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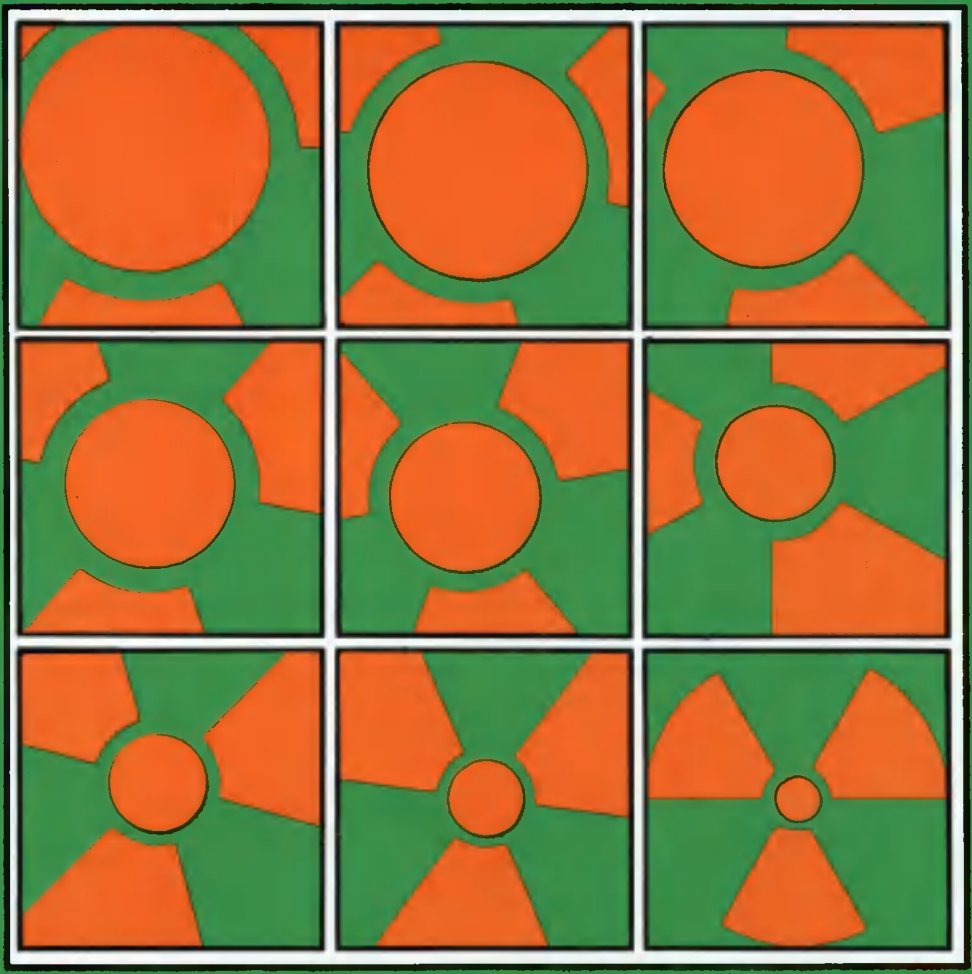
Fifth CEC Natural Analogue Working Group meeting and Alligator Rivers Analogue Project (ARAP) final workshop

Proceedings of an international workshop
held in Toledo, Spain from 5 to 9 October 1992



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Fifth CEC Natural Analogue Working Group meeting
and
Alligator Rivers Analogue Project (ARAP) final workshop

Proceedings of an international workshop held in Toledo, Spain from 5 to 9 October 1992

Edited by

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ABSTRACT

Proceedings of an International Workshop held in Toledo, Spain on 5-9 October 1992

This joint workshop combined the 5th meeting of the CEC Natural Analogue Working Group (NAWG) and the Final Workshop of the Alligator Rivers Analogue Project (ARAP), a project coordinated by OECD/NEA and managed by the Australian Nuclear Science and Technology Organisation (ANSTO).

83 specialists from 6 EC Member States (B, F, I, E, NL and UK) as well as from Australia, Finland, Japan, Sweden, Switzerland, USA and International Organisations (OECD/NEA and CEC) attended the meeting which was hosted by ENRESA (E). About 40 papers and 10 posters presented during the 5 days aimed at:

- presenting the final results of the ARAP project on site characterisation and measurements for geochemical and radionuclide transport models;
- presenting the state-of-the-art of major analogue studies and their relevance to repository performance assessments;
- discussing the concept of natural analogues in reflecting geochemical processes to include further processes of relevance to repository performance assessment;
- debating in a Panel Session the respective role of the performance assessor and the analogue worker in performance assessment.

Foreword

The 5th meeting of the CEC Natural Analogue Working Group (NAWG) was held in Toledo, Spain on 5-9 October 1992 in association with the Final Workshop of the Alligator Rivers Natural Analogue project (ARAP), a project coordinated by OECD/NEA and managed by the Australian Nuclear Science and Technology Organisation (ANSTO).

About 85 specialists came from CEC Member States (B, F, I, E, NL, UK) as well as Australia, Finland, Japan, Sweden, Switzerland, USA and OECD/NEA.

Special thanks are expressed to ENRESA (E) the host and co-organisers of the meeting for the excellent practical arrangements made and the organisation of the two field trips ("El Berrocal" research site and "El Cabril" near surface storage facility) in collaboration with CIEMAT (E).

This 5th plenary meeting provided the opportunity to:

* present the final results of the international programme of the ARAP project concerning site characterisation studies and experimental measurements for the testing of geochemical and radionuclide transport models;

* present the state-of-the-art of several major national and international analogue studies currently underway and their relevance to repository performance assessments;

* expand the concept of natural analogues in reflecting geochemical processes to include further natural processes of relevance to repository performance assessment (e.g. palaeohydrogeology, gas release, thermal alteration, neotectonics, etc.)

* debate in a panel session the respective role of the performance assessor and the analogue worker in performance assessment.

This concluding panel session arrived at a common consensus that natural analogues are currently an essential component of performance assessment and their significance will continue to increase as more focused analogue projects begin to be documented. Moreover, it was recognised that natural analogue workers and performance assessment modellers should keep working closer together to avoid communications difficulties.

The 6th plenary meeting of the Natural Analogue Working Group is planned to take place in the summer/autumn of 1994, probably in the USA or France. For this purpose, the Core Group will investigate all necessary aspects which will be announced by the CEC in due course.

These proceedings reproduce most of the papers presented at the Natural Analogue Working Group Meeting.

H. von Maravic
(CEC)

J. Smellie
(CONTERRA A.S.)

NAWG Core Group Statement

Background

The international Natural Analogue Working Group (NAWG), based on the initiative of the Commission of the European Communities (CEC), was established in June 1985 with a view to offering a scientific forum for (i) discussion of national and international natural analogue projects and (ii) evaluating their applicability as supports for repository performance assessment.

In order to achieve recognition at international level of the NAWG's activities, which are not limited to EC Member States, a Core Group of scientists active in the field of natural analogue studies was established at the first NAWG plenary meeting held in November 1985 in Brussels. A Secretariat was provided by the CEC to administer activities within the NAWG.

The initial goal of that group was to plan, organise and execute periodic workshops through which a free exchange of ideas and information would be possible. Furthermore, guidelines for new analogue studies would be provided within the framework of the NAWG.

The Core Group in its present composition comprises nine members:

Russell Alexander (RWIG, Switzerland); David Curtis (Los Alamos, USA); Peter Duerden (ANSTO, Australia); Paul Hooker (BGS, UK); Linda Kovach (NRC, USA); Henning von Maravic (CEC Secretariat, Brussels); Jean-Claude Petit (CEA, France); Peter Sargent (AECL, Canada) and John Smellie (Conterra, Sweden) who is the elected chairman of the group.

Position

The present purpose of the Core Group, further to respecting the initial goal, is to increase its effort within the NAWG to provide an additional forum for discussion and debate between natural analogue workers (earth scientists, chemists, biologists, etc.) and experts in performance (or safety) assessment. Moreover, the group is endeavouring to intensify the interaction between the NAWG and the various regulatory agencies, the funding organisations and also the public, in order to gain confidence in the "natural analogue" approach as a robust "scientific methodology" to back up safety assessments of radioactive waste disposal.

There is now a common consensus that the analogue approach is a very useful (if not the only) scientific methodology to identify processes analogous to those which could occur in the near- and far-field of a repository for radioactive waste and that data derived from natural analogue studies have been successfully used to test some of the laboratory-based models used in repository performance assessments. Most importantly, the identification, testing and validation of many processes and mechanisms which form the basis of performance assessment have been shown to be consistent with geochemical processes studied over realistic time scales.

This scientific methodology has steadily evolved through the NAWG meetings during the past seven years to a present level of awareness which the Core Group considers satisfactory, although there is still much room for improvement. Consequently the Core Group, supported by the outcome of the Toledo NAWG meeting, now feel that their efforts should be increasingly directed to ensure that information derived from natural analogue studies is adequately addressed in the light of performance assessment requirements. This demands not only that natural analogue workers integrate performance assessment objectives at the early planning stages of an investigation (i.e. to ultimately provide understanding of processes, models and data in a form that can be used in performance assessment), but also the performance assessors should more clearly define at an early stage those data (qualitative vs. quantitative) which they require as input to or as tests for the predictive models used in performance assessment.

Although a working dialogue between natural analogue workers and performance assessors has been emphasized since the first NAWG meeting held in Brussels in 1985, closer liaison is desired even today. It is fair to say that the gap has narrowed somewhat during the last seven years, but is seems nevertheless that greater appreciation and respect from both groups is still required.

The study of natural analogues is now an established part of many national radioactive waste programmes and this should be considered a significant development towards a more realistic long-term prediction of repository performance. However because of economic, bureaucratic and regulatory restraints, the use and application of natural analogue studies tend to reflect national policy. In this respect the Core Group would like to stress that the NAWG does not represent any national policy.

The present meeting in Toledo was organised to include other topics of relevance to performance assessment (e.g. palaeohydrogeology, neotectonic processes, etc.) even though these do not necessarily conform to the strict geochemical definition of a natural analogue as generally used by the NAWG. Consequently, the majority of the Core Group sees that natural analogue studies, irrespective of definition, could be applied in a broader sense to the following issues:

* issues relating to the perturbation of the natural system (geological environment) by the introduction of a technological system (repository) resulting in both near-field (e.g. canister stability, radionuclide/gas release) and far-field (e.g. radionuclide mass transport, the role of microbes and colloids) repercussions;

* issues relating to the perturbation of the technological system by disruptive processes of the natural system caused by, for example, tectonic/seismic events, climatic change and thermal processes leading to canister and backfill rupture;

* issues relating to the transfer of proven investigative methodologies from natural analogue studies to site-specific characterisation and vice-versa.

CONTENTS

Abstract III

Foreword V

NAWG Core Group Statement VII

PROGRAMME OF THE MEETING 1

INTRODUCTION AND OPENING 9

INTRODUCTION 11
H. von Maravic

USING INFORMATION FROM NATURAL SYSTEMS TO BUILD CONFIDENCE IN PERFORMANCE ASSESSMENT 15
N. A. Chapman, W.M. Miller

1. Introduction 15
2. Applying natural analogue information 15
3. Building confidence in assessments 17
   - 3.1 The illustrative role of natural analogues 18
   - 3.2 Natural geochemical fluxes 20
   - 3.3 Palaeohydrogeology 20
4. Conclusions 22

References 23

ALLIGATOR RIVERS ANALOGUE PROJECT - FINAL WORKSHOP 25

ALLIGATOR RIVERS ANALOGUE PROJECT: AN INTRODUCTION 27
P. Duerden

1. Introduction 27
2. Summary of findings 28

PERFORMANCE ASSESSMENT AND VALIDATION ASPECTS OF THE ALLIGATOR RIVERS ANALOGUE PROJECT 31
S. Wingefors

1. Introduction 31
2. Elements of a performance assessment 31
3. Some general viewpoints on validation and natural analogues 33
4. Contributions by ARAP 35
5. Conclusion 36

References 36

Setting of the Natural Analogue - Characterisation

SITE CHARACTERISATION WITH RESPECT TO GROUNDWATER FLOW 37
D.W. Emerson, K. J. Mills, M.S. Hallett

BOREHOLE TV MAPPING IN THE VICINITY OF THE KOONGARRA URANIUM ORE DEPOSIT 45
K. Miyakawa

Abstract 45
1. Introduction 45
2. Equipment and application 45
3. Results and discussions 46
    3.1 Schistosity orientations 46
    3.2 Fracture densities and apertures 46
    3.3 Fracture orientations and distribution 48
4. Conclusions 49
References 50

Hydrology

HYDROGEOLOGY OF THE KOONGARRA SITE 51
S.N. Davis

Abstract 51
1. Historical background 51
2. Hydrogeologic units 52
3. Hydrographs 53
4. Groundwater flow 53
5. Injection tests 53
6. Aquifer tests 54
7. Chemical analyses 54
8. Groundwater recharge and discharge 54
9. Direction of groundwater movement 55

HYDROGEOLOGICAL MODELLING OF THE KOONGARRA SITE 57
L. R. Townley

Abstract 57
1. Introduction 57
2. Two-dimensional modelling in vertical section 58
3. Three-dimensional modelling 58
4. Modelling in plan 59
5. Fracture flow modelling and inverse modelling 59
6. Discussion 60
7. Acknowledgements 60
References 60

EVIDENCE FOR FRACTURE FLOW AND PRELIMINARY DISCRETE FRACTURE ANALYSIS OF THE ALLIGATOR RIVERS NATURAL ANALOGUE, AUSTRALIA 63
J. L. Smoot

Solid and groundwater phases

THE CHEMISTRY AND ISOTOPIC COMPOSITION OF KOONGARRA GROUNDWATERS 65
T.E. Payne, R. Edis, A.L. Herczeg, K. Sekine, T.D. Waite, N. Yanase

Abstract 65
1. Introduction 65
2. Groundwater sampling and analysis 65
3. Main characteristics of Koongarra groundwaters 66
4. Seasonal effects and sampling variability 66
5. Spatial distribution of major parameters 67
6. ^{238}U-series radionuclides 68
7. Environmental Isotopes 69
8. Summary 70
9. Acknowledgements 70
References 70

A STUDY OF COLLOIDS IN GROUNDWATERS AT THE KOONGARRA URANIUM DEPOSIT 71
T. Seo, R. Edis, T.E. Payne

Abstract 71
1. Introduction 71
2. Field sampling 72
3. Analysis 73
4. Elemental content and mineralogy of colloids and particles 73
5. Radionuclide distributions 75
6. Summary 76
7. Acknowledgements 76
References 76

SOLID PHASE STUDIES AND URANIUM DISTRIBUTION AT KOONGARRA . 77
R. Edis, A.J. Koppi, T.E. Payne, N. Yanase

1. Introduction 77
2. Site mineralogy 77
3. Uranium Distribution 78
4. Association of uranium with minerals and elements 78
5. Uranium Series Disequilibria 80
6. Partitioning of Uranium and Thorium 81
References 82

URANIUM OREBODIES AS SOURCE TERMS FOR RADIONUCLIDES: MEASUREMENTS AND MODELS 83
J. Fabryka-Martin, D.B. Curtis

1. Background 83
2. Sample descriptions and analyses 83
3. Source-term modeling 84
4. Comparison of measurements with model predictions 85
    - 4.1 Iodine-129 85
    - 4.2 Technetium-99 85
    - 4.3 Plutonium-239 87
5. Conclusions about modeling capability 87
6. Acknowledgements 88
References 88

Mineral alteration and sorption

MINERAL ALTERATION AND URANIUM-MINERAL ASSOCIATIONS 89
T. Murakami

Abstract 89
1. Introduction 89
2. Experimental 90
3. Weathering of host rock minerals 90
4. Estimation of the reaction time and the kinetics of chlorite weathering 91
5. Uranium distribution in minerals 92
6. Calculations of uranium distribution 93
References 94

URANIUM SORPTION MODELING - A SURFACE COMPLEXATION APPROACH 95
T.D. Waite, T.E. Payne, J.A. Davis, K. Sekine

Abstract 95
1. Introduction 95
    1.1 Definitions 96
    1.2 Approach used in this study 96
    1.3 Surface complexation model 96
2. Experimental methods 97
    2.1 Preparation and properties of substrates 97
    2.2 Procedures used in obtaining pH edges 98
3. Results and discussion 98
    3.1 Ferrihydrite 98
    3.2 Quartz 99
    3.3 Kaolinite 100
    3.4 Natural substrates 100
References 100

Geochemistry

GEOCHEMICAL MODELLING OF PRESENT-DAY GROUNDWATERS 101
D.A. Sverjensky

GEOCHEMICAL MODELLING OF SECONDARY URANIUM ORE FORMATION 107
D.A. Sverjensky

DEVELOPMENT OF SECONDARY URANIUM MINERALOGY AT KOONGARRA: IMPLICATIONS WITH RESPECT TO UNCERTAINTY IN GEOCHEMICAL DATA 109
D.G. Bennett, D. Read

Abstract 109
1. Introduction 110
2. Conceptual model for the evolution of the Koongarra site 110
3. Thermodynamic data 110
4. Geochemical modelling of the Koongarra system 111
5. Coupled chemical transport modelling of the Koongarra system 112
6. Conclusions 113
References 113

Radionuclide transport

TRANSPORT MODELLING IN THE KOONGARRA WEATHERED ZONE 115
C. Golian, D.A. Lever

1. Introduction 115
2. Koongarra natural analogue 116
3. Processes 116
4. Models and results 117
5. Conclusions 120

References 120

LINKING MODELS TO PERFORMANCE ASSESSMENTS 121
D.A. Lever

1. Introduction 121
2. Parallels with the assessment process 121
3. Radionuclide transport models 121
4. Major sources of uncertainty 122

APPLICATION OF SCENARIO METHODOLOGY IN EVALUATION OF THE KOONGARRA ANALOGUE 123
K. Skagius, S. Wingefors

1. Introduction 123
2. Methodology 124
3. Application to the Koongarra Analogue 125
4. Formulation of scenarios 126
5. Conclusions 126

References 128

Regulatory objectives

THE ALLIGATOR RIVERS ANALOGUE PROJECT: A REGULATORY PERSPECTIVE 129
L.A. Kovach, G.F. Birchard, W.R. Ott

1. Introduction 129
2. Evaluating the performance of disposal systems 129
3. Application of natural analogues 130
4. The International Alligator Rivers Analogue Project 131
5. ARAP results 132
    - 5.1 Hydrology 132
    - 5.2 Geochemistry 133
    - 5.3 Performance assessment 133
6. Conclusions 134

References 134

NATURAL ANALOGUE WORKING GROUP MEETING: NATURAL ANALOGUE STUDIES 135

THE AECL/SKB CIGAR LAKE ANALOG STUDY: SOME IMPLICATIONS FOR PERFORMANCE ASSESSMENT 137
J.J. Cramer, J.A.T. Smellie

Abstract 137
1. Introduction 137
2. Cigar Lake uranium deposit 137
3. Analog features of the deposit 141
4. Modelling approach 141
5. Databases and Conceptual Models 142
    5.1 Databases 142
    5.2 Conceptual Models 143
6. Performance-Assessment-related modelling 145
    6.1 Thermodynamic codes and databases 145
    6.2 Colloids, Organics and Microbes 146
    6.3 UO_2 stability and Radiolysis 147
    6.4 Mass-transport modelling 150
7. General conclusions 151
8. Acknowledgements 151
References 152

OKLO AS A NATURAL ANALOGUE FOR RADIONUCLIDE TRANSFER PROCESSES IN A WASTE GEOLOGICAL REPOSITORY: PRESENT STATUS OF THE PROGRAM 157
P.L. Blanc

1. Field survey and sampling 158
    1.1 Preliminary 158
    1.2 Routine 158
    1.3 The reactor zones 159
2. The source term 159
    2.1 Reactor zone 10 160
    2.2 Other zones 160
3. The geochemical systems 160
    3.1 Petrographical facies 160
    3.2 Retention by clays 161
    3.3 Reconstruction of ancient fluids 161
    3.4 Thermal history of the fluid circulations 161
4. Modelling the present mass-transfer 162
5. Conclusions 162

CHARACTERISATION AND VALIDATION OF NATURAL RADIONUCLIDE MIGRATION PROCESSES UNDER REAL CONDITIONS IN A FISSURED GRANITIC ENVIRONMENT 163
J. Astudillo

Introduction 163
1. Background, objectives and organisations 164
    1.1 The site 164
    1.2 Main objectives and activities 164
2. Summary of works accomplished 165
    2.1 Drilling and geophysical activities 165
    2.2 Core analysis: lithology, fracture distribution and fissure filling 165

2.3 Lithostructural studies 166
2.4 Geochemical characterisation 167
2.5 Hydrogeological characterisation 170
2.6 Groundwater flow and radionuclide transport modelling 171
2.7 Migration experiments 171
Bibliography 173

NATURAL ANALOGUE STUDIES OF THE TONO URANIUM DEPOSIT IN JAPAN 179
T. Seo, H. Yoshida

Summary 179
1. Introduction 179
2. Outline of geology 179
3. Geological and geochemical observations 180
3.1 Chemistry of groundwater 180
3.2 Occurrence of uranium 181
3.3 Natural uranium-series disequilibria 181
4. Experimental studies 182
4.1 Impregnation experiment 182
4.2 Batch sorption experiment 182
5 Concluding remarks 183
References 183

UK HMIP NATURAL ANALOGUES PROJECT - IMPLICATIONS FOR PERFORMANCE ASSESSMENT 185
P.J. Hooker, A.E. Milodowski, D. Read

Abstract 185
1. Introduction 185
2. Natural analogues - role in performance assessment 185
3. UK sites 186
4. Lessons learned 187
5. Implications for performance assessment 187
6. Recommendations 188
7. Acknowledgements 188
References 188

THE PALMOTTU NATURAL ANALOGUE STUDY, FINLAND 191
R. Blomqvist, J. Suksi, L. Ahonen, H. Niini

Abstract 191
1. Introduction 191
2. Geological background 193
3. Activities in progress 195
3.1 Groundwater flow 195
3.2 Water-rock interaction 195
4. Future applications 199
5. Acknowledgement 199
References 200

AN OVERVIEW OF THE MAQARIN NATURAL ANALOGUE PROJECT - A NATURAL ANALOGUE STUDY OF A HYPERALKALINE CEMENT GROUNDWATER SYSTEM 203
C.J. Tweed, A.E. Milodowski

1. Introduction 203
2. Mineralogical alternation of marl as a result of interaction with hyperalkaline groundwater 204
    2.1 Objective 204
    2.2 Method 204
    2.3 Main findings 204
3. Microbiology 206
    3.1 Objective 206
    3.2 Method 207
    3.3 Main findings 207
4. Thermodynamic database testing by the modelling of trace element concentrations 208
    4.1 Objective 208
    4.2 Method 208
    4.3 Main findings 208
5. Concluding remarks 209
6. Acknowledgement 209

References 209

NATURAL CONSTRAINTS ON RADIONUCLIDE RELEASE RATES 211
D.B. Curtis, J. Fabryka-Martin, P. Dixon

Abstract 211
1. Introduction 211
2. Source terms and performance assessment modelling 211
3. Natural analogues of source terms 213
4. Natural radionuclide release rates 214
5. Discussion of results 215
6. Future work 216
7. Acknowledgements 216

References 218

PERFORMANCE ASSESSMENT SIGNIFICANCE OF NATURAL ANALOG STUDIES AT PENA BLANCA, MEXICO, AND AT SANTORINI, GREECE 219
W.M. Murphy, E.C. Pearcy

Abstract 219
1. Introduction 219
2. Peña Blanca 221
3. Santorini 222
4. Discussion 223

References 223

NATURAL ANALOGUE WORKING GROUP MEETING
NATURAL ANALOGUE SYSTEMS: PALAEOHYDROGEOLOGY 225

TIME-SCALE EFFECTS IN HYDROGEOLOGY 227
E. Ledoux, G. de Marsily

Abstract 227
1. Introduction 227
2. Trasient behaviour of a clay layer 229
3. Validation of low flow velocity in a deep aquifer 230
4. Conclusion 231
References 232

A HYDROGEOLOGIC ANALYSIS OF URANIUM ORE FORMATION IN PROTEROZOIC SEDIMENTARY BASINS 233
G. Garven, J.P. Raffensperger

1. Introduction 233
2. Methodology 233
3. Some preliminary results 234
4. Conclusions 236
References 237

EVOLUTION OF POREWATERS IN MUDROCKS 241
A.H. Bath

Abstract 241
1. Introduction 241
2. Mass transfer in mudrocks 241
3. Origins of porewaters 242
4. Examples of clay and mudrock porewaters 242
    4.1 Recent lake sediments 242
    4.2 Cross-formational flow in basinal mudrocks 242
    4.3 Near-surface Jurassic mudrocks 243
    4.4 Seawater intrusion into coastal Tertiary clays 244
5. Chemical evolution of mudrock porewaters 244
6. Porewaters and palaeohydrogeology 246
7. Acknowledgements 246
References 246

VALIDATION OF HYDROGEOCHEMICAL CODES USING THE NEW ZEALAND GEOTHERMAL SYSTEM 247
W. Glassley

Abstract 247
1. Introduction 247
2. Definition of the problem 248
3. Equilibrium regimes and implications for study sites 249
4. Modeling approach 250
5. Implications of these preliminary results for future work 250
References 251

NATURAL ANALOGUE WORKING GROUP MEETING - NATURAL ANALOGUE: A WIDER PERSPECTIVE 255

THE DEVELOPMENT OF NATURAL ANALOGUE STUDIES AND THEIR APPLICATION TO PERFORMANCE ASSESSMENT: A REVIEW 257
W.M. Miller

Abstract 257
1. Introduction 257
2. Adequate demonstrations of the validity of natural analogue studies 258
3. Repository materials 259
   3.1 Positive information 259
   3.2 Further studies 260
4. Radionuclide release and transport processes 261
   4.1 Positive information 261
   4.2 Further studies 262
5. Conclusions 263
References 264

GAS PRESSURE BUILD UP AND HOST ROCK MECHANICS - POSSIBLE IMPLICATIONS FOR THE PERFORMANCE AND PERFORMANCE ASSESSMENT OF A HIGH LEVEL NUCLEAR WASTE REPOSITORY 267
J.J.K. Daemen

1. Introduction 267
2. Stability of underground excavations 267
3. Pressurized crack propagation - Engineering 268
4. Pressurized crack propagation - Geology 269
5. Implications for repository performance - potential analog studies 270
6. Summary and conclusions 270
References 271

MAGMATIC INTRUSIONS IN CLAYS AS GEOMECHANICAL NATURAL ANALOGUES 273
F. Gera, T. Hueckel, R. Pellegrini

Abstract 273
1. Background and justification of research 273
2. Thermal alterations at Orciatico 275
3. Thermomechanical laboratory tests and modelling 275
4. Numerical simulation of thermomechanical alterations 276
5. Simulation of permeability changes due to thermal dehydration 277
6. Conclusions 277
References 278

NATURAL ANALOGUES AND NEOTECTONICS 281
R. Muir-Wood

Abstract 281
1. Introduction 281
2. Fault Rupture 281
   2.1 Strain concentration 282
   2.2 Replication 282
   2.3 Recurrence 283
3. Seismohydraulics 283
   3.1 Importance of fault style 283
   3.2 Near-fault 285
   3.3 The nature of hydrogeological change 285
4. Conclusions 286
References 286

CONCLUDING PANEL 287

WHY DO WE NOT SEE MORE RECOGNITION OF NATURAL ANALOGUES IN PERFORMANCE ASSESSMENT? 289
Chairman: I. Mc Kinley
Panelists: N. Eisenberg, I. Neretnieks, D. Lever, J. Bruno

1. Introduction 289
    1.1 Norman Eisenberg 289
    1.2 Ivars Neretnieks 290
    1.3 David Lever 291
    1.4 Jordi Bruno 291
2. General discussion 292
3. Conclusion 293

THE USE OF INFORMATION FROM NATURAL ANALOGUES IN THE PERFORMANCE ASSESSMENT OF NUCLEAR WASTE REPOSITORIES 295
J. Bruno

APPENDIX 1
SOME POSTERS PRESENTED AT THE MEETING 305

THE APPLICATION OF NATURAL ANALOGUES TO THE SWEDISH SKB-91 SAFETY PERFORMANCE ASSESSMENT 307
F. Karlsson, J.A.T. Smellie, L-O. Höglund

USE OF NATURAL ANALOGUE TEST CASES TO EVALUATE A NEW PERFORMANCE ASSESSMENT TDB 321
S.M. Pate, I.G. McKinley, W.R. Alexander

NATURAL ANALOGUE STUDY ON NATIVE IRON 333
K-H. Hellmuth

HIGH-FeO OLIVINE ROCK, A POTENTIAL REDOX-ACTIVE BACKFILL WORKING IN A NATURE-ANALOGUE WAY 343
K-H. Hellmut, A. Lindberg, E-L. Tullborg

MICROFRACTOGRAPHY OF "EL BERROCAL" GRANITE 353
M. Montoto, A. Rodríguez-Rey, B. Menéndez, A. Martínez-Nistal, V.G. Ruiz de Argandoña, L.M. Suárez del Río, L. Calleja

ELEMENT MOBILITY IN ROCK MATRIX AT PALMOTTU 359
H. Kumpulainen, P. Pitkänen, M. Valkiainen, A. Melamed, P. Manninen

MODELLING OF URANIUM TRANSPORT AT KOONGARRA WITH A MOVING WEATHERED ZONE 365
M.A. Richardson-van der Poel, H. van de Werd, S.M. Hassanizadeh

APPENDIX 2 373

ON THE EVALUATION AND APPLICATION OF GEOCHEMICAL MODELS 375
D. Kirk Nordstrom

APPENDIX 3
LIST OF PARTICIPANTS 387

PROGRAMME OF THE MEETING

Monday, 5th October

Opening
(Chairman : Henning von Maravic)

09.00-10.00	Welcome	Aurelio Ulibarri, ENRESA (E) Ramón Gavela, CIEMAT (E)
	Introduction	Henning von Maravic, CEC
10.00-11.00	Using information from natural systems to build confidence in Performance assessment	Neil Chapman, INTERA (UK)
11.00-11.30	*Coffee break*	

Alligator Rivers Analogue Project Final Workshop

Session 1: Alligator Rivers Analogue Project
(Chairman: Peter Duerden)

11.30-12.00	Alligator Rivers Analogue Project: An introduction	Peter Duerden, ANSTO (AUS)
12.00-12.30	Performance assessment and validation aspects of the Alligator Rivers analogue project	Stig Wingefors, SKI (S)
12.30-14.00	*Lunch*	

Setting of the Natural Analogue - Characterisation

14.00-14.35	Geology/Geomorphology	Karl-Heinz Wyrwoll, Univ.Western Australia (AUS)
14.35-15.10	Site characterisation with respect to groundwater flow	Don Emerson, Univ. Sydney (AUS)
15.10-15.30	Borehole TV mapping in the vicinity of the Koongarra uranium ore deposit	Kimio Miyakawa, CRIEPI (JAP)
15.30-16.00	*Coffee break*	

Hydrology

16.00-16.40	Hydrology of the Koongarra site	Stan Davis, Univ. Arizona (USA)
16.40-17.20	Hydrological modelling of the Koongarra site	Lloyd Townley, CSIRO (AUS)
17.20-17.40	Evidence for fracture flow and preliminary discrete fracture analysis of the Alligator Rivers Natural Analogue, Australia	John Smoot, PNL (USA)

Tuesday, 6th October

Session 1/ Alligator River Analogue Project, continued
(Chairman: Peter Duerden)

Solid and groundwater phases

09.00-09.30	The chemistry and isotopic composition of Koongarra groundwaters	Tim Payne, ANSTO (AUS)
09.30-09.50	A study of colloids in groundwaters at the Koongarra uranium deposit	Toshihiro Seo, PNC (JAP)
09.50-10.30	Solid phase studies and Uranium distribution at Koongarra	Robert Edis, ANSTO (AUS)
10.30-11.00	Uranium ore bodies as source terms for radionuclides: measurements and models	June Fabryka-Martin, LANL (USA)
11.00-11.30	*Coffee break*	

Mineral alteration and sorption

11.30-12.00	Mineral alteration and Uranium-mineral associations	Takashi Murakami, JAERI (JAP)
12.00-12.45	Uranium sorption modelling - A surface complexation approach	David Waite, ANSTO (AUS)
12.45-14.15	*Lunch*	

Geochemistry

14.15-14.40	Geochemical modellin of present-day groundwaters	Dimitri Sverjensky, John Hopkins Univ. (USA)
14.40-15.10	Geochemical modelling of secondary uranium ore formations	Dimitri Sverjensky, John Hopkins Univ. (USA)
15.10-15.30	Development of secondary uranium mineralogy at Koongarra: implications with respect to uncertainty in geochemical data	David Bennett, WS Atkins (UK)
15.30-16.00	*Coffee break*	

Radionuclide transport

16.00-16.45	Transport modelling in the Koongarra weathered zone	Cezary Golian, ANSTO (AUS) David Lever, Harwell (UK)
16.45-17.10	Linking models to performance assessments	David Lever, Harwell (UK)
17.10-17.30	Application of scenario methodology in evaluation of the Koongarra analogue	Stig Wingefors, SKI (S)

Regulatory Objectives

17.30-18.00	The Alligator Rivers analogue project: a regulatory perspective	Linda Kovach, US-NRC (USA)

Wednesday, 7th October

Natural Analogue Working Group Meeting

Session 2: Natural Analogue Studies
(Chairman: Russel Alexander)

09.00-09.15	Opening remarks	Russel Alexander, NAGRA (CH)
09.15-10.00	The AECL/SKB Gigar Lake analog study: some implications for performance assessment	John Smellie, CONTERRA (S)
10.00-10.45	Oklo as a natural analogue for radionuclide transfer processes in a waste geological repository: Present status of the programme	Paul Louis Blanc, CEA-IPSN (F)
10.45-11.15	*Coffee break*	
11.15-11.45	El Berrocal project: Characterisation and validation of natural radionuclide migration processes under real conditions in a fissured granitic environment	Julio Astudillo, ENRESA (E)
11.45-12.15	Natural analogue studies of the Tono uranium deposit in Japan	Toshihiro Seo, PNC (JAP)
12.15-13.00	UK-HMIP Natural Analogue projects - Implications for performance assessment	Paul Hooker, BGS (UK)
13.00-14.30	*Lunch*	

(Chairman: David Read)

14.30-15.00	The Palmottu ntaural analogue study, Finland	Runar Blomqvist, GTK Espoo (SF)
15.00-15.45	An overview of the Maqarin natural analogue project. A natural analogue study of a hyperalkaline cement groundwater system	Cherry Tweed, Harwell (UK)
15.45-16.15	Natural constraints on radionuclide release rates	David Curtis, Los Alamos N.L. (USA)
16.15-16.45	*Coffee break*	
16.45-17.30	Performance assessment significance of natural analogue studies at Peña Blanca, Mexico, and at Santorini, Greece	William Murphy, CNWRA (USA)
17.30-18.00	Wrap-up and discussion	Russel Alexander, NAGRA (CH) David Read, WS Atkins (UK)
18.15-19.15	**Poster Session**	

Thursday, 8th October

Session 3: Natural analogue systems: palaeohydrogeology
(Chairman: Emmanuel Ledoux)

08.30-08.55	Time-scale effects in hydrogeology	Emmanuel Ledoux, Ecole de Mines (F)
08.55-09.40	A hydrogeologic analysis of uranium ore formation in Proterozoic sedimentary basins	Grant Garven, Johns Hopkins Univ. (USA)
09.40-10.10	Isotope palaeohydrological constraints on groundwater movements in rocks of low permeability	Jean-Charles Fontes, Univ. Paris Sud (F)
10.10-10.40	Evolution of porewaters in mudrocks	Adrian Bath, BGS (UK)
10.40-11.10	Validation of hydrochemical codes using the New Zealand geothermal system	William Glassley, LLNL (USA)
11.10-11.40	*Coffee break*	

Session 4: Natural analogue: a wider perspective
(Chairman: Jean-Claude Petit)

11.40-12.00	Opening remarks	Jean-Claude Petit, CEA (F)
12.00-12.30	The devlopment of natural analogue studies and their application to performance assessment: a review	William Miller, INTERA (UK)
12.30-13.00	Gas pressure build-up and host-rock mechanics. Possible implications for the performance and performance assessment of a large level nuclear waste repository	Jaak Daemen, Univ. of Nevada (USA)
13.00-14.30	*Lunch*	
14.30-15.00	Magmatic intrusions in clays as geomechanical natural analogues	Ferruccio Gera, Ismes (I)
15.00-15.30	Natural analogues and Neotectonics	Robert Muir Wood, BEQE (UK)
15.30-16.00	Geochemistry of ore deposits: reservoirs, leaks and sinks	Jacques Boulègue, Univ. de Paris VI (F)
16.00	*Coffee break*	

Session 5: Concluding panel
(Chairman: Ian McKinley)

17.00-18.30 Topic: Why do not we see more recognition of natural analogues in performance assessment?

Panelists:
Jordi Bruno, MBT (E)
Norman Eisenberg, NRC (USA)
David Lever, Harwell (UK)
Ivars Neretnieks, RIT (S)

18.30	Closing remarks	Henning von Maravic, CEC
18.40	End of the meeting	

Friday, 9th October

Field trips

Wednesday, 7 October 1992

18.15-19.15 **POSTER SESSION**

"US-NRC Natural Analogue Research Programme"
Linda Kovach - US Nuclear Regulatory Commission (USA)

"The application of natural analogues to the Swedish SKB-91 safety performance assessment"
John Smellie - CONTERRA (S)
Fred Karlsson - SKB (S)

"Use of natural analogue test cases to evaluate a new performance assessment TDB"
S.M. Pate, W.R. Alexander - University Bern (CH)
I.G. McKinley - NAGRA (CH)

"Natural analogue study on native iron"

"High-FeO olivine rock, a potential redox-active backfill material working in a nature-analogue way"
Karl-Heinz Hellmuth - Finnish Centre for Radioactive and Nuclear Safety (SF)

"Fractionaction of uranium between minerals by rock weathering"
Toshihiko Ohnuki - JAERI, Tokai Research Establishment (Japan)

"3-D Discrete fracture model of Koongarra uranium ore body"
John Smoot - PNL (USA)

"Microfractography of El Berrocal granite"
Modesto Montoto - University of Oviedo (E)

"Field hydrology measurements (ARAP)"
Stanley Davis - University of Arizona (USA)

"Element mobility in rock matrix at Palmottu"
Heikki Kumpulainen - Technical Research Centre of Finland (SF)

"Modelling of uranium transport at Koongarra with a moving weathered zone"
Rikje van de Weerd, Melissa Richardson-van der Poel - R.I.V.M. (NL)

INTRODUCTION AND OPENING

Introduction to the 5th CEC Natural Analogue Working Group Meeting and Alligator Rivers Analogue Project (ARAP) Final Workshop
H. von Maravic (CEC)

Invited Opening Paper :
Using Information from Natural Systems to Build Confidence in Performance Assessment
Neil A. Chapman & William M. Miller (Intera Environmental Division)

INTRODUCTION

H. von Maravic
CEC

On behalf of the Commission of the European Communities; it is a pleasure for me to welcome you to the 5th meeting of the Natural Analogue Working Group in Toledo.

We have taken this opportunity to connect this meeting with the workshop of the Alligator River Analogue Project (ARAP), which is coordinated by OECD/NEA and managed by the Australian Nuclear Science and Technology Organisation (ANSTO). Our special welcome goes to the participants involved in this international project and I would like to thank Peter Duerden from ANSTO for ensuring the organisation of this part of our agenda.

The size of this meeting, about 90 specialists here for the next 4 days, coming from 6 EC Member States (Belgium, France, Italy, , Spain, The Netherlands and the United Kingdom) and from Australia, Finland, Japan, Sweden, Switzerland, USA and International Organisations such as OECD/NEA and CEC, show clearly the continuing interest in natural analogues.

The studies of Natural Analogues started about 10 years ago at both national and international levels involving the use of the analogy approach to investigate:

* natural occurrences of specific materials (also man-made materials affected by natural processes),
* conditions and
* processes (mainly physico-chemical)

which are the same or similar to those which could occur both in the near and far field of an underground repository for long lived radioactive waste in deep geological formations.

At that time the CEC introduced as part of the MIRAGE project (Migration of radionuclides in the geosphere) of the Community R&D programme on "Management and Storage of Radioactive Waste", a research topic on "natural geological migration systems" and has participated since 1982 in several analogue studies, especially in France, Italy, Spain and the United Kingdom in order to cover a wide range of transport and retardation processes to be considered in sedimentary and crystalline rocks.

Parallel to these activities, deeper consideration was being given to the application of natural analogues in the field of radioactive waste disposal. In 1984, a 1st comprehensive report (commissioned by SKB (S) and NAGRA (CH)) about "the potential use of natural analogues for radioactive waste disposal" was published by N. Chapman and co-workers; and also in 1984, the Lake Geneva (USA) workshop about natural analogues in granite rocks was organised by SKB(S) and US-DOE.

Considering the growing interest and demand for analogue studies and the nationally sponsored research programmes in Europe, USA and Japan, the CEC took the initiative in June 1985 of establishing the international "Natural Analogue Working Group" (NAWG) with a view to offering a forum for:

- discussion of national and international natural analogue research projects
- assessing their applicability as supports for repository performance assessment

and to build an informal alliance of experts from various disciplines, involving both researchers - people, who do the field and laboratory work - and modellers.

Since then, the NAWG has held 4 plenary meetings focusing on main items such as:

- Interaction between modellers and experimentalists, Brussels (B) 1985
- Man-made analogues, colloids and complexes, geomicrobes, Interlaken (CH) 1986
- Application of natural analogues to performance assessment, Snowbird (USA) 1988
- Review of five years natural analogue investigations and the outcome of the international Poços de Caldas natural analogue project, Pitlochry (UK) 1990

I think the feedback we have received through these workshops allows us to state that NAWG has successfully moved a considerable way towards clarifying the role and how to use and apply information and data from natural analogues in improving confidence in underground repository performance assessment and more specifically concerning a better understanding of relevant geochemical processes and increased capability of describing and modelling them.

A substantial part of this success has without doubt been due to the members of the Core Group of the NAWG, scientists active in natural analogue research and endeavouring to monitor the achieved goals and to promote the exchange of information. I trust that the Core Group, in its new composition, will also continue in this spirit, focusing on the still unanswered questions and open the door to address new aspects and areas of further development in the field of natural analogue research. To fulfil this expectation and this is my conviction not only as the representative of the CEC, scientifically responsible for research activities in the field of geological disposal of radioactive waste, also covering Natural Analogue activities, but also as a member of the NAWG Core Group.

As I mentioned before, the CEC supported, at an early stage, through its R&D programmes on "Management and Storage of Radioactive Waste" research on natural analogues.

Within its 4th cost-shared programme (1990-1994), currently underway, the CEC concentrated its efforts in this research to support mainly two large analogue studies at:

- the Oklo uranium ore deposit, Gabon, West Africa and
- the El Berrocal granite system, near the village of Numbella/Toledo, Spain

to characterise the petrographical, geochemical and hydrogeological system in order to understand and model the present migration processes.

Moreover, the CEC will support a limited research project concerning the geoenvironmental conditions of the Dunnarobba Forest, preservation of the Tiberina Valley (I) to improve the understanding of the physico-chemical conditions of the long term isolation capacity of clay.

The present status of the Oklo project, coordinated by CEA-IPSN (F) and of the El Berrocal project, coordinated by ENRESA and conducted in the field by CIEMAT, will be reported in the frame of this NAWG meeting.

I think the results obtained from all the studies up to date have led to the general consensus that natural analogues are viewed as a convincing support for validation of predictive models of relevant processes in long-term performance assessment, to increase the acceptability of disposal concepts of radioactive waste in a geological environment.

A key issue in this connection is without doubt, to be able to predict, with sufficient confidence the nature and effects of the future processes and geological events involved, from our knowledge of the past.

This not easy task implies in my understanding some crucial questions, still to be discussed:

* how to interpret the past of a complex natural system, through the examination of its present given situation, without exactly knowing, in a lot of cases, the temporal and spatial evolution of specific geochemical or hydrological processes at the site;

* how to come from those observations of natural systems towards a reliable prediction;

* how to increase confidence that the predictive models used in performance assessment are realistic when addressing the safety case to different audiences.

I guess these points mentioned above will certainly also be addressed in several of the presentations in our meeting.

The intention of this meeting is:

* to present the final work of the international programme of the Alligator River Analogue project, ended in August this year, in order to discuss the results obtained concerning site characterisation studies and experimental measurements for the testing of hydrological, geochemical and radionuclide transport models under Session 1;

* to review the progress achieved in several of the major natural analogue studies currently underway and to discuss their evident potential and limitations for developing conceptual models and validating models used in performance assessment under Session 2;

* to address the hydrogeological issue, beside the geochemical issue which has been the major concern of analogue studies, to characterise palaeo-groundwater flow

systems and to discuss the limitations in qualifying and quantifying palaeohydrological systems in the context of the natural analogue approach under Session 3;

* to open the discussion for further analogue studies which might provide information directly for application to performance assessment, by introducing several issues like the gas effects in different geological media, geomechanical processes, neotectonical or palaeoclimatological events, as well as ore formation processes which could effect the future evolution of the geoenvironmental situation of a repository for radioactive waste under Session 4.

The meeting will be concluded in a panel which represents analogue workers and performance assessment modellers and intends to focus the discussion of what they actually do by producing and using analogue data. Moreover, I assume that the panel will also pick up on some of the aspects addressed under Sessions 3 and 4.

I think this meeting has the chance to open new ways and to give recommendations for areas of further development of the analogue studies beside the geochemical issue.

The floor for this is given to you, the participants, coming from various scientific disciplines. Consequently, this is an excellent occasion to bring forward the natural analogue research as a scientific methodology to back up safety assessments of radioactive waste disposal in a geological environment. To reach acceptance not only in this community of insiders but also the outside public is a challenging goal.

In this last context, how to present the natural analogue studies to the general public, I would like to inform you, that recently NAGRA took the initiative together with SKB (S) and CEC to realise the production of a video about Natural Analogues. Up to now, about 11 organisations from Europe and outside have expressed their interest in this project. The present situation is that Dr. Güntensperger from NAGRA coordinates all the activities to realise in a 1st phase a pre-production of the video. I am happy that the producer of the video, Dr. Weiser from Switzerland and Mrs. Chris Reppmann from Germany, as well as Mr. Güntensperger, are with us at this meeting to receive 1st hand information about the state-of-the-art in natural analogue studies at an international, worldwide level and to have the possibility to come into contact with some of you during the next two days.

I would not like to close this introduction without taking the opportunity to express my gratitude to ENRESA, represented by Mr. Ulibarri, for co-sponsoring and organising this meeting and taking care of the organisation of the two field trips in collaboration with our colleagues from CIEMAT, represented by Mr. Gavela. My special thanks go to Mr. Carlos del Olmo and his co-workers from ENRESA.

I wish also to express my thanks to John Smellie, chairman of the NAWG Core Group and its members for their sustained cooperation in preparing the scientific programme of this meeting.

Finally, I hope that this meeting leads you to fruitful discussions, knowledgeable new ideas and competent symbiose of earth scientists and safety performance workers allowing us to exchange views in a very frank and friendly atmosphere.
Thank you.

USING INFORMATION FROM NATURAL SYSTEMS TO BUILD CONFIDENCE IN PERFORMANCE ASSESSMENT

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Introduction

The concept of geological disposal is based largely on our intuitive understanding that something buried in stable rock formations should be safe. It is, then, perhaps not surprising that we turn to the natural geological environment when we seek to provide examples that enhance confidence in performance assessment results. Although the majority of geological information derived from field observations, laboratory and underground experiments, in particular from site-specific studies, is generally used as *input* for the models in which we are seeking to build confidence, there are two further aspects of the use of information from natural systems in *support* of performance assessment:

- the use of 'natural analogues' in building and providing constraints on the results of performance assessment models (the familiar topic of CEC-NAWG meetings), and

- the use of natural analogues, studies of natural geochemical fluxes, and palaeohydrogeological studies to provide *illustrations* and contextual material to help us to digest the significance of performance assessment results.

This paper deals very briefly with the first of these two aspects (as this has been much debated in previous NAWG meetings), and focuses more on the second aspect. Consequently, natural analogues themselves are not discussed in depth here. Much of the discussion in this paper is derived from current reviews and analyses in which the authors are involved, with reports and papers in press (see, for example, Miller et al, 1993; Chapman, 1992; Chapman and McEwen, 1992). Miller et al (1993) provide a comprehensive review of the current state of the art of the use of natural analogues, and a summary of the contents of this major piece of work is presented by Miller later in this volume.

2. Applying natural analogue information

The two applications of natural analogues mentioned above are the technical support of the performance assessment process, and the illustrative use in presenting and setting a context in which to evaluate the results of these assessments. Looking back two or three decades, deep burial of reactor wastes seemed fundamentally sound as it could be regarded as simply putting the material, albeit considerably modified, back in the environment from which it had been extracted. The concept of the radioactivity in a spent-fuel repository decaying after a period of time to the level of the original uranium ore was used frequently in presenting disposal options. It is now recognised that such a simplistic approach is of little use in carrying out a safety assessment, but it does, nevertheless, indicate that natural analogues were being used almost unconsciously to propose a solution to the waste problem. It is now appreciated that safety must be demonstrated primarily on the basis of predictions of the likely range of future behaviour of a repository. The scientific community is, perhaps, less sanguine about the meaning of such predictions than it was a few years ago. However, the whole conceptual basis of geological disposal continues to rely on the natural evidence for the long-term stability and sluggish evolution of deep geological environments. It is common practice, where possible, to utilise natural materials rather than man-made substances in repository engineered barriers, because we believe that they are more likely to be stable and have predictable behaviour when surrounded by other natural materials in a geological environment. More fundamentally, decisions based on observations of the natural environment are deeply hidden and frequently unstated in the lower levels of performance assessment, in that they provide the whole conceptual basis for what shall be modelled; in particular, radionuclide transport phenomena.

Natural analogue studies performed to fulfil performance assessment requirements are generally aimed at three areas of developing and testing models:

- model construction,
- data acquisition for input to, or as controls on these models, and
- testing or validating the models.

The first step is essentially qualitative, the second two are quantitative. The level of importance of analogues in assisting in each step has been rather different and, to date, the use of natural analogue data in published performance assessments has been rather limited. Analysis of several integrated assessments carried out in the last ten years suggests that, for the three areas listed above:

- The role of natural analogues in setting a conceptual basis for assessment models is apparent but largely unacknowledged.

- There are probably only two clear examples of parameter values being provided by natural analogues for direct input to an assessment model (pitting ratios for copper containers for spent-fuel and matrix diffusion penetration depths). More important in the context of the second area is the 'soft quantitative' use of natural analogues in providing somewhat diffuse limits to the ranges of parameter values used or results calculated, in the sense of checking their likelihood of being correct.

- Natural analogues are only just starting to be used in a 'hard quantitative' role as test-beds against which to validate models, and, so far, only in the limited field of static geochemical modelling. These developments are so recent that they have not yet been fully absorbed in a published assessment.

In terms of direct input to performance assessment, the third area is seen as being an exceptionally powerful application, and may be the only acceptable way of providing some measure of validation of some of the more detailed aspects of assessment geochemical modelling (radionuclide speciation, solubility limitation, spent-fuel dissolution, etc). There are several important areas in assessments where analogues can provide more information than they have yet done (e.g. on irreversible or partially reversible retardation mechanisms, on volumes of rock exposed to transported radionuclides, and on the existence of fast transport pathways). This paper does not explore these further, and the reader is referred to Miller et al (1993).

3. Building confidence in assessments

Regulatory authorities are the key agencies that need to be convinced of the adequacy of a safety assessment. Such assessments may be presented from time to time as part of a rolling programme of research and development, or with the actual licensing of a repository in mind. Most agencies have, by now, set some blend of quantitative and qualitative standards against which the results of an assessment can be judged, although others are proceeding cautiously towards developing firm criteria. Quantitative standards are usually set in terms of acceptable levels of release of specific radionuclides at set points and times, or radiation doses or health risks to individuals or groups, again at various times in the future. Most waste disposers are now striving to demonstrate that specific disposal options can meet the quantitative targets set. However, a purely mechanistic engineering model that produces dose versus time projections always causes problems of belief in any audience. The lay-public are not alone in requiring some help in order to grasp the meaning of such information. Thus, acceptance is not necessarily as simple as complying with numerical targets, and a number of questions are raised:

- how confident is the assessor in the results of their assessment?
- how has such confidence been demonstrated and are the demonstrations credible?
- besides the regulators, what are the views of other concerned groups, including the scientific peers of the assessors?
- what other evidence, including qualitative information, supports the numerical conclusions of an assessment?

The evaluator of an assessment, and this could be anyone reading it, has to understand that the quantitative predictions presented are really only illustrations of what could happen, be they scenarios or time-dependent models.

The biggest uncertainty comes not from future environmental evolution, but from the development of society, over a very much shorter timescale of decades rather than millennia. The most useful way of addressing these illustrations and answering the questions above is by putting them into context with parallel processes in the evolving natural environment. Three avenues are currently open to facilitate this:

3.1 The illustrative role of natural analogues

Apart from their role in building and testing performance assessment models, discussed earlier, natural analogues can provide purely qualitative illustrations that the end result of complex, coupled processes over very long times does give the sorts of qualitative result suggested by a performance assessment model; such things are observed in nature, the assessor is not completely misguided in assuming that they might occur in a repository. They also have a much wider appeal as providers of illustrative and, in some cases, non-technical information to a broad range of audiences. From outside the confines of the performance assessment community, this aspect is probably perceived as the only reason natural analogues are studied. Natural analogues, or comparisons with natural systems, are frequently mentioned as important components of the process of evaluating and accepting disposal proposals. Among all levels of reviewer, from technical peer review panels, to non-technical audiences, there is a clear belief that predictive safety assessments are only credible if shown to have strong natural parallels. For many audiences, the nature of predictive safety assessments themselves are difficult to understand and accept. Take the following quotation from Blowers et al. (1991):

''Enormous scientific effort has been expended in Europe and North America researching and demonstrating the proposition that such repositories will be safe, for all practical purposes, for ever. Yet clearly the assertion is preposterous. The safety of an untried method cannot be proven until repositories have been constructed and monitored over many generations and the radionuclides have decayed to safe levels. Running such an empirical experiment is inconceivable. Sophisticated geological analysis, risk assessment or modelling of repository behaviour must rest upon heroic assumptions and are no substitute for empirical knowledge. Scientific predictions for periods of 10 000 years or more lie in the realm of fantasy, not rationality. In conditions of such uncertainty it must be concluded that there is no technical solution to the problem of radioactive waste.''

Although the authors come from a non-technical background, the strength of disbelief in long-term predictions voiced by all kinds of audiences cannot be dismissed by scientists. In the field of prediction, everyone has a more-or-less valid view, based on generations of widely publicised experience. No amount of scientific argument or proof is going to convince many people when a safety case is inherently very complex and extends far into the future. Doubts are not the prerogative of the non-technical audience, and are pervasive throughout the concerned community. Given this difficult position, those who have to present safety cases, or to evaluate them and base decisions on them, have found some very important uses of natural analogues. Broadly, these fall into two areas:

- As straightforward *factual examples, with a time context,* that the processes being modelled in performance assessments are not unusual or novel in the natural world, and that there is some sound basis for the time-scales involved. Such illustrations need not be quantitative, nor need they even be conclusive of any particular behaviour. They reassure that, for example, when we go to a lot of effort to model the rate of corrosion of metal canisters, then there is some basis for indicating that metals can survive in the natural environment for commensurate periods. In other words, we are not being totally misled by theory and chasing red-herrings.

- As *illustrations* that the overall result of waste disposal has natural parallels in terms of there being similar concentrations of natural radioactivity moving about in the environment, again on similar time-scales.

These two types of application are at their most valuable when used in a matter-of-fact and disinterested way to show that at least there is some sound basis in the real world for believing that geological disposal is not simply another ambitious technological enterprise, doomed to choke on its own complexity. A number of useful brochures and films have been using this approach (e.g. the UK Nirex Ltd. film *"Tunnel in Time",'* the Nagra booklet *"Observations of Nature"* and the forthcoming internationally sponsored natural analogues film). There is, however, an acute danger in either being condescending to the reader or viewer, or overstating the case; usually both can arise because material is misrepresented or simply abused. The nuclear industry itself has not always represented natural analogues honestly, sometimes tending to oversimplify and overstate the facts. No doubt it may be argued that some simplification is necessary to make the scientific data readily digestible, but there is a fine line between necessary simplification and misrepresentation of the facts. The natural analogue that is most frequently oversimplified is Oklo, often to the point of being misleading. To the scientist, Oklo does not provide unequivocal proof that a repository will be safe; the situation at Oklo is simply too complex for that conclusion to be reached. Yet, Oklo is often presented in nuclear industry literature as 'proof'. An example of 'going too far' is provided by the following quotation from 'industry' literature:

"The Oklo reactors ran gently at the kilowatt-power level for millions of years. They never blew up. The radiation and waste from them did not deter surrounding life forms. Over immense timescales, the waste has barely moved away from the reactor site. As a result, scientists today are confident that waste in man-made stores and repositories is likely to move even less . . ."

Such statements challenge belief at all levels, apart from leaving themselves open to scientific ridicule if ever they have to be defended. Caution is essential.

3.2 Natural geochemical fluxes

The core of a performance assessment looks at geochemical fluxes over long times. It is very useful for someone evaluating predicted radionuclide fluxes to have an idea of what other geochemical fluxes are occurring naturally at the same time. Over periods of 10,000-100,000 years or more, diagenesis, deep and shallow rock-water interactions, erosion, weathering, sedimentation, mineralisation and other processes are busily moving elements around within the same system that is being modelled by the assessor, independently of the presence of the repository. Comparatively, vast amounts of material are on the move, including several of the elements central to the assessment. At the limit, where the best geochemical and epidemiological data are available, it is possible to compare the health effects of these parallel processes. Even where this is impractical or illogical, it is extremely useful to be aware that these processes are active, simply to be able to put fluxes from the repository into context. Clearly, actual radiological impacts from all radionuclides need to be evaluated, but putting the overall fluxes of each element (for which it is possible to make such calculations) into a natural context can considerably aid any reviewer to grasp the significance of the processes being modelled in a repository. This point is important to communicate, for almost all audiences will have no 'feel' for the numbers (concentrations, doses and timescales) generated by performance assessment calculations.

3.3 Palaeohydrogeology

The validity of predictions made using groundwater flow models constructed using observations of present hydrogeological properties is difficult to demonstrate. These models again need to be put into context, as they look very uncomfortable in isolation. Palaeohydrogeological reconstructions of past flow systems at a repository site are perhaps the best means of supporting such models (Pearson et al, 1988; Chapman and McEwen, 1992). Palaeohydrogeology is a combination of observations on hydrochemical and isotopic differences in various groundwater zones or bodies, mineralogical data on the rock formations, and the hydraulic properties of the same formations, which are then compiled to allow interpretation of the evolution of the rock-water system over long time periods in the past. Such interpretation will require assumptions about the 'initial' conditions of the system (e.g. in sediments, about the original porewater composition at the time of deposition) together with information on the rates of various processes (e.g. diagenetic reactions), some of which may be difficult to obtain. There are inevitable ambiguities and difficulties in interpretation of so much intricately coupled information, and some well-known problems and complications need to be resolved. However, the technique is potentially exceptionally powerful because a system can usually be evaluated with a high level of confidence at a broad enough level of detail, that is adequate to define the main mechanisms and trends that have dominated its evolution. This then forms a firm foundation for any predictions made about future behaviour. The types of information which could be derived ideally from interpretation of a well-characterised site include:

- major bodies of water present in different regions of the deep geological environment

- the residence times of these bodies of water in that region, and hence their 'stability' to changes in external conditions

- the degree to which mixing of different bodies of water has occurred, and the geochemical transport mechanisms operating at their interfaces

- the principal pathways for water movement in the system (higher conductivity formations or zones) and the extent to which these have influenced the overall evolution of the groundwater regime

- regions where dilution of deeper-sourced waters may take place in shallow waters (with respect to repository releases), and the extent of such dilution

- evidence for the major forces that have perturbed the system in the past (e.g. glaciation, sea-level change, permafrost), the depth and extent of the perturbations, and the response time of the system

- the contribution of what are generally regarded as secondary mechanisms or sources to the evolution of the groundwater system (e.g. tectonic effects on flow; very deep sourced fluids affecting hydrochemistry, etc)

- evidence for groundwater transit times from shallow to deep parts of the system, and vice-versa

At the very simplest level, palaeohydrogeology can provide clear indicators of the suitability or otherwise of a site for a repository. The presence at depth of clearly 'young' waters, with high bomb tritium or anthropogenic surface water contaminants for example, and of rapid and widescale mixing of such waters with large parts of the deep flow system, would tend to exclude the site from further consideration. At this level, the information probably would not even be used in a detailed performance assessment, but would simply aid preliminary decisions on site suitability. What the waste disposer would clearly hope for would be indications of the extremely stable nature of the system over periods of tens to hundreds of millennia, with a high buffering capacity to changes wrought by external climatic forcing factors, and an overall sluggish evolution of the chemical system, and of any advective transport processes in particular. If this type of picture emerges from a site investigation it can be used in performance assessment in two ways: testing predictive models (which has not, to the authors' knowledge, been attempted) and in providing a well-founded understanding of how the site got to be the way it is today. The latter provides what must be the best demonstration of confidence in its future behaviour. If past processes have been extremely slow at repository depth, then there is very good reason to believe that they will continue to behave in the same way. Given this confidence in past stability, an assessment can be more confident about the range of future conditions likely to be experienced by the site, its range and rates of response to those conditions, and, consequently, the rates of radionuclide transport and other important fluxes in the repository system. The predictive assessment transport model can then be nested comfortably in these broader descriptions of scales and rates of natural processes. The effect of the repository itself in perturbing the natural hydrogeochemical system also clearly needs to be evaluated.

4. Conclusions

To conclude, it is worth pondering the extent to which some of the 'indirect' semi-quantitative and qualitative information discussed above can really be used by a decision-maker. Most safety submissions must, inevitably, be based primarily on quantitative predictions of dose, risk, release, concentration at a certain point at a certain time, and so on. The recipient of these numbers might suspend reality for a while and take them at face value, checking how they compare with standards, or they may try to view them in some broader context. The context may be presented to them in the submission: 'these results must be taken as stylised indicators of the nominal results of a set of possible future scenarios, using present day model receptors to calculate likely reference doses....etc'. Alternatively a context may be provided which uses information on the rate of evolution of the geological environment, the direction, scale and effects of natural processes, or the natural geochemical cycling of radionuclides or other trace elements over comparable periods of time as yardsticks against which to gauge predictions of waste radionuclide behaviour.

Putting the results into the context of what is actually observed in the natural environment is vital. The widely acknowledged non-linearity of behaviour of natural systems suggests that, whatever approach is used to produce quantitative assessments, then without this intuitive evaluation the numbers cannot be used to check compliance against a linear regulatory yardstick, no matter how much error and uncertainty treatment is included in their derivation. In other words, a safety case needs two legs to stand on. All of this looks rather imprecise, of course, and one has to admit the difficulty of devising some formal process whereby the qualitative value of a performance assessment can be accounted for in parallel with the much easier task of checking numbers against a target. However, both, on their own, are insupportable as a means of judging safety and acceptability. Perhaps, at the end of the day, the answer is nothing more complicated than ensuring extensive peer review by people well-versed in long-term processes in both the geological and the surface environments.

An alternative way round this would seem to be the use by regulators and other decision-makers of a broader and more qualitative framework within which to place the numerical result of an assessment. Not only does this make it easier for everyone to understand, but it also clearly limits our expectations of what an assessment ought to be designed to achieve, indeed of what it is ever capable of demonstrating with confidence. There has been much effort recently to 'validate' our predictive radionuclide transport models. The fact that it is taking time to develop real consensus on how this can best be addressed, and that validation has not yet been widely acknowledged to have been achieved, should lead us to be more sanguine about both our quantitative predictive capabilities, and regulations based upon them.

References

Blowers, A., Lowry, D. & Solomon, B.D. (1991) The international politics of nuclear waste. Macmillan Academic & Professional Ltd.

Chapman, N.A. (1992) Natural Analogues: The State of Play in 1992. In: High Level Radioactive Waste Management; Proceedings of the 3rd International Conference, 2, 1695-1700. American Nuclear Society, Illinois, USA.

Chapman, N. A. & McEwen, T.J. (1992, in press) The application of palaeohydrogeological information to repository performance assessment. In: Palaeohydrogeological Methods and their Applications for Radioactive Waste Disposal, OECD Nuclear Energy Agency, Paris, 1992 in press.

Miller, W.M., Alexander, W.R., Chapman, N.A., McKinley, I.G. & Smellie, J.A.T. (1993 in press) Natural Analogue Studies in the Geological Disposal of Nuclear Wastes. NAGRA (NTB 93-03) / SKB / UKDOE-HMIP Radioactive waste management series.

Pearson, F.J., Balderer, W., Loosli, H.H., Lehmann, B.E., Matter, A., Peters, Tj., Schmassmann, H. & Gautschi, A. (1988) Applied Isotope Hydrogeology - A Case Study in Northern Switzerland. Nagra Technical Report NTB 88-01, Nagra, Wettingen, Switzerland.

ALLIGATOR RIVERS ANALOGUE PROJECT

Final Workshop

Alligator Rivers Analogue Project: An Introduction
Peter Duerden, ANSTO (AUS)

Performance assessment and validation aspects of the Alligator Rivers Analogue Project
S. Wingefors, SKI (S)

Setting of the Natural Analogue - Characterisation

Site characterisation with respect to groundwater flow
D.W. Emerson, K.J. Mills, M.S. Hallett, Univ. Sydney (AUS)

Borehole TV mapping in the vicinity of the Koongarra uranium ore deposit
K. Miyakawa, CRIEPI (JAP)

Hydrology

Hydrogeology of the Koongarra site
S.N. Davis, Univ. Arizona (USA)

Hydrological modelling of the Koongarra site
L.R. Townley, CSIRO (AUS)

Evidence for fracture flow and preliminary discrete fracture analysis of the Alligator Rivers Natural Analogue, Australia
J.L. Smoot, PNL (USA)

Solid and groundwater phases

The chemistry and isotopic composition of Koongarra groundwaters
T.E. Payne[1], R. Edis[1], A.L. Herczeg[2], K. Sekine[3] T.D. Waite[1], N. Yanase[3]
[1]ANSTO (AUS), [2]CSIRO (AUS), [3]JAERI (JAP)

A study of colloids in groundwaters at the Koongarra uranium deposit
T. Seo[1], R. Edis[2], T.E. Payne[2]
[1]PNC (JAP), [2]ANSTO (AUS)

Solid phase studies and Uranium distribution at Koongarra
R. Edis[1], A.J. Koppi[2], T.E. Payne[1], N. Yanase[3]
[1]ANSTO (AUS), [2]Univ. Sydney (AUS), [3]JAERI (JAP)

Uranium ore bodies as source terms for radionuclides: measurements and models
J. Fabryka-Martin, D.B. Curtis, LANL (USA)

Mineral alteration and sorption

Mineral Alteration and Uranium-Mineral Associations
T. Murakami, JAERI (JAP)

Uranium sorption modelling - A surface complexation approach
D. Waite[1], T.E. Payne[1], J.A. Davis[2], K. Sekine[3]
[1]ANSTO (AUS), [2]US GS (USA), [3]JAERI (JAP)

Geochemistry

Geochemical modelling of present-day groundwaters
D.A. Sverjensky, John Hopkins Univ. (USA)

Geochemical modelling of secondary uranium ore formation
D.A. Sverjensky, John Hopkins Univ. (USA)

Development of secondary uranium mineralogy at Koongarra: implications with respect to uncertainty in geochemical data
D.G. Bennett, D. Read, WS Atkins (UK)

Radionuclide transport

Transport modelling in the Koongarra weathered zone
C. Golian, ANSTO (AUS) and D.A. Lever, AEA (UK)

Linking models to performance assessments
D.A. Lever, Harwell (UK)

Application of scenario methodology in evaluation of the Koongarra analogue
K. Skagius, Kemakta and S. Wingefors, SKI (S)

Regulatory Objectives

The Alligator Rivers Analogue Project: A regulatory perspective
L.A. Kovach and G.F. Birchard, US-NRC (USA)

ALLIGATOR RIVERS ANALOGUE PROJECT: AN INTRODUCTION

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1. Introduction

Previous studies funded by the US Nuclear Regulatory Commission (USNRC) and the UK Department of the Environment (UKDoE) suggested the value of studying the Koongarra uranium ore deposit in the Northern Territory, Australia, as a natural analogue of a waste repository. Simple models of radionuclide migration in the dispersion fan had suggested that the time since its formation was of the order of 1-3 My.

The Alligator Rivers Analogue Project (ARAP) was sponsored by the OECD/NEA and funded by the Australian Nuclear Science and Technology Organisation (ANSTO), the Japan Atomic Energy Research Institute (JAERI), the Power Reactor and Nuclear Fuel Development Corporation of Japan (PNC), the Swedish Nuclear Fuel Inspectorate (SKI), the UKDoE and the USNRC. During the last two years of the Project, the US Department of Energy also provided financial support and the Central Research Institute for Electric Power Industry (CRIEPI) supported a borehole TV investigation of the site.

The work focussed on the geochemical alteration of the orebody, radionuclide migration in the weathered zone and the formation of the secondary uranium mineralisation dispersion fan in the Koongarra uranium deposit. Although other important features, such as the initial alteration of uraninite in the unweathered zone may provide other relevant analogue information on near-field alteration of fuel element disposal, these were omitted from the current study.

The overall aims of ARAP were:

- to contribute to the production of reliable and realistic models for radionuclide migration within geological environments relevant to the assessment of the safety of radioactive waste repositories, and
- to develop methods of validation of models using a combination of laboratory and field data associated with the Koongarra uranium deposit.

Initially, the research was aimed at characterising the host rock properties and mineralogy, investigating the hydrogeology, evaluating groundwater flow as an input to radionuclide transport modelling, and studying the geochemistry of water and rocks, including the geochemistry of fission products and transuranics. It was expected that a range of geochemical and radionuclide transport models would then be used, with the databases generated in the Project being used in both model development and testing.

Although the overall direction of the work was unchanged, as the Project developed it was necessary to put effort into areas that initially had not been considered. For example, hydrogeological field investigations showed that the site was more complex than initially thought, hence a major investigation of structures relevant to groundwater flow using geophysical techniques was undertaken, and the "simple" flow model that had been anticipated when setting up the Project was seen to be inappropriate.

A re-evaluation of the work was also needed following the early findings of the geochemical modelling study. The original aim was to model the formation of the secondary mineralisation: the uranyl phosphate zone. It was found, however, that the present-day groundwaters are strongly undersaturated with respect to uranium-bearing minerals and should be actively dissolving the uranyl phosphate zone. Hence, these groundwaters are not responsible for the formation of the (high grade) uranyl phosphate zone, but rather for its alteration and removal into the dispersion fan. In addition, modelling of the formation of the uranyl phosphate zone suggested that formation took place in an unsaturated zone, i.e. the uranyl phosphate may have formed in a more arid climate when the groundwater table was lower than at present.

This suggested that the work at Koongarra should be divided into two categories according to their relevance to present-day geochemical processes and to those that have operated in the geologic past. It was noted, however, that the geomorphological development of the site and variations in the climate during the past million years, with their effects on the site hydrology, would also need to be considered.

The geochemical modelling also stressed the importance of better understanding the mineralogy of the "non-commercial" dispersion zone down-flow of the uranyl phosphate, which had earlier been classed as a zone of dispersed uranium adsorbed on clays. Micro-minerals of uranyl phosphates are possibly present here, but had not been identified in the earlier work. A recent result of mineralogical studies has been the highly significant association of cerium and uranium in the weathered zone, a finding completely unexpected at the beginning of the Project, and one which merits further investigation.

2. Summary of findings

The work concentrated on investigating the original weathering of the Koongarra region, groundwater flow, the alteration of the host rock and primary uranium, rock/groundwater interactions including adsorption, desorption, nuclide transport (including the relative distribution of the uranium/thorium radionuclides in the multi-phase system), the continued development of the dispersion fan, and the in-situ production and mobility of long-lived fission products such as ^{99}Tc and ^{129}I and transuranic nuclides such as ^{239}Pu.

The experimental programs resulted in substantial drillcore and groundwater databases for all the distinctive geologic units in the vicinity of Koongarra. Hydrological data were also obtained in selected parts of the area from both field and laboratory measurement programs. Although the field pumping tests provide information on the present-day (not paleo) flow system, flow patterns derived from the measurements should agree with the results of the hydrochemistry sampling and provide some validation of the techniques used. These measurements were supported by in-ground borehole TV surveys and other surface geophysical measurements.

It was also possible during the Project to test various aspects of geochemical models and databases, such as radionuclide solubility/speciation calculations, the formation of the various zones of specific secondary uranium minerals and surface complexation modelling using the results of sorption of uranium to substrates from the leached and deposited zones in the weathered zone.

A number of independent methods of estimating how the system has evolved were considered, to give confidence that an adequate understanding of the radionuclide transport process has been gained. These included a study of the geomorphology and time evolution of the site, so that the times that key geological events took place and their effects on transport could be understood. A second method was by trying to gain an understanding of how elemental transport at the site, in which groundwater flow is taking place and has taken place in the past, is related to the geochemistry of key elements. This involved laboratory experiments similar to those employed in the characterisation of sites being considered for a waste repository, such as sorption measurements using intact samples. The last method made use of the distinctive information yielded by disequilibrium in the uranium series and provided data for calibration of site radionuclide transport and performance assessment models.

Much evidence was gathered to suggest that the development of the uranium dispersion fan at Koongarra must be considered in two stages. The first, during the development of the uranyl phosphate mineralisation, occurred in an unsaturated zone above the water table with atmospheric values for O_2 and CO_2 and this may have been in a more arid climate prior to the relatively recent monsoonal climate. A possible scenario for the second phase, the development of the low level uranium concentration dispersion fan, is that initially, oxidising waters reached the unweathered schist, where flow was governed by the macroscopic fracturing seen in the borehole television mapping. This led to weathering of the fracture walls and eventually to complete weathering of the rock to a mixture of clay minerals.

PERFORMANCE ASSESSMENT AND VALIDATION ASPECTS OF THE ALLIGATOR RIVERS ANALOGUE PROJECT

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ABSTRACT

1. Introduction

The role of natural analogues (NA) in validation of concepts and models for performance assessment of repositories has been discussed thoroughly during the past decade. The objective of this presentation is to describe the possible roles of the Alligator Rivers Analogue Project (ARAP) in this context. As a basis for the discussion a short description of the elements of a performance assessment is given first, followed by some general viewpoints on validation. The subsequent part on the validation issues studied within ARAP is by necessity superficial. Above all it is not the intent to preempt the the presentations and discussions that are to follow in this final ARAP workshop.

2. Elements of a performance assessment

In the licensing of a repository for radioactive waste the application is based on a performance assessment (PA). Specific requirements on a PA may be defined by the regulatory authorities, e.g. with regard to

- scope and comprehensiveness;
- priorities among the various safety issues and scenario selection;
- quality assurance and transparency;
- validation needs and strategy;
- acceptance criteria and PA methodologies.

A PA report will contain parts describing the site and the repository system, scenario identification and results from PA calculations. However, a description of the *background knowledge* is the central and largest part of all. It should be a comprehensive treatise of all concepts, models, assumptions and data needed for the quantitative analysis. Particular attention is to be paid to uncertainties and validation aspects.

A suitable outline of the background knowledge part is given below. For those subjects where the results of ARAP is believed to play a more or less significant role, this has been denoted by an asterisc (*).

Site evaluation*

- Structural geology
- Geohydrology
- Geochemistry
- Rock mechanics (*not* treated within ARAP)
- Site evolution

Radionuclide chemistry*

Transport phenomena*, e.g.:

- retardation mechanisms for dissolved species
- colloidal transport

Near-field effects

- Heat generation
- Alteration of host rock*, including formation and behavoiur of weathering/redox fronts
- Alteration of buffer/backfill*
- Container failures
- Radiolysis
- Dissolution of waste form*

Near-field transport

- Release of radionuclides from the waste form*
- Modelling of transport through buffer and near-field host rock

Far-field transport

- Advection-dispersion phenomena
- Modelling of far-field migration*

Biosphere transport and exposure

- Transport processes and modelling
- Calculations of doses and other safety indicators

Already from the above outline it is evident that the ARAP has covered many issues of importance in a PA.

3. Some general viewpoints on validation and natural analogues

It is nowadays recognized globally that the models employed in a performance assessment must be validated. The meaning of this statement more or less automatically depends on, (1), how we define a model, and (2), how we define validation. The answers to these to fundamental questions are not very simple, however.

Considering the first question, a model might be any of the following (and the list is most probably far from exhaustive):

- A theory: the description of a given process in physical and chemical terms
- A set of assumptions needed to transform the generally accepted physical or chemical principles into a relevant description of the actual situation.
- A description of system structure, e.g. a 3-D representation of the hydraulic permeability field of a site.
- A mathematical formulation of a process, including all necessary approximations and bounding and/or conservative assumptions.
- Thermodynamic data, which, in fact, include models for description of speciation and other chemical interactions.

{- A computer code.}

The last of these items, i.e. a computer code, is put within brackets just to point out that it is nonsense to speak about validation of codes. A code can *never* be validated in a general sense. It is only the concepts being built into the code and, above all, *how it is used* that can be validated.

The objectives and meaning of *validation* have been discussed at length during the last decade, e.g. within the INTRAVAL project [1] and the GEOVAL symposia [2, 3]. Attempts to define validation have been made with varying success. Examples of such definitions are [4]:

[A model is validated when ...]

- it "provides a good representation of the actual processes occuring in a real system" (IAEA);
- it is assured that it is "a correct representation of the process or system for which it is intended" (NRC).

The first of these is too soft and can in a polite way be applied to most attempts to describe reality. The NRC definition is more useful in pointing out that it is how the model is used that really counts. However, without a long list of qualifiers such definitions are not very illustrative. On the other hand, the recent discussions have come up with some, according to my view, important conclusions, e.g. that progress in science is based on attempts to *invalidate* theories or models, not to actively trying to validate them. Thus, a model can never be "valid" in the absolute sense - it is either *not valid* or *not invalid* [4]. Most important of all may be the now well-established notion by Kuhn [5, 6] that validity is based on *consensus* among experts.

All this might seem very disappointing considering all the efforts taken to validate performance assessment models. In fact, it turns out that no simple recipe is available how to show when a model is validated for a given licensing application. However, this is not the end of the story. The focus should be shifted from trying to validate in the absolute sense to what has actually been done in order to validate a model or the like. Such well-documented *validation strategies* will probably be required by the applicants in future licensing processes.

A strategy for validation must involve testing of a model in many applications as well as establishing its limits of applicability. The final step in a validation strategy is to show that the model is also applicable for its intended use, for the particular disposal concept and the given site.

Concerning the general role of natural analogues in validation most seems to have been said already [7, 8]. Thus I will turn directly to the role of ARAP in this context.

A particular feature of ARAP is that it involves many disciplines and studies on a wide range of scales, from studies of specific processes to evaluation of site evolution. Being such a multi-disciplinary and broad study the ARAP has given the opportunity both to look for new phenomena and for testing of "established" concepts. It should be noted that integrated NA studies like ARAP may also give experiences useful for site characterisation and evaluation. This might be thought of as validation in a more general sense: Are the methods we use for site evaluation relevant and applicable? Another important experience from ARAP is the necessity for PA-modellers to take active part in studies of NA. Their contribution is not only in focussing the work on relevant validation objectives, but they should also be able to transfer valuable experiences from PA methodologies into the evaluation of NA, e.g. by providing a systematic structuring of phenomena and in the consideration of uncertainties.

4. Contributions by ARAP

The following list of items where ARAP is believed to have contributed to an increased understanding of factors needed for a performance assessment is most probably incomplete. It is, however, an attempt to highlight the more important findings.

For site characterisation ARAP has shown

- the usefulness of a comprehensive and integrated geophysics programme, in particular for characterisation of sites for shallow (> 100 m) waste deposits;
- the importance of an integrated evaluation of geohydrology and geochemistry;
- the importance of an analysis of site evolution for understanding of observed phenomena on different scales;
- the possibilities offered by a detailed examination of the mineralogy of rocks and soils.

ARAP has contributed to a better understanding of a range of processes and their relevance, e.g.,

- the geochemistry of uranium, of potential value for modelling of spent fuel behaviour;
- the updating of thermodynamic data bases;
- the relevance of ferric oxide phases in retardation of uranium (and other trace elements);
- the improvement of thermodynamic sorption models, based on a unique combination of field studies and laboratory experiments.

The testing of models for radionuclide migration within ARAP turned out to be a harder task than expected, primarily due to the complexity of the site itself. However, the determination of timescales for formation of the fan of dispersed uranium has resulted in a range of results in reasonable agreement with other independent evidence. It has also been shown that even simple PA models are able to describe the present day distribution of uranium based on established transport processes and sets of reasonable parameter values.

5. Conclusion

As evident from the above, many aspects of a performance assessment have been covered within ARAP. This great variety of issues puts high demands on our ability to extract the relevant information, to make use of it and to present it to a wider audience.

And that's why we are here.

References

1 NEA/SKI, The International INTRAVAL Project, Phase 1 Summary Report. OECD, Paris 1992.

2 GEOVAL 1987, Proceedings. Swedish Nuclear Power Inspectorate, Stockholm 1988.

3 Validation of Geosphere Flow and Transport Models (GEOVAL), Proc. NEA/SKI symposium, Stockholm May 1990. OECD, Paris 1991.

4 Davis, P.A., and Goodrich, M.T., in ref 3, p 580.

5 Kuhn, T.: The Structure of Scientific Revolutions, 2nd ed. Chicago/London 1970.

6 Niederer, U., in ref 3, p 29.

7 McCombie, C., in Natural Analogue Working Group Report, 4th Meeting, Pitlochry June 1990. CEC, Luxembourg, EUR 13014-EN, p 19.

8 Chapman, N.A., High Level Radioactive Waste Management, Proc. 3rd Int. Conf., Las Vegas April 1992, ASN/ASCE 1992, p 1695.

SITE CHARACTERISATION WITH RESPECT TO GROUNDWATER FLOW

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ABSTRACT

The unmined but intensively drilled Koongarra uranium deposit in the Northern Territory of Australia has been studied to evaluate the processes and mechanisms involved in the alteration of the primary uranium mineralisation and to model the formation of the secondary uranium orezone and the dispersion fan. The work has resulted in solid phase and groundwater databases, and hydrological data from field and laboratory measurements. These are being used to test a range of geochemical, hydrological and transport models.

The Koongarra uranium deposit is situated in the Alligator Rivers Uranium Province of the Northern Territory of Australia, about 200 km east of Darwin. The uranium ore is located in steeply dipping, physically anisotropic, quartz chlorite Cahill Formation schists of lower Proterozoic age and is near the base of a prominent southeast-facing sandstone escarpment. The upper 25 m of the schist is weathered. An upper clayey zone of intense weathering separates deeper partly weathered schist from the overlying Quaternary sands, silts and ferricretes. Directly to the northwest of the ore deposit, a major reverse fault, the Koongarra Fault, has upfaulted the schist against the middle Proterozoic Kombolgie Sandstone. Hydraulic properties of the fault zone have not been tested directly, but were previously considered to be a barrier or partial barrier to lateral flow of groundwater. The site is currently undisturbed by mining, but the steel casings of over 100 exploratory drillholes proved to be a source of noise in magnetic and electrical surveys and the condition of the holes precluded the use of drillhole and cross-hole geophysics in the site studies.

A number of different approaches have been made to characterise the site and to try to understand: how groundwater has moved and is moving through the orezone region; the source of the water - natural recharge or flow across the fault; how the groundwater drains out of the site; whether fluid flow is through fractured or porous media or both; and in particular, how this has influenced the transport of uranium and the formation of a prominent dispersion fan.

Seasonal variations of water levels of about 60 wells at the site have been monitored for periods up to 7 years. The levels show groundwater recharge in the wet season and discharge in the rest of the year and have defined southerly hydraulic gradients. Twelve full-scale aquifer pumping tests have also been carried out. The resulting drawdown cones were elongated and generally oriented

subparallel with the Koongarra fault; the tests provided measurements of transmissivity, storativity and the anisotropy ratio in the unweathered bedrock.

In the geophysical, petrophysical and structural program the site was studied at regional, field (local), lithological unit and core sample scales by geophysical, geological, and, where appropriate, geotechnical techniques, to determine lithological and structural features relevant to ancient and current groundwater flow. The initial focus of the study was the determination of the physical properties of 306 cores samples from 29 drillholes penetrating the various units. Dry bulk density, apparent porosity, intrinsic permeability, galvanic (water saturated) resistivity, ultrasonic compressional wave velocity and magnetic susceptibility values were measured. Clear contrasts in mass properties were apparent in the host lithologies: the clayey (upper) weathered zone had very low density, very high porosity and very low permeability; the (lower) weathered and transition zones had low density, high porosity and low-to-moderate matrix permeabilities; the deeper unweathered schist zone had typical metasedimentary densities, low porosities and very low permeabilities. These data together with the electrical, acoustic and magnetic properties of the host and other lithologies provided useful controls on the geophysical field data interpretation. The mass property data were used in hydrological modelling where a combination of pumping test results indicated that in restricted areas the schists must be significantly fractured locally to impart permeabilities one or two orders of magnitude beyond the laboratory rock-matrix results. The geophysical data show that the loci of the inferred fractures are the foci for subsurface fluid flow in the unweathered bedrock to the south of the ore deposit.

Twelve kilometres of geophysical traverses were completed on the site. Magnetic, gravity, radiometric, spontaneous potential (SP), electrical resistivity and electromagnetic techniques were used to elicit lateral and vertical lithological information, structural trends and discontinuities, and to infer hydrogeological characteristics. The SP method, in particular, proved to be very informative; it was employed to map interpreted streaming potentials associated with subsurface water flow. A complete geophysical interpretation clearly shows the main drainage, lithological and structural features of the site. Fluid channelling is interpreted to arise mainly from the southeast part of the orebody and flow occurs to the south. Orebody drainage in the weathered zone is thought to have occurred mainly through the microfractured matrix and not through major fractures. This is in contrast to the unweathered zone hydrogeology which is fracture-controlled. Very shallow movement of dispersed radionuclides in the surface unconsolidated sands is indicated by radiometric (gamma ray) results.

Field structural studies were integrated with a borehole television (BTV) mapping program of a total length of 469 m carried out in 20 boreholes to identify geological features, such as the orientations of the schistosities, fracture densities, (*in-situ*) aperture widths and orientations. Locally, the results of the borehole television measurements showed directional trends in the schistosity similar to the geophysical trends and to the directions of the axes of the aquifer test drawdown cones and this probably indicates that the aquifer tests were dominated by fractures in the deeper unweathered zone. The major drainage feature to the south of the orezone was identified. Regionally, the BTV study identified the dominant schistosity and fracturing that can account for the main SE dispersion fan. It was observed in the geotechnical and core studies and in the BTV program that the site overall is moderately fractured with the graphitic schist lithologies exhibiting the highest fracture intensities.

The spatial contours of uranium concentration in the weathered zone show that although high grade uranium concentrations can be seen to have migrated in the weathered schist from the primary zone towards the southeast direction a more extensive dispersion fan of uranium (non-oregrade but above background levels) is detected towards the south of the orebody, about 300 m from the primary source. The distribution is clearly similar to that identified from the groundwater chemistry and the geophysical measurements, both of which suggest a present-day southerly direction of flow from the orezone.

The ARAP site characterisation studies appear to have successfully identified the major features controlling groundwater flow at Koongarra. The results should prove useful to workers studying contaminants and their dispersion in other weathered sites.

The subsurface zones sampled, the tabulated petrophysical results and a resultant model of Cahill Formation porosity and permeability distributions are presented in Tables 1, 2 and 3 respectively. Fracture permeability (which could not be sampled and laboratory tested) is thought to be important in the unweathered Cahill Formation (Table 3) and indirect evidence for this is provided by the interpreted lower in situ resistivities at depth, obtained from surface geophysics, compared to the quite high resistivities measured on small laboratory samples of fresh schist.

The physical and structural characterisation of the Koongarra site considered features from small to large scale.

The site is set in an area of major ancient faults transecting Precambrian units. The regional hydrogeological role, if any, of these faults has not been studied except for the reverse Koongarra Fault which flanks the site to the northwest. There is no direct evidence that this fault, its breccia or its related splay fractures have an enhanced permeability; indirect evidence suggests that waters stored in the upper jointed part of the Kombolgie Sandstone may access the Cahill Formation through local breaches in the fault zone.

The petrophysical study of the Cahill Formation established that: the heterogeneous weathered zone has a high porosity, an erratically distributed but overall moderate matrix permeability in the lower part and characteristic electrical resistivities in the medium range; the anisotropic bedrock has a low porosity, low matrix permeability and a high electrical resistivity that is quite directional, dependent in the graphitic units. Significant fluid movement in the unweathered Cahill can only be by fracture flow; fluid movement in the weathered zone operates mainly through the matrix permeability - there being no direct evidence of effective fracturing except in the lower partially weathered transitional zone.

A consideration of the geotechnical and BTV data and the field observations indicates fracturing over the entire site with the graphitic units having the most abundant fractures. These graphitic units have a characteristic complex resistivity signature. Fracturing tends to be discontinuous at the macro- and micro-scales but some zones in the unweathered bedrock exhibit continuity and enhanced permeability.

The geophysical and geological fieldwork (including borehole core logging) showed that the site itself is a folded, faulted, variably fractured Precambrian psammitic and pelitic schist sequence with a quasi-horizontal weathered zone superimposed on the steeply dipping rock fabric. The site is flanked by a high resistivity younger sandstone unit to the northwest and by a magnetic amphibolite/ferricrete sequence to the far southeast. The data interpretations elicited the essential structural and broad lithological elements. Gravity, magnetic and electrical laboratory and field studies confirmed a broad folded fractured sequence of dipping layered host rocks, weathered in their upper parts and trending in a southwest-northeast direction. Qualitatively interpreted anomalies indicated the trend of the main groundwater movement to the south where dolomites are thought to act as a sink. These drainage features have SP, resistivity and radiometric expression. The roles of the Kombolgie Sandstone as a source of water and the Koongarra Fault as a barrier or otherwise were not established owing to the difficulty of geophysical access over the site's escarpment.

TABLE 1

PETROPHYSICAL SAMPLING ZONES

ZONE		Lithology	Number of Samples
A		highly weathered schists of the Lower Proterozoic Cahill Formation	(116)
	A1*	M and W series holes, tube samples	64
	A2**	diamond drill hole samples	52
B		lower weathered 'transitional' zone of Cahill Formation	16
C		unweathered schists of the Cahill Formation	(129)
	C1	quartz-mica-chlorite schists	111
	C1a	silicified schists	4
	C2	graphitic schists	6
	C3	amphibolites	8
D		Middle Proterozoic Kombolgie Sandstone (and some reverse fault breccia samples)	42
E		Quaternary ferricretes, lateritic surficial deposits (magnetic tests only)	3
* Zone A1 sampling was carried out by cable tool drilling in the late eighties, and the relatively fresh material is more argillaceous than the Zone A2 DDH materials from the seventies drilling program, which also provided the Zone B, C, D materials. **Zone A2 sampling favoured the more cohesive, consolidated materials ; the sampled materials may not be as representative as A1.			**Total : 306**

TABLE 2

SUMMARY OF PHYSICAL PROPERTY RESULTS

ZONE		Bulk Density g/cc *	Porosity % **	Permeability md ***	Resistivity Ωm	Velocity m/s	Mag k 10^-6 cgs ≈ SI 10^-5
A1	av	1.95	34.0	1147	53	1582	21
	r	1.60 - 2.43	16.4 - 40.5	1 - 8708 (μd)	14 - 177	779 - 2202	12 - 62
(Weath.	n	56	6	40	16	23	33
M, W)	s	0.21		1785	42	425	14
A2	av	2.21	16.1	61.2	127	2283	30
	r	1.62 - 2.55	4.4 - 38.4	2.0 - 536.8	16 - 719	1163 - 3433	13 - 50
(Weath.	n	44	33	35	19	19	33
DDH)	s	0.20	4.1	98.3	156	699	6
B	av	2.48	7.7	5.2	112	2963	47
	r	2.14 - 2.79	0.4 - 16.3	0.8 - 39.9	46 - 208	1838 - 5105	23 - 63
(Lower	n	15	12	10	6	7	11
Weath.)	s	0.21	5.6	12.2			12
C1	av	2.72	1.8	0.3	5943	4894	47
	r	2.07 - 2.98	<0.1 - 7.8	<0.1 - 2.0	50 - 122370	2895 - 6125	11 - 104
(Qtz - chl	n	105	103	95	57	32	76
mica sch.)	s	0.09	1.5	0.4	17624	1088	20
C1(a)	av	2.63	0.6	0.2	32391	5726	4
	r	2.60 - 2.64	0.3 - 1.1	<0.1 - 0.3	4020 - 99060		<1 - 7
(silic.)	n	4	4	4	4	1	4
C2	av	2.70	0.8	0.6	736	4660	36
	r	2.65 - 2.76	0.2 - 1.1	0.5 - 0.7	31 - 3230	3947 - 5079	33 - 39
(Graphitic sch.)	n	6	6	2	6	3	2
C3	av	2.97	0.7	0.2	117887	5444	145
	r	2.88 - 3.06	0.1 - 2.2	<0.1 - 0.5	8333 - 517503	4921 - 6554	76 - 387
(Amphib.)	n	8	8	8	7	4	7
D	av	2.61	2.1	0.9	6823	4466	3
	r	2.40 - 2.69	0.1 - 8.2	<0.1 - 12.2	252 - 75834	2516 - 6105	<1 - 12
(Komb. Ss.)	n	39	39	38	30	15	28
	s	0.06	2.0	1.0	14992	966	3

* For A1 wet bulk densities are cited; all other densities are dry bulk.

** Porosities are apparent except for A1, where total porosities are cited.

*** A1 water permeabilities are in microdarcys, all others are air permeabilities in millidarcys.

av : mean value ; r : range ; n : number of samples ; s : standard deviation.

Resistivities measured galvanically at 1 kHz on saturated specimens.

P-wave velocities measured at 500 kHz

TABLE 3

SCHEMATIC GENERALISED PERMEABILITY MODEL OF THE CAHILL FORMATION

Depth (m)	Cahill Fm Material	Fabric	Approx Wet bulk Density g/cc	Approx Apparent Porosity %	Est. Effective Porosity %	Matrix Permeability	Fracture Permeability
	I sands, scree		2.0	35	30	very high, several darcys	-
5_ water	II extremely weathered relatively argillaceous	obliterated	2.0	9 (total porosity 34)		very low ~1md (isotropic?)	very low
table 10_ 15_	III highly weathered and altered	relic	2.2	10	2	low ~1 - 10md (slightly anisotropic)	low (filled fractures)
20_	IV moderately weathered (disaggregated)	preserved	2.5	20	5	moderate ~50md tends to increase to ~100md with depth (anisotropic)	low (filled fractures)
25_	V incipiently weathered	intact	2.6	8	5	low, 5md (anisotropic)	inferred moderate 10 - 200md (anisotropic)
	VI fresh schist (tight matrix, anisotropic, variably fractured)	foliation intact	2.7	1	0 (slight, if fractured)	very low 0.5md (anisotropic)	ranges from low (few md) to high (several darcys) depending on location, lithology, depth and direction (anisotropic)
	Layers I, IV, V are aquifers Layers II and III are aquitards Layer VI is an aquiclude unless significantly fractured in the 25 - 100m depth range			Effective porosity is equivalent to the specific yield		1 darcy = 0.84m/d ; = 10^-5m/s = 10^-3cm/s 1md = 10^-3 darcys	

BOREHOLE TV MAPPING IN THE VICINITY OF THE KOONGARRA URANIUM ORE DEPOSIT

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ABSTRACT

The logging of Borehole TV (BTV) has the capability to map the in situ orientations of fractures and rock fabric and to measure aperture width of fractures, features which are difficult to determine from the core logging. The BTV logging was applied to the investigation of the Koongarra site for better understanding structural features and characterizing the distribution of fractures. The principal results from this study are as follows. A site scale synform-antiform fold in the schistosity, plunging shallow angle to the east was identified. The parallelism between the most common orientation of fractures and the schistosity in each individual hole indicates that the schistosity has a strong influence on fracture orientation. The agreement between the trend of fractures and the shape of draw-down cones resulting from pumping tests suggests that the direction of groundwater flow is dependent on the fracture trend pattern.

1. Introduction

Borehole TV (BTV) is well logging equipment which contains a prove with a built-in miniature TV camera and a compass to observe the inside wall of boreholes. BTV logging has the capability to map the in situ orientations of fractures, faults, rock fabric, and lithological boundaries, and aperture width of fractures which are difficult to determine from core logging.

The aims of the BTV investigation were to map and characterise fractures in boreholes in the vicinity of the Koongarra uranium ore deposit. The logging also provided geological, as well as structural data; it permitted interference to be drawn on groundwater flow.

Work presented in this report represents a part of geophysical and petrophysical studies of Alligator Rivers Analogue Project (Emarson et al., 1992).

2. Equipment and application

The Koongarra study used the RAAX BIPS-300 system, which is an expanding type BTV(Kamewada et al., 1990). This BTV prove contains a conical mirror to reflect the whole image of surrounding borehole wall to a built-in TV camera. This image is converted into a 360 degree expanding image, which is shown on a VDU monitor and digitally recorded onto magnetic tape in the field.

The BTV logging program was carried out 20 boreholes around the southwest part of the ore deposit (figure 1). As a result of the BTV logging, 931 fractures and 432 schistosity were surveyed in logging a total of 469m. The lithologies of logged boreholes are the unweathered and weathered Cahill Formation schists of the lower Proterozoic age, the Kombolgie Sandstone of the middle Proterozoic age and the breccia of the Koongarra fault.

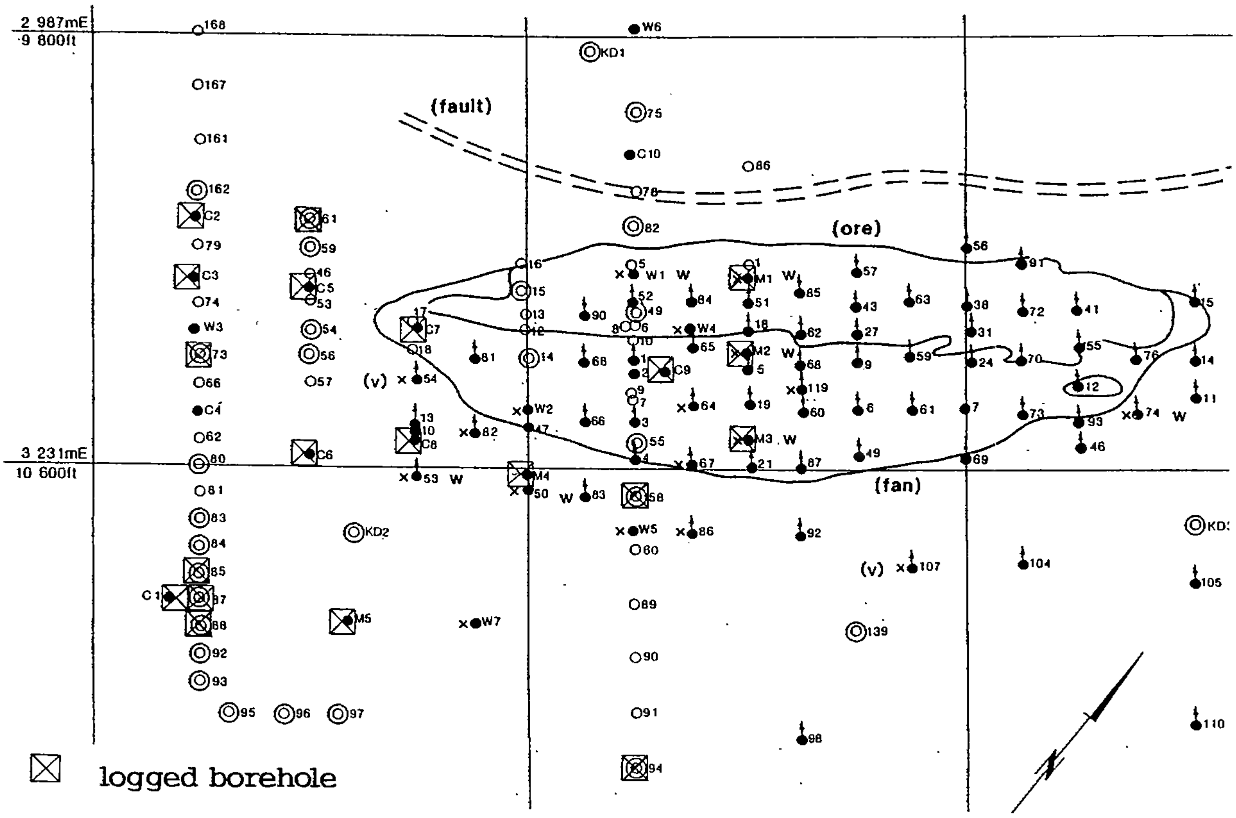

Figure 1 Location map of logged boreholes by BTV

3. Results and discussions

3.1 Schistosity orientations

The orientation of the schistosity was measured every metre in logged hole, and the result of this measurement revealed the structure of the Koongarra site. Figure 2 shows contoured diagram of poles of all 432 schistosity planes measured in the 20 holes. The shape of contours appears along a great circle, the direction of which is north-south strike and steep east dip on the diagram, and it suggests that the schistosity planes have been cylindroidally folded about a axis shallow plunging to the east. The orientations of the schistosity in each separate hole are generally uniform, while the mean orientation of the schistosity varies from hole to hole in a systematic way, therefore the fold in figure 2 indicates a site scale structure. This fold consisting of a site scale synform-antiform pair can be identified in figure 3.

3.2 Fracture densities and apertures

The overall fracture density is 2.0/m, and the aggregate aperture width is 0.7mm/m. In the unweathered lithologies, excluding the reverse fault breccia, the graphite muscovite quartz schist has the highest fracture density (4.0/m) and the most open apertures(2.0mm/m), however it is not obvious that the data is the typical fracture density and aperture of this lithology because only a short measurement interval was available. On the other hand, the muscovite quartz feldspar schist and the Kombolgie Sandstone have lower fracture densities (1.0 and 1.5/m) and tighter apertures (0.5 and 0.4 mm/m) than the others. The other lithologies show fracture densities ranging from 2.0/m to 2.5/m, and widths of aperture averaging around 1.0/mm.

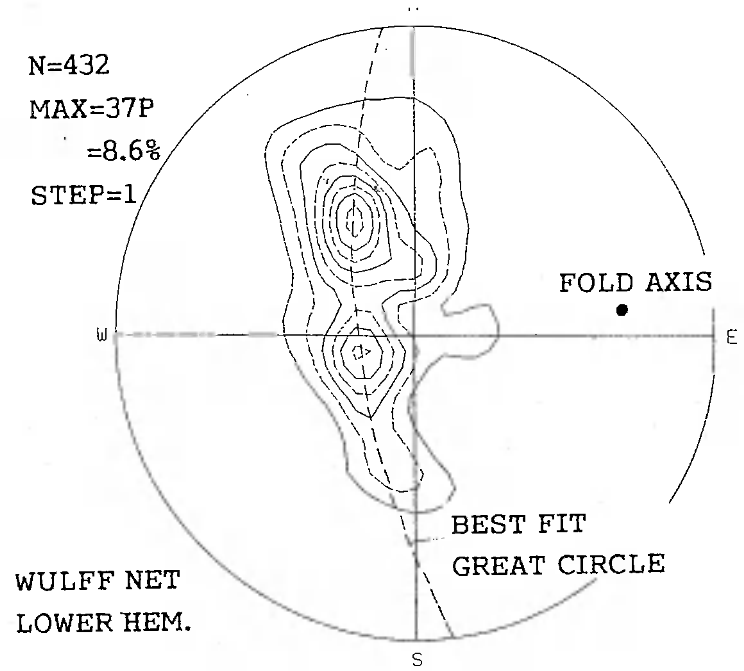

Figure 2 Contoured diagram of poles of all schistosity planes measured in 20 holes

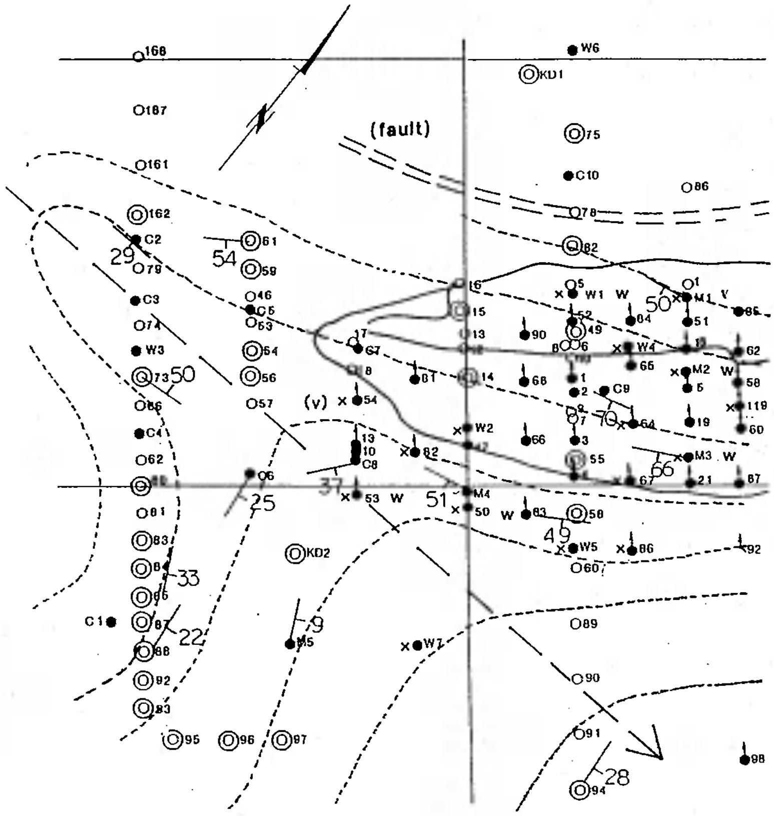

Figure 3 Site scale fold in the schistosity fabric

Fracture density appears to be more influenced by location than by lithology. The average fracture densities measured from each hole indicates that the area located south of the orebody is lower fracture densities than others (figure 4). This variation of fracture densities agrees with the shape of the draw-down cones resulting from pumping tests (Norris 1989; Marley 1990; refer to figure 7), and it suggests the variation of fracture densities may affect the direction of groundwater flow.

3.3 Fracture orientations and distribution

Figure 5 shows the contoured diagram of poles of all the measured fracture planes. The maximum concentration in the northwest quadrant indicates that the predominant orientation of fractures is the northeast strike and the southeast dip, and this orientation is subparallel to the Koongarra fault.

Other significant features in fracture orientations is the relationship with the schistosity. As compared with the schistosity orientation in each hole, one of prominent orientations of fractures is coincident with that of schistosity (figure 6). This parallelism indicates the schistosity has a strong influence on fracture orientation.

Rose diagrams representing fracture trend in each hole, presented in figure 7, show a trend pattern consisting of two distinct trends in the surveyed area. One trend is northeast-southwest at the western end of the orebody; the other trend is north-south at the south of the orebody. This trend pattern generally agrees with the shape of draw-down cones resulting from pumping tests, and it appears that the direction of groundwater flow is depended on the trend pattern.

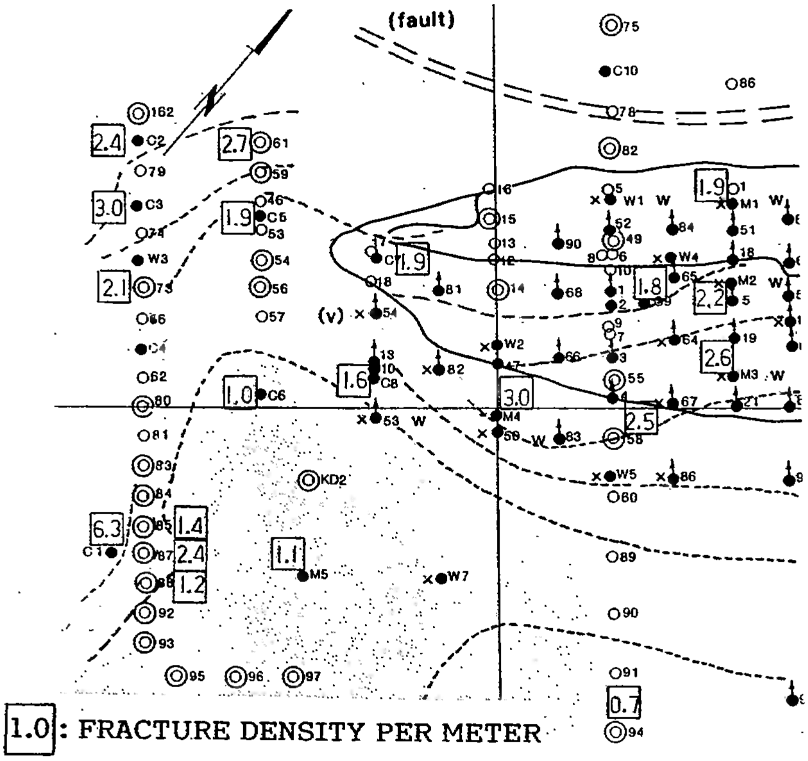

Figure 4 Average fracture density in each hole
(shaded area; below 1.0/m)

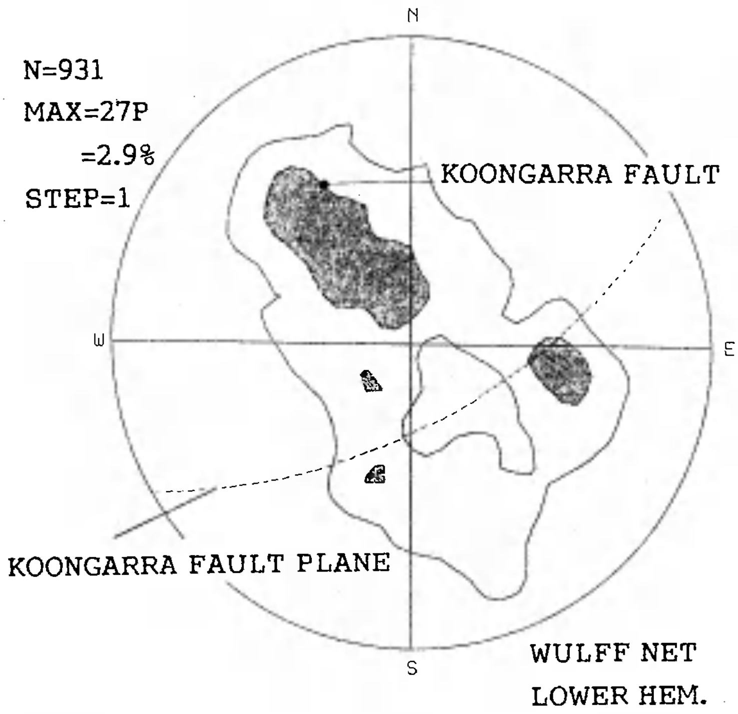

Figure 5 Contoured diagram of poles of all fracture planes measured in 20 holes

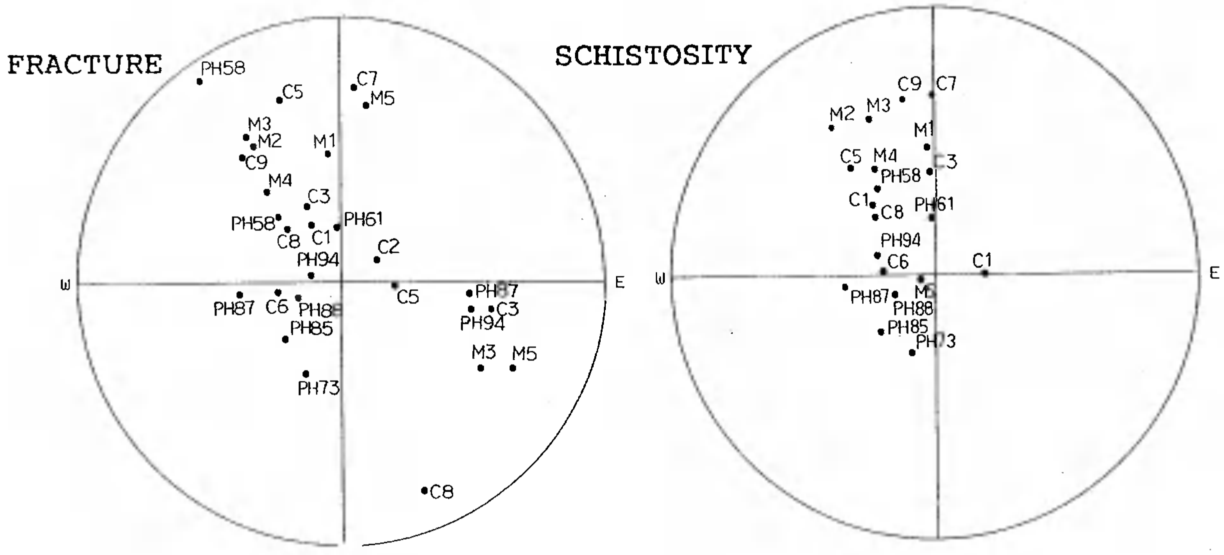

Figure 6 Prominent orientations of the fracture and the schistosity in each hole

4. Conclusions

This study was carried out based on orientations of schistosity and fractures, fracture densities and width of apertures which were surveyed by the BTV logging. The result of this study mainly contributed to better understanding structural features and characterizing fracture distribution in the vicinity of the Koongarra uranium deposit.

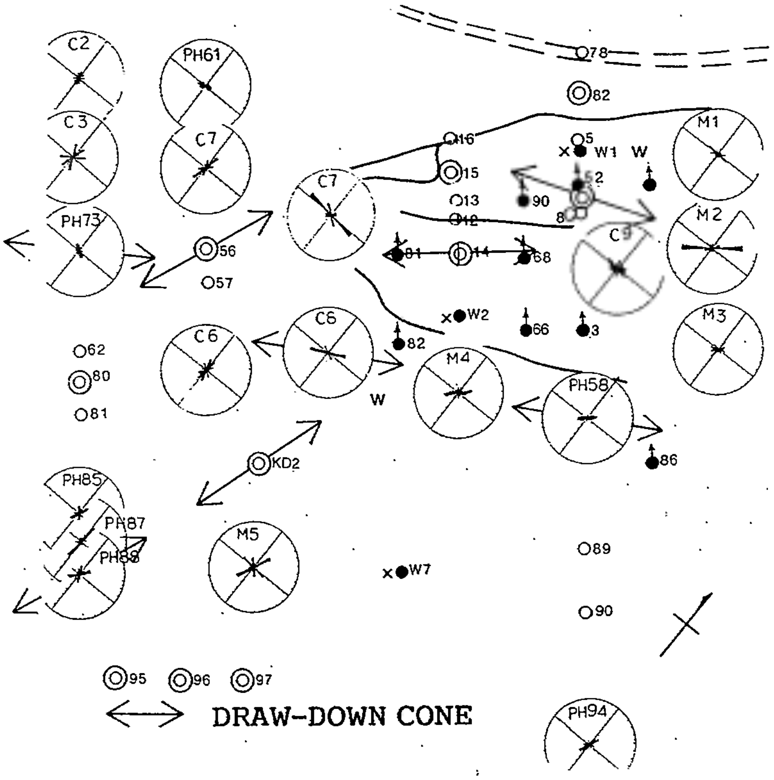

Figure 7 Rose diagrams of the fracture trends and the draw-down cones resulting from pumping tests (Norris 1989; Marley 1990) in individual boreholes

A site scale synform-antiform fold structure in the schistosity, plunging shallow angle to the east, was identified in this survey. One of prominent fracture orientations in each hole is generally parallel to the schistosity orientation. This parallelism indicates the schistosity has a strong influence on fracture orientation.

The agreement between the site scale trend of fractures and the shape of draw-down cones resulting from pumping test suggests that the direction of groundwater flow is dependent on the fracture trend pattern. A sub-area of low density, located in south of the orebody, may also affect the draw-down cone shape and the groundwater flow direction.

References

- Emarson, D.W., Mills, K.J., Miyakawa, K., Hallett, M.S., Cao, L.Q. (1992), Geophysics, petrophysics and structure, Alligator Rivers Analogue Project ,Final Report Vol.4 - *in print*
- Kamewada, S., Gi, H.S., Taniguchi ,S., Yoneda, H. (1990) Application of borehole image processing system to survey of tunnel, Rock Joint, Barton and Stephasson(Eds.), Balkma, Rotterdam,pp 51-57
- Marley, R. D., (1990), Hydrogeologic field study of the Koongarra uranium deposit in the Northern Territory of Australia, Master of Science Thesis, The University of Arizona, 115p.
- Norris, J.R., (1989). Preliminary hydraulic characterization of fractured aquifer at the Koongarra Uranium Deposit, Northern Territory, Australia, Master of Science Thesis, The University of Arizona

HYDROGEOLOGY OF THE KOONGARRA SITE

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ABSTRACT

Water-level, aquifer-test, and slug-test data indicate that the Koongarra uranium deposit is within a low-permeability, semiconfined, fractured schist. Water levels demonstrate semidurnal and diurnal fluctuations related to earth tides and evapotranspiration. Hydraulic test data were analyzed using homogeneous isotropic and homogeneous anisotropic models which allowed parameter estimation for subregions of the study area. The direction of maximum hydraulic conductivity is subparallel to lithologic layering and the Koongarra fault. Slug tests reveal regions controlled by low storate but highly conductive fractures and isolated regions of low conductivity. Hydraulic connection of the surficial sands with the underlying partly weathered schist is dependent on the continuity and clay content of the low-permeability residual clays on top of the schist.

Environmental isotopes and helium in the groundwater indicate that it has been isolated from the atmosphere for longer than 40 years and possibly several thousand years in some locations. Water-budget calculations indicate the majority of recharge must be from direct infiltration through the weathered profile to account for the calculated groundwater fluxes. Large amounts of deep subterranean recharge moving from the Kombolgie Formation through the Koongarra fault and thence into the Cahill aquifer appear unlikely. Concentrated recharge, nevertheless, seems to take place at some localities just downgradient from the fault. This recharge is from overland runoff from the uplands to the northwest of the ore deposits. Most of the water moving past downgradient wells does not originate in the ore deposit, and models which show unmodified streamtubes originating in the ore deposits and extending to Koongarra Creek are not realistic.

1. **Historical background**

The hydrogeology of the Koongarra Site was interpreted primarily from long-term hydrographs, water-level maps, water injection tests, aquifer pumping tests, logs of bore holes, and chemical analyses of groundwater samples. Data have been collected over a 21-year period starting with test drilling in 1970. The first intensive period of hydrogeologic investigations was from 1978 through 1981 and was related to anticipated exploitation of uranium ore at Koongarra. The second period was from 1986 through 1991 and was related to the international Alligator Rivers Analogue Project under the direction of the Australian Nuclear Science and Technology Organisation. From a hydrologic viewpoint, the geologic materials at Koongarra can be divided into five groups which are described below.

2. Hydrogeologic units

2.1 Kombolgie Formation, a late Precambrian sandstone with low to moderate porosity and low hydraulic conductivity

Some zones of greater conductivity are probably present along fractures that traverse the sandstone. This unit borders the site to the northwest and underlies the Mount Brockman uplands to the north.

2.2 Surficial sands, silts, and clays which cover most of the site and extend from the present-day land surface to depths of 0.5 to 9 m

The sands of the surficial sediments are probably the most permeable of the geologic materials. The thickness and nature of the surficial sediments have been determined by 234 backhoe pits and 73 auger holes. During the dry part of the year, most of the surficial materials are not saturated.

2.3 Residual clay which grades downward into moderately weathered Cahill schists

The clay has a thickness which varies from about 2 to 20 m. It is porous but has, in general, a very low hydraulic conductivity.

2.4 Partly weathered and fractured Cahill schist

Under present climatic conditions, this zone is saturated throughout the year and constitutes an aquifer which is about 10 to more than 30 m thick, depending on the location considered. The aquifer, however, is extremely heterogeneous and in many locations is dominated by fracture flow which imparts an apparent anisotropy to the flow field.

2.5 Unweathered Cahill schist in which water is generally semistatic owing to very low porosities and permeabilities

Although some fracture flow without doubt exists at depths in excess of 1.0 km, the bulk of the groundwater flow in the Cahill schist is probably at depths of less than 100 m. Thus, somewhat arbitrarily, the dense unweathered and nonpermeable schist is assumed to start at depths of about 100 m below the base of the residual clay.

3. Hydrographs

Long-term hydrographs of water levels in observation wells show seasonal fluctuations which range from about 1 m to a maximum of about 5 m. Highest water levels in the observations wells are reached about two months after the period of maximum rainfall which is normally January and February. This delayed reaction probably related to the length of time which is needed for the near-surface sediments and rocks to reach field capacity with respect to moisture. Water overflowed the tops of casings on a number of observation wells at the end of the rainy season. This suggests that the groundwater is partly confined in much of the area investigated.

4. Groundwater flow

Water-level maps show that groundwater generally flows from the base of the uplands in the north to Koongarra Creek in the south. The orientation and spacing of lines of equal hydraulic head vary locally in response to areas of rechange and discharge as well as to lateral variations in aquifer properties. Natural hydraulic gradients in the schist vary from a minimum of roughly 0.005 to a maximum of about 0.05. A groundwater mound with an elevation of about 5 m above adjacent areas is present along the Koongarra fault in the northeastern part of the study area. This mound may reflect a zone of maximum recharge which is near a known area of surface seepage of water that persists even during the dry season.

5. Injection tests

Various types of water injection tests were made on numerous bore holes. These short-term tests measured hydraulic properties of rocks close to the bore holes. Results indicated a wide variation in conductivities of the subsurface materials. A total of 45 slug tests of water-bearing zones were made in 1989 and suggested transmissivity values which varied from 3 x 10^{-5} m^2/day to 43.07 m^2/day, with a median value of 2.07 m^2/day. The depth intervals tested varied, but generally involved about 5 m of hole. Hydraulic conductivities, therefore, were, very roughly, 0.4 m/day for the water-bearing zones which were tested. In another set of 50 water-pressure tests made in 1979, hydraulic conductivities measured varied between 7.5 x 10^{-4} and 0.47 m/day and had a geometric mean of 1.3 x 10^{-2} m/day. This significant difference is due to the fact that the 45 slug tests were made in zones of known permeability and the earlier 50 water-pressure tests were made in the more weathered schist which did not generally transmit much water.

6. Aquifer tests

Long-term aquifer tests were completed at various times during 1980, 1987, 1988, and 1989 using 13 different test holes for the well which was pumped. Most of the holes were pumped for more than 1,000 minutes, and the hydraulic response of the aquifer was measured in 3 to 10 different observation holes. All drawdown cones which were produced were elongated in general north-east-southwest to north-south directions. Three of the aquifer tests showed highly localized drawdowns in a narrow band suggesting strongly that most of the groundwater flowing into the pumped well was transmitted through well-defined fractures. Transmissivities determined by the tests varied from 0.22 to 66.8 m^2/day with a median value of 26 m^2/day. Most water was pumped from the partly weathered Cahill schist. If the thickness of the water-bearing zone is assumed to be 40 m, than an average hydraulic conductivity of 0.65 m/day is suggested.

7. Chemical analyses

Chemical analyses indicate a moderately uniform water composition at any given locality. Small changes in pH, temperature, and specific electrical conductivity, however, during aquifer tests indicate a complex hydraulic system which has a variable response to pumping as a function of time. Furthermore, low concentrations of tritium and carbon-14 together with high concentrations of dissolved helium in the groundwater all suggest strongly that semistatic bodies of groundwater are present within other zones of more active circulation. In the western part of the site, considerably more dissolved solids in the form of bicarbonate and magnesium ions reflect the presence of dolomite and associated high magnesium rocks.

8. Groundwater recharge and discharge

Recharge of the groundwater appears to be primarily from the infiltration of seasonal surface runoff from the Mount Brockman uplands together with considerable direct infiltration of rainfall. Discharge of groundwater takes place in three distinct ways. During times of high water levels, groundwater seeps directly into Koongarra Creek or into riparian seasonal wetlands. Also during times of high water levels, direct soil evaporation will account for a large part of the groundwater loss. Transpiration from vegetation is significant during the entire year and is the dominant avenue of discharge during the late part of the dry season after Koongarra Creek has ceased to flow. A slow recession of groundwater levels during this season reflects use of water by plants.

9. Direction of groundwater movement

During the wet season when groundwater saturates the surficial sands, the water tends to flow through the zones of maximum sand thicknesses. These zones are not always oriented in the direction of the maximum hydraulic gradient. Thus, the direction of the gradient will not necessarily determine the direction of the maximum groundwater velocity. During the dry season, some of the thicker sands will still be saturated, but a greater portion of the groundwater flow will be through the partly weathered and fractured Cahill schist. The apparent anisotropy in these rocks should bend the groundwater flowlines in a more-or-less north-south direction which would not correspond with the direction of the maximum groundwater gradient.

Much of the groundwater is undoubtedly discharged through the surficial sands during the wet season. The total groundwater moving below the residual clay in the upper part of the weathered schist may only be a small fraction of the combined wet-weather flow through the weathered schist and the sand. Chemical evidence proves that the distal, downgradient wells do not intercept a significant amount of water that has originated from the ore bodies. In fact, models which show unmodified streamtubes originating in the ore deposits and extending to Koongarra Creek cannot be realistic.

HYDROGEOLOGICAL MODELLING OF THE KOONGARRA SITE

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Abstract

This paper summarises attempts by a number of researchers to predict rates and directions of groundwater movement near the No.1 Orebody at Koongarra under present-day climatic conditions. Rather than using a single model to explain observations, a hierarchy of different existing models was used. These included two-dimensional models in vertical section, three-dimensional models, one- and two-dimensional aquifer flow models in plan, a fracture flow model and an inverse model. Different models explained or at least illustrated different features of the flow system, but there is still much uncertainty about the source of groundwater and its rate of movement through the orebody and the dispersion fan.

1. Introduction

The secondary dispersion fan of the No.1 Orebody at Koongarra is believed to be the result of groundwater transport and chemical processes over long periods of time. A major goal of the Alligator Rivers Analogue Project (ARAP) was therefore to understand the hydrogeology of the site — both directly, through hydrogeological field studies, and indirectly, through the use of geophysics, petrophysics, water chemistry and rock chemistry as indicators of past and present hydrogeological processes. There was also a major effort to use *existing* hydrogeological flow models to interpret available data and to predict rates and directions of groundwater flow.

This paper summarises attempts by a number of researchers to predict groundwater movement near the orebody [1]. The goal of hydrogeological modelling was to use available data, both physical and chemical, quantitative and qualitative, to predict rates and directions of movement under present-day hydrogeological and climatic conditions. Paleohydrology was specifically excluded, mainly because it was perceived that there would not be enough data to make significant progress in that direction.

This paper describes a hierarchy of models applied by researchers working in various locations worldwide. The hydrogeology of the Koongarra site is complex and difficult to model because (i) subsurface flow is a miniscule component of the overall water balance of the region, (ii) significant flow occurs as fracture flow rather than as porous media flow, (iii) the region is extremely heterogeneous, with a wide range of material types and fracturing on several scales, (iv) many of the available hydrogeological measurements were collected from exploration holes, which were constructed to determine the extent of the uranium orebodies rather than specifically to understand groundwater flow, and (v) observations are concentrated near the No.1 Orebody, hence there is limited knowledge about the regional geology and about boundary conditions for regional groundwater flow.

All but one of the models are porous media models, which assume that the fractured medium acts as a continuum and that flow is governed by Darcy's Law with some effective or average hydraulic conductivity. One model is a fracture flow model, based on generating a finite number of discrete fractures with random orientations. Another model is an inverse model, which attempts to utilise data from aquifer tests to estimate heterogeneous transmissivities and aquifer storativities in a number of zones.

The hierarchy of models includes models with varying dimensionality and models which are both steady and transient. Each type of model is able to describe at least some features of the Koongarra site.

2. Two-dimensional modelling in vertical section

The first models actually applied were two-dimensional models in vertical section (Figure 1). Models developed by D.A. Lever, S.T. Morris and J.P. Raffensperger [1] showed that if a water table exists beneath the Mount Brockman Massif, flow from Mount Brockman can indeed occur towards the Cahill Schist, with flows moving generally upwards from the Koongarra Fault through the primary orebody towards the land surface. Details of the flow pattern and velocities near the orebody are quite sensitive to the assumed hydraulic conductivity of the fault zone.

The early cross-sectional models assumed a groundwater divide beneath Mount Brockman and a no-flow boundary beneath Koongarra Creek, which acts as the final discharge point for the flow system. In order to check these assumptions, another two-dimensional cross-sectional model was set up on a regional scale. This model, developed by M.G. Trefry and L.R. Townley [1], assumed boundaries on the Arnhem Land Plateau and on the far side of Mount Brockman, and also included the Sawcut Fault as another major fault system. Sensitivity studies showed that it is very likely that a local flow system exists as originally hypothesised (Figure 2).

One interesting aspect of this modelling was that it highlighted the problems which can occur when the shape of the water table is used to provide a fixed head boundary condition at the upper boundary of a two-dimensional vertical section. A given water table shape implies a particular spatial distribution of recharge and discharge across the water table. Changing the distribution of hydraulic conductivities or values of anisotropy has a significant effect on the implied distribution of recharge. The debate on this topic was initiated by Davis [2] but is often ignored. The same issues are relevant in three-dimensional modelling. It is generally better to prescribe the distribution of recharge and discharge at the upper boundary, but this was not possible using models available to researchers during this Project.

3. Three-dimensional modelling

The next models developed were three-dimensional models of steady groundwater flow. Two separate models of a region 3 km square were set up by M.G. Trefry and L.R. Townley [1]. The purpose of these models was to demonstrate that with similar assumptions to those used in two-dimensional vertical sections, flow directions could deviate significantly from a plane. By including a highly conductive zone to represent the Koongarra Fault, it was found that significant flows could occur horizontally along the Fault, at right angles to the plane previously modelled as a two-dimensional vertical section. With a less conductive Fault, a streamtube was found to flow from Mount Brockman through the Fault and towards the orebody (Figure 3).

A third three-dimensional model was developed independently, by Y. Tanaka, K. Miyakawa and M. Kawanishi [1], at a much more local scale. This model specified a completely general three-dimensional anisotropy tensor for every element in a finite element grid. Conductivities were assume to be anisotropic within the unweathered Cahill Schist, and isotropic elsewhere. Values were specified using a nearest-neighbour approach, i.e. values were assigned using the nearest location where Borehole TV measurements had allowed determination of the orientations of planes of schistosity. Just as the previous models showed that three-dimensional heterogeneity affects the details of a three-dimensional flow pattern, this model illustrated the effects of three-dimensional anisotropy.

4. Modelling in plan

Classical aquifer testing uses the concept of transmissivity in its interpretation of the response of groundwater levels to pumping. The concept of an aquifer, a layer transmitting significant quantities of water in a mainly horizontal direction, seems hard to accept in an environment as heterogeneous as that at Koongarra. But modelling of aquifers both in one dimension and two-dimensionally in plan contributed significantly to our overall understanding of the site. In retrospect, more effort should have been placed on this type of modelling, because there are many indications that the large-scale response of groundwater near the orebody is well-described by models of an effectively horizontal aquifer.

A one-dimensional model with three layers (often described as a quasi two-dimensional model) was applied by A.D. Barr and L.R. Townley [1] to flow between the Fault and Koongarra Creek. Being a transient model, this model was able to show that reverse flows can indeed occur backwards towards the Fault, as was observed in the field in December 1990, at the end of a dry season following a relatively dry wet season. But reverse flows can only occur in a one-dimensional flow system if there is distributed recharge over the orebody, as well as a mechanism for the Fault, or a region near the Fault, to remove water from the simulated one-dimensional section. The model showed clearly that the response of the three-layered system, consisting of a highly weathered clayey zone, a fractured transmissive zone and a less conductive lower schist zone, is governed mainly by the transmissivity and storage coefficient of the middle layer. The storage coefficient of the uppermost layer has little effect.

A.D. Barr and L.R. Townley [1] also developed a two-dimensional model in plan (Figure 4). This model used a description of anisotropy in transmissivity to show that reverse flows can also occur even without a conducting Fault. Borehole TV data were interpreted to indicate a shift in the principal direction of anisotropy from northeast-southwest near the Fault to north-south to the southeast of the orebody. Because Borehole TV data were available for only a small region very close to the orebody, the assumed distribution of anisotropy was a bold extrapolation from the data. Nevertheless, the model was useful because it demonstrated the effect of a number of assumptions on seasonal dynamics in groundwater levels, and reinforced conclusions about data requirements for studies of this kind in the future.

Because the three-layered one-dimensional model showed that the middle layer was the most important, the two-dimensional model can be considered to be a model of that layer. The properties of the transmissive layer control and explain the variations in observed water levels, and in a sense the water balance of the region. On the other hand, groundwater migrates in every layer, even in the least conductive layer. Thus explaining the present-day water balance is not necessarily important for the problem of radionuclide transport, if such transport is taking place in a low conductivity layer where flows are very small. It is very difficult to use water balance models alone to identify rates of flow in low conductivity layers. Coupled models of flow and transport, or of flow, transport and chemistry, are much more likely to provide information about rates of flow.

5. Fracture flow modelling and inverse modelling

A three-dimensional region near the No.1 Orebody was modelled by J.L. Smoot [1] using discrete fractures (see a separate report in these Proceedings). The modelling showed that it is certainly possible to simulate systems like that observed at Koongarra, but that large amounts of data are probably needed to obtain realistic descriptions of the fracture networks. Inverse modelling of aquifer test data by S. Braumiller [1] showed that inverse procedures may have some advantages over the fitting of analytical "type" curves to aquifer test data, especially in highly heterogeneous environments. This work was novel in the sense that data from a sequence of aquifer tests at a number of boreholes were combined into one data set for the purpose of finding the best possible spatial distribution of transmissivities and storage coefficients consistent with all the data.

6. Discussion

The objective of determining rates and directions of groundwater movement was not achieved with any degree of confidence. The most that can be said is that there are many combinations of hydrogeological and climatic variables which could produce groundwater velocities in the range apparently needed by coupled flow and transport models. In the final analysis, hydrogeological data do not contain as much information as chemical data, thus fitting of coupled models is more likely in the long term to lead to identification of the best combination of model parameters.

On the other hand, in order to interpret present-day chemistry using coupled models, it is necessary to run these models for millions of years. Since it is not possible to run three-dimensional coupled models for these time scales, it may be possible to achieve results using three-dimensional hydrogeological models that can not be achieved using coupled models. There is clearly a role for hydrogeological modelling, especially for a hierarchy of different models, but modelling is not a substitute for careful design of field experiments and careful analysis of data.

In terms of experimental design, the ARAP experience exposed the difficulties which can occur when data are collected for one purpose and used later for another. In order to quantify any water balance, hydrogeological models must be developed for a region which extends to natural hydrogeological boundaries. At Koongarra, these include the Koongarra Fault and Koongarra Creek, i.e. the region modelled two-dimensionally in plan (Figure 4). Very few hydrogeological measurements were made further than a few hundred metres from the orebody, and almost no measurements were made near the Creek, which has a very important role in the dynamics of the system. Future hydrogeological modelling of natural analogues will be more successful if field monitoring is designed in conjunction with preliminary modelling, rather than long before the modelling is commenced.

7. Acknowledgements

The author is grateful to all the co-authors of [1] for their significant contributions to the hydrogeological modelling of the Koongarra site.

References

[1] Townley, L.R., Barr, A.D., Braumiller, S., Kawanashi, M., Lever, D.A., Miyakawa, K., Morris, S.T., Raffensperger, J.P., Smoot, J.L., Tanaka, Y., and Trefry, M.G., Alligator Rivers Analogue Project Final Report, Volume 6, Hydrogeological Modelling, ANSTO, Lucas Heights, N.S.W., Australia, 1993.

[2] Davis, S.N., Discussion of a paper by J. Tóth, 'A theory of groundwater motion in small drainage basins in central Alberta, Canada', J. Geophys. Res., 68(8), 2352-2353. See also Reply by J. Tóth, 2354-2356, 1963.

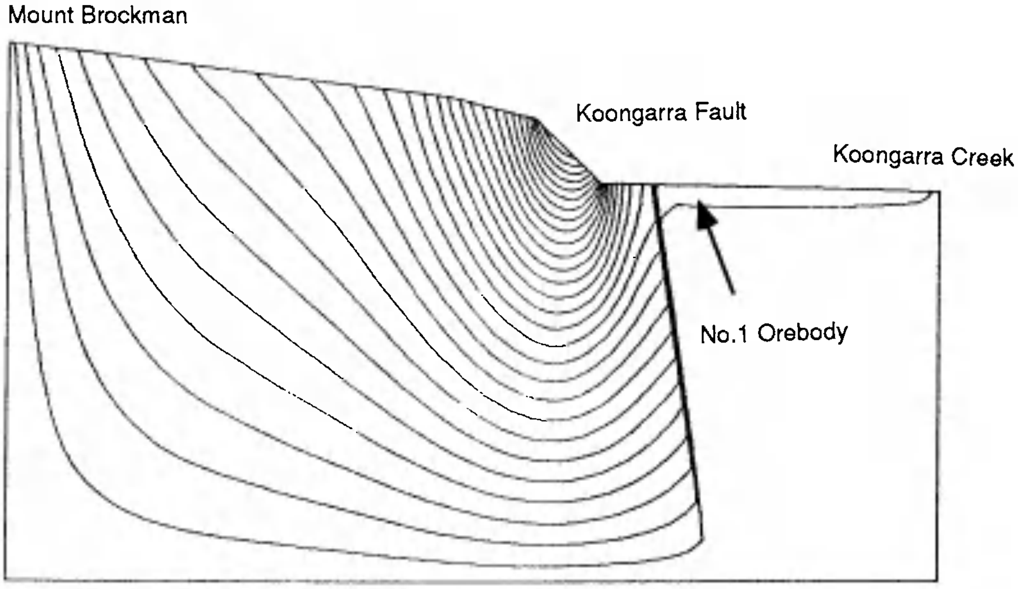

Figure 1 Streamlines calculated by two-dimensional modelling in vertical section, for the case of a highly conductive fault and a transmissive weathered layer

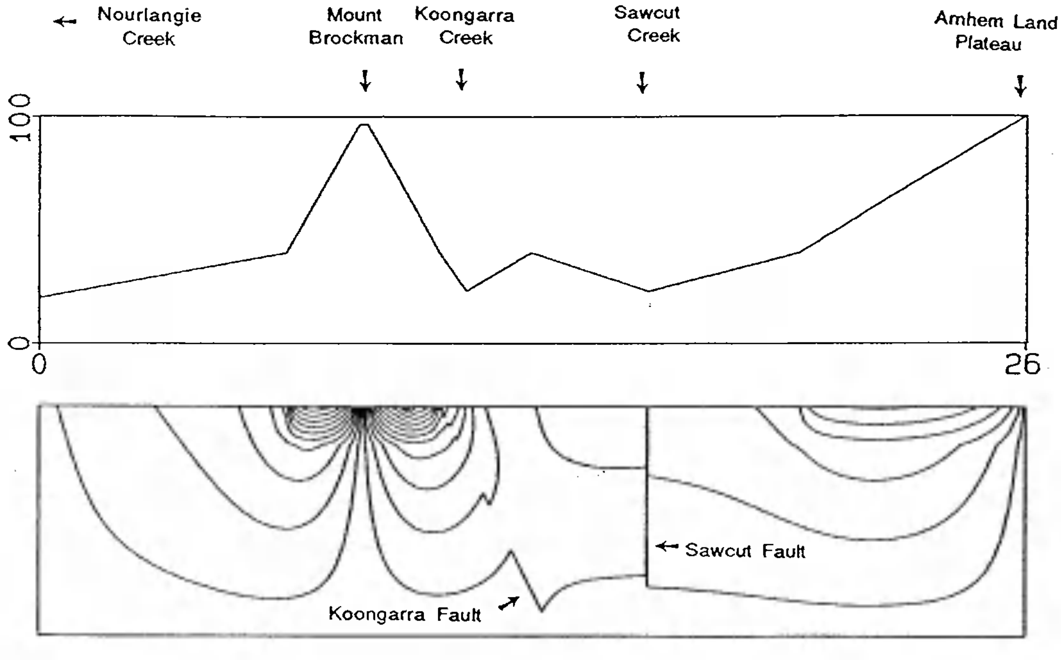

Figure 2 Streamlines for a regional scale two-dimensional vertical section 26 km long and 3 km deep. This case uses a high effective conductivity for Koongarra Fault, but the flow pattern near the orebody is relatively insensitive to fault conductivity, and also to the depth of the section. Similar results are achieved for the near field with sections 1 km or less in depth.

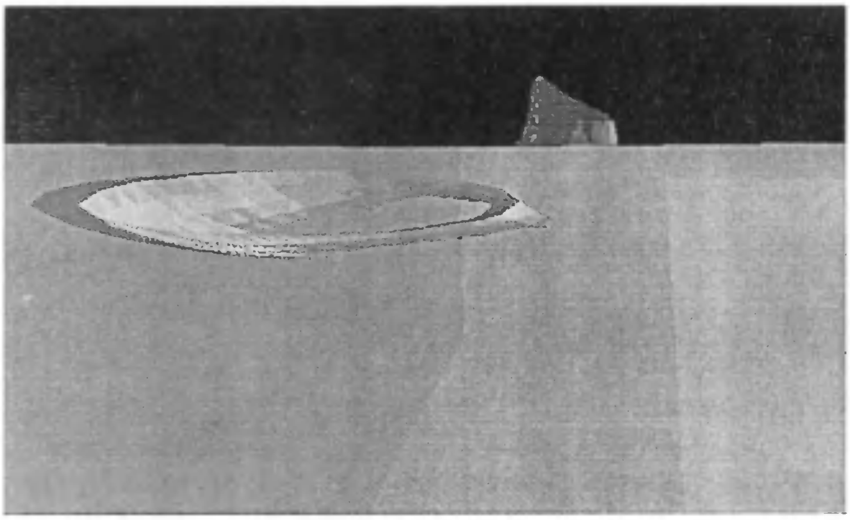

Figure 3 Three-dimensional rendered image of a streamtube approaching the No.1 Orebody.

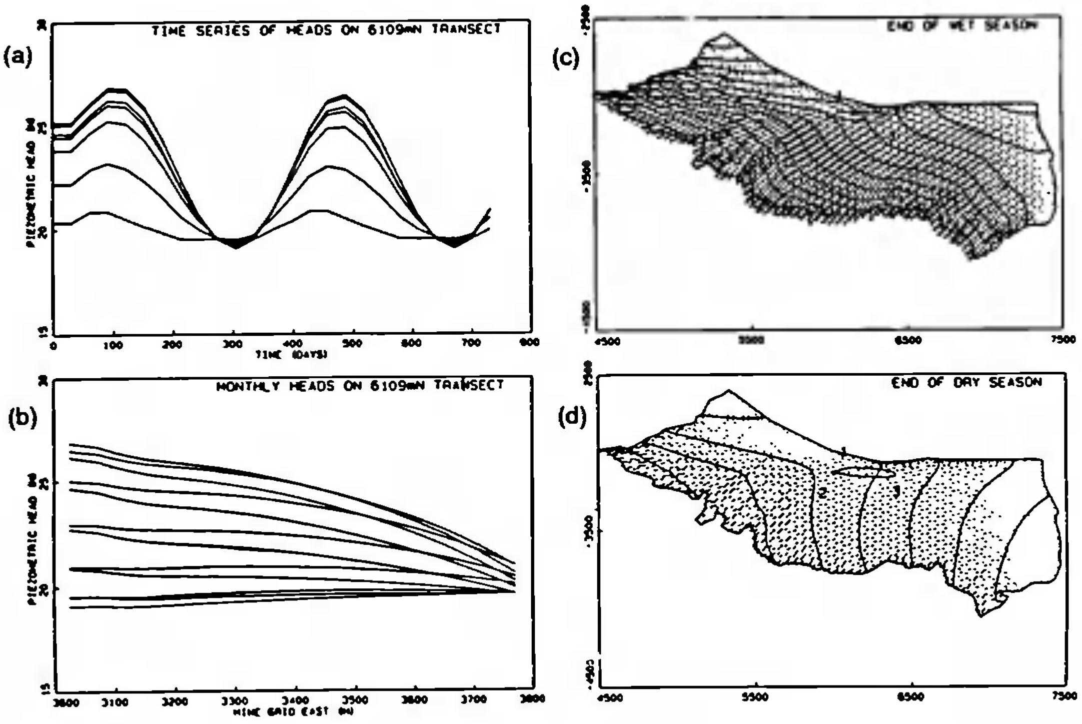

Figure 4 Sample results of two-dimensional plan modelling of a region 3 km long in the southwest-northeast direction. (a) Seven two-year time series of water levels at locations on a northwest-southeast transect, showing gradient reversal near the fault in the dry season. (b) Monthly water level distributions along the same transect, also showing the gradient reversal. (c) Water level contours at end of wet season. (d) Water level contours at end of dry season.

EVIDENCE FOR FRACTURE FLOW AND PRELIMINARY DISCRETE FRACTURE ANALYSIS OF THE ALLIGATOR RIVERS NATURAL ANALOGUE, AUSTRALIA

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Simulations of the subsurface hydrology of the Alligator Rivers Natural Analogue, Koongarra, Northern Territory, Australia, have been conducted using a model based on a discrete fracture conceptualization. The FracMan-Mafic suite of discrete fracture software was used for the analysis. The discrete fracture simulations were conducted within a cubic volume (180-m edge length) of fractured Cahill Schist. Five hundred fractures were simulated with a mean dip of 55° SE. Flow modeling of this fracture network was conducted by assigning constant head boundaries to upgradient and downgradient vertical faces of the cube; no-flow boundaries were assigned to all other faces. The fracture density across the network is 0.2 m^2/m^3. Small hydraulic gradients are generally observed across individual fractures. The mean fracture radius of 30 m is less than the cube edge length of 180 m, with a resulting small likelihood of any single fracture intersecting both constant head boundaries. Mass balance was achieved for the simulation, with a total flow of 894 m^3/day moving through the fracture network under steady-state conditions. The corresponding flux is approximately 28 mm/day through a unit area parallel to the constant head boundary planes. Preliminary results indicate that discrete fracture modeling on the field scale is computationally feasible; the availability of data will be the primary limiting factor.

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THE CHEMISTRY AND ISOTOPIC COMPOSITION OF KOONGARRA GROUNDWATERS

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ABSTRACT

The major ion chemistry of Koongarra groundwaters is dominated by magnesium and bicarbonate. Groundwater pH-values are generally between 6.0 and 7.5, and the groundwaters are quite dilute (conductivity <300 μS/cm). Groundwaters from the mineralised zones contain elevated levels of ^{238}U, up to four orders of magnitude above background concentrations. Down-gradient, there is a gradual decrease over approximately 200 m. The distribution of ^{238}U and isotopes of its decay series (such as ^{222}Rn and ^{210}Pb), suggests that dispersion occurs towards the south, at an angle to, rather than perpendicular to, the fault.

Weathered zone groundwaters have low $^{234}U/^{238}U$ activity ratios, which are often substantially below unity. Measured $^{230}Th/^{234}U$ ratios are extremely low, indicating that Th is much less mobile than U in the Koongarra system.

Groundwaters in the orebody have a low proportion of ^{14}C, and quite negative deuterium (δ^2H) values. Chemical and isotopic trends in Koongarra groundwaters appear to be adequately explained by gradual mixing with local recharge as groundwater moves away from the fault.

1. Introduction

An extensive groundwater sampling and analysis program has been undertaken at the Koongarra Uranium Deposit as part of the Alligator Rivers Analogue Project (ARAP). Elemental and isotopic data for dissolved species in Koongarra groundwaters are summarised and interpreted in this paper. Groundwater colloids are discussed elsewhere in this volume (Seo et al., 1992).

2. Groundwater sampling and analysis

During the ARAP, groundwater samples were obtained, whenever possible, from specific depth intervals. This was achieved by the use of a submersible pump suspended between inflatable packers, or by sampling from boreholes which were only open over specific intervals.

Several important parameters, such as pH, Eh, conductivity and alkalinity were determined in the field. For most chemical analyses, samples were taken after filtration through a 0.45 μm membrane, a separation accepted as defining the dissolved fraction (Batley and Gardner, 1977). Elemental analyses were carried out using a number of techniques, including ICPMS, ICPAES, anion exchange chromatography and spectrophotometry. Uranium was measured using ICPMS, α-spectrometry, and kinetic phosphorescence analysis. Other radiochemical and isotopic techniques were employed for particular isotopes. Further details are given in the final report of the ARAP (Payne et al., in preparation).

3. Main characteristics of Koongarra groundwaters

A typical groundwater analysis from borehole PH49, near the centre of the No. 1 orebody, is given in Table 1. The pH is close to neutral, and Mg^{2+} and HCO_3^- are the major cations and anions respectively. This major ion chemistry is attributed to the weathering of chlorite by CO_2-bearing groundwaters (Sverjensky, 1992). Although groundwaters from the immediate vicinity of the orebody have a high conductivity relative to other Koongarra samples, the PH49 sample is still quite dilute, compared to many natural systems. The sample is slightly oxidising with respect to U(IV)/U(VI), as is common for Koongarra groundwaters, which usually have a pH between 6.0 and 7.5 and an Eh of 100-300 mV.

Table 1. PH49 groundwater data

Borehole	PH49
Depth	28-30 m
Date	May 1988
pH	6.74
Eh (mV)	+130
EC (μS/cm)	236
Mg^{2+}	26.4
Ca^{2+}	3.9
Fe^{2+}	0.8
K^+	0.7
Na^+	1.4
Si	8.9
HCO_3^-	154
Cl^-	4.9
F^-	0.2
PO_4^{3-}	0.310
SO_4^{2-}	2
TOC	1.5
U (μg/L)	274

Units are mg/L except where otherwise stated

4. Seasonal effects and sampling variability

During the ARAP, many boreholes were sampled on several occasions, to determine whether there was any significant seasonal effect on groundwater chemistry. In general, groundwaters from the permanently saturated zone (depths greater than about 12 m) did not show a significant seasonal variation. Groundwater samples obtained from the seasonally saturated zone (within about 10 m of the surface) were generally much more dilute than the deeper samples and had a chemistry trending towards rain-water.

A complicating factor in interpreting groundwater chemistry was the variation in concentrations of some minor constituents, such as Fe and U, during continued pumping of the boreholes. This was attributed to groundwaters of slightly differing chemistry being drawn in from greater distances, and from slower draining pore-spaces, as the boreholes were pumped. In general, the change in groundwater chemistry at a given borehole during pumping of the borehole was relatively small compared to the variation of groundwater chemistry between different boreholes.

5. Spatial distribution of major parameters

In the final ARAP report, the groundwater data for key parameters will be presented both as contour plans and in cross sections. The cross-sections show data as a function of depth, and of distance from the Koongarra fault. Because of space limitations, only contour plans are included in this paper. Note that only data for samples from depths greater than 16 m are included in the contour plans.

The data for conductivity are illustrative of the approach used. Because Koongarra groundwaters are dominated by the Mg^{2+} and HCO_3^- ions, the data for these ions show similar trends to the conductivity data. Complete analytical data will be presented in the final ARAP report (Payne et al., in preparation).

The contour plan for conductivity (Figure 1) shows that the highest values are found in a band which corresponds approximately to the position of the primary ore-zone. The most dilute groundwaters occur in the region of boreholes PH94 and PH96, which are furthest from the Koongarra fault. This contour plan suggests that a zone of elevated conductivities extends towards boreholes PH80 and C1, to the south of the orebody. The highest conductivity values occurred in the groundwaters from deeper depths within the vicinity of the primary ore-zone. Shallower groundwaters, and those further away from the fault, were more dilute.

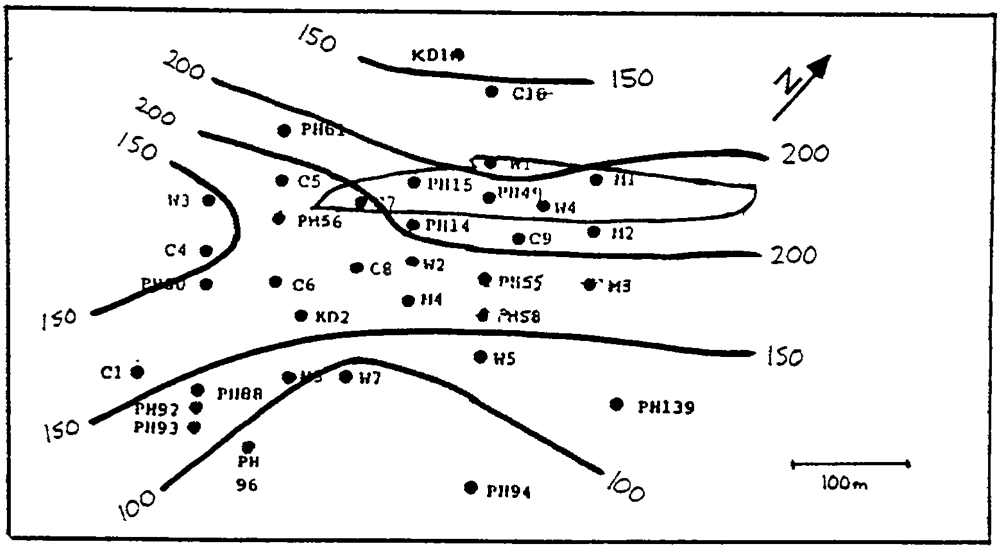

Figure 1. Groundwater conductivity (µS/cm) - contour plan. The outline of the primary ore-zone is shown.

The distribution of phosphate was studied in detail because uranyl-phosphate minerals, such as saleeite ($Mg(UO_2)_2(PO_4)_2.8\text{-}10H_2O$) are abundant at Koongarra, and because phosphate may be important in complexing uranium in solution. In some groundwater samples, PO_4 concentrations exceeded 500 µg/L. Elevated PO_4 concentrations were found in two distinct regions, one on the upstream edge of the orebody, and a second to the south-east (Figure 2). An interesting feature of the data was the relatively low phosphate concentrations found between these areas, in the region of the orebody where uranyl phosphate-containing minerals are most abundant. The elevated phosphate concentrations were generally restricted to samples from the permanently saturated zone, with much lower values, bordering on detection limits, in shallower samples

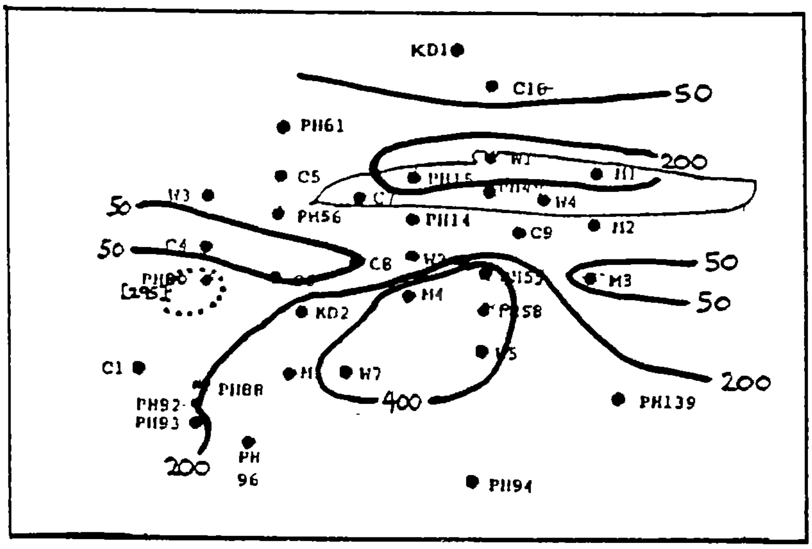

Figure 2. Phosphate in groundwater (μg/L) - contour plan.

6. ^{238}U-series radionuclides

The concentration of ^{238}U ranged from about 0.1 ppb to 1000 ppb. Uranium concentrations exceeding background levels were found over a distance extending approximately 200 m from the orebody in the direction of groundwater flow. The distribution of ^{238}U (Figure 3) was similar to the contour map of conductivity, and in general, ^{238}U concentrations tended to be correlated with conductivity. Figure 3

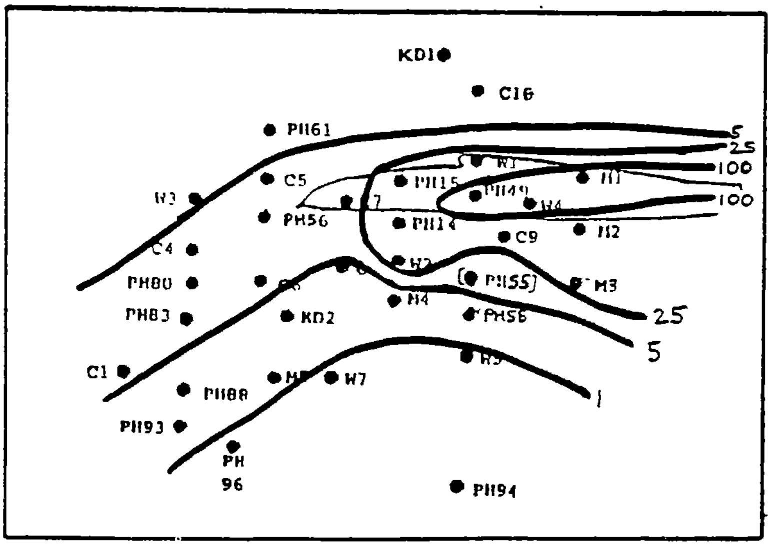

Figure 3. Uranium in groundwater (μg/L) - contour plan.

suggests that a dispersion of uranium occurs towards borehole PH80, to the south of the orebody. Similar contour patterns were obtained for other isotopes in the ^{238}U decay series, such as ^{210}Pb and ^{226}Ra. Elevated concentrations of ^{226}Ra tended to be restricted to deeper groundwaters. This was attributed to the association of radium with Fe and Mn oxides which may precipitate within the weathered zone, thus scavenging Ra from shallow groundwaters.

The activity of ^{230}Th, relative to its precursors in the ^{238}U decay series, was extremely low in Koongarra groundwaters. Typically, $^{230}Th/^{234}U$ activity ratios were in the range 10^{-4} to 10^{-2}. It was concluded that the mobility of thorium in these groundwaters is extremely low, although there is some evidence that ^{230}Th is associated with colloids (Seo et al., 1992).

Koongarra groundwaters are unusual in that the $^{234}U/^{238}U$ activity ratio is often below unity, in some cases below 0.7. Analyses of numerous samples from various depths showed that $^{234}U/^{238}U$ values below 1.0 were generally found in groundwaters of the weathered zone, whereas deeper samples had higher $^{234}U/^{238}U$ values. The $^{234}U/^{238}U$ activity ratios in groundwaters were found to be in close correspondence to the measured ratios in the accessible phases of the solid phase (Edis et al., final ARAP report, in preparation).

7. Environmental Isotopes

As well as isotopes in the ^{238}U series, a number of environmental isotopes, such as ^{14}C, ^{13}C, deuterium and tritium have also been determined in Koongarra groundwaters. An account of this part of the work has been presented (Herczeg and Payne, 1992).

Tritium values were generally low, with values exceeding 1.0 tritium units restricted to some shallower samples. Carbon-14 concentrations (expressed as percent modern carbon) tended to increase moving down-gradient, from about 55% in the centre of the deposit to 100% several hundred metres down-gradient. This was attributed to the progressive mixing and dilution of groundwaters from the ore-body with more modern water (containing greater amounts of ^{14}C). The low ^{14}C values in the centre of the orebody were attributed to the release of 'dead' carbon by weathering, or to the input of groundwaters after long transit times from the surface.

Deuterium values were generally quite negative (-25‰ to -40‰), and tended to increase with distance from the fault (Figure 4). The similarity of δ^2H values from the centre of the orezone and those from the Kombolgie formation (KD1) suggested that some of the groundwater intersecting the orebody may have moved across the Koongarra fault into the ore-zone, from the adjacent fractured sandstones of the Kombolgie formation. The δ^2H values of groundwaters tended to evolve towards the weighted mean values of rainwaters, suggesting gradual mixing with local recharge as groundwaters move down-gradient.

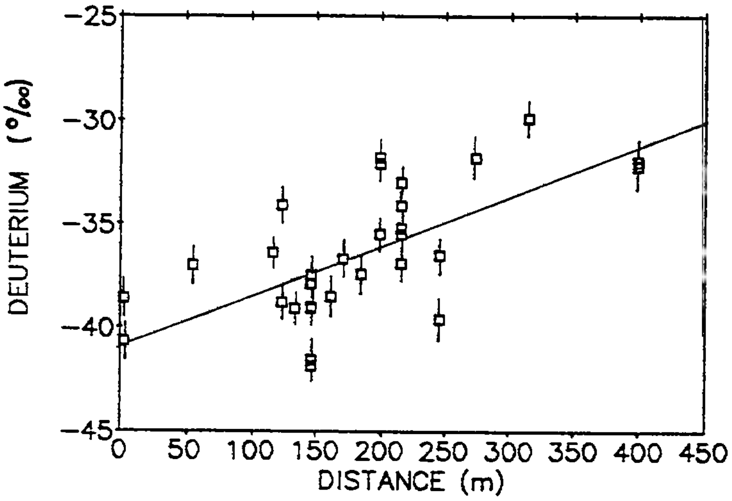

Figure 4. δ^2H composition of groundwaters as a function of distance from KD1

8. Summary

An extensive data-set of chemical and isotopic data for Koongarra groundwaters has been accumulated. Groundwaters in the centre of the orebody have a characteristic chemistry, with a major ion chemistry dominated by Mg^{2+} and HCO_3^-, and elevated concentrations of ^{238}U and members of its decay-series.

Down-gradient of the orebody, the groundwaters become even more dilute, and the δ^2H value tends to approach the average value of rainwaters and surface waters. These changes are accompanied by an increase in the radiocarbon content. Tritium is present in some shallower groundwaters. These phenomena appear to be adequately explained by a gradual mixing with local recharge as groundwater moves down-gradient.

9. Acknowledgements

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References

G.E. Batley and D. Gardner, 1977, ' Sampling and Storage of Natural Waters for Trace Metal Analysis'. Water Research 11, 745-756.

A.L. Herczeg and T.E. Payne, 1992, 'Recharge and Weathering Processes in Fractured Rock Aquifers in Northern Australia'. In: Water Rock Interaction, (eds) Y.K. Kharaka and A.S. Maest, Balkema, Rotterdam.

T. Seo, R. Edis and T.E. Payne, 1992, 'A Study of Colloids in Groundwaters at the Koongarra Uranium Deposit'. These proceedings.

D. Sverjensky, 1992, 'Geochemical Modelling of Present-Day Koongarra Groundwaters'. These proceedings.

A STUDY OF COLLOIDS IN GROUNDWATERS AT THE KOONGARRA URANIUM DEPOSIT

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ABSTRACT

Groundwaters and associated colloids were collected at several boreholes in the vicinity of the Koongarra uranium deposit. Field sampling was carried out in an oxygen-free atmosphere (2% CO_2, 98% N_2) to minimise transformations of the samples. Colloids were operationally defined as particles which passed through a 1.0 μm Nuclepore^R membrane, and were retained by an ultrafiltration membrane with a nominal cut-off at 10000 or 30000 molecular weight. Colloids (<1.0 μm) and fine particles (>1.0 μm) were characterised in terms of their mineralogy, elemental composition, and radionuclide content.

The mineralogy of the groundwater colloids reflected that of the solid phase from the vicinity of the water sampling point, and was dominated by iron oxides and clay minerals. Fine quartz particles and particles with compositions dominated by individual elements, such as lead, uranium, titanium and gold, were also observed. However, the total number of colloidal particles was quite low.

The amount of ^{238}U associated with colloids (expressed as a percentage of the total ^{238}U which passed through the 1.0 μm filter) was commonly in the range 0.1-2.5%. The corresponding figures for ^{230}Th were 10-85%. However, the total amount of dissolved and colloidal ^{230}Th, which passed through the 1.0 μm filter, was extremely small. Thorium-230 was associated to a much greater extent with larger (>1.0 μm) particles, which are unlikely to be mobile in natural groundwaters. An unexpected feature of the results was the presence of substantial amounts of ^{227}Ac in some colloid and particulate samples.

1. Introduction

The Alligator Rivers Analogue Project (ARAP) seeks to identify, and ultimately model, the major mechanisms of radionuclide migration at the Koongarra uranium deposit in Northern Australia. Koongarra is being used as a natural analogue for a nuclear waste repository. The objective of the study described in this paper was to evaluate the significance of colloids (particles below 1 μm in size) as a mechanism of radionuclide transport in Koongarra groundwaters. A previous account of the colloid study at Koongarra has been presented (Payne et al., 1992).

2. **Field sampling**

The sampling of groundwater colloids is subject to several factors which may decrease confidence in the results. Two major factors which were considered in detail prior to colloid sampling at Koongarra were (a) possible transformations of samples either during or after sampling, and (b) whether nominal filter pore-sizes (as stated by the filter manufacturer) were an accurate indication of the size range of particles retained by the filters.

The procedures adopted to minimise transformations of the samples included:

(a) In-field separation of the colloids (rather than later separation in the laboratory), to minimise the time elapsed prior to ultrafiltration.
(b) Ultrafiltration was carried out in a closed, oxygen-free system, to prevent oxidation and precipitation (particularly of Fe-oxides).
(c) The ultrafiltration equipment was provided with an atmosphere containing N_2 (98%) and CO_2 (2%) to minimise outgassing of CO_2 and possible chemical alterations in the samples.
(d) All samples were sealed under N_2/CO_2 into plastic bags or bottles and analysed with minimal exposure to the atmosphere.

Because the size-ranges of colloids are operationally defined by the filters used to separate them, it is essential that consideration be given to the types of filters used. In this work, the upper size limit of the colloids was determined by Nuclepore^R 1.0 μm filters, which have a narrow range of pore-sizes (more precisely defined than conventional depth filters). Subsequent to the field separations, these filters were subjected to an electron microscope examination, to verify that the pores had not become blocked during use, which would have reduced the effective pore-size. The lower size limit of the colloids was determined using Amicon^R ultrafiltration membranes, with a cut-off at 10000 or 30000 molecular weight (MW). These ultrafilters were employed in a recirculating system or a stirred cell, to optimise their performance with the stated particle size cut-offs.

Two different sampling systems were used to concentrate the colloids from the groundwater. In the first of these, large volumes (1000 L) were processed, with the objective being to maximise the amount of material available for chemical and physical analysis. Groundwater was passed through pre-filters (5 μm and 1.0 μm) into an Amicon DC10LA hollow fibre ultrafiltration system. This consisted of a closed loop around which groundwater was pumped, maintaining a high velocity of water along the hollow-fibre membranes. These filters had a nominal cut-off at 10000 MW (about 1.5 nm - Dearlove et al., 1991). Ultrafiltrate continuously passed through the membranes, and was replaced by an equivalent amount of groundwater. Hence, the sample was gradually enriched in colloids. Groundwater volumes of approximately 1000 litres were concentrated to about 10 litres. The colloid concentrates and ultrafiltrates were stored in airtight containers, and subsamples were subsequently mounted onto electron microscope grids. The filter membranes were backflushed between experiments with 0.1M HCl and these solutions were retained for analysis.

In the experiments with the smaller sampling system, volumes of about 600 mL were ultrafiltered through flat membranes (30000 MW) in a stirred cell. In these experiments, inflatable borehole packers were used to limit the origin of the sampled groundwaters, and a passive-filling diaphragm pump was used to minimise disturbance to the borehole. The groundwater was pre-filtered as before, and processed in a glove-box under N_2/CO_2. In some experiments, the colloids were concentrated into a small volume in the stirred cell, and then mounted onto electron microscope grids using centrifugation. Alternatively, the entire volume was passed through the ultrafilters, which were then sealed into plastic bags for analysis. Further details of sampling equipment are given in Payne et al., 1992.

3. Analysis

The colloid concentrates, and samples of filtered and ultrafiltered groundwater, were analysed using various chemical techniques, including ICPMS and α-spectroscopy. For α-spectroscopy, ^{229}Th and ^{236}U (or ^{232}U) were used as yield tracers. Electron microscope grids, filter membranes, and particles from the colloid concentrates were examined using SEM, TEM and EDS (energy dispersive spectroscopy). Ultrafiltrate samples were also examined, for evidence of particle formation after field sampling. The pre-filters were chemically leached, then ashed in a furnace, with both the leachate and residue being subsequently analysed. The chemical composition of material retained by the flat ultrafilters was determined after a chemical digestion.

4. Elemental content and mineralogy of colloids and particles

There were only minor differences between the major cation data for the ultrafiltrate (UF) and colloid concentrate (CC) fractions in the hollow fibre experiments (Payne et al., 1992). The similarity between the elemental composition of the CC, which contained colloids enriched by a factor of about one hundred, and that of the UF, suggested that most major species were not significantly associated with colloids. A significant amount of Fe (about 1% of the Fe in 1 μm filtered groundwater) was retained on the ultrafilter membrane, and was found in the ultrafilter backflush (BF) fractions. The detection of Fe-containing particles in the CC (using EDS) suggested that at least part of this Fe was colloidal, although sorption of Fe from solution on the ultrafilter membrane may have also occurred.

Because of the small amount of colloidal material present, the mineralogy of the colloids could not be directly studied. The mineralogy of the colloids was inferred from electron microscope images, electron diffraction patterns, and the elemental composition as determined by EDS. Colloids from weathered or partially weathered rock were mainly clay particles, particularly kaolinite (Si and Al in EDS spectra, crystalline platelets and spheres, 0.1-1.0 μm across). Chlorite platelets were observed in samples from less weathered rock (Si, Al, and Mg in EDS). Clay particle concentrations, estimated by manual counting, were about 10^5-10^8 particles per litre. The distribution of colloid minerals as a function of both depth and position, is presented in cross-section in Figure 1. Colloids of kaolinite occurred in the weathered zone, with chlorite, uranium, lead and uranyl silicates found in deeper samples. The presence of these minerals corresponded to their occurrence in the solid phase, with the chlorite and kaolinite being the principal minerals in the unweathered and weathered zones respectively (Murakami et al., 1991).

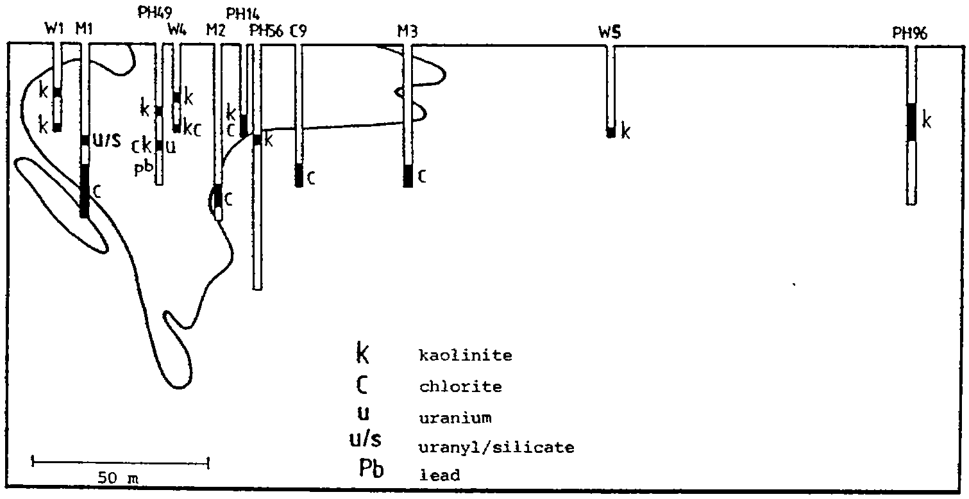

Figure 1. Distribution of some colloids detected in Koongarra groundwaters.

Fine quartz grains (highly to weakly crystalline, up to 1 μm across, blocky or spheroidal, Si in EDS) were present in groundwaters from unweathered rock, with an estimated concentration of up to about 10^7 particles per litre. Non- to weakly crystalline Fe-rich particles (probably ferrihydrite) were observed in both the CC and UF samples, with about ten times more Fe particles in the CC fractions. Their presence in ultrafiltrates indicated a proportion of post sampling formation of these colloids. Crystalline sub-angular to blocky Fe-rich particles, about 0.3 μm across, were observed in the CC samples only, and were probably present in the groundwater before sampling. Particles enriched in U and Pb were found in a CC sample from the high grade ore zone (borehole PH49). These particles were crystalline, spheroidal, 0.04-0.3 μm across, and were present at about 10^8 particles per litre. The estimated contribution of these particles to the U concentration of the groundwater was below 1%. A few titanium-rich colloids were also detected. These were probably anatase (TiO_2) particles, 0.06-0.17 μm across, often occurring in dendritic clusters up to 1 μm long. Three particles containing Si, Fe, and Mn (0.1 μm) and one particle of native gold (0.08 μm) were also observed.

Particles on the 1 μm pre-filters were examined by SEM/EDS and were found to consist of kaolinite, chlorite, mica and iron oxides. Iron oxides were present as separate particles and as coatings on clays.

It should be noted that although special procedures were developed for field sampling in this study, the colloids and particles which were detected may not be representative of the unperturbed natural system. Indeed, the large particles (above 1.0 μm in size), which were found on the 1.0 μm and 5 μm pre-filters, are unlikely to be mobile in natural groundwaters. These particles may result from perturbations caused by drilling the borehole, or by sampling activities. These possibilities should be considered in future groundwater colloid work.

5. Radionuclide distributions

The amounts of colloidal ^{238}U and ^{230}Th, based on the results of the hollow fibre experiments are given in Table 1. The data indicate the amount of these radionuclides retained by the ultrafilter, as a percentage of the total ^{238}U and ^{230}Th which passed through the 1.0 μm filter. The results show that a much greater proportion of ^{230}Th than ^{238}U was associated with colloids. However, the total amount of ^{230}Th in the <1 μm size range was very low, close to detection limits.

The data for colloidal ^{238}U and ^{230}Th in Table 1 include radionuclides found in both the CC and BF fractions. The BF may include radionuclides adsorbed from solution by the ultrafilter, as well as colloids. Therefore, the amounts of colloidal ^{238}U and ^{230}Th in Table 1 may be considered to be upper limits. If the radionuclides found in the BF are excluded from consideration, the amounts of colloidal ^{238}U and ^{230}Th (based only on enrichment in the CC) are in the range 0.1-0.4% for ^{238}U and 5-35% for ^{230}Th. Whilst these figures are substantially lower, the percentage of colloidal ^{230}Th is significant and remains much greater than the corresponding figure for ^{238}U.

The amounts of colloidal ^{238}U were also determined for the samples obtained in the stirred cell experiments with the 30000 MW membrane (Table 2). On account of the low ^{230}Th levels, and the smaller volumes processed, it was not possible to measure ^{230}Th in these samples. The proportion of ^{238}U carried by colloids was generally in the range 0.1 to 0.5%. One higher result of 6.5% was obtained for a groundwater sample obtained some distance from the ore body, where total U concentrations were much lower.

Table 1. Partitioning of ^{238}U and ^{230}Th in 1 μm-filtered groundwater (hollow fibre ultrafiltration experiments)

Borehole	^{238}U UF (ppb)	^{238}U Colloid	^{230}Th UF (mBq/L)	^{230}Th Colloid
KD2	0.079	1.8%	<0.007	-
PH55	0.40	2.5%	0.073	33%
PH14	87.7	1.4%	0.160	12%
PH14*	205	1.1%	0.062	27%
PH49	178	1.4%	0.053	82%

*There were two colloid sampling experiments at PH14.

Table 2. Uranium associated with colloids (stirred cell experiments)

Hole	Sampling Depth	U_c (ppb)	U_{uf} (ppb)	% of U on colloid
W1	23-25 m	0.24	61	0.4
W4	13-15 m	2.6	470	0.5
W4	23-25 m	1.0	300	0.3
M1	27-29 m	0.52	620	0.1
PH49	18-20 m	0.60	110	0.5
M2	42-44 m	0.12	46	0.3
W5	23-25 m	0.21	3.0	6.5

U_c - uranium on colloid U_{uf} - uranium in ultrafiltrate

A detailed study of the association of ^{238}U and ^{230}Th with particles greater than 1.0 μm in size was carried out for groundwater from boreholes PH14 and PH49 (Payne et al., 1992). This data was then compared with the corresponding data for colloids (<1.0 μm). The results showed that only a small proportion of the total ^{238}U and ^{230}Th in the sampled groundwaters was carried by colloidal particles. Almost all (65-87% of the total) of the ^{238}U was dissolved. On the other hand, ^{230}Th was mostly associated with particles above 1 μm in size, with less than 1% passing through the 1 μm filter. Of this small fraction, a major proportion was associated with colloids.

The thorium α-spectrum for many of the colloidal and fine particle fractions showed an unusual feature - prominent peaks of ^{227}Th, together with peaks of its decay products ^{219}Rn and ^{211}Bi. The measured ^{227}Th/^{230}Th activity ratio (up to about 3.0 in some samples) was almost two orders of magnitude greater than that commonly measured in bulk rock samples. As ^{227}Th has a half life of 19 days, and several months elapsed before analysis, this indicated the presence of excess ^{227}Ac in these fine particle phases. Nonetheless, the data showed that ^{227}Ac is highly immobile in these groundwaters, as at least 95% was retained by the pre-filters, and the level of ^{227}Ac in the ultrafiltrate was below detection limits.

6. Summary

This study has highlighted some of the experimental difficulties associated with sampling colloids from groundwaters. Some areas in which problems may arise include oxidation of Fe(II), or outgassing of CO_2 from groundwaters after being brought to the surface. These effects can be minimised by sampling in a closed system under an N_2/CO_2 atmosphere. Furthermore, consideration should be given to the pore-size distribution of the filters employed, and possible changes in the effective pore-size during sampling. Sorption on filter membranes may also present problems. Finally, the question of how representative the sampled colloids and particles are of the unperturbed natural system should be addressed.

Despite these uncertainties, it is possible to draw several conclusions from the present study. Colloids are predominantly clay and iron-oxide particles, and are a relatively unimportant mechanism for radionuclide transport in Koongarra groundwaters. Uranium migrates mostly as dissolved species, whereas thorium and actinium are mostly associated with larger, relatively immobile particles (>1.0 μm). However, of the small amount of ^{230}Th which passes through a 1.0 μm filter, a significant proportion is associated with colloids.

7. Acknowledgements

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References

J.P.L. Dearlove, G. Longworth, M. Ivanovich, J.I. Kim, B. Delakowitz and P Zeh, 1991. 'A Study of Groundwater-Colloids and Their Geochemical Interactions With Natural Radionuclides in Gorleben Aquifer Systems', Radiochimica Acta, 52/53, 83.

T. Murakami, H. Isobe and R. Edis, 1991. 'Effects of Chlorite Alteration on Uranium Redistribution in Koongarra, Australia'. In: Scientific Basis for Nuclear Waste Management XIV, (eds) T.A. Abrajano and L.H. Johnson, Mat. Res Soc. Symp. Proc., Vol. 212.

T.E. Payne, R. Edis and T. Seo, 1992. 'Radionuclide Transport by Groundwater Colloids at the Koongarra Uranium Deposit'. In: Scientific Basis for Nuclear Waste Management XV, (ed) C.G. Sombret, Mat. Res. Soc. Symp. Proc., Vol. 257.

SOLID PHASE STUDIES AND URANIUM DISTRIBUTION AT KOONGARRA

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1. Introduction

The chemistry and mineralogy of rock and soil at Koongarra have been investigated with the aim of gaining understanding about the migration of radionuclides. The work briefly presented here is discussed in detail in Edis et al (1992). Of central interest was the mobility and retardation of uranium over long timescales. In addition, data was collected to provide a geochemical framework of the Koongarra system. This was necessary for the application, testing and development of transport and geochemical models, and to allow a realistic evaluation of the transferability of the results.

2. Site Mineralogy

The geology of the site and the uranium mineralogy are given in Snelling (1992). The unweathered rock in the vicinity of the deposit can be divided into five major rock series;

1. Low uranium Kombolgie Formation sandstone and conglomerate;
2. Quartz chlorite schist, with siliceous bands, extending about 50 m from the sandstone and contains the primary ore;
3. Graphitic quartz chlorite hanging wall, about 5 m thick, containing pyritic and graphitic chlorite quartz breccia, and defines the SE boundary of the primary ore;
4. Quartz muscovite chlorite schist, with garnetiferous, pyritic, and graphitic sections. This extends for about 100 m from the graphitic hanging wall unit;
5. Quartz muscovite, biotite and feldspar schists, with occasional amphibolite.

Hydrothermal alteration halos have been observed about the mineralisation at Koongarra, and an inner and an outer halo have been identified. The inner alteration halo contains the primary uranium mineralisation, and extends up to 50 m from the ore. There are two main chlorite types in the schist, fine grained magnesium-rich chlorite containing little iron, and a coarser grained chlorite containing much more iron. It appears that in or near the primary ore zone, and within the inner halo of alteration, magnesium rich chlorite is dominant. However, down-gradient, the more iron-rich form is dominant. Differences in type and structure of chlorite may reflect conditions during ore genesis and hydrothermal alteration, and may give rise to a range of weathering products with differing potential for interaction with uranium. Apatite is found in the quartz chlorite schist, particularly fluorapatite. Phosphorus correlated with calcium in unweathered samples, however, there was insufficient calcium to account for all the phosphorus as apatite in some samples from within the inner alteration halo. Although the zone of secondary mineralisation in the weathered zone, is not associated with anomalously high phosphorus levels, the different forms of phosphate may affect the distribution and formation of uranyl phosphates.

Weathering of the schist has occurred to a depth of approximately 25-30 m over the site. Near the reverse fault the weathered zone extends down to about 50 m. Vermiculite, probably the major initial weathering product of chlorite, occurs at the base of weathering, in a band up to 5 m thick. Kaolinite is the dominant clay mineral in the weathered zone, resulting from the weathering of vermiculite, residual biotite, garnet, feldspar, smectite, and possibly directly from chlorite. A small amount of smectite has been found above the primary mineralised zone, and the amount increases with distance down-gradient. Differences in particle size distributions, clay mineralogy, and elemental abundances suggest that the intensity of weathering decreases with distance from the reverse fault.

Iron oxides are very important mineral phases in the weathered and weathering environment. At Koongarra they occur coating clays, fissures and remnant schistosity planes, and form nodules, ferruginous gravel and ferricrete. The different forms of iron oxide probably play different roles in the capture and storage of radionuclides. The three main iron oxides that were identified are hematite and goethite, and the "amorphous" iron oxide ferrihydrite. Hematite appears to be most abundant in the weathered primary ore zone, and down gradient goethite is the dominant crystalline iron oxide. Ferrihydrite was detected directly in one sample, using Mössbauer spectroscopy, but its presence has been suggested in many samples from extraction with Tamms acid oxalate (TAO). The amount of ferrihydrite has been estimated to be 7-29 mg/g, with 4-48% of the iron TAO-extractable. The concentration of goethite was estimated to be 2-19%.

Manganese oxide coatings were observed along fissures and remnant schistosity in weathered and partially weathered rock. Manganese oxides are most abundant down-gradient of the primary ore zone, with up to 3% MnO_2 in manganese rich samples. The main form of secondary manganese oxide appears to be lithiophorite $[(Al,Li)MnO_2(OH)_2]$. The position of the manganese phases as fissure coatings suggests a cycling of the manganese involving dissolution by reduction followed by deposition under more oxic conditions, and places them in an ideal position for contact with migrating species.

3. Uranium Distribution

Figure 1 shows the 100 µg/g uranium concentration contour line in plan-view, for three depths reflecting the unweathered, deep-weathered and shallow-weathered zones. Uranium concentrations above 100 µg/g in the unweathered rock were only detected in the vicinity of the ore body. It appears that the bulk of the apparent redistribution of uranium occurred in a SSW direction from the primary mineralisation and extended for >300 m. The degree of uranium enrichment deep in the weathered zone is similar to that higher up in the weathered zone. This suggests that much of the mobilisation and entrapment of uranium occurs near the transition zone, at the early stages of weathering. The pattern of the redistributed uranium in plan-view is similar to the pattern of the hydrochemical zones discussed by Payne et al (1992), and geophysical patterns given in Emerson et al (1992).

Figure 2 shows the uranium concentration contours for a cross-section perpendicular to the reverse fault, through the ore body. In this cross-section it can be seen that at the extremity of the uranium redistribution, most of the enrichment occurs near the surface. Outside of the zone of primary mineralisation, there is an abrupt uranium concentration boundary between the weathered and unweathered zones, demonstrating that leaching and deposition of uranium is strongly linked to the weathering process.

4. Association of uranium with minerals and elements

In unweathered rock, uranium correlated to a number of trace elements, but to no major rock forming elements. Elements that correlated to uranium in the unweathered rock were Mn, Nb, Cs, Mo, Sn, Pb, V and Ni. The area of primary mineralisation is characterised by a marked relative enrichment of heavy rare earth elements, with a maximum at dysprosium. Using α-autoradiography, an apparent diffusivity of 10^{-24} m^2s^{-1} was estimated for uranium diffusing into an unaltered and unfractured chlorite/quartz matrix from a fissure partially coated with uraninite. There was greater penetration and entrapment of uranium in secondary phases, such as talc and smectite, which occasionally coat fracture surfaces.

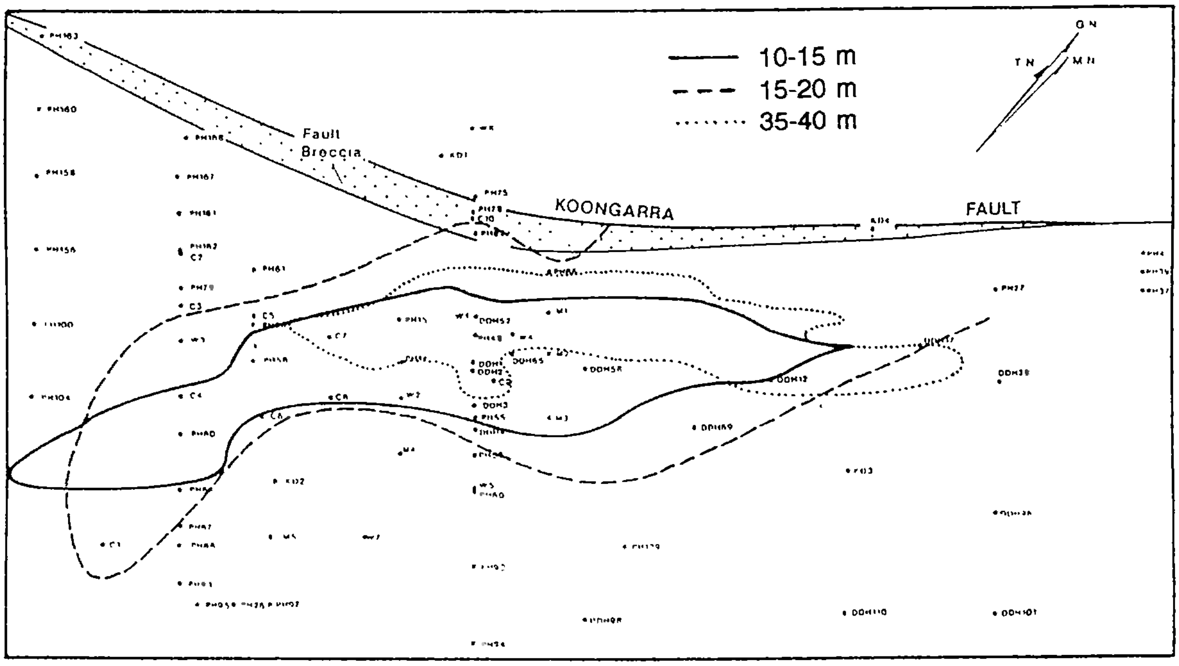

FIGURE 1 Contour lines of 100 µg/g uranium at 3 depths

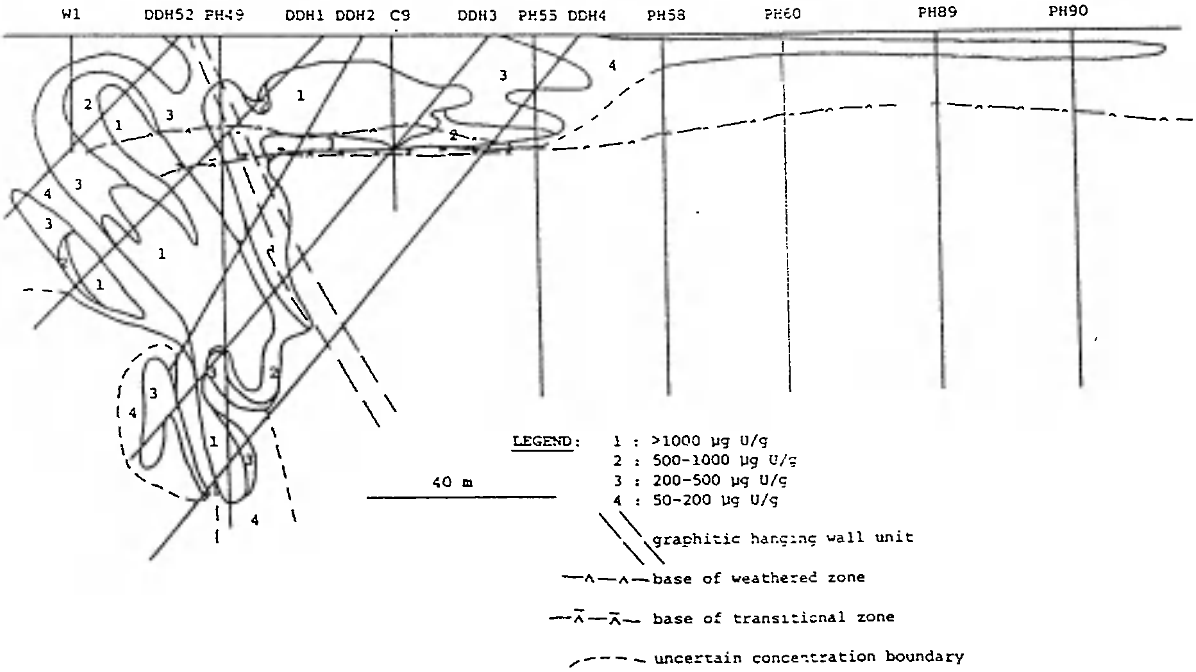

FIGURE 2 Contours of uranium concentration in cross section (section 6109mN)

In the weathered zone, uranium correlated to different elements in different areas of the site. In the leached primary ore zone, uranium correlated to P, Pb, Zn; in the zone of secondary mineralisation, where uranyl phosphate minerals have been detected, uranium correlated to P, Ni and Rb; and in the dispersed uranium zone down-gradient, uranium correlated to Fe, Ca, Ni, Zn, As, Na, Cr and Ga. In all zones, uranium and phosphorus followed similar depth and subsample trends to iron.

Electron microscopy and α-autoradiography showed the importance of oxy-hydroxides as scavengers of uranium. In the weathered zone, in the absence of uranium minerals, uranium is almost entirely associated with oxides of iron and manganese. The relationship between uranium and iron oxides appears to be of a diffuse nature, suggestive that sorption is the initial mechanism of association. Near the bottom of the weathered zone, uranium is most intensely associated with phases resembling amorphous iron oxide (possibly ferrihydrite), but at shallower depths, material resembling goethite has a more intense association with uranium. This suggests that sorbed uranium is retained as the oxide ages and transforms, as is also suggested by results of sequential extraction experiments. Within manganese oxide phases, uranium is almost exclusively associated with globules of a microcrystalline mixture of cerium and uranium oxide. The Ce/U phase was only found in association with lithiophorite zones, and probably develops through a redox sequence involving cerium and manganese, and sorption/desorption of uranium.

5. **Uranium Series Disequilibria**

Rock and soil samples (170 samples) were analysed for uranium series disequilibria in laboratories at ANSTO and JAERI. The degree of disequilibria has been determined for whole rock, chemically defined phases (two and five stage extraction schemes), mineralogically distinct zones and secondary uranium minerals. The isotopes most frequently considered were ^{238}U, ^{234}U and ^{230}Th, with some analyses of ^{235}U, ^{226}Ra, ^{210}Pb and ^{232}Th. In the unweathered zone, the ore material and the host rock were at approximate secular equilibrium, except for a small apparent depletion of ^{226}Ra. While there appears to have been negligible redistribution of uranium in the unweathered zone over the last few hundred ky, some mobility of radium is likely.

In the weathered rock, above the primary mineralised zone, high ^{230}Th/^{234}U values indicate strong leaching of uranium. In leached areas, the ^{234}U/^{238}U values are high, above unity in the bulk rock and near unity in the accessible phases (TAO-extractable). This indicates preferential mobility of ^{238}U relative to ^{234}U. The most intensely leached samples came from near the surface, near the up flow boundary of the primary ore. The most intense recent accumulation of uranium appears to have occurred about 0-50 m from the down flow boundary of primary ore, particularly near the base of weathering. Uranium deposition samples gave low ^{230}Th/^{234}U values and low ^{234}U/^{238}U values, both below unity. Further than about 50 m down-gradient, both activity ratios tend to increase with distance. Deposition of uranium greater than about 100 m from the primary ore is most pronounced near the surface. At shallow depths, low ^{230}Th/^{234}U values were associated with higher ^{234}U/^{238}U values than depositional samples deeper in the weathered zone. This may be due to different depths of source uranium; a faster flowing system and/or; the solid substrates differences.

A scenario for the development of disequilibria between ^{234}U and ^{238}U is proposed. The onset of weathering conditions may cause the rapid dissolution of the primary uranium minerals, resulting in the congruent liberation of ^{238}U and ^{234}U. This may have been followed by preferential entrapment of ^{234}U from solution and accessible sites, by various processes, including α-recoil and mechanisms involving the chemistry of ^{234}Th. This would have resulted in a preferential mobility of ^{238}U, leading to high ^{234}U/^{238}U values in leached samples and low ratios in depositional samples down-gradient.

Greater than about 50 m down-gradient, where the uranium content of groundwater and accessible phases is low, uranium mobilised from the primary ore makes a smaller contribution to the total accessible uranium. It is likely that slowly dissolving minerals that contain uranium, such as zircon and monazite, would be preferentially leach ^{234}U relative to ^{238}U, consequently increasing the $^{234}U/^{238}U$ value of the accessible uranium. It is proposed that these phases make an increasingly significant contribution to the accessible uranium with distance from the primary ore zone.

In general it appears that where the uranium content in accessible phases is high, then the accessible $^{234}U/^{238}U$ value will tend to decrease with time or distance due to preferential retardation of ^{234}U. However, where the accessible phase uranium content is low, then the accessible $^{234}U/^{238}U$ value will tend to increase due to preferential leaching of ^{234}U.

Sequential extraction data showed that most of the uranium in the dispersion fan was accessible or entrapped by crystalline iron oxides, with the crystalline phases containing the higher $^{234}U/^{238}U$ values. This indicates a mechanism of isotopic fractionation involving iron oxides. The highest activity ratios came from resistant phases with low uranium contents (after extraction with hot 6M HCl), such as quartz and muscovite. The high ratios in these essentially chemically inert phases suggests that α-recoil emplacement of ^{234}Th is a process occurring at Koongarra.

6. Partitioning of Uranium and Thorium

Various "P" ratios (functionally defined partition coefficients) have been determined, in partitioning uranium and thorium between solid and solution phases at Koongarra. The units of P are mL/g, and it should be noted that equilibrium is not implied. In-situ approaches to distribution coefficients have several limitations to their applicability (see McKinley and Alexander 1992), with the main concern being the potential overestimation of retardation of contaminant migration. By presenting several approaches for a range of groundwaters and substrates, it is hoped that such limitations can be identified.

Thorium concentrations in groundwater and crushed rock samples were compared. The resulting bulk partition values (P_B = total rock/groundwater) were high (4×10^5 to 2×10^9 mL/g), reflecting the low levels of dissolved ^{230}Th in these groundwaters. The high P_B values for thorium were considered to demonstrate its immobility in the Koongarra system as is commonly the case in geological systems, although a proportion of the rock ^{230}Th would not have been accessible to the groundwater.

Partitioning of ^{230}Th and ^{238}U between groundwater and entrained particles

Particle partition values (P_P) were obtained for particles entrained in groundwater at two locations. The particles were retained on prefilters with pore sizes of 5 μm and 1 μm, dividing the particles into two size ranges >5μm and 1-5 μm. The resulting P_P values for ^{238}U were in the range $3.7\text{-}6.5 \times 10^4$ mL/g. This relatively small range was considered to be evidence that the distribution of uranium in the system may be governed by sorption interactions. The P_P values for ^{230}Th were much higher; 7.3×10^7 to 1.6×10^9 mL/g.

The partition ratios for weak acid (0.5M HCl) extractable phases on the particles entrained in the groundwater were estimated. The P_{PA} values were lower than the P_p values; $2.6\text{-}6.5 \times 10^4$ mL/g for ^{238}U, and 2.4×10^6 to 1.1×10^9 mL/g for ^{230}Th. It was shown that the isotope content of the acid-extractable phases of these particles was consistent with these phases containing radionuclides adsorbed from the groundwater, whereas the data obtained by total digestion included some radionuclides in inaccessible phases.

Partitioning of ^{238}U between groundwater and <10 μm particles

Radionuclide migration retardation mechanisms, such as sorption, are probably controlled by the fine fraction of solid phase. Consequently, weathered zone groundwater data was compared with the fine fraction of rocks (<10 μm) from the same sampling points. The P_{PB} (bulk particle partition ratio) values were between 5.1×10^3 and 1.1×10^5 mL/g. Also determined were P_{PA} (accessible particle partition ratio) values for accessible phases only, as estimated by extraction with TAO (2.7×10^3 to 1.4×10^4 mL/g).

Partitioning of uranium between groundwater and bulk rock

Averaged bulk rock ^{238}U contents were compared with groundwater from the same borehole/depth. Bulk partition ratio (P_B) values obtained were from 1.0×10^3 to 5.2×10^4 mL/g. There appears to be a trend of decreasing $^{234}U/^{238}U$ of the groundwater with decreasing P_B for samples taken from near the base of weathering (24 m). The activity ratio in samples from the mid-weathered zone (14 m) did not appear to be affected by P_B, and this was also the case for unweathered zone samples. This data suggest that, where the concentration of uranium in the groundwater is high compared to that in the partially weathered rock (P_B approximately $< 10^4$ mL/g), development of $^{234}U/^{238}U$ values less than unity may develop.

Partitioning of ^{238}U between groundwater and rock accessible phases

Groundwater was compared with different chemically defined phases of the solid substrate, to see if the $^{234}U/^{238}U$ value of a particular component of the solid material is likely to be near equilibrium with the groundwater. TAO extractions were used to estimate the amount of uranium accessible for interactions with the groundwater. The comparisons could only be made where the rock sample was weathered and contained no uranium minerals, hence, there were only five points suitable for this comparison. However, there does appear to be a strong relationship between concentrations of uranium in groundwater and accessible phases of the rock. The accessible partition ratio (P_A) was in the range 4.6×10^2 to 1.0×10^3 mL/g total rock, and was significantly lower than the P_B or P_P values. The $^{234}U/^{238}U$ values in the accessible phases were close to those in the corresponding groundwater, giving confidence that exchange between the solute and the accessible solid phases is occurring.

References

Edis, R., Cashion, J., Klessa, D., Koppi, A.J., Murakami, T., Nightingale, T., Payne, T., Snelling, A.A. and Yanase, N. (1992): Chemistry and Mineralogy of Rocks and Soil. Volume 8 of the Alligator Rivers Analogue Project Final Report, Ansto, ISBN 0-642-59934-3 (in preparation).

Emerson, D.W, Mills, K.J., Miyakawa, K., Hallett, M.S. and Cao, L.Q. (1992): Geophysics, Petrophysics and Structure, Volume 4 of the Alligator Rivers Analogue Project Final Report, Ansto, ISBN 0-642-59930-0 (in preparation).

McKinley, I.G. and Alexander, W.R. (1992): Constraints on the applicability of "in-situ distribution coefficient" values. J. Environmental Radioactivity, 15: 19-34.

Payne, T.E., Edis, R., Herczeg, A.L., Sekine, K., Seo, T., Waite, T.D. and Yanase, N. (1992): Chemistry and Isotopic Composition of Groundwater, Volume 8 of the Alligator Rivers Analogue Project Final Report, Ansto, ISBN 0-642-59933-5 (in preparation).

Snelling, A.A (1992): Geologic Setting, Volume 8 of the Alligator Rivers Analogue Project Final Report, Ansto, ISBN 0-642-59928-9 (in preparation).

URANIUM OREBODIES AS SOURCE TERMS FOR RADIONUCLIDES: MEASUREMENTS AND MODELS

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1. Background

Among the most persistent radioactive constituents of high-level wastes from nuclear fission power reactors are plutonium-239 ($t_{1/2}$, 24,100 a), iodine-129 ($t_{1/2}$, 1.6×10^7 a), and technetium-99 ($t_{1/2}$, 2.1×10^5 a). Natural analogues, particularly uranium ore deposits, offer a means to evaluate the geochemical transport and retention properties of these radionuclides in analogous natural materials. In these natural environments, ^{239}Pu and fission-product elements have a unique geochemical history. They are produced by nuclear processes in minerals. Under certain hydrogeochemical conditions, they may be released from their host minerals, transported from their site of production, and retained at another location. However, the feasibility of using uranium minerals as analogues to characterize the behavior of these nuclear reaction products (NRP) in spent fuel relies upon a capability to characterize NRP concentrations in the host minerals.

The purpose of our study has been to evaluate the accuracy and precision with which NRP production rates can be estimated, and the degree of retention of these radionuclides by the source uranium ore.[1] Measured abundances of natural ^{239}Pu, ^{99}Tc and ^{129}I in uranium ores are compared below to calculated abundances. The comparison is formalized by calculating the fractionation factor α, which is the ratio of ratios shown in the equation below:

$$\alpha = (NRP/U)_M \,/\, (NRP/U)_{SE}$$

where NRP = nuclear reaction product; subscript M refers to measured element ratios; and subscript SE refers to element ratios calculated under the assumption of secular equilibrium, the condition in which the rates of production and decay of a radioactive species exactly balance one another. If the uncertainty in the production rate estimate is small, then the factor α is a measure of the extent of any change in NRP concentration relative to uranium over several NRP half-lives, e.g., a period of about 1×10^5 years for ^{239}Pu. An α-value of 1 manifests no fractionation between the two elements. Values less than 1 suggest preferential loss of the NRP relative to U, and values greater than 1 suggest preferential gain of the NRP relative to U. This approach is being used to provide information useful to the development and verification of source-term models used in the performance assessment of high-level waste repositories.[2]

2. Sample descriptions and analyses

Our study has focussed on samples from unweathered and unaltered zones in several different primary ore deposits, i.e., samples believed to represent systems which are closed with respect to retention of nuclear reaction products. A wide range of uranium contents and ore mineralogies were selected in order to test our understanding of factors controlling nuclide production rates and degrees of nuclide retention. The deposits investigated include Koongarra, Australia; Key Lake, Cigar Lake, and Beaverlodge, Canada; Oklo, Gabon; and Shinkolobwe, Zaire. These ores can be considered as natural analogues of spent fuel and of its alteration products as well as source terms for radionuclide migration in ground water.[1,3-7] A few analyses of NRP concentrations have also been made in samples from dynamic open systems: specifically, ores from the altered and weathered zones of the Koongarra deposit, and ground waters from Koongarra.[1,8]

Sample preparation methods are documented in Ref. 1. Iodine-129 and ^{36}Cl measurements were obtained by accelerator mass spectrometry (AMS) at the Nuclear Structure Research Laboratory of the University of Rochester.[9,10] Tc and Pu isotopic abundances were measured by thermal ionization mass spectrometry.[11-13] Measured NRP concentrations are reported below:

Table 1. Measured NRP/U ratios (x 10^{12}) in primary uranium ores[1]

SAMPLE	DEPOSIT	% U	^{239}Pu/U	^{129}I/U	^{99}Tc/U
G4674	Koongarra	11.5	1.4	1.0	n.m.
G2698	Koongarra	19.1	2.6	1.3	≤ 1.8
KL756	Key Lake	22.4	2.6	0.75	n.m.
KL785	Key Lake	9.0	1.3	n.m.	n.m.
CS235L	Cigar Lake	54.6	1.9	2.1	n.m.
W83A	Cigar Lake	40.8	3.0	1.8	≤ 1.8
W83C	Cigar Lake	46.8	2.8	2.8	n.m.
Z9-005	Oklo Zone 9	62.8	0.8	n.m.	n.m.
Z9-028	Oklo Zone 9	62.2	3.0	2.7	n.m.
NBL-6	Skinkolobwe	45.4	5.2	7.2	1.6*
BL-5	Beaverlodge	7.1	3.1	n.m.	n.m.

n.m. not measured
* Ref. 14

3. Source-term modeling

In order to assess NRP mobility, measured NRP concentrations are compared to those expected if the ores had behaved as closed systems with respect to uranium and its products. Under conditions of secular equilibrium in closed systems, NRP concentrations are solely a function of neutron flux, uranium content, and NRP decay rates. Fission products ^{99}Tc and ^{129}I are produced by three mechanisms: spontaneous fission of ^{238}U, which is a function of the uranium concentration, and neutron-induced fission of ^{235}U and ^{238}U. For ^{239}Pu, the only production mechanism is neutron-capture by ^{238}U; ^{36}Cl is produced by neutron-capture by ^{35}Cl and is of interest as a possible in-situ monitor of the neutron flux and as an indigenous water tracer. The physical and chemical properties that affect the in-situ neutron flux were measured in each sample, including abundances of major elements, selected minor and trace elements, and neutron production rates.[1] Using this data as input, the Monte Carlo Neutron and Photon (MCNP) transport code[15] was used to calculate neutron fluxes and neutron-capture reaction rates for the ore samples.

Modelling was conducted for two geometries:

(a) The "infinite model" was used to estimate NRP abundances by modelling the sample as homogeneous material with the elemental composition of the sample and infinite dimensions. In cases where the material surrounding the sample has a lower uranium concentration--which is true for nearly all of the samples in this study--the infinite model results should generally serve as upper limits for the true NRP abundances. This approach nearly always led to a substantial over-estimate of the NRP production rates.[1]

(b) The "geometry model" was used to obtain more realistic estimates of NRP abundances. In these cases, each sample was modelled as high-grade material bordered by material with different, generally lower, U contents.

4. Comparison of measurements with model predictions

4.1 Iodine-129

Measured $^{129}I/U$ ratios in unweathered primary ores investigated in this study (Table 1) exceed minimum ratios predicted from spontaneous fission of ^{238}U ($^{129}I/U = 6 \times 10^{-13}$). However, concentrations are variably less than amounts predicted by the source-term model under a wide variety of assumptions (Figure 1). Although production of ^{129}I by neutron-induced fission of ^{235}U and ^{238}U is difficult to estimate with any accuracy, the measurements suggest that ^{129}I may be depleted to a larger extent in samples from Koongarra than in samples from Cigar Lake. Samples from weathered primary ore from Koongarra contain quantities of ^{129}I that are well below the minimum abundance expected for spontaneous fission, an unambiguous indicator of loss of this fission product from its site of production.[1,16] The mobility of radioiodine is also apparent by its high concentrations in ground waters flowing through the Koongarra deposit.[8]

4.2 Technetium-99

Predictions of the source-term model indicate that ^{99}Tc production in uranium ores is dominated by spontaneous fission of ^{238}U. Production of ^{99}Tc by induced fission of ^{235}U is 5-25% of the total for the samples studied, and that by neutron-induced fission of ^{238}U is generally ≤ 4 %. The dominance of the spontaneous fission component simplifies interpretation of measured ^{99}Tc concentrations in uranium minerals. The validity of the source-term model prediction is borne out by three preliminary analyses of ^{99}Tc in primary ores, which suggested ^{99}Tc abundances about the levels predicted by the model, no more than 10% above that expected for spontaneous fission alone ($^{99}Tc/U = 1.6 \times 10^{-12}$).

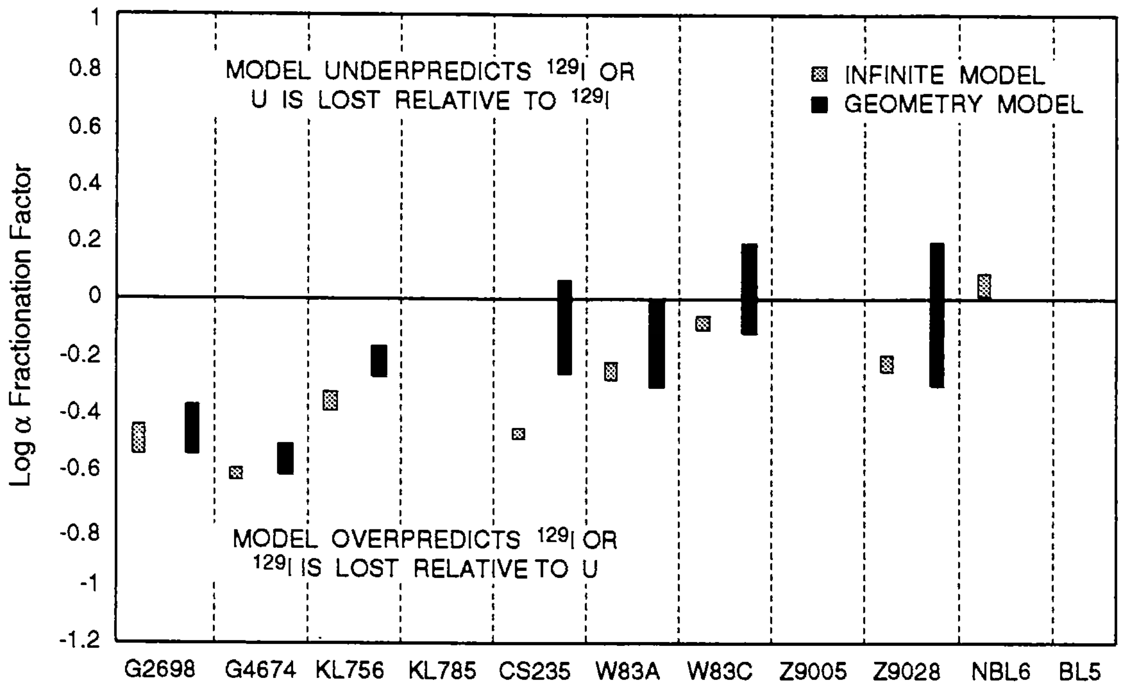

Figure 1. Comparison of measured and predicted ^{129}I/U ratios for primary uranium ores, assuming negligible contribution from induced fission of ^{238}U. See text for definition of α.

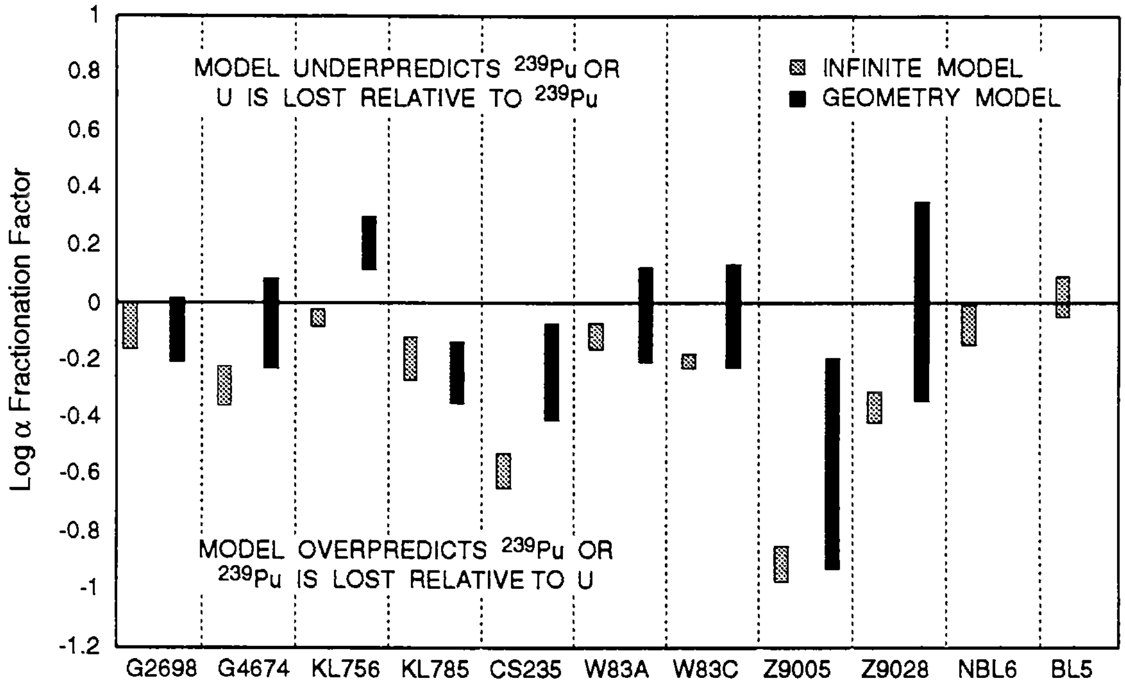

Figure 2. Comparison of measured and predicted ^{239}Pu/U ratios for primary uranium ores.

4.3 Plutonium-239

Source-term models predicting ^{239}Pu abundances in uranium minerals lead to ambiguous conclusions. Measured abundances are generally, but not always, within the range of predicted values (Figure 2). In very heterogeneous media such as that typical of uranium ore deposits, chemical parameters critical for determination of ^{239}Pu production rates are difficult to characterise with sufficient accuracy to use the results for evaluating degree of retention or loss of ^{239}Pu from the orebody.

5. Conclusions about modeling capability

The source-term model is most useful as a predictive tool in cases where the sample represents a volume of material that is large relative to the mean path length of a neutron (e.g. NBL-6 and BL-5, which have been distributed as certified reference ores for uranium assays), or where the sample is derived from relatively homogeneous material. The model also provides useful predictions, although with greater uncertainties, of NRP abundances in samples taken from well-specified locations in geometrically well-defined environments. In the latter case, realistic results are only obtained when the model incorporates additional information about sample environs. The largest uncertainties attend calculations of NRP abundances in small samples taken from heterogeneous geologic systems; for these samples, even with detailed compositional information, the source-term model is not able to predict absolute NRP abundances with the accuracy needed to calculate NRP retention or losses unless the fractionation between uranium and its reaction products is substantial, i.e., $\alpha > 0.1$ or $\alpha < -0.1$.

Uncertainties associated with the source-term model range from low (~10%) for ^{99}Tc to moderate (~20-50%) for ^{129}I and ^{239}Pu.[1] These uncertainties are almost certainly underestimated. For example, H/U and Gd/U ratios are shown by the model results in Ref. 1 to be critical parameters in controlling ^{235}U fission rates, but varying Gd/U ratios within the ranges used in that study (80-120% of measured values) may not sufficiently reflect the true uncertainty in their concentrations. The effect of varying other elemental concentrations, such as B, F or Fe, which might also have a major influence on the neutron flux in some of the ores, has not been investigated. For the geometry model, an infinite number of cases could be proposed to model the lateral extent, thickness, and elemental heterogeneities in stratigraphic intervals, e.g. with barren, high-porosity seams cutting through dense, high-grade material or vice versa.

Even in those cases where the source-term model has not been able to provide precise estimates of the true NRP production rates, it has been invaluable for identifying the critical elemental parameters controlling these rates and establishing the conditions under which various NRP production rates should correlate with or constrain one another. For example, under most conditions, ^{36}Cl ($t_{1/2}$, 3.0×10^5 a), another long-lived neutron-capture product found in uranium ores, is shown to be an ideal *in-situ* monitor of the ^{235}U fission rate, which is the dominant source term for ^{129}I and possibly a significant one for ^{99}Tc. Similarly, ^{239}Pu/U ratios can be used to establish limits on the ^{238}U neutron-induced fission rate; the ratios measured in this study suggest that ^{238}U induced fission comprises < 4 % of the total fissions in most of the ore samples studied and hence can be neglected as a source of ^{129}I and ^{99}Tc, as was assumed in the preparation of Figure 1.

6. Acknowledgements

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References

[1] Fabryka-Martin J.T., and D.B. Curtis, 1992 (in press), Geochemistry of ^{239}Pu, ^{129}I, ^{99}Tc and ^{36}Cl, Alligator Rivers Analogue Project Final Report, Vol. 15 (Australian Nuclear Science and Technology Organisation, Lucas Heights NSW Australia), Report DOE/HMIP/RR/92/085.

[2] Curtis D.B., J. Fabryka-Martin, and P. Dixon, this volume, Natural constraints on radionuclide release rates, Proceedings of 5th Natural Analogue Working Group meeting held October 5-9, 1992, Toledo, Spain.

[3] Cramer J.J. (1986) Sandstone-hosted uranium deposits in northern Sasketchewan as natural analogs to nuclear fuel waste disposal vaults. Chem. Geol., 55:269-279.

[4] Curtis D., J. Fabryka-Martin, R. Aguilar, M. Attrep, and F. Roensch, 1992, Plutonium in uranium deposits: natural analogues of geologic repositories for plutonium-bearing nuclear wastes, High Level Radioactive Waste Management, Proc. of the 3rd Intl. Conf., Vol 1, pp 338-344.

[5] DeLaeter J.R. (1985) The Oklo reactors: Natural analogues to nuclear waste repositories, Search, 16:193-196.

[6] Ewing R.C. and Jercinovic M.J. (1987) Natural analogues: their application to the prediction of the long-term behavior of nuclear waste forms. Materials Research Society Symposia Proc., 84:67-83.

[7] Finch R.J., and Ewing R.C. (1989) Alteration of natural UO2 under oxidizing conditions from Shinkolobwe, Katanga, Zaire: a natural analogue for the corrosion of spent fuel. Swedish Nuclear Fuel and Waste Management Company (SKB). Technical Report 89-37.

[8] Fabryka-Martin J., Roman D., Airey P.L., Elmore D. and Kubik P.W. (1987) Redistribution of natural iodine-129 among mineral phases and groundwater in the Koongarra uranium ore deposit, N.T., Australia. Proc., Natural Analogues in Radioactive Waste Disposal: a Symposium (B. Côme, ed.), Commission of the European Communities, Brussels, Belgium. CEC report EUR 11037 EN.

[9] Elmore D., Fluton B.R., Clover M.R., Marsden J.R., Gove H.E., Naylor H., Purser K.H., Kilius L.R., Beukens R.P., and Litherland A.E. (1979) Analysis of ^{36}Cl In environmental water samples using an electrostatic accelerator, Nature, 277:22.

[10] Elmore D., Gove H.E., Ferraro R., Kilius L.R., Lee H.W., Chang K.H., Beukens R.P., Litherland A.E., Russo C.J., Purser K.H., Murrell M.T., and Finkel R.C. (1980) Determination of ^{129}I using tandem accelerator mass spectrometry, Nature, 286:138-139.

[11] Rokop D.J., Schroeder N.C., and Wolfsberg K. (1990) Mass spectrometry of technetium at the subpicogram level, Analytical Chem., 62:1271-1274.

[12] Attrep M., Jr., F.R. Roensch, R. Aguilar, and J. Fabryka-Martin, 1992 (in press), Separation and purification of plutonium in uranium ores for mass spectrometric measurement, Radiochim. Acta.

[13] Perrin R.E., Knobeloch G.W., Armijo V.M. and Efurd D.W. (1985) Isotopic analysis of nanogram quantities of plutonium by using a SID ionization source, Intl. J. Mass Spectrometry and Ion Proc. 64:17-34.

[14] Kenna B.T. and Kuroda P.K. (1964) Technetium in nature, J. Inorg. Nucl. Chem., 26:493-499.

[15] Briesmeister J. (ed.), 1986, MCNP - A General Monte Carlo Code for Neutron and Photon Transport, Version 3A, LA7396-M Rev. 2 (manual), Los Alamos National Laboratory.

[16] Fabryka-Martin J., Davis S.N., Roman D., Airey P.L., Kubik P.W. (1988) Iodine-129 and chlorine-36 in uranium ores, 2. Discussion of AMS measurements. Chem. Geol. (Isot. Geos. Sect.), 72:7-16.

MINERAL ALTERATION AND URANIUM-MINERAL ASSOCIATIONS

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Abstract

The weathering of chlorite, one of the major minerals of the host rock of the uranium ore deposit at Koongarra, Australia, and its effects on the redistribution of uranium were briefly reviewed. We examined the processes, mechanisms, and kinetics of the chlorite weathering, and the uranium concentrations in minerals by various methods. The observed uranium distribution in the vicinity of the ore deposit was compared to that calculated, using a one-dimensional, advection-dispersion-sorption model. We have established that the chlorite weathering, one of the geochemical processes, has affected the uranium redistribution at Koongarra, and demonstrated how geochemical processes are used for the prediction of long-term nuclide migration.

1. Introduction

The Koongarra uranium ore deposit is one of the sites for natural analogue studies of radionuclide migration (Airey, 1986, and Airey and Ivanovich, 1986). The ore deposit extends just below the surface to 60 m depth in a tropical monsoonal area, the host rock of the deposit and the uranium ore minerals have been altered (Snelling, 1980), and this has had a great influence on the uranium redistribution in the vicinity of the ore deposit. The circumstances around and downstream the ore deposit are similar to those in near-fields and far-fields of the repositories, respectively.

Quartz-chlorite schist, the host rock, has probably been subjected to weathering for more than one million years (Airey et al.,1986). Although quartz is resistant to the weathering and persists even at the surface, chlorite has been altered to clay minerals and iron minerals (Airey, 1986). The alteration products of chlorite are vermiculite, kaolinite, smectite, ferrihydrite, goethite and hematite (Airey et al., 1984). The secondary uranium ore deposit, which has been formed by alteration of the primary ore deposit and the precipitation of secondary uranium minerals, is located in the weathered zone, which is present below the surface to about 20 m deep, but not in the unweathered zone, where chlorite remains unaltered. Uranium is found as uranium phosphates in the secondary ore deposit, and to be associated with the alteration products of chlorite downstream the secondary ore deposit (Snelling, 1980).

2. Experimental

Rock samples were examined by various analytical methods: X-ray diffraction analysis (XRD), optical microscopy (OM), scanning electron microscopy (SEM), electron microprobe analysis (EMPA), transmission electron microscopy (TEM) and analytical electron microscopy (AEM) for mineralogical and crystallographical information; alpha-autoradiography, visible spectroscopy (VIS), and alpha- and gamma-spectroscopy for information on the uranium-mineral association; and chemical analysis for chemical information.

3. Weathering of host rock minerals

The secondary ore deposit has been formed by the dissolution of the primary uranium minerals and the precipitation of secondary uranium minerals for the past 1 - 3 million years (Airey et al.,1986). The groundwater interacting with the uranium minerals has also interacted with the host rock and weathered chlorite. The X-ray diffractograms shows that the conversion sequence of chlorite alteration is (1) chlorite, (2) chlorite/vermiculite intergrade, (3) interstratified chlorite/vermiculite intergrade and vermiculite, (4) vermiculite and (5) kaolinite (+ smectite) (Fig. 1). This sequence may be more simply expressed as a chlorite → vermiculite → kaolinite conversion. These minerals occur as a function of depth; near the end of the secondary ore deposit, chlorite alone is present at 25 m and deeper, but rapidly decreases in amount between 25 and 24 m, and disappears at 24 m. Vermiculite appears at 25 m depth and kaolinite begins to persist at 24 m depth. Vermiculite disappears at 20 m where kaolinite is predominant as it is in the shallower zone.

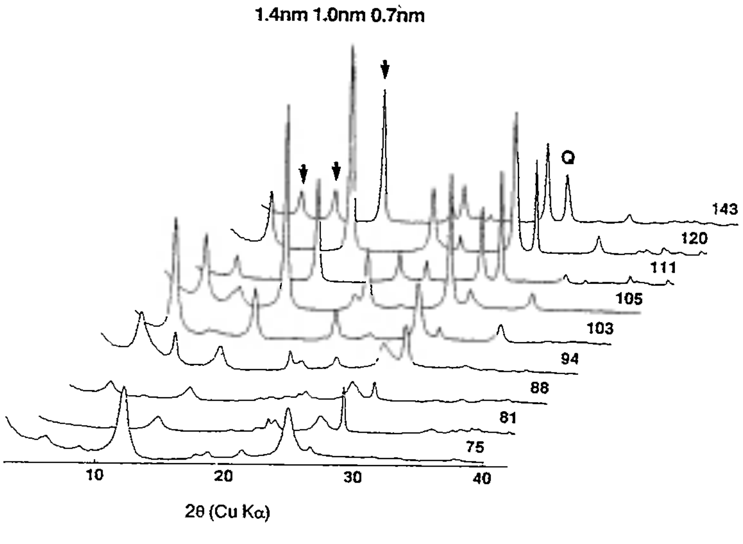

Figure 1. X-ray diffractograms of a suite of the DDH3 core. The figures in the right indicate the distances from the surface along the core in feet. Q denotes quartz. Copper with a graphite monochrometer at 35kV and 15mA.

During the weathering process, iron minerals are formed. With the proceeding of the weathering, iron minerals are present between chlorite and vermiculite layers, they precipitate between grain boundaries, and then veins of the iron minerals are formed. Because the iron minerals are closely associated with uranium as mentioned below, the distribution of iron minerals is important to understand the distribution of uranium. In order to express the chlorite alteration in the first stage, we give an example using the transformation of chlorite to vermiculite as follows:

$$(Mg_{2.24}Fe^{2+}_{2.61}Al_{1.14})(Si_{2.89}Al_{1.11})O_{10}(OH)_8 + xH_2O \rightarrow$$

Chlorite

$$(Mg_{1.36}Fe^{3+}_{0.95}Al_{0.55})(Si_{2.80}Al_{1.20})O_{10}(OH)_2 + 1.66FeO(OH).yH_2O$$

Vermiculite Ferrihydrite?

$$+ 0.88Mg^{2+} + 0.09Si^{4+} + 0.50Al^{3+}.$$

Note that the mass balance of hydrogen and oxygen ions is not considered. Because kaolinite has a similar chemical formula to the ideal one, $Al_2Si_2O_5(OH)_4$, a large amount of Fe along with that of Mg is also released during the decomposition of vermiculite to kaolinite.

4. Estimation of the reaction time and the kinetics of chlorite weathering

The reaction time of chlorite to kaolinite is the same as life time of vermiculite. The timescale of the secondary mineralization is estimated to be 1-3 My (Airey et al., 1986). Because the alteration period is probably the same as that of the secondary mineralization, we assumed the period roughly 2 My. The other assumptions for the estimation of the life time of vermiculite are: (1) No erosion has occurred during the period, (2) Kaolinization (from vermiculite) occurs at a constant rate, (3) The alteration direction is normal to the surface, and (4) The vermiculite front (25 m deep) has proceeded at a constant rate for 2 My The above assumptions and the thickness of the vermiculite layer (5 m) give 400,000 years for the life time of vermiculite, which are also the reaction time of chlorite to kaolinite.

Assuming that the chlorite to vermiculite and the vermiculite to kaolinite reactions are assumed to be first order, we calculated the mineral compositions with time for 50 wt% chlorite (an average value for the host rock). The calculated values are compared to those observed by XRD, chemical analysis and specific gravity measurement (Fig. 2). The calculations of the mineral composition with time suggest that: (1) The reaction rates from chlorite to vermiculite and from vermiculite to kaolinite are time-dependent, (2) The weathering has not proceeded under the same conditions as those in the beginning. The formation of fine-grained alteration products may result in the increase in mineral-groundwater reaction surfaces, the local change in groundwater flow rate and water chemistry, and so on.

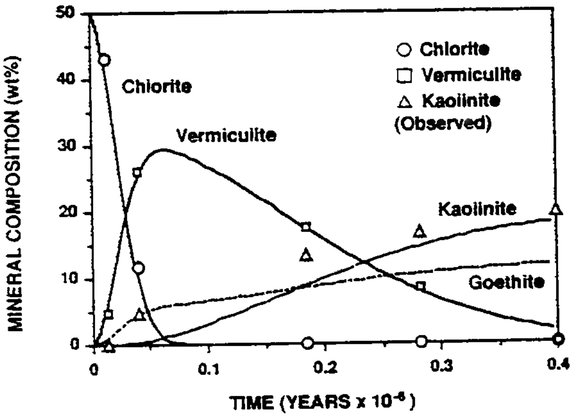

Figure 2. Changes in mineral composition with time.

5. Uranium distribution in minerals

Figure 3 shows the relevance of the extent of the chlorite weathering to the uranium concentrations on the millimeter scale. Chlorite in this sample is in the state from unweathered to completely weathered. This sample has a fracture surface at the upper end and a strongly weathered zone next to the fracture (denoted as F and A in Fig. 3a, respectively). Iron minerals, possibly ferrihydrite, goethite, and hematite, are abundant in the strongly weathered zone. Next to the strongly weathered zone, there is an intermediately weathered zone, where chlorite is weathered to vermiculite and the iron minerals are present between grain boundaries (B in Fig. 3a). In a slightly weathered zone which is in the lowest part of the figure (C in Fig. 3a), most chlorite grains are not weathered. The alpha-track map shows that uranium concentrations vary with the extent of weathering (Fig. 3b); the strongly weathered zone has a high uranium concentration, the uranium concentration decreases in the intermediately weathered zone, and uranium is much less associated with chlorite in the slightly weathered zone. The comparison strongly suggests that although chlorite itself is not a good adsorbent of uranium, it becomes a good adsorbent if it is weathered to vermiculite and further weathered. The association of uranium and minerals occurs intensively along fractures, microfissures, schistosities, and grain boundaries where the groundwater preferentially flows, i.e., where the weathering occurs intensively.

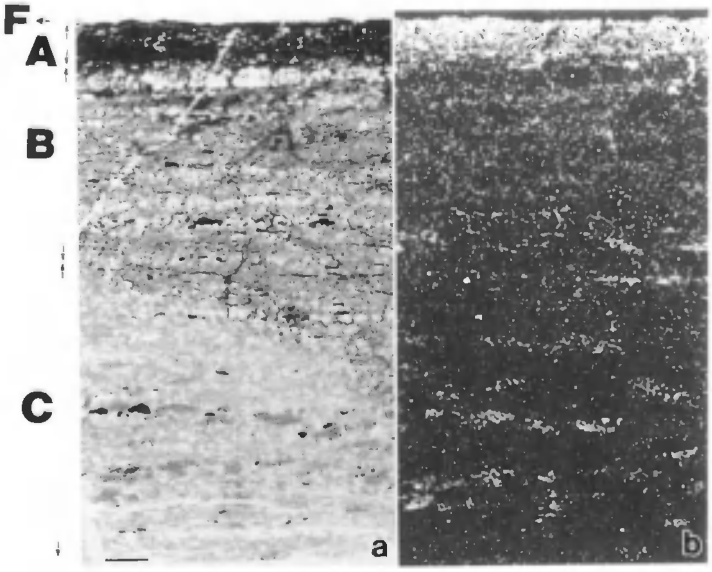

Figure 3. Comparison of a DDH4-100 thin section (a) and its alpha-track map (b). F denotes a fracture, and A indicates the strongly weathered zone (black in color), B, the intermediately weathered zone (gray), and C, the slightly weathered zone (lighter gray). White areas are those of quartz. The density of alpha tracks differs between the zones. The bar indicates 1 mm.

The SEM/VIS/EMPA studies suggest that possible main uranium fixation and redistribution mechanisms are as follows: Ferrihydrite, a direct by-product of chlorite weathering, either coprecipitates with saléeite microcrystals, or complexes with a uranyl phosphate ion which is then crystallized to form saléeite. Goethite and hematite quickly dominate ferrihydrite because the half conversion of ferrihydrite to goethite and hematite takes only about a hundred days (Schwertmann and Murad, 1983). The ferrihydrite conversion is much faster than the chlorite to vermiculite conversion. The iron minerals move to be accumulated in grain boundaries, microfissures, and fractures with retaining uranium.

6. Calculations of uranium distribution

We estimated the uranium distribution influenced by the chlorite weathering based on the mechanisms and kinetics of chlorite weathering, and the uranium concentrations and distribution in minerals. The one-dimensional advection-dispersion-sorption model considers two important factors resulting from the chlorite weathering with time; changes in distribution coefficients and porosities of the rocks. The change of a mineral composition with time by weathering is the same as that in Fig. 2. The porosity is assumed to vary with time as the apparent density of a rock, which is an average density of the coexisting minerals, varies. The distribution coefficients of uranium and thorium for a rock at a given time are expressed as average values of those of the constituent minerals at the time. Thus, the porosity and distribution coefficients change with time as the mineral composition changes.

Figure 4a shows the contours of the calculated uranium concentrations in the cross section, and Figs. 4b compares the calculated uranium concentrations to those observed for bulk rocks of two core holes. The calculated uranium concentration distribution agrees, in general, well with that observed with the reasonable values of the Darcy velocity, initial concentration of uranium in the groundwater, and dispersion length.

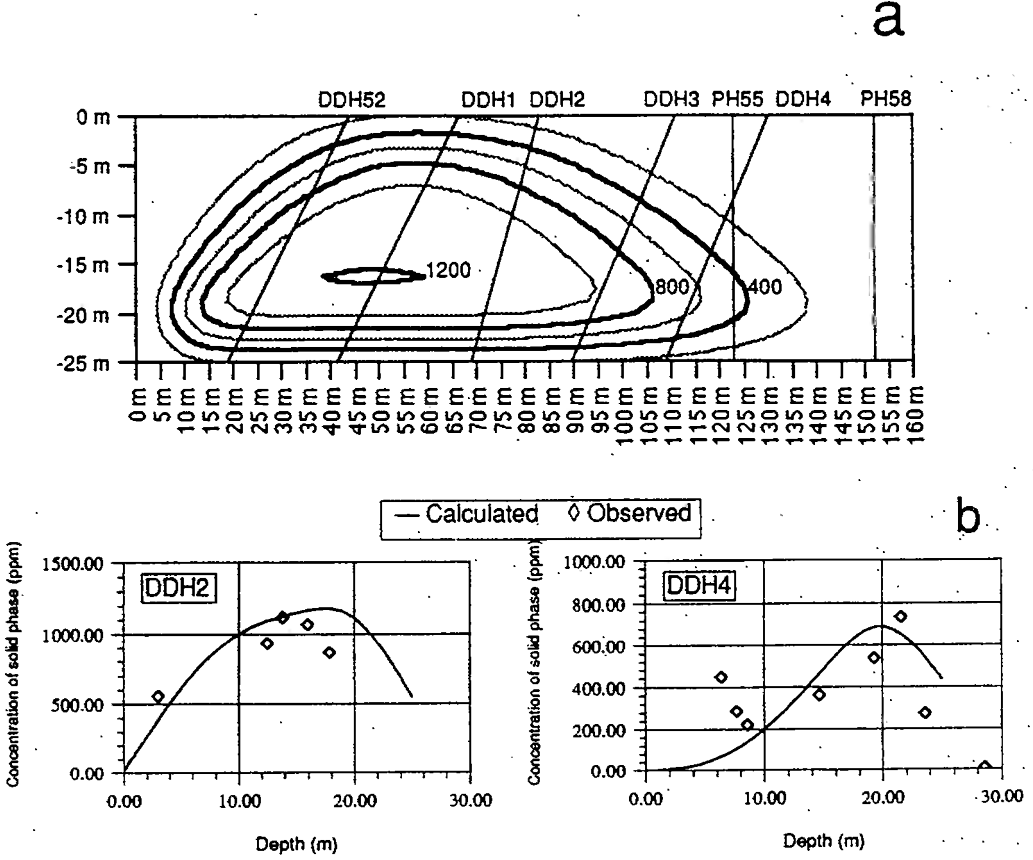

Figure 4. Calculated U-238 concentrations (ppm) in the cross section (a), and comparison of calculated and observed U-238 concentrations (ppm) in DDH2 and DDH4 core holes (b).

In this model, we considered the effects of the changes in distribution coefficients and porosities resulting from the chlorite weathering on the uranium redistribution or migration. The good consistency of the calculated and observed results indicates that the uranium migration at Koongarra has been affected by the chlorite alteration. More importantly, it may be possible to predict uranium migration for long-term, at least for a few millions of years, using the present method.

References

Airey, P. L., Chemical Geology 55, 255-268 (1986).

Airey, P. L. Golian, C. and Lever, D. A., Topical Report AAEC/C49, Australian Nuclear Science and Technology Organisation, Sydney (1986).

Airey, P. L. and Ivanovich, M., Chemical Geology 55, 203-213 (1986).

Airey, P. L. Roman, D. Golian, C. Short, S. Nightingale, T. Lowson, R. T. and Calf, G. E., NRC-04-81-172, Annual Report 1982-1983, AAEC Report C40 (NUREG/CR-3941, Vol. 1), 21-26 (1984).

Schwertmann, U. and Murad, E., Clays and Clay Minerals 3, 277-284 (1983).

Snelling, A. A., Proceedings of IAEA International Symposium Uranium in the Pine Creek Geosyncline, J. Ferguson and A. B. Goleby (Eds.), IAEA, Vienna, 487-498 (1980).

URANIUM SORPTION MODELING - A SURFACE COMPLEXATION APPROACH

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ABSTRACT

Uranium sorption (adsorption and desorption) to both single, well-defined mineral phases and selected natural substrates has been undertaken in this component of the Alligator Rivers Analog Project. Single phases used include the amorphous iron oxide phase ferrihydrite, crystalline silica and two naturally occurring kaolinites, KGa-1 and Nichika. The surface properties of these materials have been rigorously defined and adsorption studies conducted over a range of solution pH, ionic strength, carbonate content, adsorbent and adsorbate concentrations and in the presence of uranium complexants and (potentially) competing adsorbates (such as phosphate and fluoride).

Results obtained in these adsorption studies to single oxide phases have been modelled using the surface complexation approach with a diffuse double layer description of the electrical double layer. Most success has been achieved by assuming the presence of two site types - one site type corresponding to a small set of high affinity cation binding sites and the other type corresponding to the total reactive sites available for sorption of protons, cations and anions. Assignment of the hydroxylated surface complex $>SOUO_2OH^o$ as the dominant U(VI) surface species appears to give the most satisfactory agreement between model and experiment with best-fit constants being derived using the non-linear optimisation program, FITEQL.

Preliminary studies in which we assumed that all U(VI) adsorption to the natural substrates could be accounted for by uptake on amorphous (TAO extractable) iron oxides and modelled the results accordingly were reasonably successful. However, more detailed analysis of this approach has indicated significant defficiencies. Detailed consideration is thus given to identification of site types and a multi-site surface complexation approach used. While not totally satisfactory, this approach is shown to hold considerable promise and provides a framework for quantification of U(VI) partitioning over a range of solution and solid phase conditions. The results of studies into the effects of substrate ageing are also reported.

1. Introduction

While the oxidation of highly insoluble U(IV) to more soluble U(VI) followed by a sequence of U(VI) precipitation-dissolution reactions appear to have contributed to the migration of uranium away from the Koongarra ore deposit in close proximity to the deposit, adsorption-desorption processes become increasingly important in the mitigation of uranium mobility further downfield where the solubility products of U(VI) minerals are no longer exceeded. In this paper, the results of investigation into factors influencing the adsorption-desorption of U(VI) to natural substrates from the weathered zone in the vicinity of the Koongarra ore deposit are reported and the applicability of mathematical models to describe the sorption phenomena to these substrates over a range of solution conditions are assessed.

1.1 Definitions

For the partitioning relationship $J_{aq} \leftrightarrow J_{ads}$, we define the distribution coefficient as

$$K_d = \Gamma_J/[J_{aq}]$$

where $[J_{aq}]$ = concentration of all dissolved species of solute J
and Γ_J = concentration of all adsorbed A.

This expression is used under conditions where equilibrium is reached. K_d is replaced by R_d under condions where equilibrium is not attained.

Distribution coefficients may vary over many orders of magnitude depending upon solution and solid conditions. Of particular importance are the solution pH and solute to solids ratio. In addition, the partitioning of U(VI) between solid and solution phases may be dramatically influenced by complexation of the radionuclide by organic and inorganic species and by change in partial pressure of carbon dioxide.

1.2 Approach used in this study

Given the impossibility of measuring K_d's over the range of possible (past, present and future) conditions, considerable motivation exists to develop a mechanistic understanding of factors controlling partitioning (due to sorption processes).

Such an understanding should encompass solution and solid conditions and lead to a mathematical description (a model) with some predictive ability.

The following approach has been adopted in this study:

i)identify principal solids likely to play a major role in sorption (iron oxides, kaolinites, quartz); ii) undertake laboratory (batch) studies on single phases over range of conditions to provide mechanistic insight; iii) develop model that encompasses acquired mechanistic understanding (and describes data reliably); iv) undertake laboratory studies of U(VI) sorption to selected natural substrates and make deductions concerning factors controlling adsorption; and v) extend model to natural substrate data.

1.3 Surface complexation model

Surface complexation models (SCM) extend the ion-association model of aqueous solution chemistry to include chemical species on surfaces (Davis and Kent, 1990).

A number of models have been developed within the overall framework of the surface complexation approach. Differences between the models are based on the interfacial structure of the electrical double layer (EDL) and the manner in which weakly-bound ions are treated.

In this work, particular attention is given to the Diffuse Double Layer Model (DDLM). In this model, amphoteric surface hydroxyl groups are assumed to form ionised surface sites, i.e.

$$>SOH_2^+ \leftrightarrow >SOH + H^+$$

$$>SOH \leftrightarrow >SO^- + H^+$$

Surfae complexation of cations such as UO_2^{2+} by hydrous oxides involves the formation of bonds with surface oxygen atoms and the release of protons from the surface. For example, formation of a possible 1:1 surface complex between divalent cation M^{2+} and surface oxygen atoms may be represented:

$$>SOH + M^{2+} \leftrightarrow >SOM^+ + H^+$$

2. Experimental methods

2.1 Preparation and properties of substrates

The ferrihydrite, $Fe(OH)_3$, was formed by raising the pH of a Fe^{3+}/HNO_3 solution to 6.0, and then aged for 65 hours in a continuously stirred, pH - controlled vessel at 25°C. Commercially available quartz particles of narrow size range (8-15μm in diameter) were exhaustively cleaned by repeated acid and base washings. The particles were thoroughly rinsed prior to use in sorption studies. Two kaolinites, the Clay Minerals Society standard, KGa-1, and a Japanese standard, Nichika #15-27-2 were chosen for intensive study of uranium sorption. The bulk chemical composition of these clays is similar with the exception that the Nichika kaolinite contains significantly more iron than the KGa-1 standard.

Cores were obtained from a number of selected locations (W1, W2, M2 and W7) in the weathered zone in the vicinity of the Koongarra deposit using a cable-tool rig which produces intact samples. The (non-dried) sample was then crumbled by hand then gently shaken in 0.1M $NaNO_3$ solution to break it up further and render the sample homoionic. The material was then passed through a mesh of approximately 1.5 mm diameter, removing the larger size fraction ("wet sieved"). The particles were maintained at all times in the ionic medium (0.1M $NaNO_3$). All particles were then resuspended by vigorous shaking for 30 minutes and a 5 mL sample of the slurry was removed by pipette at 13 cm depth after 15 minutes settling. The application of Stoke's Law indicated that all particles over approximately 15 μm should be eliminated by this procedure.

2.2 Procedures used in obtaining pH edges

For ferrihydrite, aliquots of the pre-aged slurry were transferred directly to open polypropylene centrifuge tubes and sufficient $NaNO_3$ added to bring the suspensions to the desired ionic strength. The volume of the aliquots was such that the suspension in each tube was 10^{-3}M in iron. For studies at pH > 7.0, $NaHCO_3$ was added, sufficient to achieve equilibrium with the experimental pH of interest. The pH of the slurry was adjusted to the experimental value, and the tube was shaken for 24 hours in a water bath at 25°C. The required amount of uranium was then added.

After 48 hours, the solid and liquid phases were separated by centrifugation at 15,000 rpm. The uranium concentration remaining in solution was typically determined using kinetic phosphorescence analysis (KPA) except in cases where very low concentrations of uranium (below the KPA detection limit) were added. In these experiments, the artificial isotope ^{236}U was added and the uptake quantified using α-spectrometry after the addition of a known quantity of ^{232}U (another artificial isotope) as a yield tracer.

Similar procedures were followed for the studies of uranyl uptake on kaolinite and quartz. For the kaolinite studies, 100 mg of the kaolinite under investigation was weighed into 30 mL centrifuge tubes and, after addition of sufficient acid or base, $NaNO_3$ and for the pH > 7 studies, $NaHCO_3$, the suspension was made up to 25 mL. A quartz concentration of 100 g/L was typically used with the quartz substrate suspended in KNO_3 rather then $NaNO_3$ to avoid NaF precipitation in studies of the effect of fluoride complexation of U(VI). Solute uranium concentrations were determined routinely by kinetic phosphorescence analysis.

In the case of the natural substrates, the slurry of fine particles was vigorously agitated to fully suspend the solid. Typically aliquots containing 100 mg of particles were transferred to 25 mL polypropylene centrifuge tubes.

Sodium nitrate and $NaHCO_3$ (if required) were added and the system allowed to equilibrate for 24 hours in a shaking water bath at 25°C. At this stage, ^{236}U (84 dpm or 10^{-7}M) was added and the pH readjusted. After 48 hours of equilibration, the solid and liquid phases were separated by centrifugation. A known amount of ^{232}U tracer was added to the clear supernate and the activities of ^{238}U, ^{236}U and ^{234}U were measured by α-spectrometry.

pH edges were obtained over a wide range of solution/suspension conditions for the single and natural substrates. While most studies were undertaken under atmospheric conditions, some investigations were perfomed in a glove box with gas composition of approximately 1% CO_2/10% O_2/89% N_2.

3. Results and discussion

3.1 Ferrihydrite

Following the approach used by Dzombak and Morel (1990), we have found that best results are obtained for U(VI) sorption to ferrihydrite by adoption of a surface complexation model in which two types of binding sites are assumed, namely (1) a small set of high-affinity sites, and (2) a large population of relatively low-affinity sites. Optimal fits as indicated by FITEQL results are obtained by considering the formation of hydroxylated uranyl surface complexes, SOUO$_2$OH and TOUO$_2$OH which exhibit a squared dependency on pH, i.e.

$$SOH + UO_2^{2+} + H_2O = SOUO_2OH + 2H^+$$

at strong and weak sites (SOH and TOH) of concentrations 7 x 10^{-7}M and 2 x 10^{-4}M respectively with log(formation constants) at these sites of -1.60 and -5.21. As shown in Figure 1, good fits over a wide pH range are obtained at different total uranium concentrations. This simple model also adequately describes partitioning in the presence of elevated concentrations of CO2 and at higher solids loadings. Increased uranyl adsorption is observed in the presence of added phosphate and is modelled satisfactorily by assuming the formation of a ternary uranyl phosphate surface complex; i.e.

$$TOH^\circ + H_3PO_4 + UO_2^{2+} = TPO_4UO_2^0 + 2H^+ + H_20$$

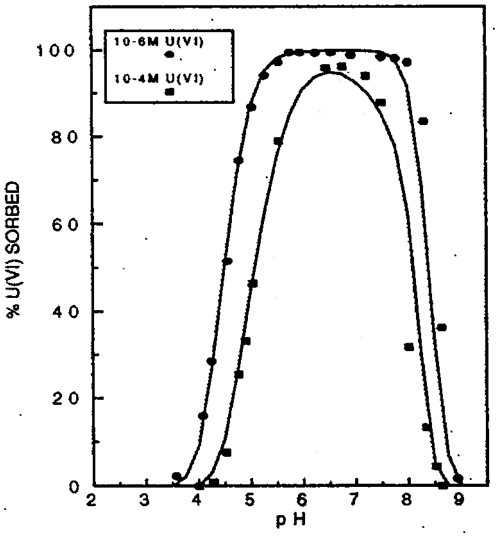

Figure 1. Adsorption of 10^{-4} and 10^{-6}M U(VI) to 10^{-3}M ferrihydrite.

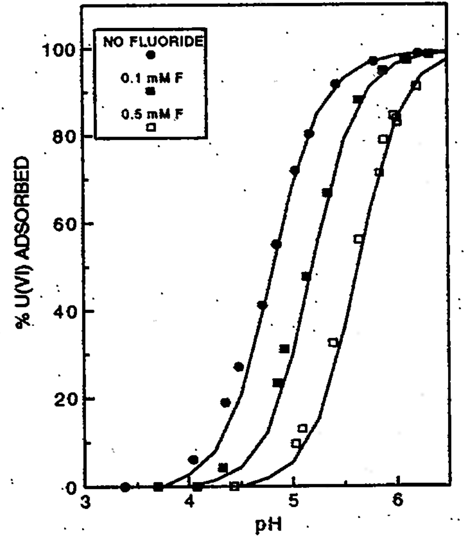

Figure 2. Adsorption of 10-6M U(VI) to 100g/L quartz in the presence of fluoride.

3.2 Quartz

Since data for adsorption of U(VI) to quartz is not available for multiple U(VI) concentrations, analysis in terms of a single site type only could be undertaken. As noted by Davis and Kent (1990), the site density used by Dzombak and Morel (1990) of 3.84 µmoles sites/m^2 for ferrihydrite closely approximates the site densities of a variety of minerals and is used here for quartz. The effect of solution phase fluoride complexation on U(VI) partitioning to quartz has also been investigated and, as shown in Figure 2, good fits obtained assuming formation of UO_2F^+.

3.3 Kaolinite

Introduction of surface reactions at ion exchange sites was found necessary in describing U(VI) adsorption to kaolinite. Reasonable fits were obtained using the following surface reactions:

$$2NaX + UO_2^{2+} = UO_2X_2 + 2Na^+$$
$$NaX + UO_2^{2+} + H_2O = UO_2OHX + Na^+ + H^+$$
$$TOH + UO_2^{2+} = TOUO_2^+ + H^+$$

3.4 Natural substrates

As indicated in Figure 3, U(VI) sorption to W2 is inadequately described either by assuming that the ferrihydrite present is the only adsorbing phase or by assuming that surface sites are evenly distributed across the complete surface area at a density of 3.84 µmoles of sites/m^2. Use of a combined ion exchange/specific adsorption model with log K's similar to those for kaolinite gives best agreement though, as shown in Figure 4, some departure is evident at low pH.

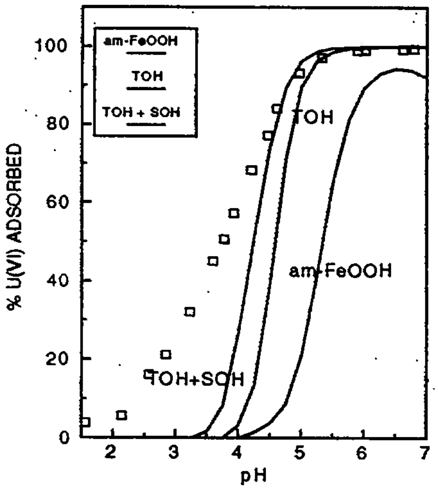

Figure 3. Comparison of experimental data with results of various models of U(VI) sorption to W2.

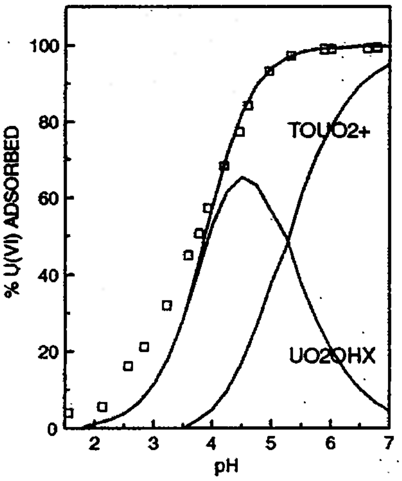

Figure 4. Comparison of experimental data with results of combined ion exchange and specific adsorption model.

References

Davis, J.A. and Kent, D.B. (1990) Surface complexation modelling in aqueous geochemistry. In Hochella M.F. and A.F. White (eds.) Mineral-water interface geochemistry. Reviews in Mineralogy, Vol.23. Washington, DC.

Dzombak, D.A. and Morel, F.M.M. (1990) Surface complexation modelling: hydrous ferric oxide, John Wiley and Sons, New York.

GEOCHEMICAL MODELLING OF PRESENT-DAY GROUNDWATERS

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The main purpose of this report is to summarize geochemical modeling studies of the present-day Koongarra groundwaters. Information on the present-day geochemistry and geochemical processes at Koongarra forms a basis for a *present-day analogue for nuclear waste migration.* The present-day analogue is built on studies of the mineralogy and petrology of the Koongarra deposit, and chemical analyses of present-day groundwaters from the deposit. The overall approach taken in the present study has been to carry out a series of aqueous speciation and state of saturation calculations for the groundwater compositions. The calculations reported in the present volume do not specifically take into account sorption processes. As such they complement the other experimental and modeling approaches taken in the Alligator Rivers Project (e.g. specifically oriented towards quantifying sorption processes). The calculations reported ihere are, of course, heavily dependent on the thermodynamic datafile used for the calculations. Aqueous speciation, saturation state and chemical mass transfer calculations were carried out using the computer programs EQ3NR and EQ6 (Wolery, 1983; Wolery et al., 1984) and a thermodynamic database generated at The Johns Hopkins University over the last eight years. In assembling all this data, considerable effort has been made to avoid inconsistencies that could introduce significant errors into the modeling calculations reported below.

Groundwaters at the Koongarra site have been sampled and chemically analyzed during the course of the Alligator Rivers Analogue Project from May, 1988 through April, 1991. The purposes of the present study are to summarize progress made in chemical modeling of the waters and to interpret the water speciation and saturation states in order to establish the factors controlling the groundwater compositions and their chemical evolution to their present state. The results of the aqueous speciation and state of saturation calculations carried out in the present study establish the dominant species thought to be present in the Koongarra groundwaters and the apparent states of saturation of the waters with respect to minerals and mineral assemblages through which the groundwaters might have migrated. These results are then used to infer specific possible water-rock interactions influencing or controlling aspects of the compositions of the groundwaters. Finally, all such inferences are tested and evaluated through reaction path calculations oriented towards studying the chemical evolution of the waters sampled at the present day.

All the speciation and state of saturation calculations carried out in the present study are reported on a diskette available on request. As a sample, complete details of the results of the calculations for representative waters at shallow depths (13 m, in the weathered zone), intermediate depths (23 m, in the transition zone), and the greatest depths sampled in the present study (37 m and more, in the unweathered zone) are available separately. Waters from these three depths are part of a continuum of compositions, speciations, and saturation states that extends towards the composition of present-day rainwater, but they also define three basic water types at the Koongarra site. The shallow waters have acidic pH, high CO_2 and SiO_2 contents, and low cation and anion contents. The main cations and anions are essentially uncomplexed. In the secondary orezone containing uranyl phosphate minerals, the shallow groundwaters contain high uranium concentrations up to about 0.4 mg/L, predominantly as the species $UO_2CO_{3(aq)}$, and low PO_4 (about 0.03 mg/L), predominantly as the species $H_2PO_4^-{}_{(aq)}$. In contrast, the deepest groundwaters have slightly alkaline pH, low CO_2, and high HCO_3^- and magnesium contents. In the main orezone containing uranyl oxide and silicate minerals, the deep groundwaters contain uranium up to about 0.1 mg/L, predominantly as the species $UO_2(CO_3)_2^{--}{}_{(aq)}$, and higher PO_4 (about 0.1 mg/L), predominantly as the species $H_2PO_4^-{}_{(aq)}$, $HPO_4^{--}{}_{(aq)}$ and $MgHPO_{4(aq)}$. Waters from the intermediate depths have characteristics intermediate to the two preceding types, but are also characterized by the highest values of SiO_2 (up to 43 mg/L) and PO_4 (up to 0.6 mg/L) at the site.

In contrast to even the most shallow groundwater, the rainwater has distinctively acid pH (about 4.4), but low levels of all other constituents. In terms of the potential of the rainwater to react with Mg-bearing minerals and rocks, it can be seen that the rainwater has the lowest activity ratio represented by the parameter $\log(a_{Mg^{++}}/(a_{H^+})^2)$. This parameter increases dramatically from rainwater through to the deepest groundwater. This suggests that weathering of chlorite-bearing schist by modified rainwater can account for the major element chemical variation in the Koongarra waters. The strongest evidence for this comes from:

(1) The simple trends of water speciation on activity diagrams. Almost all the waters plot within the kaolinite field on activity diagrams. They show a simple trend in $\log(a_{K^+}/a_{H^+})$ versus $\log(a_{Mg^{++}}/(a_{H^+})^2)$ that approaches the kaolinite/Mg-chlorite boundary. This trend suggests that the waters are part of a continous spectrum of reaction progress extending from shallow acidic relatively unreacted waters to deep slightly basic waters near equilibrium with chlorite and kaolinite.

(2) The trends of water speciation (log activity ratios) with depth, and the computed states of saturation of the waters with depth. These trends document, again, the spectrum of water saturation states. They overwhelmingly indicate that the relatively unreacted waters are the shallowest (at depths of 13 m or less, in the weathered zone proper) and that the most reacted waters are the deepest (at depths of 30-50 m in the fresh chlorite schist).

The very strong depth dependence of all the major chemical trends leads to a picture of essentially vertical recharge by rainwater that progressively evolves chemically by reaction with the chlorite schist. The principal reaction written for alteration of chlorite to kaolinite can be written as

$$\underset{\text{chlorite}}{Mg_5Al_2Si_3O_{10}(OH)_8} + 10CO_2 + 3H_2O = \underset{\text{kaolinite}}{Al_2Si_2O_5(OH)_4} + 5Mg^{++} + 10HCO_3^- + SiO_2$$

and predicts that an initial water charged with CO_2 will react with chlorite to produce waters containing $Mg:HCO_3^-:SiO_2$ in the ratio 5:10:1. The latter is a good approximation to the compositions of the deepest extensively reacted Koongarra groundwaters. Provided that there is no other source or sink for HCO_3^- (e.g. graphite or carbonates), the HCO_3^- contents of the waters are an indicator of the extent of reaction progress.

The hypothesis of acid attack on chlorite by CO_2 was further tested by carrying out reaction path calculations designed to predict the chemical evolution of Koongarra groundwaters and the trends discussed above. Chemical mass transfer calculations provide an additional tool with which to address the possible controls over the chemistry of the present-day groundwaters at Koongarra. The reactions postulated above were tested by starting with a relatively unreacted shallow acidic groundwater from within the weathered zone, and carrying out a predictive reaction path calculation to see if such a water might be expected to evolve to the state of a deeper more alkaline groundwater in equilibrium with kaolinite and chlorite. Similar calculations have also been carrried out with the same initial groundwater but with different inital rock-types. These calculations give insight into how much of the variability of the measured groundwater compositions can be attributed to reactions with a variety of rock types. In addition, they serve to illustrate how the results of the present study might have more general significance for the migration of radionuclides in nature.

BIBLIOGRAPHY

Ague, J. J., and Brimhall, G. H. (1989) Geochemical modelling of steady state flow and chemical reaction during supergene enrichment of porphyry copper deposits. Econ. Geol., 84, pp. 506-528.

Berman, R.G. (1988) Internally-consistent thermodynamic data for minerals in the system $Na_2O-K_2O-CaO-MgO-FeO-Fe_2O_3-Al_2O_3-SiO_2-TiO_2-H_2O-CO_2$: representation, estimation, and high temperature extrapolation. Jour. Petrol., 29, pp 445-522.

Berman, R.G. (1990) Mixing properties of Ca-Mg-Fe-Mn garnets. Am. Mineral., 75, pp. 328-344.

Brown, P. L., and Wanner, H. (1987) Predicted Formation Constants using the Unified Theory of Metal Ion Complexing. OECD Nuclear Energy Agency. Paris, 1987, 102 p.

Drever, J. I. (1988) Geochemistry of Natural Waters. Prentice Hall, 437 p.

Duerden, P. (1988) Alligator Rivers Analogue Project: Progress Report,1 May 1988 - 31 August 1988, 270 p.

Foy, M. F. and Pederson, C. P. (1975) Koongarra uranium deposit. In: C. L. Knight (ed.) Economic geology of Australia and Papua New Guinea, 1. Metals. Australas. Inst. Min. Metall. Monogr. Series, 5, 317-321.

Garrels R. M. and Christ C. L. (1965) Solutions, Minerals and Equilibria. Harper and Row, 450 p.

Giblin, A. M. and Snelling, A. A. (1983) Application of hydrogeochemistry to uranium exploration in the Pine Creek Geosyncline, Northern Territory, Australia. J. Geochem. Explor., 19, 33-55.

Grenthe, I., Fuger, J., Lemire, R. J., Muller, A. B., Nguyen-Trung Cregu, C (1990) Chemical Thermodynamics of Uranium. National Energy Authority, Thermoddynamic Data Base. Draft for Peer Review. March, 1990.

Helgeson, H. C. (1970) A chemical and thermodynamic model of ore deposition in hydrothermal systems: Mineralogical Society Amer. Spec. Paper, v. 3, pp. 155-186.

Helgeson, H. C., Delaney, J. M, Nesbitt, H. W., and Bird, D. K. (1978) Summary and critique of the thermodynamic properties of the rock-forming minerals. Amer. J. Sci., 278A, 229 p.

Langmuir, D. (1978) Uranium-solution mineral equilibria at low temperatures with applications to sedimentary ore deposits. Geochim. Cosmochim. Acta, 42, pp. 547-569.

Magalhaes, M. C. F., Pedrosa de Jesus, J., and Williams, P. A. (1985) The chemistry of uranium dispersion in groundwaters at the Pinal Do Souto mine, Portugal: Inorganica Chimica Acta, 109, pp. 71-78.

Markovic, M., and Pavkovic, N. (1983) Solubility and equilibrium constants of uranyl(2+) in phosphate solutions. Inorg. Chem., 22, pp. 978-982.

Moskvin, A. I., Shelyakina, A. M., and Perminov, P. S. (1967) Solubility product of uranyl phosphate and the composition and dissociation constants of uranyl phosphato-complexes. Russ. J. Inorg. Chem., 12, pp. 1756-1760.

Noller, B. N., Currey, N. A., Ayers, G. P., and Gillett, R. W. (1990) Chemical composition and acidity of rainfall in the Alligator Rivers region, Northern Territory, Australia. Sci. of the Total Envir., 91, 23-48.

Nordstrom, D. K., Plummer, L. N., Langmuir, D., Busenberg, E., May, H. M., Jones, B. F., Parkhurst, D. L. (1990) Revised chemical equilibrium data for major water-mineral reactions and their limitations. In "Chemical modelling of aqueous systems II": American Chem. Soc. Symposium Series. Ch. 31, pp. 398-413.

Payne, T. E., Davis, J. A., and Waite, T. D., Modelling of uranium sorption to substrates from the weathered zone in the vicinity of the Koongarra orebody. In Duerden, P. (ed.) ARAP 1st Annual Report, 1988-89, January, 1990, pp. 39-46.

Shock, E. L., and Helgeson, H. C. (1988) Calculation of the thermodynamic transport properties of aqueous species at high pressures and temperatures: Correlation algorithms for ionic species and equation of state predictions to 5 kb and 1000 C. Geochim. Cosmochim. Acta, 52, pp. 2009-2036.

Shock, E. L., Helgeson, H. C., and Sverjensky (1989) Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: Standard partial molal properties of inorganic neutral species. Geochim. Cosmochim. Acta, 53, 2157-2183.

Shock, E. L., and Helgeson, H. C. (1990) Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: Standard partial molal properties of organic species. Geochim. Cosmochim. Acta, 54, 915-946.

Snelling, A. A. (1980) A geochemical study of the Koongarra uranium deposit, Northern Territory, Australia. Ph.D. thesis University of Sydney (unpublished).

Snelling, A. A. (1989) Koongarra uranium deposits. In "The Geology of the Mineral Deposits of Australia and Papua New Guinea". F. E. Hughes (ed.), The Australasian Institute of Mining and Metallurgy, Melbourne, Monograph 14 (in press).

Sverjensky, D. A. (1987) Calculation of the thermodynamic properties ofaqueous species and the solubilities of minerals in supercritical electrolyte solutions. In "Thermodynamic Modelling of Geological Materials: Minerals, Fluids, and Melts" (Eds. I. S. E. Carmichael and H. P. Eugster), Reviews in Mineralogy, 18, 177-209. Mineral. Soc. America Short Course Notes.

Sverjensky, D.A., Hemley, J.J., and d'Angelo, W. M. (1991) Alkali feldspar-mica-aluminosilicate equilibria with hydrothermal alkali chloride solutions. Geochim. Cosmochim. Acta , 55, 989-1004.

Sverjensky, D. A., Shock, E. L., and Helgeson, H. C. (1992) Prediction of the thermodynamic properties of inorganic aqueous metal complexes to 1000 C and 5 Kb (in prepn.)

Tanger, J. C., and Helgeson, H. C. (1988) Calculation of the thermodynamic and transport proerties of aqueous species at high temperatures: Revised equations of state for the standard partial molal properties of ions and electrolytes: Amer. Jour. Sci. v. 288, p. 19-98.

Turner, D. R., Whitfield, M., and Dickson, A. G. (1981) The equilibrium speciation of dissolved components in freshwater and seawater at 25 C and 1 atm pressure. Geochim. Cosmochim. Acta, 45, 855-881.

Vochten, R., Piret, P., and Goeminne, A. (1981) Synthesis, crystallographic data, solubility, and electrokinetic properties of copper-, nickel-and cobalt-uranylphosphate. Bull. Mineral., 104, 457-467.

Vochten, R., Pelsmaekers, J. (1983) Synthesis, solubility, electrokinetic properties and refined crystallographic data of sabugalite. Phys. Chem. Minerals, 9, 23-29.

Wolery, T. J. (1983) EQ3NR: A computer program for geochemical aqueous speciation-solubility calculations, user's guide and documentation. UCRL-53414. Lawrence Livermore Lab., Univ. Calif., 191 p.

Wolery, T. J., Sherwood, D. J., Jackson, K. J., Delaney, J. M., and Puigdomenech, I. (1984) EQ3/6: Status and applications: UCRL-91884. Lawrence Livermore Lab., Univ. Calif., 12 p.

Zhil'tsova, I. G., Polypanov, L. I., Shmariovich, E. M., and Perlina, S. A. (1986) Physicochemical conditions of uranyl phosphate ore mineralisation. Lithology and Mineral Resources (USSR), 20, 586-596.

Zhu, C., and Sverjensky, D.A. (1991) Partitioning of F, Cl, and OH between minerals and hydrothermal fluids. Geochim. Cosmochim. Acta 55, 1837-1858.

GEOCHEMICAL MODELLING OF SECONDARY URANIUM ORE FORMATION

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The purpose of the present study was to establish how the uranyl phosphate zone at the Koongarra site was formed. The overall approach taken in the present study employed theoretical chemical mass transfer calculations and models that permit investigation and reconstruction of the kinds of waters that could produce the uranyl phosphate zone. These calculations have used the geological and mineralogical data for the Koongarra weathered zone to constrain the initial compositions and reactions undergone by groundwater during the formation of the uranyl phosphate zone. In carrying out these calculations the present-day analyses of Koongarra waters are used only as a guide to the possible initial composition of the fluids associated with the formation of the phosphate zone. However, this line of research yields results for comparison with the interpretation and evaluation of the present-day groundwaters from the Koongarra deposit. The calculations reported in the present volume are, of course, heavily dependent on the thermodynamic datafile used for the calculations. Aqueous speciation, saturation state and chemical mass transfer calculations were carried out using the computer programs EQ3NR and EQ6 (Wolery, 1983; Wolery et al., 1984) and a thermodynamic database generated at The Johns Hopkins University over the last eight years. In assembling all this data, considerable effort has been made to avoid inconsistencies that could introduce significant errors into the modeling calculations reported below.

Despite uncertainties in the thermodynamic characterization of species, all the above calculations suggest that the uranyl phosphate zone at Koongarra has not formed from present-day groundwaters. The present-day groundwaters in the weathered zone (e.g. at 13 m depth) appear to be undersaturated with respect to saleeite. Furthermore, as present-day groundwaters descend below the water-table they rapidly lose their atmospheric oxygen imprint, as is typical of most groundwaters, and become even more reducing in character. Under these circumstances, the groundwaters become more undersaturated with respect to saleeite than the shallow groundwaters. Because much of the phosphate zone is currently below the water table, under saturated zone conditions, it is suggested in the present study that the uranyl phosphate zone must have formed in the geologic past under unsaturated zone conditions.

Mass transfer calculations have therefore been used to try to delineate the optimum conditions for saleeite formation. It was found that the shallow weathered zone assemblage kaolinite + hematite + saleeite could form by the weathering of primary ore containing the hydrothermal alteration assemblage chlorite + muscovite + quartz + pyrite + graphite + apatite + pitchblende under conditions buffered by atmospheric CO_2 and O_2. Pyrite appears to be crucial under such circumstances because it keeps the pH of the fluid from rising to values consistent with saturation with respect to apatite or to silicates not found in the uranyl phosphate zone at Koongarra. The buffering by atmospheric CO_2 and O_2 is important to maintain Fe and U in their oxidised states while sufficient saleeite and hematite formed. In turn, this result is consistent with the suggestion that the formation of the uranyl phosphate zone took place in an unsaturated zone. By analogy with studies of supergene copper deposits, this suggests that the present base of the uranyl phosphate zone may represent (approximately) a paleo-water table.

The results summarised above suggest further that the uranyl phosphate zone may have formed in a more arid climate that would have been associated with a much lower water table than at present. Such a climate may have prevailed, prior to the relatively recent monsoonal climate initiated about 12,000 years ago. Although it is likely that a favorable arid climate in the geologic past would have alternated with a climate associated with a high water table and concurrent dissolution of the saleeite zone, the model suggested above would only require that the arid periods prevail. The present extent of the uranyl phosphate zone in cross-section coincides with the maximum lateral extent of graphite-bearing hydrothermal alteration assemblages. This may possibly reflect a difference in the weathering and availability of PO_4.

Based on the above results and other studies, the geochemistry and geochemical processes at Koongarra associated with the uranyl phosphate zone can be conveniently divided into two categories according to their relevance to present-day geochemical processes and those that have operated in the geologic past. Information on the present-day geochemistry of soils, weathered rock, groundwaters, and the role of sorption processes forms a basis for a *present-day analogue for nuclear waste migration.* Information and inferred reconstructions of geochemical processes thought to have operated in the geologic past form a basis for a *paleo-analogue for nuclear waste migration.*

DEVELOPMENT OF SECONDARY URANIUM MINERALOGY AT KOONGARRA: IMPLICATIONS WITH RESPECT TO UNCERTAINTY IN GEOCHEMICAL DATA

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Abstract

Over the past five years, Her Majesty's Inspectorate of Pollution (HMIP), in conjunction with other funding bodies, has sponsored the Alligator Rivers Analogue Project with the aim of evaluating the processes involved in the transport and fixation of uranium at Koongarra, Northern Australia. A broad range of research has been undertaken in order to further understanding of the Koongarra system. This has included studies of host rock mineralogy, water-rock interaction, the role of colloids in uranium transport, chemical adsorption processes and uranium-series analysis. As part of the exercise WS Atkins Science & Technology have undertaken a programme of equilibrium geochemical transport modelling with the aim of tracing the evolution of uranium mineralisation within the Koongarra system. This has entailed review of pertinent thermodynamic data, evaluation of groundwater-rock interactions and simulation of the development of secondary uranium mineralisation at the site, using the numerical coupled chemical transport code CHEMTARD.

Mineralisation at Koongarra occurs in a sequence of deformed and metamorphosed Lower Proterozoic quartz-chlorite schists and takes the form of pitchblende (UO_2) veins and disseminated ore within the chloritic alteration halos of the veins. Alteration processes within the primary ore zone have commonly led to the formation of secondary uranyl silicate minerals such as kasolite ($Pb(UO_2)SiO_4.H_2O$), sklodowskite ($Mg(UO_2)_2Si_2O_7.6H_2O$) and uranophane ($Ca(UO_2)_2Si_2O_7.6H_2O$). Immediately to the south east of the primary orebody a zone of secondary uranium mineralisation has developed, rich in uranyl phosphate minerals. Further to the south east, a zone of dispersed uranium occurs within the weathered schists. Here, it is thought that uranium is adsorbed onto the surfaces of minerals such as clays and iron oxides.

The site provides a valuable opportunity to appraise thermodynamic data for aqueous uranyl phosphate species and the oxidative weathering products of pitchblende. Assessment of available data reveals that significant errors may arise, either explicitly in calculations or implicitly by the use of erroneous constants as auxiliary data, if aqueous uranyl complexes containing the HPO_4^{2-} ligand (e.g. $UO_2HPO_4^{\circ}$ and $UO_2(HPO_4)_2^{2-}$) are considered. The project databases show a relatively high degree of consistency amongst the thermodynamic data for pitchblende, which should result in a well defined source-term for estimation of uranium migration. Few data are available for uranyl silicate minerals, though there is a fair degree of consistency in those for coffinite ($USiO_4$) and uranophane. In contrast, significant differences exist amongst the thermodynamic data for the uranyl phosphate minerals. Subsequent review of the literature has led to the derivation of a new set of thermodynamic data for minerals of the autunite group.

The results of speciation-solubility and reaction path calculations suggest that present day groundwaters flowing through the hydrologically saturated portion of the uranyl phosphate zone are dissolving saléeite ($Mg(UO_2)_2(PO_4)_2.10H_2O$) and transporting uranium away from both the orebody and the uranyl phosphate zone. They also suggest that both evaporation and weathering reactions acting in concert have played a role in the formation of the uranyl phosphate zone.

A one-dimensional coupled chemical transport model has been developed for the formation of the zone of dispersed uranium. Calculated levels of sorbed uranium are in accordance with those observed at the site. Predicted distances of uranium transport suggest that formation of the dispersed zone of uranium probably occurred over a combination of time and average groundwater velocities equivalent to between 0.1 and 0.5 m/year for 0.5 to 1.0 Ma. However, allowing for periods of dry conditions in which relatively little transport may have occurred, the overall time for the formation of the dispersed zone is almost certainly greater than these estimates suggest.

1. Introduction

Over the past five years, the Koongarra uranium deposit in the Northern Territory of Australia has been studied in order to evaluate the processes involved in the transport of uranium away from the orebody and the development of secondary uranium mineralisation in the near-surface environment. The work has been undertaken by the international Alligator Rivers Analogue Project (ARAP), sponsored by Her Majesty's Inspectorate of Pollution (HMIP) in conjunction with other funding bodies. A broad range of research has been undertaken to further understanding of the Koongarra system. This has included studies of groundwater flow, host rock alteration, water-rock interactions, the formation of secondary uranium minerals, the role of colloids in uranium transport, chemical adsorption processes and the relative distribution of uranium and thorium radionuclides in the system. As part of this research WS Atkins Science & Technology have undertaken a programme of geochemical modelling with the aim of developing an understanding of the evolution of the Koongarra system. This has entailed review of pertinent thermodynamic data, evaluation of groundwater-rock interactions, based on equilibrium speciation-solubility and sorption calculations, and simulation of the development of secondary uranium mineralisation at the site, using a numerical coupled chemical transport model.

In the following section we summarize a generalised conceptual model for the development of secondary uranium mineralisation at Koongarra. Following a description of relevant thermodynamic data, the results of a series of geochemical and coupled chemical transport modelling calculations are used to illustrate aspects of the conceptual model and the level of uncertainty inherent in the data used.

2. Conceptual model for the evolution of the Koongarra site

A stylised cross-section of the deposit, indicating the occurrence of important physico-chemical processes, is given in Figure 1. Mineralisation at Koongarra occurs in a sequence of deformed and metamorphosed Lower Proterozoic quartz-chlorite schists and takes the form of pitchblende veins and disseminated ore within the chloritic alteration halos of the veins. Immediately to the south east of the orebody a zone of secondary uranium mineralisation has developed, characterised by uranyl phosphate minerals of the autunite group (e.g. saléeite). Further to the south east, a zone of dispersed uranium occurs within the weathered schists. Here, it is thought that uranium is adsorbed onto the surfaces of minerals such as clays and iron oxides (Snelling, 1980), though an association with cerium and other rare earth element (REE) minerals has also been postulated (Edis *et al.* 1992). The spatial extent and style of mineralisation observed in the uranyl phosphate zone and the zone of dispersed uranium suggests that their formation is a result of exhumation of the deposit by erosion and the action of oxidising groundwaters on the primary ore, under near-surface conditions. This is consistent with the idea that their formation has occurred since the onset of weathering in the relatively recent past (1-3Ma; Snelling 1992) when compared to the age of the primary deposit (1550-1600 Ma; Snelling 1992). The occurrence of highly soluble autunite minerals suggests that the formation of the uranyl phosphate zone has occurred during generally dry periods, in which hydrologically unsaturated conditions prevailed. Uranium transported into this zone from the primary ore zone, as a result of the dissolution of pitchblende, is then thought to have migrated in an episodic nature due to the cyclical dissolution and re-precipitation of uranyl phosphate phases, as the prevailing conditions and in particular the level of the water table, varied in response to the climate experienced at the site (Sverjensky *et al.* 1992). The formation of the zone of dispersed uranium is assumed to have been as a result of the transport of soluble uranium in groundwaters under hydrologically saturated conditions with retardation controlled by processes of adsorption (Golian *et al.* 1992).

3. Thermodynamic data

During ARAP, a range of different thermodynamic databases have been used for geochemical modelling work. In order to allow meaningful comparison between the different results produced, and to allow an assessment of the level of uncertainty in the thermodynamic data, the current status of each of these databases has been reviewed (Bennett & Read, 1992). Detailed evaluation of thermodynamic data for uranium and thorium species has also been undertaken as these are of particular relevance to Koongarra.

The site provides a valuable opportunity to appraise data for aqueous uranyl phosphate species and the oxidative weathering products of pitchblende. Assessment of available data for the aqueous uranyl phosphates reveals that significant errors may arise, either explicitly in calculations or implicitly by the use of erroneous constants as auxiliary data, if aqueous uranyl complexes containing the HPO_4^{2-} ligand (e.g. $UO_2HPO_4^{o}$ and $UO_2(HPO_4)_2^{2-}$) are considered. Recent evaluation suggests that if these complexes do form, they are much weaker than was previously assumed (e.g. Langmuir, 1978).

The project databases show a relatively high degree of consistency amongst the thermodynamic data for pitchblende, which should result in a well defined source-term for estimation of uranium migration. Few data are available for uranyl silicate minerals although there is a fair degree of consistency in those for coffinite and uranophane. In contrast, significant differences exist amongst the thermodynamic data for the important uranyl phosphate minerals of the autunite group. For example estimates of the solubility of saléeite vary amongst the databases by approximately 5 orders of magnitude (Table 1). A review of the literature on these minerals has led to the derivation of a new set of thermodynamic data for some of the autunites (Table 1) based on the solubility data of Magalhaes *et al*, (1985), together with thermodynamic data from the CHEMVAL 4 database (Falck, 1992).

Database:- Mineral	ANSTO	NEA	JOHNS HOPKINS	THIS WORK
H-Autunite	-	-30.43	-	-29.84
Saléeite	-25.21	-	-28.66	-23.75
Na-Autunite	-28.98	-	-	-26.06
K-Autunite	-29.81	-	-	-27.85
Meta-Autunite	-	-	-33.06	-29.76
General reaction: $A(UO_2)_2(PO_4)_2.nH_2O \rightarrow A^{2+} + 2U^{4+} + 2PO_4^{3-} + (4+n)H_2O - 8H^+ - 4e^-$				

Table 1. Solubility products (Ksp) for autunite group minerals.

4. Geochemical modelling of the Koongarra system

Groundwaters collected from an array of boreholes across the deposit and the zones of secondary mineralisation are typified by high magnesium concentrations and relatively consistent, near-neutral pH values. The high magnesium concentrations have been related to the interaction of the waters with the chlorite-rich rocks of the deposit and surrounding lithologies (Sverjensky 1992; Sverjensky *et al.* 1992). Uranium concentrations in the groundwaters decrease by approximately two orders of magnitude as one moves away from the orebody into unmineralised regions.

Geochemical speciation-solubility calculations (Sverjensky *et al.* 1992) for the groundwaters indicate that;

a) in solution uranium occurs predominantly as U(VI)-carbonates; $UO_2(CO_3)_2^{2-}$, UO_2CO_3, $UO_2(CO_3)_3^{4-}$,

b) even considering the level of uncertainty in the thermodynamic data for the autunite group minerals present-day groundwaters are undersaturated with respect to saléeite,

c) solid solution between autunite and saléeite is unlikely to be an important process in fixing uranium in the uranyl phosphate zone.

It is concluded that the uranyl phosphate zone is being leached by present-day groundwaters and that its formation must have occurred under markedly different conditions in the past. Accepting this, alternate scenarios can be advanced for its formation:

a) evaporation of groundwaters in unsaturated conditions leading to the direct precipitation of uranyl phosphates,

b) weathering (oxidation) of the primary ore zone assemblages leading to groundwaters from which the precipitation of uranyl phosphates could occur.

The first of these is consistent with the observations of saléeite precipitation in surface rainwater puddles (Dickson & Meakins, 1984). The second scenario is more complex and concerns the likely weathering reactions which may act to bring the primary ore mineralogy closer to being at equilibrium with the surface environment.

Trial calculations to represent the role of evaporation (Sverjensky *et al.* 1992) in the formation of saléeite at Koongarra, indicate that because of the extreme ionic strengths reached, conventional geochemical models are not adequate for accurately describing the evaporation process. Despite this, the observations of Dickson & Meakins (1984) clearly suggest that evaporation is an important process in the formation of the uranyl phosphate zone, and are consistent with the precipitation of uranyl phosphates from brines under low temperature, laboratory conditions, as reported by Marx *et al.* (1991). Reaction path calculations (Sverjensky *et al.* 1992) representing the role of weathering reactions in the formation of autunite minerals, indicate that the dissolution of pitchblende (or amorphous UO_2), pyrite and chlorite under conditions buffered at atmospheric levels of the fO_2 and fCO_2 may result in groundwater compositions from which amorphous iron oxides and uranyl phosphate minerals are likely to precipitate. The precise results of such calculations however, are dependent on assumptions made as to the minerals involved in the reactions, the composition of the groundwater at the initiation of weathering and the thermodynamic data employed.

Thus the results of the speciation-solubility and reaction path calculations are broadly consistent with the view that present day groundwaters flowing through the hydrologically saturated portion of the uranyl phosphate zone at Koongarra are actively dissolving saléeite and are, therefore, transporting uranium away from both the orebody and the uranyl phosphate zone. They also suggest that under suitable conditions both evaporation and weathering reactions acting in concert may have played a role in the formation of the uranyl phosphate zone.

5. Coupled chemical transport modelling of the Koongarra system

The approach taken in modelling the transport of uranium and thorium through the Koongarra system has been based on the one-dimensional coupled chemical transport code CHEMTARD (Bennett *et al* 1992). Full details of the modelling undertaken are given in Golian *et al.* (1992). The observation that aqueous uranium concentrations decrease away from the primary ore zone, and the spatial distributions of the uranyl phosphate and dispersed zones, which indicate that uranium has migrated towards the south or south east, suggests that it may be possible to model the zone of dispersed uranium by tracing the evolution of a "typical ore zone water" as it flows into the rocks and waters of "regional background composition", downstream of the orebody (Figure 1).

In view of the results of speciation calculations, uranium has been modelled as $UO_2(CO_3)_2^{2-}$ and its retardation described using the Triple Layer Model (Davis *et al*, 1977) representation of the sorbing surface. Assuming iron oxides to approximate the behaviour of the surface, data have been taken from Hsi & Langmuir (1985). To include the effects of uranium series disequilibria, the following simplified decay series has been considered:

$$^{238}U\ (T½ = 4.47 \times 10^9\ \text{years}) \rightarrow {}^{234}U\ (T½ = 2.45 \times 10^5\ \text{years}) \rightarrow {}^{230}Th\ (T½ = 7.54 \times 10^4\ \text{years}) \rightarrow$$

Owing to the age of the deposit and the relatively recent period over which weathering has occurred, it has been assumed that the rocks surrounding the primary ore body were in secular equilibrium at the onset of weathering. The $^{234}U/^{238}U$ activity ratio of the typical ore zone water has been set equal to 0.7, representing the observed activity ratio at the site, which are symptomatic of the effects of preferential leaching of ^{234}U due to processes such as alpha-recoil. To represent the relatively immobile nature of Th in the natural environment ^{230}Th has been assumed to precipitate as thorianite.

Sample results from the model are illustrated in Figure 2. The predicted sorbed concentrations of uranium range between ≈100 and 400ppm (Figure 2a), and compare well with observed values from the dispersed zone (117-619ppm; Edis *et al.* 1992). The distances of uranium transport predicted from a series of calculations suggest that the formation of the dispersed zone has probably occurred over a combination of time and average groundwater velocities equivalent to between 0.1 and 0.5 m/year for 0.5 to 1.0 Ma. However, allowing for periods of dry conditions in which little transport may have occurred, the overall time for the formation of the dispersed zone may is almost certainly than these estimates suggest.

In any simulation, predicted $^{234}U/^{238}U$ activity ratios (Figure 2b) increase non-linearly from 0.7 at the ore zone to 1.0 over the distance for which transport of uranium has occurred. No chemical fractionation processes have been considered, the change in the predicted activity ratio resulting from the progressive mixing of ore zone waters with those of the regional background. Measured $^{234}U/^{238}U$ activity ratios in "accessible" solid phases of samples from the dispersed zone generally increase with distance away from the south east edge of the orebody. Thus the model reproduces this general trend. Calculated $^{230}Th/^{234}U$ activity ratios (Figure 2d) peak at values significantly >1.0, corresponding to the maximum concentration of precipitated thorium (Figure 2c) and then fall to lower values (≈ 0.7) at greater distances from the ore zone. Observed $^{230}Th/^{234}U$ activity ratios within the dispersed zone scatter widely between approximately 0.25 and 1.75, indicating the complex processes and interactions occurring at the site.

6. Conclusions

The results of speciation-solubility and reaction path calculations suggest that present day groundwaters flowing through the hydrologically saturated portion of the uranyl phosphate zone are dissolving saléeite and transporting uranium away from both the orebody and the uranyl phosphate zone. They also demonstrate that under suitable conditions both evaporation and weathering reactions may have played a role in the formation of the uranyl phosphate zone.

A one-dimensional coupled chemical-transport model has been developed for the formation of the zone of dispersed uranium. Calculated levels of sorbed uranium are in accordance with those observed at the site. Predicted distances of uranium transport suggest that the formation of the zone of dispersed uranium probably occurred over a combination of time and average groundwater velocities equivalent to between 0.1 and 0.5 m/year for 0.5 to 1.0 Ma. However, allowing for periods of dry conditions in which little transport may have occurred, the overall time for the formation of the dispersed zone is almost certainly greater than these estimates suggest. Predictions of $^{234}U/^{238}U$ activity ratios fall between 0.7 at the ore zone and 1.0, and increase over the distance for which the transport of uranium has occurred. Measured $^{234}U/^{238}U$ ratios for rock samples from the weathered zone at Koongarra scatter widely between approximately 0.6 and 1.0, and generally increase with distance from the orebody. Thus the model reproduces the observed trend on the basis of the mixing between ore zone waters with low $^{234}U/^{238}U$ activity ratios, possibly developed as a result of the preferential leaching of ^{234}U over ^{238}U via alpha-recoil processes, with shallow regional groundwaters initially in secular equilibrium.

Refinement of the models presented and the development of an understanding of the relationships between the various zones of secondary mineralisation at Koongarra will require further detailed mineralogical study of the sinks for the elements of interest and their spatial distributions.

References

Bennett D G, Liew S K, Mawbey C S & Read D. (1992). UK. DoE. Report No. DoE/HMIP/RR/92.036.
Bennett D G & Read D (1992) Geochemical Databases. ARAP Volume 10.
Falck W E (1992) UK. DoE. Report No. DoE/HMIP/RR/92.064.
Davis J A, James R O & Leckie J O (1977) Journal of Colloid Interface Science, Vol. 63, 480-499.
Dickson B L & Meakins R L (1984). Nuclear Instruments & Methods in Physics Research, Vol. 223, 593-597.
Edis R, Murakami T, Yanase N, Koppi A J, Klessa D A, Payne T E, Snelling A, Cao L Q & Nightingale T (1992) Chemistry and Mineralogy of Rocks and Soil. ARAP Volume 8.
Golian C, Lever D A, Baker A J, Bennett D G, Ohnuki T, Read D & Skagius K (1992) Radionuclide Transport. ARAP Volume 14.
Hsi C D & Langmuir D (1985). Geochimica et Cosmochimica Acta, Vol. 49, 1931-1941.
Langmuir D (1978). Geochimica et Cosmochimica Acta, Vol. 42, 547-569.
Magalhaes M C F, Pedrosa de Jesus J & Williams P A (1985). Inorganica Chimica Acta, 109, 71-78.
Marx G, Bischoff H, Esser V, Kramer-Schnabel U, & Ruihua Xi (1991). EMRS. Strasbourg, Symp C, P3.
Snelling A (1980). A geochemical study of the Koongarra uranium deposit, Northern Territory, Australia. PhD Thesis, University of Sydney.
Snelling A (1992) Geologic setting of the Koongarra Natural Analogue. ARAP Volume 2.
Sverjensky D A, Bennett D G & Read (1992) Geochemical Modelling of Secondary Uranium Ore Formation. ARAP Volume 11.
Sverjensky D A 1992) Geochemical Modelling of Present-Day Groundwaters. ARAP Volume 12.

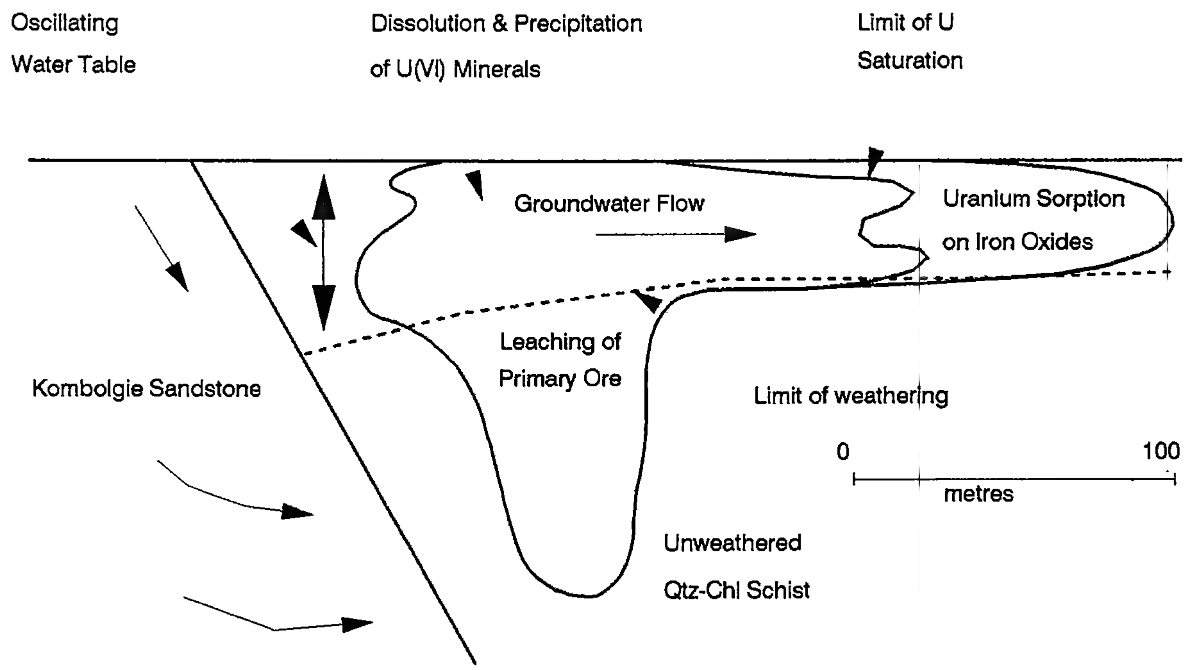

Figure 1: Conceptual model of the Koongarra uranium deposit

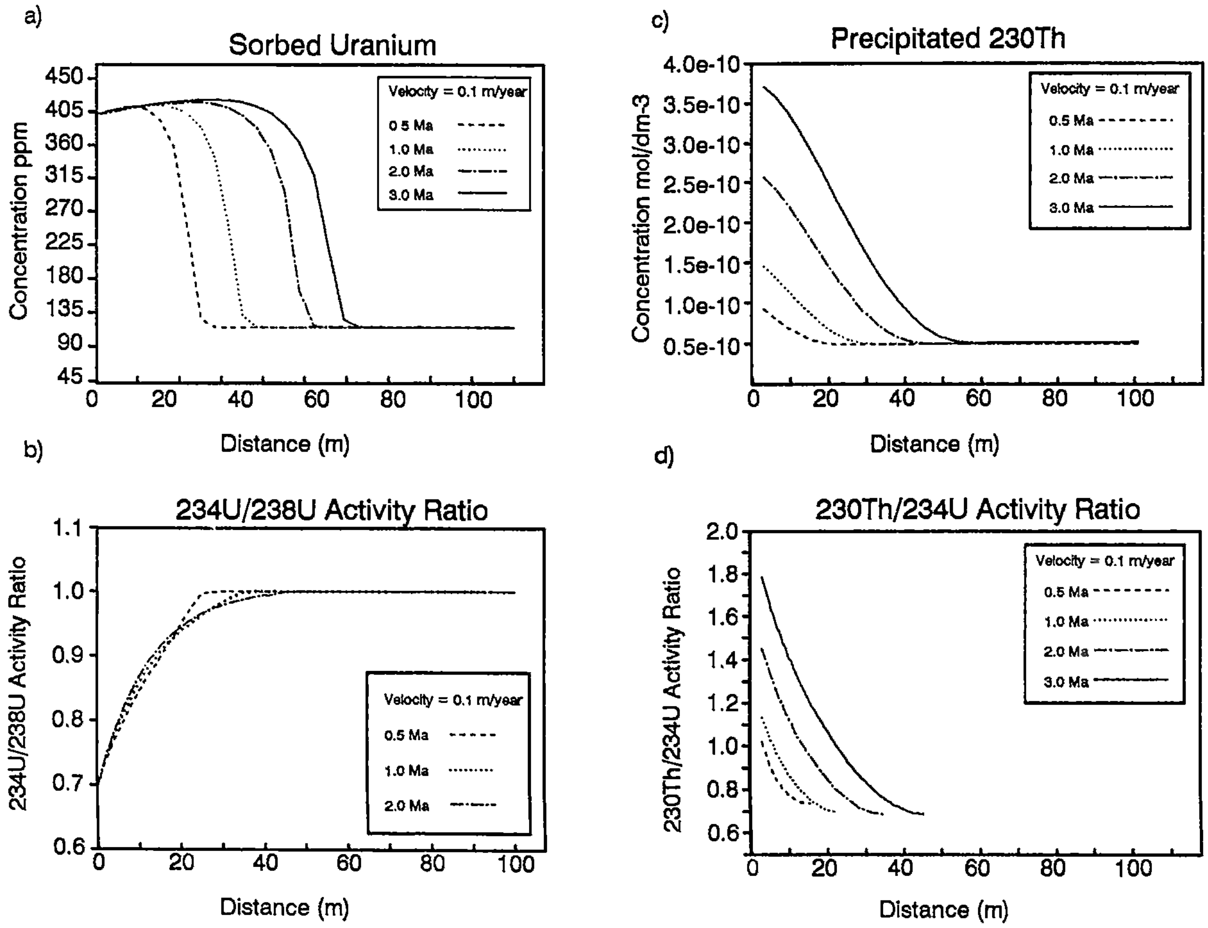

Figure 2: Sample results from coupled chemical transport modelling of the zone of dispersed uranium

TRANSPORT MODELLING IN THE KOONGARRA WEATHERED ZONE

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1. Introduction

Process of building confidence in the applicability of models used in safety assessments for radioactive waste repositories, is often termed model validation. Studies of laboratory experiments, field experiments and natural analogues can all contribute to model validation. However, the great advantage of natural geochemical systems over the other validation tools is that they give access to the long timescales required for repository safety assessments. Furthermore, the studies of geochemical systems contribute to an understanding of the processes controlling the migration of radionuclides away from a radioactive waste repository.

Four pathways have been identified internationally as being of importance in returning radionuclides to the biosphere: transport in groundwater; natural disruptive events; release of radioactive gases; and human intrusion into the repository. The main pathway to which an analogue such as Koongarra is relevant is return by groundwater flow. It is therefore appropriate to consider the relevance of modelling of radionuclide transport in the Koongarra system to similar modelling undertaken for groundwater flow paths around proposed repositories.

The Koongarra system offers the opportunity for relatively sophisticated modelling, directed at understanding the geochemistry of the system, the processes controlling the extent of uranium transport and the bounds of the timescale over which this mobilisation occured.

A large number of models (Table 1) have been employed as part of the ARAP, to interpret the substantial database available for the concentrations of uranium series radionuclides in the groundwater and in the solid phases. Value has been seen in the diversity of modelling approaches.

A number of approaches to the modelling of the transport of uranium series radionuclides have been presented in the literature (see review by Ku et al., 1992). Modelling approaches have also been applied to other natural analogues (e.g. Chapman et al., 1991) and in research associated with other repository research programmes (e.g. Latham and Schwarcz, 1987) in order to simulate the transport of uranium series radionuclides.

2. Koongarra natural analogue

The Koongarra uranium ore deposit can be divided into a number of zones. In the original orebody at depth, the uranium is in the form of pitchblende and uranyl silicates. In the weathered zone, uranium is known to be present in a number of forms; these include uranyl phosphates, other uranium-rich minerals, uranium as a minor component of other crystalline phases and sorbed uranium. Uranium transport at Koongarra is taking place in a zone of active weathering. The transport studies have focused on the ^{238}U series, and to a lesser extent on the ^{232}Th and ^{235}U series.

Modelling of the system is complicated by a number of uncertainties about the evolution of the system with time. In particular, uncertainties in groundwater flow patterns and flow rates over geological timescales present a major unknown. Climatic variations could have resulted in substantial lowering of the water table so that no horizontal uranium transport occurred. There is also uncertainty in the evolution of hydrogeological parameters with time as a result of the formation of clays, and in the rate at which the weathering front moved downwards.

The modelling work undertaken has some implications for the range of possible 'scenarios' that may be used to explain the evolution of the fan. In general, the transport modelling does not enable a choice between different 'scenarios', but serves to illustrate the possible consequences of different processes and to determine parameter ranges that are consistent with analytical data.

3. Processes

In the dispersion fan, there are a number of processes controlling the amount of radionuclides that are removed from the groundwater. These include equilibrium sorption, which is sometimes modelled by a simple K_d approach and sometimes by a more detailed model, chemical incorporation into iron oxides, uranium minerals or other crystalline phases, and recoil transfer of daughter products resulting from α-decay. It is observed that uranium in some of the crystalline phases is not in isotopic equilibrium with the groundwater, whereas in other phases it is in isotopic equilibrium. These are termed inaccessible and accessible phases respectively.

Potentially, kinetic processes are of particular importance in a safety case, because they could substantially reduce the impact of key radionuclides. An example of such a kinetic process is irreversible precipitation; this could result in radionuclides being permanently retained in rocks that constitute the geological barrier around the repository.

It is often the case in analogue studies that the initial and boundary conditions are poorly characterised and there may be a number of changes in conditions in the intervening time that are also difficult to characterise. In addition, a number of processes may be coupled together, making the analysis more complicated. These problems apply to studies of the Koongarra analogue.

4. Models and results

The models used in the uranium mobilisation study (Table 1) can be divided into three groups: the first involving partitioning of uranium between groundwater and one solid phase; the second involving partitioning between groundwater and third involving a more realistic representation of the geochemical processes determining partitioning between groundwater and rock.

The first type of model is similar to simple (and conservative) models used in safety assessments and is easy to represent mathematically. The transport equation for this sort of model usually contains a simple equilibrium sorption term that relates to the whole rock matrix.

The second type of transport model considers separate groundwater accessible and inaccessible mineral phases in the rock. This type of model is more consistent with available analytical data. However, it is more complicated mathematically, has more free parameters and requires more data on the system than the one phase models. A variety of assumptions are possible. Different models reported here have incorporated recoil processes and kinetically limited chemical exchange between groundwater and a crystalline phase. To achieve anything more than a very crude representation of the processes controlling and retarding radionuclide transport at Koongarra, it is necessary to use a model with at least this degree of complexity.

A number of modelling attempts have sought to concentrate on data from specific horizons. This procedure was adopted for two reasons; first it was hoped that this would

TABLE 1 List of modelling approaches.

model	structure			transport processes			retardation processes			
name	dim	path	couplg	adv	disp	m.diff	sorpt	precip	phase	recoil
open system		1					x			
multiphase		1					x		x	x
retarded velocity	1			x			x			
transport time	1			x			x			
simple two phase	1			x			x		x	
simple models	1			x			x			
one phase, box	1	1		x	x		x			
access phase, box	1	1		x	x		x		x	
modif. tr. time	1	1		x			x			
m.tr.time-access	1	1		x			x		x	
perform. assess	1			x	x		x			
two-phase access transport	1	1		x	x		x		x	x
two-phase transp.	1			x			x		x	x
adv-disp-sorp-fix	1			x	x		x		x	
Th fixation	1			x			x		x	x
prefer pathways	2(q)	2		x	x		x		x	
adv-disp-sorption	2(q)			x	x		x			
evolving tr zone	2(q)			x			x		x	x
NAMMU	2			x	x		x			
saleeite dating	1							x		
CHEMTARD	1		x	x	x		x	x		

minimise problems arising from heterogeneity and secondly there is some evidence for preferential flow in some layers. If data are selected for one depth interval, it may be that this corresponds to flow along one streamline and the data are less heterogeneous. However, restricting analytical data to one depth limits available data and does not allow a full assessment of the effects of heterogeneity.

Some models have considered flow to be concentrated in the lower part of the weathered zone. These models are not able to represent precisely the evolution of the weathered zone as data are not sufficient to constrain the model. However, it is possible to construct a two-dimensional picture of the dispersion fan over time using a number of one dimensional models. Other evidence indicates that flow may be concentrated in the surface layers and a quasi-2D model has been constructed from two one-dimensional models with a connection between them. These models serve to illustrate possible histories of the dispersion fan in a qualitative manner.

Some two-dimensional modelling in a vertical cross section has been carried out with the multi-dimensional groundwater flow and radionuclide transport code, NAMMU, to explore the shape of the radionuclide plume and its evolution with time. This has enabled examination of the consistency of the choice of hydrogeological parameters with the current shape of the dispersion fan.

A simplified dating model has been applied to saleeite crystals to derive a distance-time relationship for the secondary dispersion fan. It was assumed that these crystals were to a large extent isolated from groundwater. This approach is different to the other modelling attempts, but is subject to uncertain assumptions concerning the geochemical behaviour of the saleeite crystals subsequent to growth.

An alternative model to those incorporating recoil was also proposed. This invoked the chemical partitioning of ^{234}Th into an unidentified phase rather than the recoil of alpha decay products into phases where the daughter radionuclides were not in equilibrium with the fluid.

Both the ^{234}Th and the recoil models are able to explain the decreasing ^{234}U/^{238}U activity ratios in rocks in the direction of transport. Models including recoil are also capable of explaining an increase of rock ^{234}U/^{238}U activity ratios in the direction of flow, as found in many other case studies (Osmond et al., 1983), with different parameter choices.

A quantitative, geochemically rigorous, one-dimensional coupled chemical transport model was also applied. The development of the model necessitated consideration of the geochemical processes likely to be of importance at the site. The model is based on the retardation of uranium (VI) carbonate species during groundwater flow, by equilibrium sorption onto iron oxides. This process has been approximated using the Triple Layer Model representation of the sorbing surface, together with laboratory measurements and thermodynamic data from the literature, to describe the properties of the surface itself.

Nearly all the models assume constant groundwater flow parameters with time. It is known that this assumption is not correct. However, the assumption is not of serious concern if the period of climatic oscillations is fairly small compared to the half lives of ^{234}U and ^{230}Th.

The investigation of the present-day groundwater flow regime has confirmed the complicated nature of the system hydrogeological . Most of the models used a time-averaged prevailing flow direction in a N-S direction. This direction is implied by the shape of the dispersion fan, although there is some evidence for flow in another direction.

Dispersion was omitted from many of the models, since it was considered to be of much less importance than advective transport. For similar reasons, matrix diffusion was not included in the models. However, there is some evidence for back flow of waters from the dispersion fan towards the Koongarra Fault at certain times. This could be accounted for by incorporating dispersion in the models. Consequently, dispersion was included in several simple box models by allowing a component of the radionuclide transport to proceed in the direction determined by the local concentration gradient. Dispersion was also incorporated in the 2D NAMMU modelling.

In most models the timescale has been treated as a fitted parameter. By assuming that the groundwater flux is constant and making an assumption about the boundary condition concentration, it is possible to arrive at an age estimate of the fan. These results are summarised in Figure 1. Best estimates of erosion rates seem to agree broadly with the general range of the transport model estimates. The geomorphological evidence suggests that the dispersion fan is between one and six million years old.

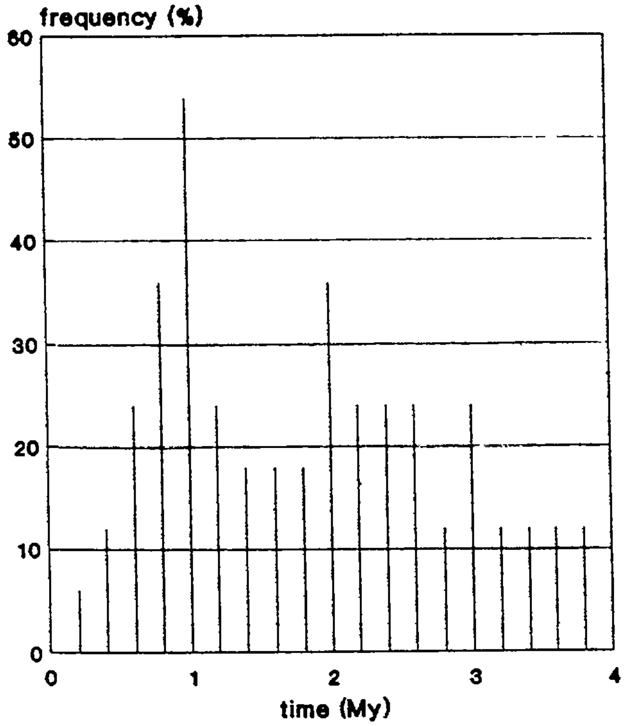

FIGURE 1 Distribution of migration time estimates

Partitioning of uranium into a crystalline phase in which uranium is not in equilibrium with the groundwater is of great importance in determining the concentrations of uranium in solution. The rate of radionuclide transfer from one phase to another was in general treated as a fitted parameter. The rate of transfer was shown to be comparable to the half-lives of ^{230}Th and ^{234}U. Recoil transfer of alpha decay products within the ^{238}U decay chain into this crystalline phase or phases is also of considerable importance. It was found that high recoil factors of up to 0.4 were required in order to explain analytical data (i.e. up to 40% of decays resulted in transfer of the alpha decay product to the crystalline phase).

5. Conclusions

In summary, a number of different models have been shown to be capable of representing different aspects of the system. The more complex models are more realistic, but require more data than are available. The simpler models are capable of crudely representing the system, but have the advantage of requiring less data.

The fact, that most of the uranium has moved only of the order of 50 to 100m over a timescale of the order of millions of years lends confidence to the practice of deep disposal of geological waste. However, some uranium has moved up to 400m, and it is possible that some uranium bearing fluids have been lost from the system.

The Koongarra system is very heterogeneous and this has lead to difficulties in selecting data for modelling. Some approaches have been adopted in order to attempt to minimise such uncertainties; for instance by selecting data from only one depth interval. The difficulties encountered because of the heterogeneity of the Koongarra weathered zone mirror those encountered in assessing radionuclide transport in deep geological systems.

Further progress in radionuclide transport modelling of the Koongarra natural analogue requires additional data on the hydrogeological system and its variation with time, on the form of uranium within the dispersion fan and on the heterogeneity of the system.

References

Chapman, N.A., McKinley, I.G., Shea, M.E. and Smellie, J.A.T. (1991) The Pocos de Caldas Project: Summary and implications for radioactive waste management. Pocos de Caldas Report No 15, NAGRA NTB 90-33, SKB TR 90-24, UK DOE WR 90-055.

Ku, T.L., Luo, S., Leslie, B.W. and Hammond, D.E. (1992) Decay-series disequilibria applied to the study of rock-water interaction and geothermal systems. In Harmon, R.S. and Ivanovich, M. (editors), Rest of reference to be provided)

Latham, A.G. and Schwarcz, H.P. (1987a) On the possibility of determining rates of removal of uranium from crystalline igneous rocks using U-series disequilibria 1. a U leach model and its applicability to whole-rock data. Applied Geochemistry 2, 55-66.

LINKING MODELS TO PERFORMANCE ASSESSMENTS

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1. Introduction

One of the main reasons for participating in a natural analogue project, such as the Alligator Rivers Analogue Project (ARAP), is to build confidence in the methods and models used in the performance assessment of a potential site for a radioactive waste repository. Either the models could be for direct application as part of the performance assessment, or they could be used to underpin the detailed understanding of a particular aspect of the system. As the ARAP has now drawn to a close it is proper to ask how the links have been made between the models used in the analogue study and those used in performance assessments.

2. Parallels with the assessment process

There are many parallels between an analogue study, such as the ARAP, and the characterization of the site of a potential repository. There are a number of aspects for which an understanding has to be developed; these include:

- the geology and geomorphology of the site, and their regional context;
- the historical evolution of the site on relevant timescales;
- the hydrogeology of the site, again on different scales ranging from the scale of the ore body to the regional context;
- the geochemical processes controlling the mobilization of the uranium in the ore body (the source term);
- the geochemistry of the processes controlling the transport and retardation of the uranium as it migrates with flowing groundwater.

Most of these involve the complementary approaches of laboratory studies, field studies and modelling. Such use as part of the ARAP has been seen in the earlier presentations to this meeting; a similar approach is frequently used in site characterization to provide the information required for performance assessments. Within the ARAP the aim has been to develop a consistent picture of the evolution of the site from the different disciplines involved.

3. Radionuclide transport models

Two of the key features of interest at Koongarra are the mobilization of uranium in the ore body and the transport of uranium in the dispersion fan. Radionuclide transport is an important feature of many performance assessments, with uranium and its daughters often being radionuclides of interest.

There are a number of processes that may be incorporated into radionuclide transport models:

- one-dimensional advective transport;
- simple models of sorption;
- molecular diffusion;
- hydrodynamic dispersion;
- radioactive decay;
- multi-dimensional radionuclide transport;

- interaction with more than one rock phase;
- detailed geochemical models (including non-linear and kinetic effects);
- α-recoil.

The first two of these are a minimum requirement if there is to be an adequate description of the distance moved by a particular radionuclide over a given timescale. Some of the others (such as dispersion and decay) are common to many transport models. Other are only found in some models when they are required to account for processes relevant to a particular application.

Sometimes more detailed models of a particular aspect of the system are developed to provide support for a simpler treatment incorporated into an overall model of the system. This approach is used in both analogue studies and performance assessments.

4. Major sources of uncertainty

In attempting to come to an understanding of the development of the Koongarra site a number of sources of uncertainty have had to be addressed. These have included:

(a) Heterogeneity. Measurements of the hydrogeological properties of the strata of interest have shown them to vary by orders of magnitude (see the contribution by Emerson et al. earlier in this volume). Similar heterogeneity is seen in the mineralogy (see the contribution by Edis et al.).

(b) Time evolution and variation. There is uncertainty in the development of the system, for example in the evolution of the weathering front, and in the timescales for the mobilization of the uranium. The climate has changed over recent geological time, which potentially has implications for the nature of the groundwater flow. On a far shorter timescales, with a monsoon climate there are significant variations in climate over the annual cycle.

(c) Patterns of groundwater flow. Characterization of the site has shown that the groundwater flow pattern is not a simple uni-directional flow. It has many three-dimensional characteristics, whose implications have to be considered (see the contribution by Davis). There is also considerable uncertainty in the magnitude of the horizontal transport velocity.

(d) The nature of the uranium in the dispersion fan. There is some uncertainty in the nature of the association of uranium with the solid phase in this important part of the system (see the contribution by Edis et al.).

Although some of these have particular relevance to Koongarra (e.g. seasonal variations arising from the monsoon climate), many of them have also to be addressed in other investigations. Their significance has had to considered, and the implications for developing an understanding of the site assessed.

In considering the implications of the various uncertainties at Koongarra and in performance assessments, it is important to understand which conclusions are legitimate in the context of the established uncertainties, which questions remain open, and which are the important outstanding issues.

Participation in the ARAP has provided valuable experience in the understanding and application of field data, in the membership of a multi-disciplinary team, and in the construction, application and testing of system models, in seeking to develop an adequate understanding of the key processes determining the evolution of the distribution of uranium at Koongarra.

APPLICATION OF SCENARIO METHODOLOGY IN EVALUATION OF THE KOONGARRA ANALOGUE

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ABSTRACT

1. Introduction

The study of natural analogues is recognized as one of the most important methods for validation of concepts and models for performance assessment of repositories for nuclear waste. The objectives of such studies range from detailed investigations of processes and features on a small scale to attempts of explaining the evolution of whole sites. Especially in the latter case it is quite obvious that the analogue studies have many features in common with a performance assessment of a repository. However, for studies of detailed processes it may well be as important to consider the larger scale settings when transforming the results of an analogue study into a better understanding of repository performance in the long-term. These are a few, but not all, reasons why it should be valuable to utilize methodologies developed for performance assessments also in the evaluation of analogues. Another important aspect is the need to ensure that the proper questions are being asked and that the investigations are being focussed on phenomena relevant for validation objectives.

In many respects the study of the Koongarra uranium orebody within the Alligator Rivers Analogue Project [1] involves a full spectrum of challenges and possibilities of this kind, e.g., it is a multi-disciplinary project covering studies of small scale processes as well as attempts of explaining and modelling the evolution of the site and the release and dispersion of uranium from the primary ore-body. Thus, the present work was initiated with the objective to apply experiences from development of scenarios for performance assessments in the evaluation of Koongarra. Two main partial objectives have been,

- establishing of a systematic description of the analogue, i.e. a description of how different processes have contributed to and caused the development of the dispersion fan;

- attempting a logical derivation of alternative evolution scenarios for the analogue.

The purpose of a systematic description of the analogue is to facilitate the exchange of information and ideas between the different scientific disciplines and modellers. It is also believed that such an approach will be of help in focussing the evaluation on issues relevant for performance assessments.

A major difficulty in trying to model the evolution of a natural analogue, including dispersion of natural radionuclides, is to define the time-frame and initial and boundary conditions. Information on the history of the site and the time-frame may be obtained from analysis of, e.g., radioactive disequilibria. However, for validation of transport models and concepts independent information about these conditions are needed. It is then important to test not one, but several possible alternatives of the site history, i.e. scenarios. The testing of several models *and* scenarios will contribute to a better understanding of the ability and limitations of different concepts and models to describe processes relevant for performance assessments.

In conclusion, it should be noted that the present study has been made with the objective to apply a scenario methodology *in the evaluation of natural analogues*. It has *not* been an objective trying to validate such methods in any sense.

A full presentation of this study is found in the Vol 16 of the ARAP Final Report series [1].

2. Methodology

The methodology adopted in this work is similar to that used in a joint SKI/SKB scenario development project [2]. The technique was originally developed by Sandia [3]. The initial activities comprised the following steps:

- Identification of all features, events and processes (FEPs) that may have had an influence on the evolution of the analogue, involving several research groups engaged in ARAP in order to cover all relevant disciplines.

- Documentation of each FEP in a short memo-text containing a description of the FEP, the causes and effects of the FEP, modelling aspects and references to literature.

- Screening of FEPs based on well-defined criteria regarding importance and role in the evolution of the uranium mineralisation.

- Classification of the remaining FEPs depending of the nature of the FEP and lumping of related FEPs into subgroups.

Subsequent steps involved the work on a systematic description of the analogue and formulation of scenarios.

3. Application to the Koongarra Analogue

In total, 242 FEPs were identified by five groups or persons. The preparation of memo-texts was found to be very time consuming, and, in addition, depending on contributions from many sources and groups within the ARAP. Thus, the following steps were carried out in parallel to preparations of memo-texts.

It was found that each FEP could be screened into one of the following groups:

- OUT, i.e. screening out for reasons such as duplication, poor definition, low probability or low consequence. (52 FEPs)

- PROCESS SYSTEM, defined as comprising all deterministic chemical and physical phenomena that might have influenced the formation of the secondary uranium mineralisation and the dispersion in the weathered zone. Typical examples are the major FEPs "Groundwater flow" and "Adsorption". (138 FEPs)

- EXTERNAL CONDITIONS, i.e. FEPs having occurred independent of the phenomena in the PROCESS SYSTEM. Examples are "Rainfall range and intensity" and "Erosion to major peneplanation". (39 FEPs)

- EXTERNAL FEATURES, i.e. FEPs reflecting the history of the region but not influencing the evolution of the analogue. Examples are "Talus deposits" and "Old coastline". (13 FEPs)

The FEPs in the PROCESS system were subsequently employed in the systematic description of the analogue in terms of schematic diagrams displaying the interconnections and links of causes and effects between different processes. Two diagrams have been developed,

- for the SOURCE, i.e. the combination of phenomena which have influenced the distribution of uranium between solid and liquid phase at the location of the primary ore (Fig. 1), and,

- for the MIGRATION, i.e. the combination of processes directly involved in the formation of the dispersion fan (Fig. 2).

A similar description of the processes influencing indirectly on the uranium dispersion, e.g. weathering, will be a next step. This is in line with experiences from development of scenarios for performance assessments, where it has been shown fruitful to describe the process system in terms of an *inverted tree of events* [4].

4. Formulation of scenarios

The attempted formulation of scenarios has been based on the EXTERNAL CONDITIONS and EXTERNAL FEATURES. A rapid weathering of the host rock, i.e. the chlorite schist, is assumed to have started around the onset of the Pleistocene Ice Age (ca 1.6 Ma BP). The eventual oxidation and mobilization of the uranium ore could then have occurred under unsaturated or saturated conditions. This leads to the following major scenarios:

- Uranyl Phosphates Formed under Unsaturated Conditions, with a periodical evolution of the dispersion fan in conjunction with alternating dry (glacial) and wet (interglacial) periods during the Pleistocene Ice Age.

- Uranyl Phosphates Formed under Unsaturated Conditions as a Single Event, taking place either early or late during the Pleistocene Ice Age.

- Uranyl Phosphates Formed under Saturated Conditions, in conjunction with periods of higher and lower flow due to the climatic cycling.

In addition to these major scenarios there are alternatives, e.g. depending on the water table level in relation to the weathering front.

5. Conclusions

It should be noted that the development of scenarios, including a description of the process system, must be regarded as a continuous and iterative process. As long as the evaluation of an analogue proceeds, scenarios may be rejected or added to the list. In this respect the present work is a first step. Application of the scenarios for modelling of the analogue would be an obvious next step providing more evidence of their viability. More work is needed before the possibilities of the chosen approach are explored in full. The methodology is complex and simplifications would make it more practical.

Although the original objectives may not have been fully achieved, this work is believed to contribute to a better understanding of the Koongarra Analogue as well as to give a basis for further scenario work.

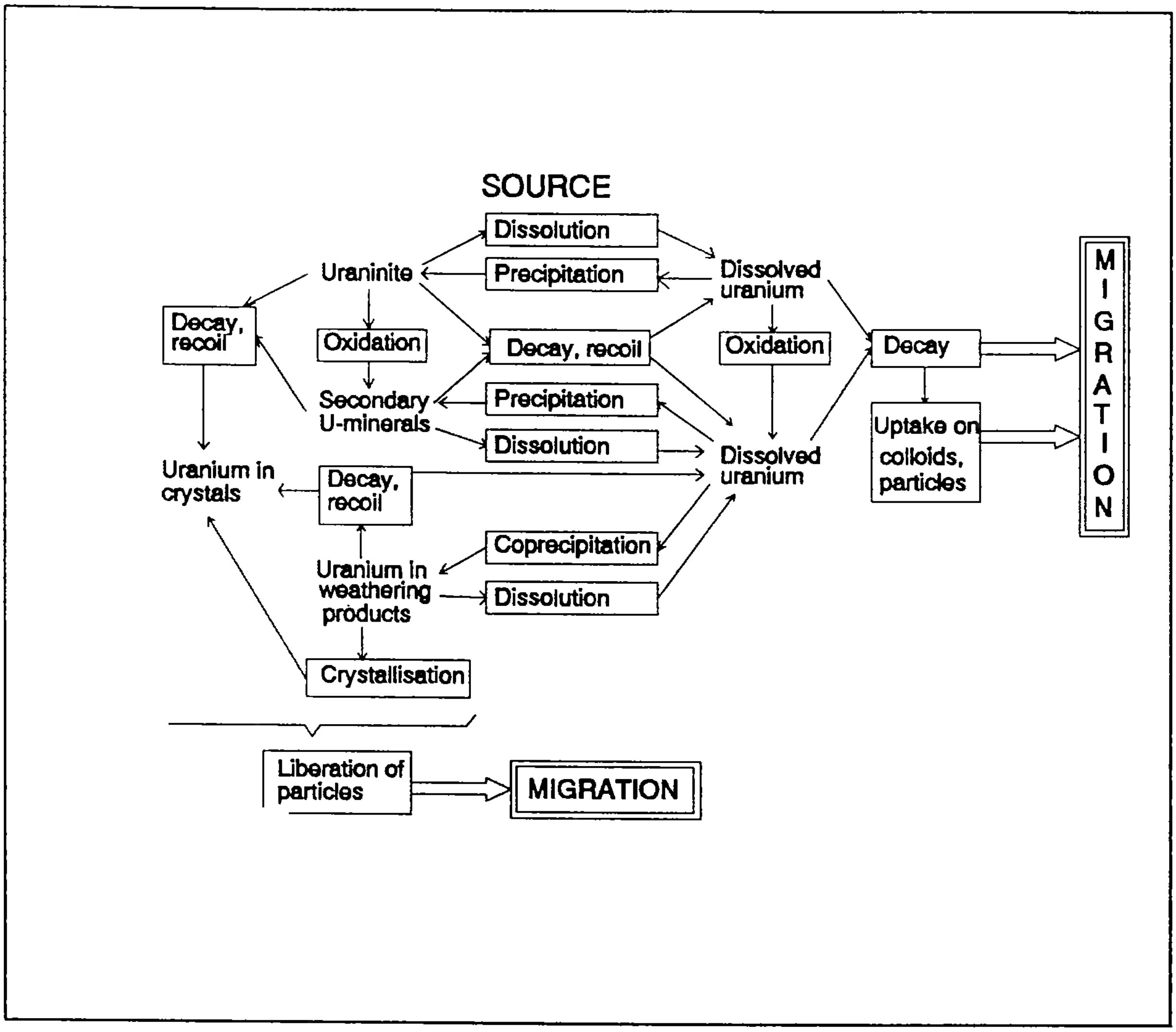

Figure 1 Schematic description of the SOURCE

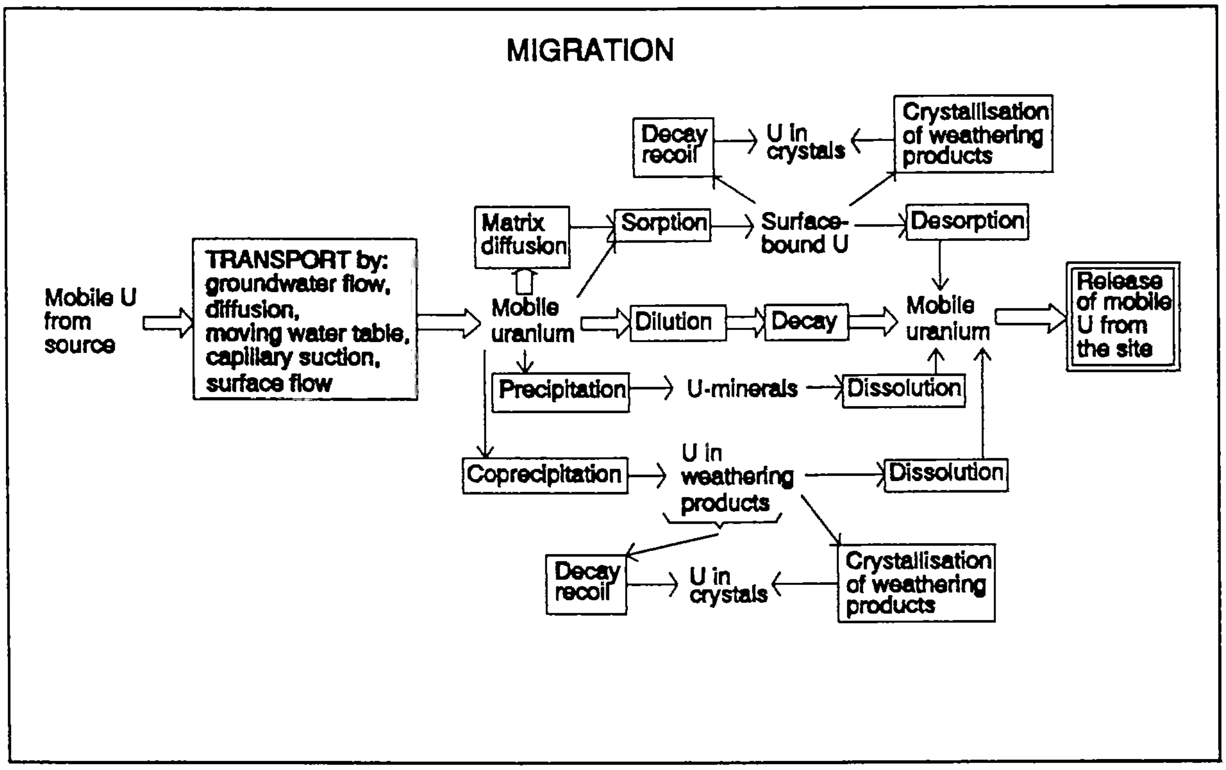

Figure 2 Schematic description of the MIGRATION

References

1 Alligator Rivers Analogue Project, Final Report. OECD/NEA - ANSTO 1992.

2 Andersson, J., Carlsson, T., Eng, T., Kautsky, F., Söderman, E., and Wingefors, S.: The joint SKI/SKB scenario development project. SKI Technical Report 89:14, Swedish Nuclear Power Inspectorate, Stockholm 1989.

3 Cranwell, R.M., Guzowski, R.V., Campbell, J.E., and Ortiz, N.R.: Risk methodology for geologic disposal of radioactive waste: Scenario selection procedure, SAND80-1429, NUREG/CR-1667. Sandia National Laboratories, Albuquerque 1990.

4 Skagius, K., and Höglund, L.O.: Scenario identification and formulation for radionuclide release from the SFR repository, SKB Progress Report SFR 91-04. Swedish Nuclear Fuel and Waste Management Co, Stockholm 1991.

THE ALLIGATOR RIVERS ANALOGUE PROJECT: A REGULATORY PERSPECTIVE

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1. Introduction

The US Nuclear Regulatory Commission is interested in research on natural analogues because the regulatory time frames over which it must assess the safety of a disposal facility far exceed the time frame available in which to test materials and performance assessment predictions. Specific time frames used within the US regulatory framework (10 CFR Part 60) [1] include 300 to 1000 years for the engineered barrier system and 10,000 years for overall system performance and performance of the waste form. These regulations do not call for validation of predictive models but they do require a finding of reasonable assurance with regard to compliance with regulatory requirements. Among the methods suggested in the NRC regulations for attaining this reasonable assurance is the investigation of natural analogues.

2. Evaluating the performance of disposal systems

The challenge for geoscientists and modelers involved in the high-level waste disposal program is to exploit the knowledge gained from natural analogue studies to increase the credibility of simulations of long-term disposal system performance. Care must be taken in this effort to identify the data needed from the field investigations to characterize the analogue system properly with regard to input requirements for performance assessment models. Data sets for these complex natural systems can be used to challenge the performance assessment teams to use their models and understanding of geologic systems to simulate the observed long-term performance of the natural system. In conducting these modeling efforts, areas of strength and weakness can be isolated both in the analytical tools and the data sets which can then be used to focus additional work. The strengths can be used to help focus site characterization programs and the weaknesses to focus needs for performance assessment capability or technological (scientific, engineering, or data collection) improvement. Developing the conceptual and computational framework for the modeling exercise demands an interdisciplinary integration of skills to represent the performance of the fully integrated natural system. Observing the benefits from overall integration of the analogue studies can help formulate well integrated investigation programs for disposal sites. All of these efforts taken together can improve the effectiveness and credibility in both site investigation programs and the validity of the modeling strategies and codes that will be used to evaluate disposal system performance.

The licensing process for a disposal facility can be simplified as shown in the diagram in Figure 1. The important concept displayed is the branch called "Auxiliary Analyses." Computational complexity can defeat even the most powerful computer systems if the system models try to incorporate detailed physical or chemical models of every process occurring in the repository. Most performance assessment system models are built on the principle that complexity is added only if absolutely necessary. Geoscientists often experience frustration when they see systems which they know are combinations of complex physical and chemical processes being represented in a performance assessment calculation by a single parameter or constant. The objective of auxiliary analyses is to find a way to bring the benefits of understanding complex processes into the performance assessment arena in a way that makes that performance assessment simulation approach reality without unacceptably decreasing computational efficiency. This is one place where analogues can help by allowing the testing and development of complex models to the point where simplified modelling approaches can be developed and tested for inclusion in more computationally efficient system codes. Detailed auxiliary analyses

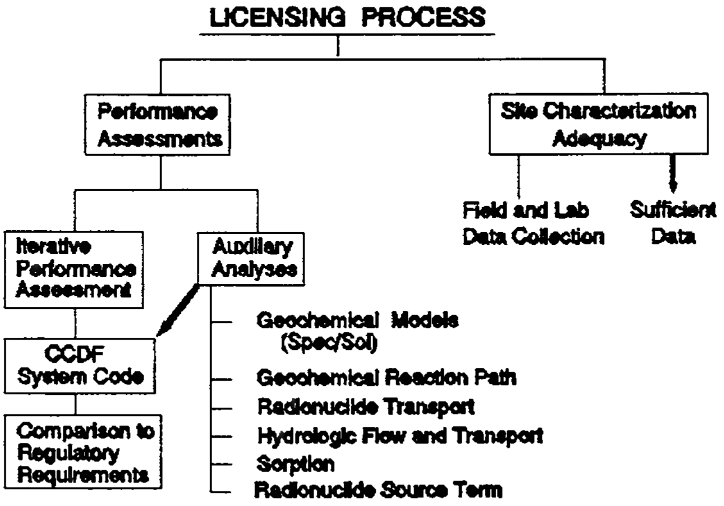

Figure 1: Simplified Diagram of Licensing Activities

which can be used include geochemical models (speciation and solubility), geochemical reaction path models, radionuclide transport models, hydrologic flow and transport models, sorption models and models of the radionuclide source term.

One aspect of natural systems that must be addressed is the natural spatial and (in some cases) temporal variability of parameters. Auxiliary analyses can include conceptual and computational models that form a basis for the range of values that feed the larger system codes and for the distribution of values within that range that should be sampled. It is then up to the PA teams to exercise the system code to generate different "realizations" of the system and combine these to generate a risk profile for the operational life of the disposal system and to conduct sensitivity studies over the range of credible parameter values.

3. Application of natural analogues

Assumptions and bounding conditions often constrain simulations of disposal facility performance. For an unperturbed disposal site it is not possible to test many of these assumptions and bounding conditions. Analogue investigations can be undertaken in geologic systems where critical parameters exceed those at the disposal site but still remain within the bounds of potential disposal site operating conditions. By judicious choice of analogue studies it is possible to undertake "reality testing" of assumptions and bounding conditions for a range of potential realizations of the disposal system. Insights gained from testing these assumptions can be used to improve performance assessment conceptual models and site characterization programs.

Site characterization can be viewed from the performance assessment perspective as an attempt to constrain the possible range of disposal system configurations by increased knowledge of the processes and events that will control disposal system performance. A mathematical analogy would be the solution of a set of simultaneous equations connecting multiple unknowns. The more equations which can be found relating the unknowns, the fewer the degrees of freedom for the set of possible solutions. Another way of looking at the same concept is by a simple application of set theory and the use of a Venn Diagram. Figure 2 shows the effect of combining information from different scientific studies to reduce the possible system models by requiring mutually acceptable solutions for the information sets generated by complementary site characterization studies. From the site characterization perspective this means that a well planned site investigation along several different directions may constrain the conceptual system

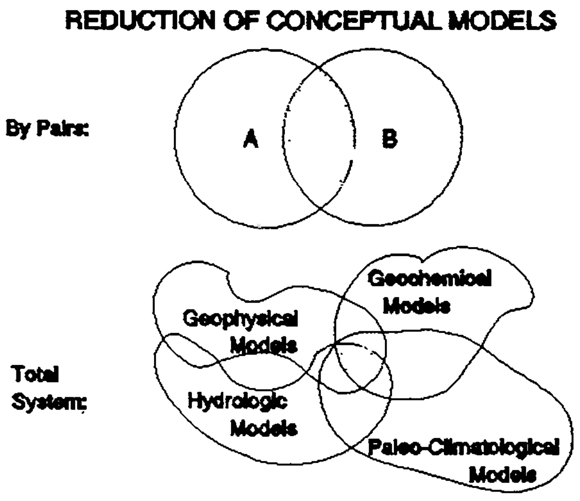

Figure 2: Combination of Data Sets to Constrain Models

model far more than one or two highly intensive studies which ignore potentially important processes or events.

This concept shows the importance of the proper integration and coupling of interactive processes and conditions. Oversimplified models and overly conservative parameter assumptions, which may include unlikely combinations of geologic parameter values, may lead to performance assessments that show violations of regulatory limits when a more scientifically correct treatment would show compliance with all limits. Conversely, over simplified performance assessment calculations which fail to account for the sets of integrated processes that could lead to extreme values in transport velocities and radionuclide fluxes could show compliance for a site that would fail a more realistic analysis. An important role of natural analogue studies is to help develop: (1) a necessary set of significant parameters and processes, including important couplings; and (2) a minimum set, not containing impossible combinations of parameter values and insignificant processes. The integrated efforts of earth scientists and performance assessment modelers is needed to avoid these extremes.

4. The International Alligator Rivers Analogue Project

The stated objectives for ARAP were: 1) to develop and test realistic models for radionuclide migration, and 2) to develop methods of model validation using laboratory data and field data [2]. The Koongarra uranium ore body, which has suffered over the past million years from active leaching and transport by infiltrating, oxidizing groundwater, was selected to serve as an analogue to a breached HLW repository for the purposes of testing and analyzing HLW site characterization and performance assessment methodologies. All parties to ARAP recognized that near surface attack by significant quantities of oxidizing groundwater on the Koongarra ore body is a condition that is far more severe than would be expected for any geologic HLW repository site.

The NRC staff involved in ARAP viewed the validation objectives of ARAP as a research tool in terms of its contribution to a long-term process of testing and improving methodologies that will be used in determining reasonable assurance with regulatory requirements. An important role of ARAP is its potential for helping to improve the capability of its participants to make sound judgments. Such judgments involve both numerical and conceptual analyses, quantitative and qualitative assessments. The scientific rigor required for acceptable numerical modeling of Koongarra was essential to the qualitative value of ARAP.

5. ARAP results

The full value of the ARAP to the NRC staff is not expected to be realized until well after the completion of the project. The extensive data and insights from ARAP will continue to be analyzed for many years to come in light of new data, methods and models. The ARAP results are a resource available to the research and regulatory communities. Because of time constraints and the necessarily limited project focus, ARAP data have not been fully analyzed. In some ways the ARAP came too soon to be fully used by the INTRAVAL project which primarily focused on groundwater hydrology modeling problems that did not involve geochemical processes. When the international model validation community's focus moves to reactive contaminant transport and coupled hydro-geochemical models, the ARAP data will be available for further analysis.

5.1 Hydrology

The Koongarra ore body is located in a complex hydrologic environment. Hydrologic testing produced results that were difficult to interpret. Multiple conceptual models could fit the data. At Koongarra a number of multidisciplinary characterization methods were applied to supplement the hydrologic tests (Fig. 3, personal communication Fabryka-Martin). The extensive hydrologic analysis and modeling indicated that overall flow rates are low through the Koongarra area despite high rainfall and fracture flow conditions, in part, because the clay-rich weathered zone limits infiltration rates.

In the opinion of the NRC participants, one of the major achievements of the ARAP was its successful approach to integrating multidisciplinary data to constrain hydrologic conceptual models. This interdisciplinary characterization and modeling methodology will be essential to understanding complex HLW sites. The ARAP showed that hydrologic tests alone are hard-pressed to provide sufficient data to constrain conceptual hydrogeologic models of complex low-permeability faulted and fractured rock [3,4]. Geophysical data helped to understand the effects

FIELD MEASUREMENTS APPLIED TO FLOW MODELING

INDEPENDENT FLOW TECHNIQUES / MODEL COMPONENTS	U-Series Solid Phase	Petrophysics Geophysics	Borehole Television	Large Scale Aquifer Tests	Chemistry	Isotopes	Hydraulic Tests
Direction of Flow (Divergent to Gradient)	X	X		X	X	X	X
Dominance and Orientation of Permeable Fracture Zones		X	X	X		X	
Velocity Field	X					X	X
Residence Time in Ore Zone					X	X	
Role of Reverse Fault				X	X	X	
Stratification of Flow		X				X	
Degree of Mixing Down-Gradient					X	X	X
Complexity of Flow Pat		X		X		X	

Figure 3: Contributions from ARAP

of faults and fractures on groundwater flow [5,6]. Isotopic data, geochemical data and modeling were invaluable to constraining the possible groundwater flow paths of possible past and future changes in flow directions. Geochemical data and modeling were used to develop the conceptual model that the weathered parts of the Koongarra ore body have been subjected to extensive periods of drying during low sea level stands in glacial periods [7]. Thus geochemical, geophysical and paleoclimatolical data [8] provided insights to understanding hydrology and transport of uranium.

Koongarra data have been used in the development and testing of a coupled hydrogeochemical transport model [9] which has provided a quantitative understanding of the process of the formation of unconformity type uranium ore bodies. This model couples thermal, hydrological and geochemical processes which caused the flow of fluids and the precipitation of ore minerals in Australian and Canadian basins. These processes may also occur in the near field of a HLW repository. This effort demonstrates the potential of numerical modeling to describe and possibly predict complex coupled long-term processes affecting a HLW repository.

5.2 Geochemistry

The hydrochemistry and mineralogy [10,11,12,13] of the weathered zone showed a distinctive vertical profile that was simulated by numerical geochemical reaction-path modeling (EQ3/EQ6) assuming the successive reaction of oxidizing rainwater containing soil concentrations of dissolved carbon dioxide with the quartz - chlorite host rock [8]. A conceptual model of downward water flow through the weathered zone is implicit in this geochemical modeling. Thermodynamic geochemical modeling with a new thermodynamic data base for uranium phosphate minerals provided an improved and acceptable fit with observed hydrochemistry and mineralogy [7,12]. The thermodynamic data base for uranyl silicate minerals was judged in need of improvement because reaction-path modeling produced different uranyl silicate minerals than are observed at Koongarra. The data may be modeled again by the NRC staff following improvements anticipated in the database. An important conclusion to the NRC staff is that the long-term stability of the Koongarra ore body is in part a function of the low solubilities of the uranyl silicate minerals that comprise the majority of the ores and that similar minerals will exist at Yucca Mountain following loss of containment. Limited measurements of plutonium activities in Koongarra ores are consistent with plutonium undergoing solid solution with uranium in uranyl silicate phases [13]. If plutonium and other high-valence state actinides, which are potentially mobile hazardous radionuclides, coprecipitate with uranium to form uranyl silicate minerals, their rates of release from the near field of disposed spent fuel at would be greatly reduced. However, this process might not effect radionuclides released from glass waste forms produced from reprocessed wastes. Thus, the long-term stability of the Koongarra ore body under near surface conditions may have important implications for glass and spent fuel disposal at a disposal site.

Koongarra weathered zone samples have been studied extensively in research on radionuclide adsorption [14,15]. Single mineral adsorption of uranium has been modeled using mechanistic surface complexation models [15]. Research is progressing well, but is not complete, on using these models to understand the complex natural materials. This research has the potential of greatly improving capabilities to model radionuclide transport. Because most radionuclides for a variety of wastes are subject to sorption and sorption may greatly reduce transport rates and concentrations, this research may help improve the regulatory community's ability to assess the safety of proposed waste disposal sites.

5.3 Performance assessment

A number of performance assessment and conceptual models were applied to Koongarra [16]. These are pioneering efforts to test the application of models that are intended for

regulatory use. The simplification of hydrogeologic and geochemical data and conceptual models involved in performance assessment modeling is a process involving qualitative judgment. Communication between geoscience specialists and performance assessment specialists is required for effective application of performance assessment models. ARAP was an important step in building better communications and in developing a better understanding of interdisciplinary approaches. The specific results of the performance assessment calculations are of no general significance but the effort was a significant step in focusing performance assessment on a field site where long-term radionuclide transport has taken place. ARAP participants have an improved appreciation and understanding of the process of integration required for performance assessment of a "real" site. From the regulatory perspective, improved judgment that may emerge from participation in ARAP is more important than any quantitative result.

6. Conclusions

The multidisciplinary approach demonstrated at Koongarra will be essential to understanding infiltration and transport of radionuclides at nuclear waste disposal sites. The combination of geological, geochemical, isotopic and geophysical data which included high resolution down-hole televiewer [6,17], provided strong constraints on hydrologic conceptual models and boundary conditions. NRC viewed this project as research to gain understanding of long-term processes that might affect the stability of a nuclear waste repository. That objective has been achieved and the data acquired can continue to provide new insights. In addition, limited highly focused work will continue which will involve compilation and modelling of the data, and additional sorption studies.

References

1. United States Nuclear Regulatory Commission, "Disposal of High-Level Radioactive Waste in Geologic Repositories," Title 10, Part 60, United States Code of Federal Regulations.
2. Duerden, P., D.A. Lever, D.A. Sverjensky and L.R. Townley, 1992, "Summary of Findings," ARAP Draft Final Report, (ANSTO) Vol 1.
3. Townley, L.R., 1992, "Hydrogeological Modelling", ARAP Draft Final Report,(ANSTO) Vol 2.
4. Davis, S.N., 1992, "Hydrogeological Field Studies", ARAP Draft Final Report, (ANSTO) Vol 5.
5. Emerson, D.W., 1992, "Geophysics, Petrophysics and Structure", ARAP Draft Final Report, (ANSTO) Vol 4.
6. Miyakawa, K., 1992, "Borehole TV mapping in the vicinity of the Koongarra uranium ore deposit", 5th CEC NAWG Meeting and Alligator Rivers Analogue Project (ARAP) Final Workshop Proceedings, EUR series pp. 37-42.
7. Sverjensky, D.A., 1992, "Geochemical Modelling of Secondary Uranium Ore Formation", ARAP draft Final Report (ANSTO) 11:1-49.
8. Wyrwoll, K-H., 1992, "Geomorphology and Paleoclimatic History", Draft Final Report, (ANSTO) Vol 3.
9. Garven, G. and J.P. Raffensperger, 1992, "A hydrogeologic analysis of uranium ore formation in proterozoic sedimentary basins.", 5th CEC NAWG Meeting and Alligator Rivers Analogue Project (ARAP) Final Workshop Proceedings, EUR series pp. 185-191.
10. Payne, T.E., 1992, "Groundwater Chemistry", ARAP Draft Final Report, (ANSTO) Vol 7.
11. Edis, R., 1992, "Chemistry and Mineralogy of Rocks and Soils", ARAP Draft Final Report, (ANSTO) 8:1-250.
12. Sverjensky, D.A., 1992, "Geochemical Modelling of Present-day Groundwaters", ARAP Draft Final Report, (ANSTO) 12:1-54.
13. Fabryka-Martin, J.T., and D.B. Curtis, 1992, "Geochemistry of ^{239}Pu, ^{129}I, ^{99}Tc and ^{36}Cl", ARAP draft Final Report, (ANSTO) 15:1-82.
14. Murakami, T., 1992, "Weathering and its Effects on Uranium Redistribution", ARAP Draft Final Report, (ANSTO) 9:1-136.
15. Waite, T.D., 1992, "Uranium Sorption", ARAP Draft Final Report, (ANSTO) 13:1-91.
16. Golian, C. and D.A. Lever, 1992, "Radionuclide Transport", ARAP Draft Final Report, (ANSTO) Vol 14.
17. Snelling, A.A., 1992, "Geological Setting", ARAP Draft Final Report, (ANSTO) Vol 2.

NATURAL ANALOGUE WORKING GROUP MEETING

NATURAL ANALOGUE STUDIES

The AECL/SKB Cigar Lake Analog Study: Some implications for performance assessment
J.J. Cramer[1], J.A.T. Smellie[2]
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Oklo as a natural analogue for radionuclide transfer processes in a waste geological repository: Present status of the program
P.-L. Blanc, CEA-IPSN (F)

El Berrocal Project: Characterisation and validation of natural radionuclide migration processes under real conditions in a fissured granitic environment
J. Astudillo, ENRESA (E)

Natural analogue studies of the Tono uranium deposit in Japan
T. Seo and H. Yoshida, PNC (JAP)

UK HMIP Natural Analogue project - Implications for performance assessment
P. Hooker[1], A.E. Milodowski[1], D. Read[2]
[1]BGS (UK), [2]WS Atkins

The Palmottu natural analogue study site, Finland
R. Blomqvist[1], J. Suksi[2], L. Ahonen[1], H. Niini[3]
[1]GTK Espoo (SF), [2]University of Helsinki, Dpt. of Radiochemistry (SF),
[3]Helsinki University of Technology, Lab. of Engineering Geology and Geophysics

An overview of the Maqarin natural analogue project - A natural analogue study of a hyperalkaline cement groundwater system
C.J. Tweed[1], A.E. Milodowski[2]
[1]AEA-Harwell (UK), [2]BGS (UK)

Natural constraints on radionuclide release rates
D.B. Curtis, J. Fabryka-Martin, P. Dixon, Los Alamos N.L. (USA)

Performance Assessment significance of natural analogue studies at Peña Blanca, Mexico, and at Santorini, Greece.
W.M. Murphy, E.C. Pearcy, CNWRA (USA)

THE AECL/SKB CIGAR LAKE ANALOG STUDY: SOME IMPLICATIONS FOR PERFORMANCE ASSESSMENT

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ABSTRACT

This paper provides background information and summarizes the results of a three-year AECL/SKB analog study on the Cigar Lake uranium deposit in northern Saskatchewan, Canada. The emphasis is on the analog aspects and the implications of modelling activities related to the performance assessment of disposal concepts for nuclear fuel wastes developed in both Canada and Sweden.

1. Introduction

AECL has been conducting analog studies at Cigar Lake since 1984. In 1989, AECL and the Swedish Nuclear Fuel and Waste Management Company (SKB) began a collaborative three-year study. The Los Alamos National Laboratory (LANL) joined the program in 1991 with funding from the United States Department of Energy. The data from these studies are currently being interpreted and documented in a joint publication (Cramer and Smellie 1993).

This paper summarizes some of the modelling activities carried out during the past few years and their implications for the performance assessment of disposal concepts for nuclear fuel wastes developed in both Canada and Sweden. The modelling is founded on an extensive and quantitative database including the results of AECL's research prior to 1989 (e.g. Cramer 1986, 1988; Cramer et al. 1987).

2. Cigar Lake uranium deposit

The Cigar Lake uranium deposit (Figure 1) is located in northern Saskatchewan at the southwestern tip of Waterbury Lake. The deposit is of hydrothermal origin and Proterozoic age, and is one of many unconformity-type, sandstone-hosted uranium deposits that characterise the Athabasca Basin uranium province (Fouques et al. 1986; Bruneton 1985, 1986). These deposits are all relatively high-grade, with some containing average ore grades reaching several tens of percent uranium. The Cigar Lake deposit is notable because it is located well below the surface at a depth of about 430 m, and the deposit has no direct surface signatures to indicate its presence.

The ore deposit, comprising primarily uraninite and pitchblende with subordinate coffinite, formed about 1.3 Ga ago (Cumming and Krstic 1992) at an estimated depth of more than 3 km below surface in hydrothermally altered sandstone. The mineralization is located at the unconformity contact of the host sandstone of the Athabasca Basin Formation and the metamorphic Precambrian basement (metapelites and calc-silicate gneisses), and is currently situated at a depth of ~430 m below the surface following millions of years of erosion. The uranium mineralization forms an irregular-shaped lens ~2000 m long, 25 to 100 m wide and 1 to 20 m thick, and has an average grade of around 12 wt.% U, with local concentrations reaching values as high as 55 wt.% U. The present ore reserve has been calculated to be $1.5x10^5$ Mg U. The Cigar Lake deposit has many features in common with the other unconformity-type deposits in the region, which all tend to consist of long linear deposits that straddle or flank traces of graphitic metapelites subcropping at the unconformity (Hoeve and Quirt 1984; Sibbald et al. 1990).

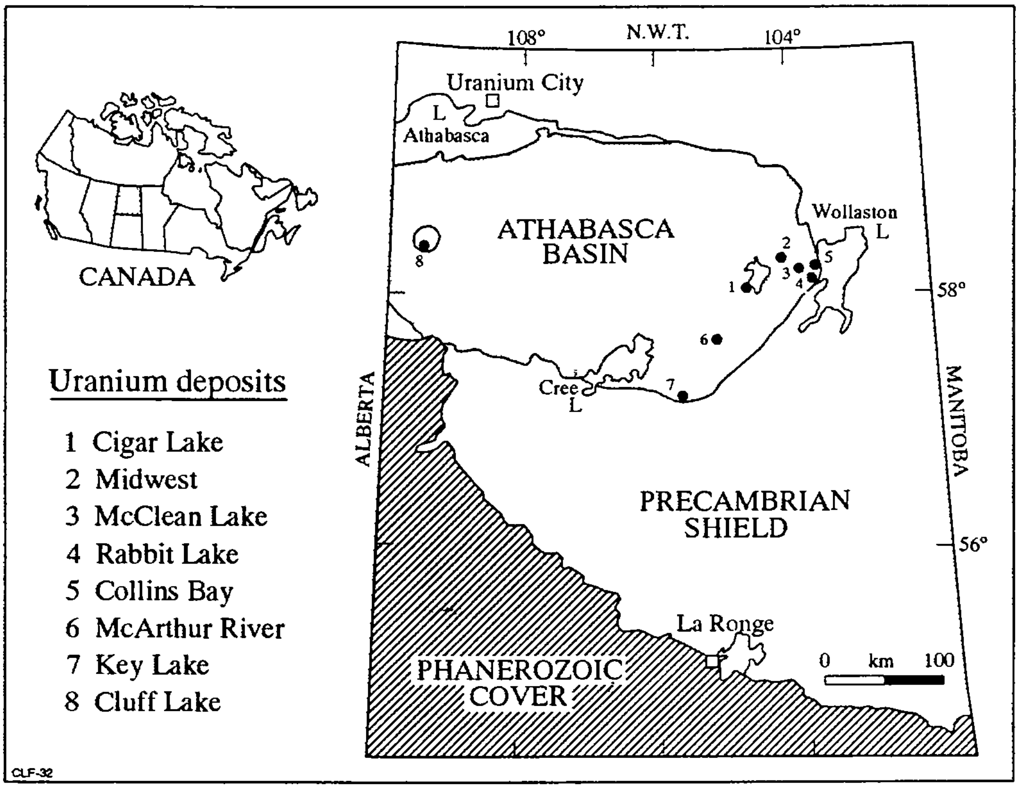

FIGURE 1 Location map showing uranium deposits of the Athabasca Basin in northern Saskatchewan, Canada.

The ore zone consists of the uranium mineralization in a very clay-rich matrix which is dominated by illite and chlorite with minor carbonates (siderite and calcite) and accessory phases (e.g. zircon, rutile, phosphates etc.). In addition to uranium, the ore contains elevated concentrations of sulphides, arsenides and sulph-arsenides incorporating a broad suite of elements (e.g. Ni, Co, Mo, Pb (radiogenic), Zn, Mn and Fe). Three stages of mineralization can be recognised (Bruneton 1986), of which at least the first two are considered to be of a hydrothermal nature: I) euhedral uraninite and pitchblende associated with primary As-S minerals of Ni, Co and Fe, II) pitchblende associated with secondary As-S minerals, in addition to Cu, Mo, Pb, Zn and Fe sulphides, and III) pitchblende and coffinite associated with ferrihydrites. The first stage produced the bulk of the Cigar Lake mineralization, whereas the last stage occurred on a local and uneconomic scale, dispersing ore above (perched mineralization along fractures) and also below (minor basement mineralization) the primary ore body. The first two stages have been dated at 1362 Ma and 1287 Ma respectively (Cumming and Krstic 1992). The last stage of mineralization is characterized by a low-temperature assemblage, and is much younger, dated at 293 Ma ago (Cumming and Krstic 1992).

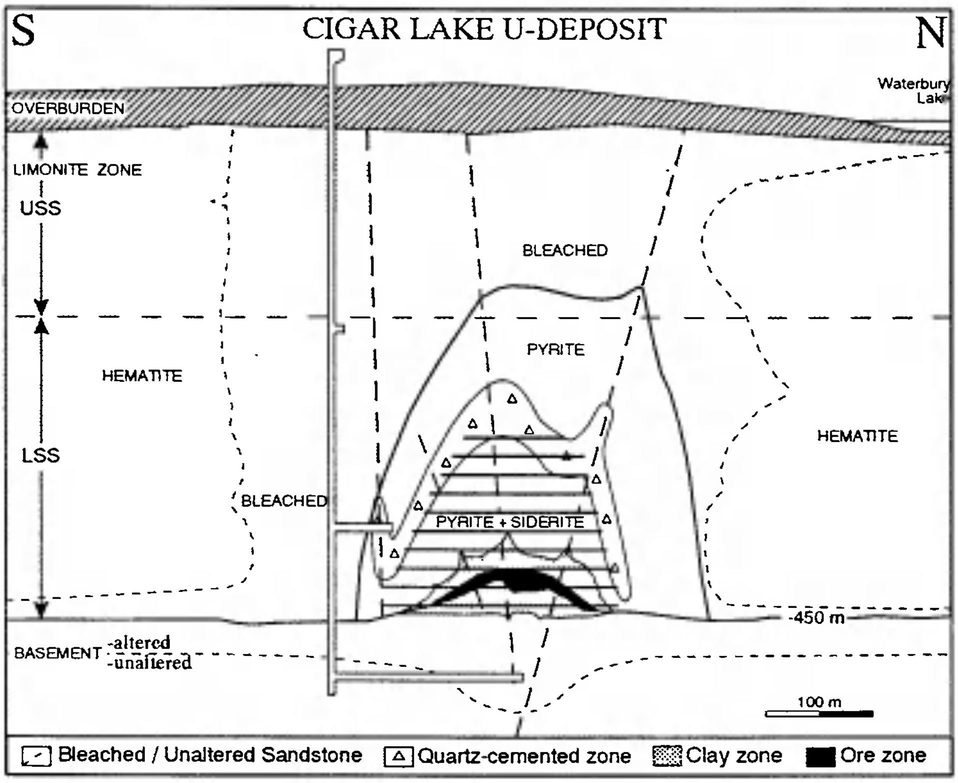

FIGURE 2 Schematic cross section through the Cigar Lake deposit showing the uranium mineralization and its host rocks, including the lithologic characteristics related to hydrothermal alteration and weathering. (USS= upper sandstone; LSS= lower sandstone).

The hydrothermal event associated with the formation of the Cigar Lake uranium mineralization was responsible for the characteristic alteration of the host sandstones (Figure 2). Reducing hydrothermal fluids (150 to 200°C), after having been in contact with the graphite-containing metapelites in the basement, were discharged along a major lineament into the sediment basin where they interacted with the more oxidising diagenetic uranium-bearing solutions of the red-bed-type sandstones. The resulting alteration of the sandstone includes the following main characteristic features: a) reduction of Fe(III) from hematite to Fe(II) in marcasite/pyrite, forming a nearly symmetrical plume of "bleached" sandstone above and parallel to the lineament, b) dissolution and mobilization of matrix quartz from the sandstone causing a progressive enrichment of refractory clay and accessory minerals toward the high-temperature side, and reprecipitation of the dissolved silica toward the cooler side of the hydrothermal system, and c) intense fracturing caused by volume readjustments in response to the quartz redistribution mentioned under b). Thus, upon descending and approaching laterally through the host sandstone, alteration of the sandstone is characterized by increasing clay-mineral contents reaching 80 to 100% locally in and around the mineralized zone. However, a quartz-cemented zone (or "quartz cap") marks the location of the silica reprecipitation in the altered sandstone before the zone reaches a clay-mineral content of about 30 %. Below this quartz cap, the altered sandstone is highly permeable, densely fractured and locally friable until the clay-mineral content reaches about 60% in the so-called clay-rich halo (or "clay zone"). This clay zone is 5 to 30 m thick, contains elevated uranium contents and surrounds the high-grade uranium mineralization. The hydrothermal alteration also affected the basement rocks underneath the mineralization, extending the clay-rich zone past the unconformity into the basement regolith. This alteration and the paleo-weathering (producing the ~50-m-thick regolith) of the basement resulted in local obliteration of the original metamorphic textures and mineral assemblages. The effects of hydrothermal alteration extend upwards about 300 m into the sandstone and down into the basement to about 100 m below the unconformity.

At present, the different lithologies are characterised as follows (Bruneton 1986):

1- The pink/red-to-purple **unaltered sandstone** is competent and hard, and contains hematite, subequal amounts of illite and kaolinite, and has a clay-mineral content of about 10 to 15 %.

2- The grey-white **bleached sandstone** is competent and hard, and contains finely disseminated marcasite/pyrite, more illite than kaolinite, and may have a clay-mineral content >15 % (however, intercalated beds and zones of less-altered (less "bleached") sandstone do occur within this unit).

3- The grey **quartz-cemented zone** is hard and highly fractured, contains euhedral quartz on fracture surfaces, in cavities and interstitially in the matrix, and is somewhat lower in clay-mineral content than the surrounding bleached sandstone.

4- The grey **altered sandstone** is less competent, even soft and friable in places, is intensely fractured and contains generally up to 30% clay-minerals both in the matrix and in fractures, with illite dominating over kaolinite. The presence of faults may be indicated by massive clay layers or pockets.

5- The pink-grey/white **clay zone** is almost entirely composed of clay with rare sandstone remnants. Localized oxidised areas are common (faults?). Illite is the dominant clay mineral with minor amounts of kaolinite, and chlorite appearing toward the ore zone. Siderite and marcasite/pyrite are common constituents. This zone has elevated uranium contents and is mineralized locally (up to 1% U).

6- The **clay-ore contact** is sharp (both upper and lower contacts of the ore zone), and is characterized by the disappearance of kaolinite and by a marked increase in chlorite content. The upper clay-ore contact is red-green in colour and may be 1 to 3 m thick, with the greater thickness correlating with the presence of faults. This upper contact obtains its reddish colouration from Fe(III) phases including both hematite and amorphous to poorly-crystallized ferrihydrites. Locally, siderite may form up to 50% of the rock.

The ~ 100-m-thick **limonite zone** at the top of the sandstone formation (Figure 2) is a late alteration (glacial and post-glacial) superimposed on both unaltered and bleached sandstones. It represents a zone in which downward infiltration of oxidising, surface-derived waters causes precipitation of ferrihydrites (including limonite), giving the rocks an orange colour.

3. Analog features of the deposit

The Cigar Lake uranium deposit has a number of features analogous to aspects considered in the performance assessment (PA) of concepts for the disposal of nuclear fuel waste at depth in crystalline rock (Cramer 1986, 1993; Cramer et al. 1987; Goodwin et al. 1989). In particular, the analogy with the excellent long-term isolation of UO_2 ore in this deposit is of great interest to Canada and Sweden, who are developing similar concepts (both considering granite as a host rock) for disposal of their UO_2-based fuel waste. In what may be termed a "worse-case scenario", the Cigar Lake ore has been well-preserved without specially designed, man-made barriers inside a major aquifer, and without showing any direct evidence of its existence at the present-day surface. Since the current topography and overburden were formed during the last glaciation, any potential migration of radionuclides from the ore has not reached the surface environment during at least 10^4 a. This time frame is in accordance with quantitative predictions in performance assessment as required by regulatory guidelines (10^4 a in Canada and 10^6 a in Sweden). Thus, the spatial arrangement of the UO_2 ore surrounded by natural barriers, including a clay zone and several hundreds of metres of host rock in a tectonically stable formation, is similar to that of the disposal scenario in the concepts being considered in both Canada and Sweden.

In addition to this general analogy, many analogous processes and materials can be found and studied in more detail in the Cigar Lake deposit (e.g. Goodwin et al. 1989). These include both processes that occur in the present-day system and those that occurred during the ~ 1-Ga history of the deposit since its formation. For example, current processes that have been studied include water-rock interaction, evolution of groundwater compositions, redox geochemistry, stability and dissolution of uranium and clay minerals, sealing by clay, formation and properties of colloids, activity and role of microbes etc. On the other hand, paleo-processes that can be studied from the geological record include the effects of erosion, uplift and glaciation, paleo-hydrology, water-rock interaction, redox buffering, mineral stability and radionuclide mass transport. A comprehensive record of the studies carried out on many of these processes is given in the final report of the AECL/SKB analog program (Cramer and Smellie 1993).

4. Modelling approach

The analog studies in the joint AECL/SKB program were subdivided into a number of tasks, with each task covering one particular discipline or related disciplines (Figure 3). The goal for each task was to produce specific databases and conceptual models, and to carry out modelling to further improve the understanding of the observed processes in each discipline. The main databases and conceptual models produced are the geological and hydrogeological databases, a mineralogical and lithogeochemical database, and a set of reference groundwater compositions. The main conceptual models produced include the geological, hydrogeological and hydrogeochemical models. In addition, the various databases and conceptual models were subsequently integrated in modelling for four PA-related objectives:

1- The evaluation of equilibrium thermodynamic codes and databases.

2- The evaluation of the role of colloids, organics and microbes in transport processes for radionuclides (near- to far-field analogy).

3- The evaluation of UO_2 stability and the influence of radiolysis on UO_2 dissolution and radionuclide migration (near-field analogy).

4- The evaluation of generic mass-transport models for potential radionuclide migration through clay-based sealants (near-field analogy).

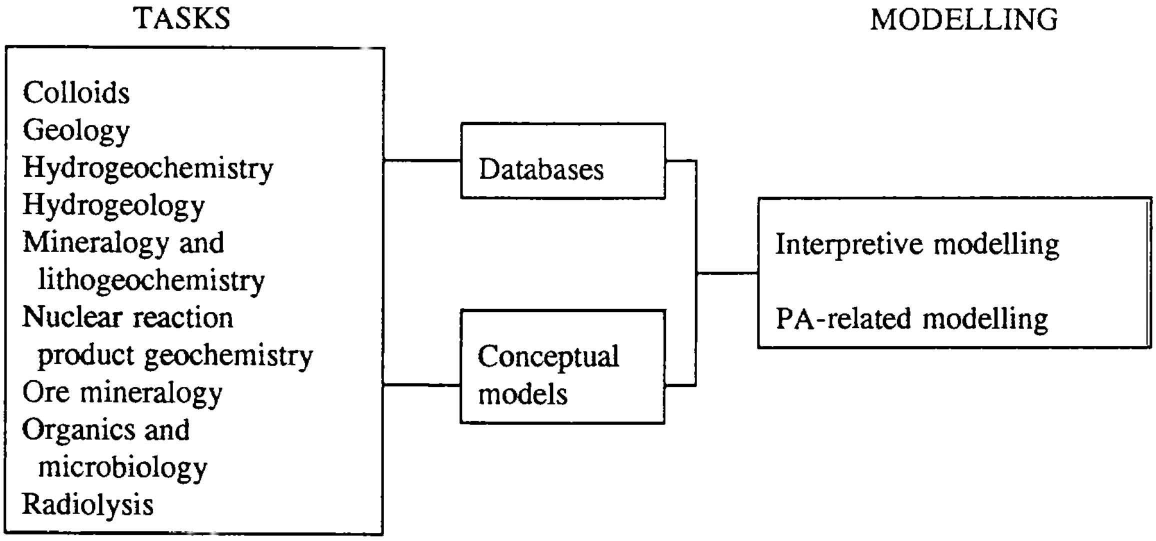

FIGURE 3 Relationship between Tasks and Modelling activities in the Cigar Lake analog study.

5. Databases and Conceptual Models

5.1. Databases

The **geological** and **hydrogeological databases** for the Cigar Lake deposit consist mainly of the vast collection of information, data and reports collected and produced by the exploration and mining companies. A large amount of work was done on the geological and hydrogeological characterization of the site, including geological, geochemical, petrological, mineralogical, geophysical, hydrological and geotechnical studies, as well as some studies of the Quaternary geology. This work involved the drilling of over 200 boreholes, conducting in-hole measurements and experiments, installing tens of piezometers, carrying out pump tests and excavating a shaft and horizontal drifts. Additional hydrogeological data were also collected as part of this analog study.

The **mineralogical** and **lithogeochemical database** was compiled from the existing mineralogical and geochemical data available with the mining company, from a PhD study on the clay mineralogy and geochemistry in this deposit (Percival 1990), and from additional work carried out as part of the analog study.

The set of **reference groundwater compositions** was produced from an extensive hydrogeochemical database collected by AECL over a period of 7 years, during which time samples were collected regularly from surface and groundwaters at the site. This carefully reviewed reference set was produced primarily for all the modelling activities of the project to provide representative compositions for all the lithological units and for the overburden.

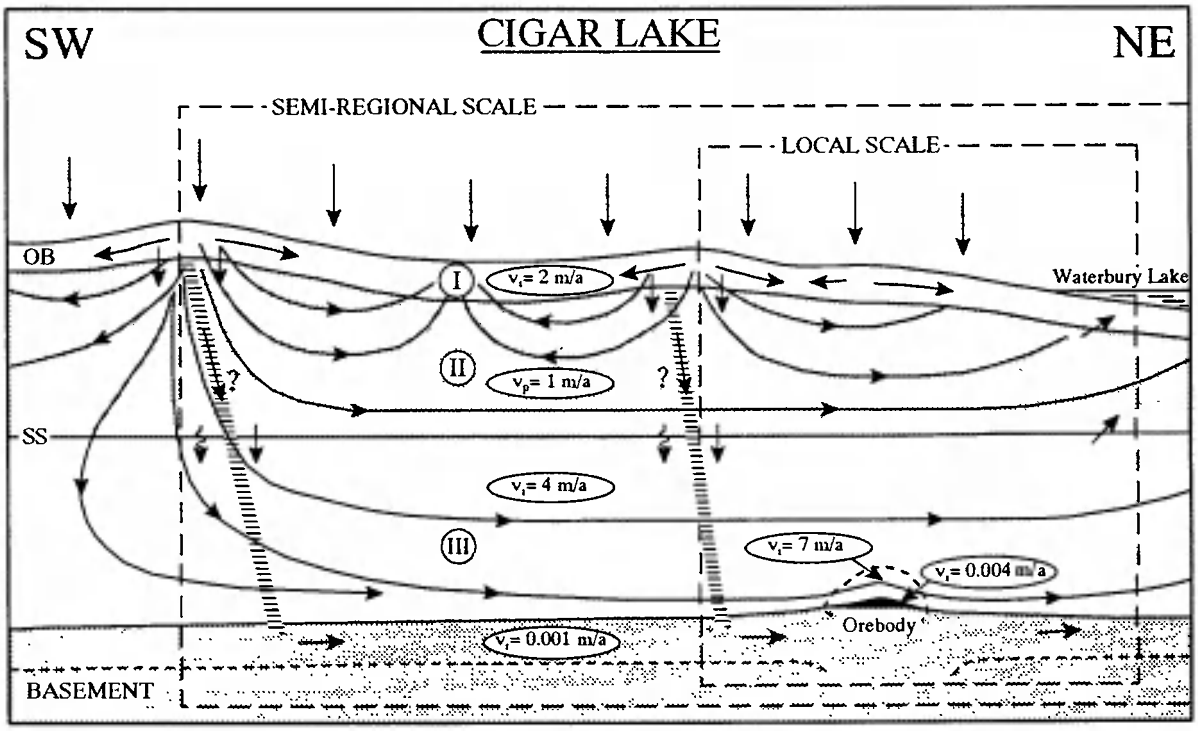

FIGURE 4 Schematic section through the Cigar Lake deposit showing the conceptual hydrogeologic model with three distinct flow regimes (I-III) and calculated particle velocities (v_i= integrated velocities, v_p= point velocities). (OB= overburden, SS= sandstone).

5.2. Conceptual Models

The **conceptual geological model** is illustrated in the schematic cross section of Figure 2, which shows the various lithological, mineralogical and structural units comprising the deposit. This south-to-north cross section represents the East Zone, the 800-m-long part of the deposit containing the richest and largest uranium mineralization. Its extension toward the west, or West Zone, is about 1200 m long, but contains only about one third of the total ore reserve, and has a less-extensive alteration halo in the sandstones. Because much of the exploration and test-mining effort was focussed on the East Zone, the best data are available for this part of the deposit, therefore, the modelling has been concentrated here.

Several conceptual hydrogeological models were already available at the onset of the AECL/SKB program. Further development of these models and analyses of existing data was carried out, leading to the construction of 2D and 3D models both on a regional and local scale (Winberg and Stevenson 1993). Maps of the hydraulic head and of particle velocities and tracks were produced, and sensitivity analyses were carried out on the boundary conditions, the geometry of the uranium mineralization and the material properties of the rocks.

The resulting **conceptual hydrogeological model** is illustrated by the schematic 2D section through the deposit, based on the 3D local model, in Figure 4. Three distinct flow regimes are shown: I) the local regime, restricted to the overburden, II) the intermediate regime, restricted to the Upper Sandstone unit, and III) the semi-regional regime, restricted to the Lower Sandstone unit. Some hydraulic interconnection occurs between each flow regime, primarily along faults or fracture zones. Also shown on the section in Figure 4 are the calculated particle velocities (v_p/v_i) for each lithologic unit. Note the very low velocities calculated for the clay and ore zones and for the regolith. Corresponding residence times for the clay and ore zones were calculated for particles released within the ore, and range between 18,000 and 85,000 years. These values correspond with residence times estimated from ^{36}Cl data for groundwaters from the ore zone.

The geochemistry and evolution of groundwaters at Cigar Lake are described in detail by Cramer and Nesbitt (1993a-c). In general, the groundwaters in and around the uranium deposit are characterized by neutral to near-neutral pH ($\sim$6-8), by low contents of total dissolved solids ($\sim$60-240 mg/L), by decreasing redox potentials toward the ore zone (from about +0.25 to -0.25 V), and by overall low U content (usually $\ll$30 μg/L or $10^{-6.5}$ mol/L). Within the ore zone groundwaters, marked increases in the contents of certain isotopes (e.g. ^3H and ^{36}Cl) are observed as a result of nuclear reactions occurring in situ.

The **conceptual hydrogeochemical model** for the evolution of groundwater compositions at Cigar Lake is illustrated by the redox diagram in Figure 5. This evolution is characterized by the interaction of the waters primarily with the clay and iron minerals in the rocks. Surface precipitation (rain and snow) reacts with illite and kaolinite, dissolving iron from various minerals in the overburden and producing a recharge water to the Upper Sandstone unit that is already equilibrated with the main clay minerals and is rich in iron (point **A** in Figure 5). Reaction of this oxidizing recharge water with the Upper Sandstone produces precipitation of ferrihydrites down to a depth of about 100 m, overprinting both the unaltered and bleached sandstone ("limonite" zone; **B** in Figure 5). Upon approaching the clay and ore zones of the deposit, subsequent reaction of the waters with Fe sulphides and siderite in the bleached sandstone reduces the oxidation potential of these waters (decreasing pO_2: **B→C→D/E** in Figure 5) to well within the UO_2 stability field. The redox-buffering capacity of the Fe sulphides in the ore and its host rocks plays an important role in maintaining reducing conditions, and thus preserves the stability of the uranium mineralization.

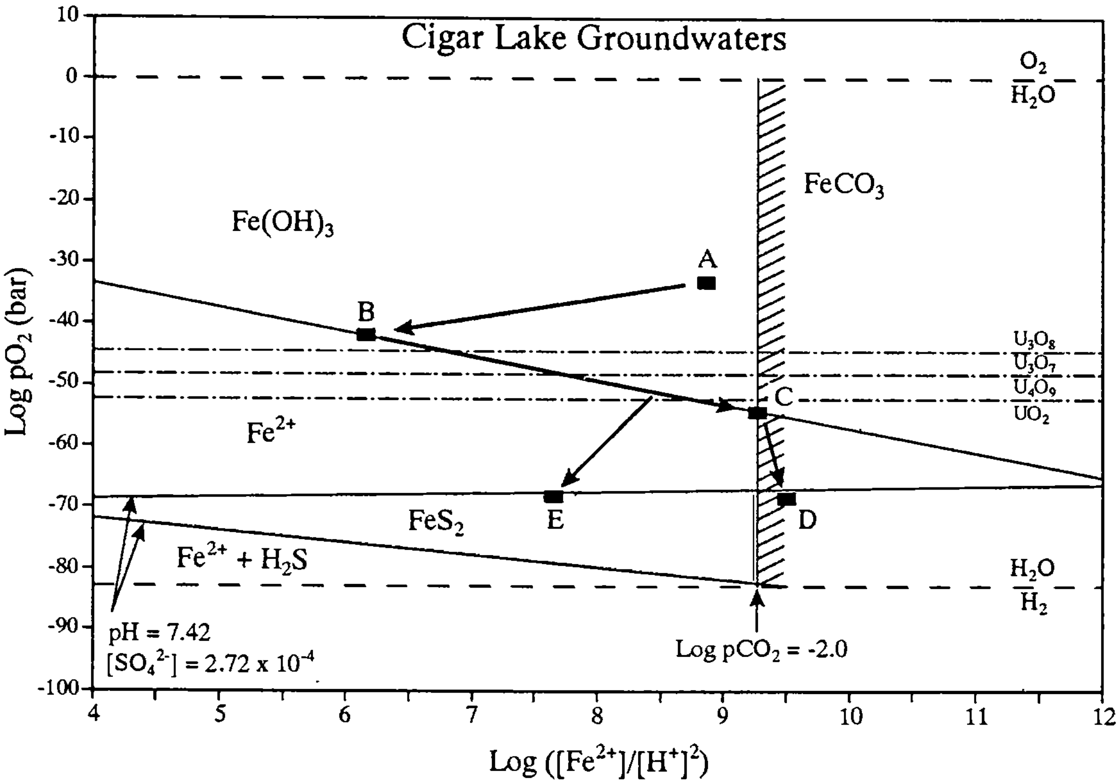

FIGURE 5 Redox diagram for water-rock interaction in the Cigar Lake deposit. Groundwater compositions evolve from A (overburden) to B (unaltered sandstone and limonite zone), to C (altered sandstone), to D/E (clay and ore zones). Semi-dashed lines represent stability boundaries for various solid uranium oxides. See text for further explanation.

6. Performance-Assessment-related modelling

6.1. Thermodynamic codes and databases

Thermodynamic codes and their databases are tools used in the performance assessment of disposal concepts to provide two main types of chemical information: 1) solubility and 2) speciation of dissolved elements and radionuclides. The solubility of an element or radionuclide determines its release rate from a solid host phase under certain conditions, and the speciation of that element/radionuclide in solution provides information on its transport properties.

To test such codes, a series of "blind" predictions was carried out in a fashion similar to that described by Bruno et al. (1990). Compositions of representative groundwaters from the Cigar Lake deposit were used as input to predict the solubility and its limiting solid phase, and the speciation of U, Pu and other elements considered important in performance assessment. The codes and databases used include PHREEQE (Parkhurst et al. 1980), ZZ-HATCHES (Cross and Ewart 1991) and SKBPU (for Pu, Puigdomènech and Bruno 1991).

The results generally showed that the predicted solubilities are in reasonable agreement with the measured concentrations, in particular for those elements that have a good thermodynamic database (Casas and Bruno 1993). Good agreement was found for U, Th, Ba and Cu. Limited success was found for Sr, Mo and As, mostly because of to a lack of relevant thermodynamic data for the critical solubility-limiting phases, which resulted in the concentration of the dissolved species being overpredicted. Similarly, the uncertainty in the redox potential for the Cr^{6+}/Cr^{3+} couple resulted in an underprediction of the concentration of the dissolved species. The analytical detection limits for Ni and Pb were insufficient to succesfully predict their solubilities.

Further improvements to be considered for this evaluation exercise include a) a comparison of the thermodynamic databases used in each code, b) better detection limits for certain elements dissolved in the groundwaters, and c) measuring the speciation for the dissolved elements of interest.

6.2. Colloids, Organics and Microbes

Although theoretical considerations indicate that radionuclide mobility may be affected by the presence of particles (through sorption), dissolved organic compounds (through complexation) and microbial activity (through redox buffering), there is a very limited database on these processes in deep natural systems. The Cigar Lake deposit provides an opportunity to study these aspects in a deep natural system containing a relatively concentrated source of uranium and other radionuclides.

The **colloid studies** at Cigar Lake (Vilks and Bachinski 1993a; Vilks et al. 1988, 1993) were focussed on determining the concentration, size and composition of particles throughout the deposit, and on determining the trace element and radionuclide sorption on the particles. Aspects of particle migration were addressed by determining particle-size distributions, looking for evidence of particle dispersion away from the ore zone, studying particle behaviour in a flow field, and assessing mechanisms of particle generation. The results of these studies include the following observations:

- In the case of reversible radionuclide sorption onto the particles, the average particle contents in the dilute Cigar Lake groundwaters are too low to have a significant impact on radionuclide migration;

- In the case of irreversible sorption, some radionuclides (e.g. U, Th, Ra) can remain fixed on particles for thousands of years (up to 8000 a) and may thus contribute to radionuclide migration;

- A large portion of natural particles in Cigar Lake groundwaters are generated by erosion of fragments from minerals and alteration products from the host rock. Thus, particle concentrations are highest in friable rock and lowest in well-consolidated rock; and

- The composition of groundwater particles in the ore zone is distinct from that in the host sandstone, indicating that the transport of particles from the ore through the clay zone has been negligible, and the mobilization of clay particles from the clay into the sandstone has not been important.

The studies at Cigar Lake lead to an overall conclusion on the role of colloids that they are not important in radionuclide migration, at least on a time scale of 10^4 a based on the 8000-a-old particles found in the ore zone waters.

The characterization of **organic compounds** in the Cigar Lake groundwaters (Petterson et al. 1993; Vilks and Bachinski 1993b) included the determination of total organic carbon (TOC) in all waters, of volatile and solvent extractable organics and of humic compounds, and detailed characterization of fulvic acids (including ^{14}C ages). The results of these studies include the following observations:

- The TOC content in all surface and groundwaters is ≤ 2 mg/L, except in ore zone waters (up to ~11 mg/L). Volatile and solvent-extractable organics account for «10% of the TOC (most of which are probably contaminants), and only 15 to 25% of TOC are humic substances except in the altered sandstone (<10%) and in the ore zone (<2%);
- The humic fraction in all groundwaters consists largely of low-molecular-weight fulvic acid, with the oldest ^{14}C ages measured for humics from the ore zone (ranging up to 15,000 a); and
- The abundance and complexing capacity of fulvic acids in all groundwaters is insufficient to have a significant influence on the speciation of either U^{4+} or U^{6+}.

From the studies at Cigar Lake, the overall conclusion on the role of organics is that the humics in the groundwaters are unlikely to play any significant role in either speciation or mobilization of uranium or any other actnide with a valency of ≥ 4.

Microbial studies on both water and rock samples from the Cigar Lake deposit (Stroes-Gascoyne et al. 1993) were focussed on the identification and quantification of micro-organisms, and on evaluating the effect of microbial activity on the redox and uranium chemistry. The results of these studies include the following observations:

- Despite low nutrient contents in the groundwaters, micro-organisms are present in all groundwaters and seem capable of surviving in radiation fields;
- Anaerobe bacteria are, on average, about 10 times more abundant than aerobe bacteria, in agreement with the prevailing reducing chemical environment in the deposit; and
- Sulphate-reducing, iron-related and denitrifying bacteria are common in both groundwaters and rocks from the most reducing parts of the deposit, and their mediation in redox reactions may contribute to the redox-buffering capacity of the system.

From the studies at Cigar Lake, the overall conclusion on the role of micro-organisms is that bacteria can survive in natural radiation fields and their activity may contribute toward maintaining a reducing chemical environment, thereby reducing the potential for dissolution and mobilization of redox-sensitive radionuclides.

6.3. UO_2 stability and Radiolysis

In both Canada and Sweden, the waste consists of used fuel made up of a crystalline UO_2 matrix that incorporates most of the fission and activation products from the nuclear reaction processes. The long-term stability of the UO_2 matrix under disposal conditions is thus of primary importance for the retention of both uranium and the contained nuclear reaction products inside the repository. The occurrence of "old" UO_2 (uraninite) minerals in the Cigar Lake deposit containing both natural-decay and natural-fission products provides an excellent opportunity for an analog study on UO_2 stability and on what controls this stability.

Canada and Sweden, in their respective performance assessment codes, have different models for the dissolution of the UO_2 matrix and the resulting release of radionuclides from the fuel waste. In Canada, the dissolution model is based on congruent dissolution of the UO_2 matrix through limited oxidation of UO_2 to U_4O_9-U_3O_7 (Johnson et al. 1993). Thus, the analog information being sought for this UO_2-dissolution model includes whether UO_2 is a stable phase and under what conditions, whether UO_2 has suitable low solubility, whether dissolution of UO_2 occurs congruently, and what the retention capability of UO_2 is for natural-decay and natural-fission products. In Sweden, the dissolution model is based on radiolysis-induced oxidation of UO_2 proceeding beyond the U_3O_7 stage (SKB 1992). When oxidation proceeds beyond U_3O_7, the corresponding change in the crystal structure strongly affects the release of radionuclides from the UO_2-U_3O_7 fuel matrix. Therefore, to further test the Swedish model, additional analog information includes evaluating the occurrence of radiolysis in the Cigar Lake deposit, its potential effects on UO_2 stability and, in the case of dissolution, the predominant speciation of dissolved uranium.

Characterization studies of the uranium minerals from the Cigar Lake ore zone (Sunder et al. 1988, 1992) show that uraninite (natural UO_2) exposed to interaction with fluids and/or groundwaters has a surface-oxidation layer of micro-crystalline U_4O_9-U_3O_7, corresponding to U^{VI}/U^{IV} values in the range of 0.20 to 0.57 (as determined by XPS) and to dissolved-U concentrations of $< \sim 10^{-7}$ mol/L (as measured in groundwaters from the ore zone). This information indicates reducing conditions for the natural water-rock interaction, and corresponds to the low redox potentials measured in present-day groundwaters (Eh $< \sim 0.2$ V; Cramer and Nesbitt 1993c). Thus, the dissolution, and therefore the stability, of UO_2 appears to be controlled by a thin surface layer of higher oxides (up to U_3O_7). This is supported by: **a)** experimental work and theoretical considerations (e.g. Shoesmith and Sunder 1991; Garisto and Garisto 1986) showing that the oxidative dissolution rate of UO_2 does not become significant until it is oxidized beyond the $UO_{2.33}$ (U_3O_7) stage, and by **b)** the predictive calculations (using measured groundwater compositions) of the uranium phases at equilibrium, which mostly give U_3O_7 with some overlap to U_4O_9 (see also Section 6.1).

Geological, geochronological and petrological information shows that the oxidation layers observed on exposed uraninite surfaces resulted from only a few discrete, major disturbances, of which the youngest can be dated at 293 Ma (Cumming and Krstic 1992). Thus, the composition of the uranium minerals observed in the ore zone today reflects the result of water-rock interaction over a period of millions of years. The composition of the uraninites is characterized by: a) $^{234}U/^{238}U$ and $^{230}Th/^{234}U$ activity ratios ranging between 0.98 and 1.00, and between 1.05 and 1.11 respectively (Cramer et al. 1993), b) high contents of radiogenic Pb (Janeczek and Ewing 1993; Cumming and Krstic 1992), and c) relatively high contents of ^{129}I and ^{239}Pu from naturally occurring nuclear reactions (Curtis et al. 1993). These three characteristics suggest both good retention of the isotopes in the natural-UO_2 matrix, and congruent dissolution of the matrix, at least over a period of 10^6 a.

The redox conditions of current water-rock interaction in the mineralized zones at Cigar Lake are controlled mainly by the Fe^{2+}/Fe^{3+} redox couple and are buffered by Fe-sulphides (pyrite/marcasite) and siderite (Cramer and Nesbitt 1993c). The corresponding measured redox-potentials of $< \sim 0.2$ V thus favour the solubility-controlled dissolution of UO_2, which is in agreement with calculated redox potentials of >0.2 V (also using pyrite and siderite) required for oxidative dissolution of UO_2 (Bruno and Casas 1993). This suggests that any radiolysis occurring in the Cigar Lake ore zone does not have a strong effect on the redox potential. In fact, calculations using SKB's current radiolysis models with a threshold redox-potential of 0.12 V for UO_2 dissolution show that the Cigar Lake ore should have been totally oxidised within 18 to 170 Ma. As this is not the case, and as recent development of SKB's radiolysis models suggests, the 0.12 V threshold potential appears to be unreasonably low, and the 0.2 V potential would allow a more realistic treatment of radiolysis effects. This is further supported by recent experimental work (Sunder et al. 1992) indicating that oxidative dissolution of UO_2 does not become important until the redox potential reaches values above -0.1 V versus SCE or +0.14 V versus NHE.

Model calculations for different radiolysis scenarios in the deposit were carried out (Christensen et al. 1993) to test a model for the formation of the red clay/ore contact (see #6 in Section 2). This model explained the red colouration (from precipitation of ferrihydrites) through scavenging of radiolysis-produced oxidants by dissolved Fe^{2+} in the ore-zone waters (Cramer 1986). Although the calculations confirm that products from α-radiolysis of water can oxidise dissolved Fe^{2+} to Fe^{3+}, it is uncertain whether the ferrihydrites (and hematite) in the clay/ore contact can be accounted for by this process. In fact, the initial model scenario, based on α-radiolysis, had to be revised to also consider γ-radiolysis when it was observed that most of the uranium ore is encapsulated inside the clay matrix of the ore zone. The alternate scenario includes groundwaters being subjected primarily to γ-radiation inside the more permeable, and more common, water-bearing horizons or fractures instead of the water having large areas of direct contact with the ore minerals as required for significant α-radiolysis.

The conclusions of the radiolysis modelling are that the effects of α- and/or γ-radiolysis are insufficient to cause significant oxidation of the UO_2, even when integrated over the lifetime of the deposit (Christensen et al. 1993). This is supported by the observations, mentioned earlier, that major dissolution and mobilization of uranium occurred since the ore was formed during distinct events in which the system underwent major perturbations. However, the extent of radiolysis taking place in the steady-state system of the ore zone is still an open question, and what causes the red oxidized clay/ore contact is also unresolved at this time. The established importance of dissolved Fe^{2+} as a fast oxidant-scavenger, combined with the measured high concentrations of dissolved H_2 in groundwaters from the ore zone (Cramer and Nesbitt 1993b), suggest that, if radiolysis takes place locally and only on a minor scale, the natural system of clay and ferrous minerals can buffer the redox potential to maintain reducing conditions to well within the stability field of UO_2.

Therefore, the net changes resulting from radiolysis are probably overestimated considerably in SKB's current PA models based on radiolytic oxidation of UO_2 fuel waste.

6.4. Mass-transport modelling

One of the objectives for the detailed litho- and hydro-geochemical studies on the Cigar Lake deposit was to identify the occurrence and location of radionuclide migration from the mineralized zones. However, no evidence was found from studies of the ore-clay-altered sandstone sequence of significant radionuclide-migration taking place, neither currently nor during the recent ~ 1-Ma history of the deposit. In contrast, active radionuclide migration may occur at shallower depths as the result of lateral groundwater flow through the limonitic and bleached sandstones (see Figures 2 and 4). To test this hypothesis, uranium-series data (Smellie et al. 1993) for rock samples from potential transport paths (i.e. fractures and obviously permeable horizons) in the ore, clay and altered sandstone units were obtained. The uranium-series data indicate that some mobilization of uranium, and possibly radium, has taken place, but only on a small, localized scale (i.e. both preferential removal and deposition of isotopes occur side by side). This is supported by the isotopic composition of the reducing groundwaters (from the permeable zones) in these rock units (Cramer and Nesbitt 1993a), where high $^{234}U/^{238}U$ values likely result from α-recoil rather than from dissolution processes. Furthermore, the amounts of dissolved uranium and other radionuclides in groundwaters from either side of the clay zone can be compared to give concentration gradients across the clay zone that are positive, zero and negative. Thus, the general conclusion with regard to radionuclide migration at Cigar Lake is that any modelling of mass transport in the deposit must be considered as being only hypothetical.

Although mass transport is included in current PA-codes (e.g. SKB), there were no specific mass-transport models available that could be directly tested in the Cigar Lake analog study. Therefore, a series of iterative, generic models had to be developed for potential mass-transport scenarios in the Cigar Lake deposit (Liu et al. 1993). These generic models are based on the assumption that any potential radionuclide migration takes place from the ore zone through the clay zone to the aquifer in the altered sandstone (i.e. a positive concentration gradient accross the clay zone). The models that were developed consider a range of scenarios for the source term and transport processes, including solubility-controlled and oxidative dissolution of UO_2, diffusion and advection, and coupling of mass-transport and geochemical processes. The results from this generic modelling include the following general conclusions:

- The extent of a uranium plume breaking through the clay/altered sandstone interface would not exceed 0.5 m into the altered sandstone;
- The one-dimensional modelling results in a good agreement for most measured parameters;
- At the dissolved-O_2 levels measured in the ore zone waters, the modelling predicts that oxidation of the clay/ore contact over a distance of 1 m is reasonable; and
- The low-permeability clay zone surrounding the mineralization is <u>the</u> most important parameter in limiting radionuclide mass transport.

7. General conclusions

The analog studies on the Cigar Lake uranium deposit have provided valuable information and insight on a number of performance assessment aspects common to the disposal concepts in both Canada and Sweden. The important general conclusions can be summarized as follows:

1- UO_2 dissolution and stability:
  - long-term thermodynamic stability under reducing conditions;
  - little dissolution achievable during 10^8 a; and
  - congruent dissolution controlled by surface alteration.

2- Clay sealing:
  - clay (in this case illite) can provide effective, long-term sealing;
  - long-term stability of illite; and
  - clay is an efficient barrier to radionuclide and colloid migration.

3- Colloids:
  - colloid and particle contents in groundwater are generally lowest in competent rock and highest in friable rock;
  - only a small fraction of radionuclides in water is attached to colloids;
  - colloids can be effectively sealed in by clay-rich rocks; and
  - colloids were not important in radionuclide migration at Cigar Lake, at least on a time scale of 10^4 a.

4- Organics and Microbes:
  - low humic-contents in dilute water are unlikely to play significant role in either speciation or mobilization of radionuclides;
  - microbes can survive in radiation fields, and they can mediate in redox control and buffering; and
  - organics and microbes are unlikely to adversely affect radionuclide migration in the near field.

5- Groundwater chemistry:
  - interactions with clay minerals control the bulk composition of groundwater;
  - redox geochemistry is strongly controlled and buffered by the iron redox couple; and
  - the evolution of groundwater compositions can be predicted by existing geochemical codes.

6- Radiolysis:
  - radiolytic-oxidation models for UO_2 dissolution appear overly conservative in SKB's current PA code; and
  - dissolved Fe^{2+} is an important scavenger of radiolytic oxidants.

7- Radionuclide migration:
  - natural hydrologic barriers and appropriate geochemical conditions in a relatively open, natural system are effective in limiting radionuclide migration over any significant distance; and
  - clay sealing is an important barrier to radionuclide migration.

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References

BRUNETON, P. 1985. Petrographic, mettalogenic and geochemical study of the Cigar Lake mineralized zones, Volume 1. COGEMA Canada Ltd. Internal Rep., 8479-8529.

BRUNETON, P. 1986. Geology of the Cigar Lake uranium deposit (Saskatchewan, Canada). In: Economic Minerals of Saskatchewan. Eds: C.F. Gilboy and L.W. Vigrass. Sask. Geol. Soc. Spec. Publ., **8**, 99-119.

BRUNO, J., CROSS, J.E., EIKENBERG, J., McKINLEY, I.G., READ, D. SANDINO, A. and SELLIN, P. 1990. Testing of geochemical models in the Poços de Caldas analogue study. Svensk Kärnbränslehåntering AB Tech. Rep., **TR 90-20**.

BRUNO, J. and CASAS, I. 1993. Testing of spent fuel dissolution codes. In: Final report of the AECL/SKB Cigar Lake analog study. Eds: J.J. Cramer and J.A.T. Smellie. AECL/SKB Rep., **AECL-10851** (in preparation.

CASAS, I. and BRUNO, J. 1993. Testing of solubility and speciation codes for trace elements. In: Final report of the AECL/SKB Cigar Lake analog study. Eds: J.J. Cramer and J.A.T. Smellie. AECL/SKB Rep., **AECL-10851** (in preparation).

CHRISTENSEN, H., SMELLIE, J.A.T. and CRAMER, J.J. 1993. Model calculations of α- and γ-radiolysis in the Cigar Lake ore zone. In: Final report of the AECL/SKB Cigar Lake analog study. Eds: J.J. Cramer and J.A.T. Smellie. AECL/SKB Rep., **AECL-10851** (in preparation).

CRAMER, J.J. 1986. A natural analog for a fuel waste disposal vault. In: 2nd International Conference on Radioactive Waste Management, Winnipeg, Sept. 1986. Can. Nucl. Soc. Proc., 697-702.

CRAMER, J.J. 1988. Natural analog studies on the Cigar Lake uranium deposit: an update. In: Proc. 3rd CEC/NAWG meeting, Snowbird, Utah, June 1988. Com. Eur. Commun. Rep., **EUR 11725-EN**, 50-56.

CRAMER, J.J. 1993. Natural analogs in support of the canadian concept for nuclear fuel waste disposal. Atomic Energy of Canada Ltd. Rep., **AECL-10291**, 109p.

CRAMER, J.J. and NESBITT, H.W. 1993a. Hydrogeochemistry of the Cigar Lake uranium deposit: hydrologic and isotopic constraints. In preparation.

CRAMER, J.J. and NESBITT, H.W. 1993b. Hydrogeochemistry of the Cigar Lake uranium deposit: groundwater evolution. In preparation.

CRAMER, J.J. and NESBITT, H.W. 1993c. Hydrogeochemistry of the Cigar Lake uranium deposit: redox geochemistry. In preparation.

CRAMER, J.J. and SMELLIE, J.A.T. 1993. Final report of the AECL/SKB Cigar Lake analog study. AECL/SKB Rep., **AECL-10851** (in preparation).

CRAMER, J.J., TAYLOR, P. and SUNDER, S. 1993. Characterization of Cigar Lake ore minerals. In: Final report of the AECL/SKB Cigar Lake analog study. Eds: J.J. Cramer and J.A.T. Smellie. AECL/SKB Rep., **AECL-10851** (in preparation).

CRAMER, J.J., VILKS, P. and LAROCQUE, J.P.A. 1987. Near-field analog features from the Cigar Lake uranium deposit. In: Natural Analogues in Radioactive Waste Disposal. Eds: B. Côme and N.A. Chapman. Com. Europ. Commun. Rep., **EUR 11037-EN**, 59-72.

CROSS, J.E. and EWART, F.T. 1990. HATCHES - A thermodynamic database and management system. Radiochim. Acta, **52/53**, 421-422.

CUMMING, G.L. and KRSTIC, D. 1992. The age of unconformity-related uranium mineralization in the Athabasca Basin, northern Saskatchewan. Can. J. Earth Sci., **29**, 1623-1639.

CURTIS, D.B., FABRYKA-MARTIN, J., ROENSCH, F., AGUILAR, R. and ATTREP, M. 1993. Radionuclide retention in the Cigar Lake spent fuel analogue. In: Final report of the AECL/SKB Cigar Lake analog study. Eds: J.J. Cramer and J.A.T. Smellie. AECL/SKB Rep., **AECL-10851** (in preparation).

FOUQUES, J.P., FOWLER, M., KNIPPING, H.D. and SCHIMANN, K. 1986. The Cigar Lake uranium deposit: Discovery and general characteristics. In: Uranium deposits of Canada. Ed: E.L. Evans. Can. Inst. Min. Metall. Spec. Vol., **33**, 218-229.

GARISTO, N.C. and GARISTO, F. 1986. The dissolution of UO_2: a thermodynamic approach. Nucl. Chem. Waste Manag., **6**, 203-211.

GOODWIN, B.W., CRAMER, J.J. and McCONNELL, D.B. 1989. The Cigar Lake uranium deposit: An analogue for nuclear fuel waste diposal. In: Natural Analogues in Performance Assessment for the Disposal of Long Lived Radioactive Wastes. Int. Atom. Ener. Agency Tech. Rep., **304**, App. B, 37-45.

HOEVE, J. and QUIRT, D. 1984. Mineralization and host rock alteration in relation to clay mineral diagenesis and evolution of the Middle-Proterozoic, Athabasca Basin, northern Saskatchewan, Canada. Sask. Res. Council Tech. Rep., **187**, 187p.

JANECZEK, J. and EWING, R.C. 1993. Uraninite from Cigar Lake: drill cores 220 and FH-18. In: Final report of the AECL/SKB Cigar Lake analog study. Eds: J.J. Cramer and J.A.T. Smellie. AECL/SKB Rep., **AECL-10851** (in preparation).

JOHNSON, L.H., D.W. SHOESMITH, D.M. LENEVEU, N.C. GARISTO, D.W. OSCARSON, M.N. GRAY and R.J. LEMIRE. 1993. The Vault Model for postclosure assessment for disposal of Canada's nuclear fuel wastes. Atomic Energy of Canada Ltd. Rep., **AECL-10714**, in preparation.

LIU, J., NERETNIEKS, I.E. and YU, J. 1993. Modelling of potential radionuclide migration in the Cigar Lake deposit. In: Final report of the AECL/SKB Cigar Lake analog study. Eds: J.J. Cramer and J.A.T. Smellie. AECL/SKB Rep., **AECL-10851** (in preparation).

PARKHURST, D.L., THORSTENSON, D.C. and PLUMMER, L.N. 1980. PHREEQE - a computer program for geochemical calculations. U.S. Geol. Surv. Water-Resour. Invest., **80-96** (revised 1985), 193p.

PERCIVAL, J.B. 1990. Clay mineralogy, geochemistry and partitioning of uranium within the alteration halo of the Cigar Lake uranium deposit, Saskatchewan, Canada. Carleton Univ., Ottawa, Canada. PhD Thesis, 343p.

PETTERSON, C., ALLARD, B., EPHRAIM, J. and VILKS, P. 1993. Humic substances in groundwaters from the Cigar Lake area. In: Final report of the AECL/SKB Cigar Lake analog study. Eds: J.J. Cramer and J.A.T. Smellie. AECL/SKB Rep., **AECL-10851** (in preparation).

PUIGDOMÈNECH, I. and BRUNO, J. 1991. Plutonium solubilities. Svensk Kärnbränslehåntering AB Tech. Rep., **TR 91-04**.

SHOESMITH, D.W. and SUNDER, S. 1991. An electrochemistry-based model for the dissolution of UO_2. Atomic Energy of Canada Ltd. Report, **AECL-10488**.

SIBBALD, T.I.I., QUIRT, D.H. and GRACIE, A.J. 1990. Uranium deposits of the Athabasca Basin, Saskatchewan. Geol. Surv. Can. Open File, **2166**, 56p.

SKB 1992. Final disposal of spent nuclear fuel. SKB-91. Importance of bedrock for safety. Swedish Nuclear Fuel Waste Management Co., SKB Tech. Rep., **TR 92-20**.

SMELLIE, J.A.T., CRAMER, J.J. and MACKENZIE, G. 1993. The Cigar Lake uranium deposit: geochemical and isotopic features of the host sandstones and clay halo. In: Final report of the AECL/SKB Cigar Lake analog study. Eds: J.J. Cramer and J.A.T. Smellie. AECL/SKB Rep., **AECL-10851** (in preparation).

STROES-GASCOYNE, S., FRANCIS, A.J. and VILKS, P. 1993. Microbial research on the Cigar Lake uranium deposit. In: Final report of the AECL/SKB Cigar Lake analog study. Eds: J.J. Cramer and J.A.T. Smellie. AECL/SKB Rep., **AECL-10851** (in preparation).

SUNDER, S., TAYLOR, P. and CRAMER, J.J. 1988. XPS and XRD studies of uranium rich minerals from Cigar Lake, Saskatchewan. In: Proc. 11th Symp. Scientific Basis for Nuclear Waste Management. Mater. Res. Soc. Proc., **112**, 465-472.

SUNDER, S., CRAMER, J.J. and MILLER, N.H. 1992. X-Ray Photo-electron Spectroscopic study of uranium minerals from the Cigar Lake uranium deposit. In: Proc. 15th Symp. Scientific Basis for Nuclear Waste Management. Mater. Res. Soc. Proc., **257**, 449-457.

SUNDER, S., SHOESMITH, D.W., MILLER, N.H. and WALLACE, G.J. 1992. Determination of criteria for selecting a UO_2 fuel dissolution model for nuclear fuel waste management concept assessment. In: Proc. 15th Symp. Scientific Basis for Nuclear Waste Management. Mater. Res. Soc. Proc., **257**, 345-352.

VILKS, P. and BACHINSKI, D.B. 1993a. Colloid studies. In: Final report of the AECL/SKB Cigar Lake analog study. Eds: J.J. Cramer and J.A.T. Smellie. AECL/SKB Rep., **AECL-10851** (in preparation).

VILKS, P. and BACHINSKI, D.B. 1993b. Total organic carbon and other organics. In: Final report of the AECL/SKB Cigar Lake analog study. Eds: J.J. Cramer and J.A.T. Smellie. AECL/SKB Rep., **AECL-10851** (in preparation).

VILKS, P., CRAMER, J.J., BACHINSKI, D.B., DOERN, D.C. and MILLER, H.G. 1993. Studies of colloids and suspended particles in the Cigar Lake uranium deposit. Accepted for publication in Applied Geochemistry.

VILKS, P., CRAMER, J.J., SHEWCHUK, T.A. and LAROCQUE, J.P.A. 1988. Colloid and particulate matter studies in the Cigar Lake natural-analog program. Radiochimica Acta **44/45**, 305-310.

WINBERG, A. and STEVENSON, D. 1993. Compilation of hydrogeological data and 2D and 3D conceptualisation and 2D modelling of the groundwater flow conditions in and around the Cigar Lake uranium deposit. In: Final report of the AECL/SKB Cigar Lake analog study. Eds: J.J. Cramer and J.A.T. Smellie. AECL/SKB Rep., **AECL-10851** (in preparation).

OKLO AS A NATURAL ANALOGUE FOR RADIONUCLIDE TRANSFER PROCESSES IN A WASTE GEOLOGICAL REPOSITORY: PRESENT STATUS OF THE PROGRAM

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The uranium ore body in Oklo has now been for twenty years a unique scientific subject, and still is: fission reactions occurred there spontaneously two billion years ago, and provide us with opportunities for the study of natural analogy with deep radioactive waste disposal, specially radionuclides mass transfer processes to the surface.

The initial scientific program on Oklo ("Franceville project") dealt mainly with the reality of the phenomenon and the study of the natural reactors. The present radioactive waste analogy program was re-initiated in mid-1988 and has been co-funded by the CEC since 1991.

The responsibility for the coordination of this program was vested in the IPSN, though individuals or teams belonging to other directorates in the CEA are involved.

Access to the program was also offered to other nuclear agencies, mainly SKB (Sweden), ONTARIO-HYDRO and AECL (Canada), and more generally to research establishments interested, such as the universities of Tokyo (Japan), of Arizona and of New-Mexico (U.S.A.).

The tasks have been subdivided into several different categories:

1°- *IN SITU* OBSERVATION AND SAMPLING, both for solid rock and for hydrology, have to be done in close collaboration with the mining company (C.O.M.U.F., COmpagnie des Mines d' Uranium de Franceville, Mounana, Gabon).

2°- STUDY AND CHARACTERIZATION OF THE SOURCE TERM (mostly in CEA laboratories) rely heavily on the results obtained by the "Franceville project", but adjustments have to be done to take into account the differences between the shallow (when discovered) reactor zones 1 to 6 (plus 7-9), now mined out, and the deeper ones, still open.

3°- STUDIES ON THE GEOCHEMICAL SYSTEMS RULING THE MIGRATIONS can be split into studies on ancient migrations, reconstructed from solid state geochemistry, *versus* recent-to-present migrations (hydrology and hydrogeochemistry). Both imply collaboration between CEA laboratories and other institutions: CREGU (Centre de REcherches sur la Géologie des matières premières minérales et énergétiques, formerly "de l'Uranium", Nancy), Centre de Géochimie de la Surface (CNRS, Strasbourg), and Ecole Nationale Supérieure des Mines de Paris (ENSMP, Centre de Géologie Générale et Minière & Centre d'Informatique Géologique, Fontainebleau).

4°- **MODELLING** will in part take place in each laboratory involved, but the final coupling of models will be the responsibility of IPSN and ENSMP.

1. Field survey and sampling

1.1 Preliminary

In April, 1989, a conservatory mission took place, in order to avoid the loss of valuable, and as yet undeciphered, scientific information, as the mining company was working out depleted uranium, for which they had a market at the time, from reactor zones discovered after the climax of the Franceville project, and thus unsufficiently sampled.

During that mission, wall face surveys and sampling have been conducted in forewinning drifts D73S in reactor zone 10 and SD37 in reactor zone 13. Small diameter cores were taken from reactor zone 10 (for a length of 23.03 m) and from reactor zone 13 (8.59 m).

Furthermore, an additional coring program in reactor zone 10 was defined, to be carried out, in larger diameter, by the exploration team of the mining company. This was done during summer and fall the same year (cores SF82 to SF85, overall 90 m approx.).

1.2 Routine

From september 1989 on, we have kept in Oklo a standing mission, *i.e.* a post-M.Sc. student has been appointed each year to follow the progress of the mining works, do the necessary surveys and some sampling, and advise us on the need and best periods for more specialised field missions or for orders of heavier work from the COMUF company.

Because of the shrinking market for depleted uranium, the year 1990 did not bring much on the reactor zones, despite the thoroughness with which the drifting works in the Okélobondo area have been followed.

On the other hand, 1991 was marked by two important achievements:

the OK84bis reactor zone has been sampled by new boreholes: DF15 to DF 17 (each about 20 m long) in small diameter, of which two (DF 16 & 17) actually crossed the R.Z. and SF 94 & 95 in larger diameter, of which only SF 95 reached the R.Z

reactor zone 16 was casually discovered, in an area where exploration boreholes had previously missed all clues to the presence of a reactor zone, and has been sampled, both on wall-face and by eight small diameter cores (PX 1 to 8, averaging 5m in length).

The year 1992 has already provided us with a good opportunity to sample the lower levels and closure of reactor zone 10, as a circulation drift had been mined in this direction (D81). A heavy hydrology campain, initially planned for this summer, is actually taking place at this very moment.

1.3 The reactor zones

From 1972 to 1991, 16 numbers have been allocated to reactor zones in the Oklo mine, but some numbers (11, 12, 14) appear to be void. More reactor zones, which have not been reached yet by the works, but are known by exploratory coring, are designated by their borehole number, in the Okelobondo area, close to the south-east of Oklo. An isolated one is known below the Bangombé plateau, close to the Moanda manganese deposit, about 20 kilometers from Oklo.

Reactors numbered 1 to 9 and 15 have been mined out. There is at present no specific mining of the remaining reactor zones. The present accessibility of the reactor zones remains thus as follows:

-. Reactor zone 10 is situated in the center of the bearing, 70 to 80 m north of the Dolerite dyke, downhill from the quarry, between the 120 and 150 m elevations (slices D65 to D81). It has been estimated to about 300 tons of depleted uranium, of which 40 % have already been taken. As a circulation drift has recently been mined in the direction of the lower levels (D81), it has been possible to observe and sample the lower closure of this reactor zone.

-. Reactor zone 13 was also situated downhill from the quarry, but about 35 m to the south of the Dolerite dyke, at an elevation of 230 to 218 m. Very little of this reactor zone, if any at all, may remain at level SD38.

-. Reactor zone 16 was discovered in may 1991, at level D75N, i.e. at mid-level of reactor zone n°10, but about 150 m to the north. No indication of the presence of a reactor zone was known there before. As drift D75N is intended for ventilation, we can expect an easy access to the zone for some time.

-. The "OK 84" reactor zone lies 500 m to the south-east of the quarry, at an elevation of about 60 m. Several drifts come close to it, but none did actually cut through it up to now.

-. The "Bangombé" (rather than "Bagombé") reactor zone is located a few kilometers to the south-east of the town of Moanda, itself 20 kilometers south of Mounana and the Oklo deposit.

2. The source term

The work undertaken with the Ionic Probe since 1989 bear on zone 10 and Zone 13.

The U/Pb ratios have made it possible to confirm the two important dates in the history of the bearings: 1970 Mega-annum (Ma) for the fission reactions (zone 10) and 750 Ma for the major lead mobility episode, probably linked to the emplacement of the dolerite dykes.

The age of the fission reaction also allows to recalculate the $^{235}U/^{238}U$ ratio at the time: this was 3.68%, five times the present value.

2.1 Reactor zone 10

The reactor-core facies boundaries have been accurately drawn, thanks to measurements done on numerous wall-face and borehole samples. The reactor zone spreads from level 144 above (slice D65) to level 118 downslope (slice D82). Upslope, the observed depletion remain rather moderate, with $^{235}U/^{238}U$ ratios from 0.670 to 0.725 % (atom %). Lower down more important depletions are observed, with 0.562 % in core SF84 and 0.46 % at level 91.65 in core SF29,an exploratory borehole the study of which had already begun before the present program.

2.2 Other zones

Reactor zone 13 shows several peculiar features:

it is an uraninite layer, from 20 to 30 cm thick, about 5 m wide and only 12 m from top to bottom, which rests directly on the sandstones, with the only intercalation of a very thin bed of black clay and organic matter. The richest uraniferous layer reaches a density of 7, with a peak depletion ratio ($^{235}U/^{238}U$) of 0.382% and an overall average of 0.46 % !

Despite a similar facies, zone 16 does not seem to quite reach the same depletion in Uranium-235 ($^{235}U/^{238}U$= 0.65%).

New UF_6 isotopic measurements done on samples from old exploratory boreholes in Bangombé have reconfirmed the presence of a reactor zone there (BA145, 11.60 m: $^{235}U/^{238}U$= 0.6552; BA145 bis ,11.20 m: $^{235}U/^{238}U$= 0.6983 in atoms %).

3. The geochemical systems

3.1 Petrographical facies

The petrographical and mineralogical facies of the deep reactors zones are similar to those of the earlier-discovered ones (1 to 9), apart from a few specific features, which can be interpreted as related to the lack of supergene weathering

The rocks surrouding the reactor zones are sandstones. They are made up of quartz, some biotite grains, less feldspar and few accessory minerals (zircon, uranium oxides, titanium oxides, organic matter). The claey fraction is made of ferrous chlorite and illite, and calcite is present as fissure infillings.

The reactor-clay facies shows areas of cryptocristalline magnesian chlorite, with a few corroded quartz grains. Secondary minerals (coffinite, zircon? uraniferous titanides) develop from primary accessory minerals. Apatite may also be met. By comparison to reactor zones 1 to 9, kaolinite remains less than scarce in the deep reactors, as it has been observed in only one borehole above zone 10.

In the reactor-facies, the main mineral phases are uranium oxide and white micas.

3.2 Retention by clays

The study of the retention of fission products by phyllosilicate minerals has progressed when enriched uranium has been evidenced in the acid leaching residue of a clay sample from the roof of reactor zone 10.

The uranium linked to the cristalline lattice of the chlorite is enriched ($^{235}U/^{238}U = 0.01051$), while the uranium extracted with the soluble fraction, which was only adsorbed on the surface of the clay particles, is depleted ($^{235}U/^{238}U = 0.00681$).

Plutonium-239 created during the fission reaction was mobilized by the contemporary reducing fluids. It was then trapped by the crystallisation of the chlorite and decayed on the spot to Uranium-235, thus causing the observed enrichment. The half-life of ^{239}Pu (24400 years) gives an estimate of the maximum time elapsed between the nuclear reaction and the chlorite crystallisation.

3.3 Reconstruction of ancient fluids

The study of trace elements contents in hydrothermal minerals in the vicinity of the reactor zones has been undertaken, with the aim of using these elements as tracers of the fluids which were circulated in the bearings. The analyses are done mainly by neutron activation.

The minerals studied are sulphides (pyrite and galena), in order to observe chalcophilous fission products. A simultaneous examination of the contents in arsenic, antimony, cobalt, nickel, molybdenum and silver shows that the samples gather into well-defined clusters. This can be explained in different ways:

- either it shows the evolution of an initial fluid, which undergoes differentiation through interaction with the surrounding rocks: but the monotonous surrounding sandstones argue against this interpretation;
- or it shows the circulations of different fluids in the sandstones and fissures, most probably also at different times in the history of the bearings.

3.4 Thermal history of the fluid circulations

Preliminary microthermal analysis of fluid inclusions have been conducted on samples from FA sandstones and quartz veins in Okélobondo, and from the sandstones to reactor clay contact in Oklo reactor 10.

In the sandstones and quartz veins, the size of the fluid inclusions ranges from 3 to 10 µm, with melting temperature from -1 to -6°C, indicating salinities from .1 to 7.8 % NaCL weight equivalent, and homogeneization temperatures of 160 to 200°C.

The fluid inclusions, in the silica overgrowth of quartz grains from the contact between sandstone and reactor clay in zone 10, reach homogeneization temperatures of 280 to 480°C, with melting temperatures from -6 to -10°C, indicating salinities of 9 to 14% NaCl weight equivalent.

4. Modelling the present mass-transfer

We hope to follow directly the water circulations responsible for the transfer of elements,and to characterize the geochemical system which rules these transfers, by identifying natural tracers of the reactor zones in the environment.

The first stage of this task has been the compiling of an hydrogeological synthesis, taking into account all the available information on:

- the morphological and topographical frame,
- the geological frame, including the general structure, the stratigraphy, the rock fracturation and geometry of the levels with a potential hydraulic role,
- the hydrological frame, including the meteorology, the runoff, the position of the water occurrences in boreholes or in the underground works,
- the hydrochemical frame, with an inventory of all the analyses done to-date.

These data have made it possible to propose a diagramatic hydrogeological section, and to launch a preliminary hydrodynamic modelling.

A drilling campain was initially planed for this summer, which also happens to be the dry season in Gabon. Due to some combination of circumstances, we are late, and this campain is now under way. We will then proceed with the sampling and hydrochemical and isotopical analyses of the waters, in order to identify an active geochemical system involving some reactor zones end products, and do in situ tests and measurements to obtain the quantitative information necessary to the validation of the hydrogeological diagramatic model proposed.

5. Conclusions

Such an overview does not quite do justice to the efforts of the participants. Some results have had to be neglected at this stage, because they will need a broader synthesis: let us, for an example, mention the fact that the CNRS team in Strasbourg did not restrict themselves to the dating of the occurrence of the nuclear reactions, but extended their scope to the history of the Franceville basin as a whole: it is not irrelevant.

We are now confident that the solid rock part of the program is well on its way, but our attention and efforts must now go to the hydrology part of the program, both in Oklo-Okélobondo (because the largest wealth of rock-geochemistry data was obtained there) but also in the Bangombé area, because this is where we have the highest chance of observing present-day leaching of a reactor zone.

EL BERROCAL PROJECT
CHARACTERISATION AND VALIDATION OF NATURAL RADIONUCLIDE MIGRATION PROCESSES UNDER REAL CONDITIONS IN A FISSURED GRANITIC ENVIRONMENT

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Introduction

The general aim of the international El Berrocal Project is to understand and model the migration processes controlling the distribution of naturally occurring radionuclides in a fractured granitic environment, using an approach that fully integrates the geochemical, structural and hydrogeological features of the site. The current phase of the Project was initiated on 1st March 1991 and is scheduled to run for two years. This two-year phase forms the first part of an intended four-year programme of work to be carried out collaboratively and with the financial participation of the Commission of the European Communities DG XII (Project FI2W0080), by five European organisations:

. Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas (referred to here as CIEMAT), Madrid, Spain.

. Centro Internacional de Métodos Numéricos en Ingeniería, Universidad Politécnica de Cataluña, Departamento de Ingeniería del Terreno (referred to here as CIMNE), Barcelona, Spain.

. Commissariat à L'Energie Atomique, Institut de Protection et de Sûreté Nucléaire (CEA/IPSN), Cadarache, France

. AEA Technology Isotope Geoscience Section, Harwell, United Kingdom.

. British Geological Survey, Fluid Processes Research Group (BGS), Keyworth, United Kingdom.

The project is being co-ordinated by the Empresa Nacional de Residuos Radiactivos, S.A. (ENRESA), Madrid, Spain, who have contracted Intera Information Technologies (INTERA), Melton Mowbray, United Kingdom, to provide support with the overall scientific management of the Project.

In addition, the Joint Research Centre of the Commission of the European Communities, based in Ispar, Italy (JRC/CEC-Ispra), is co-operating scientifically with the Project participants.

This first phase (1991-1993) of the Project was preceeded by a smaller-scale two-year (1989-1990) joint project (CEC Contract n° FIW280), primarily involving ENRESA, CIEMAT, JRC/CEC-Ispra and CEA/IPSN. Results of this earlier work, summarised in references [1-2], indicated the potential of the site for a study of this type.

1. Background, objectives and organisations

1.1 The site

The experimental site of "El Berrocal" is located 92 Km to the southwest of Madrid, near the village of Nombela (Toledo), in the southeastern part of the Sierra de Gredos, Central Mountain System. The El Berrocal granite is of late Hercynian age, and has intruded through the older granodiorities which are the dominant rock in this area (Fig. 1)

The 22 km^2 granitic intrusion contains a uranium-rich quartz dyke that was extensively mined some 30 years ago. The main access gallery has a lenght of about 70 m and intersects the quartz dyke at 46 m.

In the Preliminary study (1988-1990), two 60-m-deep boreholes were drilled in the gallery at distances of 13 m (borehole S1) and 20 m (borehole S7) from the quartz dyke, and a 30-m-long subhorizontal borehole (S2) was drilled at the end of the gallery (Figure 2). Seven further shallow boreholes were drilled in the gallery (S3-S6, S8-S10) and two deeper boreholes (AT-1, AT-2) 150 m to the south of the gallery.

1.2 Main objectives and activities

Phase 1 of the project consists of a set of closely inter-related tasks designed:

- To characterise the geology, geochemistry and hydrogeochemistry of the site of depths of 200-250 m,
- to develop a three-dimensional groundwater flow and radionuclide transport code, and
- to make preliminary predictions of the hydrogeological and hydrochemical behaviour of the site, with a view toward the planning of Phase 2 investigations, and the validation of concepts and models developed in Phase 1.

Phase 2 is designed as a logical continuation of Phase 1, with the aim of building up a comprehensive three-dimensional picture of the hydrogeological and hydrochemical behaviour of the site.

The five Phase 1 tasks include:

- Characterisation of the physical environment at the site, through surface and borehole studies,
- characterisation of the geochemical environment at the site, through hydrogeochemical sampling in boreholes, groundwater colloidal phase sampling and characterisation, uranium series disequilibrium studies, and chemical characterisation of fracture-filling material,
- radionuclide migration studies, involving analysis of the distribution of natural series radionuclides in the field, laboratory tests of radionuclide mobilisation and retardation processes, and in situ migration experiments,

- characterisation of the hydrogeological environment at the site, through assessment of borehole conditions, hydraulic testing of local groundwater heads and transmissivities, crosshole interference tests and refinement of groundwater flow models, and

- preliminary modelling of groundwater flow and radionuclide transport at the site, including development and testing of appropriate computer codes, an initial analysis of uncertainties caused by spatial heterogeneity, an initial analysis of flow and transport in a single fracture zone, and development of a conceptual model(s) for the El Berrocal site, for the purpose of developing validation tests in Phase 2 of the Project.

2. Summary of works accomplished

During the first 18 months of the project, the work was focussed on surface based site characterisation (geophysical, geological and geochemical mapping), geochemical and migration studies in the previous boreholes in the gallery; drilling, logging an instrumentation of the new boreholes for hydrogeochemical, hydrogeological and migration field data and lab adquisition.

2.1 Drilling and geophysical activities

At the start of Phase 1, it was planned to drill a group of 5 boreholes up to 250 m in depth at predetermined locations. According to the preliminary data obtained for these boreholes, two further boreholes have been drilled using a percusion technique. In addition one of the phase 1 boreholes (n° 16) was successfully deepened using full coring at a depth of more than 600 m for phase 2 of the project. All of these boreholes have been drilled vertically with the exceptions of boreholes 13 and 15, which were inclined at 30° and 20° respectively, so as to intersect the mineralised zone beneath the gallery.

All the boreholes (except 17) were fully logged using downhole geophysical equipment and, in addition, a televiewer system was used to provide detailed information on fracture orientations. Additional geophysical studies were performed in borehole 17 by CEA/IPSN. In parallel combined helicopter borne magnetic, electromagnetic a VLF survey and surface gravimetric methods was applied to obtain regional structural data.

All data obtained are under interpretation. A compilation of the first results have bee used to stablish the main fractures zones associated to the groundwater flow, considering the core data analysis.

2.2 Core analysis: lithology, fracture distribution and fissure filling

During the drilling activities the borehole core obtained was studied in a field office by CIEMAT people. The fractures and the mineral distribution was studied in relation with the depth. Number of fractures, petrological description of the rock matrix, and alteration products (magnesium a iron oxides and hydroxides, sericite, moscovite, chlorite, quartz, sulphure, carbonates, kaolinites, clay, uranium minerals, etc.) are described for each borehole. The main characteristics observed are:

- The lithology of the core boreholes is similar than that two mica granite of the gallery (alkaline feldspar granite with dominant muscovite). The iron oxides are found as fractured filling and impregnating the rock in the higher part of the core (depths lower than 60 m). The carbonates appear as diaclase filling at depths higher than 60 m, but the amount is very variable. The chloritization is located in zones with quartz dykes, calcite and in certain zones with numerous subvertical fractures. The clay filling appears in some fractures, in all breccia zones to bre related to important water flow zones. The mineralized quartz dyke has been crossed by boreholes 13, 15 and the root zone of the mineralized quartz dyke has been crossed by borehole n° 16.

According to the core observation and the geophysical profiles, the more interesting and characteristic cores boreholes fracture zones were selected and storaged for detailed studies.

2.3 Lithostructural studies

To regional scale 8 fracture families have been stablished related with the hercinian and alpine movements. At the local scale, three main fractures named F1, F3 and F4 divide the are in four morphotectonic blocks.

The mineralogy of the fissural filling are related with the fracture family, but more precise date are under consideration. The more important structural fracture on the Berrocal site is the fracture F-1 (N70-75W) denominated Berrocal Fissure. The uranium dyke is associated at this fissure. A 3-D structural preliminary model has been constructed (Fig. 2).

Field works and microscopic and chemical analysis studies from sampled collection from otucrops, El Berrocal uranium mine gallery, and core boreholes have been used for this geological characterisation.

To regional scale four granitic facies have been differenced: the porphyritic biotitic San Vicente type granite, the leucogranites, the quartz dikes and the Berrocal granites. In the Berrocal granites can be distinguished: pegmoapilites (under study) and the two mica granite, muscovite predominating over biotite. Two mica granite is the main facies of el Berrocal pluton. It can be classified as an alkaline feldspar, highly evolved, SiO_2-rich, peraluminous,hypocalcic granite, with an evolutive tendency from a potassic to a more sodic end. The granite is enriched in incompatible elements, including Li, F and Sn, with a K/Rb ration ranging between 80 and 89 like pegmatites, and $U/Th > 2$, like in U fertile granites, most of the U being held in uraninite.

The three facies that constitutes El Berrocal, two mica granite, pegmoapilite and leucogranite pluton seem to have been originated by differentiation from a peraluminic, hypocalcic, alkaline magma. The aplitic dyke is later than the San Vicente-type granite and earlier than "El Berrocal" pluton (Fig. 3).

The two mica "El Berrocal" granite is the only facies fertile in U found until now. This element is mostly held as uraninite.

The "El Berrocal" pluton is affected by a set of post-hercynican fractures, the most developed being: N70-75W, N75-80°E, N60°E, N35°E and N145-150°E. Fractures N100-110°E and N75-80°E are mineralized by the hydrothermal quartz lodes.

2.4 Geochemical characterisation

Groundwater hydrogeochemistry

To perform the groundwater characterisation the "Geochemical Transport Working Group" (GTWG) of the Berrocal Project, decided to stablish a set of Referenced Zones for groundwater sampling, colloidal studies and fissured filling characterisation and radionuclide distribution. These reference zones were stablished according to the study of the number of open and close fractures, nature of fracture filling, geophysical parameters as resistivity in cores: 13, 14, 15 and 17 and the compiled data of the hydraulic conductivity carried out by BGS staff in 13, 14 and 15 were the most important hydraulic fractures (higher permeability) were selected.

Prior to sampling analysis of new boreholes, the pre-existing boreholes were sampled and analyzed to groundwater and colloid to obtain information of the geochemical processes between the surface to 60 m depth.

TABLE 1

HYDRAULIC FRACTURE DEPTH (m). REFERENCE ZONES OF THE GROUNDWATER SAMPLING IN EL BERROCAL BOREHOLES

BOREHOLE 13		BOREHOLE 14	BOREHOLE 15	BOREHOLE 16
A	43.14-43.64	33.5-36.4	19.14-20.41	65.4-65.7
B	45.11-50.55	-	29.9-30.0	91-92
C	67.97-68.01	74.5-74.7	36.9-37.1	166-167
D		94.6-95.1	38.3-38.8	229-236
E		106.8-107.05	109.3-110.1	279-280
F		120.7-121.6	110.4-111.3	334-335
G		129.0-130.0	112.4-112.6	386-387
H		-	126.6-129.6	442.09
I		215.8-216.5		446.0
J		219.1-219.4		460-480
K		235.8-236.0		525-532
L		238.3-238.4		550-555
M				586-594

All samples will be collected, with equipment supplied by BGS, by CIEMAT staff. In order to avoid the organic contamination from the downhole packers and the sampling lines, the packers, in contact with the isolated zone, will be coated with spray teflon. The pump rates will be the least as possible ones, in order to avoid the leakage through the fractures.

Before sampling the groundwater it is necessary to establish whether the groundwater is in equilibrium or not. Every selectd zone needs to be pumped several times controling the concentration of the tracer (Br^- and I^-). When this concentration arrive to the background level of the zone, the sample will be representative. Some measurements will be made in the field in a closed line flow through cell flushed with an inert gas to avoid chemical changes in the sample. These parameters include pH, two measures of Eh, temperature, electric conductivity and dissolved oxygen. Groundwater samples will be filtered by an in line cartrigde filter 0.45 microns prior to all the measurements. A groundwater sampling and in situ analysis protocol has been stablished by the GTWG.

Colloids Study

The colloidal studies are performed by CIEMAT and AEA-HARWELL.

Separation of suspended particles and colloids will be carried out by a 450 nm Millipore filter in a glove-box in order to prevent oxidation processes. Composition of particles retained in the filter will be made by X-ray diffraction (XRD). A direct characterisation of the nature of the colloids will be carried out by the study of membrane filters with SEM and EDAX.

The techniques used so far in this study to characterise particle size and number are photon correlation spectroscopy (PCS) and transmission electron microscopy (TEM).

Each concentrate will be separate in several aliquots in order to analyse major cations and trace elements (ICP-AAS), cations (IC), uranium by fluorimetry method and DOC by organic carbon analyser. Samples were prepared in AEA-HARWELL for electron microscopy analysis by a novel ultracentrifugation method.

The majority of particles are small being less than 100 nm in diameter. The total number of particles per litre is approximately 10^{10} to 10^{12}.

The data obtained for boreholes S-7 and S-2 indicate that the colloidal populations are relatively low (10^{12} particles per litre) and the size distribution is broad with a lot of large particles. The average particle diameter measured by this method is about 800 nm.

U and Th partition calculations indicate that more than 88% of total U and more than 92% of total Th are in true solution; there is virtually no loading of colloids in these boreholes.

The $^{234}U/^{238}U$ activity ratios for colloid, solution and particulate phases are similar (about 2 to 2.5) confirming that these phases are in chemical equilibrium with respect to U.

Natural Radionuclide distribution

According to the data obtained by CIEMAT the U in essential and accessory minerals represents 20.5% of the total U in El Berrocal granite, so the remaining 79.5% is shared between uraninite (≈ 63%) and labile U (≈ 16.5%). The latter comes from the oxidation of uraninite and the partial remobilization of U from the mineral.

The natural radionuclide migration/retention processes in the clayey materials, fractions $<60\mu m$ and $<2\mu m$, associated with the N100°-110°E fractures, in El Berrocal U mine, have been studied. These fractures are critical because the uranium mineralization dyke are with the same direction.

The neoformed clay minerals and accessory minerals and mineraloids play an important role in the retention, either by adsorption or precipitation, of the radioactive (U and Th), heavy elements (mainly P and organic C), released during the hydrothermal alteration of the granite and weathering of the sulfide and uraniferous mineralizations. The organic C could be due to present biological activity in the clays or to organic acids transported, from the topographic surface, by the percolating water. In this last cas, organic-clay complexes would probably be formed.

Among the natural radionuclides, U is precipitated as UO_2^{++} phosphates, mainly autunite and torbernite, as UO_2^{++} sulfates, like uranopilite, and adsorbed by the clay minerals and Fe, Al and Si gels. Th can be found in the minerals inherited from the granite and mainly absorbed by the clay minerals and/or precipitated as Th huydroxides and/or cryptocrystalline silicates.

Uranium series isotopic analysis of fractures infill materials

In order to establish the natural radionuclide distribution in the mineral phases of the fracture infill materials in the El Berrocal batholith a number of water-bearing horizons have been selected and core material from these sampled. The radiometric data base currently being set up should serve as the data base for planned rock/water interaction modelling at El Berrocal. These works have been performed by AEA-HARWELL with a colaboration of CIEMAT.

The fracture in-fill materials analysed so far indicate high uranium content ranging from 20 to 400 ppm. Thorium concentrations are typical of near surface crystalline rocks with a range of 5 to 15 ppm. The $^{234}U/^{238}U$ activity ratios greater than unity are indicative of recent uranium uptake from the fracture fluids by these fracture wall mineral assemblages. However, judging by the $^{230}Th/^{234}U$ activity ratios most of which are within 2σ uncertainty of unity, the observed uptake may have taken place on the timescales of many thousand of years allowing ^{230}Th to grow into secular equilibrium with its parent ^{234}U, or alternatively the U uptake has been slow allowing ^{230}Th daughter to maintain itself in secular radioactive equilibrium.

2.5 Hydrogeological characterisation

To characterise the natural radionuclide migration processes in the Berrocal pluton it is necessary to obtain a detailed information about the groundwater flow in the site.

To obtain the hydrogeological information several activities were accomplished:

- Develop a preliminary conceptual model for groundwater flow, to discuss the more suitable borehole situation.
- Design the hydrogeological program and the specific instrumentation for data adquisition, according with the objective of the projects, the characterisation of the site (previous data) and the founding availability.
- Develop the hydraulic testing program with a preliminary introduction of data obtained in the unreal groundwater flow code.

These activities were performed mainly by BGS with a very intensive field work during 1992, with the collaboration of CIMNE and CIEMAT.

Single borehole testing of boreholes S13, S14, S15, T1 and T2 has been performed using the straddle packer system designed for the site. Each borehole was tested using an 11 metre overlapping straddle interval. Great care was used to identify and eliminate leakage around packers. Zones with a significant transmissivity was re-tested using a shorter straddle interval, usually 3 meters, in an attempt to identify particular flowing features.

The preliminary hydrogeological modelling, undertaken by BGS, was done in two dimensions, using a section perpendicular to the hill, i.e., parallel to the access gallery to the mine, and a constant value of hydraulic conductivity (Fig. 3).

CIMNE and CIEMAT have also been contributing to the development of the conceptual model for groundwater flow at the site. For example, information from field observations and aerial photogeological interpretations have been used by CIMNE to provide the following contraints on the groundwater flow boundary conditions:

To the East, a strike-slip fault which forms the eastern valley and intersects the quartz dyke. To the south, the Tarica quartz dyke system. To the north the surface water divided and to the west an artificial boundary needs to be imposed because groundwater flow seems to be driven towards the west.

Preliminary conclusions from the BGS field-work suggest that the site comprises a series of poorly permeable blocks. A small amount of recharge is able to maintain steep hydraulic gradients in both the horizontal and vertical directions. The distribution of hydraulic conductivity is non-uniform, appearing higher in the upper 100 m than at depth, and higher within specific features, such as the main quartz dyke. Groundwater flow is generally from the top of the hill towards the bottom, with some groundwater being intercepted by the dyke, an extensive feature which, as noted above, drains water through the rock mass. Excavations in the dyke complicate the natural head conditions.

The head in the dyke at depth (where penetrated by borehole 15) is lower than in the gallery. This indicates that the dyke drains the mine, rather than the dyke carrying water to the mine. The outflow point of the dyke is unknown.

Boreholes connect transmissive zones (usually associated with faults or dykes), which tend to have different water levels and act as conduits, transporting groundwater from zones of high head to zones of low head. As the conductivity is generally low 10^{-9} m/s, flows from or into such zones are relatively small.

2.6 Groundwater flow and radionuclide transport modelling

These activities are performed by CIMNE. The specific objectives of these activities are:

> The modelling of the groundwater flow system at the site with the specific objectives of (a) developing a stochastic formulation for flow and transport in fractured media by superimposing a three-dimensional continuum on a two-dimensional medium (high-permeability fracture zones), and (b) implementing the formulation in a computer code (called TRANSIN-III) able to analyse real cases and, specifically, to apply this code to the site. The work has been organised into four tasks:
>
> 1. flow and solute transport inversion, 2. flow and transport through isolated fractures, 3. flow and transport through fracture networks, and 4. hydrogeology of the site, focussed on hydraulic test interpretation.

CIMNE has a preliminary version of TRANSIN-III running, and work is underway to improve the numerical algorithms employed. As more data from the site become available over the next six months, the preliminary hydrogeological conceptual models of the site will be refined in collaboration with BGS. In addition, the TRANSIN-II code will be fully documented and the TRANSIN-III code further refined.

The specific work in relation to task 4, was included in the preliminary modelling, in collaboration with BGS and CIEMAT presented before.

2.7 Migration experiments

In the Berrocal Project the activities in relation with the migration experiments include:

- Application of borehole tools
- Cross-hole migration test with conservative tracer
- Laboratory experiments on column migration

Borehole tools

The objective of these activities performed by CEA are to obtain the chemical parameter, in situ, in relation with the strategy to be used for geological barrier characterisation.

A substantial field campaign involving full-scale testing of a suite of novel downhole tools for site characterisation was undertaken by CEA/IPSN in borehole 17, and supporting laboratory analysis were inititated. The main tools tested in this period were AUTOLAB and CHROMATOLAB. AUTOLAB is capable of in situ measurements of chemical diffusion coefficients, and CHROMATOLAB provides a variety of in situ chemical analyses. Furthermore, in situ radar measurements were obtained toward the end of the reporting period.

In addition, other more standard downhole measurements in boreholes 14 and 17 were undertaken. In particular, Eh and pH data obtained indicate, inter alia that:

. 30-35 days were needed for the boreholes to re-equilibrate after the cessation of drilling, and

. at least two distinct groundwater exist, with the separation between the groundwater systems occurring at a depth of about 150 m in borehole 17 and a depth of about 120 m in borehole 14.

Cross-hole migration test

In the previous of works performed in the Berrocal site, a reference zone for in situ migration test was selected between the boreholes S-1 and S-7. A conductive fracture connects both boreholes..

A first crosshole tracer test was performed by JRC/CEC-Ispra in September-October 1991, using a conservative non-radioactive bromide tracer. Work in this period was aimed at further interpretation of the results obtained, and in formulating the conceptual design of a second in situ tracer test. Major shortcomings of the first test were that pumping from the withdrawal well was only possible in daytime hours, and taht the fracture geometry between the two holes was only partially understood. Steps have been taken to remedy these problems. In particular, it is planned that BGS undertakes a detailed hydrological characterisation of the two holes prior to the next racer test. In view of the problems experienced with the first test, it is currently considered that the second test will not make use of a non-conservative tracer. Rather, the test will bre repeated with the same bromide tracer, and control during the experiment will be greatly improved, for example by the introduction of double-packer systems in both boreholes.

Laboratory experiments

The objectives of the studies performed by CIEMAT is to compare the field and laboratory data in relation with the uranium migration.

The work to be performed in the lab included the design and characterisation of granit column, using Berrocal granite, column migration experiments, development under different conditions, and modelling, in collaboration with CIMNE, the data obtained.

Two granitic columns have been selected from core borehole 17. These two columns included a longitudinal fracture, and will be used to study migration of ^{75}Se, ^{137}Cs, ^{60}Co and ^{233}U, in the fracture and in the altered rock adjacent to the fracture.

In addition, initial sorption-desorption studies using the same isotopes have begun in batch experiment on crushed fresh granite and fractured in filling material from the site.

Bibliography

[1] Migration Radionuclides on Fissured Granitic Environment 1989-90 (Preliminary Draft), CIEMAT, 1991 - Madrid.

[2] Laboratory and in situ Determination of the Migration Processes of Actinide Complexes and Colloids in a Fissured Granitic Environment (Contract FI1W0230-E-(E1) Annual Progress Report December 1988-December 1989. ENRESA, 1991 - Madrid.

[3] El Berrocal Project Co-ordinating Committee Minutes of the Third Meeting (Jerez de la Frontera, 17th - 18th October 1991) (EB-INTERA-(91)9). INTERA, 1991 Melton Mowbray

[4] El Berrocal Project Co-ordinating Committee Minutes of the Fourth Meeting (Santa Cruz de la Palma, 28th - 29th January 1992) (EB-INTERA-(92)2). INTERA, 1992, Melton Mowbray.

[5] L. Pérez del Villar, B. de la Cruz, J. Pardillo and J.S. Cózar, (1991). An approach to the calculation of U (Th) mineralogical distribution in the fresh granite from "El Berrocal" pluton (Toledo, Province, Spain). El Berrocal Project Topical Report (EB-CIEMAT-(91)26) CIEMAT - Madrid.

[6] El Berrocal Project Quality Assurance Requirements (EB-INTERA-(91)10). INTERA, 1991, Melton Mowbray.

[7] "El Berrocal Project" Phase 1. First Six-Monthly Progress Report. 1-3-91 to 31-8-91 ENRESA, 1991

[8] "El Berrocal Project" Phase 1. Second Six-Monthly Progress Report. 1-9-91 to 29-2-92 ENRESA, 1992

[9] "El Berrocal Project" Phase 1. Third Six-Monthly Progress Report. 1-3-91 to 31-8-92. ENRESA, 1991

[10] L. Pérez del Villar, B. de la Cruz, J. Cózar, J. Pardillo, P. Gómez, Mª Jesús Turrero (1992). Characterisation of clayey materials associated with N100-110E

fractures in El Berrocal site (Gredos, Spain). Genesis and U, Th and other elements retention capacity. El Berrocal Project Topical Report (EB-CIEMAT-(92)-34)

[11] L. Pérez del Villar, J. Pardillo (1992) "Lithological map of the Berrocal site". El Berrocal project Topical report (EB-CIEMAT ()2)-46(I)

FIGURES

FIGURE 1: Regional geology (a) and detailed lithostructural map (b)

FIGURE 2: 3-D structural block (a) and detail of the gallery zone

FIGURE 3: Preliminary modelling: a) heads and water table, (b) particle pahtlines (c) groundwater flow rates.

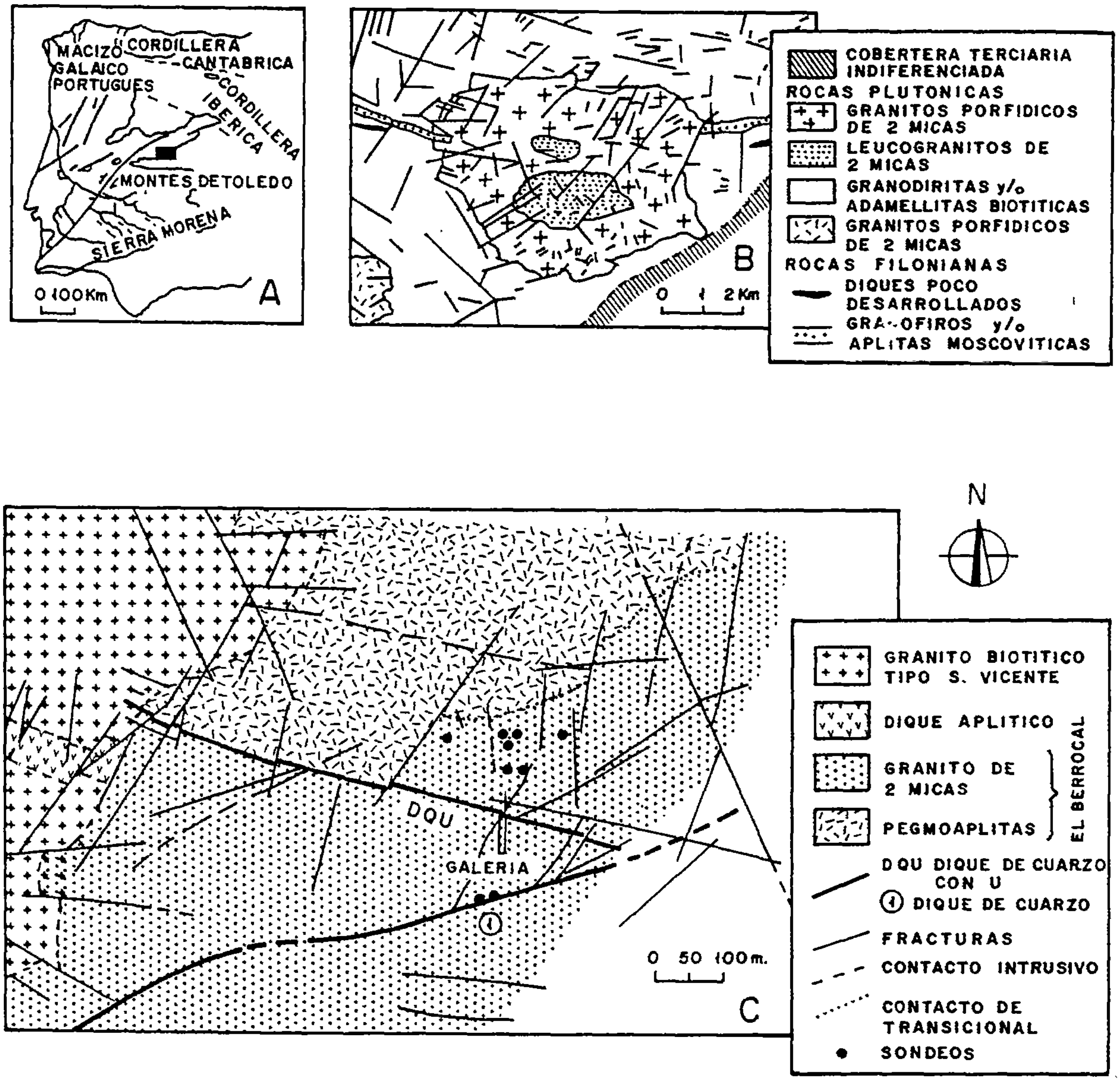


FIGURE 1A) Geological situation map, B) Geological Scheme of the Berrocal plutonium (Julivert et al., 1974 and Varea & Iglesias, 1989) C) Lithological Map of the Berrocal Experimental Station area (Pérez del Villar & Pardillo, 1992)

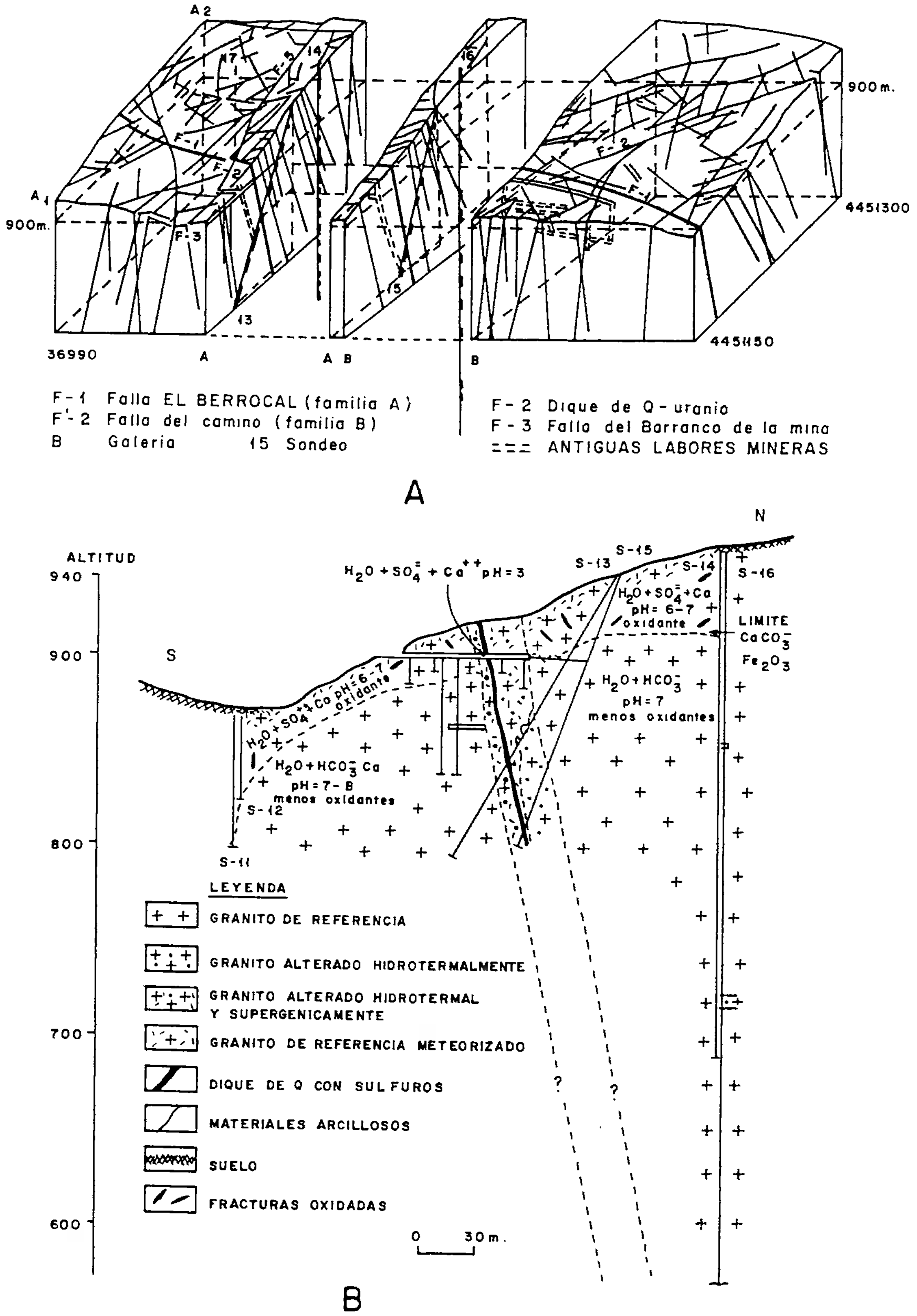
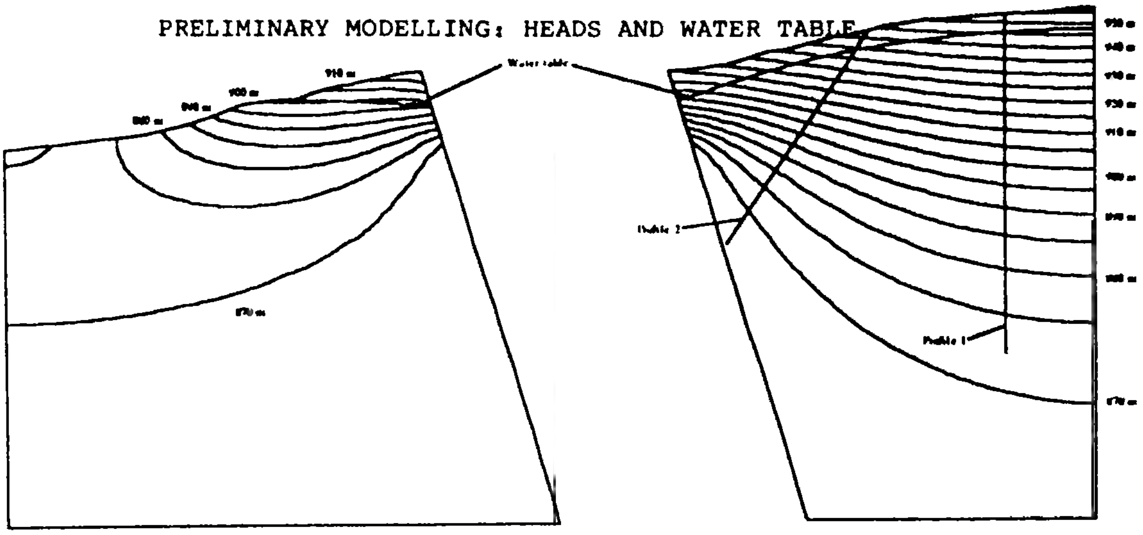


FIGURE 2A) Diagram block of the Berrocal zone (Marín, 1993) B) Lithogeochemical Scheme of the Berrocal Station (Pérez del Villar et al., 1993)

Berrocal section: heads and water table.

FIGURE 3a)

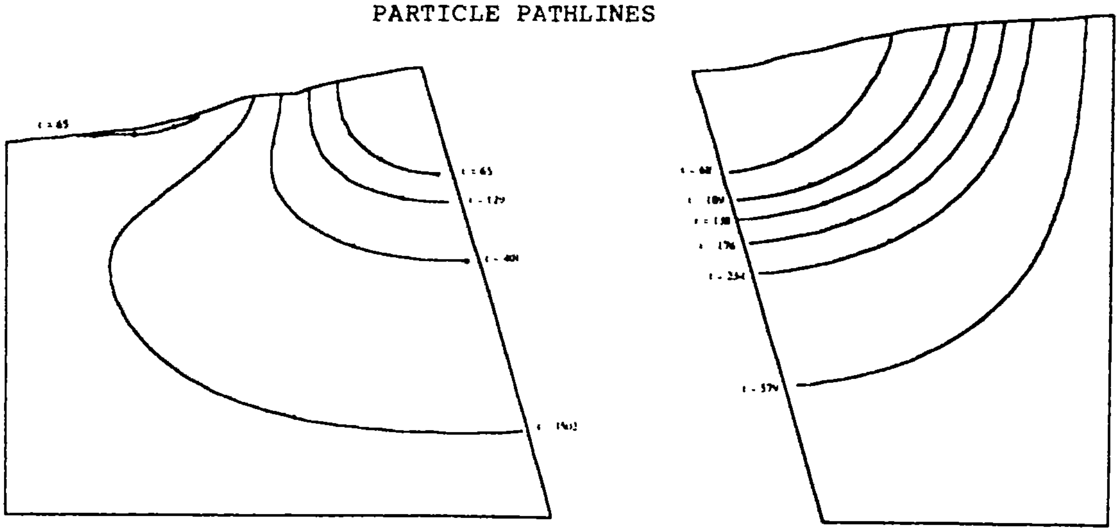
PRELIMINARY MODELLING: HEADS AND WATER TABLE



Berrocal section: Particle pathlines.

FIGURE 3b)

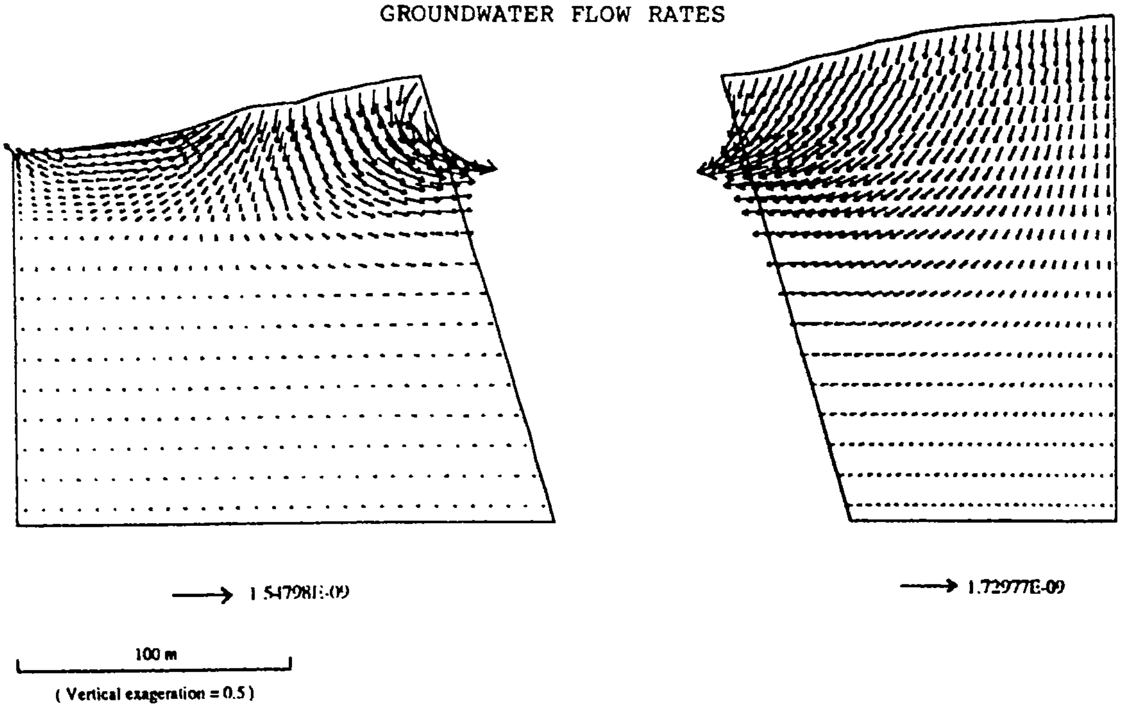
PARTICLE PATHLINES



Berrocal section: Groundwater flow rates.

FIGURE 3c)

GROUNDWATER FLOW RATES



NATURAL ANALOGUE STUDIES OF THE TONO URANIUM DEPOSIT IN JAPAN

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Summary

This paper presents an overview of natural analogue related studies in the Tono uranium deposit, Japan, which can be considered a result of natural nuclides migration. The studies were carried out with observations and experiments in order to reveal the processes of natural nuclide migration. This combination of observations and experiments is considered to be helpful for the development of a basic conceptual model on nuclide migration in the geosphere.

1. Introduction

The Tono uranium deposit, located in central Japan, is hosted by Tertiary sedimentary rocks (Figure 1). The uranium mineralization occurs as a stratiform body approximately 130 meters below ground surface. The advantages of this deposit for analogue studies include its relatively undisturbed nature (not commercially excavated) and infrastructure (accessible shaft and gallery), which provide favorable conditions to investigate the behavior of natural uranium-series nuclides in an undisturbed geological environment.

The uranium is considered to have been leached from the basement granitic rocks, and then transported by groundwater, and deposited in the sedimentary rocks. Therefore, the Tono uranium deposit can be considered to be a result of the natural migration of nuclides. Preliminary work consisting of the combination of observations and experiments was carried out in order to reveal the underlying processes.

2. Outline of geology

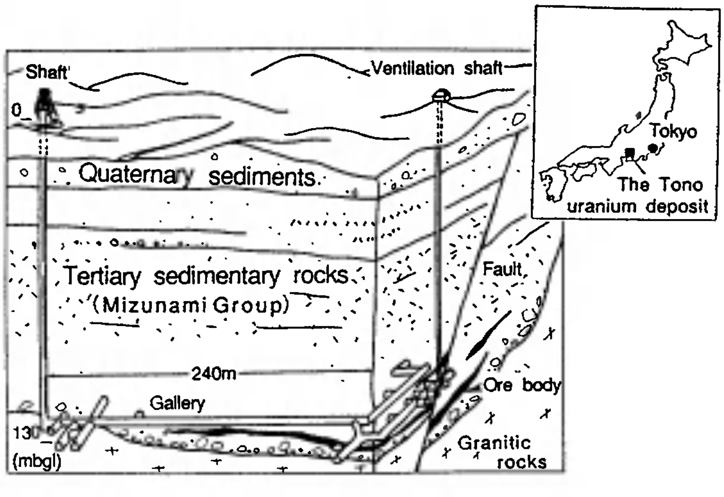


Figure 1. Conceptual view of the Tono uranium deposit.

The Tono area is lithologically divided into three parts: the Cretaceous basement granitic rocks (60Ma-100Ma), Tertiary sedimentary rocks and unconsolidated Quaternary sediments (Figure 1). The Tertiary sedimentary rocks are called the Mizunami Group (20Ma-15Ma). The lower part of the Mizunami Group consists of lacustrine or fluviatile sediments which are overlain by marine sediments of the upper part of the Mizunami Group. The uranium ore body is situated in the lower part of the Mizunami Group. The length of ore body is 3km and the width is 0.5km with thicknesses up to 10m [1,2].

3. Geological and geochemical observations

Geological and geochemical observations, of such things as chemistry of groundwater, occurrence of uranium, and uranium-series disequilibria have been carried out. The results obtained are as follows.

3.1 Chemistry of groundwater

The chemical composition of groundwater in the Mizunami Group collected from boreholes using a multiple packer system, varies from Na^+,Ca^{2+}-HCO_3^- enriched nearer the surface to Na^+-HCO_3^- enriched at depth. The pH value also changes from neutral to mildly alkaline with depth.

Detailed characteristics of groundwater were investigated in the ore zone. A sample was collected using a double packer system installed at the level of the ore body from a borehole which was drilled from the gallery. Concentration of major elements and uranium were determined from this sample. The physicochemical parameteres, such as pH , Eh and electric conductivity also have been measured in-situ by a monitoring system developed in-house. The characteristics of the groundwater are given in Table 1. Noteworthy characteristics of this sample are its strongly reducing (Eh=-300mV) and mildly alkaline (pH=9.2) nature. Na^+ and HCO_3^- are dominant and uranium content is lower than 1.0 ppb [3,4].

Table 1. Characteristics of groundwater in the ore zone.

Sampling point : -153~-155m (G.L.)
Temperature : 18.5℃
Eh : -300mV
pH : 9.2
DO* : 0.0ppb
EC** : 168 μS/cm

Ion	Concentration (ppm)	Ion	Concentration (ppm)
Si	8.1	Na^+	45
Al	<0.02	K^+	0.29
Fe^{2+}	<0.02	F^-	4.1
Fe^{3+}	<0.02	Cl^-	1.06
Mn^{2+}	<0.01	SO_4^{2-}	1.26
Mg^{2+}	0.02	HCO_3^{2-}	79
Ca^{2+}	1.98	CO_3^{2-}	8
U	0.15 (ppb)		

DO* : Dissolved Oxygen EC** : Electric conductivity

3.2 Occurrence of uranium

A microscopic study using alpha autoradiograph and EPMA has revealed that uranium is accumulated in the spaces between detrital grains such as quartz, feldspar and lithic fragments, and closely associated with pyrite, iron oxides and altered biotite. In particular, high concentrations of uranium, occurring as coffinite and pitchblendeare present associated with pyrite. However, almost no uranium was observed in the interstices lacking pyrite or other iron oxide minerals. These occurrences indicate that uranium concentrations and fixation processes have a close relationship with mineralogical phases controlling redox condition [5].

3.3 Natural uranium-series disequilibria

A study of the radioactive disequilibria of the rocks was carried out in order to examine the geochemical behaviour of natural uranium-series nuclides under reducing conditions. A total of 256 rock specimens were collected from 8 boreholes and a gallery in the uranium ore body zone. The activity ratios range between 1.2 and 0.8 for $^{234}U/^{238}U$ and $^{230}Th/^{234}U$ (Figure 2). The average values of these ratios are close to unity. Since isotopic data show relative radioactive equilibrium states, these results suggest that reducing conditions of the groundwater have been maintained for a long time, and that the uranium and thorium nuclides have not migrated significantly during the last one milion years. On the other hand, the activity ratio of $^{226}Ra/^{230}Th$ falls within a wide range from 0.3 to 5.1 (Figure 3). This result indicates that radium has been redistributed during the past several thousand years.

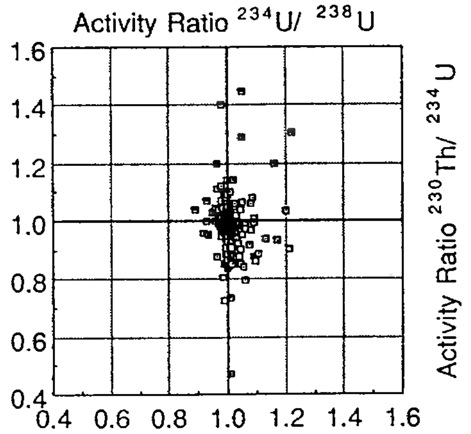


Figure 2. Activity ratio $^{234}U/^{238}U$ against $^{230}Th/^{234}U$ for 256 rock samples from the Tono uranium deposit.

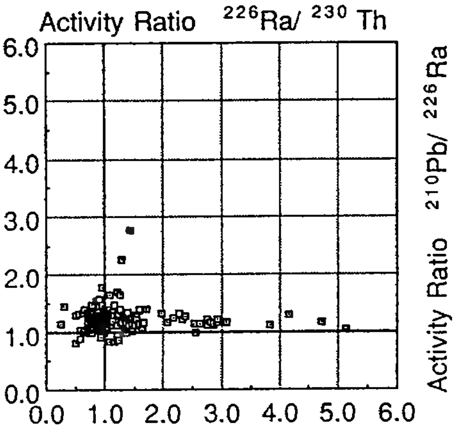


Figure 3. Activity ratio $^{226}Ra/^{230}Th$ against $^{220}Pb/^{226}Ra$ for 256 rock samples from the Tono uranium deposit.

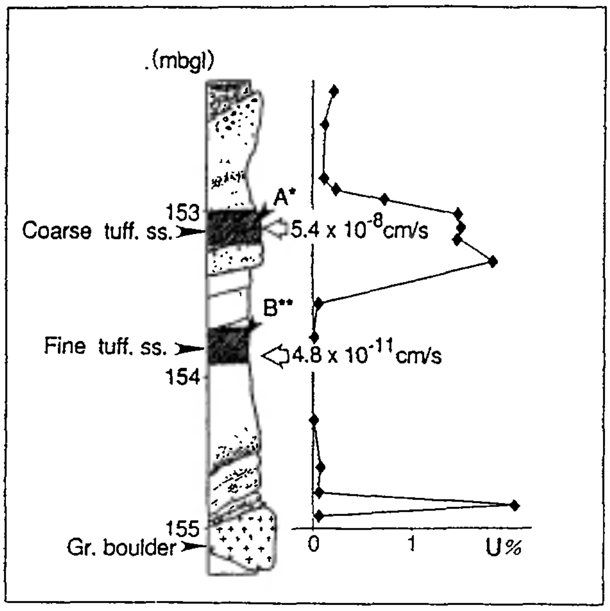
The depth profiles of uranium contents and activity ratios of $^{234}U/^{238}U$ and $^{230}Th/^{234}U$ on core specimens from a borehole were also obtained. This borehole was drilled from the gallery. These profiles show that some mineralized samples have low activity ratios of $^{230}Th/^{234}U$, although the activity ratio of $^{234}U/^{238}U$ is close to unity. This result indicates that uranium has been redistributed during the past several hundred thousand years but any removal of uranium must be occuring at a sufficiently rapid rate to prevent the development of $^{234}U/^{238}U$ disequilibrium. Such uranium redistribution can be recognized along the fault plane and along many fractures. This suggests that faulting is one of the pathways for the redistribution of uranium [6].

4. Experimental studies

The geosphere acts as a massive physical and chemical buffer for nuclide migration. Nuclide migration will be controlled by geometrical factors, such as path structure, and geochemical factors, such as sorption and desorption along the path ways. In order to identify the importance of these factors to nuclide migration, an impregnation experiment and a sorption experiment were carried out.

4.1 Impregnation experiment

An impregnation experiment using red colored resin was carried out in order to elucidate the influence of geometrical factors on nuclide migration in the sedimentary rocks. Two core specimens were examined in this experiment. Samples were collected from the high uranium concentration zone (HCZ) and the low uranium concentration zone (LCZ). The levels of both sampling points are adjacent in the tuffaceous sandstone within similar hydro-geochemical conditions. They are lithologically similar excluding the grain size. The hydraulic conductivity of the HCZ is higher than that of the LCZ by three orders of magnitude (Figure 4).



▨ Measurement point of hydraulic conductivity

☐ Sampling points for experiment

A*: Sample taken from the high U conc. zone (HCZ)

B**: Sample taken from the low U conc. zone (LCZ)

Figure 4. Geological background of rock sampling point for experiments.

The rock sample collected from the HCZ shows that impregnated pores and micro-fractures are present in the detrital grains such as quartz and biotite or in the spaces between these detrital grains. It suggests that such pores and micro-fractures in the HCZ are interconnected. EPMA and Cathodoluminescence studies of the rock sample collected from the HCZ show that uranium accummulation is coincidently observed along the impregnated pores and micro-fractures. On the other hand, resin could not be impregnated into the rock sample collected from the LCZ. This indicates that pores or micro-fractures in the LCZ have poor connectivity. The impregnation experiments imply that the pores and micro-fractures have functioned as a preferential path for natural uranium transport [7].

4.2 Batch sorption experiment

A batch sorption experiment using ^{233}U as a tracer was carried out in order to estimate sorption value which will assist in the interpretation of the chemical retardation and fixation capability (geochemical factor) of natural uranium in the sedimentary rock. The rock samples for this experiment were the same as were used to the impregnation experiment.

The results from this experiments are shown in Figure 5. It clearly shows that the sorption partition coefficients (Rd) of the sample collected from the LCZ is at least 40 times greater than that of the HCZ, although the Rd of the LCZ was not reached at saturation value. The low Rd of the HCZ shows that almost no retention capacity can be expected. This is probably due to the fact that the sorption sites are almost fully occupied by natural uranium. On the other hand, the Rd of the LCZ shows a similar chemical retention capability which can be explained as the original capacity in tuffaceous sandstone. However, uranium could not accummulate due to poor connectivity of pores and micro-fractures in the LCZ [5].

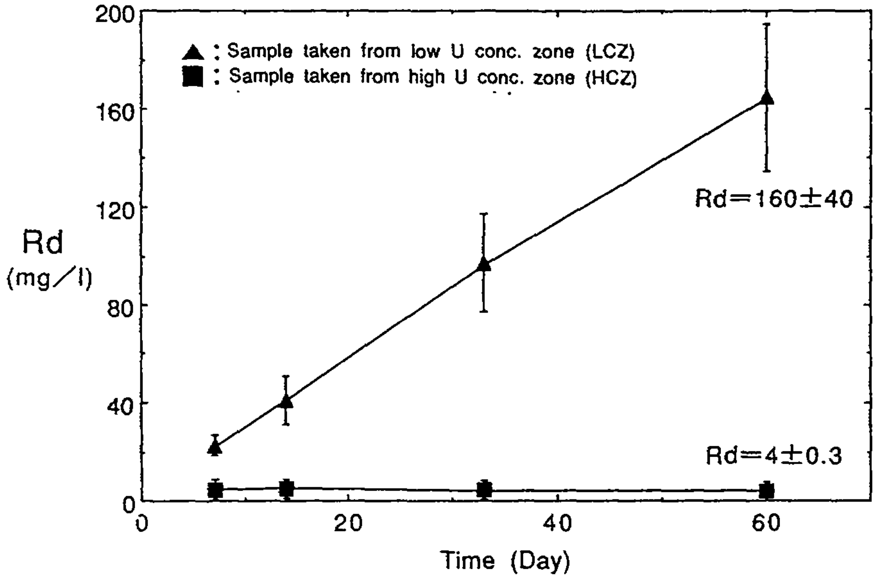


Figure 5. Sorption partition coefficients (Rd) time dependence on the rock samples.

5. Concluding remarks

The combination of observations and experiments discussed above shows that uranium concentrations are not simply controlled by geochemical retention capability but also by geometrical characteristics such as the connectivity of pores. The distribution of natural uranium in the samples studied confirms this observation.

Preliminary data from this work suggests that this approach is a helpful method to understand the elementary process on nuclide migration. This method will be further developed in order to increase confidence for a model of nuclide migration in the geosphere.

References

[1]Yamakawa, M. (1991) : Geochemical behavior of natural radionuclides in the geological formation. Proceedings of the 3rd International symposium on advanced nuclear energy research -Global environment and nuclear energy-, Mito(Japan), 13-15th March 1991, pp150-158.

[2]Hirose, K., Uchida, M. and Takeda, S. (1991) : Review of geological problems on radioactive waste isolation in Japan. Geological problems in radioactive waste isolation, A world wide review, Witherspoon (ed.), Earth sciences division Lawrence Berkeley laboratory, Univ. of California, pp93-101.

[3]Ochiai, Y., Yamakawa, M., Takeda, S. and Harashima, F. (1989) : A natural analogue study on Tono uranium deposit in Japan, CEC natural analogue working group 3rd meeting, Snowbird near Salt Lake City (USA), 15-17 June 1988, Final Report, pp.126-138.

[4]Seo, T., Ochiai, Y., Takeda, S. and Nakatsuka, N. (1989) : A natural analogue study on Tono sandstone-type uranium deposit in Japan. Proceedings of the 1989 joint international waste management conference, 22-28 Oct. 1989, Kyoto (Japan), Vol. 2, pp.353-358.

[5]Yoshida, H., Yui, M. and Shibtani, T. (1991) : A study of influence factor on uranium fixation in the Tono uranium deposit. PNC technical report, PNC TN7410 91-061.

[6]Nohara, T., Ochiai, Y., Seo, T. and Yoshida, H. (1992): Uranium-series disequilibrium studies in the Tono uranium deposit, Japan. Radiochimica Acta, (in press).

[7]Yoshida, H., Komuro, K., Yamamoto, M. and Ohtsuka, Y. (1992) : Influence of micro path structure on nuclides migration in sedimentary rocks. Abstracts of 29th International geological congress, 24 Aug.-3 Sept. 1992, Kyoto (Japan), Vol. 1, p.226.

UK HMIP NATURAL ANALOGUES PROJECT - IMPLICATIONS FOR PERFORMANCE ASSESSMENT

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ABSTRACT

Within the United Kingdom, Her Majesty's Inspectorate of Pollution (HMIP) funds an extensive programme of research in order to assess, independently, proposals made by UK Nirex Limited for underground disposal of radioactive waste. At present, these proposals relate to deep disposal of low- and intermediate-level wastes at Sellafield in Cumbria, England. Owing to the temporal and spatial scales involved, HMIP safety assessment procedures rely heavily on computer-based models [1], including those which simulate groundwater movement, contaminant transport and a range of other geological processes. These models are supported by corresponding laboratory and field programmes, in particular investigations centred around occurrences of high natural radioactivity. The HMIP natural analogue project focusses on a diversity of such geochemical systems in the UK and provides essential information on the adequacy of current models and enhances our understanding of the transport mechanisms which underpin performance assessment. This paper presents a brief summary of the research carried out at the UK natural analogue sites, and describes the lessons learnt from the different investigations and the various implications for performance assessment.

1. Introduction

In 1985 a reconnaissance was undertaken [2] to identify some UK locations where the migration of natural decay series radionuclides and elements analogous to radionuclides could be recognised and the governing proceses could be quantified using numerical models. Four accessible sites, all showing evidence of transport of uranium or other elements of interest in near-surface sediments, were deemed to merit more detailed research. Three of the sites are in Scotland (Broubster in Caithness, Loch Lomond and Needle's Eye on the Solway Firth coast); the other one is in Cornwall at the disused South Terras Uranium Mine (Fig.1). At the request of HMIP, a natural analogue co-ordinating group was convened (UKNACG) to oversee the necessary research at each site. The organisations involved and their respective roles were:

British Geological Survey (BGS)	Project management, site characterisation;
AEA Technology, Harwell (AEA)	Colloid sampling, U/Th series analysis;
Scottish Universities Research and Reactor Centre, East Kilbride (SURRC)	Loch Lomond sediment study, chemical and U/Th series analyses;
WS Atkins Science and Technology (Atkins S & T)	Model development, numerical analysis;

Under the CEC MIRAGE I programme, the Ecole des Mines de Paris (EMP), Fontainebleau, carried out some coupled chemical-transport modelling of the Needle's Eye site [3].

2. Natural analogues - role in performance assessment

Post-closure performance assessments of radioactive waste disposal in deep engineered repositories are characterised by the time-scales over which safety criteria have to be demonstrated, typically up to one million years into the future. In recognition of the inherent uncertainties involved in making predictions over such time-scales, HMIP has funded the development of probabilistic procedures in order to predict long-term evolution of the natural environment [1]. The current probabilistic risk assessment (pra) methodology employs Monte Carlo simulation to generate samples of possible "futures" using the TIME4 code [4] and then quantifies the effect of time-dependent environmental change on radiological risk using VANDAL [5]. The VANDAL model represents groundwater flow, radionuclide leaching, water-borne transport, dispersion in the biosphere and exposure pathways to people. TIME4 simulates surface hydrology and geomorphological processes that define the boundary conditions for the transport calculations.

More detailed deterministic models are used to support the necessarily simplified representations in VANDAL. Among these, thermodynamic models provide information on radionuclide leaching, solubility and the aqueous speciation pertaining for a given set of equilibrium conditions [6]. Structured procedures have been formulated for combining these models in a risk assessment framework (Fig.2) and have been implemented successfully, at least in trial simulations [1]. However, confidence in the results of such simulations can only be gained through observations on natural systems which have evolved over comparable time-scales.

Côme and Chapman [7] identify four areas in which "natural analogues" of radioactive waste disposal situations can contribute to the modelling process, by:

- allowing extrapolation of laboratory observations to larger spatial and temporal scales
- placing realistic bounds on parameter values to be used in modelling
- indicating the dominant mechanisms operating in groundwater systems similar to those envisaged for waste disposal
- representing the net effect of many complex processes operating over protracted lengths of time.

To these may be added the stimulus provided for more complete and realistic model development by feedback from studies of natural geological systems. The Broubster investigation is one such example [8].

A problem common to all natural analogue studies is how to relate them to a performance assessment (PA). One possible approach is to use an interaction matrix [9] as shown in Fig.3. The principal factors on the diagonal have different bearings on the PA and in turn the PA begs various questions of the principal factors, including the characteristics of the natural analogue study being investigated.

3. UK sites

The UK sites were chosen to pursue geochemical studies of the distributions of the uranium and thorium decay series radionuclides and other elements (e.g. iodine) in near-surface sediments and groundwaters. The different studies were designed to increase our understanding of the migration behaviour (processes, rates and distributions) of these radionuclides and elements in different sediment environments, and to improve our confidence in modelling uranium speciation and mass transport of different elements using PA-relevant computer codes (e.g. PHREEQE, CHEMTARD, NAMMU) and the CHEMVAL thermodynamic database. A review of the sites is given elsewhere [10].

There are different time and distance scales at each site. The Loch Lomond sediments consist of a marine band enriched in iodine and other halogen elements which are slowly moving into the pore water and then upwards by diffusion through the overlying lacustrine deposits. The layers are a few metres thick and the migration processes have been continuing for the last 5,400 years since the retreat of the sea. At Broubster the U anomaly in the peat has formed over the last 5,000 years or so representing the end result of mobilisation from mineralization present in the Devonian sandstone and subsequent groundwater transport over a distance of 100-200 m. The pitchblende veins in the cliff at Needle's Eye are being leached of U which is being carried by groundwater into the post-glacial flood plain sediments (<10, 000 years old) stretching for a distance of about 80m from the cliff to a tidal creek. The South Terras Uranium Mine was worked between 1873 and 1929, and the abandoned spoil heaps on the surface have been leaching U into the ground. This effect and the influence of the operations of the surface treatment plant used for extracting radium from the dump material between 1922 and 1925 has been the object of the South Terras study. All these time-scales are geologically very short, thus reducing uncertainties surrounding initial boundary conditions.

The Broubster investigation saw a successful interplay between modelling and experimental work [8]. Translocated uranium has been fixed and concentrated in post-glacial peat (Fig.4). It has been estimated on the basis of comparing U concentrations in the unweathered sandstone and the leached bedrock within the fault breccia zone that about 1000 kg of U has been lost, mainly to groundwater. The speciation of the soluble uranium has been modelled on the basis of U-fulvate complexation in the groundwater. The fulvic acid (MWt 1860) molecule is regarded as having a carboxylic and a phenolic site that can bind to the uranyl cation. If the mean concentration of U in the peat is about 400 ppm, the extent and thickness of the peat suggest that 600 kg of U are present in the peat anomaly. Assuming a constant groundwater flow rate of 10 m per year along the fault and a dissolved U load of 24 ppb (10^{-7} M), 60,000 years would have been required to accumulate the observed anomaly in the peat. Clearly, the flows must have been faster in the past and/or the supply of U was from other contributing sources covering a wider area.

4. Lessons learned

- Improved techniques for analysing halogens and U and Th in groundwaters have been developed e.g. SURRC now has a HPLC/ICPMS method for small (0.1ml) porewater samples containing I, Br [11].
- Filtration and alpha spectrometry techniques have shown that colloids can be important for Th but not for aqueous U uptake.
- Autoradiography, fission track registration, SEM and alpha spectrometry have proved to be a powerful combination for describing the distribution of alpha-emitters in sediment samples.
- The mobilisation or loss-rates of Th from mineralisation are much less than those for U e.g. U loss from the Needle's Eye pitchblende veins occurs at an estimated rate of 5×10^{-5} to 10^{-6} per year whereas the Th radionuclides are static [12].
- A first order loss-rate of about 2×10^{-7} per year has been estimated for iodine migration from the Loch Lomond marine band; it would take a further 2 million years to become 50% depleted [13].
- Organics can play a large role in U geochemistry and migration: low pH groundwaters can contain stable and mobile U-fulvic acid complexes; peat concentrates U by reversible complexation; plant roots create small-scale local environments where U-As-Cu minerals can form; biomineralization is a common occurrence in shallow sediments in the root-zone [14].
- Current codes have limited applicabilities; geochemical concepts are ahead of mathematical modelling.
- The K_D concept is inadequate for modelling U retardation.
- Successes in these studies were founded on the adoption of a multidisciplinary approach, the application of focussed laboratory and field research work and, wherever possible, by interacting modelling with experiments in an *iterative* way.

5. Implications for performance assessment

- It takes time to develop concepts, to establish the site-pertinent mechanisms and controls and to define the scales and ranges of influence of hydrogeology and particular geochemical processes.
- Accurate and comprehensive thermodynamic databases are a pre-requisite for modelling; gaps should be filled e.g. the inclusion of solubility product data etc. for some uranyl minerals in CHEMVAL.
- The project has provided a stimulus for the development of new mathematical models e.g. the incorporation of diffuse layer models into PHREEQE [15] and CHEMTARD

for describing U-organic acid complexation; the BGS code PHRQORGV is new and uses Falck's model and Model V of Tipping [16]; the DIAGEN program was designed for modelling halogen migration in an accumulating sediment [17].

- The project should provide a stimulus for new data e.g. parameters for surface complexation models involving U on silica and organic surfaces.

6. Recommendations

- Further applications of CHEMTARD, a coupled chemical transport code, are required for modelling migration of U at the Broubster and Needle's Eye sites.
- Mathematical modelling developments are required to catch up with geochemical concepts e.g. for co-precipitation.
- Measuring migration rates of U/Th series radionuclides in different hydrogeological environments is essential background knowledge.
- Transfers between the geosphere and biosphere could be studied in more detail, especially at Needle's Eye and Broubster where significant biomineralization has been observed.
- Quantifying uncertainties in different migration processes is an area that requires more work; this is especially important when predicting the effects of future climate changes.

7. Acknowledgements

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References

[1] Sumerling, T.J. & Thompson, B.G.J. 1992. Application of a probabilistic system-model based methodology for the performance assessment of deep underground disposal of nuclear wastes. Proc. IHLRWM Conf., Las Vegas, 1647-1657.
[2] Hooker, P.J., *et al.* 1987. Natural analogues of radionuclide migration: reconnaissance study of sites (May 1985-March 1986). UK Department of the Environment Report DOE/RW/87.098.
[3] Ledoux, E. *et al.* 1991. Hydrogeochemical modelling of the Needle's Eye, natural analogue (Scotland). In: Source, Transport and Deposition of Metals, M. Pagel and J.L. Leroy (eds.), Balkema, Rotterdam, 65-68.
[4] Ringrose, P.S., *et al.* 1990. Probabilistic simulation of the long term evolution of radioactive waste disposal sites. Proc. NEA/IAEA/CEC Symp. 'Safety Assessment of Radioactive Waste Repositories', Paris, 427-436.
[5] Laurens, J.M., *et al.* 1990. The development and application of an integrated radiological risk assessment procedure using time-dependent probabilistic risk analysis. Proc. NEA/IAEA/CEC Symp. 'Safety Assessment of Radioactive Waste Repositories', Paris, 627-635.
[6] Read, D., *et al.* 1987. A structured programme of research into the chemical aspects of radioactive waste disposal. Mat. Res. Soc. Symp. Proc., 94, 343-354.
[7] Côme, B. & Chapman, N.A. (Eds.) 1989. CEC Natural Analogue Working Group. Third Meeting Report. CEC EUR 11725EN.
[8] Read, D. *et al.* (in press). The migration of uranium into peat-rich soils at Broubster, Caithness, Scotland. Journal of Contaminant Hydrology.
[9] Hudson, J.A. 1989. Rock Mechanics Principles in Engineering Practice. CIRIA ground engineering report. Butterworths. 72pp.
[10] Hooker, P.J. 1991. An overview and assessment of the British Geological Survey's

research work on natural analogue studies in Great Britain. Radiochim. Acta 52/53, 341-347.

[11] MacKenzie, A.B. *et al.* 1989. Development of an analytical method for the analysis of I$^-$ and Br$^-$ ion concentrations in lacustrine sediment interstitial water. British Geological Survey Technical Report WE/89/65 and UK Department of the Environment Report DOE/RW/89.099.

[12] Scott, R.D. *et al.* 1991. Uranium transport and retardation at the Needle's Eye natural analogue site, southwest Scotland. Radiochim. Acta 52/53, 357-365.

[13] Falck, W.E. & Hooker, P.J. 1991. Quantitative interpretation of halogen porewater concentration profiles in lake sediments. Mat. Res. Soc. Symp. Proc. Vol. 212, 757-764.

[14] Milodowski, A.E. *et al.* 1990. Uranium-mineralized microorganisms associated with uraniferous hydrocarbons in southwest Scotland. Nature Vol.347, No.6292, 465-467.

[15] Falck, W.E. 1989. Two modified versions of the speciation code PHREEQE for modelling macromolecule-proton/cation interaction. BGS Technical Report WE/89/57.

[16] Tipping, E. and Hurley, M.A. (in press). A unifying model of cation binding by humic substances. Geochimica et Cosmochimica Acta.

[17] Falck, W.E. & Hooker, P.J. 1990. Quantitative interpretation of Cl, Br and I porewater concentration profiles in lake sediments of Loch Lomond, Scotland. BGS Technical Report WE/90/3 and UK Department of the Environment Report DOE/RW/90.030.

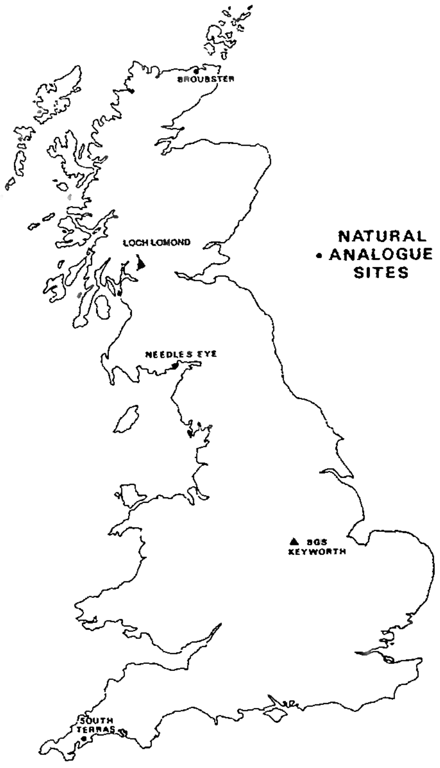

Figure 1. Natural analogue sites in the UK.

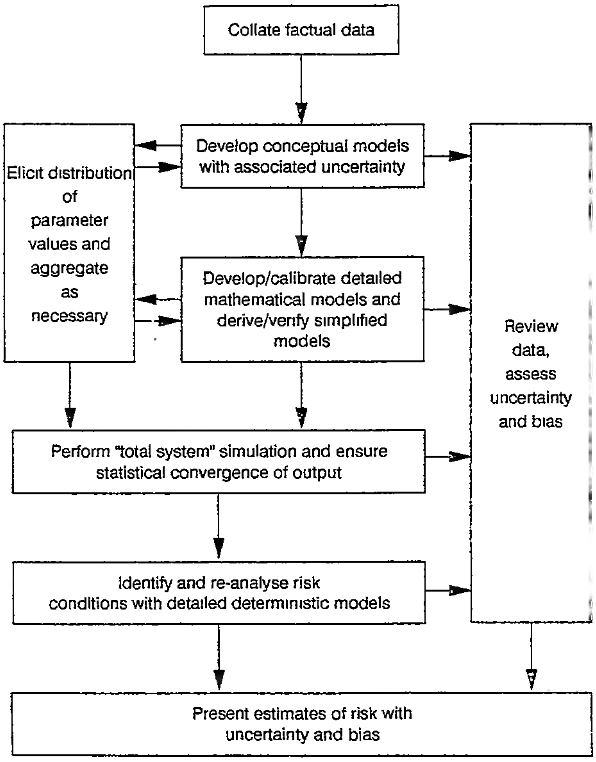

Figure 2. The HMIP assessment procedure.

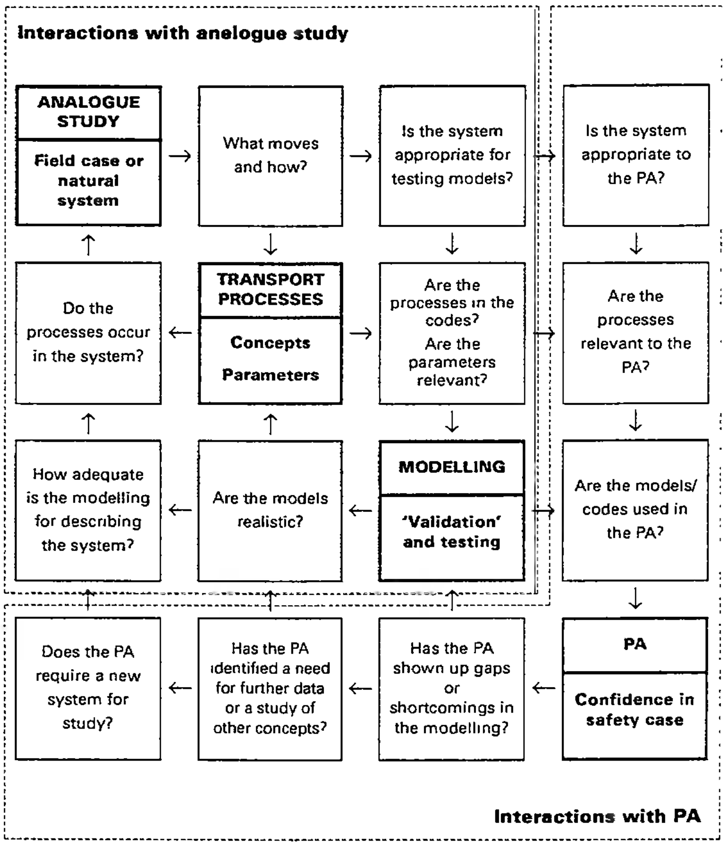

Figure 3. An interaction matrix of questions relating an analogue study to PA.

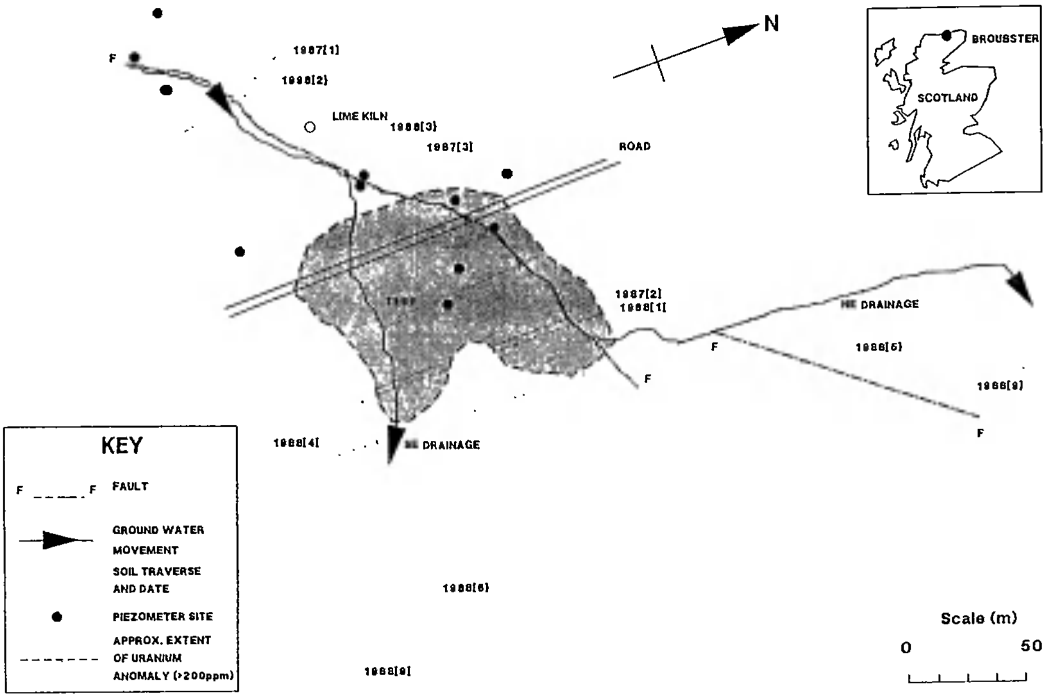

Figure 4. A plan of the Broubster site and its peat-uranium anomaly.

THE PALMOTTU NATURAL ANALOGUE STUDY, FINLAND

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ABSTRACT

The natural analogue study around the small U-Th mineralization at Palmottu, SW Finland, aims at a more profound understanding of radionuclide transport processes in fractured crystalline bedrock. The essential factors controlling transport are groundwater flow and interaction between water and rock. Accordingly, the study includes (1) structural interpretations partly based on geophysical measurements, (2) hydrological studies including hydraulic drill-hole measurements, (3) flow modelling, (4) hydrogeochemical characterization of groundwater, uranium chemistry and colloid chemistry, (5) mineralogical studies, (6) geochemical interpretation and modelling, (7) studies on radionuclide mobilization and retardation including matrix diffusion, and (8) modelling of uranium series data. Palaeohydrogeological aspects, due to the anticipated future glaciation of the Fennoscandian Shield, are of special interest. Quaternary sediments are studied to gain information on post-glacial migration in the overburden.

1. Introduction

The final disposal of nuclear wastes is an extensively studied aspect of the Finnish nuclear waste management policy. A repository for nuclear waste is planned to be excavated deep in crystalline bedrock. The spent fuel will be isolated from the biological environment by multiple technical and natural barriers. The bedrock is the ultimate natural barrier retarding and diluting any radioactive matter possibly released. In assessing the performance of the system, the possibilities of failure of the technical barriers, and the effects of subsequent chemical processes such as dissolution, mobilization and retardation of spent fuel in the bedrock, are also considered (*e.g.* Vieno *et al.*, 1992). The Palmottu study aims at the identification and quantification of similiar chemical processes (natural analogues) in a crystalline bedrock environment.

During the 1980's several international projects dealing with natural analogues of high-level radioactive wastes were established and a large amount of information on radionuclide behaviour was subsequently obtained from these sites: Alligator Rivers, Australia (Duerden, 1992), Poços de Caldas, Brazil (Chapman *et al.*, 1992), Cigar Lake, Canada (Cramer and Smellie, 1993). More recent studies have been centred around the Oklo natural reactors in Gabon (Blanc, 1993), the Tono uranium deposit, Japan (Seo and Yoshida, 1993) and the El Berrocal granite, Spain (Astudillo, 1993). Many of above studies have been undertaken in proximity to uranium deposits, but most of these studies concentrate on geological and hydrological conditions that differ substantially from those of the fractured crystalline bedrock of the Fennoscandian Shield. Therefore, a more relevant natural analogue study was initiated in Finland at the U-Th deposit of Palmottu in the southwestern part of the country.

After a brief feasibility study, the first phase of the Palmottu analogue project commenced in 1988 and terminated at the end of 1991, and the present 3-year phase of the study was started in 1992 (Blomqvist *et al.*, 1991; Suksi *et al.*, 1992a; Ahonen *et al.*, 1993a). This study is a co-operational research programme financed by the Finnish Centre for Radiation and Nuclear Safety and the Ministry of Trade and Industry of Finland. The principal target of the present project is to obtain a sound knowledge of the factors affecting radionuclide mobilization and retardation in crystalline rock. Moreover, the Palmottu site offers the possibility to understand the effects of various palaeohydrogeological conditions during glacial and interglacial cycles. It is also hoped that all these studies will lead to improved research methods particularly applicable to nuclear waste disposal problems in crystalline rock. Finally, through such an analogue project it should be possible to present a more reliable and palatable concept of radioactive waste disposal and its consequences to the general public.

In terms of repository performance assessment, the following major applications are relevant:

1. Near-field spent fuel solubility/dissolution.
   * geochemical modelling of ore dissolution (uranium solubility/dissolution).
   * geochemical modelling of additional trace elements that may be present in solution and considered important in safety disposal (e.g. Th, Tc, Pu, Cu, Mo, As, Cs, Sr).

2. Far-field radionuclide mobilisation/transportation.
   * the role of uranium minerals and fracture mineralogy (e.g. Fe-bearing phases) on the groundwater redox chemistry
   * the effects of groundwater redox chemistry on the dissolution and transportation of radionuclides (and other trace elements)
   * the role of colloid/organic material on the up-take and transportation of radionuclides
   * the role of microbes on the groundwater redox chemistry
   * the role of matrix diffusion on the retardation of radionuclides

The research strategy of the project can be presented as a hierarchical system of activities aimed ultimately at a more profound understanding of radionuclide transport processes (Fig. 1). Fundamental tasks include fracture-mineral, groundwater, sorption and matrix diffusion studies. Groundwater flow and water-rock interaction are the principal factors contributing to migration of radionuclides. Various models for describing water-rock interaction processes are used. At present, the nature and location of groundwater flow is to be emphasized. The final target will be the estimation of time scales of radionuclide transport. The study of Quaternary sediments aims at acquiring information on post-glacial radionuclide migration in the biosphere.

The research institutes involved include the Geological Survey of Finland, acting as the co-ordinating organization, the Department of Radiochemistry of the University of Helsinki, the Laboratory of Engineering Geology and Geophysics of Helsinki University of Technology, and the following three laboratories of the Technical

Research Centre of Finland: Reactor Laboratory; Road, Traffic and Geotechnical Laboratory; Nuclear Engineering Laboratory. In addition, an increasing international contribution is anticipated.

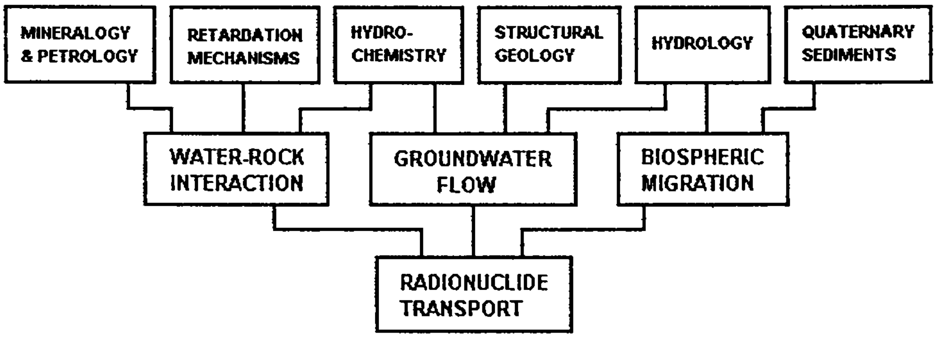

Fig. 1. Research strategy of the Palmottu Analogue Project.

2. Geological background

The study area occurs within a zone of metamorphosed supracrustal volcanic and sedimentary rocks that extends from SW Finland into Central Sweden, including the intensively studied Stripa mine area. The Palmottu U-Th mineralization type is related to the latest stages of orogenic events about 1.8—1.7 Ga ago. The surroundings of Palmottu are characterized by granites and highly metamorphosed migmatitic rocks, schists, and metavolcanites (Räisänen, 1986; Kuivamäki *et al.*, 1993). The discontinuous uranium mineralization, which has a total length of about 400 m, was intersected by a large number of drill holes during exploration. The outcropping parts of the U-Th mineralization are mainly located SE of Lake Palmottu, but a minor part is also located under the lake (Fig. 2). The thickness of the mineralized zones vary up to 15 metres. Uranium occurs mainly as disseminated uraninite (UO_{2+x}) in microcline granite dykes cutting the migmatitic gneiss. Uraninite has been altered along grain boundaries and fractures, evidently resulting from hydrothermal activity, and a rim composed mainly of coffinite is found in almost practically all uraninite crystals (*e.g.*, Blomqvist *et al.*, 1992b).

During recent geological history the area has been subjected to several glaciations (Ehlers, 1983), the latest of which ended 10,000 years ago, and the bedrock is in many places covered by a thin glacial till cover. Before and between the glaciations weathering and river erosion were active, and during the glaciations thick continental ice sheets resulted in an unevenly eroded bedrock surface. Erosion was preferentially concentrated in the old deeply weathered fractures and fracture zones, which commonly transected each other, leaving intervening more elevated bedrock blocks of variable size. Regionally Palmottu is located within a bedrock block topographically slightly higher than its surroundings; the terrain drops most steeply southward and eastward from the study area, the largest gradient being some 50 m/km. The northwestern corner of the Palmottu block was encroached upon by a large glaciofluvial delta formation consisting of sand and gravel. This thick sand and gravel deposit forms a huge surface water reservoir which also contributes to the inflow of Lake Palmottu (Niini *et al.*, 1993).

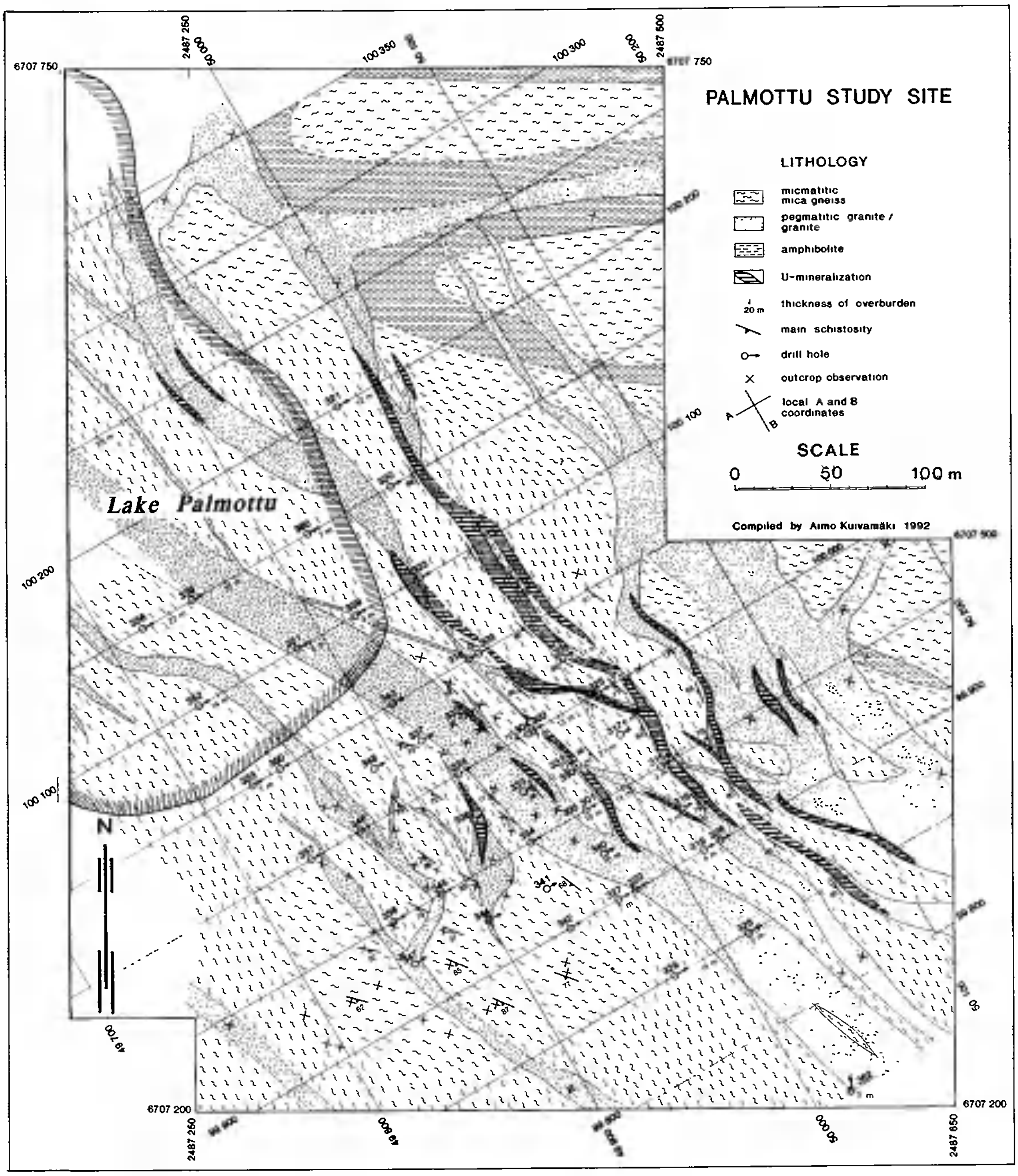

Fig. 2. Geological map of the Palmottu study area (Kuivamäki *et al.*, 1993).

Repeated glaciations are known to have affected the Fennoscandian Shield during the last few hundreds of thousands of years; the next glacial advance is expected to commence in about 10,000 years, and to end some 100 ka later (*e.g.*, Eronen and Olander, 1990). As the decay activity of the proposed high-active nuclear waste disposal will still be reasonably high at the end of the next glaciation, it is important to obtain a thorough understanding of the hydrogeological effects within a glacial cycle. Accordingly, one of the important applications of the Palmottu study is to try to further increase our knowledge of the various palaeohydrogeological conditions during a glacial cycle. The first steps of such studies have already been taken within the site-selection studies in Finland (Blomqvist *et al.*, 1992a), and Palmottu, due to its high uranium concentration, should therefore offer an excellent study forum.

3. Activities in progress

3.1. Groundwater flow

The structural features of the Palmottu U-Th-deposit have been studied by drill core logging and geophysical measurements, the main focus being in recognizing fractures or fracture zones that might be important pathways for groundwater flow. In order to determine the geometry of possible hydraulic zones, charged-potential (mise-à-la-masse) measurements were carried out in ten drill holes at the central part of the drilling site (Paananen, 1993; Paananen and Kuivamäki, 1993). On the basis of the measurements, the location and orientation of 6 or 7 separate galvanic (and possible hydraulic) connections were discerned within one of the drilling profiles. The dips of these structures are mostly parallel or subparallel to the general dip of the geological structures, but some structures are interpreted as cutting the formation at a low angle. The galvanic connections with a subsequent profile also indicated possible hydraulic connections. The next step will be a hydrology programme based on pumping tests.

The surface-hydrological study aims to determine the annual water infiltration and surface runoff of the Palmottu drainage basin. During 1990—1992 systematic monthly water-table measurements were carried out in 29 drill holes intersecting the uranium deposit. Based on variations of water level with time, the area drilled can be divided into three subareas which indicate different hydraulic connections, either fracture or surface controlled, between the various holes and Lake Palmottu.

A method for determining the detailed areal variations of the deep groundwater flow was developed, based on assessing the water-balance component modelling of the 12 most significant fracture zones which act as channels for bedrock groundwater flow in the Palmottu area (Niini *et al.*, 1993). The flow direction varied according to the direction of hydraulic gradient: the groundwater flow is mostly outwards from the Palmottu catchment but in the westernmost section it is partly towards the centre. This interpretation is still inadequate and further hydrological observations are required.

3.2. Water-rock interaction

Hydrogeochemistry and uranium chemistry. Hydrogeochemical results show that the chemistry of groundwater varies strongly within small areas at Palmottu indicating relatively isolated fracture-controlled flow systems (Blomqvist *et al.*, 1992b). Bicarbonate, chloride and sulphate waters with total dissolved solids (TDS) from 0.2 to 1.5 g/l have been sampled from the four drill holes depicted in Fig. 3. Drill hole 324 contains a dilute Ca-HCO_3 water throughout its length, whereas drill hole 304 has slightly saline Ca-Na-SO_4-HCO_3-Cl water up as far as the groundwater table. The two drill holes 346 and 357 have fresh groundwaters of Ca-HCO_3 or Na-HCO_3 type close to the surface of the bedrock and slightly saline groundwaters deeper down in the system, the former being a Na-SO_4 and the latter a Na-Cl-SO_4 water. The pH values are generally 8—9 and the Eh values -35— -125 mV. The waters of drill hole 324 have lower pH values and higher Eh values compared to the other drill holes (pH: 6.6—7.0; Eh: 55—100 mV).

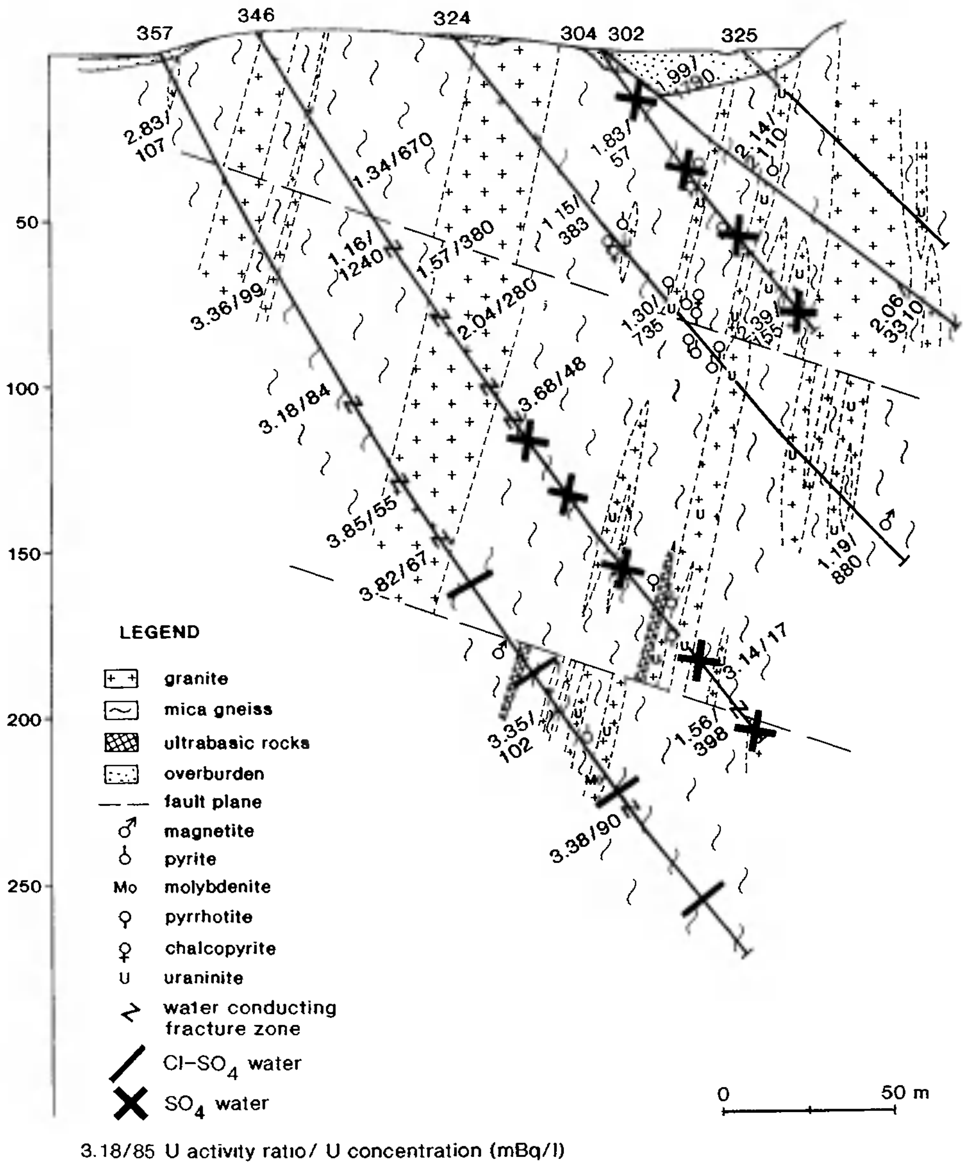

Fig. 3. Distribution of groundwater types, $^{234}U/^{238}U$ activity ratios and U concentrations in groundwater in drill holes 302, 304, 324, 346, and 357 of the Palmottu U-Th ore deposit. Data from Blomqvist *et al.* (1992b).

The uranium concentrations of the filtered waters vary within two orders of magnitude from 17 mBq/l to 3310 mBq/l. Also, a large variation of $^{234}U/^{238}U$ isotopic activity ratios are observed (from 1.15 to 3.85), (Fig. 3). Generally, a decrease in uranium concentration with depth is evident, in good agreement with decreasing Eh values (Suutarinen *et al.*, 1991; Blomqvist *et al.*, 1992b). A concomitant increase in $^{234}U/^{238}U$ activity ratios is also apparent. The groundwaters from drill hole 324, however, behave independently, and the uranium concentrations and $^{234}U/^{238}U$ activity ratios do not show such a systematic change as compared to the other drill holes.

In a recent test for the oxidation state for soluble uranium, the relative amount of hexavalent uranium decreased with increasing depth from 97 % to 7 %. Good agreement between calculated oxidation state of uranium, based on measured Eh and pH, and analyzed oxidation state of uranium, was observed (Ahonen *et al.*, 1993b).

Geochemical interpretation and modelling. The hydrogeochemical research at Palmottu is aimed primarily at providing a better understanding of the processes affecting the chemical composition of groundwater. Fracture minerals give important information on water-rock interaction. Fracture calcites are in equilibrium with the slightly basic groundwaters (pH: 8—9), while the slightly acidic waters are distinctly undersaturated with respect to calcite. Kaolinite is a typical fracture mineral, but the concentrations of aluminum and silica in groundwater are not controlled by kaolinite. Also, the common fracture mineral pyrite is not in equilibrium with groundwater (Ahonen *et al.*, 1992). Recently Pitkänen (1993) used the mass-balance model (NETPATH) to model

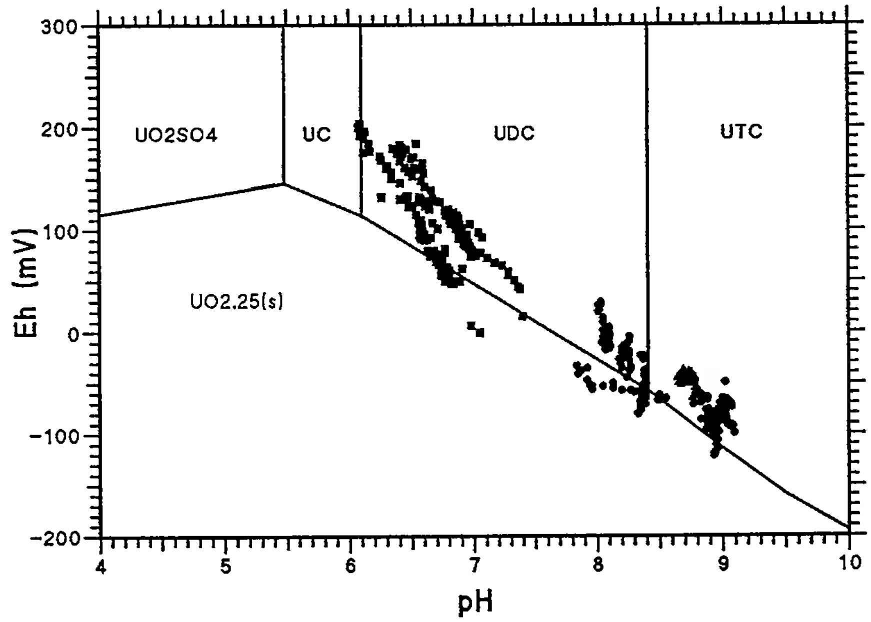

Fig 4. Scatter diagram of measured Eh-pH values from three drill holes (324, 346, 357). Solid lines separate the calculated stability field of uraninite ($UO_{2.25}$), and the predominant fields of soluble uranyl species. The phase boundary is drawn for 10^{-8} M of soluble uranium. Assumed concentrations are representative for the slightly saline groundwater in Palmottu: H_4SiO_4 = 1.3×10^{-4} M, total carbonic acid = 2×10^{-3} M, sulphate = 10^{-2} M. Data from Ahonen *et al.* (1993b).

the groundwater evolution. The calculations, based on water chemistry of two drill holes, indicated that the production of sulphate by oxidation of sulphides is improbable under present ambient conditions. The simultaneous increase of the concentrations of Na, SO_4, and Cl with increasing salinity indicate a common source for these elements. Hence, fluid inclusions (or soluble salts) are considered potential contributors to the salinity of groundwater. Some mixing with relic sea water may also have taken place.

The study of the groundwater redox systems is an essential part of water-rock interaction investigations as the behaviour of uranium is strongly dependent on the redox conditions. The results obtained indicate that soluble uranium species are in redox equilibrium with groundwater. Measured Eh and pH values indicate equilibration between the common uranium minerals, iron oxyhydroxides, and groundwater (Fig. 4.)

Characterization of groundwater colloids and organics. Further characterization of colloids were carried out in three new groundwater samples (Vuorinen and Kumpulainen, 1993). The colloids were characterized by various microscopical and microanalytical methods (SEM, TEM, EDS, XRD, and AFM (atomic force microscopy). Image analyses methods were also tested to assess colloid size distribution.

The concentration of TOC (Total Organic Carbon) in groundwater was about 1.5 mg/l. Evidence of organic colloids in the colloid concentrate in the size range between about 2 nm and 500 nm was obtained. Nevertheless, a significant part of the organic matter in the groundwater samples was of very small size as it passed through the 30,000 NMWC (Nominal Molecular Weight Cut-off) filter, and was found in the filtrate at concentrations almost equal to those in the groundwater. The colloid concentrate also had colloid-size particles with a distinct mineral character such as plagioclase, mica and quartz. TEM preparates analyzed with EDS indicated large amounts of spherical Ca-containing colloids in the 150 nm size range, both in the colloid concentrate and in the ultrafiltrate.

Radionuclide retardation. Evidence for uranium sorption and matrix diffusion around fractures had been obtained in earlier studies (Suksi *et al.*, 1991; Suksi *et al.*, 1992b). These studies indicated that retardation of dissolved U is controlled by the characteristics of the rock around the fracture. In altered granitic rock, uranium is accumulated in a zone where the most intense alteration has taken place.

Mineralogical work, α-particle radiography, phase selective dissolution techniques and dissolution kinetics studies have been used to provide information about radionuclide fixation during groundwater flow along fractures. The results indicate that a considerable part of the uranium attached to fracture surfaces occurs in phases easily accessible to groundwater. Adsorption onto solids coated by iron oxyhydroxides, and co-precipitation with calcite, seem to be most common fixation mechanisms for uranium.

Interpretation of uranium series data. In the studies of uranium transport and retardation in the rock/groundwater system at Palmottu, emphasis has been directed to a proper interpretation of the information inferred from the measured disequilibria between radionuclides of the uranium decay series. The mechanisms and processes which may cause and maintain radioactive disequilibrium in decay series are, in general, rather well understood, providing a sound theoretical basis for the interpretation. To further improve the interpretation, however, a computer code URSE (uranium series disequilibrium) has been developed to simulate inventories of a 4-member (or shorter) radioactive decay chain in simplified systems. The system may consist of periodically open or continuously open subsystems which can be combined into continuous scenarios (Rasilainen and Suksi, 1992).

As a very first modelling attempt, the standard matrix diffusion theory was used to interpret the observed radionuclide concentration profiles in an altered rock core around a natural fracture (Suksi *et al.*, 1992b). In the modelling, the uranium series disequilibrium code URSE and the migration code FTRANS were used in conjunction. The concentration profiles from the fracture surface into the rock were simulated. The system was characterized using available site-specific data from Palmottu. Measured concentration profiles of ^{238}U, ^{234}U and ^{230}Th could be explained by matrix diffusion assuming realistic initial and boundary conditions and diffusion times of about 300 000 years (Rasilainen and Suksi, 1993).

Palaeohydrogeological studies. The existing oxygen and carbon isotope data for fracture calcites was supplemented by 50 additional samples, and stable isotope data (^{18}O and ^{13}C) from some 100 calcite samples are presently available. When compared to groundwater values, stable isotopes of calcite should yield information on formation conditions and eventual subsequent modifications of calcite coatings. Additionally, the information of $^{87}Sr/^{86}Sr$ will be used. Young calcites (< 300 ka) are important when interpreting relatively recent palaeohydrogeological conditions. Accordingly, several fracture calcite samples were selected for $^{230}Th/^{234}U$ dating studies. The calcite samples were collected from drill cores corresponding to the previous sampling sites for groundwater, making it possible to compare the $^{234}U/^{238}U$ activity ratios of groundwaters and fracture-coating calcites.

4. Future applications

The present study is aimed at the understanding of radionuclide mobilisation and retardation processes. During the on-going phase of the project, groundwater flow will also be emphasized. The target of this subproject is to locate possible flow channels in and around the central part of the study area. The idea is to evaluate whether the Palmottu study could be developed towards an *in situ* transport analogue study for radionuclides where geochemical processes could be coupled with mass transport considerations. The second application is developed by studying the U-Th rich parts of the mineralization as an analogue for spent nuclear fuel. The release of elements during secondary and low temperature mineral formations could yield important implications on the long-term behaviour of spent fuel.

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References

GSFR = Geological Survey of Finland, Nuclear Waste Disposal Research, Report YST

Ahonen, L., Blomqvist, R., Ruskeeniemi, T., Vesterinen, M., and Pitkänen, P., 1992. Geochemical processes controlling the groundwater composition at Palmottu study site, SW-Finland. *In* Water-Rock Interaction (eds. Y.K. Kharaka & A.S. Maest), A.A. Balkema, Rotterdam, 763—766.

Ahonen, L., Blomqvist, R., and Suksi, J. (eds.), 1993a. The Palmottu Analogue Project. Progress Report 1992. GSFR 82, 98 p.

Ahonen, L., Ervanne, H., Ruskeeniemi, T., Jaakkola, T., and Blomqvist, R., 1993b. Uranium mineral - groundwater equilibration at the Palmottu natural analogue study site, Finland. *In* Scientific Basis for Nuclear Waste Management XVI (eds. C. Interrante & R. Pabalan), Materials Research Society (in print).

Astudillo, J., 1993. "El Berrocal Project": Characterisation and validation of natural radionuclide migration processes under real conditions in a fissured granitic environment. *In* Proceedings of 5th Natural Analogue Working Group Meeting and Alligator River Analogue Project (ARAP), Final Workshop, Toledo, Spain 1992 (eds. H. von Maravic and J. Smellie). CEC Report EUR (in print).

Blanc, P.-L., 1993. Oklo as a natural analogue for radionuclide transfer processes in a waste geological repository: Present status of the program. *In* Proceedings of 5th Natural Analogue Working Group Meeting and Alligator River Analogue Project (ARAP), Final Workshop, Toledo, Spain 1992 (eds. H. von Maravic and J. Smellie). CEC Report EUR (in print).

Blomqvist, R., Jaakkola, T., Niini, H., and Ahonen, L. (eds.), 1991. The Palmottu Analogue Project. Progress Report 1990. GSFR 73, 147 p.

Blomqvist, R., Nissinen, P., and Frape, S.K., 1992a. Dating of fracture minerals from Olkiluoto, Eurajoki. TVO/Site Investigations, Technical Report 92-27 (mainly in Finnish), 117 p. + 9 Appendices. Teollisuuden Voima Oy, Helsinki.

Blomqvist, R., Pilviö, R., Ahonen, L., and Ruskeeniemi, T., 1992b. Groundwater conditions and uranium mobility in Palmottu analogue study site in Finland. GSFR 78, 33—67.

Chapman, N.A., McKinley, I.G., Franca, E.P., Shea, M.E., and Smellie, J.A.T., 1992. The Poços de Caldas Project: an introduction and summary of its implications for radioactive waste disposal. J. Geochem. Explor. 45, 1—24.

Cramer, J.J. and Smellie, J.A.T, 1993. The AECL/SKB Cigar Lake Analogue Study: Some implications for performance assessment. *In* Proceedings of 5th Natural Analogue Working Group Meeting and Alligator River Analogue Project (ARAP), Final Workshop, Toledo, Spain 1992 (eds. H. von Maravic and J. Smellie). CEC Report EUR (in print).

Duerden, P. (ed.), 1992. The Alligator Rivers Natural Analogue. The International Intraval Project: To study validation of geosphere transport models for performance assessment of nuclear waste disposal, Phase 1, Test Case 8. Organization for Economic Co-operation and Development (OECD), Nuclear Energy Agency (NEA), and the Swedish Nuclear Power Inspectorate (SKI).

Ehlers, J., 1983. The glacial history of north-west Germany. *In* Glacial Deposits in North-West Europe, (ed. J. Ehlers). A.A. Balkema, Rotterdam, 229—238.

Eronen, M. and Olander, H., 1990. On the World's ice ages and changing environments. Nuclear Waste Commission of Finnish Power Companies, Report YJT 90-13, 72 p.

Kuivamäki, A., Paananen, M., and Kurimo, M., 1993. Bedrock structures and lithology around the Palmottu uranium deposit. GSFR 83 (in print).

Niini, H., Blomqvist, R., Kuivamäki, A., Vesterinen, M., Tuokko, T., and Hakkarainen, V., 1993. Deep groundwater flow at Palmottu. GSFR 82, 23—32.

Paananen, M., 1993. Mise-á-la-masse measurements and galvanic connections as a part of flow path investigations at Palmottu U-Th-mineralization, southwestern Finland. GSFR 81, 18 p. (in Finnish).

Paananen, M. and Kuivamäki, A., 1993. Structural interpretation for mapping of groundwater flow paths at Palmottu U-Th-mineralization. GSFR 82, 33—40.

Pitkänen, P., 1993. Geochemical modelling of $NaSO_4$ type groundwater at Palmottu using a mass balance approach. GSFR 82, 79—86.

Rasilainen, K. and Suksi, J., 1992. On the quantitative interpretation of uranium series disequilibria. Technical Research Centre of Finland, Research Notes 1404, 63 p. + 2 Appendices (in Finnish).

Rasilainen, K and Suksi, J., 1993. Modelling in-situ matrix diffusion at Palmottu. GSFR 82, 87—98.

Räisänen E., 1986. Uraniferous granitic veins in the Svecofennian schist belt in Nummi-Pusula, Southern Finland. Technical Committee Meeting on Uranium Deposits in Magmatic and Metamorphic Rocks, Salamanca 1986. Report IAEA-TC-571, 12 p.

Seo, T. and Yosida, H., 1993. Natural analogue studies of the Tono uranium deposit in Japan. *In* Proceedings of 5th Natural Analogue Working Group Meeting and Alligator River Analogue Project (ARAP), Final Workshop, Toledo, Spain 1992. CEC Report EUR (in print).

Suksi, J., Ahonen, L., and Nimi, H. (eds.), 1992a. The Palmottu Analogue Project. Progress Report 1991. GSFR 78, 138 p.

Suksi, J., Ruskeeniemi, T., Lindberg, A., and Jaakkola, T., 1991. The distribution of natural radionuclides on fracture surfaces in Palmottu analogue study site in SW Finland. Radiochim. Acta 52/53, 367—372.

Suksi, J., Ruskeeniemi, T., and Rasilainen, K., 1992b. Matrix diffusion - evidences from natural analogue studies at Palmottu in SW Finland. Radiochim. Acta 58/59, 367—372.

Suutarinen, R., Blomqvist, R., Halonen, S., and Jaakkola, T., 1991. Uranium in ground-water in Palmottu analogue study site in Finland. Radiochim. Acta 52/53, 373—380.

Vieno, T., Hautojärvi, A., Koskinen, L., and Nordman, H., 1992. TVO-92 safety analysis of spent fuel disposal. Nuclear Waste Commission of Finnish Power Companies, Report YJT-92-33, 250 p. (in Finnish).

Vuorinen, U. and Kumpulainen, H., 1993. Characterization of natural groundwater colloids at Palmottu. GSFR 82, 41—63.

AN OVERVIEW OF THE MAQARIN NATURAL ANALOGUE PROJECT - A NATURAL ANALOGUE STUDY OF A HYPERALKALINE CEMENT GROUNDWATER SYSTEM

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1. Introduction

Current design concepts for low/intermediate level radioactive waste disposal (and some high-level waste disposal) in many countries involve emplacement underground in a cementitious repository. Chemical conditions in the near field are expected to be hyperalkaline, dominated by the alkalinity of the cement porewaters for long periods of time. This alkaline porewater will leach out of the near-field environment and, by interaction with the repository host rock, may significantly alter the original physical and geochemical properties of the host formation and therefore influence the retardation of radioelements within the 'disturbed zone'.

In the safety assessment of a potential waste repository, it is important to have an understanding of the chemical and retardation properties of the near field and disturbed zone. Experimental studies and observations of cement aggregate systems give information on reaction mechanisms and provide kinetic and thermodynamic data for computer models. However, it is important to complement laboratory studies, which are necessarily performed over short timescales, by study of chemically similar natural systems, which have evolved over geological timescales.

This paper presents a summary of a programme of work carried out since 1990 at Maqarin in Northern Jordan. At this unique site, naturally-occurring hyperalkaline groundwaters are in contact with marl and bituminous limestone. The site thus represents an analogue for the repository near field and disturbed zone.

A comprehensive report of the research activities of this project is given elsewhere [1]. For the purposes of this paper three areas of the research programme associated with Maqarin will be highlighted:

i) an investigation of the mineralogical alteration of unmetamorphosed bituminous marl and limestone host rocks as a result of their interaction with hyperalkaline groundwater which aids our understanding of likely mineralogical and flow-path changes in the repository 'disturbed zone';

ii) a study of the indigenous microbiological populations of the hyperalkaline springs, which will provide an indication of the potential role of microbes in the cement-dominated environment of a repository;

iii) a modelling study of the solubility of a series of trace elements of potential importance in determining the repository safety case to provide limited validation of the thermodynamic codes and databases which underpin research models.

2. Mineralogical alteration of marl as a result of interaction with hyperalkaline groundwater.

2.1 Objective

The work described here was undertaken as a follow-up to the 1990 study (Phase I) with the specific objective of investigating the mineralogical alteration of unmetamorphosed bituminous marls and limestone host rocks as a result of their interaction with hyperalkaline groundwaters emanating from the combustion metamorphic zones [2]. It was a precursor and feasibility study into the potential of the Maqarin site for testing and validating the coupled solubility and transport models CHEQMATE [3,4] and MPATH [5] during 1992/93. (This coupled code testing is now in progress.)

2.2 Method

Analysis of rock samples was carried out using standard geochemical, mineralogical and petrographic techniques. In particular, detailed mineralogical and petrographic analyses were carried out by X-ray diffraction, X-ray powder diffraction photography, backscattered scanning electon microscopy and electron microprobe analysis and analytical transmission electron microscopy.

2.3 Main Findings

The main observation from the investigation summarised above is that, although the overall paragenesis of the hyperalkaline-marl interaction at Maqarin is complex, the marls, limestones and quartz, show significant evidence of reaction. The reaction sequence is illustrated schematically in Figure 1 and can be summarised in the Stages described below:

Stage 1
Hyperalkaline water saturated with calcium hydroxide is formed by hydration of localised zones of high-temperature combustion-metamorphosed rocks within the

Bituminous Marl formation [6]. These groundwaters percolate through fractures into the non-metamorphosed host-rock marl and limestone.

Stage 2

Initial alteration of the marl with the inflowing hyperalkaline waters results in the precipitation of colloidal portlandite on the fracture walls. Calcite in the wallrock then begins to dissolve.

Stage 3

Ca and OH migrate from the hyperalkaline water into the wallrock. Colloidal, gel-like CSH (calcium silicate hydrate) and CASH (calcium aluminium silicate hydrate) phases are precipitated in the wallrock alteration zone and as fracture

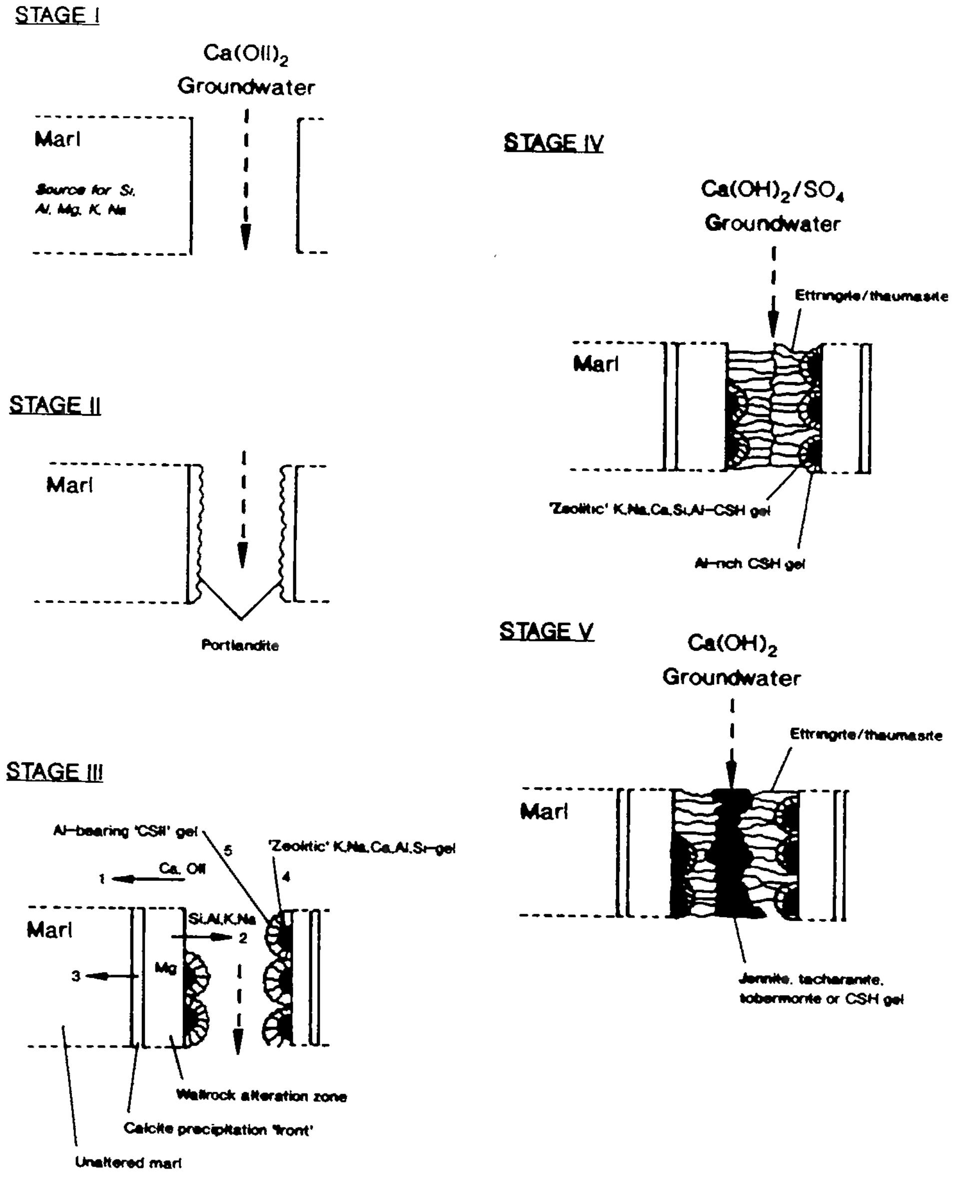

Figure 1 Schematic representation of the mineralogical changes which occur when a hyperalkaline groundwater interacts with a marl.

linings as Si, Al, K and Na leached from clay minerals, and silica minerals react with portlandite or calcium hydroxide water. The early CASH phases have zeolitic compositions but these gradually transform to Al-substituted CSH phases. Calcite is also dissolving, and thus wallrock porosity increases. The calcite is reprecipitated at the interface between the reaction zone and unaltered marl. Mg is immobile and precipitates as oxide phases such as brucite.

Stage 4

The groundwater evolves as these processes continue becoming enriched in silica and/or sulphate. Ettringite or thaumasite (or a solid-solution of these two minerals) then precipitates, replacing the earlier CSH and sealing the fractures.

Stage 5

Further groundwater flows through reactivated fractures. Ettringite and thaumasite react again to form a later generation of CSH phases similar in composition to jennite or tobermorite.

The reaction sequence described above has shown that interaction between hyperalkaline water and the Maqarin host rocks tends to lead, in general, to the sealing of fractures by secondary phases such as ettringite, thaumasite, jennite, tobermorite and other similar phases. In contrast, dissolution of calcite and primary silicate minerals tends to increase microporosity. However, the precipitation of secondary phases along the margin with unaltered rock may inhibit groundwater movement from the fracture zone into the host rock.

Changes in primary porosity may lead to localisation of regional groundwater flow into a few large fractures. This could reduce the overall barrier capacity of the far field. Further, changes to the secondary porosity (i.e. rock matrix porosity) could be of significance to radionuclide retardation. In many marls, secondary calcite seals fracture surfaces so reducing matrix diffusion. In this system, however, the production of increased microporosity observed in the carbonate-rich rocks would be beneficial with respect to increasing retardation through matrix diffusion.

The more silicate-rich rocks studied here show significantly-decreased secondary porosity following reaction with obvious impact on rock matrix diffusion.

3. Microbiology

3.1 Objective

The aim of this work was to study the indigenous microbiological populations of the hyperalkaline springs, which will provide an indication of the potential role of microbes in the cement-dominated environment of a repository [7]. Particular emphasis was placed on sulphate-reducing bacteria as these can participate in steel corrosion and may affect concrete by their hydrogen sulphide production. They are also known to withstand high pH. The results are also useful for the testing of microbiological codes, such as EMMA [8].

3.2 Method

Samples were collected from the hyperalkaline springs at Maqarin during the 1990-91 field programme. Attempts were made to isolate and identify the various types of microbes present using standard cultures.

3.3 Main findings

The enrichments for denitrifying and sulphur-reducing bacteria, alkalophilic photosynthetic bacteria, algae and also fungi were all negative. Tests for heterotrophs and oligotrophs (aerobic and anaerobic) were all negative. However, the on-site tests did reveal the presence of low numbers of heterotrophs in samples from all the sites although this did vary with sampling methodology. Sulphate reducing bacteria were detected in all samples using the qualitative Postgate's B medium but these could not be isolated.

These results are not surprising in the light of the hydrochemistry of the Maqarin waters. The major elements for microbial growth and metabolism in an aqueous environment are carbon, phosphorus, sulphur and nitrogen. Electron donors and acceptors are also required for energy generation. Carbon levels are low (total organic carbon levels typically less than 1.8 mg dm^{-3}). These low carbon levels could support only a very low heterotrophic population. Low levels of phosphate are also available. The samples with the higher phosphate, nitrate, sulphate and organic carbon also show the highest microbial counts which could be attributed to the higher nutrient values with carbon possibly acting as the limiting factor on growth. It is also of interest that Se levels are high, as Se appears to be used by the microbes in preference to S, to the extent that the microbes are possibly poisoned by high levels of Se.

Further work is ongoing in the Maqarin Phase II, atempting to provide enough data to test EMMA, a microbiology code which was designed to define the effects of microbes on the repository system.

4. Thermodynamic database testing by the modelling of trace element concentrations

4.1 Objective

The objective of the modelling work reported here was to test geochemical codes and databases under chemical conditions of relevance to the cementitious repository environment to provide limited validation of the codes and databases.

4.2 Method

Geochemical modelling was carried out at two main stages in the programme. At the beginning of the project, prior to the field trip, modelling was performed to predict the likely levels of trace elements in the Maqarin waters [9]. This modelling was used to guide the experimental programme by giving an indication of which trace elements were likely to be present in measurable concentrations and whether sample preconcentration before analysis was likely to be needed. As several modelling organisations were involved, a database intercomparison was also possible at this stage. At the end of the analytical programme, a series of 'blind' modelling runs were performed and the model predictions were then compared with field observation.

4.3 Main findings

The main finding from the modelling study was that the observed solution concentrations of trace elements were two or three orders of magnitude less than would have been predicted assuming that the concentrations were controlled by the solubility of a simple oxide or hydroxide phase listed in the current databases i.e. thermodynamic databases behaved, in general, in a conservative manner. Uranium was, however predicted to be oversaturated with respect to $CaUO_4$. This is a phase which is not observed in nature. Choice of an oxide as the solubility-limiting phases, as recommended by Lemire [10] for a natural system, would lead to a conservative prediction of uranium solubility.

The main limitation of these geochemical codes in predicting element solubilities was the representation of the solid phase. Most of the solids contained in the databases are pure end-members and these are not generally observed in nature. Furthermore, mineralogical study of the secondary mineral assemblages at Maqarin showed that many of the trace elements were incorporated in major element solid phases such as CSH phases and sulphate minerals. Coprecipitation of these trace elements with these major minerals is of paramount importance in dictating the concentrations of these elements in the groundwaters.

The value of comparing laboratory measurements with field data is also highlighted here in the results of Sn and Ni modelling. The AEA Technology Sn database [11] was refined in the light of laboratory data to include Sn(IV) hydrolysis products [12]. Comparison with field data showed good agreement, which provides some support for the AEA Sn database. However, it must be stressed that this is not a rigorous validation of the database, due mainly to the lack of relevant minerals in the current databases.

5. Concluding remarks

The work descibed above has demonstrated the value of the Maqarin site as an analogue of a cementitious repository. Investigation of the processes occurring here aids our understanding of the processes likely to occur in the repository near field and disturbed zone. A second Phase of the Programme is currently underway, aimed specifically at providing data for testing the detailed research models which underpin performance assessments.

6. Acknowledgement

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References

1. Alexander,W.R.(Ed). Nagra Report NTB 91-10 (1992)
2. Milodowski,A.E. Nagra Internal Report NIB 92-50 (1992)
3. Haworth, A., Sharland, S.M., Tasker, P.W. and Tweed, C.J. Nirex Safety Studies Report NSS/R113 (1988)
4. Haworth,A., Sharland, S.M., Tasker, P.W. and Tweed, C.J. Nirex Safety Studies Report NSS/R115 (1988)
5. Lichtner,P.C. Nagra Internal Report
6. Khoury, H.N., Salameh, E and Abdul-Jaber, Q. J. Hydrology **81** 79-91 (1985)
7. West J.M. et al Chapter 4 in Reference 1
8. EMMA model - Nagra Internal Report
9. Tweed, C.J. et al, Chapter 5 in Reference 1
10. Lemire,R.J.Atomic Energy of Canada Ltd Report AECL-9549 (1988)
11. Cross, J.E. and Ewart,F.T. Radiochemica Acta **52/53** 212-213 (1991)
12. Pilkington N.J.and Stone,N.S. Nirex Safety Studies Report NSS/R186 (1991)

NATURAL CONSTRAINTS ON RADIONUCLIDE RELEASE RATES

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Abstract

A strategy is developed to constrain alteration rates of radionuclide host phases used in performance assessment models of geologic repositories for high-level radioactive waste. The constraints will be established by characterizing natural radionuclide release rates. We suggest that release rates can be determined from measures of secular equilibrium/disequilibrium between ^{99}Tc and U, and ^{129}I and U. Interpretation of equilibrium/disequilibrium between ^{239}Pu and U is likely to be complicated by the geochemical behavior of plutonium in natural systems. We will seek to confirm the proposed strategy by analysis of ^{99}Tc,^{129}I,^{239}Pu, and U in rock and water samples from uranium deposits in varied hydrological and physiochemical environments.

1. Introduction

A decision to inter high-level radioactive waste in geologic repositories is common among countries with responsibility for safe disposal of radioactive by-products of nuclear power generation. The objective of such a repository is to isolate the wastes from humans and the environment to ensure that no potential future releases of radioactive substances constitute an unacceptable risk. Redundant containment is the strategy inherent in a geologic repository; a combination of engineered and natural barriers provide assurance that radioactive constituents have decayed to some pre-determined level before they are re-introduced into the human mileau. The required periods of isolation range from 10^4 to 10^5 years, depending upon regulatory levels. Assessing the effectiveness of geologic repositories over such extended times is an unprecedented activity. Performance assessment methodologies have been, and continue to be, developed for this purpose.[1] The process involves development of a repository design, identification of processes that may affect the integrity of the proposed repository, quantification of the processes to assess their radiological impact, and comparisons of the results of these predictions with regulatory limits. One difficulty with performance assessments of high-level radioactive waste repositories is the inability to assess the validity of results; a long-term prediction can only be verified in the long-term. It is the general applicability of theories to explain results derived from laboratory experiments, studies of natural systems, and models that provides verification of the validity of performance assessment methods.[1,2]

Our work is intended to provide information from natural systems to assist in development and verification of performance assessment source term models, specifically those process models used to predict radionuclide release rates from engineered barrier systems. We are characterizing "apparent "release rates of three naturally occurring radionuclides, ^{99}Tc, ^{129}I, and ^{239}Pu, from their site of production in varied hydrological and geochemical environments. The objective is to confirm that processes and mechanisms that are the basis for performance assessment source term models are consistent with processes that operate on the long time and large space scales of earth systems, and to provide a basis for selecting and justifying the choice of parameters to model these processes.

2. Source terms and performance assessment modelling

The initial Sandia Total System Performance Assessment (TSPA)[3] develops scenarios of radionuclide release to the accessible environment by considering "well-defined connected sequences of features, events, or processes. *Features* are the geologic or hydrologic properties of the site or system, which are expected to be durable. *Processes* are phenomena that have gradual, continuous interactions with the system. *Events* are occurrences that have a specific starting time (and usually a duration shorter than the time being simulated)."[3] Detailed modeling of scenarios requires selection of conceptual models and parameters to describe the component features, events, and/or processes. Variability and uncertainty of site parameters are addressed by using the Monte Carlo method, a stochastic simulation technique involving repeated random sampling from distributions of variables that appear in the mathematical models.

One scenario considered in the TSPA is aqueous transport from a repository with features that simulate a potential repository at Yucca Mountain, Nevada, as it is currently understood. For this scenario, mathematical descriptions of radionuclide release from an engineered barrier system, groundwater flow, and radionuclide transport are coupled in computer based models. Predictions of cumulative releases to the accessible environment, expressed as probability distributions, are the measure of performance from these coupled models.

Source term models in support of the TSPA, calculate radionuclide releases from the engineered barrier system into the far-field region.[3,4] Models are developed around conceptual processes that simulate failures of the engineered barrier system, radionuclide exposure, and transport from the near field environment. Containment system breach exposes *radionuclide bearing materials* to the near field environment. Once failure has occurred, release rates depend upon *radionuclide* exposure rates to the near field environment and maximum rates of transport from the waste package. In the TSPA, exposure rates are a function of alteration/dissolution rates of radionuclide host phases; oxidation of reduced uranium oxide is assumed to be the operative chemical process for alteration of reactor fuel where the majority of radionuclides reside. In gaps and boundaries of fuel, where smaller portions of the inventory are diffusively driven under high temperature conditions of reactor operation, radionuclides in unspecified phases are assumed to be rapidly exposed in the event of containment failure. Once exposed, two transport processes are considered: In localized regions of the repository where there is moisture, but no flowing water, radionuclide release is exclusively controlled by diffusion. In locally saturated areas where there is flowing water, release may be by both advection and diffusion. The TSPA model inventory for aqueous transport is comprised of nine radionuclides. Release processes for four of them, ^{79}Se, ^{99}Tc, ^{129}I, and ^{135}Cs, are characterized as alteration limited. These are considered to be soluble and thus, upon contact with groundwater, are contained exclusively in the aqueous phase; their aqueous concentrations are controlled by host phase alteration/dissolution. Tin-126, ^{234}U, ^{237}Np, ^{239}Pu, and ^{243}Am form insoluble phases under many natural conditions and thus, upon exposure, groundwater concentrations are limited by solubility of secondary hosts. Sorption is a critical process controlling transport rates of both alteration limited, and solubility limited radionuclides.

Rates of processes controlling releases are functions of hydrogeological and physiochemical conditions of the repository site. Groundwater is a factor in both rate of container failure, and rate of mass transport. To encompass extremes of groundwater flow at Yucca Mountain, TSPA considers two alternative models. " The composite-porosity model, a model based on Darcy's law........ allows unrestricted water movement between fractures and the tuff matrix; .... the weeps model, ... depicts essentially all of the percolating water traveling down fractures."[3] Physiochemical conditions affect alteration of radionuclide host phases, solubility, and adsorption of radionuclides. In the initial TSPA, matrix alteration rates were input as a log-normal distribution, with values based upon results of laboratory experiments of spent fuel leaching. Parameters for solubility of the four actinides and tin were input as log-normal distributions, bounded by results from laboratory measurements and geochemical models. Information regarding range, mean and variability of sorption coefficients was elicited from experts. Radionuclides were placed in one of three categories: those with little or no tendency to sorb, (^{99}Tc, ^{129}I) were given singular sorption coefficients of zero; those with small but variable sorptive tendencies (^{79}Se, ^{234}U, ^{237}Np, and ^{135}Cs) were given sorption coefficients parameterized as distributions as a function of rock type; those with large but variable sorptive properties (^{126}Sn,^{239}Pu, and ^{243}Am) were assigned constant minimum sorption coefficients, following the philosophy of minimum K_d.[5]

3. Natural analogues of source terms

Technetium-99, ^{129}I, and ^{239}Pu are juvenile radionuclides. They are products of naturally occurring nuclear fission, and neutron capture by uranium. The three nuclear products are radioactive nuclides formed *in-situ* in host phases of the parent element, uranium. In closed systems, nuclear processes of production and destruction establish states of secular equilibrium between uranium and its radioactive daughters. In such systems, relative abundances of daughter and parent nuclides are fixed by relative rates of the nuclear processes. If the parent/daughter abundances are not in secular equilibrium, it is a manifestation of open system processes. For instance if the relative abundance of a daughter nuclide is less than its secular equilibrium abundance, the deficiency manifests faster rates of daughter loss by physiochemical processes than by radioactive decay at secular equilibrium. Figure 1 is a schematic representation of the geochemical cycle of juvenile radionuclides. It illustrates the analogy with source term models. Our strategy focuses on *processes* in the TSPA aqueous release scenario. By characterizing "apparent" release rates of ^{99}Tc, ^{129}I, and ^{239}Pu in different geochemical and hydrological settings, we seek to confirm our understanding of processes controlling radionuclide release rates, and relationships between these *processes*, and site or system *features*.

In uranium deposits the overwhelming majority of nuclear reaction products are produced, and thus initially contained, in uranium-bearing phases. The situation is analogous to radionuclides in spent fuel matrix. The degree to which the analogy is applicable depends upon the extent to which natural host-phases have properties analogous to spent fuel. The best natural analogue is probably the natural spent fuels at Oklo. Ores in reduced environments are analogous to unirradiated fuel. In oxidized environments, altered ores are analogues of breached repositories. In a manner completely analogous to the TSPA conceptual model, the exposure rate - the rate at which radionuclides are exposed to the local environment is controlled by the rate of alteration/dissolution of host minerals. Once a radionuclide is exposed, its rate of removal from site of production is controlled by rate of mass transport - primarily a function of groundwater velocity and sorptive properties of the radionuclide in the rock matrix. The exposure (alteration/dissolution) rate is the rate limiting process; the

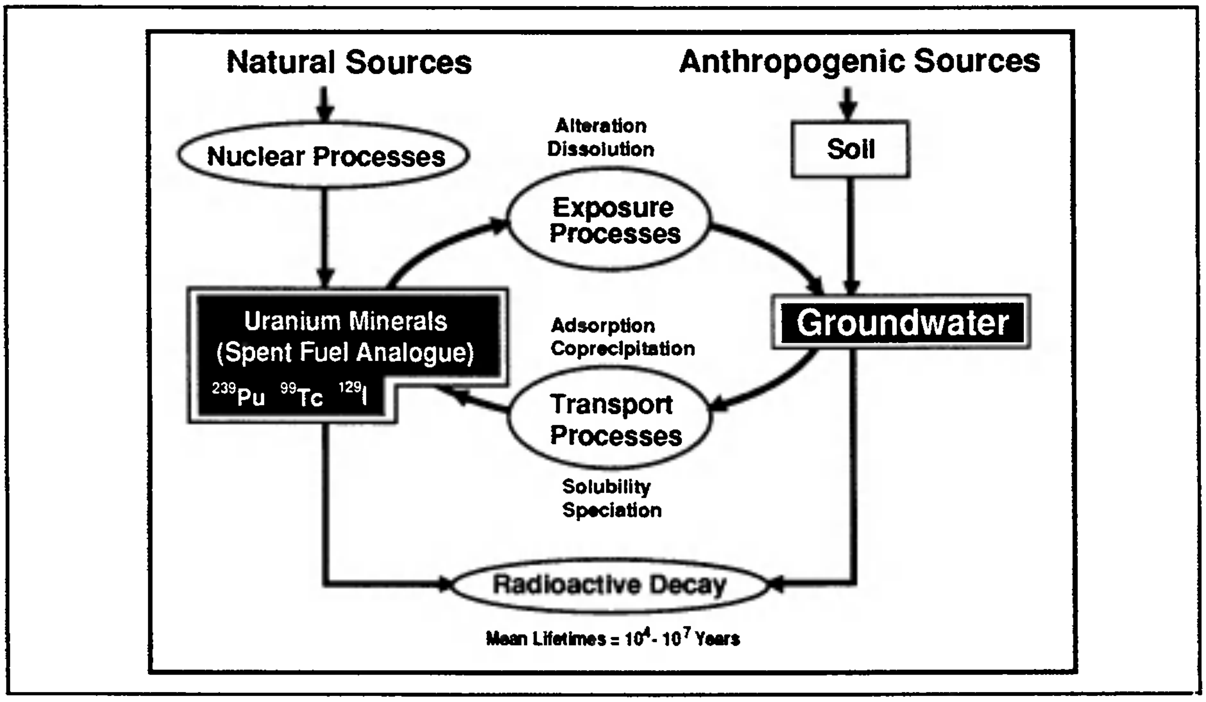

Fig. 1. Juvenile radionuclide geochemical cycle.

rate of radionuclide release can never be faster than the rate of exposure. Hence, measured natural radionuclide release rates are minimum limits on host phase alteration/dissolution rates.

The nuclear products that we are investigating are three of nine radionuclides considered in the aqueous transport scenario of the TSPA, and are thus perfect chemical analogues of the radioactive constituents of spent fuel. However, spent fuel inventories are dramatically different from those in uranium deposits. Model spent fuel inventories are: 12 *Ci* ^{99}Tc/MTHM (metric ton heavy metal), 0.03 *Ci* ^{129}I/MTHM, and 308 *Ci* ^{239}Pu/MTHM. In uranium deposits these radionuclides are present at levels that are about 10^{-12} of their level in spent fuel: approximately 7 *pCi* ^{99}Tc/MTU (metric ton uranium), 0.1 *pCi* ^{129}I/MTU, and 60 *pCi* ^{239}Pu/MTU.

4. Natural radionuclide release rates

Ratios of daughter to parent, ^{99}Tc/U, ^{129}I/U, and ^{239}Pu/U, in a system closed for several half-lives of the daughter, will achieve a state of secular equilibrium in which rates of production and decay are equal. Periods required to achieve secular equilibrium are approximately 10^5 yr for ^{239}Pu, 10^6 yr for ^{99}Tc, and 10^8 yr for ^{129}I. Deviation from secular disequilibrium is produced by open system processes. The degree of disequilibrium may be expressed as a fractionation factor;

$$\alpha = (\text{daughter/parent})_M / (\text{daughter/parent})_{SE} \qquad (1)$$

where M refers to measured abundances of parent and daughter nuclides, and SE refers to secular equilibrium abundances. In a closed system, α is unity. If α is greater than unity, open system processes have enriched daughter relative to parent. If parent is enriched relative to daughter, α is less than unity. A condition of disequilibrium results from three conditions: the system must have been open in the window of time between the present and several daughter half-lives in the past; the process had to proceed at a significantly greater rate than radioactive daughter decay at secular equilibrium; the two nuclides had to be fractionated by the operative physiochemical processes.

A simple mathematical expression can be formulated to determine the rate of the open system processes from measures of α;

$$\Delta = \lambda_d (1-\alpha) \qquad (2)$$

where Δ is process rate, expressed as fraction per year, and λ_d is the radioactive decay constant of the daughter element. Assumptions inherent in this formulation are that Δ is independent of quantity of daughter element, and that disequilibrium is the result of a process, rather than an event (in the sense discussed above with regard to TSPA scenario development). It is impossible to distinguish between an ongoing process, and events that were operative at faster rates for shorter periods of time. Equation (2) is a lower limit on rates of events.

These formalisms are equally applicable to more familiar studies of disequilibrium between radioactive parents and daughters in uranium and thorium decay chains. Significant differences between radionuclides in natural radioactive decay chains and those in our studies are their chemical properties. Long-lived decay products of uranium and thorium are unlikely to meet the assumption that Δ is independent of quantity of daughter element. Most of the decay products have stable or very long-lived primordial components in natural systems. These elements form solid phases, are likely to be sorbed on the surfaces of solid phases, or have radioactive precursor elements that are chemically active, particularly in uranium deposits. In contrast, ^{99}Tc and ^{129}I are likely to be chemically benign. At abundances in nature, solubility is unlikely to be a factor in determining their aqueous concentration. Chemical homologues, which might induce coprecipitation, are rare in most natural systems. The elements are generally poorly sorbed in natural systems. Consequently, we hypothesize that ^{99}Tc and ^{129}I release from their site of production will be the result of the same processes. Their release rate will simply be a function of rate of alteration/dissolution of uranium bearing host phases, and water velocity. If these assumptions are valid, measures of α for ^{99}Tc and ^{129}I directly manifest rates of radionuclide release, as calculated by equation (2). Calculated values of Δ represent lower limits on mineral alteration rates, a critical and highly uncertain parameter in source term models.

Plutonium quantities in uranium ores are so small, that concentrations in groundwaters will always be less than the solubility of primary plutonium solid phases. However, uranium and thorium in various oxidation states are chemical homologues of plutonium, and it is likely that aqueous plutonium concentrations in natural systems are controlled by coprecipitation in secondary minerals of other actinides. In addition, plutonium has variably large sorption coefficients in natural systems. These properties negate assumptions that are the basis for formulating equation (2), and interpretations of ^{239}Pu disequilibrium will not be straightforward.

5. Discussion of results

Inspection of equation (2) demonstrates limits on the ability to quantify radionuclide release rates by measuring disequilibrium of different radionuclides. If α is zero, that is the sample contains no daughter, a lower limit is established on Δ by the decay constant of the daughter nuclide. An upper limit is established by uncertainty in α. If α is unity i.e. if the sample contains secular equilibrium abundance of daughter, then Δ is limited by the uncertainty in the measure of α. Uncertainties in α for these nuclear products are greater than for decay chain radionuclides, because of uncertainties in secular equilibrium abundances[6] and increased analytical uncertainties resulting from the extremely small quantities of these nuclides in nature. Assuming that a state of secular equilibrium can be determined with an uncertainty of 25%, bounding rates for Δ determined by ^{99}Tc are 3.3 x 10^{-6} and 8 x 10^{-7} yr^{-1} and by ^{129}I, 4.3 x 10^{-8} and 1 x 10^{-8} yr^{-1}. It is apparent that if assumptions regarding the validity of equation (2) are correct, there should never be partial disequilibrium of both ^{99}Tc and ^{129}I in the same sample. Process rates that would partially deplete ^{129}I, would be too slow to result in ^{99}Tc disequilibrium. Conversely, processes at rates that would deplete ^{99}Tc to any degree, must occur at a rate that would effectively remove all ^{129}I . This concept is illustrated by plots of Δ vs. (1–α) for ^{99}Tc and ^{129}I in Figure 2. If assumptions of no sorption and no solubility controls are correct, there should be no process that would enrich either of the two radionuclides in solid phases. All ^{99}Tc and ^{129}I removed from host phases should remain in groundwater.

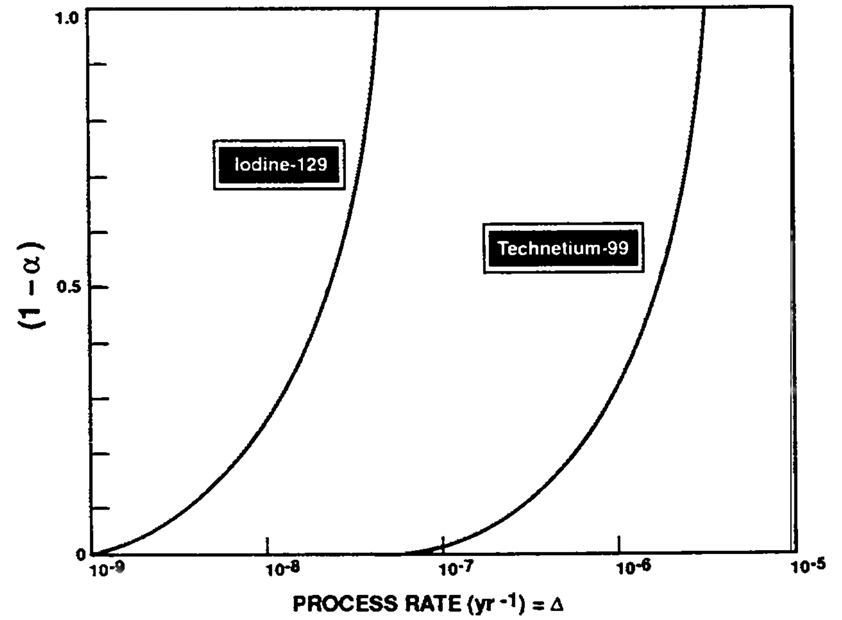

Fig. 2. Graphical representation of the relationship between process rate and fractionation factor for iodine-129 and technetium-99.

An extensive discussion of measurements of α for ^{129}I and ^{239}Pu in uranium deposits may be found in Fabryka-Martin and Curtis.[6] The data provide an opportunity to examine the concepts discussed here. Determinations of α are imprecise because of the inherent difficulty in determining secular equilibrium abundances for products of natural nuclear fission and neutron capture reactions. All analyzed samples from unweathered regions of four uranium deposits contained measurable concentrations of ^{129}I and ^{239}Pu. For ^{239}Pu, α values encompass, or nearly approach, unity, a result that is consistent with ^{239}Pu retention. Samples from a fossil reactor at Oklo, and from the reduced uranium ore body at Cigar Lake, Saskatchewan, Canada, have α values for ^{129}I at or near unity, suggesting release rates $<10^{-8}$ yr^{-1}. Samples from the weathered zone and the underlying altered zone of uranium mineralization at Koongarra, NT, Australia, and from an altered uranium ore body at Key Lake, Saskatchewan, Canada, are partially depleted in ^{129}I. Values of a range from 0.2 to 0.5, suggesting radionuclide release rates around 10^{-8} yr^{-1}. Groundwater from Koongarra deposit contains abundant ^{129}I, consistent with deficiencies in rock.

6. Future work

We are currently developing comprehensive data sets at three deposits: Cigar Lake, an ancient deposit of reduced uranium oxide minerals; Koongarra, a deposit with modern weathering zone; and Oklo, the unique deposit in which ancient natural fission reactions produced natural spent fuels. The diversity of environments provided by these deposits will provide the opportunity to evaluate the concepts put forth in this paper. We are also working on methods to decrease uncertainties in the determination of secular equilibrium values, and to improve the sensitivity of the measurement methods so that they can be used in a greater diversity of geologic settings.

7. Acknowledgements

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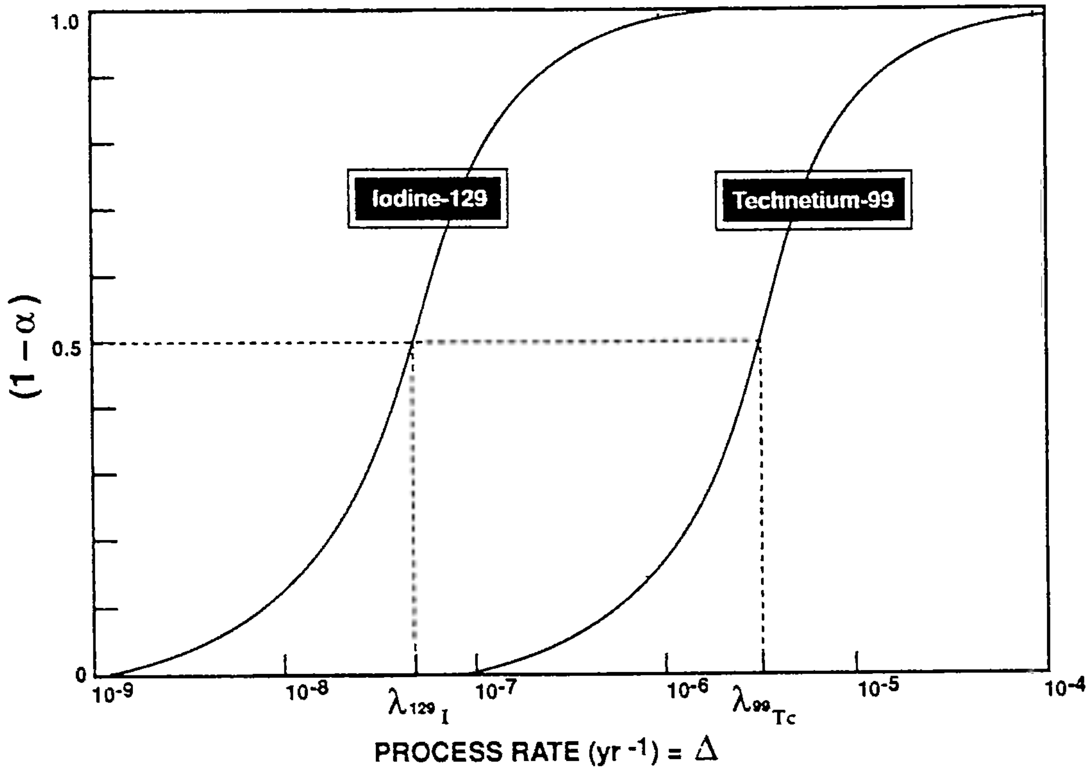
Equation (2) is incorrect. The correct formulation should be:

$$\Delta=\lambda_d(1-\alpha/\alpha) \qquad (2)$$

The correct formulation of Equation 2 assumes that only the daughter radionuclide is removed by an ongoing, continuous process. Δ is the process rate, expressed as the fraction of daughter lost per year. It is impossible to distinguish between losses from a continuous process and episodic losses occurring at faster rates for shorter periods of time. Consequently values of Δ calculated from Equation 2 are lower limits on process rates that preferentially remove daughter radionuclides from their site of production.



Amended Fig. 2. Graphical representation of the relationship between process rate and fractionation factor for iodine-129 and technetium-99.

Because of the error in Figure 2, a correct graphical representation of the relationship between process rate and fractionation factor is shown in the amended version of Figure 2: It is apparent from the figure that for $1 > \alpha > 0.5$, the process rate is $<\lambda 99_{Tc}$, as $\alpha \rightarrow$ unity, $\Delta \rightarrow 0$, the closed system case. For $\alpha < 0.5$, the rate of radionuclide loss is greater than the rate of radioactive decay. Given the current uncertainties in values of α, quantitative estimates can be calculated if ^{99}Tc losses occur at rates between 10^{-5} yr^{-1} and 10^{-6} yr^{-1} and if ^{129}I losses occur at rates between 10^{-7} yr^{-1} and 10^{-8} yr^{-1}. If ^{99}Tc and ^{129}I are being depleted by the same processes, then if $1 > \alpha > 129_{I} > 0$ then $\alpha\ 99_{Tc}$ must equal unity. Conversely if $1 > \alpha\ 99_{Tc} > 0$ then ^{129}I must equal zero.

Acknowledgements: We thank Henry Shaw for pointing out the error in the formulation of Equation 2.

References

1. Radioactive Waste Management Committee of the OECD Nuclear Energy Agency and the International Radioactive Waste Management Advisory Committee of the International Atomic Energy Agency, *Can long-term safety be evaluated,* **NAGRA bulletin, 1/1992**, pp. 4–21.

2. Ewing, Rod, *Natural systems prediction of radionuclide migration,* **Proceedings of the third International symposium on advanced nuclear energy research – Global environment and nuclear energy**, March, 1990.

3. R. W. Barnard, M. L. Wilson, H. A. Dockery, J.H. Gauthier, P.G. Kaplan, R.R. Eaton, F.W. Bingham, and T. H. Robey, *An initial total-system performance assessment for Yucca Mountain,* Sandia Report, SAND91-2795-UC-814.

4. Richard Kossik, Ian Miller, and Mark Cunnane, *Integrated performance assessment model for waste package release and radionuclide release,* **Proceedings of the Third International Conference on High Level Radioactive Waste Management**, Las Vegas, Nevada, April 12–16,1992, 2, pp. 1786-1791.

5. Meijer, A., *A strategy for the derivation and use of sorption coefficients in performance assessment calculations for the Yucca Mountain site,* in **Proceedings of Workshop on Radionuclide Adsorption** held in Los Alamos, NM, September 11–12, 1990, LA-UR-91-3747, Los Alamos National Laboratory, Los Alamos, NM

6. Fabryka-Martin, June, and David Curtis, *Uranium orebodies as source terms for radionuclides: measurements and models,* **Proceedings of 5th natural analogue working group meeting** held October 5–9, 1992, Toledo, Spain.

PERFORMANCE ASSESSMENT SIGNIFICANCE OF NATURAL ANALOG STUDIES AT PENA BLANCA, MEXICO, AND AT SANTORINI, GREECE

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ABSTRACT: The Nopal I uranium deposit at Peña Blanca, Mexico, and the Akrotiri archaeological site at Santorini, Greece, are being studied as natural analogs of the proposed high-level nuclear waste repository at Yucca Mountain, Nevada, U.S.A. Reliable transfer of information from the analog studies in support of repository performance assessment modeling is likely to be enhanced because of similarities in the physical settings among the analogs and the proposed repository. All sites are above the water table in silicic tuffaceous environments in relatively dry climates. Technical issues in performance assessment modeling of a geologic repository for nuclear waste include the source term and the processes of contaminant transport. Uranium mineralization at Peña Blanca provides the opportunity to study mechanisms of the alteration of uraninite (an analog of spent nuclear fuel) and controls on uranium solubility, which are processes likely to affect the source term. Uranium distribution at Peña Blanca and the rate and mechanism of uranium transport over geologic time scales can contribute to an understanding of contaminant transport. The geochemical environment of buried archaeological artifacts at Santorini is likely to provide a record of trace element migration from well constrained and exotic sources over a well defined period of time with repository significance (3600 years). Trace contaminant transport processes can be investigated, and in particular, it is anticipated that transport models of significance to performance assessments can be exercised and tested using data from the Santorini site.

1. Introduction

In the Nuclear Waste Policy Act of 1982, as amended in 1987, the government of the United States of America mandated investigation of Yucca Mountain, Nevada, as the sole national candidate site for permanent disposal of high-level nuclear waste (HLW). The United States Environmental Protection Agency (EPA) regulations stipulate that compliance with HLW cumulative release requirements for a period of 10,000 years is to be demonstrated by performance assessments. Performance assessment analyses are to identify all significant processes and events and to examine their effects on the performance of the disposal system. Regulations promulgated by the United States Nuclear Regulatory Commission (NRC) require that predictive analyses and models developed by the repository license applicant (e.g., the U.S. Department of Energy) shall be supported by an appropriate combination of methods such as field, laboratory, and natural analog studies. Furthermore, the demonstration of compliance with objectives and criteria for repository performance over long times in the future is stipulated to involve use of predictive models that are supported by such measures as field, laboratory, and natural analog studies.

Despite clear philosophical (e.g., Ewing, 1992; Petit, 1992), technical (e.g., McKinley, 1989), and regulatory bases for natural analog studies, tenable information transfer from analog systems to repository modeling is a persistent challenge. Difficulties arise in the characterization of complex natural analog and repository systems (e.g., initial and boundary conditions for relevant processes) and in accommodation for differences between analog and repository systems. Predictive models for repository performance depend on the characteristics and properties of the natural repository setting. Therefore, applicable and justifiable support for these models is best provided by natural analog studies conducted in environments that are similar to the repository setting and that permit identification and quantification of processes of significance to repository performance.

Yucca Mountain is located 150 kilometers northwest of Las Vegas, Nevada, on federal land that includes part of the Nevada Test Site, the national reservation for nuclear weapons testing. The geologic setting of the proposed repository at Yucca Mountain consists of fractured, silicic, volcanic tuffs, above the permanent water table, in a region of arid to semiarid climate (DOE, 1988). The silicic tuffs are variously glassy, devitrified to alkali feldspar and silica polymorphs, or altered to a zeolitic assemblage, and have a minimal reducing capacity (e.g., Broxton et al., 1987; Bish and Chipera, 1989). The vadose zone gas is rich in oxygen and carbon dioxide, and the vadose zone water is a dilute, oxidizing, Na-bicarbonate solution (e.g., Kerrisk, 1987; Thorstenson et al., 1990; Yang, 1992).

The selection of two areas for natural analog research by the Center for Nuclear Waste Regulatory Analyses (CNWRA) has been guided by the geological, geochemical, hydrologic, and climatic characteristics of the candidate repository environment at Yucca Mountain and recognition of processes that are likely to affect repository performance. Sites at Peña Blanca, Mexico, and at Santorini, Greece, are both in oxidizing, unsaturated, silicic volcanic environments in relatively dry climates (Murphy et al., 1991). Technical issues in performance assessment modeling of a geologic repository for nuclear waste include the source term and the processes of contaminant transport. Uranium mineralization at Peña Blanca provides the opportunity to study mechanisms of the alteration of uraninite (an analog of spent nuclear fuel) and controls on uranium solubility, which are processes likely to affect the source term. Uranium distribution at Peña Blanca and the rate and mechanism of uranium transport over geologic time scales can contribute to an understanding of contaminant transport. The geochemical environment of buried archaeological artifacts at Santorini is likely to provide a record of trace element migration from well constrained and exotic sources over a well defined period of time with repository significance (3600 years). Trace contaminant transport processes can be investigated, and in particular, it is anticipated that transport models of significance to performance assessments can be exercised and tested using data from the Santorini site.

The object of this communication is to describe CNWRA natural analog investigations at Peña Blanca and at Santorini with an emphasis on the identification of analog information that may be useful in support of performance assessment models for the proposed Yucca Mountain repository. Table I displays a list of general issues in performance assessment modeling correlated with anticipated and possible contributions to resolution of these issues through natural analog research at Peña Blanca and at Santorini. The following sections of this report provide descriptions of the manner in which issues in Table I are being addressed in the context of a general introduction to the two analog study areas.

Table I. Performance Assessment Significance of Peña Blanca and Santorini analogs

PERFORMANCE ASSESSMENT ISSUES	ANALOG SYSTEMS	ANTICIPATED CONTRIBUTIONS TO PERFORMANCE ASSESSMENT	POSSIBLE CONTRIBUTIONS TO PERFORMANCE ASSESSMENT
Spent fuel properties and stability/ source term	Peña Blanca	•Model for rate-limiting source-term processes •Mechanisms of alteration of uraninite •Secondary mineralogy	•Primary and secondary phase properties
Container performance	Santorini		•Corrosion rates and mechanisms
Fluid flow and transport processes	Peña Blanca	•Characterization of flow systems affecting uraninite alteration and uranium transport	•Water chemistry •Unsaturated system processes •Migration of chemical homologs
	Santorini		•Applications and evaluations of transport models •Migration of chemical homologs

2. Peña Blanca

Research at Peña Blanca has focused on a uranium deposit at the Nopal I site where a suite of uranium minerals and their geologic environment have been well exposed by interrupted mining operations. Geologic, petrographic and mineralogic relations at Peña Blanca have been summarized by Calas (1977), Goodell (1981), Ildefonse et al. (1990), and George-Aniel et al. (1991). Current research confirms many of the conclusions reached by these authors concerning the geologic setting and paragenesis of uranium mineralization at Peña Blanca (e.g., Pearcy et al., 1992).

A large mass of oxidized uranium (e.g., 320 metric tons; George-Aniel et al., 1991), occurring mostly as uranophane, weeksite, soddyite, and schoepite encloses small (e.g., centimeter scale) remnant pods of reduced uranium as partially oxidized uraninite at Nopal I. Textural relations indicate that uraninite formed during primary hydrothermal mineralization and that subsequent alteration led to generation of the secondary uranyl silicate and oxide phases. Preservation of the secondary assemblage indicates that the rate of uraninite oxidation, dissolution, and growth of the secondary uranyl oxide and silicate minerals must have exceeded the rate of dissolution of the secondary phases and transport of uranium out of the system. The rate-limiting step for uranium migration appears to have been advective transport in groundwaters with uranium contents controlled by interactions with uranyl silicate minerals such as uranophane (Murphy and Pearcy, 1992). Analogous rate-limiting processes are likely to affect the source term for contaminant release in a repository at Yucca Mountain, and should provide realistic constraints on source term modeling.

Uraninite at Nopal I typically occurs in fractures but is also present in the matrix of host rock fragments where it has apparently replaced feldspar. X-ray diffraction data for uraninite from Nopal I show that most uraninite is oxidized to $UO_{2.25}$ with a lesser amount of $UO_{2.33}$. Microprobe analyses of uraninite reveal significant concentrations of Si (0.46 to 2.64 atom percent), Al (0.01 to 0.77 atom percent), and Ca (1.39 to 1.77 atom percent) (Pearcy et al., 1992). These elements may be present in mineral phases that are intergrown with the uraninite at a scale too small to be differentiated by scanning electron microscopy, or these elements may be incorporated by solid solution into the uraninite structure. The structure and composition of partially oxidized uraninite at Peña Blanca are likely to be analogous to altered spent nuclear fuel in the Yucca Mountain environment.

Oxidation of the Nopal I uraninite has produced a coherent sequence of secondary uranyl oxide and uranyl silicate minerals (e.g., Ildefonse et al., 1990; Pearcy et al., 1992; Leslie et al., 1992). Uranyl oxide hydrates are the earliest minerals in the alteration sequence and occur as direct replacements of uraninite and in voids rimmed by uraninite. Uranyl oxide hydrates are subsequently replaced by uranyl silicates. Uranophane is the predominant uranyl silicate with lesser amounts of soddyite, weeksite, and boltwoodite. This pattern of alteration and suite of secondary minerals are close analogs of spent fuel alteration under similar conditions. Notably, uranophane and uranyl oxide hydrates and other silicates have been detected in experimental studies of the alteration of spent nuclear fuel and UO_2 at 85° to 90°C in water related to the Yucca Mountain environment (Wilson and Bruton, 1989; Wronkiewicz et al., 1992). Convergence of results for mechanisms of UO_2 alteration among experimental and natural analog studies provides a measure of confidence in repository related models for spent fuel alteration that invoke these mechanisms.

The host rocks at Peña Blanca and at Yucca Mountain are commonly fractured, particularly in welded zones. A subset of the fractures at Peña Blanca shows signs of hydrothermal or low-temperature alteration. Late occurring processes that may have occurred under unsaturated conditions, e.g., those associated with caliche, appear to be concentrated along the latest through-going fractures. Larger scale field evidence in the form of seeps and springs emanating at surface manifestations of fractures indicates the presence of a discontinuous, ephemeral, perched water table that roughly mimics the topography. These observations suggest that connectivity of fracture porosity is a key factor controlling episodic, unsaturated fracture flow in the Peña Blanca environment. Studies of the effects of this hydrologic system on uraninite alteration and uranium transport at Peña Blanca should elucidate analogous processes in a repository at Yucca Mountain and aid development of transport models.

The margins of the orebody at Nopal I are sharp. The transition to unmineralized tuff occurs over a distance of about 0.5 meter as indicated by field and laboratory gamma ray measurements. Relatively minor amounts of uranium are present outside the central orebody. The distribution of uranium outside the orebody is related to the presence of discrete fractures and inferred fracture zones. It is interpreted that flow of primary uranium-bearing fluids was largely restricted to the permeable zone of the central orebody, with later redistribution of uranium caused by fluid movement along fractures that intersect the orebody. Field observations of rock alteration indicate movement of fluids through the matrix of the host rocks perpendicular to the fractures along which uranium was transported. This alteration suggests that uranium was transported through the rock matrix as well as along fractures, which is consistent with the occurrence of uranium minerals within the orebody as pervasive replacements of pre-existing minerals in a pattern unrelated to fractures.

The great similarity of present geochemical, structural, and hydrological environments at Yucca Mountain and Peña Blanca prompts interest particularly in processes that have occurred recently. Investigations of uranium and thorium series disequilibrium relations among the alteration phases at Nopal I are being conducted to identify systems that have been open over the last 10^3 to 10^6 years, and to attempt to provide constraints on the rate of contaminant transport. These studies should permit identification of chemical and transport processes that have occurred in the present environment, and by analogy, under conditions similar to those in a geologic repository at Yucca Mountain.

In summary, information obtained from the Peña Blanca analog with regard to rate-limiting processes, the nature of uraninite oxidation, and the paragenesis of secondary oxidized minerals offer clear support for source term modeling for performance of the spent fuel waste form proposed for the Yucca Mountain repository. Furthermore, the convergence of results from analog and laboratory studies offers a measure of validation for models of the processes of spent fuel alteration. Information on fluid pathways for uranium transport at Peña Blanca, the distribution of uranium, and the timing and rate of migration provides clear support for development of models for contaminant transport at the proposed repository at Yucca Mountain.

3. Santorini

Approximately 3600 years ago, 30 to 40 cubic kilometers of silicic volcanic ash erupted from a volcano in the Aegean Sea enlarging a caldera, one rim of which now forms the island of Santorini (Manning, 1990; Hubberton et al., 1990; Sigurdsson et al., 1990; Pyle, 1990; Heiken and McCoy, 1984). A Minoan city on the Akrotiri peninsula of the island was buried in the tuffs of the eruption and has now been partially excavated. The archaeologic research site is located approximately seven meters above the present groundwater table and less than five meters below the present ground surface. An ephemeral stream flowed over and through portions of the presently excavated city, although the stream is now diverted. The Minoan people living at Akrotiri apparently anticipated the eruption and fled the island leaving numerous artifacts which have been discovered among their partially collapsed buildings. A survey of the excavations, examination of the records of archaeological digs over the past decades, and, particularly, discussions in the field with the director of the investigations at Akrotiri, Professor Christos Doumas of the University of Athens, have led to the identification of sites where artifacts were buried in proximity to the pre-Minoan volcanic rocks. Trace element migration from these artifacts may provide a well constrained data base for validation of models for elemental transport in this unsaturated, silicic volcanic environment over a period of thousands of years.

A hoard of artifacts was discovered in September of 1970 in room 3 of the Delta (Δ) house at Akrotiri. It comprises three ewers, two baking dishes, and one goblet all made of bronze, and other lead and stone artifacts. The bronzes were extracted from an area between the collapsed first story floor of room $\Delta3$ and an earthen floor of the ground level, which was packed on an excavated surface of silicic tuffaceous rock of the pre-Minoan volcanic series. Material enclosing the bronzes consisted of collapsed building debris (volcanic rock and earth), ash from the Minoan eruption which filtered into the buildings through doors and windows, and alluvial sediments deposited by the ephemeral stream that passed over and adjacent to room $\Delta3$ subsequent to the Minoan eruption.

The bronze artifacts, which are on display at the National Archaeological Museum in Athens, range up to 50 centimeters in maximum dimension. Although they have been severely corroded, their original cumulative mass is estimated grossly at twenty kilograms. Perhaps one third of their original mass has been removed. The distribution of the lost material is presently unknown in detail. Some, perhaps much of it, was discarded with earth and rock materials excavated from the immediate vicinity of the artifacts. However, leaching tests on selected earth and rock samples collected from the floor of room $\Delta3$ are being conducted to detect a contaminant plume that may have emanated from the artifacts.

A fundamental component of predictive assessments of repository performance at Yucca Mountain is a model for trace element transport in an unsaturated silicic tuff. Given initial and boundary conditions, differential equations describing flow and transport are solved to obtain the distribution of chemical species as a function of time. A model for trace element migration at the $\Delta3$ site is under development to enable predictions of the current distribution of contaminant species. Site investigations will provide best estimates of the properties of the system and its evolution and will be used to establish initial and boundary conditions for the model. Effects of variations in parameters, and initial and boundary conditions will be tested to explore the range of possible distributions predicted by the model. The well constrained location of the contaminant source, the well constrained time scale for transport processes, and the relatively well known physical characteristics of the site should facilitate development of models for contaminant transport using the tools provided by and for repository performance assessment modeling.

Following model development and determination that a contaminant plume is discernible, a systematic sampling of the tuffaceous materials surrounding the Δ3 room is proposed. Materials will be analyzed and the extent of the plume will be mapped. Detailed comparisons of model results and plume properties will contribute to validation of the modeling. Further characterization of the plume should provide basic information on contaminant transport mechanisms such as transport pathways and sorption processes.

4. Discussion

Natural analogs can contribute to nuclear waste repository performance assessment modeling both by providing qualitative identification of processes and by contributing to quantitative model validation. Model validation requires confirmation that models include correct and significant components, and that models provide quantitative predictions within the required limits of accuracy or conservatism. Validation of models must occur over the range of parameters, conditions and processes of significance for repository performance. Modeling must be site specific in most respects, because of the unique geochemical, hydrological, and geological features of each geologic repository site. Physical and temporal similarities of analog and repository sites and systems augment the range of useful model support and validation. In general, transfer of information from analog systems is enhanced in studies of well constrained systems and in studies where the similarity of systems is high.

As illustrated in Table I, analog sites at Peña Blanca and Santorini are complementary in the types of information that are likely to be extracted and applied to support performance assessment for the proposed repository at Yucca Mountain. Two technical issues of particular concern in performance assessment modeling of a geologic repository for nuclear waste are the source term and the processes of contaminant transport. As described above, source-term constraints can be derived at the Peña Blanca site through evaluations of the mechanisms of uraninite alteration and the rate-controlling processes for uranium transport out of the mineralized zone. Identification and characterization of flow paths, decay series isotopic studies, and the distribution of uranium in solid minerals at Peña Blanca also contribute to an understanding of transport processes that would affect waste isolation at a Yucca Mountain repository. Detailed observations of contaminant migration from artifacts at Santorini should yield information on transport processes and provide a particularly well constrained test example for model validation exercises.

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References

Bish, D.L., and Chipera, S.J. (1989) Revised mineralogic summary of Yucca Mountain, Nevada. Los Alamos National Laboratory LA-11497-MA, UC-271, 68 pp.

Broxton, D.E., Bish, D.L., and Warren, R.G. (1987) Distribution and chemistry of diagenetic minerals at Yucca Mountain, Nye County, Nevada. Clays and Clay Min., v. 35, p. 89-110.

Calas, G. (1977) Les phénomènes d'altération hydrothermale et leur relation avec les minéralisations uranifères en milieu volcanique: Le cas des ignimbrites tertiaires de la Sierra de Peña Blanca, Chihuahua (Mexique). Sciences Géologiques Bull., v. 30-1, p. 3-18

DOE (1988) Site characterization plan. Department of Energy, DOE/RW-0199, 8 volumes.

Ewing, R.C. (1992) The role of natural analogues in performance assessment: Applications and limitations. High Level Rad. Act. Waste Mgmt. Proc., Amer. Nucl. Soc., p. 1429-1436.

George-Aniel, B., Leroy, J.L., and Poty, B. (1991) Volcanogenic uranium mineralizations in the Sierra Peña Blanca district, Chihuahua, Mexico: Three genetic models. Econ. Geol., v. 86, p. 233-248.

Goodell, P.C. (1981) Geology of the Peña Blanca uranium deposits, Chihuahua, Mexico. In Goodell, P.C., and Waters, A.C. (eds.) Uranium in Volcanic and Volcanoclastic Rocks. AAPG Studies in Geology, no. 13, p. 275-291.

Heiken, G., and McCoy, F. Jr. (1984) Caldera development during the Minoan eruption, Thera, Cyclades, Greece. Jour. Geophys. Res. v. 89, B10, p. 8441-8462.

Hubberton, H.-W., Bruns, M., Calamiotou, M., Apostolakis, C., Filippakis, S, and Grimanis, A. (1990) Radiocarbon dates from the Akrotiri excavations. In Hardy, D.A. (ed.) Thera and the Aegean World III. The Thera Foundation, London, v. 3, p. 179-187.

Ildefonse, P., Muller, J.-P., Clozel, B., and Calas, G. (1990) Study of two alteration systems as natural analogues for radionuclide release and migration. Engineering Geol., v. 29, p. 413-439.

Kerrisk, J.F. (1987) Groundwater chemistry at Yucca Mountain, Nevada, and vicinity. Los Alamos National Lab., LA-10929-MS, 117 pp.

Leslie, B. W., Pearcy, E. C., and Prikryl, J. D. (1992) Geochemical natural analogs. In Patrick, W.C. (ed.) NRC High-Level Radioactive Waste Research at CNWRA January 1 through June 30, 1992. CNWRA 92-01S, p. 7-1 to 7-18.

Manning, S.W. (1990) The eruption of Thera: Date and implications. In Hardy, D.A. (ed.) Thera and the Aegean World III. The Thera Foundation, London, v. 3, p. 29-40.

McKinley, I.G. (1989) Applying natural analogues in predictive performance assessment. In Saltelli, A. (ed.) Risk Analysis in Nuclear Waste Management, ECSC, Brussels, p. 359-375.

Murphy, W.M., and Pearcy, E.C. (1992) Source-term constraints for the proposed repository at Yucca Mountain, Nevada, derived from the natural analog at Peña Blanca, Mexico. Mat. Res. Soc. Symp. Proc. v. 257, p. 521-527.

Murphy, W.M., Pearcy, E.C., and Goodell, P.C. (1991) Possible analog research sites for the proposed high-level nuclear waste repository in hydrologically unsaturated tuff at Yucca Mountain, Nevada. Fourth natural analogue working group meeting and Poços de Caldas project final workshop, Commission of the European Communities Report EUR 13014 EN, p. 267-276.

Pearcy, E.C., Murphy, W.M., Green, R.T., Leslie, B.W., and Prikryl, J.D. (1992) Geochemical natural analogs. In Patrick, W.C. (ed.) Report on Research Activities for Calendar Year 1991. CNWRA 91-01A, p. 7-1 to 7-32.

Petit, J.-C. (1992) Reasoning by analogy: rational foundation of natural analogue studies. Applied Geochem., Sup. Issue 1, p. 9-11.

Pyle, D.M. (1990) New estimates for the volume of the Minoan eruption. In Hardy, D.A. (ed.) Thera and the Aegean World III. The Thera Foundation, London, v. 2, p. 113-128.

Sigurdsson, H., Carey, S., and Devine, J.D. (1990) Assessment of mass, dynamics and environmental effects of the Minoan eruption of Santorini Volcano. In Hardy, D.A. (ed.) Thera and the Aegean World III. The Thera Foundation, London, v. 2, p. 100-112.

Thorstenson, D.C., Weeks, E.P., Haas, H., and Woodward, J.C. (1990) Physical and chemical characteristics of topographically affected airflow in an open borehole at Yucca Mountain, Nevada. Proc. Nuclear Waste Isolation in the Unsaturated Zone Focus '89, Amer. Nuclear Soc., p. 256-270.

Wilson, C.N., and Bruton, C.J. (1989) Studies on spent fuel dissolution behavior under Yucca Mountain repository conditions. LLNL preprint UCRL-100223, 19 pp.

Wronkiewicz, D.J., Bates, J.K., Gerding, T.J., Veleckis, E., and Tani, B.S. (1992) Uranium release and secondary phase formation during unsaturated testing of UO_2 at 90°C. Jour. Nucl. Mater., v. 190, p. 107-127.

Yang, I.C. (1992) Flow and transport through unsaturated rock -- data from two test holes, Yucca Mountain, Nevada. High Level Rad. Act. Waste Mgmt. Proc., Amer. Nucl. Soc., p. 732-737.

NATURAL ANALOGUE WORKING GROUP MEETING

NATURAL ANALOGUE SYSTEMS: PALAEOHYDROGEOLOGY

Time-scale effects in hydrogeology
E. Ledoux[1] and G. de Marsily[2]
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A hydrogeologic analysis of uranium ore formation in proterozoic sedimentary basins
G. Garven and J.P. Raffensperger, The Johns Hopkins Univ. (USA)

Evolution of porewaters in mudrocks
A.H. Bath, BGS (UK)

Validation of hydrogeochemical codes using the New Zealand geothermal system
W. Glassley, LLNL (USA)

TIME-SCALE EFFECTS IN HYDROGEOLOGY

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ABSTRACT

In low permeability media, flow and transport conditions may more often than not be in a state of non-equilibrium because of relatively recent geologic changes to which these media have been subjected and which may still be influencing the behaviour of the system. Our predictions of its future behaviour could be very much in error if what we observe today were interpreted as a stable situation, thus ignoring the very long transient response of such systems. However, such transient behaviours can be of great interest for the validation of our models, if we can use them to reconstruct the present observed state of the systeme, as the calculated result of the succession of events that have occured in the past. In particular, if the transport models used to predict movements of radionuclides in the geosphere were also used to reconstruct the transient movements of those chemical species or environmental tracers, that are active on the sites considered as potential repositories, this would constitue a great step forward in the validation and confidence build-up of these models and the resulting performance assessments.

Examples are given of transient behaviour and use of chemical species migration in the Belgian Boom Clay and the Paris Basin.

1. Introduction

It is known that in low permeability media and/or large aquifer systems non-equilibrium conditions could exist even if present observations show constant measurements with time. This is due to the slow transmission of perturbations in such systems and to the relatively short duration of our observations.

As an example Dieng et al. (1990) reported that the famous piezometric depression of the Ferlo in the Senegal Basin, which is a closed cone 40 m below sea level, can be explained by the change in the sea level that occured about 12,000 years ago as a result of the melting of the ice. The relatively large distance to the sea and the relatively low hydraulic conductivity of the medium combined to the small rate of recharge of the aquifer explain why the depression is still filling up today. But this process is so slow that the rate of filling cannot be detected at the historic scale.

Orders of magnitude of time laps needed for the transmission of perturbations in an aquifer system can be obtained from the equations describing the transfer phenomenon which is considered. For instance, for water movement, the diffusivity equation shows that the steady state is reached when thousands of years, so that a true steady state was reached which had, for example, a more or less constant head profile in the Boom clay (figure 2, profile 1). Suppose then that 10,000 years ago, the ice melted and that the head in the Rupelian aquifer fell almost instantly to its present value. This "perturbation" will slowly propagate itself through the Boom clay, and the present head profile in the clay could be the second one shown in figure 2. This is a transient profile, the final steady-state value has not yet been reached.

This hypothetical example does not by any means prove that the Boom clay is in a transient state of flow at present ; it only shows that the apparent discrepancy between two values for the hydraulic conductivity of the clay, determined by two different methods, could be made consistent if paleohydrogeological processes are considered.

One way to determine which is the good hypothesis would be to get undisturbed piezometric measurements inside the clay. A second way would be to adress another phenomenon linked to water movement such as the transport of environmental tracers. We shall given an example of the use of such data in the Paris basin.

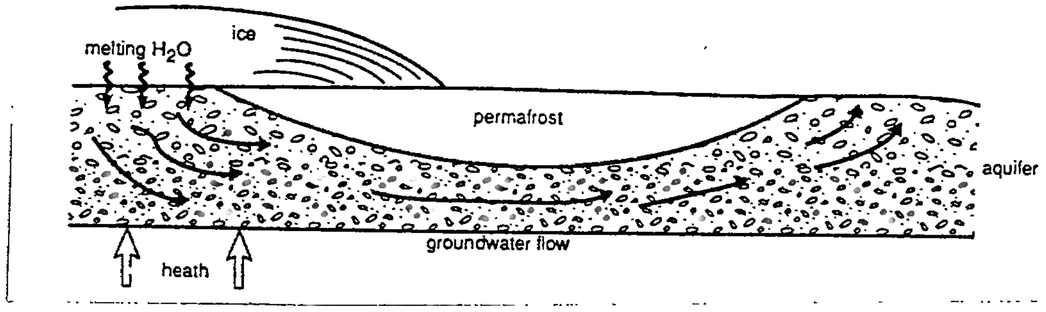

Fig. 1. Groundwater flow under (semi) artic conditions (after Glasbergen, 1990)

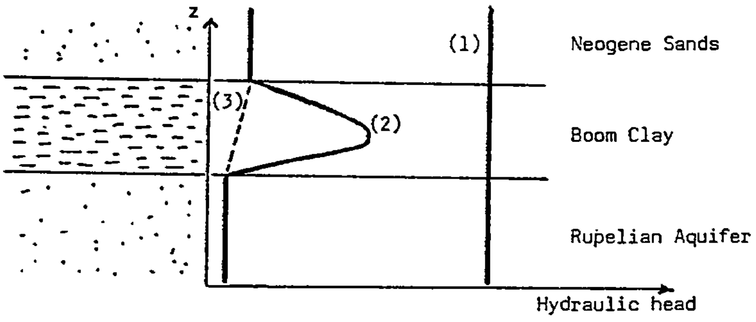

Fig. 2. Possible piezometric profiles in the Boom Clay :

(1) Initial steady state profile during glaciation
(2) Possible present transient profile
(3) Final steady state profile.

the elapsed time since the start of perturbation is larger than $t = \frac{x^2 S}{T}$ where x is the distance, T the transmissivity and S the storage coefficient. Chosing representative values for a phreatic aquifer ($T = 10^{-4}$ m^2/s ; $S = 0,01$ and $x = 100 \times 10^3$ m) one obtains $t \simeq 30,000$ years. If we now consider the advective transport through a clay layer, a tracer will move in about 30,000 years through a medium 100 m thick, if the permeability is 10^{-10} m/s, the kinetic porosity is 0.1 and the hydraulic gradient is 0.01.

These numerical values are in the range of those of a potential host rock for waste disposal. It is then clear that "recent" geological events such as those which have occured since the last glaciations can still have an effect on the behaviour of the systems and thus must be considered in safety analysis.

We shall give two examples of such a behaviour, one in the Boom Clay in Belgium and the other in the Basin of Paris.

2. Transient behaviour of a clay layer

We shall considerer the hypothetical example of the Boom Clay which is a potential host rock formation for nuclear waste disposal. The 100 m thick Boom clay is surrounded by two aquifers, the Neogene sands above and the Rupelian sands below. Piezometric surveys in each aquifer show that, in the central part of the system, the head in the upper aquifer is higher than the one in the lower aquifer by approximately 2 to 5 m ; under steady state assumptions, this would mean that the leakage flux from one aquifer to the next through the Boom clay must be oriented downwards in that area.

A steady-state multilayered aquifer model (Patyn, 1985 ; Patyn and al., 1990) was fitted on the observed piezometric data. A permeability of 10^{-10} m/s for the clay was necessary to obtain the needed leakage in the steady-state assumption. This value was regarded as controversial since most laboratory measurements gave values in the order of 10^{-12} m/s. This discrepancy can be explained invoking a scale effect between the measurements on small cores and average values on meshes of several kilometers used by the model. It can be also explained considering that the steady-state assumption is wrong.

Recent studies in the Netherlands concerning the hydrologic regime during a glaciation have produced the following plausible scenario (Glasbergern, 1990) : when the permafrost develops in front of and around the edge of an ice cap during a glaciation, the upper aquifers of the systeme become frozen ; however, further upstream, beneath the ice cap, the insulating quality of the ice prevents the ground from freezing and high water pressures develop, in equilibrium with the thickness of the ice (figure 1). The water is then forced to flow deep into the ground, in the lower aquifers, below the permafrost. Suppose that, due to the permafrost in the upper Neogene aquifer, the flow of water was much higher in the lower Rupelian sands 100,000 years ago. In that case, we can assume that the head in the lower Rupelian sands was 100 m above its present value and that it remained identical for tens of

3. Validation of low flow velocity in a deep aquifer

In recent years, the hydrology of the deep aquifers of the Paris basin has attracted continuous interest. One reason for this is the development of the geothermal resources of the Dogger and Triassic aquifers for space heating in the Paris area. Wei (1990), Wei et al. (1990) developed a multilayered aquifer model of the entire Paris basin, representing six successive aquifers : Triassic, Dogger, Lusitanian, Portlandian, Neocomian and Albian. Between each of these aquifers, low permeability layers form aquitards, through which vertical leakage fluxes can occur, as in the case of the Boom clay. The hydrologic model was calibrated by trial and error, based on the following information :

- piezometric measurements in each aquifer ;
- transmissivity data from pumping tests in each aquifer ;
- estimates of the recharge rates on the outcrops of each aquifer.

The uncertainty in the true parameter values after calibration was, however, considered important, given the paucity of hydrologic data and the large number of unknowns : since the transmissivity and storage coefficient of each aquifer and the vertical hydraulic conductivity and specific storage coefficient of each aquitard are all potentially variable in space. Three environmental tracers were used to try to validate the flow model : Sodium Chloride, Helium and ^{14}C.

We will discuss here the use of ^{14}C for the validation of the very low flow velocity that was obtained from the hydrodynamical model. A dozen measurements of ^{14}C in the water of the Dogger aquifer were available. Given the half-life of ^{14}C (5,570 years), the only possible origin of ^{14}C in the Dogger water is the recharge on the outcrops because the transit time of the leakage water through the Liassic aquitard is too long to contain any ^{14}C. If the flow model is able to reproduce the observed C^{14} content of the Dogger, it will bring a partial validation of the recharge rate and water velocity in this formation.

The measured ^{14}C concentrations are very small giving groudwater ages between 22,000 and more than 40,000 years which is the detection limit. However, a consistent picture from a few repeated measurements shows that there is a measurable gradient in ^{14}C ages in the Dogger towards the center of the basin.

The convective transport of decaying ^{14}C was calculated with the model, and the product thickness $*$ porosity was adjusted so that the calculated ^{14}C concentrations matched the observed ones. Figure 3a and b show the calculated and measured ^{14}C concentrations and the adjusted effective thickness of the aquifer, assuming a constant porosity value of 15 % (value measured on cores in the center of the basin). This adjusted effective thickness is in good agreement with the measured value at the center of the basin, and its reduction towards the periphery is consistent with what is known of the aquifer.

The unquestionable evidence of ^{14}C deep in the center of the Paris Basin, in the Dogger, which initally came as a great surprise, forced us to admit that the Dogger was indeed a flowing system and not a confined and immobile one. This information is of interest for the estimation of groundwater travel times in a near-by aquifer, if for example a waste disposal site were to be considered in the Liassic formation.

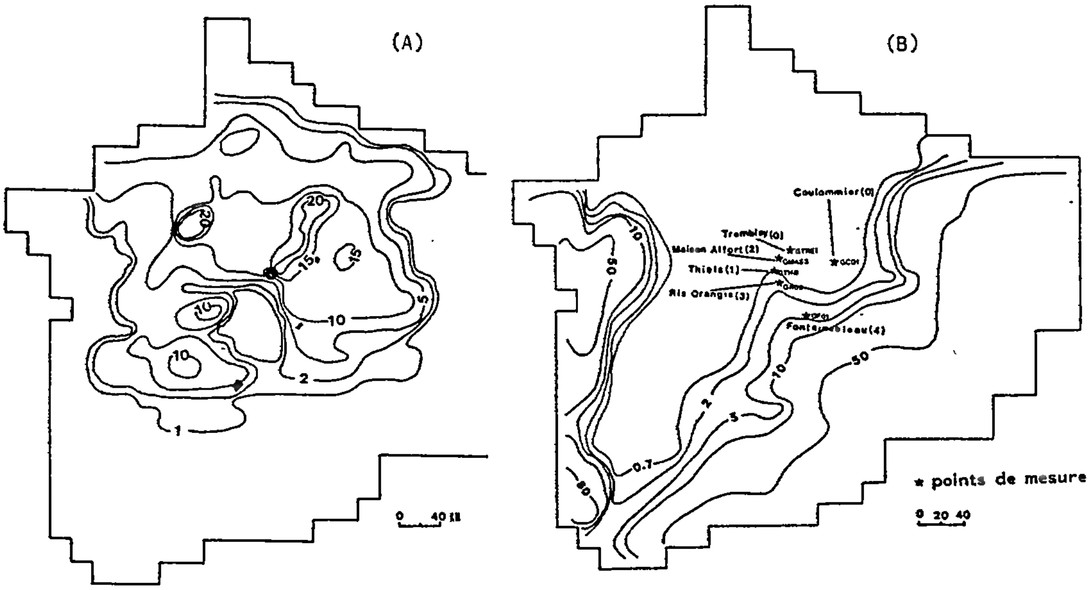

Fig. 7. (after WEI, 1990)

A : effective thickness of the Dogger, m, calculated from the ^{14}C data

B : measured and calculated ^{14}C activity in the Dogger, in % modern ^{14}C

4. Conclusion

Paleohydrogeological story of an aquifer system leads to difficulty when interpreting the present state which can be observed. Particularly the behaviour of low permeability media which are considered in waste disposal can be predicted on a wrong way if we ignore the transient response of the system.

However the simulation of transient behaviour adressing long duration transport phenomena can be very useful if one can show that the present can be correctly reconstructed as the calculated results of events that have occured in the past. The ability of reconstructing the post is a way to convince that the dominant natural features of a site have been incorporated into the model.

References

Dieng, B., Ledoux, E., Marsily, G. de : "Paleohydrogeology of the Senegal sedimentary basin. A tentative explanation of the piezometric depression", Journal of Hydrology, 118, 357-371, 1990.

Glasbergen, P. : "The interaction between diapirism, caprock growth and salt solution in the Netherlands as an example of a sedimentary basin" To appear in : Proc. Symp. on Diapirism, Teheran, Dec. 1990.

Patyn, J. : "Contribution à la recherche hydrogéologique liée à l'évacuation de déchets radioactifs dans une formation argileuse", Doctoral Thesis, Paris School of Mines, Fontainebleau, 1985.

Patyn, J., Ledoux, E., Bonne, A. : "Geohydrological research in relation to radioactive waste disposal in an argilaceous formation", Journal of Hydrology, 102, 1990, 267-285.

Wei, H.F. : "Modélisation tridimensionnelle du transfert d'eau, de chaleur et de masse dans l'aquifère géothermique du Dogger dans le Bassin de Paris", Doctoral Thesis, Paris School of Mines, Fontainebleau.

Wei, H.F., Ledoux, E., Marsily, G. de : "Regional modelling of groundwater and salt and environmental tracer transport in deep aquifers in the Paris Basin". J. of Hydrology, 120, 341-358, 1990.

A HYDROGEOLOGIC ANALYSIS OF URANIUM ORE FORMATION IN PROTEROZOIC SEDIMENTARY BASINS

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EXTENDED ABSTRACT

1. Introduction

The study of uranium ore deposits as natural analogues for geologic repositories of nuclear waste requires a basic understanding of the hydrologic systems responsible for ore formation and subsequent periods of geochemical alteration. Although it is generally believed that the huge unconformity-type uranium deposits of the Athabasca Basin and the McArthur Basin formed through the transport of uranium in hot, saline groundwater (Hoeve and Quirt, 1984; Kyser et al., 1989), until now no study had examined the palaeohydrology of ore formation nor examined the coupling between fluid flow, heat transport and reactive solute transfer. The overall goal of this presentation is to discuss our progress in quantifying the palaeohydrology of Proterozoic sandstone basins through theoretical research, particularly as it relates to natural analogues (ore districts) in basins of northern Canada and Australia.

2. Methodology

Key issues concerning the palaeohydrology of unconformity-type uranium deposits include the relationship between basin tectonics and flow systems, the factors controlling regional groundwater flow, the effects of fluid flow on the thermal regime, and the geochemical scenarios for ore mineralization and subsequent phases of alteration. To address these issues, we have developed a numerical model that solves the coupled equations of variable-density groundwater flow, heat transport, and multicomponent reactive solute transport (Fig. 1). The hydrogeochemical model is based on the method of finite elements for groundwater flow, heat transport, and solute transport, and on the assumption of local chemical equilibrium between the aqueous phase and mineral phases within reactive porous media. Compilations of thermodynamic data are derived from the literature and the work of Sverjensky (personal communication). Hydrogeologic parameters are based on geologic lithology and known ranges in the governing parameters for modern environments. Details concerning the numerical approach in modelling reactive flows in porous media are described by others, many of which apply simultaneous solution or sequential iteration methods (Walsh et al., 1984; Liu and Narasimhan, 1989; Yeh and Tripathi, 1989). Our model is unique in its ability to efficiently solve variable temperature, reactive flow problems on a workstation using a predictor-corrector method (Raffensperger and Garven, 1991).

3. Some preliminary results

Our calculations presently are restricted to simulating two dimensional flow and transport along vertical cross sections through sedimentary basins (Fig. 2). A major goal here is to apply the coupled transport model so as to define palaeohydrologic conditions for uranium ore mineralization in large Proterozoic basins, thereby providing initial and boundary conditions on the far field environment which can be used in repository performance assessment scenarios.

Results from dozens of palaeohydrogeologic simulations of deep topography-driven groundwater flow and thermally-driven free convection suggest that both mechanisms were important agents for chemical mass transport in the Proterozoic sedimentary basins of northern Australia and Canada. Simulations have been conducted for basin-scale (100-1000 km) and regional-scale (1-10 km) hydrologic systems. Free convection probably played a more important role in primary ore mineralization, which later evolved to forms of mixed convection, and finally gravity-driven flow alone as the sedimentary basins were gradually uplifted by tectonic forces. Transport of fluids and heat along major fracture zones had an important role in ore formation, at least within the fractured metasedimentary basement. It should be noted that the simulations presented here are currently handicapped because they cannot portray the three-dimensional hydrology as might be required for a repository setting.

One smaller scale 2-D flow simulation is described also to illustrate the potential application of the reactive flow model in understanding geochemical scenarios of uranium mobilization in the near field, primary mineralization, and the formation of a redox front. The region modelled is a 2 km deep by 4 km wide box, with three units: a basement unit, a graphite zone, and an upper sandstone aquifer unit. Two hundred finite elements are used to discretize the flow domain. No flow boundaries were assumed on all sides of the domain. A constant temperature of 100°C is assigned to the top boundary and a basement heat flux of 80 mW/m^2 is assigned to the bottom boundary. The sandstone unit contained nearly all of the groundwater flow within the region caused by free convection because of the natural permeability contrast, with Darcy flow rates up to 2 m/yr. Flow is driven downward at the sides and upward at the domain center, above the more thermally conductive graphitic shear zone. Transport of multicomponent reactive solutes, subject to local equilibrium, is modelled also, including the precipitation of primary and secondary mineral phases. Twelve chemical components are involved, including about 60 aqueous species and 10 minerals. About 25 hours of CPU time were required to run the FORTRAN code on an IBM RS/6000-560 workstation.

After simulating 200,000 years of flow and transport, a large uranium ore body forms at the unconformity surface between the sandstone and graphitic basement. The source of the uranium is the far-field sandstone and uraninite is precipitated through reduction of uranyl and its complexes by methane generated from hydrothermal alteration of graphite. A stable redox front develops in the vicinity of ore deposition, while the carbonate concentration in the groundwater increases well above the ore body due to the precipitation of ore. Without significant groundwater flow into the basement, less uraninite is deposited, and ore deposition near the unconformity is constrained by rates of diffusion of methane up from the graphitic zone. Significant transport of groundwater must occur therefore through the basement metasediments, partcularly through the graphitic shear zones which probably formed narrow palaeoaquifers and focused hydrothermal groundwater into basal sandstones. Time scales of 100,000 years or more are required to concentrate the large ore bodies such as Jabiluka (230,000 tons) in the McArthur Basin and Cigar Lake (100,000 tons) in the Athabasca Basin.

4. Conclusions

The ramifications of the hydrogeologic setting to uranium migration and mineralization are being evaluated through transport simulations that account for coupled advection, dispersion, diffusion, aqueous reactions, and mineral dissolution and precipitation at pressure, temperature, and salinity conditions that are analogous to environments surrounding the far-field of a nuclear waste repository in the deep saturated zone.

Directions for future research include:

- Three-dimensional flow and transport modelling of palaeohydrologic systems.
- Treatment of fracture networks within a porous-medium framework.
- Application to present-day analogue sites to understand weathering processes.
- Expansion of the hydrochemical model to include reaction kinetics and isotopic fractionation.
- Stochastic treatment of permeability so as to better characterize uncertainty in model scenarios of mass transport.

The results presented here are preliminary, but clearly they illustrate the utility of coupled, reactive-flow modeling in understanding palaeo-conditions for mineralization. No other tool is available which has the ability to integrate geologic, hydrologic, and geochemical processes in a single assessment. Proper evaluation or characterization of subsurface data requires an integrated approach in performance assessment, as no single set of data alone (whether it be hydrologic or geochemical) can be used to independently understand mass transport in the near or far field without taking into account how processes overlap or affect each other. Our numerical model represents the type of new software available today which can executed on workstations to better assess ancient, present-day, and future scenarios of chemical mass transport in the subsurface. Future performance assessment work on natural analogues as repository scenarios ought to make use of this frontier technology.

REFERENCES

Hoeve, J. and Quirt, D., 1984, Mineralization and host rock alteration in relation to clay mineral diagenesis and evolution of the middle-Proterozoic Athabasca Basin, northern Saskatchewan, Canada: Saskatchewan Research Council Technical Report No. 187, 187 p.

Kyser, T.K., Wilson, M.R., and Ruhrmann, G., 1989, Stable isotope constraints on the role of graphite in the genesis of unconformity-type uranium deposits: Canadian Journal of Earth Sciences, v. 26, p. 490-498.

Liu, C.W. and Narasimhan, T.N., 1989, Redox-controlled multiple-species reactive chemical transport: 1. Model development: Water Resources Research, v. 25, p. 869-892.

Raffensperger, J.P. and Garven, G., 1991, (abstract), Coupled hydrochemical modeling of hydrothermal systems: Application to uraninite precipitation: Geological Society of America Abstracts with Programs, v. 23, p. A382.

Yeh, G.T. and Tripathi, V.S., 1989, A critical evaluation of recent developments in hydrogeochemical transport models of reactive mulitchemical components: Water Resources Research, v. 25, p. 93-108.

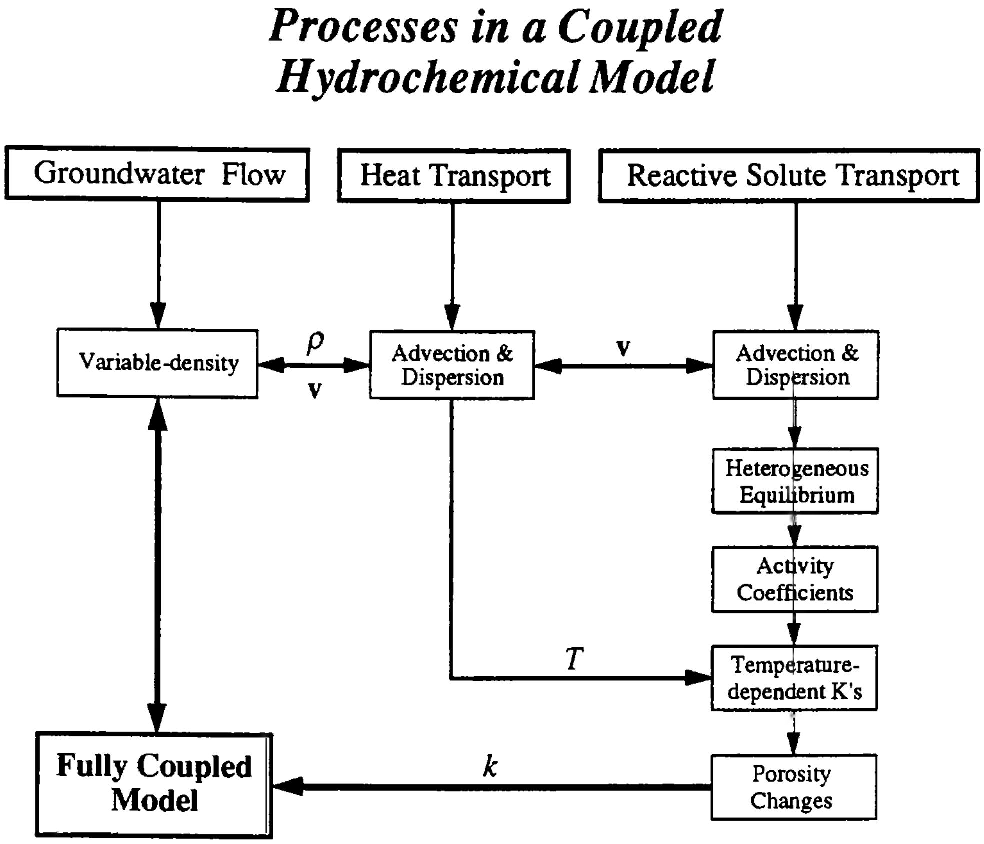

Fig. 1. Flow chart showing the organization of the coupled reactive flow model. The symbols are as follows: T is temperature, v is groundwater velocity or flow rate, ρ is groundwater density, k is intrinsic permeability, and K is equilibrium constant for chemical reaction. A finite element algorithm is used to solved the coupled flow-transport problem.

Conceptual Hydrothermal Model for the Origin of Unconformity-Type Uranium Deposits

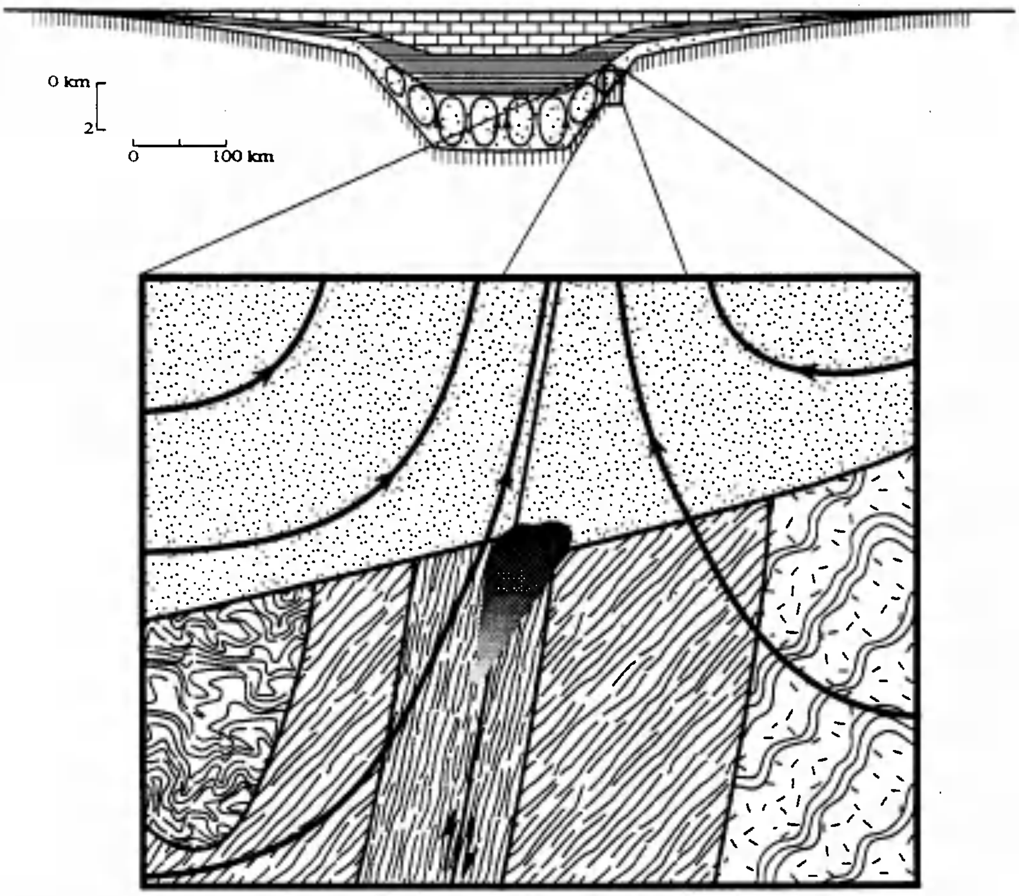

Fig. 2. Schematic section across a Proterozoic Basin showing the style of free convection driven by thermal gradients, along with an expanded view of the flow field near the unconformity between younger sandstone and crystalline basement containing graphitic shear zone.

EVOLUTION OF POREWATERS IN MUDROCKS

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ABSTRACT

The palaeohydrogeology of mudrocks is of significance to safety assessment in various ways. The beneficial physical and chemical properties of clay-rich sedimentary rocks make them potential hosts for repositories. Such rocks often constitute a large part of sedimentary rock sequences which constitute the 'far field' for a repository at some locations in underlying basement. They provide a hydraulic 'buffer' which records the hydrochemical, isotopic and pressure histories of the groundwater system. This cumulative record must be interpreted alongside present-day conditions to increase confidence in long-term behaviour of the groundwater system.

Concepts for the palaeohydrogeology and geochemistry of mudrock porewater systems require many hydraulic, isotopic and chemical data to test their validity. Representative porewater samples need to be taken for analysis and in situ experimentation is necessary; both tasks present many difficulties and uncertainties.

1. Introduction

Mudrocks are fine- to very-fine grained siliciclastic sediments or sedimentary rocks. They have varying proportions of sand, silt and clay grains. These and other properties such as degree of diagenetic induration and cementation determine their physical properties. Of particular relevance to geological disposal of hazardous and radioactive wastes is the low permeability to groundwater movement in mudrocks. The high clay content and compaction also make mudrocks strongly anisotropic to flow. Fracturing and microfissuring will also influence mechanical and hydraulic properties. Thus it is not possible to generalise about water flow and solutes in mudrocks, as the following examples demonstrate.

Hydrochemical measurements on porewaters have been carried out for investigations of mudrocks at various sites in southern and eastern England. The extraction method used to sample porewaters has been described elsewhere, as have some of the limitations on hydrochemical studies in low permeability rocks [1]. This paper summarises the results of these studies and what they indicate about the evolution of the porewaters and the hydrogeological history of the mudrocks sequences.

Amongst the issues which are important to the 'far field' performance of mudrocks are:

- advective or diffusive transport of groundwater and solutes;
- fissuring and preferential flow paths with matrix exchange;
- source and age of water and solutes in mudrock matrix;
- salinity and concentration gradients across mudrocks;
- water-rock reactions including sorption and dissolution;
- reactions which buffer pH and redox conditions in the matrix;
- trace element geochemistry and radionuclide analogues.

2. Mass transfer in mudrocks

The driving forces which control groundwater and solutes movements through mudrocks are:

- compaction: pore volume reduction and advection outwards;
- cross-formational flow: advection along a hydraulic gradient between the upper and lower boundaries;
- diffusion: random motion of water and solutes causing net mass transfer along concentration gradient;
- dilation: pore expansion due to elastic rebound in overconsolidated rocks, causing inwards advection.

Other processes also become significant in the particular physical conditions of mudrocks. Osmosis is a 'coupled' process which creates a pressure gradient across a low permeability clay 'membrane' separating porewaters with different concentrations. For example, thermodynamics predicts a pressure differential of 6 MPa when two brines with chloride concentrations of 70 and 35 g/l are separated by an ideal semi-permeable membrane. Conversely, ion filtration or reverse osmosis occurs when solutions are advected through a clay in which pore spaces selectively exclude some of the larger hydrated ions. This process is likely to affect pore waters being extracted for analysis. Further consideration of the coupled processes is outside the scope of this paper.

3. Origins of porewaters

The origins of porewaters depends on the age, depositional environment and subsequent hydrogeological history of mudrocks. A simple set of porewater categories and the distinguishing characteristics is:

- depositional, either seawater or fresh, in marine or lake clay deposits
  - unmixed only in recent sediments (e.g. deep seabed)
- meteoric, i.e. originating as rainwater which has infiltrated the mudrock
  - old sediments which have been flushed by fresh water
  - characterised by low/variable salinity and the stable oxygen and hydrogen isotopic ratio of the water
- marine intrusion, either at present-day or in the geological past
  - coastal sediments, caused by density contrast between sea and fresh water
  - distinctive chemistry and isotopic compositions
- mixed porewaters ("connate")
  - very old porewaters with complex origins, histories and chemistries
  - found in large scale basinal sediments with cross formational flow

4. Examples of clay and mudrock porewaters

4.1 Recent lake sediments

The investigations of the Loch Lomond sediments have been reported elsewhere [2]. The Holocene glacial and fresh water lake clays have an intercalated marine band dating back to a marine incursion about 6900 - 5400 years ago. The saline porewater in this band is now dispersing into the adjacent fresher porewaters. A 1-D finite difference model has been able to simulate chloride transport by diffusion, although the porewater data for iodide indicate release from a solid phase and kinetic retardation. These are essentially stagnant porewaters, with negigible hydraulic gradient, in which solutes migrate by diffusive transfer.

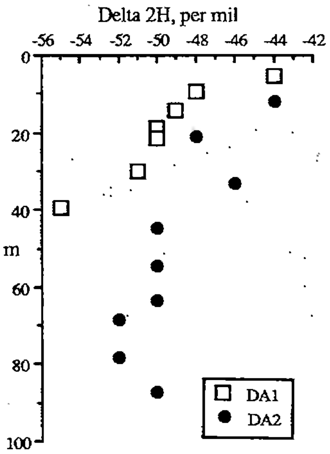
4.2 Cross-formational flow in basinal mudrocks

The groundwater conditions in the Cretaceous-Jurassic sediment sequence at Harwell, on the edge of the London Basin, were investigated by a series of boreholes. Hydrogeological measurements in the limestones and in the lower permeability mudrocks showed that hydraulic gradients converge towards the Corallian limestone aquifer as do the gradients of salinity [3]. The origin of the increasing salinity (around 8000 mg/l chloride) in porewaters is mixing with chloride-rich relicts, altered by water-rock reaction, of the marine depositional environment of the sediments up to 200 my ago. However the chemical and stable oxygen and hydrogen isotopic compositions of the porewaters show that these are now complex 'connate' mixtures which have evolved by cross-formational solute transport and lateral migration in the aquifer strata [4]. The stable isotopic ratios suggest a dominantly meteoric origin for the water. The palaeohydrogeology is difficult to disentangle, being a record of post-depositional sediment burial followed by basin uplift and inversion which allowed fresh water to begin flushing the depositional saline waters. Overall, the rapid increase with depth in porewater salinity shows that the water fluxes have not been great, and that the total basinal groundwater system may be approximated as being 'closed' for much of its geological history. The mass transport mechanism has not been quantified, but the salinity gradient is consistent with the calculated hydraulic transit time from depth to surface of around a million years [5].

4.3 Near-surface Jurassic mudrocks

Shallow sequences of Jurassic mudrocks-limestones have been investigated at various locations in central and eastern England. These are at Fulbeck [6], Elstow [7] and Down Ampney [8]. High salinity gradients in the porewaters indicate that there has been very low mass transport through the systems. However, no timescales can be put on this groundwater history because solute transport mechanisms, pathways and boundary conditions are not known. At each site, stable isotopes show that meteoric water dominates, even as salinity increases. The data from Fulbeck and Down Ampney, which were sampled to greater depths, show shifts in stable O and H ratios to isotopically lighter values which suggest that meteoric waters now at these depths were recharged at lower temperatures during the last glacial episode some tens of thousands years ago (Figure 1).

The Down Ampney site was investigated specifically to evaluate the effect of faults on mudrock hydrogeology. Geophysical, hydrochemical and hydraulic methods were applied [9, 10]. A fault across the site causes the Oxford Clay to be downfaulted against older Jurassic limestones and mudrocks in the sequence; the displacement is about 50m. Although the data are rather heterogeneous, probably reflecting the complex sequence of sediments and localised faulting both of which influence groundwater movement, they suggest that the chloride gradient is lower in the upfaulted block (Figure 2). This suggests that there might be either enhanced advective flow within the fault zone or that there has been accelerated flushing of the thinner block since uplift, erosion and weathering.



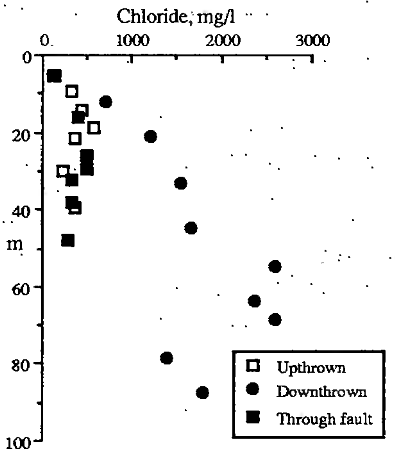


Figure 1. Depth variation of stable hydrogen isotope ratio in porewaters from Oxford Clay at Down Ampney site. Decreasing delta value corresponds to palaeoclimatic change.

Figure 2. Depth variation of chloride in porewaters from Oxford Clay at Down Ampney site, showing effect of faulting on salinity gradient. Clay profile in downthrown block is thicker and further from fault.

4.4 Seawater intrusion into coastal Tertiary clays

Porewaters were sampled in two profiles through Tertiary clays and silts (about 80m thick) overlying a Chalk limestone aquifer at the Bradwell site on the coast of south-eastern England [11]. There is presently an upwards hydraulic gradient from the Chalk through the mudrock sequence. The mudrocks were deposited in marine conditions but have since experienced fresh water flushing. Modelling with a 1D advection-diffusion model [12] shows that this would be achieved in a million years or so by diffusion alone. Holocene sea level rises are known to have affected this region, and would have caused seawater intrusion into the sediments from the surface at about 9000 y ago. Vertical profiles of porewater chloride concentrations show that intrusion has occurred, most notably affecting the profile nearer to the present shoreline (Figure 3). Both chloride profiles can be simulated by diffusion with boundary concentrations varying over time consistent with their relative coastal positions and with palaeoclimatic changes [12]. Stable O and H isotopic compositions can be similarly modelled with palaeohydrological values for fresh water sources (Figure 4). Though the modelling does not give unique simulations, it can be concluded that solute mass transport has been controlled by diffusion over a timescale of at least 10000 y.

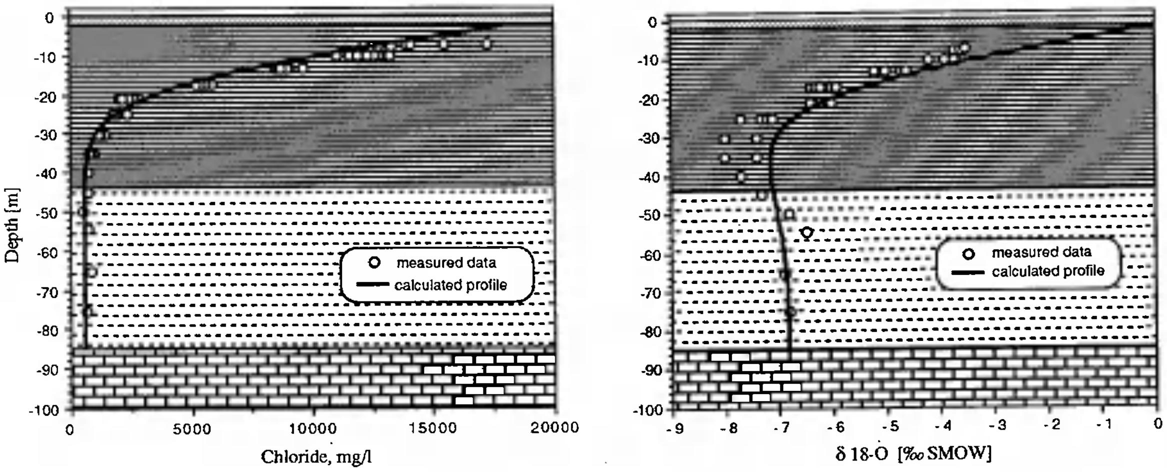
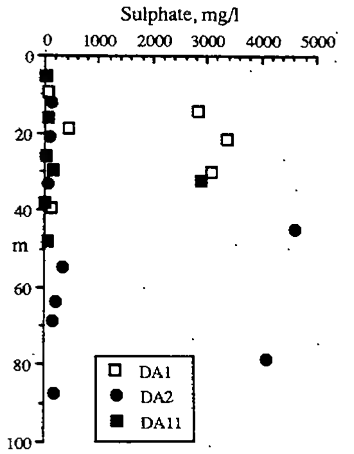


Figure 3 and 4. Depth profiles of chloride and stable oxygen isotope ratios in porewaters from Tertiary mudrocks at Bradwell site. Curves calculated with a diffusion model, using boundary conditions consistent with palaeoclimatic changes, are also shown.

5. Chemical evolution of mudrock porewaters

The hydrochemical evolution of mudrock porewaters is interlinked with the alteration and 'neoformation' of matrix minerals. Hydrochemistry and mineralogy together form the record of palaeofluid changes, and are more strongly linked because of the reactivity, low fluid fluxes and low water:rock ratios in mudrocks.

Deeper mudrock porewaters are dominantly Na-Cl composition but also have substantial and variable sulphate contents, higher than in samples from flowing groundwater (Figure 5). In some cases pyrite oxidation has occurred during porewater extraction. However pyrite oxidation and high sulphate may also occur 'in situ' by inwards diffusion of oxygen. Acidity generated during pyrite oxidation is partly buffered by the dissolution of carbonate or reaction with other matrix minerals, though lower pH values are observed to be correlated with high sulphates (Figure 6). It is possible that, in some mudrocks, the matrix porewater is chemically distinct from water being advected through fissures, and more variable in composition.



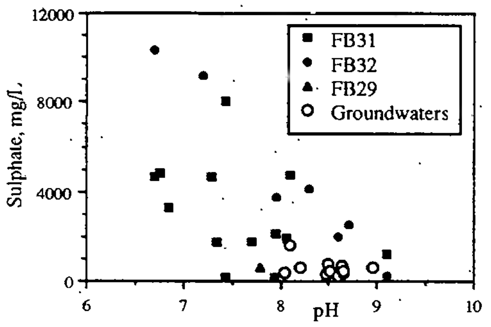


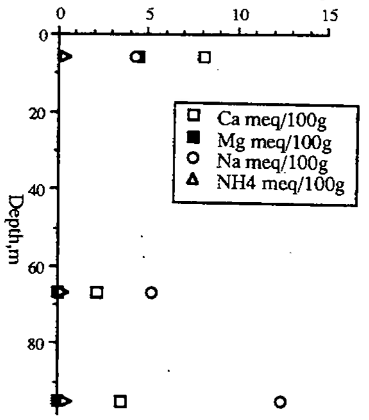
Figure 5. Sulphate variation in porewaters through three drillcore profiles at Down Ampney site.
Figure 6. Correlation between high sulphate and low pH in porewaters from Lias mudrocks at Fulbeck.

High contact area between mineral surfaces and porewaters, with many of the minerals being clays, dictates that cation solutes are controlled by sorption and double-layer effects. Thus exchangeable cations may buffer the dissolved species, but have themselves been progressively modified during the history of solute transport through the mudrock. This is demonstrated by solid phase data from the Tertiary (Bradwell) and Jurassic (Fulbeck) mudrocks (Figures 7). Exchangeable Na tends to increase with depth at the expense of sorbed Ca; for example at Fulbeck:

Exchangeable Ca > Na ~ Mg > NH_4 at 5m depth,
Exchangeable Na > Ca > Mg > NH_4 at 70m depth and >5000 mg/l Cl.

The normally rather high pH values observed in most mudrock porewaters, in the range 7 to 9, may also be buffered by ion exchange although there is not a model to quantify this.

Mudrocks often contain abundant sources of organic and colloidal material which can pass into porewater solution, resulting in relatively high observed concentrations of dissolved Total Organic Carbon (50 to >100 mg/l TOC) (Figure 8). The presence of organic material and sulphide minerals suggests that the mudrock matrix is able to buffer reducing conditions in porewaters. This is reflected in the trace element contents of porewaters, though these may be overprinted by oxidation reactions during extraction of porewater unless anaerobic conditions are used in the laboratory. Localised high concentrations of trace elements may be buffered by specific diagenetic equilibria, for example localised U anomalies (e.g. 340 µg/l) in porewaters corelate with occasional rhabdophane (cerium phosphate) in Fulbeck mudrock [6].



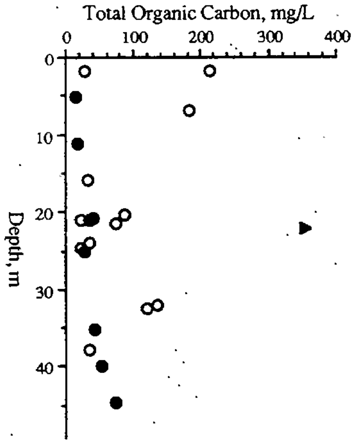


Figure 7. Exchangeable cation loadings on Lias mudrocks from Fulbeck site, showing change from Ca to Na dominance with increasing depth.
Figure 8. Dissolved organic carbon (TOC) concentrations in porewaters from Lias mudrocks from Fulbeck site.

6. Porewaters and palaeohydrogeology

The conclusions of this overview of porewater hydrochemistry in mudrocks, particularly with respect to the history of groundwater movement and solute transport, are:

- older mudrocks have more complex mixed origins of water and solutes;
- diffusion may dominate mass transfer across thick uniform mudrocks;
- high salinity gradients indicate low mass transfer;
- coupled processes and transient effects are important but difficult to quantify;
- groundwater advection in fissures enhances matrix porewater flushing;
- hydrochemistry is dominated by high reactivity and ion exchange;
- diagenetic mineralogy is an indicator of palaeohydrogeology;
- local equilibria may control trace element chemistry.

7. Acknowledgements

Many colleagues in BGS contributed to the studies on mudrock porewaters and palaeohydrogeology. This paper is published with permission of the Director, British Geological Survey (NERC).

References

[1] Entwisle, D.C. and Reeder, S. (1993) New apparatus for pore fluid extraction from mudrocks for geochemical analysis. Chapter 15 in *Geochemistry of Clay - Pore Fluid Interactions* (D.A.C. Manning, P.L. Hall & C.R. Hughes, eds), pp 365-388. The Mineralogical Society Series, Vol 4. Chapman & Hall, London.

[2] Falck, W.E. and Hooker, P.J. (1991) Quantitative interpretation of halogen porewater concentration profiles in lake sediments. *Mat. Res. Soc. Symp. Proc.* Vol. **212**, pp. 757-764.

[3] Black, J.H., Holmes, D.C., Alexander, J. and Brightman, M.A. (1985) The role of low permeability rocks in regional flow systems - the Harwell area study. In *Hydrogeology of Rocks of Low Permeability. Proc. Congress Intl Assoc Hydrogeol.*, Tucson, USA, Jan 1985. IAH Memoires Vol XVII Part 1, pp 107-117.

[4] Brightman, M.A., Bath, A.H., Cave, M.R. and Darling, W.G. (1985) Pore fluids from the argillaceous rocks of the Harwell region. *Rep. Fluid Processes Res. Group Br. Geol. Surv.* FLPU **85-6**, 77pp.

[5] Alexander, J., Black, J.H. and Brightman, M.A. (1987) The role of low-permeability rocks in regional groundwater flow. In *Fluid Flow in Sedimentary Basins and Aquifers* (J.C.Goff and B.P.J.Williams, eds). Spec. Publ. No. **34**, pp173-183. Geological Society, London.

[6] Bath, A.H., Ross, C.A.M., Entwisle, D.C., Cave, M.R., Green, K.A., Reeder, S. and Fry, M.B. (1989) Hydrochemistry of Porewaters from Lower Lias Siltstones and Limestones at the Fulbeck Site, Lincolnshire. *Report Brit. Geol. Surv.*WE/89/27. 28pp.

[7] Ross, C.A.M., Bath, A..H., Entwisle, D.R., Cave, M.R., Fry, M.B., Green, K.A. and Reeder, S. (1989) Hydrochemistry of Porewaters from Jurassic Oxford Clay, Kellaways Beds, Upper Estuarine and Upper Lias Formations at the Elstow Site, Bedfordshire. *Nirex Safety Studies Research Report* NSS/R172. 31pp.

[8] Metcalfe, R., Ross, C.A.M., Cave, M.R., Green, K.A., Reeder, S. and Entwisle, D.C. (1990) Porewater and groundwater geochemistry at the Down Ampney fault research site. *Nuclear Science and Technology*, EUR 14335, Commission of the European Communities, 52pp.

[9] Brightman, M.A., Sen, M.A. and Abbott, M.A.W. (1990) Hydrogeological measurements and modelling of the Down Ampney fault research site. *Report Brit. Geol. Surv.*WE/90/25 40pp.

[10] Sen. M.A. and Abbott, M.A.W. (1991) Hydrogeological investigations of a fault in clay. *Quarterly J. Eng. Geol.*, **24**, 413-426.

[11] Bath, A.H., Ross, C.A.M., Entwisle, D., Cave, M.R., Green, K.A., Reeder, S. and Fry, M. (1989) Hydrochemistry of Porewaters from London Clay, Lower London Tertiaries and Chalk at the Bradwell Site, Essex. *Nirex Safety Studies Research Report* NSS/R170. 22pp.

[12] Falck, W.E. and Bath, A.H. (1989) Vertical Changes in Chloride and Stable Isotope Compositions of Groundwater: Theoretical Modelling and Evaluation of Data from Coastal London Clay. *Nirex Safety Studies Research Report* NSS/R174. 39pp. UK Nirex Ltd.

VALIDATION OF HYDROGEOCHEMICAL CODES USING THE NEW ZEALAND GEOTHERMAL SYSTEM

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Abstract

Evaluation of the performance of a nuclear waste repository requires that numerous parameters be evaluated over a broad range of conditions using computer codes. The capabilities of these codes must be demonstrated using complex natural systems in which the processes of interest have already occurred or are occurring. We have initiated such a test of geochemical and hydrological simulation codes, using the geothermal areas of the Taupo Volcanic Zone, New Zealand. Areas that have been evolving for a few tens to a few tens of thousands of years are of particular interest. This effort will help determine the extent to which simplified modeling approaches can be used in performance assessment calculations.

To guide the selection of natural systems, we are attempting to map potential repository regions dominated by equilibrium processes and those dominated by kinetically controlled processes. To do so, fluid velocities and temperatures were computed using the V-TOUGH code assuming an equivalent continuum, dual porosity model. These results were then used to compare advective fluid flow rate with silica dissolution/precipitation rates, using Damköhler numbers. Only the first 5000 years of repository operation were considered. The results identify a migrating envelope of kinetically dominated activity several meters wide in the vicinity of waste packages that contrasts with other parts of the repository.

The Lake Rotokawa region, New Zealand, has been used in our first test effort, since it contains environments that are examples of kinetic and equilibrium processes. The results of tests involving equilibrium processes show excellent correspondence between simulated and observed mineral alteration sequences, although discrepancies in some mineral parageneses demonstrate that operator decisions in conducting simulations must be considered an integral part of validation efforts; pure "code validation" is impossible when considering complex natural systems. The extent to which simplification of models may be possible will be evaluated as further simulations are completed.

1. Introduction

Predicting the behavior of nuclear waste repositories over their service lifetimes requires codes that simulate the response of the enclosing geological environment to a broad range of physical and chemical processes. However, it is unrealistic to expect that these codes will rigorously simulate the detailed behavior of these repositories because: 1.) many of the processes of interest are coupled in complex ways that are not yet fully characterized by functional relationships; 2.) many of the parameters that need to be measured are difficult or impossible to obtain (e.g., the rate of precipitation of mineral phases in the natural setting, or the surface roughness of pore spaces); 3.) probabilistic functions that describe the distribution of properties or parameters can seldom be determined due to the variability of the natural setting, and the fact that the number of points at which the parameters can be evaluated is insufficient to satisfy statistical requirements for representative sampling. Furthermore, the number of separate computer runs required to provide a statistically valid probabilistic model of the performance of a repository is prohibitively large.

It thus becomes necessary to determine the extent to which models of natural processes can be simplified. To do this requires determining which parameters have a significant influence on the performance of the repository, and defining the precision that is required for characterizing or measuring these significant parameters.

Simulations of processes in natural settings are particularly important for accomplishing this task. Natural systems are the only "experiments" available for evaluating the relative importance of specific parameters in complex, heterogeneous environments, and in which the time duration is comparable to repository lifetimes. The principle shortcoming of such systems is that they are difficult to characterize, since they seldom have sufficient information preserved to allow adequate measurement of the parameters of interest.

To address some of these issues, we have begun a long term study of geochemical and hydrothermal processes at the active Taupo Volcanic Zone on the North Island of New Zealand[1]. The intent of this study is to determine the extent to which geochemical and hydrothermal models can be simplified and still provide accurate predictions of geochemical and hydrological properties. This effort is also designed to accomplish rigorous code validation by comparing the results of simulations with observed processes.

2. Definition of the problem

Processes and characteristics that are important for nuclear waste repositories include, but are not limited to, reaction kinetics, ion exchange and sorption, aqueous speciation, rock and fracture permeability, imbibition characteristics, connectivity, and fracture roughness. Values for these variables span many orders of magnitude. Evaluation of the ability of a code to simulate processes in a nuclear waste repository thus requires that the natural systems used for study somehow provide a test of the capabilities required to simulate repository behavior.

There are specific characteristics of the proposed repository design at Yucca Mountain that are useful in selecting natural sites for study. Rocks and packing material in the vicinity of waste packages will undergo a period of rapid heating followed by a long cool-down period (Fig. 1). In the fractured rocks that may make up the repository, fluid velocities will be very different between intact blocks and the fractures, and these velocities will vary greatly as heating and cooling proceed. This situation generates two distinct domains that will be important for understanding the evolution of chemical and hydrological environments.

Of particular interest to us is the extent to which chemical equilibrium will be achieved within domains of the repository. We have compared the different flow regimes by computing, as a function of time and position with respect to a waste package, the distance a fluid would be required to move to achieve chemical equilibrium.

The computations were carried out in a two dimensional array that extends away from waste packages 24 meters in a vertical direction, and 18 meters in a horizontal direction. The simulations first established the flow regime and thermal history, using the VTOUGH code[2]. The resulting fluid velocities and temperatures were then used to compute the distances over which fluid must flow before equilibrium would be closely approached, by inverting the Damkohler Group 1 number for length. The Damkohler Group 1 number is a dimensionless number that is the ratio between reaction rate and fluid velocity, for the temperature, fluid velocity, exposed reactive surface area, distance over which the fluid flows, reaction rate function, and the equilibrium fluid composition for the system being considered[3], and is expressed as:

$$D_I = v_{ij} S_j K_j (a_{H+})^n L/c_{eq} V,$$

where v_{ij} is the stoichiometry of the ith component in the jth reaction, S_j is the surface area, K_j is the reaction rate, $(a_{H+})^n$ is the hydrogen ion activity for the respective nth order reaction, c_{eq} is the equilibrium concentration of the ith component, and V is the fluid velocity.

Large Damkohler numbers (> 1000) characterize systems that will approach thermodynamic equilibrium, while small Damkohler numbers (< 1) characterize systems that will be dominated by kinetics.

We assumed a D_I value of 1000, the reaction kinetics appropriate for cristobalite dissolution and precipitation, that the solution remains near neutral in pH, and solved for the equilibrium length. This allowed us to map those regions in the vicinity of waste containers in which fluid velocities were high enough to require large equilibrium lengths. Regions that had this feature would be unlikely to achieve chemical equilibrium, and provided us with a guide for selecting particular types of systems in New Zealand for detailed study and use in code validation activities.

3. Equilibrium regimes and implications for study sites

Within a few years after waste emplacement, fluid velocities in *fractures* a few meters away from the waste containers are high enough (>1 meter/year) to result in very large length values (10-10,000 meters; shaded region in Fig. 2). This regime migrates outward over a period of about 100-400 years, and into regions where equilibrium may have been achieved. As it migrates the halo eventually dissipates in regions that are at the same elevation as the waste containers. Above and below the containers, however, these areas persist until they eventually dissipate at about 400 years. In contrast, there are no regions in which the velocity of fluids in the rock *matrix* requires lengths greater than a millimeter. This suggests that equilibrium will be achieved in the rock matrix.

With these features in mind, the initial site we selected for reconnaissance study was Lake Rotokawa in the Rotokawa geothermal field[4]. Lake Rotokawa fills a 6000 year old hydrothermal eruption vent. The lake water has a slightly elevated temperature, with a pH of 2.3. The high pH is due to condensation and oxidation of upwardly streaming H_2S-rich fluids that are interacting with atmospheric gases. The H_2S fluids are derived from boiling alkaline chloride fluids that are at deep levels in the hydrothermal system. Sulfur, which is one of the oxidation reaction products, is actively being deposited at the site.

The upward flowing fluids have caused the development of alteration zones that represent different degrees of rock-water interaction. These zones represent different liquid to rock ratios, and can be used as a means of testing the ability of codes to accurately model fluid-rock interaction.

This system is phenomenologically similar to those that may develop in regions surrounding waste packages, at the potential repository site at Yucca Mountain, where increased saturation may develop in response to pore-fluid vaporization, migration and condensation. The attractive aspect of the Rotokawa site for testing geochemical simulation capabilities is the ability to monitor the kinetics of reactions in natural systems, and the quantity of reaction products that develop.

4. Modeling approach

Our initial effort focused on modeling the evolution of the fluids and solid reaction products, as a function of fluid-rock ratio and temperature. Our goal was to determine the conditions under which sulfur would be deposited in the relative proportions observed at various temperatures using the observed gas and liquid compositions at the site, and to compare the observed mineral assemblages at the site with the minerals predicted to occur by the reaction path geochemical modeling code EQ3/6[5,6].

Since it was unknown the extent to which sulfur deposition reflected free evolution of atmospheric gases and volcanic fluids, or interaction of fluids with rock, we considered several different scenarios. The cases we considered allowed free evolution of the fluids (volcanic gases/waters and atmospheric gases) with and without controls on certain gas species. We then repeated the simulations, but included the local rock (Taupo ignimbrite) as a reactant.

Under no conditions did sulfur form in the simulations, if any of the gas fugacities were fixed at some constant value. If the gas fugacities are allowed to freely evolve (i.e., are unbuffered by any mineral assemblages) sulfur deposition occurs. Of course, it was only in the runs that had the Taupo ignimbrite present that secondary alteration mineral sequences formed.

The secondary minerals that form, and the quantity of sulfur deposited depends directly on the amount of fluid-rock interaction (Fig. 3). The correspondence between observed and simulated secondary mineral assemblages is excellent. The absence of anhydrite in the simulations, however, is an important contrast between models and observed phase relationships, since it represents the presence of an oxidized sulfur species. This suggests that the models do not accurately represent fluid-rock-atmospheric gases interaction.

5. Implications of these preliminary results for future work

With respect to code validation activities, this exercise emphasizes the well known problem that there is seldom sufficient information available from natural sites to allow a test of codes modeling capabilities alone. Validation activities also become a test of the knowledge of the individuals designing the validation runs. In this particular instance, guesses had to be made as to how gases behaved during evolution of the system (i.e., were gas fugacities buffered or were they allowed to evolve as the system evolved?). Such situations may be advantageous, however, since the computer simulations generate vast bodies of predictive information that can be tested by further field work. When conducting simulations for validation efforts, plans should therefore include field studies that will be conducted after the simulations, in order to test code predictions.

With respect to the simplification issue, it is apparent that the greater the number of variables that can be treated as constants during the simulations, the simpler are the computations. The effort we are undertaking in New Zealand is focused on this problem, with the intent of establishing the range of values for particular chemical parameters of importance to the system, as a means of defining limits for chemical conditions. It is not yet known, however, if it will be possible to accomplish significant simplification of the systems we are studying; the preliminary results we have to date have not provided any clear indication of particular chemical variables that may be amenable to such a treatment.

Work performed under the auspices of the U.S. DoE by Lawrence Livermore National Laboratory under Contract W-7405-ENG-48. Prepared by Yucca Mountain Site Characterization Project (YMP) participants as part of the Civilian Radioactive Waste Management Program.

References

1. W.E. Glassley and B.W. Christenson, 1992, Water-rock interaction in New Zealand hydrothermal systems: Comparison of some simulated and observed geochemical processes. In, Proceedings of the Third International Conference on High Level Radioactive Waste Management, Las Vegas, Nevada, American Nuclear Society, p. 352-356.

2. J.J. Nitao, 1989, V-TOUGH - An enhanced version of the TOUGH code for the thermal and hydrologic simulation of large-scale problems in nuclear waste isolation. Lawrence Livermore National Laboratory, UCID-21954, Livermore, CA, p. 1-24.

3. R. B. Knapp, 1989, Spatial and temporal scales of local equilibrium in dynamic fluid-rock systems. Geochim. Cosmochim. Acta, v. 53, p. 1955-1964.

4. R.E. Krupp and T.M. Seward, 1987, The Rotokawa geothermal system, New Zealand: An active epithermal gold-depositing environment. Econ. Geol., v. 82, p. 1109-1129.

5. T.J. Wolery, 1979, Calculation of the chemical equilibrium between aqueous solution and minerals: The EQ3/6 software package. Lawrence Livermore National Laboratory UCRL-52658, Livermore, CA.

6. T.J. Wolery, K.J. Jackson, W.L. Bourcier, C.J. Bruton, B.E. Viani, K.G. Knauss, and J.M. Delany, 1990, Current status of the EQ3/6 software package for geochemical modeling. American Chemical Society Symposium Series 416, D.C. Melchoir and R.L. Bassett, eds., p. 104-116.

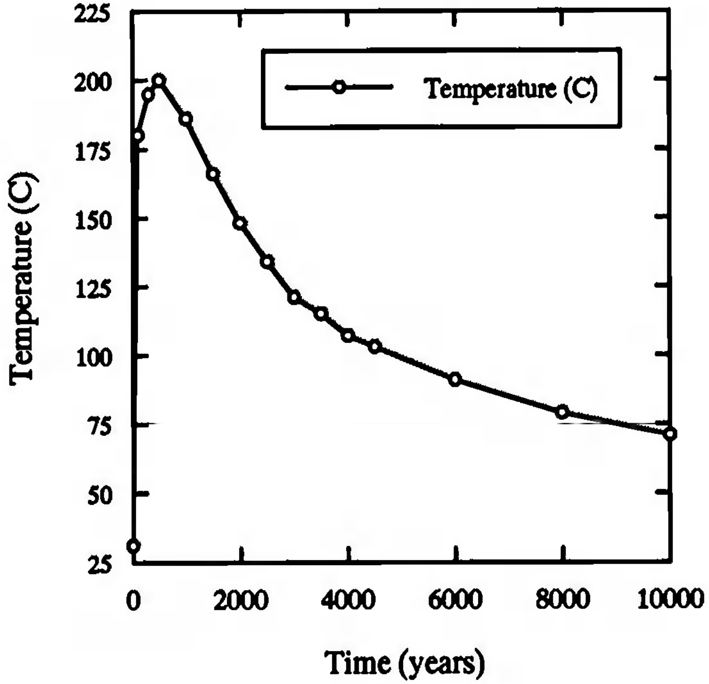

Figure 1. Temperature of the center of a high level radioactive waste repository at the potential repository site at Yucca Mountain, Nevada, as a function of time. Temperatures computed for 30 year old fuel, and an assumed areal power density of 114 kw/acre, with no recharge flux (computed by J. Nitao and T. Buscheck, using the VTOUGH code[2]).

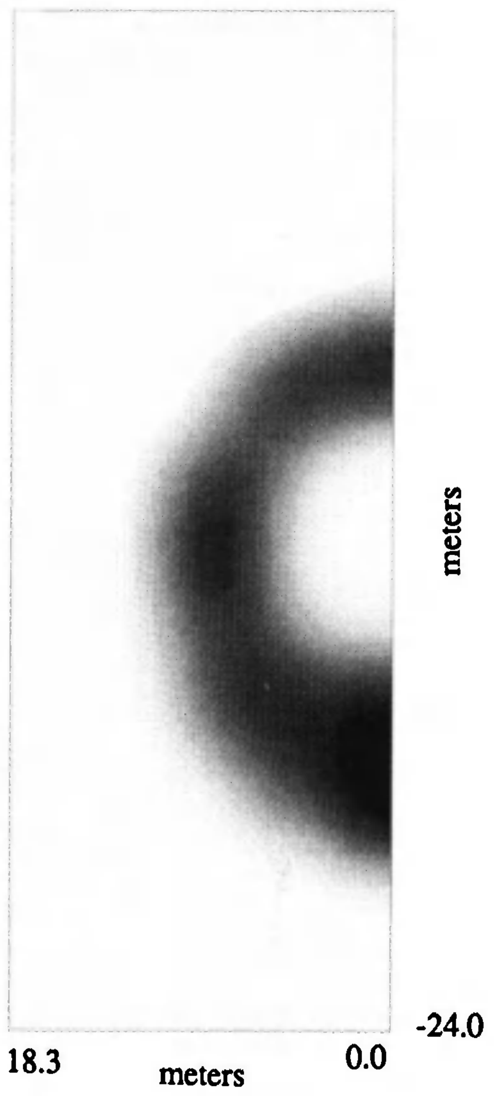

Figure 2. Fluid flow distances in fractures 25 years after waste emplacement. Darkest shading is for distances >10,000 meters, lightest shading is for distances of 10m.

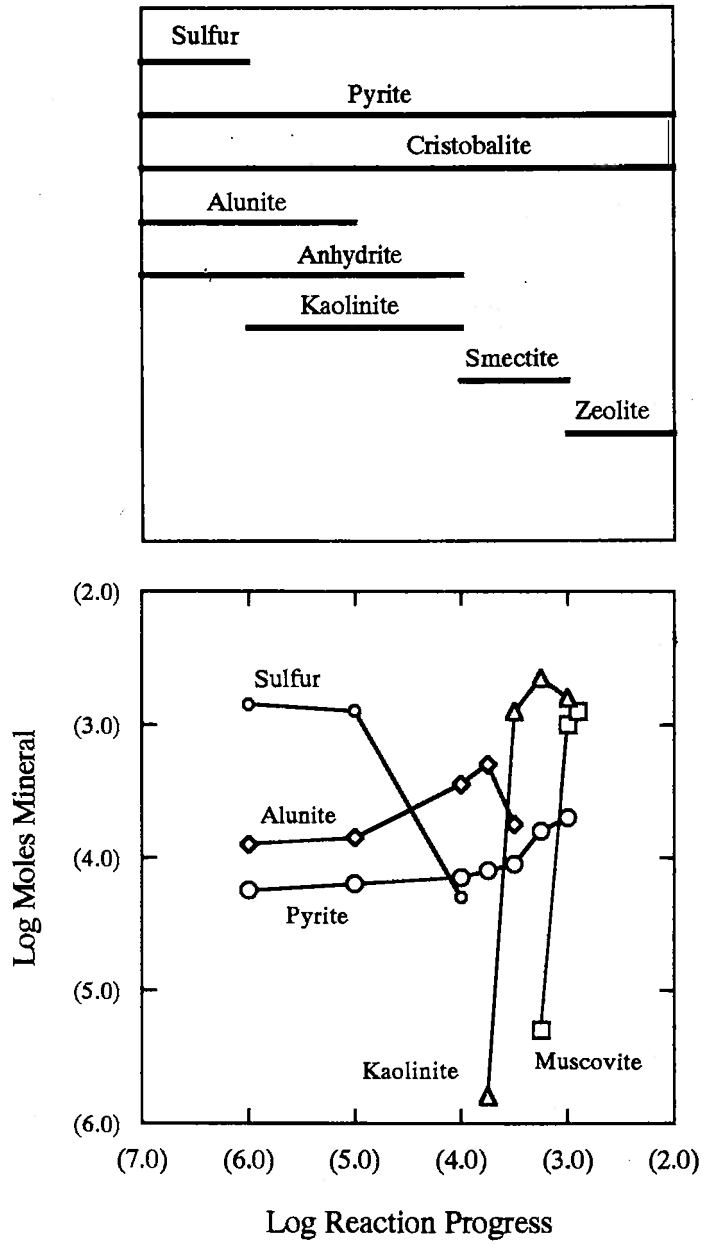

Figure 3. Comparison of the observed mineral assemblages at the Rotokawa geothermal system (top) with the assemblages predicted to occur in the EQ3/6 simulations (bottom). The horizontal axis in the top figure is schematic, and represents the transition from water-dominated conditions (left side of figure) to rock-dominated conditions (right side of figure). Bars identify approximate conditions over which different minerals coexist. Numbers in parentheses in the bottom figure are negative.

NATURAL ANALOGUE WORKING GROUP MEETING

NATURAL ANALOGUE: A WIDER PERSPECTIVE

The development of natural analogue studies and their application to performance assessment: a review
W.M. Miller, INTERA (UK)

Gas pressure build-up and host-rock mechanics. Possible implications for the performance and performance assessment of a high level nuclear waste repository
J.J.K. Daemen, Mackay School of Mines, Nevada (USA)

Magmatic intrusions in clays as geomechanical natural analogues
F. Gera[1], T. Hueckel[2], R. Pellegrini[3]
[1] Ismes, Rome (I), [2] Duke Univ., Durham (USA), [3] Ismes, Bergamo (I)

Natural analogues and neotectonics
R. Muir-Wood, BEQE (UK)

THE DEVELOPMENT OF NATURAL ANALOGUE STUDIES AND THEIR APPLICATION TO PERFORMANCE ASSESSMENT: A REVIEW

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Abstract

Over two decades of study on natural analogues of repository materials and radionuclide release and transport processes has produced a large volume of information. Much of this information potentially has direct application to performance assessment, although little of it has every been used in this manner. This review of natural analogue studies distils out the most important conclusions that could be applied to performance assessment and identifies areas where further analogue studies are most needed.

1. Introduction

It is well understood that both the near and far-fields of any repository are highly complex systems characterised by a legion of coupled processes operating on a wide range of different materials (both natural and man-made). The complexity of both the near and far-fields clearly makes the modellers job extremely difficult for they must attempt to construct a relatively simple model of these systems in terms of discrete components to which numerical values can be attributed but without loosing any of the vitally important couplings between them. Furthermore, these models must be capable of describing the evolution of the near and far-fields over 10^6 years or more; that is to say they must be predictive.

Evidently, development of models that adequately describe the behaviour of a repository (performance assessments) does not occur in a vacuum, and can only be undertaken on the back of a thorough understanding of both geochemistry and materials science. Yet, the requirement for models to predict so far into the future, means that 'standard' scientific methods (*i.e.* laboratory studies) are, by themselves, an inadequate tool for the practical study of repository-relevant processes and materials: hence the advancement of natural analogue studies. It follows that the construction of satisfactory performance assessments requires three elements (i) model development, (ii) laboratory studies, and (iii) natural analogue studies. No one element is sufficient alone, and no one element can be omitted if the final performance assessment is to be defensible.

In an ideal world, the two prime applications of natural analogues to performance assessment would be (i) model construction, and (ii) model testing and validation. Yet, a common cry of anguish from the natural analogue fraternity is that very few of the results from analogue studies are ever explicitly applied to performance assessment in either way. In order to answer the question why this is so, it is first necessary to take stock of the results from these natural analogue studies and to assess whether they actually provide the information that modellers require and, so that further studies are better received, to identify specific areas where further natural analogue-derived data would be of particular value to the modellers. This assessment should allow future natural analogue studies to be more closely focussed, with well defined and specific aims relevant to performance assessment in the manner defined in the very first NAWG meeting (Côme & Chapman, 1986).

The remainder of this paper partially attempts to fulfil this assessment, and examines the current state of development of natural analogue studies, specifically addressing studies on repository materials and radionuclide release and transport processes. As such, this paper is only concerned with the quantitative application of natural analogue studies to performance assessment; the more qualitative uses (*e.g.* as illustrative material for use in demonstrations to lay audiences), whilst important, are not considered here.

This paper represents a condensed version of some aspects of a very much more detailed review of natural analogue studies (Miller *et al.,* 1993) of relevance to the Swiss, Swedish and United Kingdom radioactive waste disposal programmes and is, therefore, not intended to be comprehensive of *all* natural analogue studies. However, as the three countries of interest are, between them, developing disposal concepts for L/ILW, HLW and spent fuel, it is probable that some of the discussion in this paper will have relevance to the disposal programmes being developed by many other countries.

The larger review is shortly to be published simultaneously in the Nagra NTB, SKB TR and UK DoE RW report series.

2. Adequate demonstrations of the validity of natural analogue studies

To help persuade modellers to take note of the results from natural analogue studies it is necessary that all analogue studies should explicitly demonstrate the validity of the analogue under investigation. This means showing that the materials or system being studied have real significance to a repository, for this is the only way that modellers can be confident that analogue-derived information has direct relevance to performance assessment.

Adequate demonstration of the validity of an analogue study requires that the following two guidelines be met:

1) The physico-chemical characteristics of the analogue materials (rock, metal, clay, cement *etc.*) must be sufficiently similar to those of the repository materials.

2) The physico-chemical characteristics of the environment in which the analogue study is performed must be sufficiently similar to those of the repository near or far-field in question and must always have been so.

If one or both of these guidelines are not met then, simply, it is not possible to extract any quantitative data from the analogue study that would have any value in performance assessment. This restriction may seem harsh but it is consistent with the need for all data used in performance assessment to be defensible in the eyes of the licensors.

The requirement to prove 'sufficient similarity' is a key problem, for how similar does an analogue material or system need to be to its repository equivalent, bearing in mind that, by definition, an analogue is *not* the same as the object to which it is compared. This problem is illustrated by studies of natural glasses as analogues of the borosilicate glass waste-form. Clearly, there are important compositional differences between borosilicate glasses and natural glasses; after all, as their name suggests, borosilicate glasses may contain, in addition to the waste itself, between 10 and 30% B_2O_3 which is almost totally lacking from natural glasses. Yet, solely on the basis of low silica content, natural basaltic glasses are usually identified as being the closest analogues to borosilicate glass and have, therefore, received the most attention. However, the key question is:

Has it ever been adequately demonstrated that the compositional differences between these two glass types does not cause them to exhibit different physico-chemical properties, which would invalidate the results of the natural analogue studies ?

The answers to questions such as this are unavoidably subjective and can only be determined by consensus between modellers and analogue researchers. On the other hand, there are numerous natural analogue studies which have been performed that clearly do not meet these two guidelines. As an example, in an attempt to demonstrate the longevity of borosilicate glasses, the million year plus ages of many natural basaltic glasses have been cited as supportive if not conclusive evidence. However, in most cases data on the compositions of the glasses or the chemistry of the environment from which they were taken is either inadequate, inappropriate or totally lacking and so defensible quantitative conclusions cannot be drawn from them. Similar criticisms can be made against a number of analogue studies of other repository materials and also at some studies aimed at investigating radionuclide release and transport processes.

Despite the apparent difficulty in demonstrating the validity of natural analogue studies, useful information actually has been gained from examination of analogues of repository materials and analogues of radionuclide release and transport processes. However, many more areas have been identified where information is lacking and further research is needed. The reminder of this paper very briefly highlights some of these issues.

3. Repository materials

3.1 Positive information

Positive information derived from natural analogue studies of repository materials includes, but is not limited to, the following issues.

- Corrosion rates of metals and pitting factors.
  A number of studies of archæological artefacts composed of copper and iron (or iron alloys) have yielded very similar corrosion rates. For copper (Tylecote, 1979; Johnson & Francis, 1980) corrosion rates are typically 0.15 to 0.25 $\mu m\ yr^{-1}$. In contrast, corrosion rates for iron (Johnson & Francis, 1980) are typically an order of magnitude greater, about 1 to 10 $\mu m\ yr^{-1}$. Pitting factors (ratio between pit depths and mean corrosion rate) for copper have been found to be about 3 (Bresle *et al.*, 1983), meaning that the value of 25 used in KBS-3 is very conservative.

- Dissolution rate of uraninite.
  Studies of uraninite stability at uranium ore deposits such as Cigar Lake (Cramer, 1991) show that at low temperatures and in a reducing environment, uraninite can exist for many millions of years and remain stable. Significant dissolution or alteration only occurs at higher (hydrothermal) temperatures or under oxidising conditions, environments that are not relevant to most disposal concepts or performance assessments.

- Smectite to illite transformation rate.
  The rate of alteration of bentonite to illite is controlled by the temperature and the availability of potassium in groundwaters to exchange with the sodium in the bentonite. This process has been studied in thick sequences of bentonite (*e.g.* Pusch & Karnland, 1988) and in bentonites adjacent to igneous intrusions (*e.g.* Benvegnù *et al.*, 1988). These studies show that where groundwater is poor in potassium and

fluxes are low, the illitisation process is extremely slow. On this basis it has been calculated that it may take 10^7 years for the bentonite in a granite hosted spent-fuel repository to alter completely.

- Longevity of calcium silicate hydrate (CSH) compounds in cement.
  CSH compounds occur naturally (although infrequently) in some rocks and some of these have been found to be tens of millions of years old (*e.g.* Milodowski *et al.*, 1989). This longevity of CSH compounds in the geological environment points to their potential stability in the near-field of a deep repository. Although much younger (c. 2000 years old), pristine CSH compounds have been found in many Roman cements (*e.g.* Hadrian's Wall).

- Hydraulic barrier function of bitumen.
  Bitumen can preserve organic materials by efficiently isolating them from air and water (Hellmuth, 1989). Pleistocene fossils (up to 2 million years old) have been preserved in tars pits in California and Peru (Rolfe & Brett, 1969; Behrensmeyer, 1980). Ever since the Babylonians (1300 B.C.) first discovered bitumen, it has been used to waterproof houses, ships *etc.* (Forbes, 1934). Many of these early bitumen coated materials are still completely intact.

- Hydraulic barrier function of clays.
  There are several eye-catching examples of organic material having been preserved in clay environments, two of which are particularly interesting. In Italy, fossil trees some 1.5 million years old have been discovered in a lacustrine clay horizon (Benvegnù *et al.*, 1988). These trees are still composed of hard-wood, despite freely circulating oxidising waters in the sandy beds above and below. In China, a 2100 year old burial-tomb has been unearthed which was lined with a thick clay layer (Lee, 1986). The cadaver found inside had been so well preserved the skin retained its elasticity and the joints were still movable. Furthermore, vegetable and meat foodstuffs were also excellently preserved.

3.2 **Further studies**

Further natural analogue studies of repository materials are needed in, at least, the following areas:

- Direct incorporation of radionuclides into waste-form (glass or spent fuel) alteration phases.
  When a waste-form degrades, the radionuclides may be directly incorporated into the newly forming alteration minerals which then become the solubility-limiting phases. In order correctly to model the source term, these secondary phases deserve further investigation. As an example, early glasses were coloured by doping them with uranium, it may be possible to examine these glasses with a view to measuring uranium diffusion in the glass and incorporation in any secondary phases.

- Hydrogen production from iron corrosion.
  In Project Gewähr (Nagra, 1985), it was calculated that the cementitious low and intermediate-level waste repository would evolve some 8.2 x 10^7 m^3 of hydrogen due to corrosion or iron and steel in the first 10 000 years. It is possible that this gas production process could be investigated by study of reinforcing rods in old concretes, possibly in foundations where conditions would be both reducing and alkaline.

- Cementation of bentonite.
  Natural analogue study of bentonite (Pusch *et al.*, 1987; Pusch & Karnland, 1988) has revealed that at c.150°C, dissolution of smectite and subsequent precipitation of siliceous phases causes partial cementation of the bentonite over a time period of only a few months. This process has potentially important consequences for the behaviour of the near-field and so requires urgent further natural analogue investigation.

- Cement pore-water evolution.
  In the lifetime of the repository, cement pore-waters are expected to change from 'early' NaOH/KOH leachates to 'late' $Ca(OH)_2$ leachates. No laboratory or analogue studies have addressed the exact relationships between these two distinct pore-waters or the relative effects of the migration of these pore-waters into the far-field. The Maqarin site in Jordan has both these types of water, consequently some relevant investigations may be performed there.

- Radionuclide sorption onto cement.
  Although laboratory studies have addressed this issue (*e.g.* Allard, 1985), no natural analogue studies have been performed despite the obvious importance of this process. It is probable that some useful information could be gained by examination of cements in Roman baths located at radionuclide-rich hydrothermal springs.

- Interaction between different waste-forms / repository materials / host rock.
  Few natural analogue studies of repository materials examine how interaction between different materials may affect their behaviour, although those that have often indicate that near-field performance may be impaired. For example, Mazurek (1990) shows that the concrete liner of a ventilation tunnel in a marl host-rock was completely recrystallised at the contact zone, resulting in a significant increase in porosity. Further effort should be made to investigate similar detrimental interactions between different waste-forms, host-rocks and other repository materials.

4. Radionuclide release and transport processes

4.1 Positive information

Positive information derived from natural analogue studies of radionuclide release and transport processes includes, but is not limited to, the following issues.

- Testing and evaluation of thermodynamic solubility-speciation codes and databases.
  This has been one of the most useful applications of natural analogues to performance assessment. Both backfitting exercises and 'blind' predictions, *e.g.* at Poços de Caldas (Bruno *et al.*, 1991) and at Maqarin (Alexander, 1992), show that the codes and databases are often not accurate but normally over-estimate solubilities and are, therefore, conservative. These analogue studies also prove invaluable for testing the modellers, giving them experience in the art of using the codes.

- Matrix diffusion in fractured rock.
  Matrix diffusion has been studied in samples of many different granites using numerous physico-chemical techniques. One of the most useful techniques is uranium-series disequilibrium studies of the rock adjacent to open fractures. Encouragingly, most studies give comparable results which indicate that the depth of interconnected porosity is finite and restricted in fresh granites to 10 to 50 mm but which may be greater in altered granites.

- <u>Redox front processes.</u>
  Redox front processes were investigated in detail at the Osamu Utsumi mine as part of the Poços de Caldas natural analogue study (Chapman *et al.*, 1991). This study showed that redox front movement was slow, equivalent to the erosion rate c.1m per million years. The redox front proved to be an effective trap for redox sensitive elements such as uranium but, less intuitively, also for many non-redox sensitive elements which were enriched at the redox front due to incorporation in secondary UO_2, or sorption onto iron-oxyhydroxides. Thermodynamic modelling of these redox front processes (Cross *et al.*, 1991) showed that these models were poor at simulating the complexity of trace element behaviour and, consequently, further work is needed on this issue.

- <u>Diffusion in clays.</u>
  Two studies have shown that diffusion of radionuclides in clays is extremely slow but measurable. The well known Loch Lomond study (Mackenzie *et al.*, 1990) examined migration of nuclides from a c. 5400 year old marine bed overlain and underlain by freshwater sediments. The pore-water concentrations of Br and I decreased with distance from the marine bed in a profile which was modelled to give an apparent diffusivity of 8×10^{-7} cm^2 s^{-1} for Br. In another study of nuclide migration in turbidite sequences in the North Atlantic (Colley & Thomson, 1985; 1991) diffusion coefficients for ^{226}Ra of between 6×10^{-9} cm^2 s^{-1} and 1×10^{-9} cm^2 s^{-1} were determined.

- <u>Colloidal populations in deep groundwaters.</u>
  Colloid populations have been measured in deep and shallow groundwaters as part of several natural analogue studies, *e.g.* Cigar Lake, 8 mg l^{-1} (Vilks *et al.*, 1991); Alligator Rivers, 1.4 µg l^{-1} (Seo, 1991); Poços de Caldas, 0.8 mg l^{-1} (Miekely *et al.*, 1992). Generally the populations measured are considered to be low. However, if these colloids occurred in the repository environment and were mobile, a significant quantity of radionuclide could be carried over the lifetime of the repository despite the low populations.

- <u>Microbiological populations in hyperalkaline environments.</u>
  The population and behaviour of microorganisms in hyperalkaline environments has been studied as part of two natural analogue studies, one in Oman (Bath *et al.*, 1987) and the other at Maqarin (Alexander, 1992). In both cases, total populations were low but the microorganisms were well adapted to the ambient conditions. Of particular note were the populations of sulphate reducing bacteria which, in a repository, would exacerbate steel corrosion and concrete degradation. It was concluded in these studies that the controlling influence on the microbiological populations was not the extreme chemical environment but, rather, a lack of the primary nutrients (C, N, P and S).

4.2 **Further studies**

Further natural analogue studies of radionuclide release and transport processes are needed in, at least, the following areas:

- <u>Better methods for measuring *in situ* distribution coefficients (K_d).</u>
  Three methods for measuring *in situ* K_d values have been tried: (i) from radionuclide concentrations in rock-water pairs, (ii) from radionuclide concentration profiles, and (iii) from isotope ratios. The first of these methods is the technique commonly used for measuring K_d values in fractured rocks and sometimes, in an attempt to distinguish between sorption and precipitation, selective leachants are used (for discussion

see Chao, 1984). This is a good first step towards determining 'real' K_d values but this method is not yet fully proven because there is still concern that the leachants used are not totally specific and that redistribution of radionuclides may occur during the leaching operation.

- Colloid migration in the far-field.
  Laboratory and field experiments have shown that colloids exist at depth, albeit in low populations, and that radionuclide uptake may occur onto colloids. However, it has not been shown that colloids can represent a feasible transport mechanism over long distances in deep rocks. A natural analogue study is needed to show if colloids are capable of long-distance migration in a repository-relevant environment where several groundwater compositional boundaries would need to be crossed by the colloids (locations where colloids would become unstable). If the colloids cannot migrate long distances or cannot cross these chemical boundaries, then colloid transport is not important.

- Radionuclide release and transport processes in sedimentary rocks.
  Most recent natural analogue studies have concentrated on fractured crystalline rock environments but it is not possible to transfer information derived from these studies to either argillaceous rocks or to evaporites. It is necessary to perform parallel analogue studies to those in crystalline rocks to investigate general radionuclide transport and retardation processes in the sedimentary rocks. Specific attention should be paid to redox fronts and to matrix diffusion in the secondary porosity.

- Radionuclide transfer processes at the geosphere-biosphere interface.
  It is possible to apply the natural analogue methodology to biosphere studies in general but specifically it would be informative to examine the geosphere-biosphere interface because this is an area not clearly in the realm of either the far-field modeller or the biosphere modeller; as a result this interface could be overlooked. Numerous analogues exist for radionuclides migrating downwards into the geosphere from the biosphere (*e.g.* fallout from Chernobyl; Gustafsson *et al.,* 1987) but here the processes may well be different for the radionuclides are travelling in the opposite direction to that of interest to performance assessment.

- Far-field gas migration.
  It was discussed earlier that large volumes of hydrogen will be evolved from L/ILW repositories. This migration of this gas through the far-field may influence radionuclide transport either by direct transport of gaseous species or by perturbing the flow of groundwaters. Furthermore, the gas may be involved in reactions with the rock. Natural analogues of gas migration may be found in the vicinity to hydrocarbon reservoirs and considerable expertise exists in the petroleum industry for interpreting gas migration (*e.g.* Philp & Crisp, 1982) which could be tapped.

5. Conclusions

This short review has highlighted the fact that a considerable volume of positive information has been derived from natural analogue studies which could be applied to performance assessment. Furthermore, there are a number of areas for which adequate data are lacking which could be practically studied using the natural analogue methodology.

It is recommended that modellers take note of the current review of natural analogue studies and revisit some of the positive data obtained with a view to applying these data to performance assessment. However, perhaps more importantly, modellers should take note of the possibilities for obtaining further data in new natural analogue studies and modellers should become involved at an early stage in planning these studies so that they become focussed on performance assessment requirements right from the outset. It would appear that, only if a strategy of dialogue is followed, can both modellers and the natural analogue community be assured that future natural analogue studies do indeed obtain the data that are required and that these data are used to their full advantage.

References

Alexander, W.R., Dayal, R., Eagleson, K., Eikenberg, J., Hamilton, E., Linklater, C.M., McKinley, I.G. & Tweed, C.J. (1992 in press) A natural analogue of high pH cement pore waters from the Maqarin area of northern Jordan II: results of predictive geochemical calculations. *Journal of Geochemical Exploration.*

Allard, B., Eliasson, L., Höglund, S. & Andersson, K. (1984) Sorption of Cs, I and actinides in concrete systems. *SKB Technical Report,* **TR 84-15**.

Bath, A.H., Christofi, N., Neal, C., Philp, J.C., Cave, M.R., McKinley, I.G. & Berner, U. (1987) Trace element and microbiological studies of alkaline groundwaters in Oman, Arabian Gulf: a natural analogue for cement pore-waters. *Nagra Technical Report,* **NTB 87-16** and *BGS Technical Report,* **FLPU 87-2**.

Behrensmeyer, A.K. (1980) Fossils in the making. *Chicago University Press.*

Benvegnù, F., Brondi, A. & Polizzano, C. (1988) Natural analogues and evidence of long-term isolation capacity of clays occurring in Italy: contribution to the demonstration of geological disposal reliability of long--lived wastes in clay.*CEC Nuclear Science and Technology Report,* **EUR 11896**.

Bresle, A., Saers, J. & Arrhenius, B. (1983) Studies in pitting corrosion on archæological bronzes. *SKB Technical Report,* **TR 83-05**.

Bruno, J., Cross, J.E., Eikenberg, J., McKinley, I.G., Read, D., Sandino, A. & Sellin, P. (1990) Testing of geochemical models in the Poços de Caldas analogue study. *SKB Technical Report,* **TR 90-20**; *Nagra Technical Report,* **NTB 90-29**; *UK DoE Technical Report,* **90-051**.

Chao, T.T. (1984) Use of partial dissolution techniques in geochemical exploration. *Journal of Geochmical Exploration,* **20**, 101-119.

Chapman, N.A., McKinley, I.G., Penna Franca, E., Shea, M.J. & Smellie, J.A.T. (1992 in press) The Poços de Caldas project: an introduction and summary of its implications for radioactive waste disposal. *Journal of Geochemical Exploration.*

Colley, S. & Thomson, J. (1985) Recurrent uranium relocations in distal turbidites emplaced in pelagic conditions. *Geochimica et Cosmochimica Acta,* **49**, 2339-2348.

Colley, S. & Thomson, J. (1991) Migration of uranium daughter radionuclides in natural sediments. *CEC Nuclear Science and Technology Report,* **EUR 13182**.

Côme, B. & Chapman, N.A. (editors) (1986) Natural analogue working group; First meeting, Brussels, November 1985. *CEC Nuclear Science and Technology Report,* **EUR 10315**.

Cramer, J.J. (1991) Cigar Lake project: progress report for the period May-October 1991.

AECL Cigar Lake Report, **CLR-91-5.**

Cross, J.E., Haworth, A., Lichtner, P.C., MacKenzie, A.B., Moreno, L., Neretnieks, I., Nordstrom, D.K., Read, D., Romero, L., Scott, R.D., Sharland, S.M. & Tweed, C.J. (1991) Testing models of redox front migration and geochemistry at the Osmau Utsumi mine and Morro do Ferro analogue study sites, Poços de Caldas, Brazil. *SKB Technical Report*, **TR 90-21**; *Nagra Technical Report*, **NTB 90-30**; *UK DoE Technical Report*, **WE 90-052.**

Forbes, R.J. (1934) Aus der ältesten Geschichte des Bitumens. *Bitumen*, 6-11.

Gustafsson, E., Skålberg, M., Sundbland, B., Karlberg, O., Tullborg, E-L., Ittner, T., Carbol, P., Eriksson, N. & Lampe, S. (1987) Radionuclide deposition and migration within the Gideå and Finnsjön study sites, Sweden: A study of the fallout after the Chernobyl accident. Phase I, initial survey. *SKB Technical Report*, **TR 87-28.**

Hellmuth, K-H. (1989) Natural analogues of bitumen and bitumenized waste. *Finnish Centre for Radiation and Nuclear Safety*, **STUK-B-VALO 58.**

Johnson, A.B. & Francis, B. (1980) Durability of metals from archæological objects, metal meteorites and native metals. *Battelle Pacific Northwest Laboratory*, **PNL-3198.**

Lee, C.F. (1986) A case history on long-term effectiveness of clay sealant. *In:* Côme, B. & Chapman, N.A. (editors) Natural analogue working group; Second meeting, Interlaken, June 1986. *CEC Nuclear Science and Technology Report*, **EUR 10671**, 172-190.

MacKenzie, A.B., Shimmield, T.M., Scott, R.D., Davidson, C.M. & Hooker, P.J. (1990) Chloride, bromide and iodide distributions in Loch Lomond sediment interstitial water. *BGS Technical Report*, **WE/90/2.**

Mazurek, M. (1990) OBS: the interface between marl and concrete lining in Seelisberg tunnel. *Nagra Technical Report*, **NIB 90-08.**

Miekeley, N., Coutinho de Jesus, H., Porto da Silveira, C.L., & Degueldre, C. (1992 in press) Chemical and physical characterisation of suspended particles and colloids in waters from the Osamu Utsumi and Morro do Ferro analogue study sites, Poços de Caldas, Brazil. *Journal of Exploration Geochemistry.*

Miller, W.M., Alexander, W.R., Chapman, N.A., McKinley, I.G. & Smellie, J.A.T. (1993 in press) Natural analogue studies in the geological disposal of radioactive wastes. *Nagra/SKB/UK DoE-HMIP Report Series.*

Milodowski, A.E., Nancarrow, P.H.A. & Spiro, B. (1989) A mineralogical and stable isotope study of natural analogues of ordinary portland cement (OPC) and CaO-Si_2-H_2O (CSH) compounds. *Nirex Radioactive Waste Disposal: Safety Studies*, **NSS/R240.**

Nagra (1985) Project Gëwahr. Nuclear waste management in Switzerland: feasibility studies and safety analyses. *Nagra Technical Report*, **NTB 85-09.**

Philp, R.P. & Crisp, P.T. (1982) Surface geochemical methods used for oil and gas prospecting: a review. *Journal of Geochemical Exploration*, **17**, 1-34.

Pusch, R., Börgesson, L. & Erlström, M. (1987) Alteration of isolating properties of dense smectite clay in repository environment as exemplified by seven pre-quaternary clays. *SKB Technical Report*, **TR 87-29.**

Pusch, R. & Karnland, O. (1988) Geological evidence of smectite longevity. The Sardinian and Gotland cases. *SKB Technical Report*, **TR 88-26**.

Rolfe, W.D.I. & Brett, D.W. (1969) Fossilization process. *In:* Eglinton, G. & Murphy, M.T.J. (editors) Organic geochemistry. *Springer Verlag*, Berlin.

Seo, T. (1991) Uranium distribution in the colloidal and solute phases at the Koongara uranium deposit. *In:* Duerden, P. (editor) Alligator Rivers Analogue Project: second annual report 1989-1990. *Australian Nuclear Science and Technology Organisation.*

Tylecote, R.F. (1979) The effect of soil conditions on the long-term corrosion of buried tin-bronzes and copper. *Journal of Archæological Science*, **6**, 345--368.

Vilks, P., Cramer, J.J., Bachinski, D.B., Doern, D.C. & Miller, H.G. (1991) Studies of colloids and suspended particles in the Cigar Lake uranium deposit. *Migration 1991.*

GAS PRESSURE BUILD UP AND HOST ROCK MECHANICS - POSSIBLE IMPLICATIONS FOR THE PERFORMANCE AND PERFORMANCE ASSESSMENT OF A HIGH LEVEL NUCLEAR WASTE REPOSITORY

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1. Introduction

Gas pressure in rock around underground excavations affects the stability of the excavations. Presumably repository site selection will assure that excessive natural in situ gas pressures are not likely to be encountered at a repository site. The question remains as to whether the emplacement of waste might induce effects similar to those associated with naturally ocurring gas pressurization. One possibility is pressurization of air and steam as a result of the temperature rise induced by radioactive decay of the emplaced waste. In a host formation of low permeability and high porosity, especially if the rock contains a large amount of water, i.e. is partially but significantly saturated, it may be possible that the potential pressurization resulting from evaporation of groundwater can not be released sufficiently fast to prevent fracturing of the host rock. For such a repository situation it may be necessary to evaluate the risk of fractures propagating as a result of pressurization. Such fractures could affect the stability of excavations, e.g. waste emplacement holes or drifts, and could affect the isolation capability of a repository host formation.

Analogs may be found in nature, namely in the geological record, where fracture propagation as a result of internal pressurization may have occurred, e.g. during intrusive sequences and near volcanic events. An investigation of the conditions near volcanic and intrusive heating and/or pressurization that induce, or do not induce, fracturing of the rock, with the result of creating potential preferential flowpaths may be a useful endeavor within the context of analog studies aimed at predicting the performance of HLW repository host rock formations.

A major challenge in predicting the long term performance of repositories for the disposal of HLW (High Level radioactive Waste) is to provide reasonable assurance that no excessive fracturing will take place in the rock around the repository. Excessive fracturing could affect repository performance in a number of ways: fracturing around emplacement holes or drifts could lead to excessive loading of waste packages; the development of long pervasive fractures could create preferential flow paths for gas or liquid flow towards or away from emplaced waste. Excessive fracturing could complicate retrieval, if necessary.

Rock engineering has had a considerable interest in rock fracturing for a variety of applications. Few traditional engineering applications deal with structures on a timeframe anywhere near that required for nuclear waste repository performance predictions. We can invoke the experience gained in analog studies to identify possible parallel approaches aimed at determining the risk of excessive fracturing developing at some future time around a HLW repository.

Two candidate environments suggest themselves for potential analog studies: intrusions, and volcanic areas. For both basic conditions have existed that may bear on repository performance: a rock mass has been heated internally, pressurized, and deformed. Such combinations of conditions should allow for analog studies aimed at evaluating under what conditions fracturing of a rock mass may develop and may propagate.

2. Stability of underground excavations

Gas pressures and gas releases can affect underground mining and construction. A common approach to analyze the stability of a mine roof in flat bedded deposits (e.g. Hoek and Brown, 1980, p. 235-6) is to consider the roof as a beam that spans the excavation, and is loaded by its own weight and by a gas (or water) pressure acting on top of the beam. Even a modest gas pressure can suffice to cause roof failures.

In many mining districts, for example in the potash mines in Southern New Mexico, pressure relief holes are drilled routinely into the back of mine entries, particularly at intersections, to relief such pressures. Under extreme conditions gas pressures can cause major outbursts, involving extensive damage. Major gas outbursts most commonly have been encountered in coal, salt, and potash mines (e.g. Obert and Duvall, 1967, Section 19.9; Ribicic et al, 1991). Methane, particularly dangerous because of its susceptibilty to ignition, has been encountered in a very wide variety of underground mining and construction environments (e.g. Edwards, 1991; Warren et al, 1991).

Brady and Brown (1985, Chapter 9) present a method to analyze whether a block of rock around an underground excavation is in equilibrium, or might fall or slide into the excavation. Again, if a gas or water pressure acts along the faces of a potentially unstable wedge, the effect will be de-stabilizing: the fluid pressure adds to the driving forces loading the wedge, and the fluid pressure decreases any effective frictional resistance that counteracts sliding along the wedge faces.

An engineering approach to evaluate the influence of a fluid (e.g. gas) pressure on the stability of rock is by performing the stability analysis in terms of the effective stress. The strength of rock, when influenced by fluid pressure acting within the rock pores, is determined on the basis of the effective stress, i.e. the total stress reduced by the pore pressure. While this effective stress approach may be oversimplifying, e.g. Patterson, 1978, Section 5.2, and should more appropriately be referred to as the "conventional" effective stress approach, the widespread engineering use of the method suggests its adequacy to at least illustrate the fundamental importance of fluid pressure in rock failure analysis. The frictional resistance against sliding along a weakness plane is reduced by reducing the total normal stress by the fluid (e.g. gas) pressure acting across the weakness. The effective stress approach is well established in engineering practice (e.g. Jaeger and Cook,1979,Section 8.9; Goodman, 1989, Section 5.6) and for the analysis of the development of geological structures (e.g. Roberts, 1969; Shaw, 1980).

3. Pressurized crack propagation - Engineering

Propagating fractures in rock by means of pressurizing cracks or fractures finds a number of applications in rock engineering:

- hydraulic fracturing

Hydraulic fracturing is used to enhance the production of oil and gas from tight formations, to stimulate water flow in water wells, and to measure the state of stress in rock: a section of a borehole is isolated by means of packers, the isolated interval is pressurized, thus causing a tensile stress in the borehole walls, and the pressure is increased until the rock fails, i.e. until a tensile fracture is induced. For production purposes the pressurization may be continued in order to propagate the fracture to great distances, thus enhancing the permeability of the rock formation, and facilitating flow towards the borehole.

- waste injection

Brines, chemical wastes, and some low level radioactive wastes are injected in tight (low permeability) rock formations through boreholes, by means of a hydraulic fracturing procedure very similar to the one described above (e.g. Weeren et al, 1985).

- blasting

A significant aspect of the propagation of fractures around boreholes in which explosives are detonated is the driving force exerted by the explosive gases. Research on this subject has included extensive investigations of the propagation of pressurized cracks in rock (e.g. Ghosh, 1990; Fourney, 1983).

- grouting

Cement, chemical and clay grouts are injected into rocks and soils with the objective of reducing the permeability of the rock or soil, e.g. around and underneath hazardous waste sites. Some grouting methods intentionally apply a high pressure during injection in order to fracture the ground, and thus facilitate grout penetration over greater distances. On occasion fracturing is induced unintentionally, and then may be counterproductive in terms of attaining the intended permeability reduction.

- geothermal energy production

The "Hot Dry Rock" concept (e.g. Bowen, 1989, Section 5.5) relies on creating a network of hydraulic fractures in a rock mass with low natural permeability and at high temperature. A potentially attractive feature of geothermal energy research is that much of the induced fracturing is pursued at temperatures that are in the general range of those that may be encountered relatively close to a HLW repository.

In sum, pressurized fracture propagation finds application in a variety of rock engineering applications. Considerable research has been conducted on many of these applications. It should be of benefit to evaluate the risk of rock fracturing in a repository host formation based on the information available in other contexts.

Shortcomings in the engineering literature on induced rock fracturing with regard to repository performance analogies may be a lack of detail with regard to the influence of time, at least very long time, with regard to the influence of temperature, and with regard to the influence of corrosive crack propagation. The time scale frequently studied by geologists far exceeds the time scale of primary interest for repository performance, which may pose similar problems in relating mechanics and mechanisms of fracture formation from the geological time scale to the repository performance time scale.

An aspect of fracture propagation in rock seldom accounted for in engineering practice is the influence of chemical effects, notably interactions with water, near or at the tip of a propagating fracture. Such effects have been shown to be potentially significant, especially for fractures that propagate slowly (e.g. Spetzler et al, 1981). Many of the rate or time effect and the water or corrosion effect studies have been performed within the general framework of geological investigations, suggesting a natural extension of possible analogs within the fields where long-term mechanical behavior of rock have been investigated.

4. Pressurized crack propagation - Geology

The development of fractures in the earths' crust is a basic topic of investigation in many areas of geological inquiry. A brief review of some literature quickly allows one to identify many studies that could appropriately be considered for further investigation within the context of analog studies aimed at predicting and evaluating the eventual performance of the host rock formations surrounding HLW repositories. The prime objective of the following discussion is to briefly highlight a few topics that are directly relevant to possible fracture formation around a HLW repository.

Knipping(1989) presents results of calculated temperature distributions near an intruding dike, and discusses physico-chemical changes in the rock within which the intrusion has occurred. Although short-term heating tests have shown considerable success with calculated temperature field distributions as compared to the measured ones, such experiments of necessity involve a relatively small rock volume, and so far have been limited to a few years, at most. It seems likely that many natural analogs of this type must exist, and may provide validation information for thermal predictions.

Decker and Kinoshita (1971) compare surface deformations near volcanos with predicted (calculated) results, and demonstrate the feasibility of calibrating the theoretical models to simulate deformations induced by a hot magma core. Visualizing a repository as a heat source, and resulting pressure source, the general thermal and mechanical similarities would seem sufficient to warrant further investigations of volcanic pressure and heat sources as possible analog models for repository host rock behavior. Similar deformation models and calculations have been presented by Johnson, 1970.

Roberts (1960) places most emphasis on the development of fractures in brittle rock resulting from magmatic intrusions, and further examples of detailed analyses of the development of fractures are given by Aucott (1969). Given that one concern about repository host rock performance is the risk of inducing fractures, particularly fractures that might propagate great distances, at, what are by engineering standards, possibly very slow rates, it seems reasonable to postulate that extensive possibilities exist for conducting analog studies in characteristic potential repository host rock formations aimed at understanding specifically the fracture formation history. A full understanding of the mechanics that have caused fracturing in the past, and of the conditions that did not result in fracturing, should assist in providing confidence about the future behavior of the rock mass surrounding emplaced HLW waste.

5. Implications for repository performance - potential analog studies

A number of areas can be suggested as potentially useful and productive for further investigation from the point of view of identifying possible analog models of future repository host rock behavior and performance.

A topic that would seem to be a fairly obvious candidate for the Yucca Mountain site is the investigation of rock fracturing within areas relatively close, but not immediately adjacent, to the main pressurization location associated with volcanic activity. It needs to be determined whether or not the pressure and temperature ranges in such locales may correspond to those to which a repository host rock formation might be subjected. If the similarities are within an acceptable range, it might be possible to gain insight into the risk of developing fracturing around a repository by studying the conditions that caused fracturing in areas near volcanoes.

More generally, the mechanics of intrusion can be used for analog studies, particularly from the point of view of associated fracture, e.g. joint and fault, development. While the time duration of the events may be very long compared to likely events induced by a repository, it may be possible to treat fracturing on this time scale, and extremely low strain rates, as one type of bounding condition. Alternatively, it is possible that some rock fracturing induced by intrusions may develop fairly rapidly. As a minimum, the topic deserves investigation.

A number of possibilities exist for engineering analog studies. Examples of such studies that have been performed in the past include the study of ancient cements in order to investigate the durability of cementitious repository components (e.g. Malinowski, 1982; Roy and Langton, 1983). A much broader approach to the use of ancient materials has been argued for forcefully and persuasively by Winograd (1986), who suggests multiple avenues for possible analog-type studies that could improve our understanding of the long-term behavior of materials and of the natural host environment under conditions similar to those near a repository.

An area of investigation that deserves attention is the long term stability of underground excavations. Recent design approaches for underground excavations have seen a dramatic increase in the use of classification methods. Such classification approaches, implicitly, use the concept of analogs, by postulating that the performance of future underground excavations can be predicted from the past performance of similar excavations. Again, within the context of conventional engineering practice, not much need has existed for performance predictions exceeding a few decades. As a result, the data bases of the widely used classification methods do not include case studies of excavations that have been standing for centuries, or that have failed in the course of such a timeframe. Many underground openings are available to perform long-term stability studies. Examples include natural caves, as well as ancient excavations, e.g. mines, water conveyance tunnels, dwellings and temples.

6. Summary and conclusions

Assessing and predicting the performance of the host rock mass within which a HLW repository is located requires predicting mechanical behavior of rock for a duration which is very long compared to that of engineering structures in or on rock, and relatively short compared to geological timeframes. An approach to provide reasonable assurance about the behavior of the rock mass over a timeframe of the order of millenia is to perform analog studies. Most analog studies conducted to date have emphasized geochemical analogs. It is suggested here that a broader range of analog studies could productively implemented. Highlighted examples focus on topics that will improve our understanding of the conditions under which rock fracturing around a repository may develop. Analog studies can pursue natural environments, such as fracturing near volcanic and intrusive events or histories. Analog studies also might be conducted with the objective of improving our understanding of the stability of underground excavations based on the performance of ancient manmade or geological underground openings.

References

Aucott, J.W., 1970, Tectonics of the Galway Granite, Mechanism of Igneous Intrusion, Proceedings of the Symposium, Liverpool, 1969, Ch. 4, pp. 49-66, Gallery Press, Liverpool.

Bowen, R., 1989, Geothermal Resources, 2nd edit., Elsevier Applied Science, London

Brady, B.H.G., and E.T. Brown, 1985,Rock Mechanics for Underground Mining, George Allen & Unwin, London

Cleary, M.P., 1983, Modelling and Development of Hydraulic Fracturing Technology, Rock Fracture Mechanics, CISM Courses and Lectures No. 275, H.P. Rossmanith, Ed., Ch. XIV,pp. 383-475, Springer-Verlag, Wien.

Decker, R.W., and W.T. Kinoshita, 1971, Geodetic measurements, The surveillance and prediction of volcanic activity, pp. 47-74, Unesco, Paris.

Edwards, J.S.,1991, Potential hazards resulting from the presence of methane dissolved in groundwater, pp. 223-231, Vol 1, Proceedings, 4th International Mine Water Congress, Ljubljana, Slovenia, Yugoslavia, September

Fourney, W.L., 1983, Gas Well Stimulation Studies, Rock Fracture Mechanics, CISM Courses and Lectures No. 275, H.P. Rossmanith, Ed., Ch. XII, pp. 353-369, Springer-Verlag, Wien.

Franklin, J.A., and M.B. Dusseault, 1991, Rock Engineering Applications, McGraw-Hill, Inc., New York.

Ghosh, A., 1990, Fractal and Numerical Models of Explosive Rock Fragmentation, Ph.D. Dissertation, University of Arizona, Tucson.

Goodman, R.E.,1989,Introduction to Rock Mechanics, Second Edition, John Wiley & Sons, New York.

Hoek, E. & E.T. Brown, 1980, Underground Excavations in Rock, The Institution of Mining and Metallurgy, London.

Kesseru,Z., 1991, Spontaneous Hydrofracturing: a Frequent Way of Failure in Natural and in Engineered Rock/Soil Barriers and New Ways for Process Control, pp.245-255, Vol 1, Proceedings 4th International Mine Water Association Congress, Ljubljana(Slovenia)-Portschach(Austria), September.

Khristianovich,S.A., and R.L. Salganik, 1983, "Several Basic Aspects of the Forming of Sudden Outbursts of Coal(rock) and Gas," Proc. 5th Int. Cong. Rock Mech., Vol E, pp. E41-50.

Knipping, B., 1989, Basalt Intrusions in Evaporites, Lecture Notes in Earth Sciences 24, Springer-Verlag, Berlin.

Malinowski, R., 1982, Ancient Mortars and Concretes: Aspects of their Durability, pp. 89-100, History of Technology, 7th Annual Vol, A.R. Hall and N. Smith, Eds., Mansell Publishing Ltd., London.

Murrell, S.A.F, 1970, Global tectonics, rock mechanics, and the mechanism of volcanic intrusions, Mechanism of Igneous Intrusion, Proceedings of the Symposium. Liverpool, 1969, Ch. 17, pp. 231-44. Gallery Press, Liverpool.

NEA/OECD, 1990, Disposal of Radioactive Wastes - Can Long-Term Safety be Evaluated ?, Radioactive Waste Management Committee, Paris.

Obert,L., and W.I. Duvall, 1967, Rock Mechanics and the Design of Structures in Rock, John Wiley & Sons, Inc., New York.

Paterson, M.S., Experimental Rock Deformation - The Brittle Field,
Minerals and Rocks 13, Springer-Verlag, Berlin.

Ribicic,M., M. Kocevar and R. Hoblaj, 1991, Hydrofracturing of Rocks as a Method of Evaluation of Water, Mud, and Gas Inrush Hazards in Underground Coal Mining, pp. 291-303, Vol 1, Proceedings, 4th International Mine Water Association Congress, Ljubljana (Slovenia) - Poertschach (Austria), September.

Roberts, J.L., The intrusion of magma into brittle rocks, Mechanism of Igneous Intrusion, Proceedings of the Symposium, Liverpool, 1969, Ch. 20, pp. 287-338. Gallery Press, Liverpool.

Roy, D.M., and C.A. Langtòn, 1983, Characterization of Cement-Based Ancient Building Materials in Support of Repository Seal Materials Studies, Report BMI/ONWI-523, Office of Nuclear Waste Isolation, Columbus, Oh.

Scholz,C.H.,1990,The Mechanics of Earthquakes and Faulting, Cambridge University Press, Cambridge, England.

Spetzler, H., C. Sondergeld and I.C. Getting, 1981, The Influence of Strain Rate and Moisture Content on Rock Failure, Anelasticity in the Earth, F.D. Stacey, M.S. Paterson, and A. Nicholas, Eds., Geodynamics Series Volume 4, pp. 108-112, American Geophysical Union, Washington, DC and Geological Society of America, Boulder, CO.

Warren,C.D., G.P. Birch, A. Bennett, & P.M. Varley, 1991, "Methane studies for the Channel Tunnel," Quart. Jnl. Eng. Geol., Vol. 24, pp. 291-309.

Weeren, H.O., E.W. McDaniel, and L.C. Lasher, 1985, "Recent Hydrofracture Operations at Oak Ridge National Laboratory," Waste Management '85, Vol 2, pp. 465-471, Proceedings of the Symposium, Tucson, March 1985.

Winograd, I.J., 1986, Potential Contributions of Archaeology to Evaluation of Thick Unsaturated Zones of Arid Regions for Toxic Waste Disposal, U.S. Geological Survey Open-File Report 86-0136, Reston, Va.

MAGMATIC INTRUSIONS IN CLAYS AS GEOMECHANICAL NATURAL ANALOGUES

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ABSTRACT

Uncertainty about predicting the behaviour of host media for radioactive waste repositories over extended periods of time is one of the most troublesome aspects of the process of building a consensus over nuclear waste disposal. Neither laboratory experiments nor numerical simulations based on these experiments, and not even in situ tests lasting several years can provide the basis for understanding the long-term (thousands of years) performance of the host rocks in the near field.

To a certain extent, through their reference to existing situations, natural analogues are instrumental in describing phenomena, predicted to occur in repositories, in a way which is convincing to the researchers and appealing to the general public.

Thermal alterations of argillaceous materials can be studied in all cases where clays have undergone thermal metamorphism. Intrusions of magma within clay bodies are relatively common. A similar situation may be the flow of lava on clay outcrops. Useful information may be provided also by the study of argillaceous sediments exposed to geothermal heat.

Most studies of processes and phenomena occurring in natural analogues, and relevant to argillaceous materials, regard their geochemistry and mineralogy. Geomechanical features of natural analogues have received considerably less attention. Geomechanical data regard possible fracturation and thermoconsolidation, related changes in density and porosity, permeability and strength. These parameters, and in particular the last two, are the basic parameters for the engineering analysis of the thermal impacts of radioactive waste disposal in argillaceous materials.

Any mechanical or hydraulic property of the argillaceous materials that is altered irreversibly by the thermal transient due to the proximity with the magma is amenable to be the subject of a geomechanical, natural analogue study.

1. Background and justification of research

The heating caused by the intrusion of magmatic material into argillaceous sediments may be considered as a natural analogue of the thermal effects of radioactive waste disposal in clays. Although not all conditions are precisely analogous in the observed geological sites and in the planned repositories, many useful conclusions may be drawn from the analogy. A particularly interesting example is the study of geochemical and mineralogical alterations within a thermometamorphic halo around a magmatic intrusion in clay at Orciatico in Tuscany [Leoni et al, 1986; Benvegnù et al, 1988].

A similar analogue has been identified at Cerillos, New Mexico, where a series of monzonite plugs intrude Cretaceous sedimentary rocks, including the Mancos shale. The shale is composed by mixed layer smectite-illite; approaching the magmatic material the degree of illitization increases regularly [Brookins, 1987].

Both at Orciatico and Cerillos the temperatures at the contact with the magmatic body were much higher than temperatures expected in a waste repository.

There are many instances where argillaceous sediments have been contacted by lava. A typical case is that of Busachi in central Sardinia, where a bentonite bed, about 10 m thick, has been very significantly heated (more than 200°C) for several days when rhyolitic lava flowed on it. Analyses showed that smectite content was not reduced to less than 60% in any part of the bed and only slight cementation took place in the uppermost level by precipitation of heat-released silica [Pusch and Karnland, 1988].

In this paper the feasibility of analysing the field observations in a heated clay body from a thermomechanical viewpoint is examined. For example, given the advance in thermo-geomechanical modelling of clay behaviour, a numerical simulation of the thermomechanical alterations of the Orciatico clay could provide interesting and useful results.

In general terms the geomechanical simulation of the effects of magmatic intrusions into clay bodies should focus on the outer metamorphic zone, farther away from the heat source, where temperatures are expected to have been in the same range as in clay near waste packages. In this zone the thermo-geomechanical modelling has the greatest experimental support. In the zone of higher temperatures, very close to the magma, where processes of melting and vitrification are believed to have occurred, the thermomechanical clay response is known only in very general terms. Thus, it is of primary importance to determine the evolution of isotherms during the process, or at least the value of the temperature peak at a given location.

The interest in a quantitative analysis of a natural analogue is twofold. Firstly, such analysis provides a basis for verification of a number of hypotheses concerning the short-term and long-term modelling of thermal, hydraulic and thermomechanical clay behaviour, as established by means of laboratory testing. Secondly, it may furnish a tool for quantitative assessment of the hypothetical long-term thermo-hydromechanical performance of the clay mass around a heat source.

Finally, it must be remembered that natural analogues of the type discussed here are nothing more than the final outcome of a heating-cooling cycle, with possible subsequent alterations due to weathering and unloading, as a consequence of erosion of the overburden. A successful geomechanical simulation might provide an insight into the thermomechanical part of the evolution process starting at the moment of magmatic intrusion into the clay mass and followed by heating and subsequent cooling till stabilization of temperature.

It is conceivable that a well characterized natural analogue could be used for the validation of a thermo-mechanical model; increasing, therefore, the confidence in the engineering analysis of repositories and in performance assessment, at least as far as modelling the near field is concerned.

2. Thermal alterations at Orciatico

At the Orciatico site, a small magmatic intrusion, with an estimated initial temperature around 800°C, penetrated pliocenic argillaceous sediments. Several boreholes have been drilled at the site, to investigate the metamorphic contact zone from the chemical and mineralogical viewpoints. The boreholes were situated at different distances from the outcrop of magmatic rock. Thus, the boreholes passed through a sequence of zones differently affected by heat. It was therefore possible to compare a zone of highly altered clay, at the contact with the heat source, to a more remote zone of less affected clays and to completely unaffected clay.

Assuming that the clay body had originally the same properties throughout the whole mass, changes introduced by heating in rock mineralogy and geochemistry were evaluated. Some of this evaluation may be used for a geomechanical analysis as discussed below.

Three different types of thermometamorphism have been identified: crystallization of pyroxene, plagioclase and biotite; crystallization of K-feldspar; and crystallization of K-smectite. The first kind of metamorphism occurred only very close to the contact, while the other two occurred all over the metamorphic halo and involved only fine sized mineral grains.

On the basis of physical alterations, two distinct zones have been identified. In zone I (0.5 to 1.5-3.0 m directly around the heat source) the clay became extremely compact, with scarce fracturation associated with re-crystallization and loss of plasticity. In zone II, further away from the heat source, an extensive fracturation of the argillaceous rock occurred. It has been suggested that, in the early stage, an intense migration of interstitial water took place, followed by extensive, diffuse micro-cracking caused by stress. It is suggested that cracking may have caused an increased permeability and convective water circulation. This in turn led to the formation of smectite and probably also to accelerated cooling. The smectitization, that causes a rise above the reference value of the cation exchange capacity, is a totally unexpected phenomenon that may enhance the role of the clay as a barrier. If confirmed in other circumstances, it could be considered an added bonus of argillaceous barriers employed for the isolation of heat-generating radioactive waste.

3. Thermomechanical laboratory tests and modelling

Some thermomechanical phenomena described above, such as irreversible compaction of clays, thermally induced hydraulic fracturation associated with dilatancy and thermal change in permeability, have been studied experimentally in the laboratory at temperatures ranging up to 120°C [Hueckel and Baldi, 1990]. In drained tests at constant stress it was found that slow heating up to 120°C may cause very different volumetric irreversible strain responses depending on whether the material is stressed or not. For high confining stresses, the response to heat consists in a dramatic thermal consolidation. At low confining stress the material dilates when heated. Rapid heating or undrained heating in the presence of some differential stress, in a material with relatively undeformable skeleton, may lead to high water pressure rise and to possible skeleton fracturation and failure.

The above types of skeleton behaviour are caused by the thermal reduction of the elastic domain or yield limit, i.e. the stress range in which skeleton reacts elastically to stressing. When the elastic domain during heating shrinks so much that the stress in the skeleton reaches the yield limit, clay irreversibly consolidates or dilates (and fractures) depending on the confining stress. To quantify such behaviour, a thermo-plasticity model for saturated clays has been developed [Hueckel and Borsetto, 1990]. This model has been combined with Darcy's formulation of seepage through porous media and Terzaghi's effective stress principle to simulate numerically the response of clay and interstitial water to heating, using a computer code based on the Finite Element Method [Baldi et al, 1987].

In a separate effort, effects of dehydration and re-hydration of smectite during heating, and cooling were studied. In particular, the removal of adsorbed water from interlamellar spaces, collapse of clay clusters and related changes in porosity and permeability, observed by Pusch [1987], were mathematically modelled. A mixture theory of a fluid interacting with an elastic solid of variable porosity was adopted [Hueckel, 1992; Ma and Hueckel, 1992]. The dehydration was simulated as interconstituent mass transfer, making the adsorbed water gradually a part of freely flowing water. The link between porosity and permeability was expressed by the Carman-Kozeny equation, which gives reasonable results for Boom clay (hydraulic conductivity about 10^{-12} m/s).

4. Numerical simulation of thermomechanical alterations

The above mentioned computer code has been applied to study the effects on clay of a cylindrical, infinitely long, centrally located heat source [Baldi et al, 1990]. The results of this simulation will be analyzed now from the viewpoint of the Orciatico intrusion.

The intruded magmatic body has the shape of an ellipsoid with the long axis oriented north-south. It should be realized that the clay cover at the time of the intrusion was thicker than at present, since a significant amount of overburden has been removed by erosion. The surroundings of the intrusion can be idealized as a cylindrical, centrally heated body having its axis coincident with that of the axis of the currently exposed ellipsoid. One can assume also that the radial flow of heat and water away from the heat source, as assumed by the model geometry, does not deviate excessively from the actual flow which occurred in situ. Therefore, the thermomechanical response at Orciatico was, at least qualitatively, and with all the possible reservations due to the above simplifying assumptions, similar to that simulated in the heating, boundary-value problem with axial symmetry. The quantitative analogy is impossible in this case, because the simulation was performed assuming that the heating surface was located 0.15 m from the axis, that the heat output was constant at this radius and that the resulting temperature was never more than 180°C. The fundamental features of the simulation are the zones of different volumetric response to heating, concentrically formed around the heater. The first zone, characterized by strong thermoplastic consolidation, is formed at the contact with the heat source. After the initial elastic changes in pore pressure, a plastic dilatancy occurs and, with the drastic reduction of the elastic domain, the material is again forced into thermoplastic consolidation. The corresponding evolution of the effective stress profile indicates that the dilatancy zone is generated in the first year and that reconsolidation does not occur before the first 50 years. The width of the high shear stress zone at 100 years corresponds almost to the whole thermally affected area, with peak values, that may induce cracking, extending over the first 5 m. It must be remembered that the size of the heating element is much smaller than in the analogue, and thus the actual sizes cannot be expected to correspond.

5. Simulation of permeability changes due to thermal dehydration

Permeability changes and their effects on the evolution of water pressure during radial heating by an exponentially decaying heat source with a half-life of 30 years and an initial strength of 325 W/m were studied for Boom clay [Ma and Hueckel, 1992]. An infinitely long cylinder with a central line heat source and an imposed effect-free perimeter at 100 m were assumed. The calculated temperature reached nearly 200°C at the contact and did not fall below 100°C for the first hundred years. As a result of heating, the permeability near the heat source (0.8 m) increased over one order of magnitude within 3000 days (temperature rise at this point was about 80°C), by comparison with the reference permeability, and then upon cooling returned to the original value, as shown in Figure 1. These changes were in addition to those caused by thermally induced changes on water viscosity. Still, a ten meters ring of high pore pressure increase (about 1.6 MPa) developed in one month and propagated to 50 meters, dropping to 0.6 MPa in 50 years, as shown in Figure 2. It can be concluded that the permeability changed during heating from values typical of smectite to those typical of illite and returned, after cooling, to smectite-like values.

6. Conclusions

Some geomechanical alterations induced by heating argillaceous materials at temperatures lower than 200°C appear to be irreversible and, therefore, amenable to natural analogue studies.

The results of two previous numerical analyses of heating effects in Boom clay indicate the feasibility of detailed analyses of the thermomechanical behaviour of natural clay bodies contacted by magmatic materials. Considering the Orciatico case as an example, it is necessary to point out that the simulation results discussed above referred to conditions only qualitatively similar to those existing in situ. However, such phenomena as consolidation at about 200°C, fracturation at temperature as high as 100°C, and thermal permeability changes at 80°C were shown to be modellable.

Clearly, the simulations discussed above were not based on the material properties of the Orciatico clays and the geometrical formulation of the problem was only remotely analogous to the Orciatico site. Therefore, in case of a future study, to obtain a physically meaningful simulation, pertinent data should be gathered regarding the actual site. In particular, field evidence regarding topography, mineralogy and geodynamics of the site should be collected. More detailed geochemical analyses of the thermal history of the site should be made. Rock properties should be mapped in three dimensions across the site to detect their spacial variations. This should include porosity, density, water content, specific surface area and a measure of fracturation. In addition, experimental data should be obtained in the laboratory on thermal and hydraulic conductivity and on thermo-mechanical and geomechanical parameters of the rock samples from different locations throughout the site. Issues that should receive particular attention are: the duration of the thermal transient, the rate of cooling and the extent of subsequent unloading of the clay body due to erosion.

References

Baldi G., M. Borsetto, T. Hueckel and A. Peano, 1987. Coupling of thermoplastic and hydraulic effects in a clay repository: Near field analysis, in: Coupled Processes Associated with Nuclear Waste Repositories, ed.: C.F. Tsang, Chapter 41, pp. 565-580, Academic Press, Orlando, Fa.

Baldi G., T. Hueckel, A. Peano and R. Pellegrini, 1990. Developments in modelling of thermo-hydro-geomechanical behaviour of Boom clay and clay - based buffer materials, CEC Report EUR 13365/1 & 2.

Benvegnù F., A. Brondi and C. Polizzano, 1988. Natural analogues and evidence of long-term isolation capacity of clays occurring in Italy, CEC Report EUR 11896.

Brookins D.G., 1987. Natural and archeological analogues: A review, proceedings of a CEC symposium on "Natural Analogues in Radioactive Waste Disposal", CEC report EUR 11037.

Hueckel T., 1992. Water-mineral interaction in hydro-mechanics of clays exposed to environmental loads: A mixture approach, Canadian Geotechnical J. 29 (4), in print.

Hueckel T. and G. Baldi, 1990. Thermoplasticity of saturated soils and shales: Constitutive equations, J. Geotech. Engineering 116 (12), 1765-1777.

Hueckel T. and M. Borsetto, 1990. Thermoplasticity of saturated clays: Experimental constitutive study, J. Geotech. Engineering 116 (12), 1778-1798.

Leoni L., C. Polizzano and F. Sartori, 1986. Nuclear waste repositories in clays: The Orciatico metamorphic aureole analogy, Applied Clay Science 1, 385-408.

Ma C. and T. Hueckel, 1992. Thermomechanical effects of adsorbed water in clay around a heat source, Int. J. of Numerical and Anal. Methods in Geomechanics, in print.

Pusch R., 1987. Permanent crystal lattice contraction: A primary mechanism in thermally induced alteration of Na bentonite, in Scientific Basis for Nuclear Waste Management X, eds.: J.K. Bates and W.B. Seefeldt, MRS v. 84, pp. 791-802, Pittsburgh, Pa.

Pusch R. and O. Karnland, 1988. Geological evidence of smectite longevity. The Sardinian and Gotland cases. SKB report 88-26.

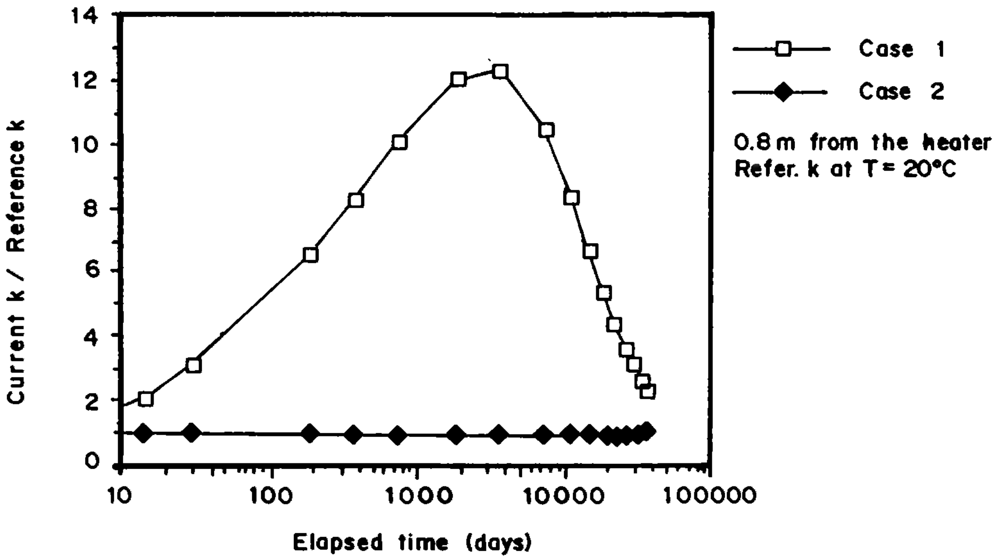

Figure 1 - Ratios of current to reference permeabilities at 0.8 m away from the heater. Case I : with heating . Case 2 : reference values.

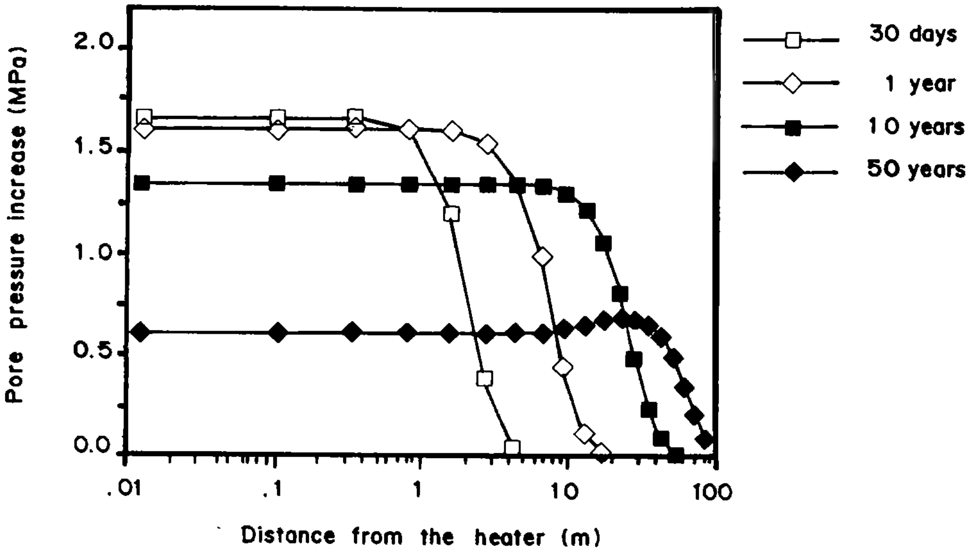

Figure 2 - Excess pore pressure distribution with mass transfer at 30 days, one, ten, and fifty years.

NATURAL ANALOGUES AND NEOTECTONICS

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ABSTRACT

Neotectonics concerns ongoing crustal deformation, principally related to episodes of coseismic (earthquake-related) fault-displacement. Two classes of neotectonic phenomena are of particular significance for radioactive waste disposal: fault rupture and seismohydraulics (hydrogeological changes accompanying earthquakes). Empirical evidence provides the most useful resource for exploring these phenomena. The definition of fault rupture hazard requires an exploration of the degree to which strain is concentrated on specific faults; the replication of rupture from one event to the next and the duration of rupture-recurrence. Seismohydraulic changes are primarily determined by fault style and proximity to the fault rupture. There are profound regional contrasts between extensional (normal-fault) and compressional (reverse-fault) earthquakes, while the most significant hydrogeological effects are found in proximity to the fault. Natural analogue studies have not previously recognised the importance of tectonic setting for determining fundamental aspects of the dynamical hydrogeological system in which they have been located and should now be specifically targetted to explore subsurface hydrogeological processes in the immediate vicinity of active faults.

1. Introduction

Natural analogue studies reflect a phenomenological approach to the understanding of the long-term behaviour of geochemical systems considered representative of buried radioactive waste. The exploration of the hazards posed to a radioactive waste repository by active tectonics demands a comparable approach, primarily employing observations collected from scientific investigation in the aftermath of important earthquakes. This paper sets out to highlight some of the preliminary conclusions that can be gained from these studies and also proposes how neotectonics and natural analogue studies should come together.

There are three distinct phenomena associated with earthquakes that can provide hazards to radioactive waste repositories: ground motion, ground rupture and seismohydraulic (hydrogeological) changes. The second and third of these are likely to be the most significant for long-term repository performance and are the subject of this paper.

2. Fault Rupture

A fault is a planar zone of weakness that suffers sudden rupture when the shear-strain in the surrounding rockmass excedes the strength of the fault-rock, thereby generating an earthquake. Shear-strain accumulates as a result of regional deformation, principally associated with the large-scale convection of the Earth's mantle concentrated by the movements of the lithospheric plates. The earth's crust is full of faults, but at any one period it appears that only those that are particularly sensitive to the prevailing deformation field are activated. Displacement to length ratios of long-lasting faults are typically in the range 10^{-2}-10^{-3} whereas displacement to length ratios of individual fault rupture events are in a range typically of 10^{-4} - 10^{-5} (Scholz, 1990). Hence faults must undergo repeated displacement events. This simple observation provides the justification that past fault movements are likely to be indicative of future hazard.

Fault rupture has a number of implications for radioactive waste disposal, in particular with respect to cavern stability, disruption of waste packaging and the creation of new fractures, or the reactivation of older fracture systems or faults, that may act as new pathways to fluid transport. An underground repository acts as a 'soft inclusion' in the rock mass which may tend to focus deformation, attracting failure, much as fractures radiate from window-openings in a building deformed by earthquake vibration.

2.1 Strain Concentration

The potential influence zone of fault-rupture is determined by the degree to which shear-strain is concentrated along a narrow fault-zone. There is a large quantity of scientific observations collected in the aftermath of more than one hundred earthquakes over the past century from which it is possible to explore the nature of coseismic strain localisation. A number of categories of coseismic faults can be recognised.

The primary fault is the one on which the main seismic energy release occurs. In the simplest case the displacement is concentrated along a single fault that passes through to the surface. However no fault is a simple two dimensional plane, but comprises a series of sub-parallel fault sections, that show a fractal distribution of sizes (Scholz, 1990). At bends, jogs (where fault displacement passes from one sub-parallel fault to another) and fault terminations the fault rupture will tend to develop new paths along pre-existing faults and fractures.

Secondary connecting faults emerge off the primary fault, either with a sub-parallel (synthetic) or near orthogonal (antithetic) orientation. Sometimes the primary fault itself splits into a series of synthetic faults as it passes towards the surface. Secondary superficial faults do not directly connect with the primary fault but are generated deformation resulting from faulting. Many reverse faults and reverse-strike-slip faults are 'blind' and do not break surface, instead generating overlying folds. Deformation within the overlying folds tends to be superficial (faults disappearing with depth) and can be distributed over zones as much as 5km in width as seen in the 1989 Loma Prieta, California and 1980 El Asnam, Algeria earthquakes.

Sympathetic fault rupture involves the displacememt along a very sensitive subsidiary fault not directly connected with the primary fault. as a result of regional strain or even ground motion. Aftershocks and displacements triggered by the first fault displacement may also fall into this category. Other superficial faults form as a result of geotechnical processes in unconsolidated deposits resulting from strong ground vibration.

The degree to which strain is localised appears to be primarily determined by the style of faulting: the highest strain concentrations being associated with normal faults, the most distributed effects found in conjunction with reverse faults. Hence tectonic context provides an important control of the potential hazard posed by fault rupture.

2.2 Replication

There is much evidence to suggest that fault ruptures are predominately replicated from one displacement event to the next. However fault geometry also evolves, and hence some proportion of each fault rupture is likely to be new. Explorations of one fault rupture relative to the previous event are now commonplace, in particular through trenching recent fault scarps, although no specific study has been focussed on the problem of replication alone. However from what is already known it appears that typically ca. 95% of the fault rupture replicates itself, although this proportion is probably variable from one fault type to another. There are obvious locations along a fault where changes in rupture path are most likely: at bends, jogs and fault terminations. Jogs are particularly likely to evolve because they are unstable systems, involving internal rotation and growth.

2.3 Recurrence

The recurrence interval between one fault displacement and the next is principally determined by the regional rate of deformation. Along plate boundaries, where rates of displacement can be several tens of millimetres each year, fault-rupture can recur every 100-200 years. However in one or two examples far from plate boundaries, fault rupture recurrence has been shown to have been in excess of 100,000 years.

3. Seismohydraulics

Profound hydrogeological changes can accompany earthquakes. In order to explore these changes we have undertaken a major study collecting hydrological observations from more than 200 earthquakes in many different parts of the world. We have also developed a general theory of earthquake-induced changes in hydrogeology that has been tested against the empirical observations.

In order to find useful data it is necessary to focus on continental regions of exposed igneous, metamorphic or well-lithified sedimentary rock in which unconfined near-surface aquifers extend without interruption into the fractured crystalline rocks of the upper crust. In all such areas changes in fluid pressures in the upper crust have the potential to communicate with the surface. Excluded however are those regions in which there is an impermeable (generally unlithified) sedimentary cover, in particular of evaporites, or clays. The best data concerns detailed observations of pre- and post-seismic river flows in arid regions that sample broad (>100km^2) and heterogeneous regions of the crust surrounding a major earthquake.

Hydrogeological changes accompanying earthquakes can be shown to be a consequence of coseismic strain. In typical upper crustal rocks, mobile water is held and transported in fractures. Variations in stresses and their consequent strain changes are accommodated in crystalline rocks by alterations in fracture separation.Strain alters both the dynamic porosity and the permeability, the latter being constrained by the dilatation and interconnectivity of fractures.

We have found that the primary factor in determining the nature of the hydrogeological changes accompanying earthquakes is the style of faulting. The most striking contrast in hydrological signatures is found between normal and reverse fault earthquakes.These changes can best be understood in terms of far-field and near-fault components.

3.1 Importance of fault style

In regions where the crust is being pulled apart, in the interseismic period the crust is subject to extensional strain (see Figure 1, until at the time of fault rupture this strain is transferred into permanent displacement along a normal fault-plane. In response the surrounding rock-mass undergoes elastic rebound in compression. Reverse fault earthquakes occur where tectonic forces are pushing rocks horizontally against some resistance. Before earthquake failure has occurred there is an accumulating interseismic component of compressional horizontal strain. At the time of the fault rupture the strain that was formerly distributed through a large

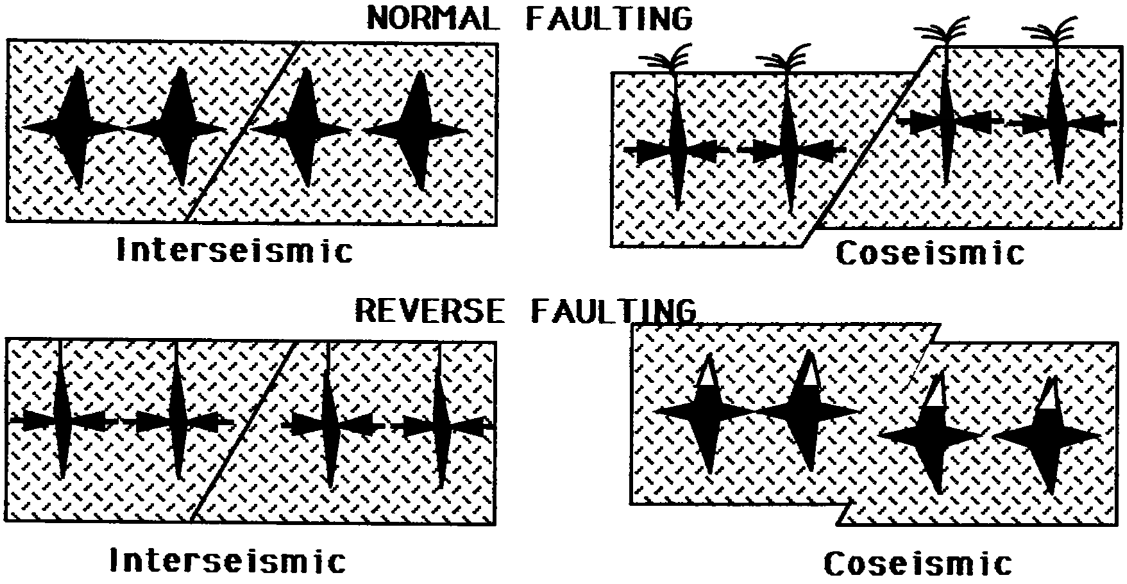

Figure 1. Simplified model of strain changes and consequent variations in crustal porosity through the earthquake cycle.

volume of rock becomes transferred onto displacement on the fault plane and the elastic rebound of the surrounding crust is extensional.

Hence one can predict that in a region of extension the cracks within the rock slowly open up between earthquakes increasing the crustal porosity. At the time of an earthquake the cracks suddenly close squeezing water up to the surface. In a region of compressional tectonics cracks should slowly close between earthquakes as the water is squeezed out and then suddenly open after the earthquake, drawing more water into the crust.

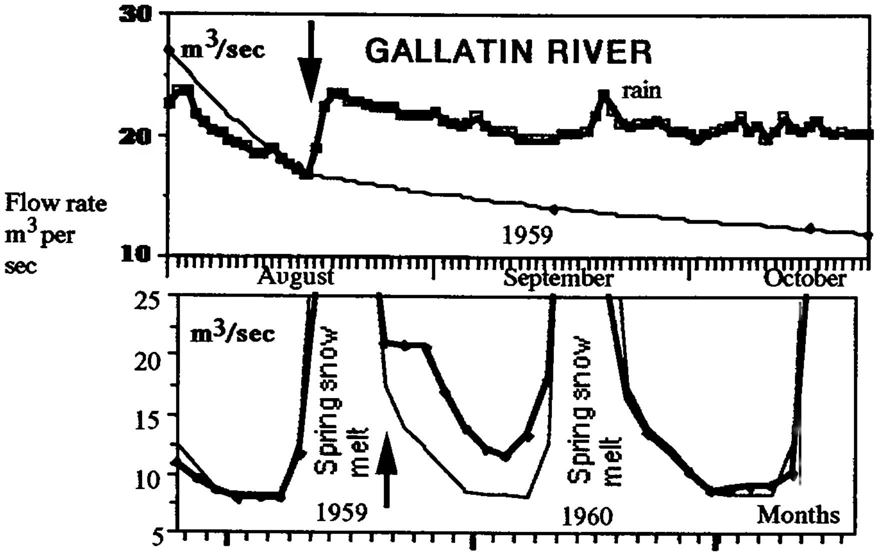

Figure 2: Impact of the 1959 August 17th Hebgen Lake earthquake on flow in the Gallatin River, Montana. Arrow indicates earthquake. Expected flows shown as thin line.

The 1959/8/17 Hebgen Lake earthquake (M7.3) in Montana is a typical normal fault earthquake that had a profound impact on river-flows in the surrounding region. Following the earthquake flows reached higher levels than ever recorded at this time of year, that had no explanation in levels of precipitation. The daily and monthly river flow data for one catchment in the region surrounding the fault are shown in Figure 2. From detailed river flow information for all the catchments surrounding the causative fault, and by comparing the flow prior to the earthquakes, and the trend of flows in previous years, it has proved possible to calculate the total excess discharge for each catchment. These flows can be normalised for the area of the catchment into 'rainfall equivalents' that were more than 100mm in the vicinity of the fault, but more typically 20-40mm out to distances of up to 100km around the location of the earthquake. Adding excess discharges from all the individual catchments shows that around 500 million cubic metres (0.5 km3) of water was expelled over an area of ca. 10,000km2 and over a time-period of about 8 months following the earthquake. Water release following other major normal faults earthquakes has shown closely comparable hydrological effects (Muir Wood and King, 1993). No such increased discharge occurs in the vicinity of purely reverse fault earthquakes.

These strain changes can be modelled and the volumetric strain compared with the actual geographical distribution of water-release revealing volumetric strain surrounding the fault typically around 10^{-5}. By perfecting this comparison it is possible to estimate the depth over which the hydrogeological system undergoing strain is connected with the surface (Muir Wood and King, 1993). From the overall form of the rise-time and decay function of the fluid flows it is also possible to explore the'characteristic' fracture size that dominates crustal drainage, that is found to have a width typically of around 0.03mm.

3.2 Near-fault

In the vicinity of a fault rupture there is the potential for high levels of strain to become localised where there is a change in the displacement vector (as at the end of a fault), a change in orientation of the fault, or a change in the plane of the displacement. As a recent example of fault-related strain in the October 28th 1983, M7.2 Borah Peak normal fault earthquake, some springs located above the dipping fault, about 5km from the surface fault trace, which were dry before the earthquake, fountained at an estimated 12 $m^3 s^{-1}$ within a few hours, with water emerging at the surface at least 30m above the valley floor. It is likely that a compressional jog in the underlying fault was the primary cause of the water-release.

A second phenomenon encountered in the vicinity of a fault displacement is the generation of new thermal springs: highly conductive conduits that communicate with a deeply buried recharging aquifer. A number of hot springs have been observed to form at the time of an earthquake and to have continued to exist thereafter. The large majority of non-volcanic hot springs for which the geological context has been established are located on, or closely related to, faults. While it is not always possible to demonstrate that they owe their existence to movement along the fault, this remains perhaps the simplest explanation as to how a conduit of the appropriate conductivity can be generated.

3.3 The nature of hydrogeological change

Hydrogeological changes accompanying earthquakes are of three categories: cyclical, transient and permanent.

In the region surounding a fault, strain accumulated through the interseismic period is then relieved at the time of fault rupture. Hence there will be a cycling of hydrogeological properties such as permeability and porosity, with a slow change through the interseismic period followed by a sudden return to the original state following fault displacement. In a compressional tectonic regime these cyclical changes involve interseismic decreases in porosity and permeability followed by post-seismic recovery. In extensional tectonic environments the cycle is reversed. The direction of this cycle can determine whether recharge of the upper crust is from oxygenated surface waters or deeper water already saturated with dissolved minerals.

In the immediate aftermath of coseismic strain the change in porosity displaces fluid. In the region around the fault water is either squeezed out of the crust (following normal faulting) or sucked into the crust (following reverse faulting). These transient effects can cause the movement of large bodies of water. In regions in which the water displaced out of the crystalline crust cannot simply emerge at the surface fluid will be displaced laterally away from the region of the fault. The fluid flux through any formation will be dependent on porosity, confinement, geometry etc. but simple calculations suggest that these fluxes may be very considerable and can oppose normal fluid flow regimes. This in turn could have important implications for the dispersal of a plume of contaminated water emerging from a repository.

In the immediate vicinity of fault rupture strain may be permanent, just as fault displacement itself is not relieved between earthquakes. This in turn can lead to permanent changes in hydrogeology. The most notable of such changes involves the generation of new long-lasting thermal springs, but other permanent changes in hydrogeological connectivity and permeability will also occur subsurface.

4. Conclusions

Earthquakes provide a principal motivation for dynamic hydrogeology. The impact of earthquake-related strain on the hydrogeology in the vicinity of a repository, or natural analogue, located in crystalline rock, involves three critical factors: the regional tectonic style, the location of the repository relative to the fault rupture and the nature of the fracture flow system.The tectonic context of a natural analogue site can have a profound impact on its long-term hydrogeological and geochemical evolution just as it would have on a real waste disposal facility. Pre-existing natural analogue studies have inadvertently sampled a variety of different tectonic settings, without recognising the potential impact of seismohydraulic processes on long-term dynamic hydrogeology. This is particularly apparent when comparing studies in compressional tectonic settings, such as Japan, with those in extensional tectonic settings, as in northern Mexico or Nevada. All the properties of dynamic hydrogeology associated with tectonics have the potential to be explored in well-located natural analogue systems. Hydrogeological and geochemical studies should be undertaken subsurface in proximity to major active faults and the impact of fault rupture investigated in underground workings that have been intersected by faults since their excavation.

References

Muir Wood R. and King G.C.P. (1993) Hydrological signatures of earthquake strain. Journal of Geophysical Research (in litt). (also see Tectonic Hazards for Nuclear Waste Repositories in the UK, Report for UK HMIP: 1992).

Scholz C.H. (1990) The Mechanics of Earthquakes and Faulting, Cambridge University Press, Cambridge, 437p.

CONCLUDING PANEL

Why do we not see more recognition of natural analogues in performance assessment?
Panelists: N. Eisenberg, NRC (USA), I. Neretnieks, RIT (S), D. Lever, AEA Harwell (UK) J. Bruno, MBT (E)
Chairman: I. McKinley, Nagra (CH)

The use of information from natural analogues in the performance assessment of nuclear waste repositories
J. Bruno, MBT (E)

WHY DO WE NOT SEE MORE RECOGNITION OF NATURAL ANALOGUES IN PERFORMANCE ASSESSMENT?

Chairman:: I. Mc Kinley
Nagra, Wettingen, Switzerland

Panelists: N. Eisenberg[1], I. Neretnieks[2], D. Lever[3], J. Bruno[4]
[1]NRC, Washington, USA - [2]RIT, Stockholm, Sweden
[3]AEA, Harwell, UK - [4]MBT, Barcelona, Spain

1 Introduction

The Chairman's introduction provocatively provided background to the question posed, contrasting papers presented by the panelists at various previous analogue workshops which advocated wide applicability of analogues in performance assessment (PA) with the very limited (or non-existent) mention of analogues at performance assessment meetings or in reports describing major performance assessment projects. The following text very briefly summarises the responses of the individual panelists (in the order in which they were presented) and then reviews the subsequent discussions.

1.1 Norman Eisenberg

A natural analogue may be considered as any natural occurrence which, by analogy or some degree of similitude, can support the assessment of repository safety. However, human-induced analogues, both archaeological and more recent, are also important. There appears to be no reason to limit, nor does the NRC limit, the definition of natural analogues by timescale, phenomena, discipline, etc. The NRC staff considers natural analogues to be an important potential support for performance assessment.

Natural analogues have the potential to support performance assessment in several significant ways, including:

1) Determination of data and data uncertainties, including the characterisation of parameters by ranges and distributions
2) Qualitative conceptualisation of natural systems
3) Quantitative and qualitative determination of physico-chemical processes, their interactions and importance
4) Determination of previous environments as a guide to future states for the repository environment
5) Support for model validation and testing
6) Insights into the limitations and important aspects of site characterisation.

Natural analogues do not appear to be used to the extent possible or desirable to support performance assessment for several possible reasons. It should be recognised that the investigators and investigations have a different focus in performance assessment and natural analogue studies. In performance assessment a "model" has the rôle of a model in engineering; i.e. the fundamental laws are known, but a model is used to represent a system's behaviour in place of extensive testing of the system. In natural analogue studies the "model" has the rôle of a model in the natural sciences; i.e. a tentative hypothesis which, if not invalidated, could be the basis for a fundamental law. Because natural analogue studies are nearly always isolated occurrences, the point of view of the investigators is to define and explain that occurrence. The point of view in performance assessment is to consider various outcomes from a system subject to differing events, environmental conditions, or initial conditions. Natural analogue studies tend to evaluate the detailed aspects of occurrences. For example, precise aspects of changes in mineralogy may be determined and analysed. Performance assessment modelling, especially the modelling used to obtain quantitative estimates of performance, tends to be coarse with regard to spatial scale, timescale, geometric definition and processes considered. Even the more robust analyses used to support the quantitative estimates of performance tend to be less precise in several aspects than many natural analogue studies.

Other factors affecting the use of natural studies in performance assessment include organisational constraints. Both natural analogue and performance assessments tend to be labour-intensive activities conducted in different departments; this tends to limit interactions, especially in larger programmes. Proof of safety using natural analogues is an important adjunct to, and support for, performance assessment, but alone is unlikely to carry the day for licensing. The differences between an analogue and the repository are too numerous to make a robust licensing case. Inherently, natural analogues provide anecdotal evidence; performance assessments apply general principles to obtain predictions of repository performance.

1.2 Ivars Neretnieks

In the Swedish programme, where the repository will be located at about 500 m depth in fractured crystalline rocks, some key issues have been identified in the performance assessments. The strong retardation due to nuclide uptake in the rock matrix has been shown to be the main retardation effect in the rock. This mechanism has been seen to take place over long times and distances in several natural analogues (El Berrocal, Palmottu, Poços de Caldas and others). Effects of radiolysis have been seen in Oklo and in Cigar Lake within the range of expected values. Clear imprints of channeling were seen in Poços de Caldas over long distances. In Cigar Lake, where the uranium ore body is surrounded by clay, much as in some proposed repository designs, the release rates of dissolved constituents emanating from the ore are in the range of values predicted by present models.

These observations have considerably increased our confidence that we have conceived these mechanisms and processes correctly.

1.3 David Lever

I believe we are seeing increasing use of analogues in support of performance assessments. In answer to the points raised in the Chairman's introduction, I would not expect to find many references to analogues in high-level summaries of performance assessments. The place I do expect to find analogue studies, and reference to such studies, is in supporting documents that serve one of two purposes. First there are some documents that describe in detail the models either used directly in assessments or that support simpler assessment models. Then secondly there is the justification for the choice of data for a particular site-specific study. Part of the justification will be interpretation of the analogue data, often from a different site with different conditions, and consideration of the appropriate ways in which those data can be used, complementing other more site-specific data obtained from laboratory and field investigations.

Perhaps it would be helpful to list some of the areas in the Nirex safety assessment research programme where analogues are currently being studied. This research programme supports the possible development of a deep geological repository at Sellafield in the UK for low- and intermediate-level waste, in which cement will be a major material. The areas in the research programme are:

- The Maqarin analogue in Jordan as an analogue of the cementitious near field, and surrounding disturbed zone
- Analogues of the oxidised disturbed zone, in particular providing an understanding of the time sequence of secondary iron oxyhydroxide minerals
- Use of the uranium series radionuclides to examine rock-matrix diffusion in fractured rocks and to provide information on the behaviour of uranium in rock/water systems over very long timescales
- Colloid characterisation in natural systems, such as El Berrocal
- Microbiological populations in naturally alkaline systems, such as alkaline lakes.

1.4 Jordi Bruno

In my opinion the rôle of natural analogue studies in performance assessment exercises is to test the solidity, robustness and consistency of the performance assessment submodels.

Natural analogue studies also have a very specific rôle in checking the validity of the non-anthropogenic scenarios devised for the repository.

The integration of natural analogue information in performance assessment studies will be very dependent on the solidity of the assumptions used in describing the paleo-conditions of the system. Furthermore, a thorough dialogue should be established between natural analogue and performance assessment modellers to allow an over-the-border integration. This could be achieved practically by establishing a specific task in one of the forthcoming exercises in which performance assessment submodels are tested involving performance modellers.

The limits of the applicability of natural analogue studies in performance assessment exercises are set by our capability to describe the hydrogeochemistry of the natural analogue systems in the fourth dimension, which is the one that links natural analogue and performance assessment ambitions (c.f. extended discussion in a companion paper).

2 General discussion

Key points made can be briefly summarised as:

1) Some discrepancies in the extent to which analogues are actually used in performance assessment are related to the size of the programmes involved. In very small European programmes, the same people are involved in performance assessment and analogue studies, while in larger programmes (e.g. in the USA or France) this work is carried out by different groups and hence a communication problem exists. Nevertheless, a need to get performance assessment groups more involved in analogue studies was recognised.

2) The lack of **recognition** of analogue studies in performance assessment documentation could be attributed to a number of factors:
    a) The tacit use of analogues in the early development of conceptual models which is recognised as important but corresponds to an aspect not normally described in detail in such documentation
    b) The focus of performance assessment documentation on quantitative analysis, an area in which analogue input has been limited to date
    c) The probabilistic nature of some performance asssessments - again an area in which analogues have not yet been able to make significant contributions
    d) The early stage of documentation of many of the "2nd generation" analogue studies which have been planned explicitly to contribute to PA.

3) In addition to formal performance assessment documentation, safety must also be demonstrated to the general public in a more "public relations" oriented manner. Although care must be taken to avoid over-interpretation of the significance of particular analogues, this aspect has been widely utilised in many national programmes (e.g. Sweden, Switzerland and the UK) and its increasing rôle is well illustrated by the presence at this meeting of the film crew who are currently making a natural analogues video with extensive international support.

4) It was pointed out that, in the US, there is an explicit regulatory requirement for the incorporation of natural analogues in PA. In other countries without such an explicit requirement, natural analogues become essential because of the lack of cut-off times for performance assessment - safety requiring to be demonstrated "for all times". In this latter case, it is clear that models extrapolated from laboratory timescales become little more than semi-quantitative indicators of performance which critically require support from natural analogues in order to demonstrate any "robustness".

   Validation of performance assessment models over very long timescales was thus recognised as a particularly complex topic, but one where analogues must play an increasing rôle.

5) Fundamentally, the aspect of recognition in written documents is less important than ensuring that the analogue workers get feedback which allows them to see that their work has application and to iteratively improve its applicability, and that the funding organisations are aware of the input which analogue studies are providing.

   In this regard, the Natural Analogue Working Group plays an important rôle and special initiatives such as this panel session can be very valuable.

3 Conclusion

The consensus of the panel is that natural analogues are currently an essential component of performance assessment and one whose significance (and explicit recognition) will certainly increase with time as more focused analogue projects are documented and as their methodology matures.

THE USE OF INFORMATION FROM NATURAL ANALOGUES IN THE PERFORMANCE ASSESSMENT OF NUCLEAR WASTE REPOSITORIES

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Introduction

The safe disposal of high level nuclear waste requires the isolation of the waste and its components from the biosphere for very long periods of time. This is to ensure that no substantial amounts of radiochemical components are added to the already existing present levels in the biosphere. The periods of time involved in the safety assessment of HLNW disposal ar far beyond the normal horizon for social and technical planning (NEA-IAEA-CEC collective opinion release, 1992)[1].

It has been previously identified (Chapman et al, 1991)[2] that the prediction of the future behaviour of a repository will be facilitated by comparison with the evolution of natural geochemical systems, containing some of the radiochemicals of interest. This approach of looking for circumstantial evidence in Nature has been developed under the name of Natural Analogue studies.

Natural Analogue studies can be used in the four main elements of the safety assessment of a high level nuclear waste repository, namely:

1) In the definition of the disposal concept and its components. Most of the *realistic* disposal concepts are based on the general idea of putting back the radionuclide content of the waste matrix back where it belonged at the beginning of the nuclear cycle. The deep burial in geological formations as an isolation and stability factor is a clear *analogy* to the stability of ore deposits.

Some of the key components of the widely accepted disposal concepts are based on analogy to geochemical situations. Specifically, the waste matrix (for spent fuel) and the clay (bentonite) barrier.

2) In the identification of the possible processes and events that may affect the integrity of the system. In these respect the rôle of natural analogues is very clear in terms of defining the most probable non-anthropogenic processes affecting a potential repository.

3) In the qualification of the radiological impact by predictive modelling. Here is where Natural Analogue studies should have its key application. In terms of testing

both the scientific and technical paradigms as well as the computer codes used in the current models.

4) In the description of the associated uncertainities. Natural Analogue studies can be used in some cases to identify sources of uncertainity. In some other (more favourable cases), to narrow down these uncertainities.

The objective of this paper is to discuss to which extent Natural Analogue studies contribute to bring *circumstantial evidence* in the various areas of safety assessment and in particular in the qualification of radiological impact by predictive modelling.

How do we use predictive modelling in the performance assessment of nuclear waste repositories?

The models used for the qualification of the radiological and chemical impact of nuclear waste repositories are build up as a chain of different models which take into account the different compartments in which we divide our intellectual view of the repository system. These models are often simplified in order to make them numerically bearable to our present computers. However, the PA models are build up from solid and rigorous submodels which contain the main scientific and technical paradigms of our present civilization.

Natural Analogue systems should provide a framework of observations where these submodels may be tested against.

The submodels are constituted by both the concepts and the numerical (computer aided) tools used to handle them. For instance, a solubility controlled model for the definition of source term from the waste matrix includes chemical solution thermodynamics as the concept and geochemical equilibrium codes (EQ3, PHREEQE, MINIQL) as the tools.

How do we check the correctness of our PA submodels by using NA studies?

The predictive models we use in performance assessment should be tested both conceptually and numerically. A full validation of the models will be rarely achieved, however the correctness of the theoretical assumptions and numerical solutions may be checked against these long-term hydrogeochemical settings. Hence, areas which require conceptual and/or numerical development identified and sometimes uncertainities in the submodels narrowed down.

The extent of succes on the model/checking is unfortunately very dependent on our ability to describe not only the present hydrogeochemical situation but also the past one.

The credibility and consequently the usage of NA studies in PA exercises will be very critically dependent on how well we will be able to describe the paleohydrogeochemistry of the system. The involvement of experienced scientists in this area should be a priority in future studies.

Some specific examples of the usage of NA information in PA exercises.

Recently, the Swedish Nuclear Fuel and Waste Management Co has gone through a PA exercise under the generic title of SKB 91[3]. The main purpouse of this PA exercise was to assess the sensitivity of the disposal system to the variability of the geological setting.

Source term concentrations from the waste matrix were defined for two average granitic groundwaters with a different salinity content (defined as saline and non-saline). Furthermore, the thermodynamic solubilities of the different elements were calculated under oxic and anoxic conditions (Eh: +200 mV and Eh=-200 mV respectively).

The Tables 1 and 2 show the result of these calculations (Bruno and Sellin, 1992)[4].

SALINE	Oxidizing conditions		Reducing conditions	
	conc/lim phas	dom. spec	conc/lim phas	dom. spec
U	$3x10^{-6}$ Schoepite	$UO_2(CO_3)_2^{2-}$ $UO_2(CO_3)_3^{4-}$	$2x10^{-7}$ UO_2(fuel)	$U(OH)_4$
Pu	$3x10^{-8}$ $Pu(OH)_4$	PuO_2^+	$5x10^{-8}$ $Pu(OH)_4$	Pu^{3+} $PuSO_4^+$
Np	$4x10^{-4}$ $NaNpO_2CO_3$	NpO_2^+ NpO_2Cl	$2x10^{-8}$ $Np(OH)_4$	$Np(OH)_4$
Am	$6x10^{-8}$ $AmOHCO_3$	$AmCO_3^+$ Am^{3+}	$5x10^{-8}$ $AmOHCO_3$	$AmCO_3^+$ Am^{3+}
Th	$2x10^{-10}$ ThO_2	$Th(OH)_4$	$2x10^{-10}$ ThO_2	$Th(OH)_4$
Ra	$2x10^{-7}$ $RaSO_4$	Ra^{2+}	$2x10^{-7}$ $RaSO_4$	Ra^{2+}
Sn	$2x10^{-8}$ SnO_2	$Sn(OH)_4$	$2x10^{-8}$ SnO_2	$Sn(OH)_4$
Tc	high	TcO_4^-	$2x10^{-8}$ TcO_2	$[TcO(OH)_2]_2$

SALINE	Oxidizing conditions conc/lim phas	dom. spec	Reducing conditions conc/lim phas	dom. spec
Zr	$9x10^{-11}$ ZrO_2	$Zr(OH)_5^-$	$8x10^{-11}$ ZrO_2	$Zr(OH)_5^-$
Se	high	SeO_4^-	$1x10^{-4}$ Fe_3Se_4	HSe^-
Ni	$2x10^{-4}$ $NiFe_2O_4$	Ni^{+2}	$2x10^{-5}$ Ni_3S_4	Ni^{+2}
Sm	$7x10^{-4}$ $Sm(OH)_3$	Sm^{+3}	$7x10^{-4}$ $Sm(OH)_3$	Sm^{+3}
Pa	$3x10^{-7}$ Pa_2O_5	$PaO_2(OH)$	$3x10^{-7}$ Pa_2O_5	$PaO_2(OH)$
Pb	$2x10^{-5}$ $PbCO_3$	$PbCl^+$	$7x10^{-16}$ PbS	$PbCl^+$
Nb	$1x10^{-5}$ Nb_2O_5	$Nb(OH)_5$	$1x10^{-5}$ Nb_2O_5	$Nb(OH)_5$
Pd	$1,5x10^{-6}$ $Pd(OH)_2$ (s)	$Pd(OH)_2$ (aq)	$1,5x10^{-6}$ $Pd(OH)_2$ (s)	$Pd(OH)_2$ (aq)

FRESH	Oxidizing conditions		Reducing conditions	
	conc/lim phas	dom. spec	conc/lim phas	dom. spec
U	$3x10^{-4}$ Schoepite	$UO_2(CO_3)_2^{2-}$ $UO_2(CO_3)_3^{4-}$	$2x10^{-7}$ UO_2(fuel)	$U(OH)_4$
Pu	$3x10^{-9}$ $Pu(OH)_4$	PuO_2^+	$2x10^{-8}$ $Pu(OH)_4$	Pu^{3+} $PuSO_4^+$
Np	$2x10^{-3}$ $NpO_2(OH)$	NpO_2^+ NpO_2CO_3	$2x10^{-9}$ $Np(OH)_4$	$Np(OH)_4$
Am	$2x10^{-8}$ $AmOHCO_3$	$AmCO_3^+$ Am^{3+}	$2x10^{-8}$ $AmOHCO_3$	$AmCO_3^+$ Am^{3+}
Th	$2x10^{-10}$ ThO_2	$Th(OH)_4$	$2x10^{-10}$ ThO_2	$Th(OH)_4$
Ra	$1x10^{-6}$ $RaSO_4$	Ra^{2+}	$1x10^{-6}$ $RaSO_4$	Ra^{2+}
Sn	$3x10^{-8}$ SnO_2	$Sn(OH)_4$	$3x10^{-8}$ SnO_2	$Sn(OH)_4$
Tc	high	TcO_4^-	$2x10^{-8}$ TcO_2	$[TcO(OH)_2]_2$

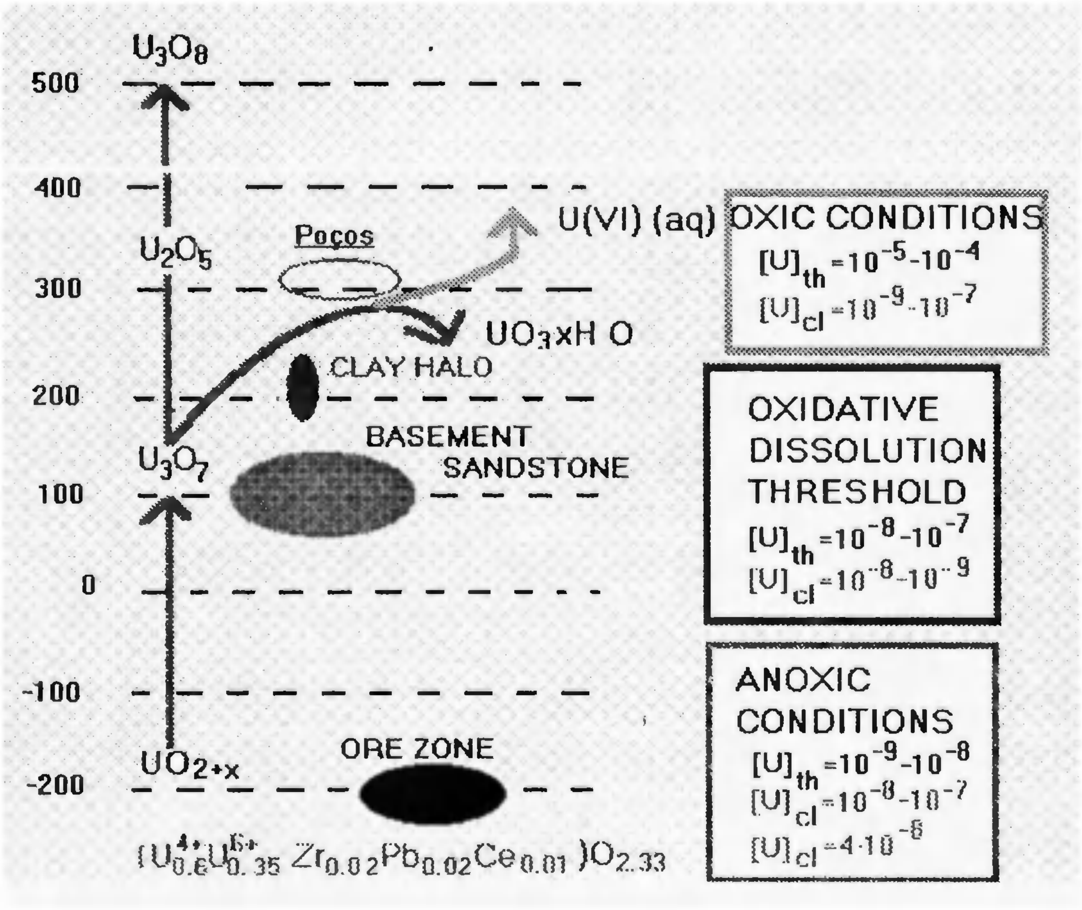
FRESH	Oxidizing conditions		Reducing conditions	
	conc/lim phas	dom. spec	conc/lim phas	dom. spec
Zr	$2x10^{-11}$ ZrO_2	$Zr(OH)_5^-$	$2x10^{-11}$ ZrO_2	$Zr(OH)_5^-$
Se	high	SeO_4^-	$1x10^{-9}$ Fe_3Se_4	HSe^-
Ni	$9x10^{-5}$ $NiFe_2O_4$	Ni^{+2}	$1x10^{-4}$ Ni_3S_4	Ni^{+2}
Sm	$1x10^{-4}$ $Sm_2(CO_3)_3$	Sm^{+3}	$1x10^{-4}$ $Sm_2(CO_3)_3$	Sm^{+3}
Pa	$3x10^{-7}$ Pa_2O_5	$PaO_2(OH)$	$3x10^{-7}$ Pa_2O_5	$PaO_2(OH)$
Pb	$2x10^{-6}$ $PbCO_3$	$PbCO_3$	$2x10^{-15}$ PbS	$PbCO_3$

Nb	$1x10^{-5}$ Nb_2O_5	$Nb(OH)_5$	$1x10^{-5}$ Nb_2O_5	$Nb(OH)_5$
Pd	$1,5x10^{-6}$ $Pd(OH)_2$ (s)	$Pd(OH)_2$ (aq)	$1,5x10^{-6}$ $Pd(OH)_2$ (s)	$Pd(OH)_2$ (aq)

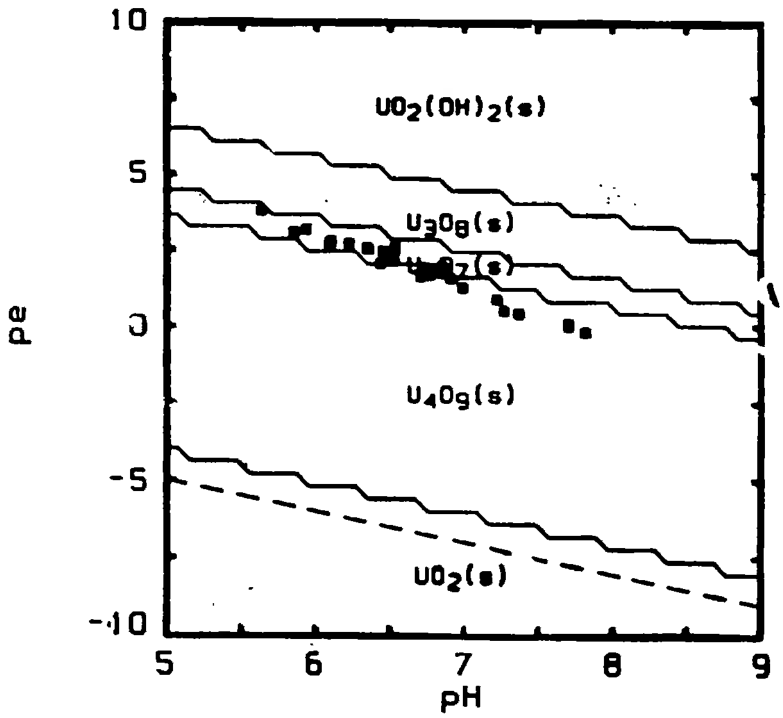
In all cases the results of the calculations were contrasted with the information from either NA studies like Poços de Caldas and Cigar Lake or data on radionuclide concentrations in natural water systems of similar characteristics. This was possible because the data from Poços de Caldas and Cigar Lake sites had undergone an extensive test-study on the predictability of geochemical codes and their associated databases. Therefore, the limits for the applicability of determined solubilities and radionuclide speciation were well defined.

Another case of potential application of NA findings in PA exercises constitutes the challenge posed by the Cigar Lake and Poços de Caldas observations to current paradigms on waste matrix dissolution from spent fuel disposal. The current models assume that the UO_2 matrix will become unstable when, due to radiolytic oxidation, the redox potential rises over 100 mV in the NHE scale. This is based on carefull experiments where the alteration of the surface of UO_2 electrodes has been correlated to their corrosion potential (Shoesmith and Sunder, 1992)[5]

In the following Figure I have put together the information collected in the Poços de Caldas and Cigar Lake analogue sites, in terms of mineralogy, groundwater geochemistry and uranium concentrations, as well as the electrochemical model for the dissolution of UO_2



It is clear from this comparison that in Cigar Lake we find uraninite stable in redox environments over 200 mV with the corresponding uranium concentrations expected for the stability of uraninite. However, in Poços de Caldas the alteration had gone up to U_3O_8(s) in oxic groundwaters with measured Eh ranging between 300 to 400 mV. This clearly indicates that the threshold for the oxic dissolution of UO_2 is well beyond the 100 mV barrier previously proposed and that uraninite with U(IV)/U(VI) ratios which correspond to ideal stoichiometries of U_4O_9 to U_3O_7 are stable in the Eh range +100-+200 mV in natural water conditions. This is exactly what is predicted from the thermodynamic model for the stability of uranium phases. Figure 2 illustrates the point by plotting the selected Eh/pH field data from Cigar Lake in a predominance diagram of the uranium system.



These findings should be transferred to the submodels for the stability of the spent fuel matrix in order to narrow down uncertainities and to decrease the level of "conservatism" which at the present dominates these particular submodels.

How can we integrate more NA information in PA studies and where are the limits?

According to my opinion the rôle of NA studies in PA exercises is to test the solidity, robustness and consistency of the PA submodels.

NA studies have also a very defined rôle in checking the validity of the non-anthropogenic scenarios devised for the repository.

The integration of the NA information in PA studies will be very dependent on the solidity of the assumptions used in describing the paleo-conditions of the system. Furthermore, a thorough dialog should be established between NA and PA modellers to do an over the border integration . This could be practically achieved by establishing a specific task in one of the forthcoming exercises in which PA submodels are tested involving PA modellers.

The limits of the applicability of NA studies on PA exercises are set by our capability to describe the hydrogeochemistry of the NA systems in the fourth dimension, which is the one that links NA and PA ambitions.

References

[1] NEA-IAEA-CEC collective oppinion release, NAGRA Bulletin 1992

[2] Chapman, N.A., McKinley, I.G. and Smellie, J.A.T. 1984. The potential of natural analogues in assessing systems for deep disposal of high level waste. SKBF/KBS TR 84-16. (Stockholm, Sweden) and NAGRA TR 84-41, (Baden, Switzerland).

[3] Final disposal of spent nuclear fuel. Importance of the bedrock for safety, SKB 91. SKB TR 92-20 (Stockholm, Sweden).

[4] Bruno, J and Sellín, P. (1992). Radionuclide solubilities to be used in SKB 91. SKB TR 92-13 (Stockholm, Sweden).

[5] Shoesmith, D. and Sunder, S. An electrochemically-based model for the dissolution of UO_2.SKB TR 91-63 (Stockholm, Sweden).

APPENDIX 1

Some posters presented at the meeting

The application of natural analogues to the Swedish SKB-91 safety performance assessment
F. Karlsson[1], J.A.T. Smellie[2], L-O. Höglund[3]
[1]SKB (S), [2]Conterra (S), [3]Kemakta (S)

Use of natural analogue test cases to evaluate a new performance assessment TDB
S.M. Pate[1], I.G. McKinley[2], W.R. Alexander[3]
[1]Napier University (UK), [2]Nagra (CH), [3]RWIG, Univ. Bern (CH)

Natural analogue study on native iron
K-H. Hellmuth, Finnish Centre for Radioactive and Nuclear Safety (SF)

High-FeO olivine rock, a potential redox-active backfill working in a nature-analogue way
K-H. Hellmuth[1], A. Lindberg[2], E-L. Tullborg[3]
[1]Finnish Centre for Radioactive and Nuclear Safety (SF)
[2]Geological Survey of Finland (SF), [3]Terralogica (SF)

Microfractography of El Berrocal granite
M. Montoto, A. Rodriguez-Rey, B. Menéndez, A. Martínez-Nistal, V.G. Ruiz de Argandoña, L.M. Suárez del Río, L. Calleja, University Oviedo (E)

Element mobility in rock matrix at Palmottu
H. Kumpulainen[1], P. Pitkänen[2], M. Valkiainen[1], A. Melamed[2] , P. Manninen[1]
[1]VTT-Reactor Laboratory (SF), [2]VTT-Traffic and Geotechnical Laboratory (SF)

Modelling of uranium transport at Koongarra with a moving weathered zone
M.A. Richardson-van der Poel, H. van de Weerd, S.M. Hassanizadeh, RIVM (NL)

THE APPLICATION OF NATURAL ANALOGUES TO THE SWEDISH SKB-91 SAFETY PERFORMANCE ASSESSMENT

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1. Introduction

SKB-91 is a safety performance assessment of a Swedish repository for spent nuclear fuel (SKB-91, 1992). Similar assessments of spent fuel disposal were made in 1979 and in 1983; the basic concept has essentially remained unchanged since then. It comprises an underground repository in granitic rock were the spent nuclear fuel is encapsulated in copper canisters and emplaced in vertical deposition holes drilled from horizontal tunnels at a depth of roughly 500 m. Compacted bentonite clay is emplaced around the canisters and a sand bentonite mixture is used to backfill the tunnels. This arrangement is often referred to as the "KBS-3 concept" (KBS, 1983). Over the years only minor changes to this original concept have been implemented and these have been mainly geared to improving canister design and its manufacture. For example, the recent development of the inner steel outer copper canister concept developed in cooperation with TVO in Finland (Salo and Raiko, 1989).

The aim of the SKB-91 analysis was to assess the relative importance of the rock properties at a certain disposal site for the long-term safety of spent fuel. Since the late seventies considerable emphasis has been put on the selection of a rock mass with a very low hydraulic conductivity. As a result of the SKB-91 analysis, however, it was concluded that relatively large variations in rock hydraulic properties could be tolerated due to the predicted excellent performance of the canisters and backfill. Consequently, this will provide a large freedom of choice when final site selection for the repository is carried out. Site properties that remain important include a sufficiently large volume of hydraulically conductive rock to locate the deposition holes, the presence of oxygen-free reducing groundwaters, and a safety distance of around 100 m from a bounding system of major fault zones which are expected to buffer tectonic movement and any resulting changes in groundwater flow. A first step towards a final repository for spent nuclear fuel in Sweden will probably be through the construction and operation of a demonstration facility.

References to natural analogues have been made in all safety performance assessments made by SKB, such as KBS-1 on vitrified waste, KBS-2, KBS-3 and SKB-91 on spent fuel, the final safety report (FSR) for the low- and intermediate-level waste repository (SFR), and a supplement to the FSR report which is in fact a renewed safety assessement. Natural analogue applications have been mostly concerned with the near-field environment, e.g. the stability of the copper canister and the bentonite overpack. These and other applications are documented in the literature and a summary is given by Smellie (1989).

In the SKB-91 performance assessment, highlighted in this presentation, reference is made to:

- the reliability of groundwater redox measurements and the importance of anoxic groundwater conditions in near-field radionuclide stability,
- the Poços de Caldas analogue study to support the statement that far-field colloid transport is of little concern, and
- the Cigar Lake analogue study to support the statement that the current near-field spent fuel leaching model, based on radiolysis oxidation of uranium, is too conservative.

2. Groundwater redox conditions

For a deep repository hosting spent fuel, such as described by the KBS-3 concept, it is an advantage if the groundwater is reducing in character. The presence of oxygen will cause pitting corrosion of the copper used as a canister material, it will increase the solubility of the uranium dioxide, the waste matrix for spent fuel, by four orders of magnitude, and it will result in the higher solubility and lower sorption of redox-sensitive nuclides such as neptunium and technetium in their oxidised states (i.e. as neptunyl and pertechnetate).

It has always been difficult to measure redox conditions in groundwater because of the generally very low concentrations of redox active species. For example, concentrations of iron(II) ions are usually present at the microgram per litre level. In reality the redox buffering capacity of the system depends more on the concentration of mafic minerals that supply, for example, the iron to the water.

Prior to 1984, in situ redox potential measurements in the Swedish radioactive waste programme were carried out in groundwaters pumped to the bedrock surface and subsequently passed through a sealed, flow-through electrode measuring cell. Since 1984, new developments have allowed downhole measurements of pH and Eh within isolated, pre-determined borehole section lengths, the redox-sensitive elements being simultaneously measured in a mobile laboratory at the surface to which water from the same packed-off section was being pumped.

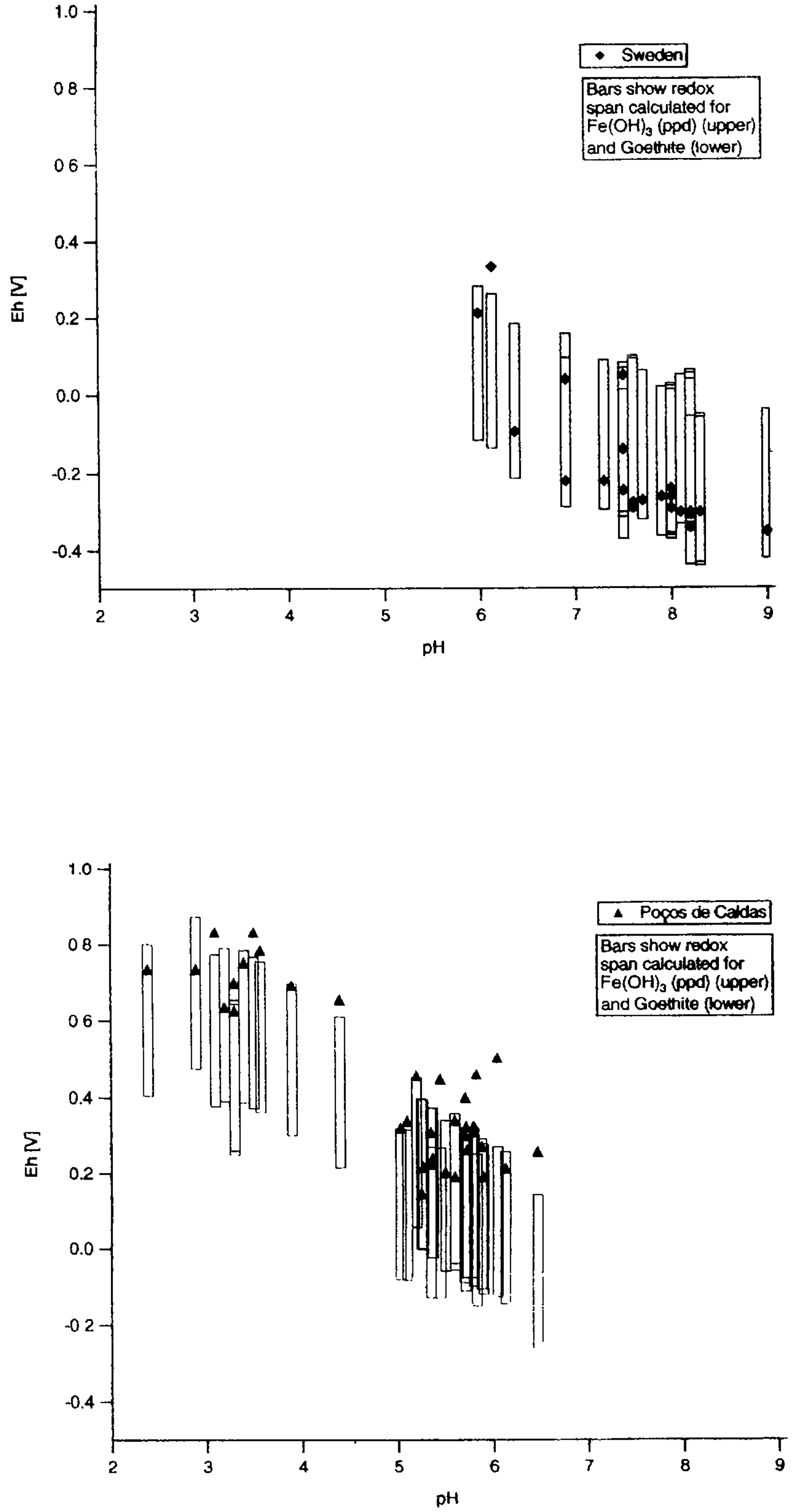

Figure 1: Measured vs. calculated redox potentials of groundwaters from Sweden and Poços de Caldas, Brazil.

In an evaluation of Swedish redox potential data collected over several years, Grenthe et al. (1992) showed there was a close correlation between measured and calculated redox potentials. It was found that the redox conditions could be characterised by simple analysis of Fe(II), pH, HCO_3 and temperature, in combination with field observations of the age and crystallinity of fracture filling iron minerals.

This hypothesis has presently been tested on data both from the Swedish site investigation programme and from the natural analogue study site at Poços de Caldas. In Figure 1 the calculated redox potentials for different solid mineral phases of Fe(III) are compared with the redox potentials measured in the field using platinum and/or glassy carbon electrodes. Most of the Eh measurements are made at the bedrock surface; the downhole probe measurements have only been available during the latter part of the Swedish programme.

Considering the age and crystallinity of fracture filling minerals observed in rock at the different sites, a good correlation was found between calculated and measured redox potentials. The Swedish groundwaters were found to correspond to equilibrium conditions with aged Fe(III) precipitates, such as crystalline goethite. The groundwater samples from Poços de Caldas indicate active precipitation of $Fe(OH)_3$ which is also observed in the field as a result of the continual precipitation of ferric oxides. Notable is the low pH at Poços de Caldas compared to the Swedish sites.

2.1. Conclusions

Testing the redox model shows that:

- the model is validated for a wide range of deep groundwater conditions, especially variations in pH and alkalinity,
- as the model is reliable, it should therefore be possible to simplify groundwater redox conditions by omitting direct measurement of Eh, provided that the other parameters are accurately determined,
- the uranium concentration in the groundwaters at the different sites is low, in accordance with the Eh as defined by the model.

The existence of an acceptable model for determining deep groundwater redox conditions considerably facilitates site assessment. The reducing character of the groundwater is ultimately controlled by the fracture-filling mineralogy thus establishing a stable oxygen-free environment where uranium and similar elements are reduced to their lowest soluble valencies.

3. Colloids

Most of the radionuclides in radioactive waste with long enough half lifes to be of concern for safety assessment are limited by their solubility in groundwater. Even if they are released at concentrations below their solubility limits, sorption on the rock mineral surfaces will further lower their concentrations. Solubility in groundwater and sorption on mineral surfaces are important retention mechanisms to prevent extensive dispersion of radionuclides if they become released in groundwater. For the deep disposal of high-level waste underground, water can reach the waste if a canister unexpectedly fails.

In principle, colloids can cause dissolution of radionuclides above their solubility limits and prevent sorption on rock mineral surfaces. If this occurs to any notable extent, then the colloids would act as a "short circuit" to the important barriers of solubility and sorption.

The release of radionuclides as colloids at the surface of the leached waste form is of less concern if an overpack, essentially impermeable to colloids such as bentonite clay, is chosen. Outside the clay overpack the radionuclides in the form of ions or inorganic complexes can reach the flowing groundwater in the rock fractures by diffusion. At that point, their concentrations will have diminished well below their saturation limits. Thus, pure radionuclides are not likely to be formed by super- saturation outside a clay overpack. However, there is a third possibility to address; that radionuclides are taken up by sorption on particulate matter already existing in the groundwater. These aggregates are sometimes referred to as pseudocolloids of radionuclides. The formation of pseudocolloids and rapid migration of such species has been observed in laboratory experiments and field tests.

The relative importance of this for waste disposal safety can be assessed in the following way (Allard et al., 1991). The concentration of dissolved radionuclides at the exposed waste surface is calculated. The corresponding amount of groundwater flow per year that would carry these radionuclides out of the near-field is also calculated. From groundwater analyses the concentration and kind of natural colloidal particles in the groundwater is obtained. From laboratory measurements the uptake of different radionuclide elements on natural colloids is measured. With these parameters it is relatively straightforward to calculate a maximum fraction of released radionuclides that could be carried as colloids. This has been done for spent fuel assuming a leaky copper canister. No dose consequences (calculated doses below ICRP limits) were obtained even if irreversible uptake and no retention of the colloid transported radionuclides were assumed. However, the result depends on the assumptions made and the measurements carried out. Important factors include the canister failure scenario, the sorption of radionuclides on the colloids and the colloid concentration. The last parameter is probably sensitive to water composition in general. Especially dilute waters tend to stabilise colloids, and at low enough concentrations of cations even the bentonite clay used for backfill can release colloidal clay particles. This phenomenon is referred to as the critical coagulation concentration, ccc. The ccc is less for divalent than monovalent ions, so calcium is more efficient in preventing colloid formation than sodium.

The Morro do Ferro site at Poços de Caldas (Fig. 2) was well suited to investigate the role of colloid transport (Chapman et al., 1990). The thorium/rare-earth mineralisation characterising Morro do Ferro contains three- and tetravalent elements (lanthanides and thorium) with strong tendencies to sorb onto particulate matter. It also contains uranium which is the main component of spent nuclear fuel; observations of the particulate migration of uranium have been reported elsewhere (Eisenbud et al., 1984). The intense lateritic weathering at Morro do Ferro generates iron hydroxides and clay minerals which form colloids and particles. The surface waters are also rich in humic substances which can either form organic particles or stabilise inorganic colloids. The groundwater at Morro do Ferro (Chapman et al., 1990) is very dilute with, for example, calcium concentrations in the range of 0.1 to 7 mg/L as compared to 20 to 4000 mg/L in average Swedish groundwaters at repository depths.

At depth the colloid concentration in the Morro do Ferro groundwaters is less than 1 mg/L which is not much different to that measured in groundwaters from Sweden or elsewhere. Thorium, lanthanides and uranium are associated with the colloids, for example 97 % of the Th and 80 to 90 % of the lanthanides. Only minor amounts of uranium is associated with the colloids.

Compared to the assumptions made for the colloid transport model used in performance assessment, it is interesting to note that the uptake of three- and tetravalent elements are much higher than anticipated from laboratory experiments. The sorption coefficient used in the colloid transport model for three- and tetravalent actinides was 30 m^3/kg which would suggest that only 3 % of these elements were attached to the colloids. The difference may be explained by the high organic content of the Morro do Ferro colloids which gives them strong sorption properties.

The relative concentration of lanthanides form a characteristic pattern. It is possible to measure and compare this pattern for the lanthanides on the particles, in the rock and dissolved in the groundwater (see Fig. 3). Colloidal lanthanides have the same pattern as the truly dissolved fraction and both are different to the rock. This would infer equilibrium between lanthanides on the colloids and in the water. This indication of reversible uptake is further strengthened by the observation of a difference in patterns of colloidal lanthanides near the surface and at greater depths in the Morro do Ferro formation (Fig. 3). Alternatively, completely different colloids may characterise the near-surface and deep groundwaters. In any case it is negative proof of colloid transport. According to colloid transport modelling, a reversible uptake on the migrating colloids will make the radionuclide dispersion insignificant. If the sorption of a radionuclide on a particle moving with the flow of water is reversible then the particle will sooner or later lose the nuclide by desorption. As the desorbed nuclide will be retarded by sorption onto the rock mineral surfaces, then colloid transport is of little concern.

Uranium has two isotopes, ^{238}U and ^{234}U, where the ratio between them can vary due to rock/water interactions, i.e. the radioactive processes that generate ^{234}U from ^{238}U. The isotopic ratios of uranium on suspended particles, on the rock and dissolved in groundwater, have been compared. The $^{234}U/^{238}U$ isotopic ratio lies within the same range for water and particles (1.5 to 2.1) but different to the rock (0.9 to 1.2). This would support reversible uptake of uranium on the particles.

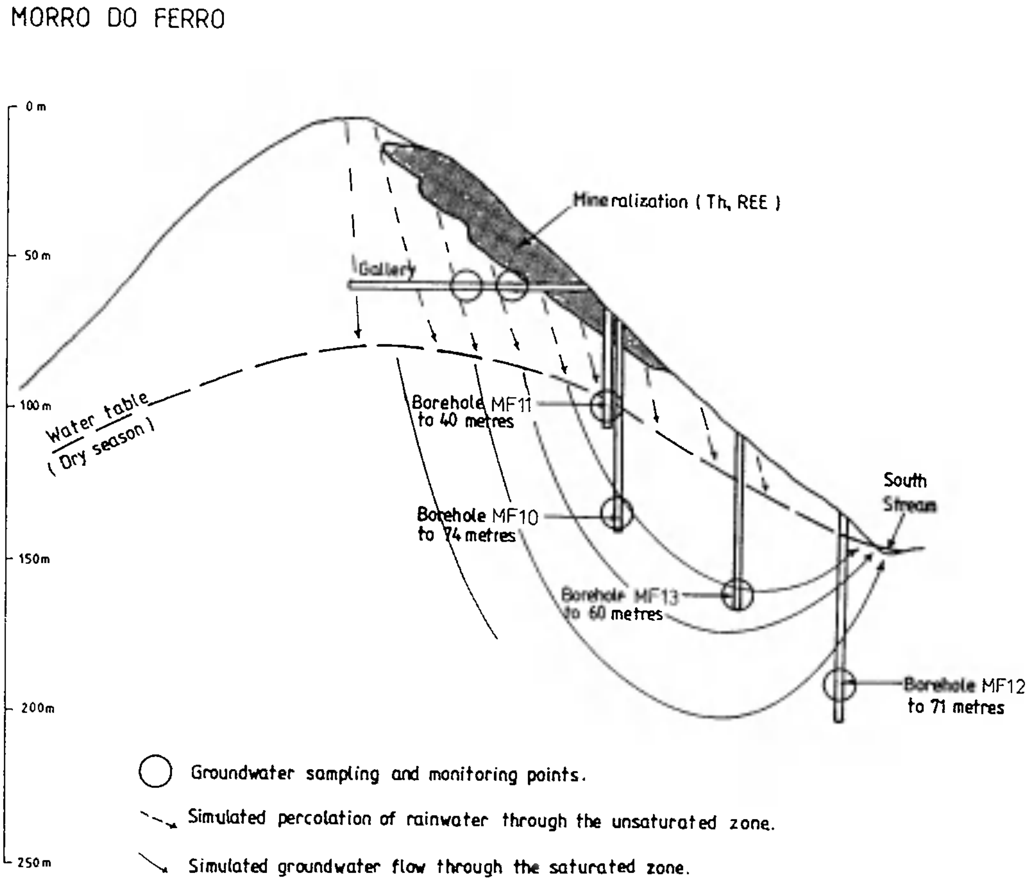

Figure 2: Seasonal relationship of the water table to the topography and main groundwater flow gradients at Morro do Ferro.

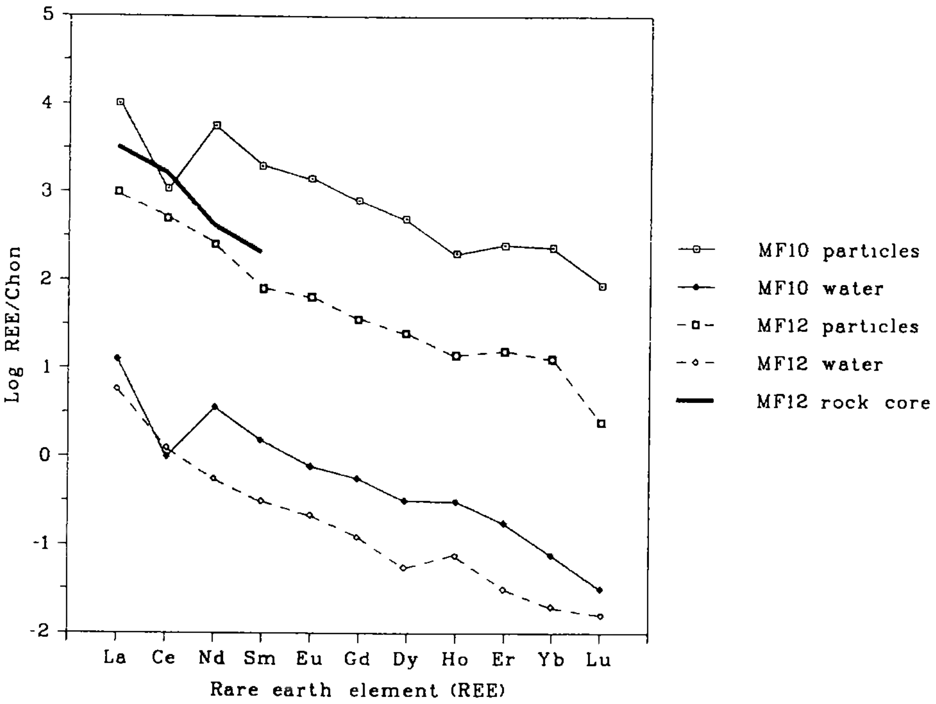

Figure 3: Chondrite-normalised REE patterns in representative rocks, groundwaters and corresponding suspended particles from boreholes MF10 and MF12 at Morro do Ferro.

3.1. Conclusions

The observation of colloids in association with thorium, lanthanides and uranium at Morro do Ferro, show that:

- three- and tetravalent elements and uranium are taken up by the colloidal particles in the groundwater. The uptake of three- and tetravalent elements is stronger than anticipated,
- the concentration of colloidal particles is normal despite the intense weathering and dilute character of the groundwater, and
- the uptake of uranium, thorium and lanthanides on colloids is either reversible or colloidal particles are immobile.

The migration of uranium and three- and tetravalent ions of lanthanides and thorium by sorption on mobile colloidal particles is unimportant at Morro do Ferro.

4. Radiolysis

The large amounts of concentrated high-grade uranium ore at Cigar Lake presented the possibility of evaluating the potential influence of radiolysis (both alpha and gamma radiation effects) on uranium ore (UO_2) dissolution and radionuclide transport from the ore into the surrounding clay halo.

Assuming that radiolysis of water is occurring at the ore/massive clay contact, oxidants will be generated (e.g. OH-radicals, H_2O_2 and O_2) and hydrogen. As hydrogen is not very reactive at ambient temperatures, it is expected to escape from the ore zone by diffusion through the water-filled matrices of the ore and the surrounding clay halo. The net chemical effect of radiolysis will be oxidation of components in the groundwater, contact rock and ore minerals (see Fig. 4).

In principle, the following reductants present at Cigar Lake can react with the oxidants produced by radiolytically generated reactions:

a) In the groundwater: Fe^{2+}, HS^-, DOC.

b) In the minerals: Fe(II) (e.g. siderite), sulphide (e.g. Fe_2S, PbS), SOC (Solid Organic Content), U(IV) (uraninite).

Mineralogical and geochemical observations note that Fe(III), present as amorphous ferrihydrites and hematite, has been precipitated in the clay near the ore/massive clay contact (Percival and Kodama, 1989). Furthermore, the uranium ore shows signs of surface alterations to mixed oxides of stoichiometries in the range of U_4O_9 to U_3O_7 (Sunder et al., 1988). Hydrogen has also been analysed in groundwaters sampled from the ore/clay zone (Cramer per. comm., 1992). The presence of these oxidation and other products can, in principle, be generated by radiolysis.

General model calculations (Christensen, 1990) confirm that the radiolysis products of water oxidise Fe(II) to Fe(III), which may then precipitate due to low solubility. These findings support the field evidence, although it is uncertain as to whether all the Fe(III) minerals can be accounted for by this process.

Laboratory experiments indicate that no radiolytic oxidation occurs at the UO_2 surface beyond a certain corrosion potential (Shoesmith and Sunder, 1991). This may explain the lack of significant quantities of higher valency uranium oxides at the uraninite mineral surfaces. The radiolytic model originally proposed for the oxidation of UO_2 by alpha radiolysis was consequently modified (Christensen et al., 1992), showing that the oxidation of UO_2 had been overestimated by an order of magnitude in the earlier calculations.

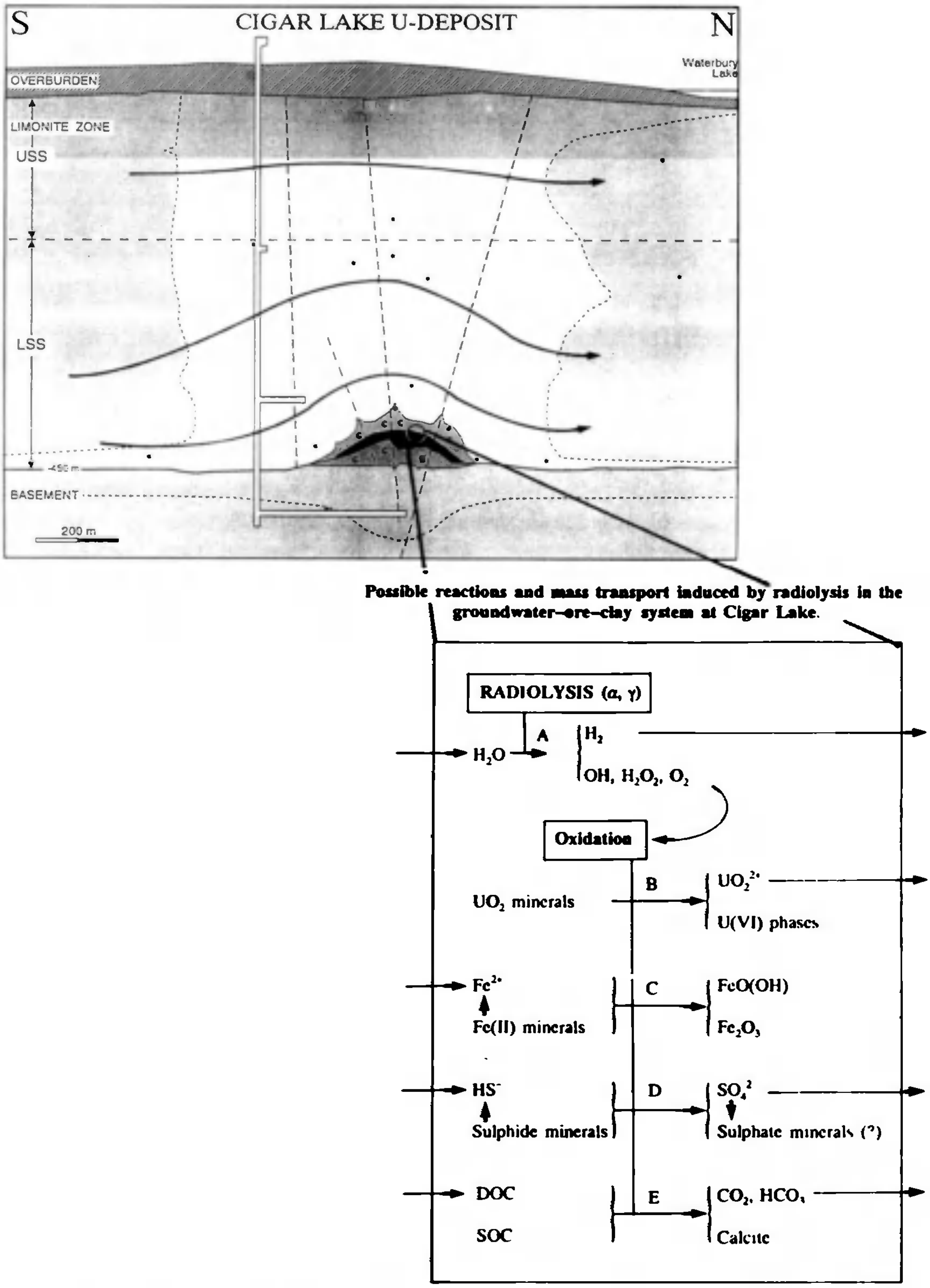

Figure 4: Diagramatic vertical profile through the Cigar Lake uranium deposit showing the major rock units, the clay (c) and ore (black) zones, the vertical shaft and the main groundwater flow directions. The clay/ore contact, where radiolytic reactions might be expected, is ringed (modified after Vilks et al., 1991).
Schematically illustrated is an analysis of possible oxidation reactions caused by radiolysis; the production of hydrogen and oxidising species (reaction A), and some possible oxidation reactions accounted by these species (reactions B-E).

The surface oxidation of uranium ore (UO_2) to higher mixed oxides is of interest from a performance assessment viewpoint. If oxidation proceeds beyond U_3O_7 to U_3O_8 it will alter the crystal lattice structure. Spent nuclear fuel consists of UO_2 with radionuclides contained in the crystal matrix. If the matrix is changed by oxidation these radionuclides can become available for dissolution through release. A further mechanism for release would be the oxidation of U(IV) to U(VI) and thereby the dissolution of uranium as uranyl ions. However, evidence from Cigar Lake shows that only minor quantities of higher mixed oxides (U_4O_9 to U_3O_7) are present on the ore surfaces (Sunder et al., 1988). Furthermore, there is no indication of extensive uranium loss by oxidation to uranyl ions.

In summary, at Cigar Lake radiolysis may be accountable for:

- the oxidation of the uranium ore (UO_2) to higher mixed oxides. This process appears to be very limited as the threshold value of the corrosion potential has not been exceeded, and

- the presence of dissolved hydrogen in groundwaters from the ore zone.

Whether small amounts of dissolved uranium have also accompanied the outward "redox front" movement of Fe^{3+} into the clay layer, forming co-precipitates with ferrihydrites, is not, however, established.

4.1. Conclusions

With regard to the performance assessment of spent nuclear fuel disposal, observations at Cigar Lake support the following conclusions:

1. Only very thin surface layers of higher uranium oxides are observed on the natural uraninite. This indicates that no change in the UO_2 crystal lattice will occur until U_3O_7 is exceeded (e.g. to U_3O_8 or UO_3).

2. It is important to bear in mind that if the observed oxidation of iron in the near-field at the Cigar Lake ore body is a result of radiolysis (and not influenced to any major degree by microbial mediation), then the total amount of Fe(III) oxides generated is still minor compared to predictions of the total net oxidation using current models employed to assess the amount of spent fuel oxidation by radiolysis (SKB-91).

3. Oxidation of U(IV) is not the only oxidant-comsuming reaction occurring in the ore zone. Oxidants, including those possibly produced by radiolysis, can also react with components of the groundwater (e.g. Fe^{2+}, HS^-, DOC etc.) or diffuse out into the surrounding rock to react with mineral reductants such as siderite, uraninite and the various sulphide phases.

Taken collectively, present results from the Cigar Lake study support the fact that radiolytic oxidation in the near-field of exposed spent nuclear fuel, within the concept of an underground repository, cannot be ruled out. However, the net changes are considerably overestimated by models currently used for performance assessment. The presence of some oxidation in the ore body indicates that the UO_2 in spent fuel will not necessarily consume all the oxidants generated.

5. Acknowledgements

We would like to thank Jan Cramer (AECL) for constructively reviewing the section on radiolysis.

References

Allard, B., Karlsson, F. and Neretnieks, I., 1991. Concentrations of particulate matter and humic substances in deep groundwaters and estimated effects on the adsorption and transport of radionuclides. SKB Tech. Rep. (TR 91-50), Stockholm.

Chapman, N.A., McKinley, I.G., Shea, M.E. and Smellie, J.A.T., 1990. The Poços de Caldas project: Summary and implications for radioactive waste management. Nagra Tech. Rep. (NTB 90-33), Wettingen, SKB Tech. Rep. (TR 90-24), Stockholm, UKDOE Tech. Rep. (WR 90-055), London.

Christensen, H., 1990. Calculation of the effect of α-radiolysis on UO_2 oxidation. Studsvik Tech. Rep. (NS-89/117), Studsvik Material AB.

Christensen, H., Sunder, S. and Shoesmith, D.W., 1992. Calculation of radiation induced dissolution of UO_2. Adjustment of the model based on α-radiolysis experiments. Studsvik Status Rep. (M-92/20), Studsvik Material AB.

Cramer, J.J., 1988. Natural analogue studies on the Cigar Lake uranium deposit: An update. In: Proc. 3rd. CEC/NAWG Meeting, Snowbird, Utah (June 15-17). CEC Rep. EUR 11725 EN, 50-56.

Eisenbud, M., Krauskopf, K., Penna Franca, E., Lei, W., Ballad, R., Linsalata, P. and Fujimori, K., 1984. Natural analogues for the transuranic actinide elements: An investigation in Minas Gerais, Brazil. Environ. Geol. Water Sci., 6, 1-9.

Grenthe, I., Stumm, W., Laaksoharju, M., Nilsson, A-C. and Wikberg, P., 1992. Redox potentials and redox reactions in deep groundwater systems. Appl. Geol. (In press).

KBS-3, 1983. Final storage of spent nuclear fuel - KBS-3. SKBF/KBS (5 volumes), Stockholm.

Percival, J.B. and Kodama, H., 1989. Sudoite from Cigar Lake, Saskatchewan. Can. Miner., 27, 633-641.

Salo, J-P. and Raiko, H., 1989. The copper/steel canister design for nuclear waste disposal. TVO/KPA Tech. Rep. (TR 89-14), Helsinki.

Shoesmith, D.W. and Sunder, S., 1992. The prediction of nuclear fuel (UO_2) dissolution rates under waste disposal conditions. J. Nucl. Mat. (submitted).

SKB-91, 1992. Final disposal of spent nuclear fuel. Importance of the bedrock for safety. SKB Tech. Rep. (TR 92-20), Stockholm.

Smellie, J.A.T., 1989. Some Swedish natural analogue studies: A review. In: Proceedings of the Third CEC-NAWG Workshop, Snowbird, Utah, USA. CEC Tech. Rep. (EUR 11725 EN), 96-103.

Sunder, S., Taylor, P. and Cramer, J.J., 1988. XPS and XRD studies of uranium rich minerals from Cigar Lake, Saskatchewan. Mat. Res. Symp. Proc. Vol. 112, 465-472.

Vilks, P., Cramer, J.J., Bachinski, D.C., Doern, D.C. and Miller, H.G., 1991. Studies of colloids and suspended particles in the Cigar Lake uranium deposit. Migration '91 (Oct. 1991), Jerez, Spain.

USE OF NATURAL ANALOGUE TEST CASES TO EVALUATE A NEW PERFORMANCE ASSESSMENT TDB

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Abstract

Natural analogue studies carried out to date provide a range of well defined test cases which can be used to verify and, to some extent, validate chemical thermodynamic models and their associated thermodynamic databases (TDBs). This paper illustrates how this approach is applied to a new Nagra TDB which will be used as a reference standard in calculations to support the Kristallin-I performance assessment and the evaluation of a potential L/ILW repository site at Wellenberg.

1. Introduction

Chemical thermodynamic models are widely used in radioactive waste management - for example to interpret field geochemical measurements, to help plan laboratory experiments and to predict radionuclide solubility in a repository environment. These models and, especially, their associated thermodynamic databases (TDBs) are in constant development and are regularly updated as new information becomes available. At specific times the model/TDB may be "frozen" and documented to ensure that a reference is available for quality control (QC). For performance assessment usage, this QC aspect is particularly important and the procedure for freezing TDBs may be formalised (e.g. Pearson and Berner, 1991; Pearson et al., 1992).

TDBs are notorious for some of the major errors which they contain. Apart from the difficulties involved in measuring thermodynamic data, many TDBs originate in hand calculations or unit conversions which commonly contain arithmetic or transcription errors. This is not helped by the fact that the TDB files are commonly held in an extremely user-unfriendly format (betraying the card-based ancestry of some of the common codes used) which makes them very difficult to check. In addition, the key parameter used in many codes is the reaction equilibrium constant (K), which is extremely sensitive to errors in the free energies of reactants from which it may be calculated. Errors found in established databases have occasionally included K values which are incorrect by over **100 orders of magnitude** - an error inconceivable in almost any other area of science!

Apart from errors in the database, major difficulties can arise when correct data are incorrectly applied in a simulation - for example calculating solubility based on a solid phase which is kinetically hindered from forming or assuming redox equilibration between inappropriate couples.

When a new TDB is "frozen", it must be checked for possible errors accumulated during its compilation and it should be further tested for applicability to the particular environment to be modelled. The two testing methods available are "verification" - comparision of results from the new code/database with those from other (independent) codes/databases - and "validation" - comparison of model predictions with reality. In fact, it is not possible to validate a thermodynamic code/database in a rigorous sense, but repeated testing builds confidence in its applicability.

Thermodynamic model testing has been a major component of many analogue studies (e.g. Oman (Bath et al., 1987); Poços de Caldas (Bruno et al., 1991); Maqarin (Alexander et al., 1992)). Such studies have been modelled ("blind") by several independent groups. Running such cases with a new TDB allows both comparison with the previous modelling results (verification) and comparison with reality as reflected by field measurements.

This paper illustrates such testing of the new Nagra reference database (Pearson and Berner, 1991; Pearson et al., 1992). This TDB will be used as a reference for performance assessments carried out as part of the Kristallin-I evaluation of HLW disposal in the crystalline basement of Northern Switzerland and the site characterisation of the marl of Wellenberg as a potential host for a L/ILW repository.

2. Procedures

The modelling work was carried out with RIPP2 which is a user-friendly interface for the code PHREEQE (Parkhurst et al., 1980). A particular advantage of RIPP2 is that it allows simulations to be easily run for a range of different TDBs. Major element water chemistry for a series of test cases was supplied to the modeller who was required to predict the limiting concentration and speciation of a range of trace elements "blind" - as was the case in the original analogue studies. This aspect of blind testing is particularly important as, in many cases, the manner in which the simulation is carried out can be very objective and, if the "answer" is known, can be biased either consciously or subconsciously. The difference between blind testing of model **predictions** and testing if a model can **simulate** particular observations is fundamental, although often not evident from the literature.

The new Nagra database NTB9118 (Pearson and Berner, 1991; Pearson et al., 1992) is being verified via intercomparison with two databases previously used in the Nagra programme: NAI0289 (Pearson et al., 1989) and a version of HATCHES (version 3.0; Cross and Ewart, 1991). The three databases have been used to model five different water types, representing a wide range of environments of interest to the Swiss radwaste programme, but this paper will consider only the analogue examples.

The selected analogues waters may be paired with repository waters:

1 **HLW, far-field environment**
   a) Kristallin-I: Reference deep groundwater for the Nagra Kristallin-I safety assessment (Pearson and Scholtis, 1992)
   b) Poços de Caldas: Deep groundwater from the Osamu Utsumi mine, Poços de Caldas, Brazil used in a previous verification and validation study (Bruno et al., 1991)

2 **L/ILW, near field environment**
   a) Cement porewater: Reference porewater for the cement/concrete dominated near field (Berner, 1992)
   b) Maqarin: Hyperalkaline groundwater from the natural cement zone at Maqarin, northern Jordan (Khoury et al., 1992) used in a previous verification and validation exercise (Alexander, 1992; Alexander et al. 1992).

The precise groundwater compositions are detailed in Table 1.

A rather simple procedure was used in which the model was used to simulate the specified major element water chemistry including an element of interest at trace concentration ($1 \mu g\ l^{-1}$). This allowed identification of possible solubility-limiting phases and, from calculated saturation indices of these phases, an estimate of the limiting solubility set by these phases. In particular cases, equilibration of the water of interest with the selected solid was also simulated, but this was avoided for elements which were either highly soluble (where saturation upsets the major element chemisty) or highly insoluble (concentrations are so low as to be meaningless). Aqueous speciation calculated by the code is also reported although, as speciation may depend on the concentration of the element of interest, cross comparisons with other codes/nature must be interpreted with care.

Table 1: Water chemistry in a repository environment and in the analogue test cases

	Kristallin-I[1] reference groundwater (West region)	**Cement porewater[2] chemistry**	**Poços de[3] Caldas F5**	**Maqarin[4]**
Temp°C	55	25	24	30.0
pH	7.7	12.7	6.4	12.6
pε	-2.7	not defined	4.3	2.1
Major elements (M)				
Na	1.4e-2	1.9e-1	2.7e-5	5.8e-3
K	2.2e-4	5.8e-2	3.3e-4	1.6e-2
Ca	3.5e-4	1.9e-2	3.9e-4	2.6e-2
Mg	1.2e-3	9.5e-8	6.0e-6	4.1e-6
Cl	3.6e-3	1.9e-1	-	1.4e-3
F	6.4e-4	1.2e-4	3.5e-4	-
SO_4	3.1e-3	1.6e-2	5.5e-4	1.5e-2
$[CO_3]$	4.8e-3	1.6e-5	8.5e-4	8.4e-6
SiO_2	5.9e-4	1.6e-5	6.2e-4	3.1e-7
NO_3	-		-	6.2e-4

$[CO_3]$ total carbonate

1) Pearson and Scholtis, 1992
2) Berner, 1990 ("lining concrete at 7 cycles")
3) Bruno et al., 1991
4) Alexander et al., 1992

3. Results and discussion

3.1 Poços de Caldas

Table 2 shows the predictions made by 5 modelling groups of solubility, speciation and controlling solid for 3 elements (U, Th and Ni) in a deep groundwater from the Osamu Utsumi mine (water F5; Bruno et al., 1991). These predictions are compared with those made using RIPP2 with the new Nagra TDB and with field observations.

For U, the predicted controlling solid agrees with 4 out of the 5 other modelling groups and the predicted solubility is in the same ball park, even if at the high end of the range of predicted values. Aqueous phase speciation shows a wide range of scatter between the modellers.

Comparison with reality indicates that the predicted solubility is very high relative to observed concentrations (by 3 orders of magnitude) but, at least, this could be considered a conservative overestimate. The reason for this discrepancy could be limited availability of U, but this is rather unlikely in such an area of extensive uranium mineralisation. As discussed further by Bruno et al. (1991), a more likely explanation is the scavanging of U by iron oxyhydroxides forming in this system. Such co-precipitation cannot be modelled by current codes/databases.

Th shows a much more consistent picture, with the Nagra predicted solubility lying in the middle of the rather narrow range of predictions by the other modelling groups and agreeing well with the measured concentration. There is also fairly general agreement on ThO_2 being the limiting solid but it is noticeable, for this high fluoride groundwater, that the solubility of ThF_4 is very similar. Although not specifically observed in core from the borehole from which water was sampled, thorianite is a known mineral in this region and thus ThO_2 is a reasonable assumption for the limiting solid phase. Typically, however, there is a fair discrepancy in predicted speciation. The Nagra prediction of predominantly uncharged species in solution does not, however, match the field observation of soluble Th being predominantly cationic.

Nagra predicts very high solubility of Ni, even higher than the values specified by the other modellers. At such high solubilities, the modelling approach breaks down as dissolving an Ni mineral until saturation is reached considerably changes the major element chemistry. Nevertheless, the simple prediction that Ni would have very high solubility would be in agreement with 3 out of 4 of the other modelling groups.

Nickel ferrite ($NiFe_2O_4$) and a nickel silicate ($Ni\ Si\ O_3$) are actually contained in the Nagra TDB, but are not considered to be a potential solubility limiting phase in low temperature systems. Because of its relatively simple chemistry, there is more agreement on Ni aqueous speciation between models.

The observed low concentration of Ni could be due to solubility controlled by a phase discounted in the modelling or to its supply to the system being limited. Like U, however, the most likely explanation is coprecipitation with iron oxyhydroxides.

Table 2: Poços de Caldas test case (F5; Bruno et al., 1991)

	Solubility (M)		Solid Speciation
Uranium			
SKB	9e-6	U_3O_8	$UO_2F_2^{\circ}/UO_2F^+$
KTH	1e-8	U_3O_8	$UO_2CO_3^{\circ}/UO_2(CO_3)_2^{2-}$
PSI	2e-5	U_3O_8	$UO_2F_2^{\circ}/UO_2F^+$
Harwell	6e-6	U_3O_8	$UO_2CO_2^{\circ}/UO_2(CO_3)_2^{2-}/UO_2F_2^{\circ}$
Atkins	4E-6	Zippeite	$(UO_2)_2\,(OH)_3CO_3^-/UO_2(HPO_4)_2^{2-}$
Nagra	4e-5	UO_3	$(UO_2)_2(OH)_3CO_3^-$
Observation	*3e-8*	*?pitchblende*	*mainly anionic*
Thorium			
SKB	9e-9	ThO_2	ThF_3^+/ThF_2^{2+}
KTH	4e-10	ThO_2	$ThF_4^{\circ}/Th(OH)_4^{\circ}$
PSI	6e-11	ThF_4	ThF_3^+/ThF_4°
Harwell	2e-9	ThO_2	$Th(HPO_4)_3^{2-}/Th(OH)_4^{\circ}$
Atkins	2e-9	ThO_2	$Th(HPO_4)_3^{2-}/ThF_3^-/ThF_4^{\circ}$
Nagra	3e-10	ThO_2	$Th(OH)_4^{\circ}$
Observation	*1e-10*	-	*mainly cationic*
Nickel			
SKB	9e-13	$NiFe_2O_4$	Ni^{2+}
KTH	5e-2	$Ni(OH)_2$	Ni^{2+}
PSI	3e-3	NiO	$NiCO_3^{\circ}/Ni^{2+}$
Harwell	2e-2	$Ni(OH)_2$	Ni^{2+}
Atkins	-	-	-
Nagra	>1e-1	NiO	$Ni^{2+}/NiHCO_3^+$
Observation	*1e-7*	-	-

3.2 Jordan

Here the data (Table 3) are presented in an alternative form which still allows intercomparison of the database predictions. In the case of U, there is reasonable agreement between the Nagra and PSI aqueous speciation predictions, but significant differences with the Harwell results. In the former case this reflects the same source of most of the U data in both databases (i.e. the NEA U data set; Grenthe et al., 1992). Pearson et al. (1992) noted that agreement between the Nagra and Harwell U database was "generally not good" and this appears, in part at least, to reflect differences in the importance of the anionic hydrolysis products of U. As thermodynamic data for these complexes are estimated for high pH values (see Craig and Vaughan, 1981), there remains considerable debate as to the importance of this form of U.

Nagra predict that UO_3 2[H_2O] controls the solubility of U in this system while $CaUO_4$ is predicted by PSI and Harwell. UO_3 2[H_2O] is included in all three databases (indeed the input data are identical in all three) whereas $CaUO_4$ is absent from the Nagra database. Although the PSI and Harwell databases may be said to be less conservative here, in that they predict a greater degree of U oversaturation, recent work in the Maqarin system suggests they may, nevertheless, be more realistic as an unidentified Ca-U phase (an oxide or carbonate) has been identified in the primary mineral assemblage at this site (see Alexander, 1992, for details). However, it should be noted that, although $CaUO_4$ may indeed be present as a U source in the Maqarin groundwater, widespread secondary U (as a trace element in hydrated silicate phases and ferric hydroxides) may be acting as a U sink and be a more important control on U in solution. Consequently, until this system is better understood, the more conservative Nagra database might be preferred.

The Th results indicate $Th(OH)_4^{\circ}$ to be the sole aqueous species in all cases. In addition, higher ThO_2 oversaturation in the Harwell predictions is due to the inclusion of a more crystalline ThO_2 solid in the HATCHES database (c.f. discussion in Langmuir and Herman, 1980, on the effects of crystallinity on solubility).

To date, no discrete Th phase has been identified in the Maqarin system. It seems more likely that Th exists as an amorphous phase in this low temperature environment, suggesting the Nagra and PSI databases may be more appropriate here.

The similarity in the aqueous speciation and solubility controlling solid predictions for Se for the PSI and Harwell databases reflect the same source of the data (i.e. Baeyens and McKinley, 1989). The Nagra database rejected the Baeyens and McKinley data on relatively soluble Se salts and rare ore minerals, in favour of the results of the work of Weres et al. (1989) which suggested that the only solid likely to exert significant solubility control is elemental Se.

Table 3: Maqarin test case (MQ5: Alexander, 1992)

Modelling Group (DATABASE)	**PSI** (NAI0289)	**Harwell** (HATCHES 3.0)	**Nagra** (NTB9118)
Uranium (1 μg l^{-1})			
Aqueous species(%)			
$UO_2(OH)_4^{2-}$	4	86	12
$UO_2(OH)_2^0$	10	4	-
$UO_2(OH)_3^-$	86	-	88
Solubility controlling solid (SI)			
$CaUO_4$	+10.3	+10.4	-
$UO_3 \cdot 2[H_2O]$	-	-	+7.1
Thorium (1 μg l^{-1})			
Aqueous species(%)			
$Th(OH)_4^0$	100	100	100
Solubility controlling solid (SI)			
ThO_2	+1.2	+5.7	+1.3
Selenium (1 μg l^{-1})			
Aqueous species(%)			
SeO_4^{2-}	53	49	85
SeO_3^{2-}	47	51	15
Solubility controlling solid (SI)			
$CaSeO_3$	-5.6	-5.5	-
$CaSeO_4$	-7.7	-7.6	-
Se	-	-	-3.4

The results of the ongoing Maqarin natural analogue project indicate the presence of $CaSeO_4$ and elemental Se, among numerous other Se containing phases (e.g. Cu-K-selenite). However, the presence of $CaSeO_4$ in the secondary mineral assemblage and elemental Se in the primary mineral assemblage suggests that the former phase may be the more important control on Se in the Maqarin groundwaters.

4. Conclusions

This exercise has shown that an indication of the applicability of a database to performance assessment modelling can be assessed by using well established analogue test cases. Although a considerable effort has gone into preparing a new standard database, it is not clear that it better predicts the chemistry of near-neutral groundwaters although solubility estimates may be more conservative. This exercise also indicates that important phases may be missing from the TDB, which are important under high pH conditions.

Existing test cases are useful but could be usefully extended by inclusion of:

1) Examples with known long residence time in contact with mineral phases rich in the elements of interest

2) Groundwaters which are known to be chemically reducing

3) Better analysis of any secondary phases which may contain the elements of interest (pure phases or co-precipitations/solid solutions)

4) More rigorous techniques for measuring trace element speciation. This paper clearly shows that this is an area where major discrepancies between codes/databases exist.

Tests of geochemical models/databases are one of the most useful applications of analogues to date. Existing data from previous studies can be re-used to test new TDBs, but further improved analogues of this type are also justified.

5. Acknowledgement

The blind modelling approach to testing of geochemical models has been developed iteratively at workshops held in the Oman, Poços de Caldas and Jordan analogue projects and the authors appreciate the input from many colleagues towards improving methodology and selecting test cases. Thanks also to Andreas Gautschi, Charles McCombie, Andreas Scholtis and Piet Zuidema for their input to this manuscript.

References

Alexander, W.R., 1992 (ed): "A natural analogue study of cement-buffered, hyperalkaline groundwaters and their interaction with a sedimentary host rock - I: Source-term description and geochemical code database validation"; Nagra Technical report series, NTB 91-10, Nagra, Wettingen, Switzerland (in press)

Alexander, W.R., Dayal, R., Eagleson, K., Eikenberg, J., Hamilton, E., Linklater, C.M., McKinley, I.G., Tweed, C.J., 1992: "A natural analogue of high pH cement pore waters from the Maqarin area of northern Jordan II: Results of predictive geochemical calculations"; J. Geochem. Explor. (in press)

Baeyens, B. and McKinley, I.G., 1989: ""A PHREEQE Database for Pd, Ni and Se"; Nagra Technical report series, NTB 88-28 Nagra, Wettingen, Switzerland

Bath, A.H., Christofi, N., Neal, C., Philp, J.C., Cave, M.R., McKinley, I.G., Berner, U., 1987: "Trace element and microbiological studies of alkaline groundwaters in Oman, Arabian Gulf: A natural analogue for cement pore-waters"; Nagra Technical report series, NTB 87-16 Nagra, Wettingen, Switzerland

Berner, U., 1990: Unpublished report PSI-TM-41-90-20; Paul Scherrer Institute, Wuerenlingen & Villigen, Villigen, Switzerland

Bruno, J., Cross, J.E., Eikenberg, J., McKinley, I.G., Read, D., Sandino, A., Sellin, P., 1991, - "Testing of geochemical models in the Poços de Caldas analogue study" Nagra Technical report series, NTB 90-29, Nagra, Wettingen, Switzerland (SKB TR 90-20 / UK DOE WR 90-051)

Craig, J.R. and Vaughan, D.J., 1981: "Ore microscopy and ore petrography"; John Wiley and Sons, London, UK

Cross, J.E. and Ewart, F.I., 1991: "HATCHES - A thermodynamic database and management system"; Radiochim. Acta, 52/53, 421-422

Grenthe, I., Fuger, J., Lemire, R.J., Muller, A.B., Nguyen-Trung Cregu, C., Wanner, H., 1992: "Chemical Thermodynamics I: Chemical Thermodynamics of Uranium"; North-Holland, Amsterdam, The Netherlands

Khoury, H.N., Salameh, E., Clark, I.D., Fritz, P., Bajjali, W., Milodowski, A.E., Cave, M.R., Alexander, W.R., 1992: "A natural analogue of high pH cement pore waters from the Maqarin area of northern Jordan I: Introduction to the site"; J. Geochem. Explor. (in press)

Langmuir, D., and Herman, J.S., 1980: "The mobility of thorium in natural waters at low temperatures"; Geochim. Cosmochim. Acta, 44, 1753-1766

Parkhurst, D.L., Thorstenson, D.C., Plummer, L.N., 1980: "PHREEQE - A computer program for geochemical calculations"; USGS report no. PB 81 167801

Pearson, F.J. Jr. and Berner, U., 1991: "Nagra thermochemical data base - I. Core data"; Nagra Technical report series, NTB 91-17, Nagra, Wettingen, Switzerland

Pearson, F.J., Lolcama, J.L., Scholtis, A., 1989: ""Chemistry of waters in the Böttstein, Weiach, Riniken, Schafisheim, Kaisten and Leuggern boreholes - A hydrochemically consistent data set"; Nagra Technical report series, NTB 86-19, Nagra, Wettingen, Switzerland

Pearson, F.J., 1992: "Nagra thermochemical data base - II: Supplemental data"; Nagra Technical report series, NTB 91-18, Nagra, Wettingen, Switzerland, in press

Pearson, F.J. and Scholtis, A., 1992: "Reference waters for the Crystalline basement of Northern Switzerland"; Nagra Technical report series, NTB 93-07, Nagra, Wettingen, Switzerland, in press

Weres, O., Jaouri, A.R., Tsao, L., 1989: "The distribution speciation and geochemical cycling of selenium in a sedimentary environment, Kesterson Reservoir, California, USA"; Applied Geochem., 4, 543-563

NATURAL ANALOGUE STUDY ON NATIVE IRON

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Summary

Native iron formed at high, magmatic temperatures is rare because of the special conditions of formation. Millions of tons have survived millions of years mostly at shallow depths within the rock matrix due to mass transport limitations and/or pore water conditions favouring passivation of the metal. For a comprehensive understanding of the preservation of native iron further investigation of the nature and role of the corrosion products is needed.

Native iron formed at lower, hydrothermal to ambient temperatures during the serpentinization of ultrabasic rocks is more abundant than commonly believed. In this case preservation is due to thermodynamic stability under highly reducing groundwater conditions generated during serpentinization. High–FeO olivine used as backfill could assure favourable groundwater conditions in nuclear waste repositories.

1. Introduction

Native iron has been suggested repeatedly since the creation of the natural analogue approach and until recently (1) as a possible candidate for natural analogue studies. But no detailed studies have been performed yet. Native iron is not an easy analogue that could be used in a straight–forward manner for studying iron container corrosion in nature simply because there is no similarity with current technical barrier systems planned for nuclear waste repositories. However, important fundamental issues like the influence of corrosion products can be evaluated, and when metallic iron is considered as an indicator of very low, local redox conditions perspectives widen considerably.

Native iron has been studied intensively during the last decades to elucidate the conditions of formation, but investigators usually were not interested in the circumstances of preservation of the metal. Therefore it was considered as justified to review all available information on native iron for the purpose of extracting information useful in the field of nuclear waste management. A limited number of samples of native iron in basalt was available for experimental investigation. From the point of view of the regulatory authority demands on the quality of a natural analogue are less stringent as compared with the application of gained results in the safety analysis. An analogue can be a very important tool in decision making without delivering quantitative data for the safety analysis.

Because of their completely different nature in the following occurrences of iron formed at high, magmatic temperatures are treated separately from those formed at lower, hydrothermal to ambient temperatures. For more details see (2).

2. Native iron formed at high, magmatic temperatures in basalt

There are only two occurrences known on earth where native iron has been formed in significant amounts, the Bühl (Germany) and Disko (Greenland). Both are connected with sediment contaminated basalt volcanism. On Disko island native iron-bearing basaltic rocks are very common, about 0.5 to 1.0% of all volcanic rocks there, giving a total amount of iron metal of several millions of tons. Average contents reach up to 2.5 wt.% metallic iron. The iron of Disko occurs mostly as interconnected inclusions and cumulates of various size (mm to m) (Fig.1). The Bühl iron forms sponge-like inclusions of mostly cm-size in basalt (Fig.2). The Bühl iron has a low carbon content (0.1-0.2 wt.%) and no nickel. Disko iron with a low as well as a high carbon content has been found, nickel being low or up to about 2%. The iron can be compared with technical qualities ranging from low-carbon steel to high-carbon cast iron. In contrast to technical iron the natural mineral associations often include sulphides, various Fe-Ti oxides, magnetite and silicates. Sulphides enhance corrosion, make observed rates conservative.

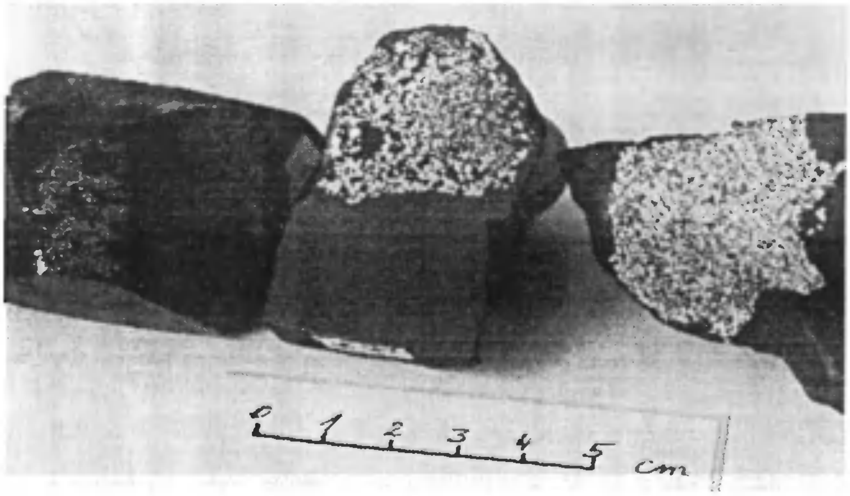

Fig.1: Samples of native iron in basalt (Bühl, Germany).

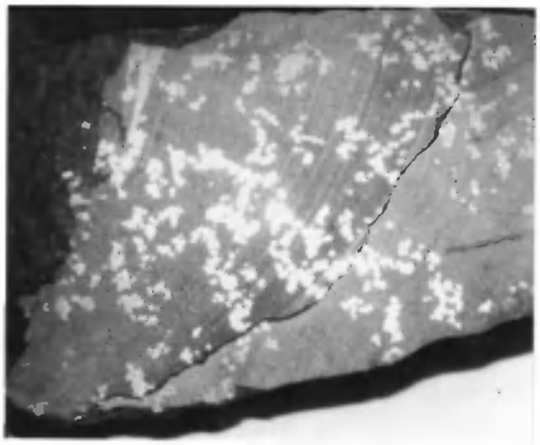

Fig.2: View of section through native iron-bearing basalt (scale: about 15 cm; Disko, Greenland).

It should be borne in mind that conditions of magma emplacement were not always favourable with respect to iron preservation: subaqueous, subaerial deposition, thickness of basalt layers containing iron sometimes as low as a few metres – almost certainly a modeler would have predicted that iron could not survive in these cases. In some cases iron has been in equilibrium with larger volumes of melt, but textural and compositional evidence of steep local redox gradients is common, too. In some other cases rapid quenching of the melt was indicated by the presence of basaltic glass containing native iron. Very steep redox gradients have been found in basalt surrounding tree-molds at Mt.Fuji, Japan, with an intermediate layer between normal and iron-bearing basalt of only 1–3 cm. Emplacement of a relatively small basalt body (diameter: about 150 m) near the surface at the Bühl implies contact of the basalt with groundwater at very early stages of the evolution of the occurrence. Pathways which enable access of water are formed when the basalt solidifies as columns. On Disko island iron-bearing basalt influenced by hydrothermal fluids (zeolite facies metamorphism) should be studied further (for references see (2)). Another feature deserving to be investigated is the surprising preservation of native iron in a well-cemented tuff layer of only 12 m thickness on the Nugssuaq peninsula (Greenland). Tuffs covering this layer were seriously affected by various processes of hydrothermal alteration and weathering. Unfortunately, in most cases the data available does not allow a detailed reconstruction of the alteration history of the iron-bearing layers.

The time scales to be considered in connection with native iron are about 13 Ma (Bühl) and 30–63 Ma (Disko) since the formation. Only a few samples have been dated yet. Both occurrences were exposed by weathering. At the Bühl the operation of a quarry has removed most of the iron-bearing basalt until far below the present groundwater level. In the collections available at museums only a few out of about a hundred samples were found to be altered/weathered. On Disko present-day weathering is proceeding, changing the iron-bearing layers superficially into marker horizons, stained by iron corrosion products. On Disko most iron inclusions are irregularly interconnected providing pathways for corrosion progress. Corrosion in the absence of hydrothermal fluids has not advanced deeper than a few mm to cm from the surface into the interior. From erosion rates under present climatic conditions at the prevailing steep slopes the time scale of exposure at outcrops can roughly be estimated to be 1,000–10,000 years. Permafrost conditions further complicate the assessment of reaction rates.

Preservation of native iron in basalt during the complete course of its evolution seems to be mainly due to an initial, high redox capacity of the basalt (excess of reductant in the melt, reacting with water) and diffusional mass transport limitations (in the melt as well as in the solid matrix and alteration products), probably in combination with favourable pore water conditions.

3. Native iron formed during serpentinization of ultrabasic rocks

Native iron in serpentinites does not seem to be much more rare than serpentinized ultramafic rocks themselves. It occurres in very old as well as in geologically young formations. The metal has often been overlooked because it frequently occurs in an extremely fine-grained form. Metal phases are absent in fresh ultramafic rocks. Serpentinization is a process involving massive infiltration of water. In the course of the reaction very low redox potentials are achieved: iron(II) is liberated from olivine, hydrogen gas develops, and metallic iron becomes stable. In contrast to the system: native iron in basalt where an external source was necessary to create a highly reducing environment, one can speak of an internal reducing source in the serpentinization system. The fact that very often instead of pure iron nickel-iron phases are found does not diminish the value of the system as a natural analogue. The simple fact that during the primary magmatic differentiation nickel follows into the ultramafic fraction explains these observations. Although the metallic nickel–rich phases do not require a redox potential potential as low as pure iron the same reactions would proceed also without the nickel content and stabilize pure iron.

From the point of view of nuclear waste disposal the serpentinization system provides an analogue for a redox–active backfill. In this case iron is only an indicator of favourable redox conditions. An integrated analogue system, Ni–Fe canister and ultramafic backfill, has been proposed earlier (3). It is doubtful, however, if such low redox conditions can be maintained with sufficient high probability over geologic periods of time. It seems to be more reasonable to rely on the general tendency of the reactions of the backfill and use a more corrosion resistant copper canister. Native copper, too, has been found in altered ultrabasic rock.

In the following some observations in nature are listed which are important from the natural analogue point of view because they characterize the properties and capability of the system:
Serpentinization is a process which is fast on a geological time scale. Signs of low redox potential have been observed in ultramafic bodies of rather small dimensions (tens of metres), under near–surface conditions and in environments of intensive weathering (high–flow conditions). Examples of large as well as small water–rock ratios have been described. If all olivine is altered native iron is oxidized first to magnetite, but the redox potential of the system is still buffered at very low values. The buffering capacity is high due to the usually large amounts of primary and secondary (originating from the serpentinization process) magnetite.

The observation of very steep redox potential gradients in nature illustrates the efficiency of the buffering system. Variations in oxygen fugacity of about ten orders of magnitude, as indicated by typical mineral assemblages, over distances as short as a couple of centimetres have been found. Correspondingly low sulphide, carbonate and proton contents occur behind the serpentinization front, conditions favourable in many respects in a waste disposal system.

Earlier it was beleived that serpentinization can proceed only at temperatures of a few hundred degrees, but in recent years evidence for ambient temperature serpentinization has been found at many locations. This is important as temperatures in the waste disposal system will be low after some hundred years in the near field and in the far field, generally. The evolution of surface water infiltrating ultramafic rock has been simulated by geochemical modeling: free oxygen and carbon dioxide are removed and the pH rises. The results could be confirmed by observations in nature. Although there might be details of water–rock reaction mechanisms which are not yet understood, the predictability of the system supports the use of high–FeO olivine rock as backfill material.

The ultimate reason for the preservation of metallic iron in partly serpentinized rocks is the thermodynamic stability of the assemblage combined with a very high redox capacity.

4. Results of the investigation of samples of native iron in basalt

The following chapter gives a summary of experimental results based on a limited number of samples. More details can be found in ref.(4).

The Bühl–iron seems to be a fairly clear–cut model system: ball–like iron inclusions in

regular columns (average diameter: about 40 cm) of homogeneous rock in contact with near–surface groundwater. A model explaining the long–term preservation of native iron needs information on:
- the formation and evolution of the system,
- the nature of basalt alteration,
- the corrosion behaviour of the iron and the nature of iron corrosion products,
- the properties of the rock matrix (diffusivity), and
- the nature of pore water in the rock matrix.

A comprehensive solution of the problem cannot be expected from this limited study. Part of the museum specimens was not available for destructive analytical methods.

Three types of samples from the Bühl were examined: (i) iron sponge without visible alteration zone (Fig.3), (ii) iron with an alteration rim (Fig.4) and (iii) heavily corroded iron with no basalt adhering (Fig.5). In sample (i) equilibrium between metal and silicate seems to exist. Unfortunately the distribution of trace elements between both phases which could give more information on the state of equilibrium of discrete iron particles could not be determined with the methods available. The iron alteration in sample (ii) is probably due to rising oxygen fugacity at the early stages of crystallization and cooling and not an effect of weathering. From the severely oxidized sample (iii) only a small fragment was available for analysis. Characterization of the corrosion products as a basis for reconstruction of the processes would require more advanced methods (isotope determinations, Mössbauer spectroscopy, etc.). The iron seems to have been located near the margin of a basalt column or an open fissure so that after high–temperature alteration low–temperature weathering was affecting the iron. The rhythmic formation of products with an alternating iron content might indicate slow, diffusion–controlled corrosion. The corrosion front is rather even. It was not possible to find out if there was a negative selection in such a way that corroded iron inclusions were not collected during the operation of the quarry.

Examination of the interface between metal and silicate in the interior of the iron sponge from the Bühl showed layers of magnetite, Fe–silicate and ilmenite which originated at higher temperatures (Fig.6). The magnetite was not always forming a continuous protective layer.

The Bühl basalt itself showed signs of slight alteration of glass phases by fluids during cooling. The yellow–brown coloured, 5–8–mm rims on the surfaces of the columns seem to be weathering rims caused by some millions of years of exposure. The borderline between fresh and weathered basalt represents a redox front.

The corrosion behaviour of native iron in basalt groundwater under ambient conditions in contact with air as well as under oxygen exclusion, even of the nickel–rich sample tested, was as expected from technical iron. Local corrosion near sulphide inclusions was observed, but could not be studied further.

The composition of the calculated local basalt porewater depends very much on the presence of olivine. The pH rises to about 10 and conditions become very reducing, mainly in the magnetite stability field (iron passivation) or even, locally, near the stability line of iron. Iron species are produced faster than they are removed by diffusion and precipitate.

The porosity of the basalt matrix is relatively high, about 2.3 vol.%, but evenly distributed, with no discrete pathways (Fig.7). From the measured diffusivity of the basalt the corrosion rate of an iron inclusion (diameter: 4 cm) caused by diffusing oxygen (10 mg/l in groundwater) at the centre of a basalt column (diameter: 40 cm) is roughly estimated at 1 mm in

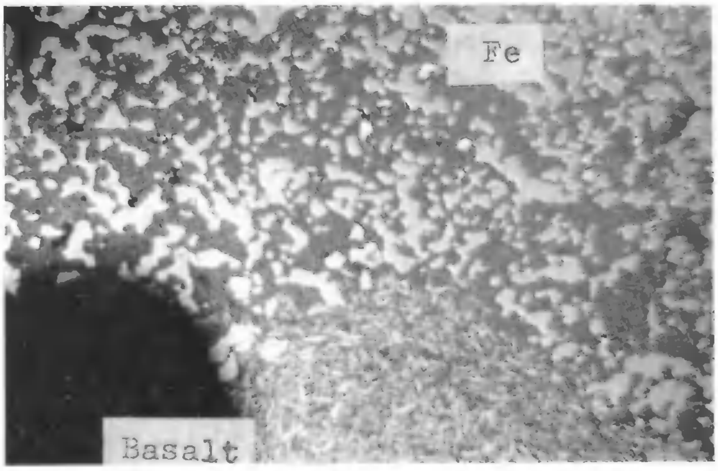

Fig.3: Iron sponge in basalt without alteration zone (width of section: 15 mm; Bühl).

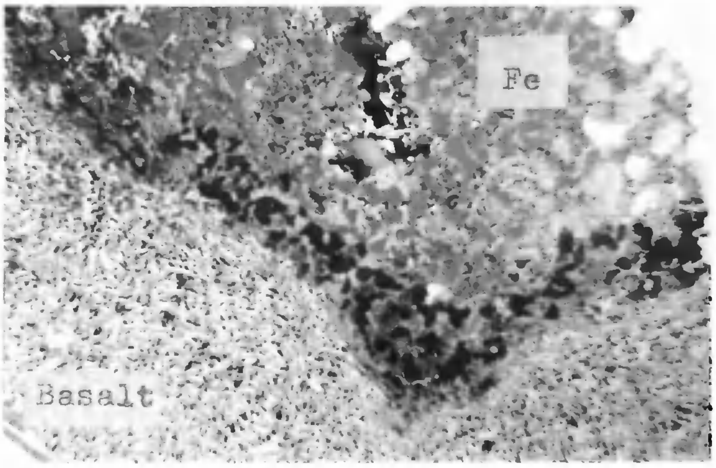

Fig.4: Iron sponge in basalt with alteration rim (width of section: 15 mm; Bühl).

Fig.5: Partially corroded native iron (Bühl; scale in cm).

10 Ma. Small inclusions near the margin would not survive: the corrosion rate is roughly 20 mm in 10 Ma for 1 cm diffusion length. However, oxygen is consumed by Fe(II) in the basalt (redox front movement for complete consumption of Fe(II): about 7.2 cm in 10 Ma) so that the actual life-time of the iron is higher. Open fissures of tens of micrometers by aperture would increase corrosion rates significantly, but precipitation of corrosion products would lower the rates down to the same orders of magnitude as in the intact basalt or an increase by a factor of two or so caused by one small fissure.

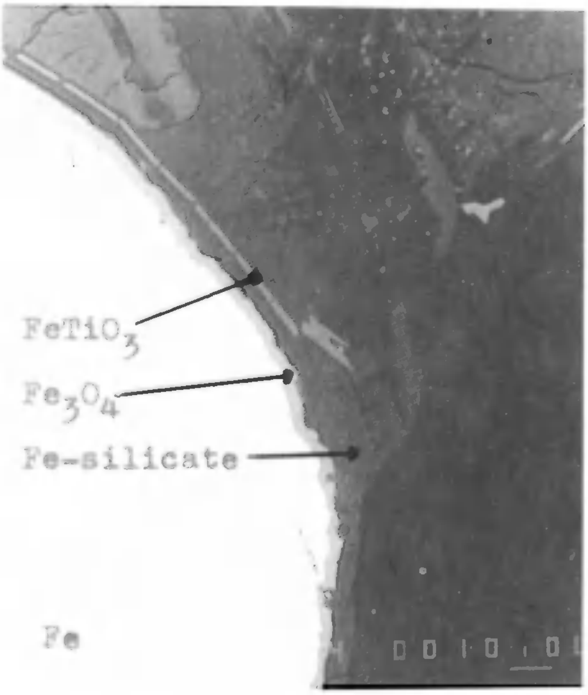

Fig.6: Metal–silicate interface within iron sponge (Bühl; backscattered electron image, scale bar, 0.01 mm).

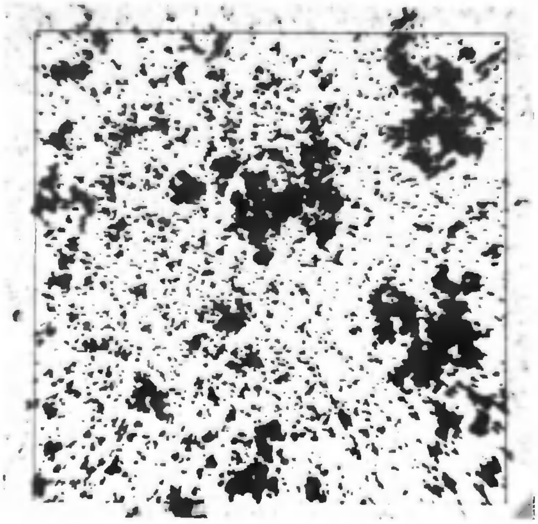

Fig.7: Spatial distribution of porosity in basalt (Bühl; binary image indicating areas above about 2% porosity by vol.; scale: frame, 20 mm).

The two different samples from the Hammers Dal complex, Disko (Greenland) were more complicated to assess. In one (GGU 175958) from an outcrop of a dike-like intrusion iron was completely corroded to a depth of a few millimetres. At greater depths from the exposed surface surficial corrosion of a part of the inclusions was observed, fissures were filled with corrosion products (Fig.8). The rusty weathering crusts containing magnetite and goethite seem to be the result of weak hydrothermal alteration and over-printing by weathering. The basalt is still rather fresh, and sulphides are preserved in the crusts.

In the other sample (GGU 175926) from the outcrop of a sill iron was pervasively oxidized, but sulphides were preserved. The corrosion products (magnetite and amorphous phases) contained also silica. Preliminary impregnation experiments using a carbon-14-labeled polymer showed a very high porosity in the corrosion products (Fig.9), but diffusivities seem to be low. The basalt showed halos around altered inclusions. These features are ascribed to hydrothermal influences originating from a nearby fault. Because of the limitations of experimental data and information concerning the hydrothermal event no further conclusions can be drawn.

The retardation of trace elements in iron corrosion products was not studied, because they were not detectable with the methods available, and, on the other hand, the traces in the metal phase origin from extraction from the silicate phase and, consequently, are more or less siderophile. Except for rhenium (as a chemical analogue for technetium) which, however, is in the ppb-range, there are no good waste nuclide analogues.

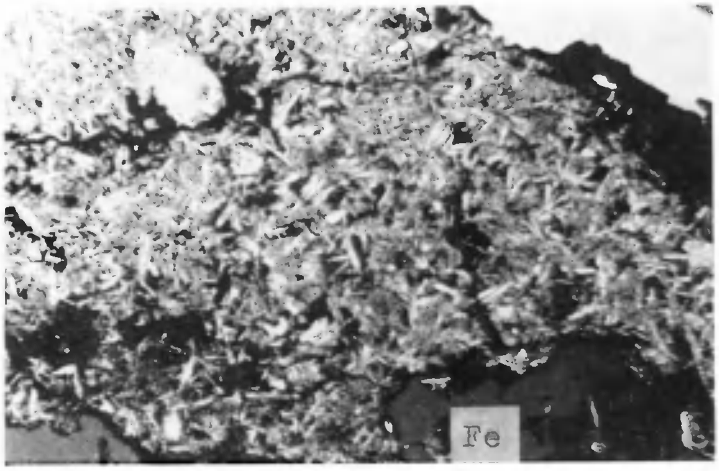

Fig.8: Native iron-bearing basalt with corrosion product-filled fissures (Disko; width of section 7.5 mm; outcrop surface above, right.

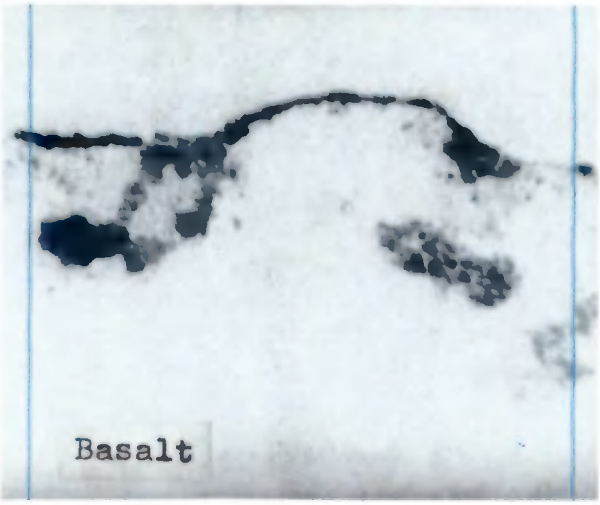

Fig.9: Spatial porosity distribution in sample of basalt with corroded native iron from an outcrop (Disko; autoradiograph; scale: frame, 30 mm). The porous rim on top of the specimen consists of corrosion products.

5. Discussion

Already the short survey of existing knowledge on native iron given above provides safety-relevant insights into and understanding of natural phenomena and processes. The experimental work presented gives additional answers and indicates possibilities for further investigations. Of particular interest in that respect would be investigations on the influence of the nature of corrosion products and the presence of sulphides and other impurities on corrosion rates at outcrops of Disko iron. Sampling and assessment of the local conditions, a major drawback of the site, should be conducted by the investigators. The preservation of iron in compacted tuffs near hydrothermally altered formations in western Greenland might be interesting for the Yucca Mountain disposal concept. The advancement of redox fronts in various matrices is another issue to be studied further. A safety-relevant issue is the question to what degree Fe(II) in minerals participates in redox reactions.

A fruitful by-product of this work was the development of the carbon-14-polymethylmethacrylate impregnation method (5) originally designed to measure properties relevant for the assessment of transport of reactants through corrosion/alteration products filling tortuous, narrow pathways. The method gives quantitative information on local porosities. Work to make diffusion profiles visible and calculate diffusivities in geometrically complicated pathways is going on.

Native iron in ultrabasic rock is a very sensitive indicator of reducing pore water conditions and redox front movement. However, because of the very fine-grained distribution it is not a practical tracer in most cases. The stabilization of metallic iron in fractured, water-saturated rock is the safety-relevant key issue. Unfortunately, ultramafic intrusions in old shield areas are, mostly, completely serpentinized, i.e. no fresh olivine is left to buffer the redox conditions at very low values. A rare exception is the Lovasjärvi intrusion in southeastern Finland. The rock is nearly unweathered and contains about 70% olivine. The fayalite content in olivine is about 50 mol%. Taking into account also magnetite, total FeO contents up to 40% (average: 28%) are achieved. Under low-flow conditions predicted in a repository in granitic rock in Finland the redox capacity of an olivine backfill of a couple of metres would last for geological periods of time. This issue needs further investigation. As a first approach an analogue study of the behaviour of high-FeO olivine rock in contact with surface and groundwater in nature on a geological time-scale has been conducted (6).

References

1. Apted MJ, Natural analogues for the predictive reliability of the engineered barrier system for high-level waste. In: Come B, Chapman NA, (edit.) Fourth Natural Analogue Working Group Meeting, CEC Report No. EUR 13014 EN, Luxemburg, (1990).

2. Hellmuth KH, The existence of native iron – implications for nuclear waste management, part I: Evidence from existing knowledge. Finnish Centre for Radiation and Nuclear Safety, Report STUK-B-VALO 67, Helsinki (1991) 41 p.

3. Apps JA, Cook GW, Backfill barriers: The use of engineered barriers based on geologic materials to assure isolation of radioactive wastes in a repository. Proc. MRS Symposium, Scientific Basis for Nuclear Waste Management III, (1980) 291-298.

4. Hellmuth KH, The existence of native iron – implications for nuclear waste management, part II: Evidence from investigation of samples of native iron. Finnish Centre for Radiation and Nuclear Safety, Report STUK-B-VALO 68, Helsinki (1991) 71 p.

5. Hellmuth KH, Siitari-Kauppi M, Lindberg A, Study of porosity and migration pathways in crystalline rock by impregnation with carbon-14-polymethyl-methacrylate. J. of Contaminant Hydrology (1992) (in print).

6. Hellmuth KH, High-FeO olivine rock, a potential redox-active backfill working in a nature-analogue way. 5th CEC Natural Analogue Working Group Meeting, Toledo (1992), (to be publ.).

HIGH-FeO OLIVINE ROCK, A POTENTIAL REDOX-ACTIVE BACKFILL WORKING IN A NATURE-ANALOGUE WAY

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Summary

The long-term behaviour of a high-FeO olivine rock proposed as a high-capacity, highly reactive redox buffer backfill in nuclear waste repositories has been studied in nature at the Lovasjärvi intrusion, south-eastern Finland.

Investigation of weathered rock at outcrops and alterated rock along fractures and fissures at various depths led to the conclusion that the olivine rock, in principle, is highly reactive on a geological time scale, although the intrusion as a whole, for reasons not yet studied, is surprisingly well preserved. The huge redox capacity of the very dense rock seems to be available at the outcrop as well as along fractures where the matrix porosity is increased. The redox conditions within the body are mostly reducing as can be concluded from the nature of fissure fillings. Unfortunately groundwater of the Lovasjärvi intrusion was not accessible.

1. Introduction

Intrusion of oxidizing and acid meteoric water is a threat to the safety of repositories for high-level radioactive waste in geological formations, making predictions of waste canister corrosion, waste form dissolution and waste nuclide migration uncertain. In fractured, crystalline rock the redox buffer capacity of the rock mass available for interaction with surface water is the key parameter which determines groundwater properties. There is no database available on these rock properties on which predictions needed in safety assessments could be based.

In Finland as well as in comparable old shield regions the total, theoretical redox buffer capacity of the dominating (about 90% of the area of Finland) acid, silica-rich rocks, as inferred from bulk FeO contents, is rather poor. The FeO content of rock in Finland is only slightly above 3%, on the average.

The process of low-temperature serpentinization of ultramafic rocks, marked by alteration of primary olivine and pyroxene to chrysotile and brucite leads to unusual, very reducing groundwater conditions under which even metallic iron is often stable (1). However, olivine not only controls the redox potential, but also the carbonate and sulphide content as well as the pH, which are relevant parameters influencing container corrosion, waste matrix dissolution and radionuclide migration in a nuclear waste repository:

detrimental groundwater component	reacts with olivine component
O_2	Fe(II)
S^{2-}	Fe(II)
CO_2	Mg^{2+}
H^+	Mg_2SiO_4.

Suitable, unweathered, high–FeO rocks are rare in Finland. Generally, ultramafic rocks are ore–critical, have a high Mg/Fe ratio, or are completely altered to serpentine or other products. Often, they occur as intrusions the lateral extension of which is in the order of magnitude of a few metres to tens of metres. An exception is the Lovasjärvi intrusion in south–eastern Finland (2,3). Crushed material from the Lovasjärvi intrusion contains on the average 28% FeO and would provide a powerful redox–active backfill in the near–field and in shafts and tunnels in repositories for nuclear waste working in a nature–analogue way (1). If reaction rates are known tailored backfills could be made by variation of grain size and addition of bentonite. The predictability of such a system could be based on laboratory and modelling efforts in combination with a natural analogue study.

A natural analogue study on the long–term behaviour of high–FeO olivine rock in nature should include:
- pre–glacial and post–glacial surficial weathering processes,
- alteration at greater depth along fractures and fissures,
- characterization of groundwaters,
- modelling of water–rock interaction
- geohydrological investigations.

The present work focusses on surficial weathering and fissure filling minerals. Unfortunately deep groundwater in the Lovasjärvi intrusion was not accessible. A report containing more details is in preparation (4).

2. Geological setting

The Lovasjärvi intrusion near Mäntyharju, south–eastern Finland, situated at the margin of the Viborg rapakivi massiv, contains in its north–western part a plagioclase–olivine body (in the following called olivine rock) with dimensions of about 1500 x 400 m. According to radiometric age determinations (1643 Ma) it is older than the rapakivi intrusion (3). A cross–section is shown in Fig.1. The most probable groundwater flow patterns as inferred from the local topography are indicated. Regional gradients are estimated to be low due to the generally low relief of the region. Only at the central, small hill outcrops are found. Even there the body is partly covered with a thin, conspicuously red–brown weathering crust and glacial till.

The olivine rock consists of olivine (about 65%) with a high fayalite content (39–58 mol%), plagioclase (about 20%), opaques (mainly magnetite; about 8%) and others (including serpentine) (2). The average serpentine content is below 3% which indicates the very low degree of serpentinization of the intrusion. The total FeO content is, on the average, about 28%; the maximum is about 42%. The nickel and sulphide values are very low. In Fig.2 a thin section shows the structure of the fresh olivine rock. A dense network of mm–sized fissures probably originating from the cooling of the body and successive intrusional phases is filled with serpentine to about 90%.

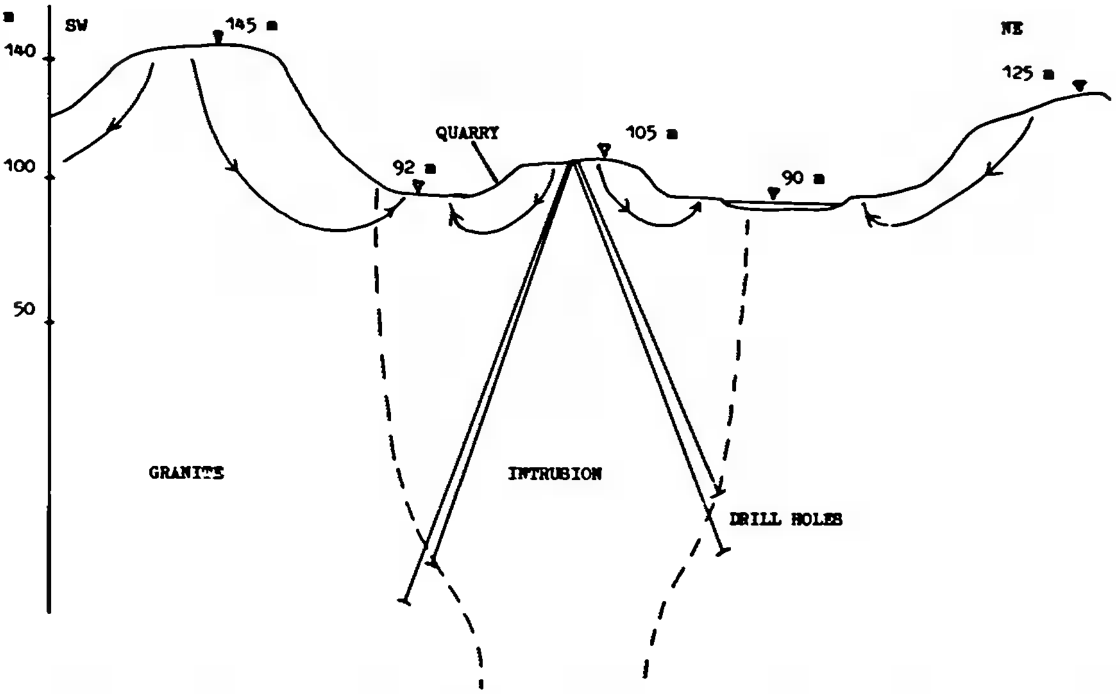

Fig.1: Cross-section through the Lovasjärvi intrusion (2) showing the probable hydrological situation as inferred from the topography. The approximate location of the drill holes is indicated. The horizontal scale is about 1200 m.

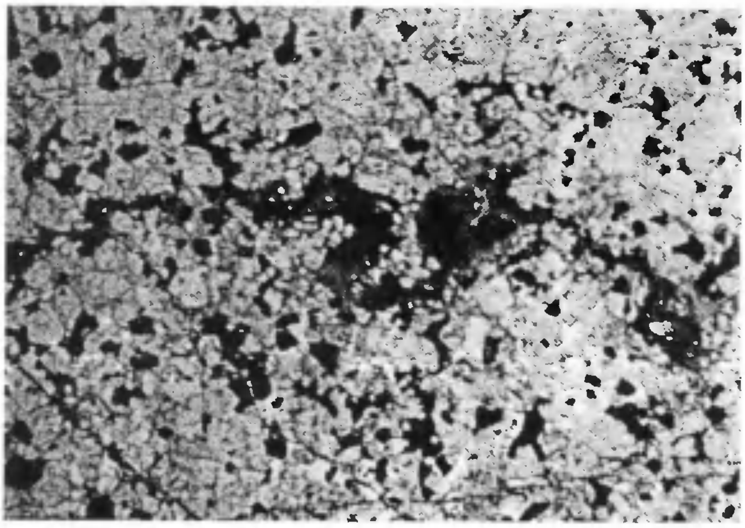

Fig.2: Thin section of fresh to slightly altered olivine rock from the quarry showing the structure of the material (olivine: colourless, primary magnetite: opaque, serpentinized zone: middle, from left to right). Scale: width, 15 mm.

Six low-angle drill holes were drilled during the year 1976 for prospecting purposes (Fig.1). They were between 200 and 265 m long, but the vertical depths reached only down to about 90–140 m below the present ground level. The holes are now blocked in their upper part.

3. Samples and methods

Olivine rock disintegrated by natural processes and weathered as well as boulders from the till were sampled at the central hill and the quarry. Fissure fillings were sampled from the drilled cores 301 to 306.

Thin sections were examined microscopically. Crushed samples were analyzed for their Fe(II)/Fe(III) ratio chemically. A limited number of fissure fillings was studied by X-ray diffraction (XRD) and microprobe. Sampling and analyses were focussed on minerals able to give most information with respect to present-day water-rock interaction and weathering: calcite, clay minerals, sulphides and oxidized Fe(II)-minerals. Calcite from open and closed fissures was analyzed for stable carbon and oxygen isotopes to allow indirect conclusions on the extend of surface water influences in the intrusion.

4. Results and discussion

Intensively coloured, red-brown remains of weathering products in pockets on top of the present erosion level of the intrusion seem to originate from warmer, pre-glacial periods of intensive weathering. Conspicuous zones of intense disintegration of about 1 m thickness, too, indicate intensive weathering, but the dominating green colour of the bulk material and the low Fe_2O_3 content imply that only a small fraction of the high redox capacity of the olivine rock is used up. Only along the visible margins of former blocks brown colour dominates, but the phenomenon is of a more surficial nature, the degree of oxidation is still low (Table 1). No Fe(III)-minerals were detected by XRD. In the till cover pervasively weathered samples were found. Weathering proceeds along microfissures in the olivines resulting in Fe(III) minerals (Fig.3). The network of porous structures could be visualized (Fig.4) and measured by impregnation with a radioactive tracer (5). Fresh olivine rock has a porosity below about 0.2% (by vol.) while in the slightly weathered sample a porosity of 0.5% was measured. The Fe(III) analyses, however, still show a low degree of oxidation (Table 1). Serpentine seems to weather easily due to its porous structure (Table 1). Locally, along fractures high-temperature serpentinization is pervasive which is illustrated by the porosity distribution (porosity above about 1%; core 301/153.3 m; Fig.5).

Surficially weathered boulders were observed in the quarry not deeper than a few metres below ground level. Oxidation has caused visible traces only in nearly vertical, conducting fractures. Intensively altered, soft, green fracture filling material at a greater depth (core 301/153.3 m) showed little oxidation, only clay minerals were identified (Table 1).

Without further investigation it is not possible to estimate the time-scales of the different weathering and alteration processes that resulted in the features observable now at the outcrop. It is likely that most of the products were formed under pre-glacial, warmer conditions, but were mostly removed during subsequent glacial periods. Boulders of fresh material, exposed by glacial activity seem to exhibit, generally, only very thin, yellow-brown weathering rinds. Compared with nearby granitic rocks the olivine rock can be

Table 1: Fe(II) and Fe(III) contents and minerals identified by XRD in weathered material from the Lovasjärvi intrusion.

	FeO (%)	Fe_2O_3 (%)	minerals
Weathering profile, outcrop, green coloured	29.9	6.82	olivine
Weathering profile, outcrop, brown coloured	29.4	7.31	olivine, smectite
Boulder from till cover, fresh	31.9	4.60	
Boulder from till cover, weathered	24.0	13.4	
Boulder from till cover, serpentine	17.5	17.7	
Drill hole 301/153.3 m, altered, green coloured	18.2	8.36	kaolinite, smectite, hornblende

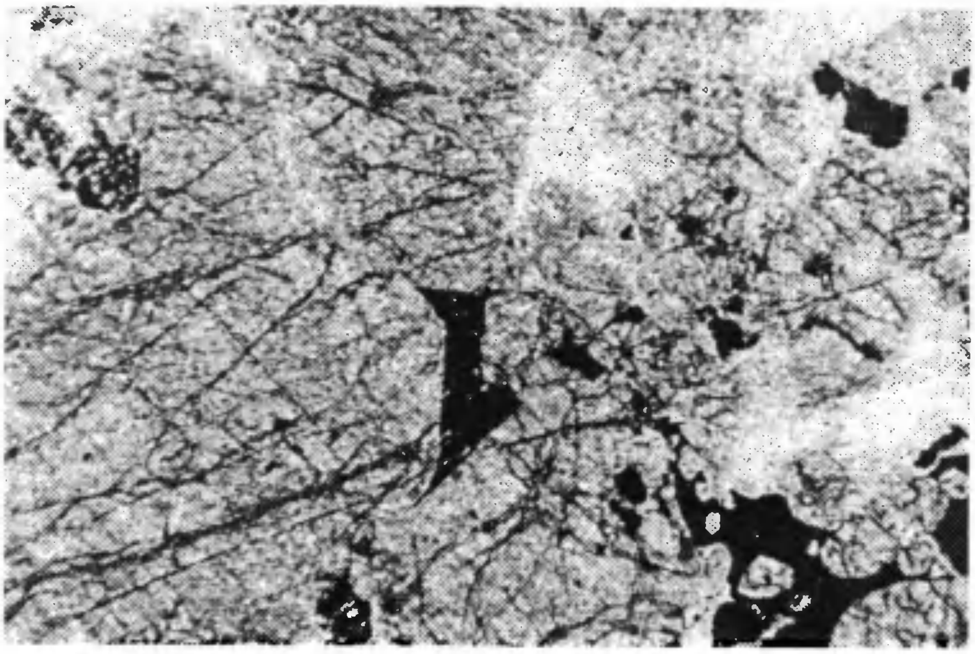

Fig.3: Thin section of weathered olivine rock from the till cover of the Lovasjärvi intrusion (scale: width, 1.8 mm).

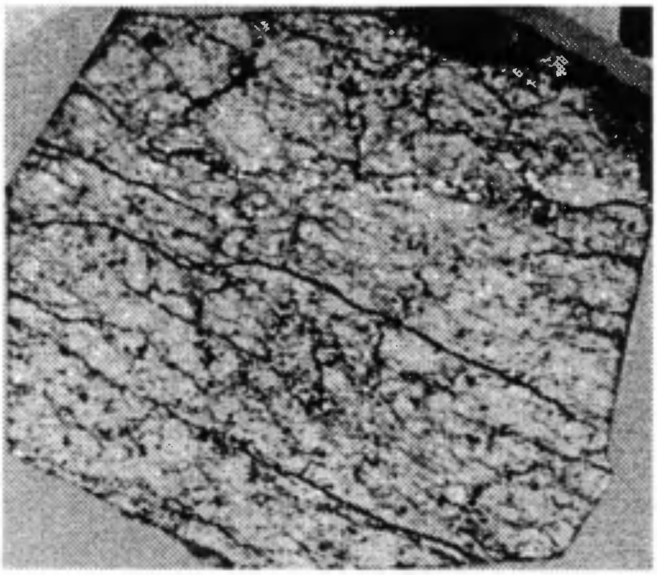

Fig.4: Autoradiograph of olivine rock from an outcrop of the Lovasjärvi intrusion impregnated with radioactive tracer making the areal distribution of open pore space visible (surface exposed to weathering: above, right). Scale: width of sample, 4 cm.

characterized as a highly reactive material on a geological time scale. Although the fresh rock matrix is dense and intact, the redox capacity of the rock is accessable as weathering proceeds along the grain boundaries and into the olivines along microcracks and zones of weakness resulting in a typical network structure.

Fissure filling minerals giving information on the extent of surface water influences on the olivine rock are summarized in Table 2. The amount of phases that might contain Fe(III) was in most cases to small to allow unambiguous characterization. Clay minerals are omitted from the table, because they could not always be distinguished from other alteration products by the methods available. A rough examination of all fissure fillings in the cores confirmed the conception that most of them originated from serpentinization processes at higher temperatures, probably, during cooling of the intrusion. Diffusion-controlled alteration fronts can often be observed. The different types of serpentine which would give information on the formation temperatures could not be distinguished with the methods available.

Minute amounts of pyrite occur along the whole length of some cores. Intergrowth and paragenesis indicate hydrothermal origin. Even at shallow depths fresh sulphide surfaces were observed in open fractures. Only in a few cases slight oxidation of pyrite was observed. These findings indicate that potentially present near-surface groundwaters are predominantly reducing.

Clay minerals were not common, although unambiguous determinations could not be made by microscopic methods alone. Clay minerals generally were not associated with Fe(III)-minerals.

Fe(III)-minerals were relatively rare compared with the number of serpentine fillings. As expected, the highest frequency was observed in the first tens of metres in the cores. Sporadic occurrences were found, mainly, at about 100 and 150 m core length. However, without knowledge of the fracture system and the hydrologic flow regime of the site interpretation remains speculative. In some cases at shallow as well as greater depth goethite was observed. Sometimes iron–oxihydroxide minerals suspected from visual inspection were not found analytically. Altogether, the oxidizing influence of surface waters can be observed only in rare cases and seems to be restricted to conducting fractures providing pathways directly from the surface or from the surrounding granitic rocks.

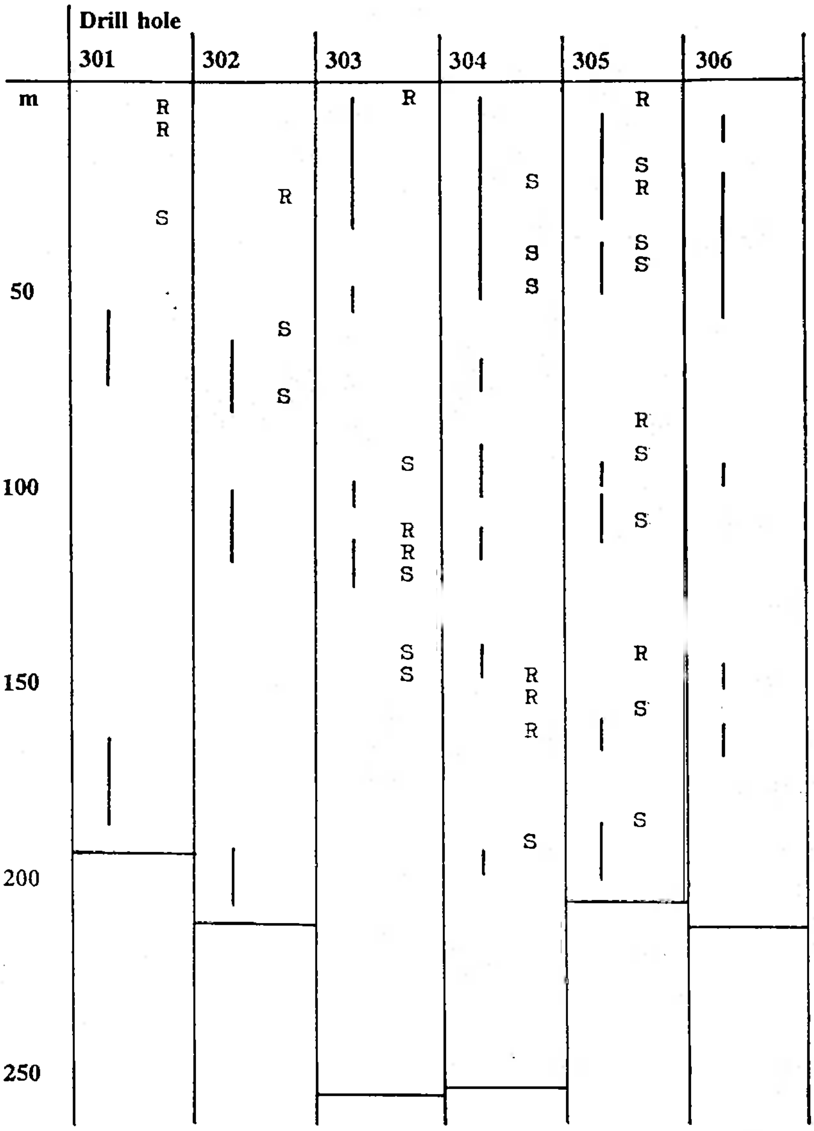

Table 2: Distribution of most conspicuous occurrences of calcite (vertical bars), sulphide (S) and iron–oxihydroxides (R, "rust") along the cores from the Lovasjärvi intrusion. The granite contact is indicated by horizontal lines.

Calcite usually dissolves at shallow depth when carbon dioxide–rich waters infiltrate, but here calcite occurs at shallow depth in open fractures. There might be precipitation of calcite when carbon dioxide comes into contact with high–pH waters originating from present–day serpentinization. In some cases intergrowth of calcite with secondary magnetite was observed, indicating a connection with serpentinization processes. The stable isotopes study did not identify high–temperature, post–magmatic/hydrothermal calcites. The isotope values are given in Table 3 and Fig.6. The alternative interpretation is that

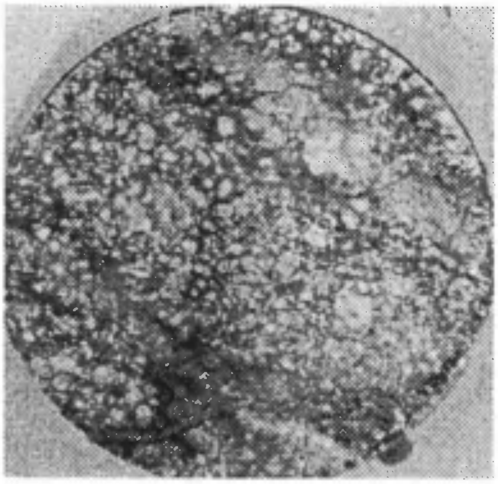

Fig.5: Autoradiograph of olivine rock from a pervasively serpentinized zone of the Lovasjärvi intrusion in core 304/143.5 m impregnated with radioactive tracer making the areal distribution of open pore space visible. Scale: diameter of sample, 32 mm.

Sample:	$\delta^{13}C_{PDB}$ (o/oo)	$\delta^{18}O_{PDB}$ (o/oo)
301: 64.5 A o	-13.7	-12.2
301: 64.5 B s	-12.1	-12.3
302:114.7 o \\	- 0.5	-14.4
302:207.2 o \\	-11.3	-10.7
302:211.5 o \\	-14.0	- 6.3
303: 6.75A o	-10.7	-12.1
303: 6.75B s	- 9.7	-13.0
303: 55.2 o xx	-16.1	- 6.3
304: 44.85A o	-15.4	-12.5
304: 44.85B s	-15.2	-12.5
304:102.8 s	-13.4	-11.3
304:205.0 o \\	-15.1	- 9.7
305: 18.0 o	-15.0	- 7.9
305: 46.5 A o xx	-15.3	-12.9
305: 46.5 B s	-15.3	-11.0
305:111.53 o xx	- 7.8	- 9.7
305:153.55 o \\	-14.2	- 7.6
305:174.95 o?\\	-17.8	-10.3
305:195.95 o?\\	-17.5	- 9.8
306: 16.0 o?	-15.0	-12.0
306: 32.3 o xx	-13.6	-11.7
306: 51.7 o xx	-15.9	-10.4

o = calcite from originally open fracture
s = calcite from sealed fracture
A,B = different generations of calcite within a single fracture (A is the younger and B is the older)
\\ = slickenside surface
xx = calcite crystals of idiomorphic shape.

Table 3: Stable carbon and oxygen isotope values in fracture filling calcites from the Lovasjärvi intrusion.

the calcites re-equilibrated subsequently at lower temperature. The plot of the carbon against the oxygen values shows that several generations of calcites are present. Most samples within the core interval 0–70 m (less than 50 m vertical depth) show a clear influence of groundwater with the same isotopic composition as expected in the local precipitation, but exceptions occur. Near the contact of the olivine rock with granite calcites differ in composition from those in contact with surface waters. Either surface water does not reach these fractures or they are sealed which is a common phenomenon in ultrabasic rocks. Further conclusions would need a present-day groundwater data base.

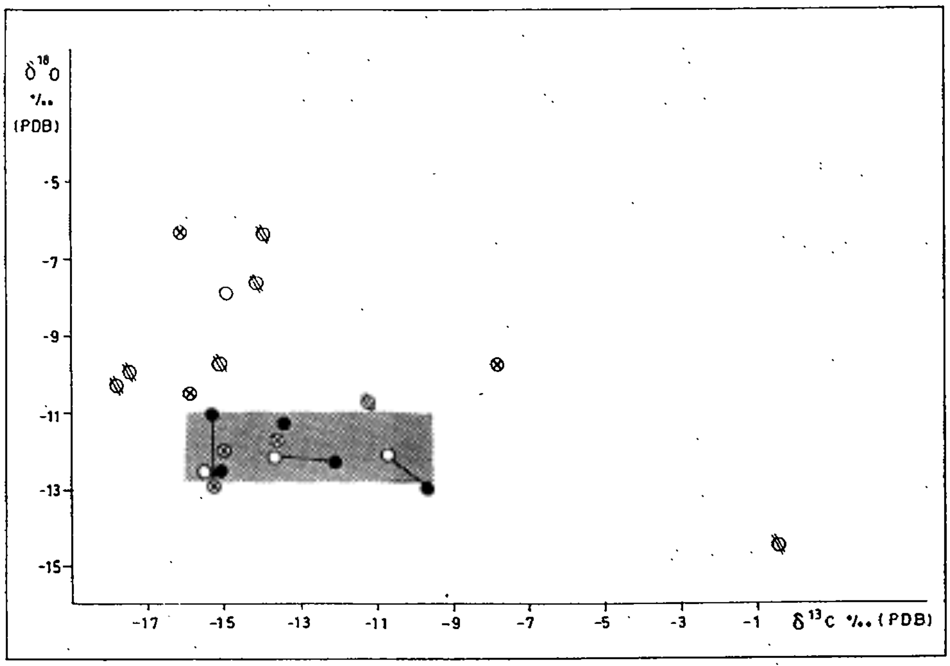

Fig.6: $\delta^{13}C/\delta^{18}O$–diagram for fracture filling calcites from the Lovasjärvi intrusion.
○ = calcite from open fracture
● = calcite from sealed fracture
⦸ = calcite from slicken side surface, open fracture
⊗ = calcite crystals of idiomorphic shape, open fracture
Ruled area represents interval of calcite precipitated from a water of $\delta^{18}O \approx -14\%$ (SMOW), assuming a temperature between 5 and 10°C and using a fractionation factor according to Craig (1965).

5. Conclusions

From the observations at the outcrop and the fissure fillings of the Lovasjärvi high–FeO olivine rock mass it can be concluded that the rock, despite of its mechanical firmness and low porosity, is highly reactive on a geological time scale towards oxidizing surface waters. Surface waters penetrate the rock body, at least locally, and become reducing. The huge redox capacity of the rock seems to be accessible and has been used up so far only in very thin surface layers at the outcrop. The reaction front proceeds along grain boundaries and zones of weakness within the olivine. The mechanisms and kinetics of the reactions have to be investigated further on the laboratory scale. Preliminary experiments show that the Lovasjärvi olivine rock is highly reactive on the laboratory time scale at only moderately increased temperatures. Further investigations including the reaction of olivine with redox-sensitive radionuclides are under way.

A comprehensive treatment of the water-rock interactions relevant to a quasi-natural analogue judgement of the long-term behaviour of this high-FeO rock would require extensive, further information on the local geohydrology, isotope geochemistry and groundwater chemistry. Such an approach should also include an assessment of the role of the geological evolution and the present-day geohydrology for the amazingly low degree of serpentinization of the intrusion.

Crushed, unweathered, high-FeO olivine rock is an ideal chemical buffer providing in many respects favourable groundwater conditions in high-level waste repositories in deep geological formations. As it reacts with water with certainty there is little possibility of failure of this robust nature-analogue barrier.

References

Hellmuth, K-H. The existence of native iron – implications for nuclear waste management. Part II: Evidence from investigations of samples of native iron. Report STUK-B-VALO 68, Finnish Centre for Radiation and Nuclear Safety, Helsinki, 1991, 71 p.

2. Alviola, R. Investigation report on the industrial mineral investigations concerning the Mäntyharju Lovasjärvi intrusion. Report M 19/3132/-81/80, Geological Survey of Finland, Espoo, 1981, 91 p. (in Finnish).

3. Siivola, J. The mafic intrusion of Lovasjärvi. Report of investigation 76, Geological Survey of Finland, Espoo, 1987, p. 121-128 (in Finnish).

4. Hellmuth, K-H., Lindberg, A., Tullborg, E-L. Water-rock interaction in a high-FeO olivine rock in nature. Report STUK-YTO-TR, Finnish Centre for Radiation and Nuclear Safety, Helsinki, 1992, (in preparation)

5. Hellmuth, K-H., Siitari-Kauppi, M., Lindberg, A. Study of porosity and migration pathways in crystalline rock by impregnation with carbon-14-polymethylmethacrylate. J. of Contaminant Hydrology (1992), (in print).

MICROFRACTOGRAPHY OF "EL BERROCAL" GRANITE

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ABSTRACT

Digital image processing and manual stereological methods have been used for the quantification of the most significant petrographic parameters in rock matrix diffusion (mineral volumetric percentage, specific surface of mineral grains, affinity index, fractal dimension of mineral boundaries and fissures, etc.) of "El Berrocal" granite. These methods have been applied on images obtained from the same zone of the rock under different techniques of microscopy (transmitted polarized light, fluorescence, scanning electron and confocal laser scanning).

1. Rationale

Radionuclides migrating in solution along hydrogeologically active fractures, in crystalline rocks, show a retardation mechanism induced by the rock matrix. That retardation mechanism has been observed to a depth of about 2 to 12 cm into the rock matrix from the fracture. The microfractography and mineralogy of the rock matrix play a decisive role, mainly the water-conducting microcracks traversing micas and altered feldspars.

To estimate the potential capacity of such retardation mechanism, in a given rock mass, those petrographic components have to be evaluated. Also for transport models.

2. Procedure

Oriented cores have been drilled in the "El Berrocal" mine gallery (Toledo, Spain). From them, oriented thin sections have been made following a non-standard procedure, both to avoid artefacts (as new cracks) and for applying very different microscopic techniques to the same area of the specimen (Fig. 1).

The different images, so obtained are studied under digital image processing and manual stereological methods, for the quantification of: Mineral volumetric percentage; Specific surface of mineral grains; Affinity index (minerals); Fractal dimension of mineral boundaries; Specific surface of intra-, inter- and transgranular fissures; Fractal dimension of fissures; and Fissure orientation. First results from both methods are here presented.

The real 3D microfractographic network can be observed under confocal-laser scanning microscopy, CLSM; strike and dip of fissures can also be measured.

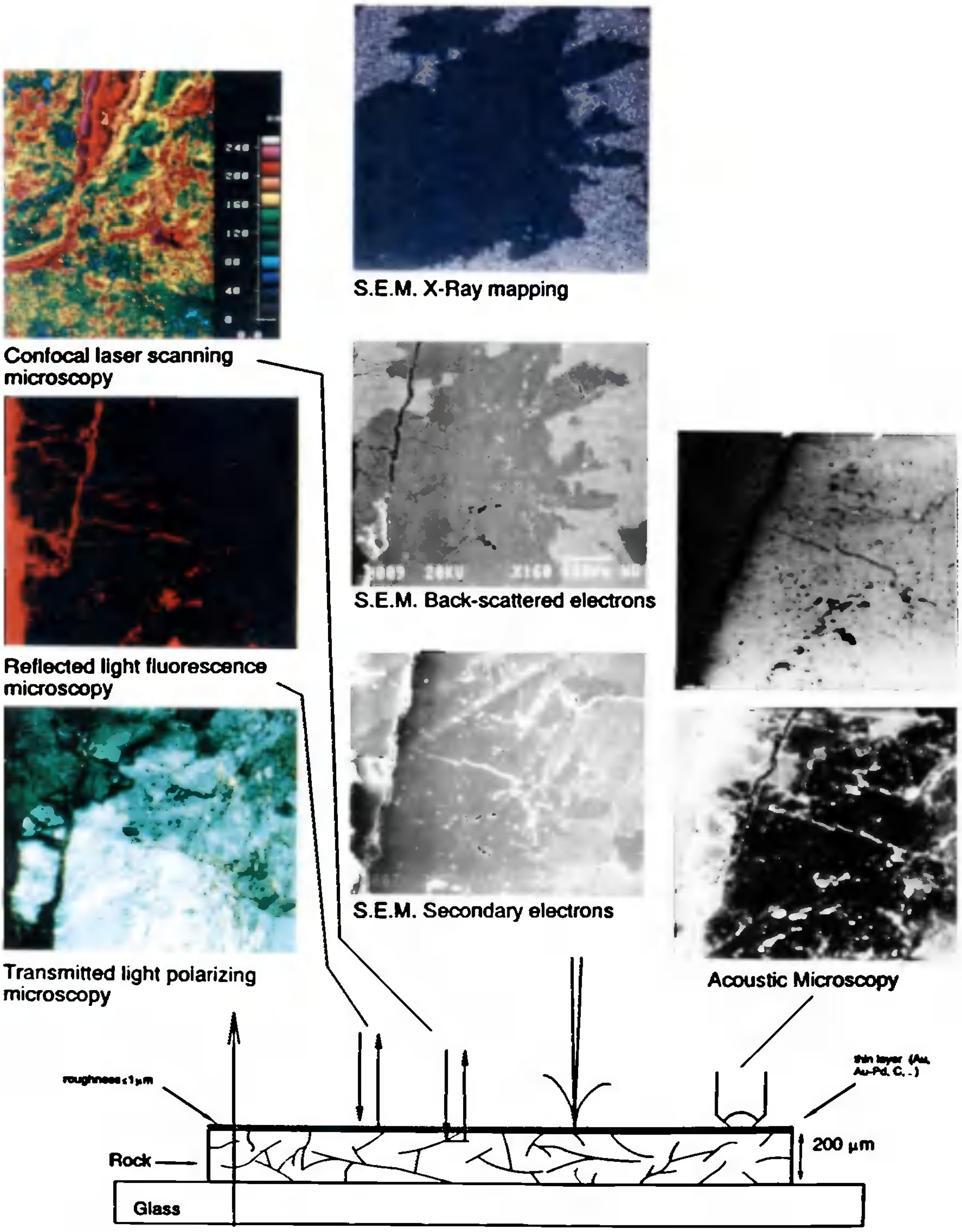

Fig. 1.- Different microscopy techniques applied to the same zone of the rock thin ("thick") section.

3. Petrography

3.1 Mineral grain quantification.

From the mosaic in Fig. 2 (obtained under polarized-light microscopy) an image of grain boundaries is interactively obtained and then digitalized; later a binary image is obtained and a thinning process is performed. Therefore, the mineral phases can be classified as well as the grain boundaries according to the minerals in contact (Fig. 3).

Fig. 2.- Micrograph mosaic of the rock texture under optical microscopy, polarized-light, crossed nicols.

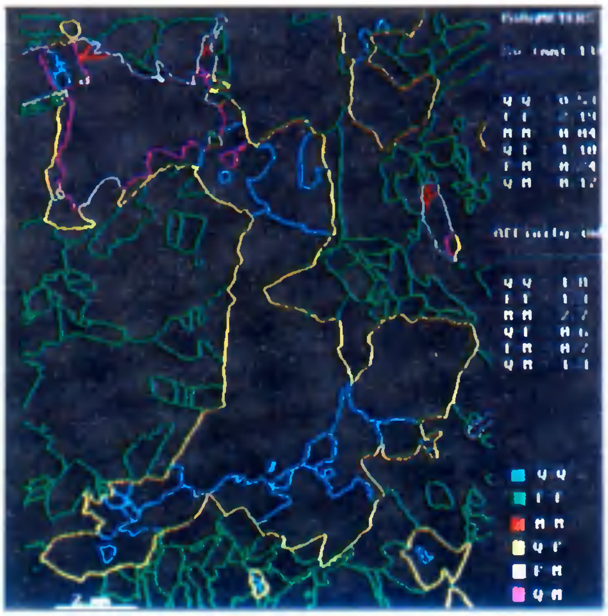

Fig. 3.- Classified image of the grain boundaries. Data for specific surface (referred to each type of mineral boundaries) and affinity index are obtained under digital image analysis.

- **Mineral volumetric percentage** (Vv) for each rock-forming mineral:

$$est(V_v)=\frac{\sum pixels(mineralphase)}{\sum pixels(totals)}$$

- **Specific surface of mineral grains** is obtained from the image of the boundaries between grains of the same phase and of different phases (data in Fig. 3).

$$est(S_v)=\left(\frac{4}{\pi}\right)\times\frac{\sum lenght\ grain\ boundaries}{\sum area\ (total)}$$

- **Affinity index**, (data in Fig. 3), from the results of Sv between mineral boundaries, is evaluated according to:

$$\theta_{AB}=\frac{Specific\ surface\ (AB)}{Expected\ specific\ surface\ (AB)\ under\ isotropic\ distribution}$$

- **Fractal dimension of mineral boundaries (D).** It is calculated by measuring the boundary length with different length units. For feldspar, a plot of total length versus length units is drawn in Fig. 4 (pixel size is 10 μm square).

- **Specific surface of the intergranular fissures** (4.41 mm^{-1}) has been obtained (by digital image analysis), it is classified according to the mineral grains in contact. The obtained data for El Berrocal granite (in mm^{-1}) are: Q-Q: 0.02; Q-F: 0.91; Q-M: 0.15; F-F: 2.02; F-M: 0.15; and M-M 0.02.

- **Specific surface of the intragranular fissures** (3.80 mm^{-1}) is classified according to the enclosing mineral: Quartz, 0.68; Feldspars, 3.63; Micas, 0.10 mm^{-1}.

- **Fissure orientation.** It is calculated, by image analysis, from the table of coordinates of its middle line approximated by a sequence of polygonal lines. The coordinates of the polygonal lines are used to calculate the histogram orientation of the fissures network.

- **Fractal dimension of fissures, (D)** is obtained in a similar way as mineral boundaries (Fig. 6).

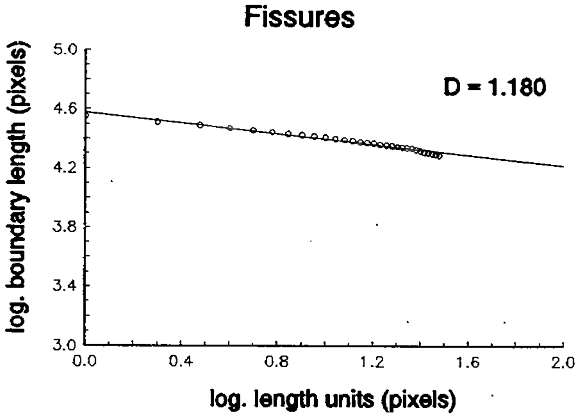

Fig. 6.- Fractal dimension of fissures.

4. Confocal Laser Scanning Microscopy

The confocal laser scanning microscope, CLSM, allows the real 3D reconstruction of the rock microfractography and to obtain quantitative information. Series of sectional images ("virtual sections") can be obtained from the rock-thin ("thick") section. The sections can be as close as 0.5 μm apart (Fig. 7).

This is an unique procedure for observing fine details of rock fissures (connectivity, tortuosity, etc.) and the whole geometry of the fractographic network. Accordingly, the potential water paths through the rock matrix can be more realistically interpreted.

Finally, the 3D relationship between the open fissures, potentially water-conducting, and the rock-forming minerals may provide more appropriate data for a better interpretation of the retardation mechanism.

The integration of data of fractures of "El Berrocal", from satellite, field geology and CLSM is planned.

The fractal dimension of the boundary is obtained from D=1-m (m is the slope of the linear portion of the plot). D values for quartz and mica are 1.075 and 1.080 respectively.

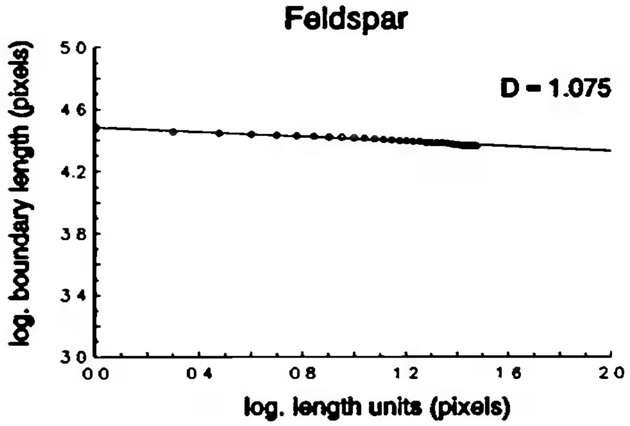

Fig. 4.- Fractal dimension of feldspar boundaries.

3.2 Fissures quantification.

Digital image analysis procedures are applied to the fissures image, obtained under fluorescence, reflected-light microscopy (Fig. 5).

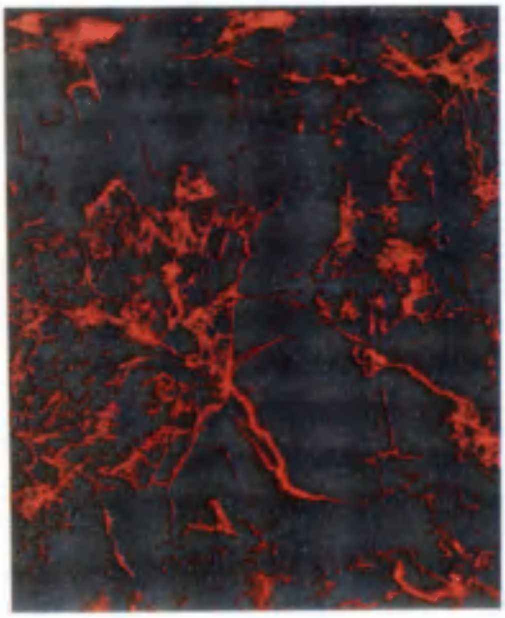

Fig. 5.- Micrography mosaic of the rock microfractography under fluorescence microscopy, reflected-light.

The fissure image and the classified texture image allow the elaboration of the fissure classification; first, fissures are classified according to their textural position: intergranular (between grains) or intragranular (inside grains).

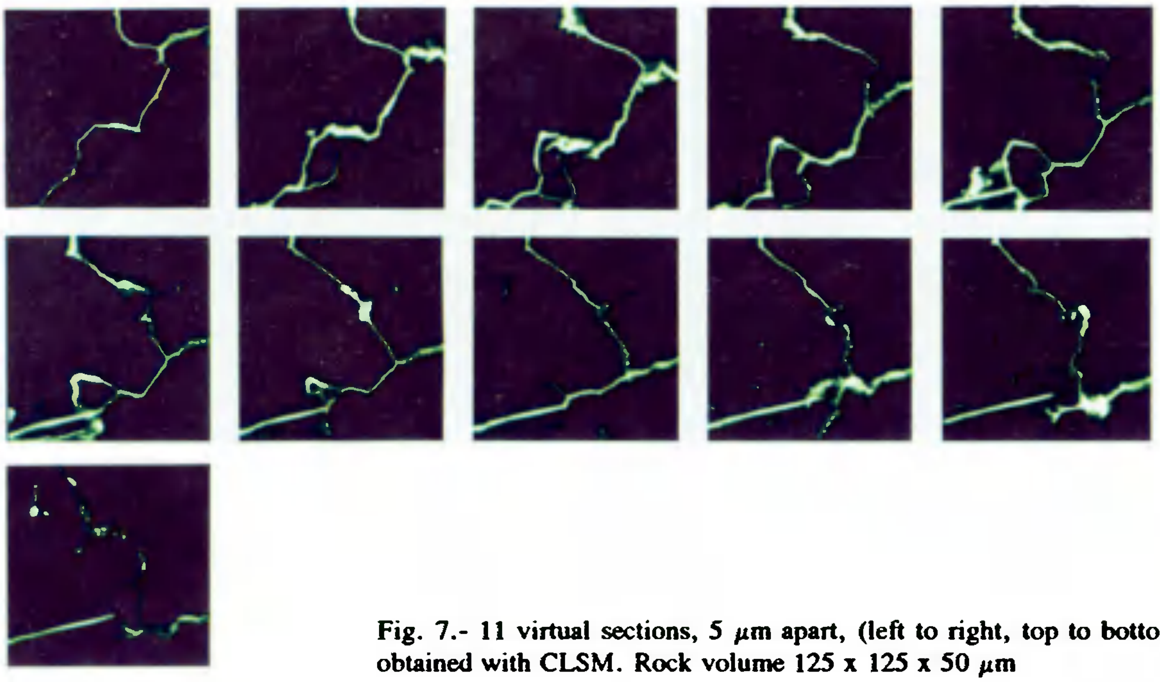

Fig. 7.- 11 virtual sections, 5 μm apart, (left to right, top to bottom) obtained with CLSM. Rock volume 125 x 125 x 50 μm

5. Petrographic data

The following petrographic parameters have been estimated by stereological procedures:

Sample		Vv (mineral percentage)			Sv (mineral specific surface) (mm^{-1})			θ_2 (mineral affinity)			Sv (fissures) (mm^{-1})		
		Q	F	M	Q	F	M	Q	F	M	Q	F	M
Core (loosen block)	Q	42 CE, 6.4%	50 CE, 3.8%	8 CE, 10.5%	3.27 CE, 7.6%	4.32 CE, 1.6%	1.04 CE, 7.7%	2,2	0,4	0,6	------------		
	F								1,7	0,9			
	M									3,2			
Core (loosen block)	Q	35 CE, 13.2%	57 CE, 7.2%	8 CE, 10.4%	2.74 CE, 15.0%	5.20 CE, 3.7%	0.88 CE, 12.7%	2,1	0,4	0,5	------------		
	F								1,5	1,0			
	M									3,0			
Core (loosen block)	Q	46 CE, 7.7%	46 CE, 10.0%	8 CE, 26.0%	4.21 CE, 10.0%	5.77 CE, 7.4%	0.65 CE, 20.3%	1,9	0,6	1,2	2,5	0,5	0,1
	F								1,4	1,5		3,8	0,1
	M									1,5			0,3
											CE, 3.7%		
Oriented cora (gallery)	Q	33 CE, 2.8%	59 CE, 1.8%	8 CE, 1.1%	3.87 CE, 9.7%	8.41 CE, 8.0%	0.94 CE, 9.4%	2,4	0,2	0,5	1.41	0.68	0.06
	F								1,8	0,8		6.36	0.15
	M									7,8			0.23
											CE, 5.5%		
S 16 38.34 m	Q	36	55	9	32,4	45,2	19,6	1,9	0,6	0,5	0.11		
	F								1,4	0,9			
	M									2,2			

CE, Coefficient of error

ELEMENT MOBILITY IN ROCK MATRIX AT PALMOTTU

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ABSTRACT

Rock specimens adjacent to two water conducting fractures at a depth of about 205 m from the Palmottu uranium deposit were studied in order to obtain information on element mobility. Concentration profiles for a number of elements were determined. Uranium series disequilibrium studies as well as petrographic studies and porosity determinations were also performed. Hardly any mobilization was observed for the lower fracture, but for the upper fracture several elements had been mobilized, while many remained immobile. Elemental concentration data analysis provided also for the alteration depth about 25 mm. The results indicate, that conditions have been reducing for long times.

1. Introduction

The Palmottu U-Th deposit is situated in south western Finland. It is characterized by highly deformed and metamorphosed migmatitic rocks, granitic gneisses, schists and metavolcanics. The geological framework of the Palmottu natural analogue study site and the groundwater conditions has been described in Suksi et al. 1992. The deposit contains some one million tons of ore with an average grade of 0.1 % uranium. The ore body is discontinuous over a total length of 400 metres, with a thickness varying from 1 to 15 metres. Uranium occurs mainly as uraninite (UO_2), which is a primary uranium mineral. In this work element mobility in crystalline rock around two open fractures at Palmottu was studied from element profiles. In addition to element analyses, petrographic studies, porosity measurements and uranium series disequilibrium measurements were performed.

2. Rock specimens

Rock specimens were obtained from drill hole 346, from which a complete section of core between depths of 205.328 m and 205.995 m was selected, see Fig.1. The section was situated between two water conducting fractures occurring a few metres away from uranium mineralization. At similar depths (140 - 212 m) groundwater is of slightly saline Na-Cl-SO_4-HCO_3-type (390-130-120-80 mg/l respectively) /Jaakkola et al.,1989/. Suutarinen et al.,1991 have measured characteristic values of Eh ≈ -300 mV (fracture water -70 mV) and pH ≈ 9 at a depth of approximately 200 m, indicating that conditions were reducing.

A series of specimens as a function of distance from the fracture were taken from the upper fracture at 205.328 m trending downwards and another series from the lower fracture at 205.995 m trending upwards. Petrographic and porosity studies as well as uranium isotope disequilibrium measurements were performed for the lower fracture series.

In all the thin sections examined, the major primary minerals were quartz, plagioclase, biotite and garnet. K-feldspar was an additional major component in the upper fracture series, as was garnet in the lower fracture series specimens. Zircon, apatite, and pyroxene (hypersthene) were present in minor amounts in the lower fracture series sections. Secondary minerals included sericite, chlorite, and carbonate (calcite), the latter usually representing alteration products of plagioclase and hypersthene, and to a minor degree, of biotite and garnet.

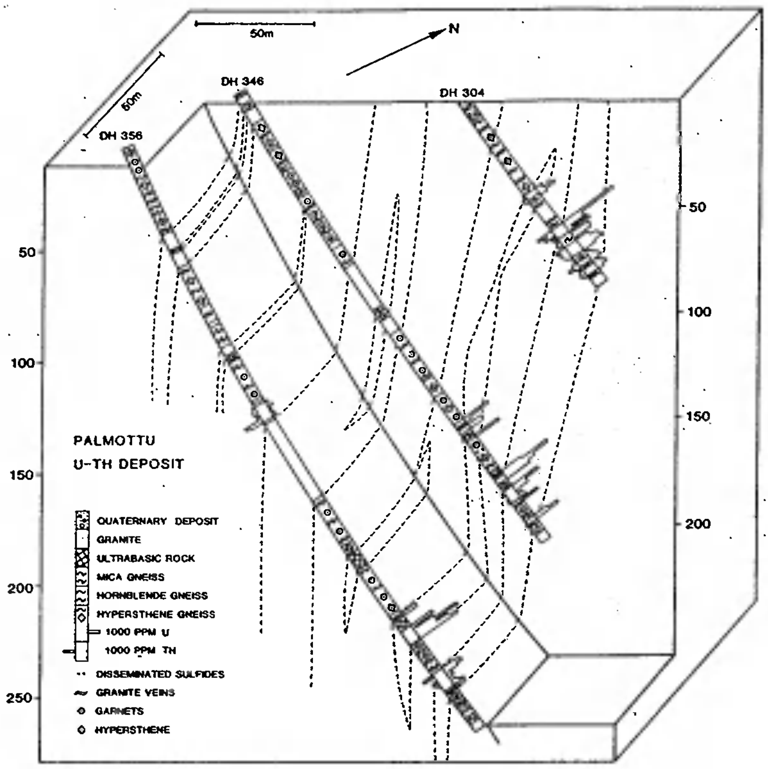

Figure 1. Lithology of the drill holes 356, 346 and 304 /Suutarinen et al.,1991/. The specimen were obtained from DH 346.

Complete alteration of hypersthene was only evident in thin section close to the fracture surface for the lower fracture series. This section also showed the highest overall total alteration and secondary crystallization (8 %). These observations correlated well with the porosity curve, which showed the highest value (0.38 %) for the part of the rock sample taken from the vicinity (3 mm) of the fracture surface, see Fig. 2. In the upper fracture series specimens the alteration of hypersthene was stronger adjacent to the fracture surface. The porosity values were low (≤ 0.1 %), for those specimens, which could be measured, but a couple of specimens were ruined during handling. No clear evidence for low temperature alteration of the specimens could be seen, which seems to be in accordance with the obtained low porosity values.

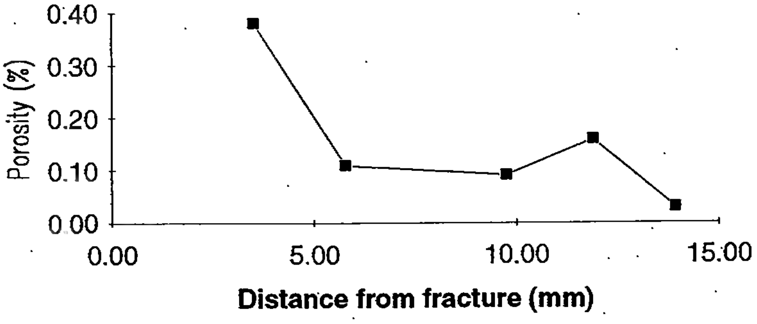

Figure 2. Porosity values as a function of distance from the fracture surface (lower fracture series).

3. Element profiles

The variations in chemical composition across each profile reflect the specimen mineralogy, the nature of each alteration process and the extent of element dissolution or accumulation. By using neutron activation analysis (NAA) and x-ray fluorescence analysis (XRF) a multitude of elements such as Fe, Sc, Br, Na, K, Rb, Cs, Ca, Ba, Al, Si, U, Th, Mn, Cu, Co, S, Au and Ti were determined. Furthermore the REE La, Ce, Nd, Sm, Eu, Tb, Yb and Lu were determined.

The concentrations were normalized against the concentraton of titanium, based on the assumption of geochemical immobility of titanium in most alteration processes /Kamineni,1986/. Fig.3 shows the curves for Ca and U. The growth at the fracture surface for the upper fracture series was strong, whereas for the lower fracture series changes have been very modest. For the upper fracture series, concentration increased 800 % for Na and some 200 percent for Ca, Al and U. For Si, Mn and Th the increases were around 70 %. The changes in the U and Th profiles near the fracture surface for the lower fracture series are very modest.

The variances of element concentrations were also dealt with principal component analysis using the computer program SIRIUS /Kvalheim et al.,1987/. Only the results for the upper fracture series are presented, since the treatment of the lower fracture series met with difficulties due to the nature of the data. Separate samples were classified according to the distance from the fracture. It was evident that the significance of the point (ie. the specimen) correlated directly with proximity to the water conducting fracture. Furthermore, the results also clearly showed that the effect of the fracture extended to a depth of about 25 mm. One could also refer to the work of Suksi et al.,1991 concerning the Palmottu investigation site where they found, on the basis of $^{234}U/^{238}U$ -activity ratio profiles, that the minimum extent of interconnected porosity was 25 - 30 mm.

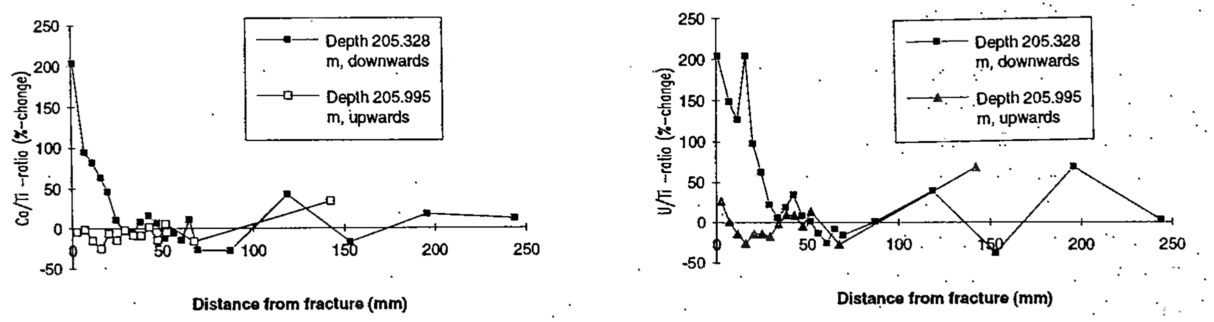

Figure 3. Titanium and "parent rock" normalized concentration profiles for selected elements.

The elements are classified in Fig.4. Elements situated furthest to the right of the origin (cross) have been most enriched due to the fracture surface. These are Na, Ca, U, Th, La, Sm, and Al. In contrast, elements located in the vicinity of Ti, the "immobile element", have not been dissolved, namely Au, Fe, Sc, Co, Cu and S. La, Sm and Th in particular are very similar in their behaviour, since in Fig.4 they are clustered together and their elemental profiles resemble one another. The elements Fe, Co and Sc as well as Rb and Cs also form similar groups.

The results are in quite good accordance with the fracture fillings and the results of interpretation of water-rock interaction at this depth. Ruskeeniemi et al.,1991 identified calcite, kaolinite, pyrite and illite as the main fracture minerals. Plagioclase dissolution and calcite and kaolinite precipitation with simultaneous release of sodium into groundwater have been interpreted as the dominant processes affecting groundwater composition at this depth /Pitkänen et al., 1991/. Although sulphate concentration is high, pyrite has not been altered

/Ruskeeniemi et al., 1991/ reflecting reducing conditions for iron and sulphide. Their immobility is also evident in Fig.4. The mobilization of Ca, Na, Si and Al close to the fracture is consistent with plagioclase dissolution. However, sodium enrichment in the vicinity of the fracture surface suggests that the element mobilization has taken place under conditions different to those prevailing at present. These might have been metamorphic, when if for instance hypersthene altered to amphibole and sericite near the fracture surface.

Evaluating the fractionation history of the REE is complicated (Fig.5). The decrease of the negative Eu anomaly and concomitant Eu enrichment on the fracture surface is obvious. Slight leaching of the other REE is possible compared to the lower fracture series. The physico-chemical conditions for alteration are not clear. They could have been hydrothermal (low grade metamorphic) in origin connected to major mineral alteration, quartz recrystallization with fluid inclusion capture, and possibly U-mineralization. Also the REE fractionation may be a result of both hydrothermal and low temperature alteration.

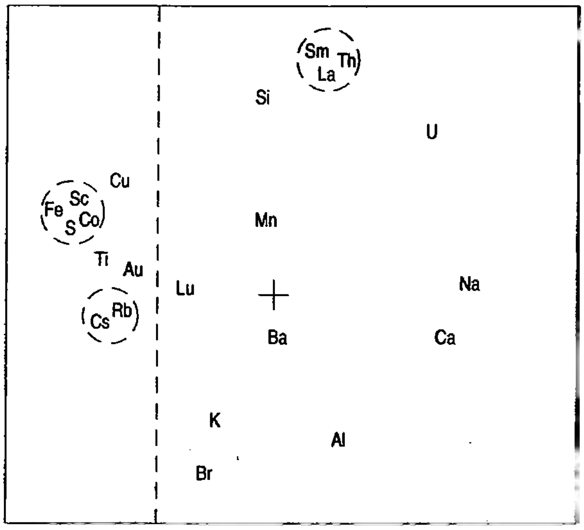

Figure 4. Element analysis results for the upper fracture series samples according to different elements by means of a chemometry computer program. Origin indicated by cross. Abscissa represents the effect of the determining variable 1 (the fracture) and ordinate the determining variable 2.

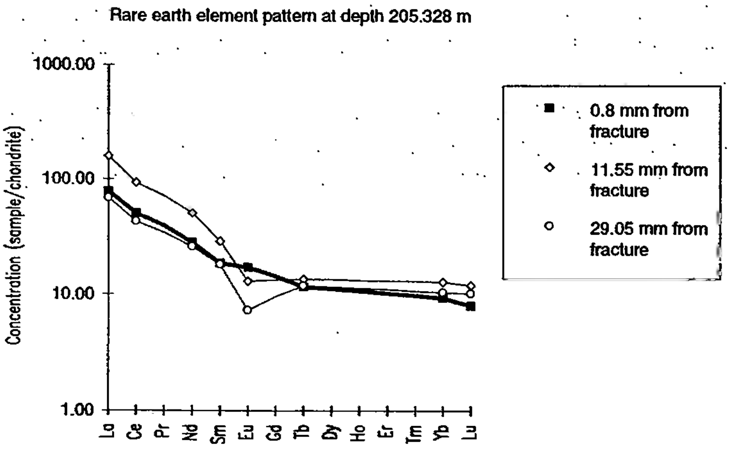

Figure 5. The chondrite normalized REE pattern for the upper fracture series at selected distances from the fracture surface.

4. Uranium series disequilibrium

For crystalline rocks the uranium series system is a sensitive indicator of recent uranium mobility, the time span for $^{234}U/^{238}U$ -ratio extending back some 1 million years /Alexander et al.,1990; Smellie et al.,1986, Ivanovich et al.,1982/. By using specimen dissolution, chemical separation and α-spectrometry the uranium isotope ratio $^{234}U/^{238}U$ was measured for the lower fracture series, and the results are presented in Fig.6 as a function of specimen distance from the fracture surface. One sigma standard deviations are also indicated. No clear disequilibrium is discernible after taking the ± 2σ error limits into consideration. A probable interpretation of the results could be that uranium has not been mobile during the last 1 million years. This is in accordance with the U concentration profile, in which there has been no obvious U enrichment close to the fracture. Unfortunately the U series disequilibrium measurements were not available for the upper fracture series.

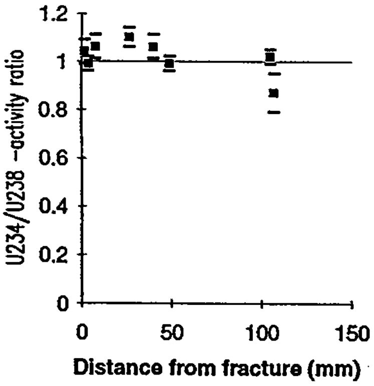

Figure 6. Uranium series activity ratio $^{234}U/^{238}U$ as a function of distance from the fracture surface for the lower fracture series.

5. Conclusions

The two open fractures studied clearly have different characteristics in spite of their close location. In the vicinity of the upper fracture the effects of element mobilization could clearly be seen. On the other hand the lower fracture did not show any significant element mobility. Near the upper fracture the U concentration was low, but very close to the fracture (< 30 mm distances) U turned out to be enriched. Several elements such as Na, Ca, Al, Si, and U were enriched adjacent to the upper fracture. However Fe, Sc, Co, S, and Cu had been immobile. For example La, Sm and Th were very similar to each other in their behaviour. The depth of alteration was 25 mm. The results indicated, that groundwater conditions have been reducing for long times.

Acknowledgement

The drill core sample has been kindly selected for this purpose by Antero Lindberg of the Geological Survey of Finland.

References

Alexander, W.R., MacKenzie, A.B., Scott, R.D., McKinley, I.G., Natural analogue studies in crystalline rock: The influence of water-bearing fractures on radionuclide immobilisation in a granitic repository, Schweiz 1990, Nagra, Nagra Technical Report 87-08.

Ivanovich, M., Harmon, R.S. (Eds.), Uranium Series Disequilibrium: Applications to Environmental Problems, Oxford University Press, Oxford 1982.

Jaakkola, T., Suksi, J., Suutarinen, R., Niini, H., Ruskeeniemi, T., Söderholm, B., Vesterinen, M., Blomqvist, R., Halonen, S., Lindberg, A., The Behaviour of Natural Radionuclides in and around Uranium Deposits. 2. Results of Investigations at the Palmottu Analogue Study Site, SW Finland, Geological Survey of Finland, Report YST-64, Espoo 1989.

Kamineni, D.C., Distribution of uranium, thorium and rare-earth elements in the Eye-Dashwa Lakes pluton - a study of some analogue elements, Chem. Geol. 55 (1986), 3/4, 361-373.

Kvalheim, O.M., Karstang, T.V., Multivariate data analysis program SIRIUS, Chemom. Intell. Lab. Syst., 2 (1987), 235-237.

Pitkänen, P., Leino-Forsman, H., Ahonen, L., Ollila, K., Hydrogeochemical interaction in Palmottu natural analogue site based on the results of borehole 346. Geological Survey of Finland, 1991, Nuclear Waste Disposal Research, Report YST-77, 39 p.

Ruskeeniemi, T., Vesterinen, M., Fractures and fracture minerals in drill core 346, in: Palmottu Analogue Project Progress Report 1990, Geological Survey of Finland, Report YST-73, Espoo 1991, 47-58.

Smellie, J.A.T., MacKenzie, A.B., Scott, R.D., An analogue validation study of natural radionuclide migration in crystalline rock using uranium series disequilibrium studies, Stockholm 1986, Svensk Kärnbränsle hantering Ab, SKB Tchnical Report 86-01.

Suksi, J., Ahonen, L., Niini, H. (Eds.) The Palmottu Analogue Project Progress Report 1991, Geological Survey of Finland, YST-78, Espoo 1992. 138 p.

Suksi, J., Ruskeeniemi, T., Matrix diffusion in situ in Palmottu, in: Palmottu Analogue Project Progress Report 1990, Geological Survey of Finland, Report YST-73, Espoo 1991, 47-58.

Suutarinen, R., Blomqvist, R., Halonen, S., Jaakkola, T., Uranium in groundwater in Palmottu analogue study site in Finland, Radiochim. Acta, 52/53 (1991), 373-380.

MODELLING OF URANIUM TRANSPORT AT KOONGARRA WITH A MOVING WEATHERED ZONE

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Abstract

In this paper, the modelling of the dispersion processes at the Koongarra uranium deposit site in the Alligator Rivers Analogue Project (ARAP) is discussed. Only the transition zone, which is believed to be the layer where the uranium dispersion takes place, is considered. The area is modelled in two dimensions as a horizontal layer, with a constant mean velocity flow field. Analysis of the field data for the determination of the model parameters suggests that the direction and velocity of the groundwater did not significantly change during the period of uranium dispersion. A mean velocity vector was determined based on this analysis, and employed in a simplified model of dispersion in the present transition zone. The preliminary modelling results displayed qualitative agreement with contour lines from measured uranium concentrations in the solid phase. In the continuation of this study, some of the present assumptions will be relaxed, and additional processes will be taken into account.

1. Introduction

The Koongarra uranium deposit is one of a number of uranium deposits in the Alligator Rivers Province, Northern Territory, Australia. The site contains two distinct uranium orebodies, separated by approximately 100 meters of barren schists. The southwestern orebody, referred to as the No. 1 orebody, contains a fan-shaped dispersion zone of secondary uranium mineralization which reaches from the surface to approximately 25-meters in depth. This dispersion zone is divided into a highly weathered and a partially weathered (transition) zone. It is presently accepted that transport occurs in the transition zone, and that the dispersion has ceased in the layers which have become highly weathered. Furthermore, it has been estimated that the dispersion process began approximately 2 million years ago (1).

2. Analysis of chemical data

Field chemical data were analyzed to aid in the estimation of model parameters and the choice of modelling approach. These data consist of uranium concentrations in the solid phase which were measured in the rock cores, as well as fluid phase data measured in the groundwater. To determine whether one general direction and a mean velocity value were appropriate, contour plots of uranium concentrations of 100 and 1000 ppm in the solid phase were made at depth intervals of 5 meters, beginning with the surface and extending to the base of the weathering zone (see Figure 1a to 1f). The contour lines have the shape of an elongated and distorted ellipse. The orebody seems to lie around one of the focal points of the ellipse. The mean direction of groundwater flow is considered to be the direction of elongation of the contour line as measured from the "center" of the orebody. The distance of dispersion is defined as the distance between the "center" of the orebody and the farthest point on the 100-ppm contour line (in the mean direction of flow).

It is apparent from the contour plots presented in Figure 1 that the distribution of uranium in the successive layers assumes a southwesterly direction, and that the base of weathering is the boundary for dispersion in this direction. The main transport direction and distance of dispersion at different depths are presented in Table 1. Therefore, it was concluded that the magnitude and direction of the groundwater flow did not vary significantly with depth, and that a steady-state, unidirectional groundwater flow field was appropriate as a first assumption for the transport modelling.

Table 1 Estimates of the main transport direction and the distance of dispersion based on uranium concentrations in the solid phase

depth (meters relative to 25 m AHD)	main transport direction (compass bearing)	transport distance (meters relative to PH49)
5 - 10	221	336
10 - 15	217	340
15 - 20	214.5	342
20 - 25	209	335

3. <u>Modelling approach</u>

Since the dispersion is believed to have taken place in the transition zone, a hypothesis that appears to be confirmed by the chemical data analysis, it was decided to only model the transition zone. The modelling region is bounded by Koongarra fault, Koongarra Creek and two non-perennial creeks perpendicular to Kongarra fault. The modelling will be carried out in steps of increasing difficulty.

To begin with, the region has been modelled as a two-dimensional, steady state groundwater flow system, using a mean flow velocity, constant in time and space. The results of this preliminary modelling are presented in the next section.

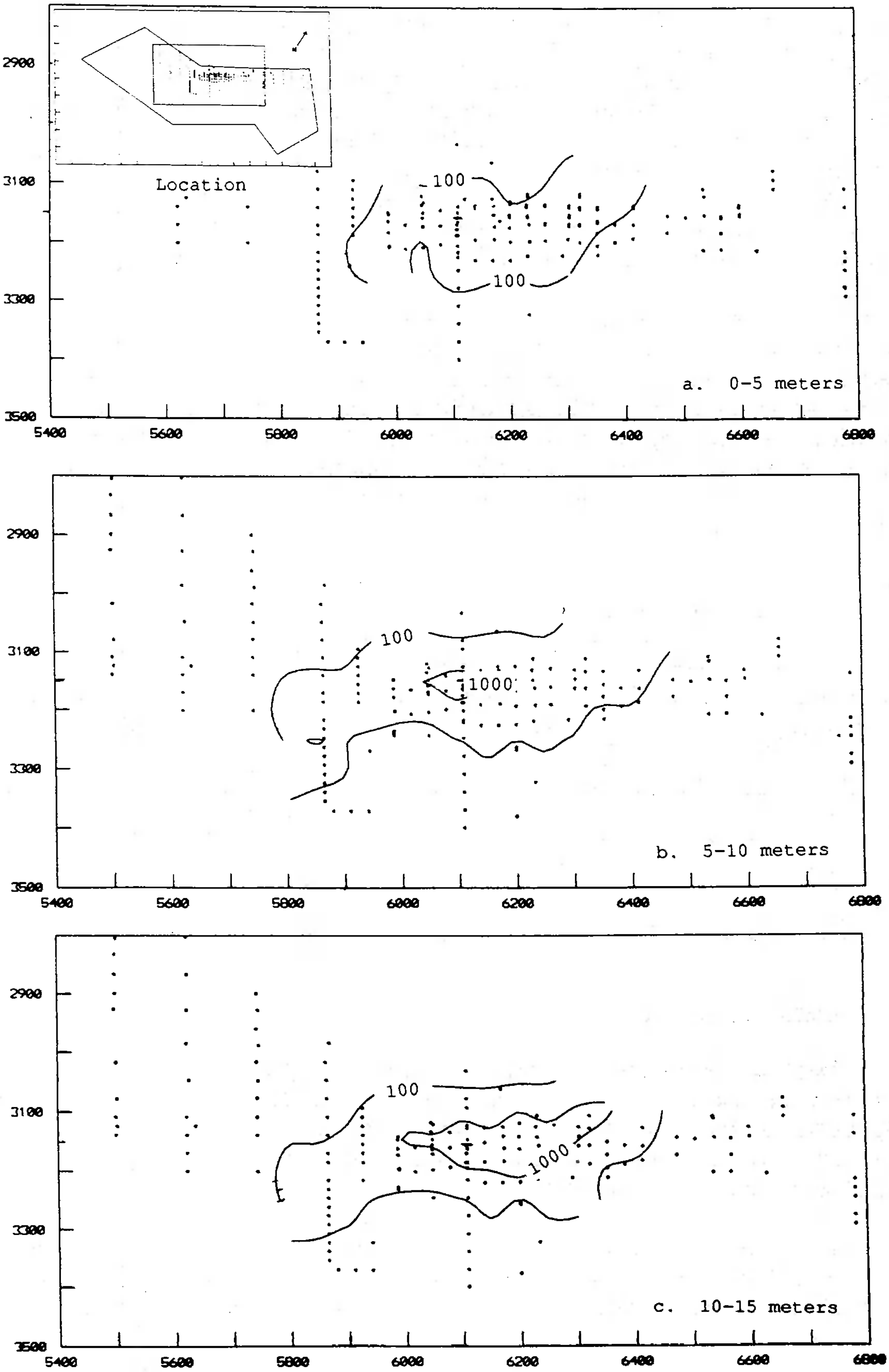

FIGURE 1a-c: Contours of 100 and 1000 mg/kg Uranium Concentration in the Solid Phase at Different Depths

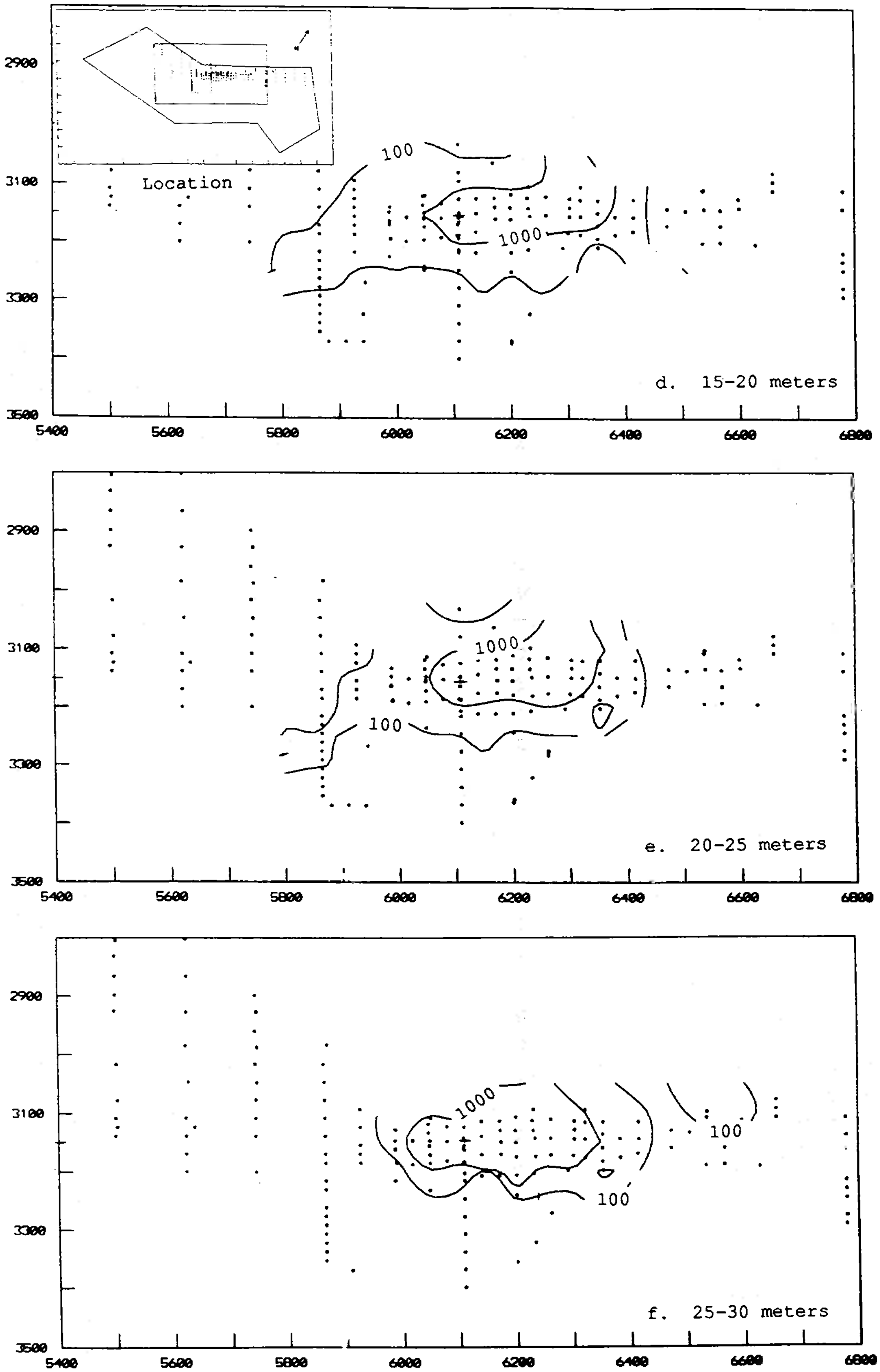

FIGURE 1d-f: Contours of 100 and 1000 mg/kg Uranium Concentration in the Solid Phase at Different Depths

Using the constant velocity model as the starting point (or base case), the effects of the velocity distribution, geochemical processes and the downward movement of the transition zone will be investigated. Different velocity distributions, beginning with a spatially variable flow field and extending to a series of steady-state flow fields based on paleo-climatological data will be modelled.

Geochemical processes which need to be incorporated in the model include: the effects of radioactive decay, non-equilibrium sorption, and geochemical equilibria.

The downward movement of the transition zone as weathering proceeds will be incorporated into the model by means of a sink term in the advection-dispersion equation. One may clarify this by noting that as the weathering progresses, uranium in the highly weathered zone will leave the model system at the top and clean schist will enter the model system at the bottom. Uranium diffusion from the highly weathered zone into the transition zone will also be taken into account.

4. Model description

In the simplified model, a mean value of velocity, constant in time and space is employed. The magnitude of the velocity is taken from the literature (1) and the direction is based on the form of the dispersion fan. The model parameters are given in Table 2, and were also assumed to be constant in space and time. The orebody was represented as a constant solute concentration of uranium in the relevant nodal points of the 2-dimensional mesh. No dispersive or diffusive mass flux was considered across the boundaries of the domain.

The modelling period was 400,000 years. This time period was based on the assumption that the base of the weathering zone has moved from the surface to 25 meters depth in 2 million years with a constant velocity. Thus, it would have taken about 400,000 years for the present transition zone, which has a thickness of 5 meters, to develop.

Table 2.: Model parameters for the first model calculation

Parameter	Value	Source
Flow velocity	1.3 $m \cdot y^{-1}$	literature (2)
Flow direction	215 compass bearing	(chemical data analysis)
Longitudinal dispersivity	30 m	assumed
Transversal dispersivity	3 m	assumed
Porosity	0.153	field data

(continued)

Table 2. (cont.)

Parameter	Value	Source
Rock density	2659 $kg \cdot m^{-3}$	field data
Adsorption coefficient	0.7 $m^3 \cdot kg^{-1}$	(chemical data analysis)
Solute concentration of orebody	$0.5 \cdot 10^{-3}$ $g \cdot l^{-1}$	assumed
Simulation period	$4.0 \cdot 10^5$ years	assumed

5. Preliminary modelling results

The results of the calculations for the simplified model are plotted in Figure 2. A plot of the dissolved uranium concentration contours are given in Figure 3. A comparison of these two figures shows that the main direction of groundwater flow in the transition zone is close to the assumed direction used in the model calculations. A qualitative agreement can be seen between the calculated and measured general forms of the contour lines and their approximate locations. However, the calculated concentration values at specific points do not correspond with the measured concentrations. Assuming that the concept is correct, the deviation between measurements and calculations may be explained by a number of possible causes:

- source concentration is too low
- retardation factor is too high
- modelling period is too short
- flow velocity is too low

It is improbable that the source concentration is too low, since the calculations were made with the highest measured concentration of uranium. The retardation factor was calculated using the partition ratio, which is the slope of the sorption isotherm (i.e., the ratio of the concentration in the solid phase to the total concentration), so it is also unlikely that the retardation factor must be changed. Although the flow velocity is based on calculations with a hydrologic model, the value obtained is very uncertain. Trial runs performed with a doubling of the assumed velocity corresponded better to the natural situation. Also, the assumptions underlying the modelling period are rather weak. A more quantitative analysis of the age of the transition zone needs to be carried out. Perhaps one of the most important improvements of the model will be achieved by working with a velocity field variable in time and space.

6. Discussion

The Alligator Rivers natural analogue has proven to be a rather complicated case,

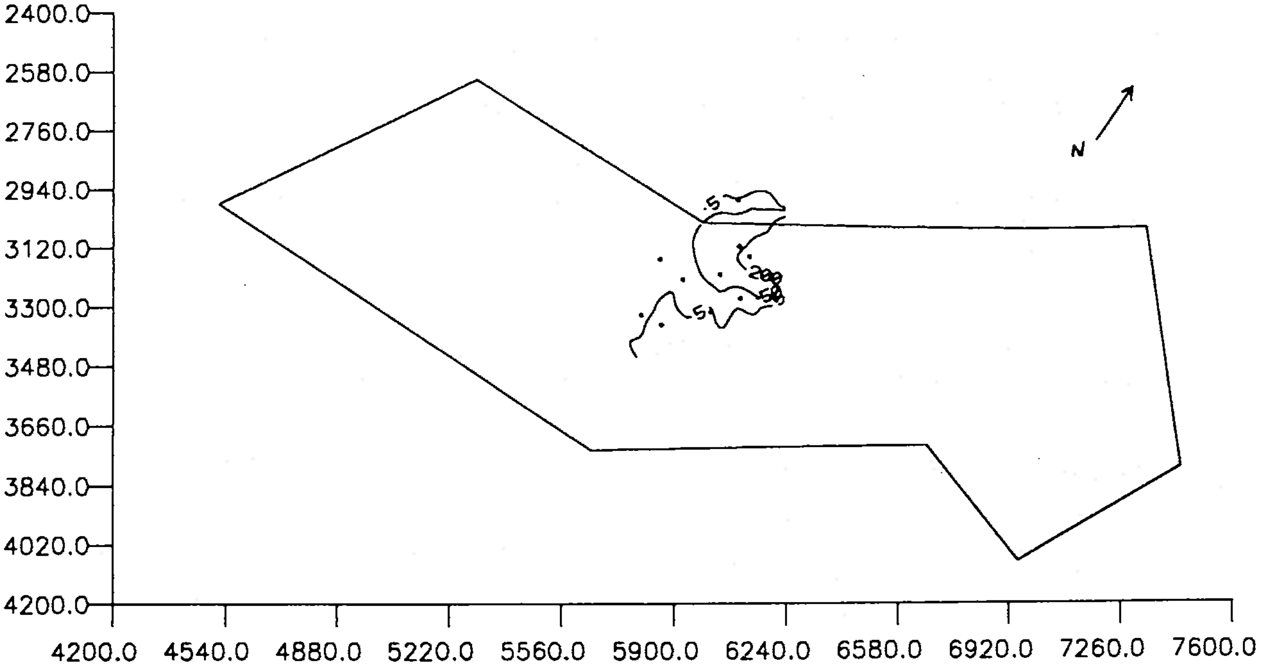

Figure 2: Measured Uranium Concentration Contours (µg/l)

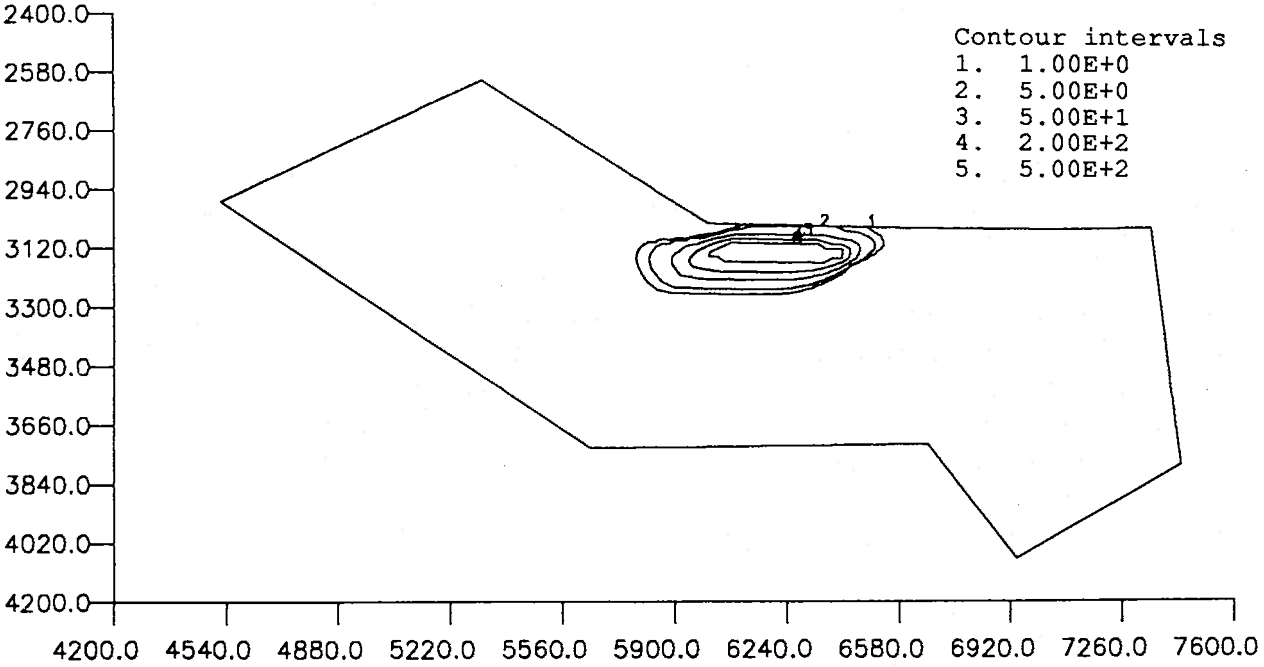

Figure 3: Uranium Concentration Contours as Calculated by METROPOL (µg/l)

and a difficult system to characterize. The interplay of many geochemical and geohydrological processes occurring over large time scales make it a formidable task to construct any deterministic and quantitative model of the history of groundwater flow and nuclide transport. The transport processes have been going on for an estimated two million years, and during this period many climatological and hydrological changes have taken place. The ongoing weathering processes have changed the nature of the rock, the uranium minerals, and the groundwater properties. To construct an accurate model of the system behavior in the past and present, a detailed quantitative knowledge of the above-mentioned processes is needed; for example, the groundwater velocity distribution, the speed of weathering, and the extent of the mineral diagenesis. Unfortunately, such information is unavailable. Therefore, the focus of modelling has to be limited to capturing the general pattern of the concentration distribution rather than an accurate calculation of concentration at specific locations and times.

7. Conclusions

In this study, the dispersion pattern at a given depth is taken as a indication of the groundwater pattern during a certain period when the transition zone was situated at that depth. The numerical modelling of the dispersion has been carried out in the simplest possible form. A mean value and direction of velocity, constant in time and space, has been used in the calculation and the movement of the weathering transision zone has been neglected. Yet, a qualitatively reasonable agreement between calculated and measured contour lines has been obtained. The agreement is, however, far from any quantitative equivalence.

8. Future work

In the continuation of the study, a constant speed of weathering will be assumed and equations for the sink term to simulate the weathering process will be incorporated in the model. Also, a series of steady state spatially variable velocities, corresponding to different geohydrological regimes in the past, will be used in the simulations.

References

1. Snelling, A.A., Geological Development of the Koongarra Uranium Deposit, ARAP Progress Report, Australian Nuclear Science and Technology Organisation, 1 September 1990-30 November 1990.

2. Townley, L.R. and A.D. Barr, Two-Dimensional Regional Groundwater Flow Near Koongarra, ARAP 3rd Annual Report, Australian Nuclear Science and Technology Organisation, Australia, 1990-1991.

APPENDIX 2

Paper under discussion:

On the evaluation and application of geochemical models
D.K. Nordstrom, US Geological Survey

ON THE EVALUATION AND APPLICATION OF GEOCHEMICAL MODELS

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ABSTRACT

A strategy is presented for the evaluation and application of geochemical models. This strategy utilizes error propagation in a sensitivity analysis to determine the limits of model applicability. Sensitivity analysis can provide a basis for the acceptable range of uncertainty from analytical determinations and thermodynamic data necessary to produce meaningful geochemical modeling for the interpretation of ground water systems. Practical, scientific, and philosophical problems plague the use of the words *verification* and *validation* to such an extent that their usage cannot be recommended for either scientific or regulatory purposes. More meaningful descriptors (model testing, model evaluation, model corroboration, and model analysis) can and should be employed, thereby avoiding the misconception that a model is a "good," "correct," "true," "valid," or "sufficient," representation of reality.

Testing geochemical models with field data to assess their "correctness" or "validity" is an essential aspect of scientific research, but it really tests their consistency with observed data, not necessarily their proximity to truth. A model that is consistent with field data, yet incorrect, is certainly conceivable. Field observations are not a sufficiently robust source to validate geochemical models. True field validation is not possible because of the complexities of natural systems, the inadequacy of field data, and because the meaning of validation implies an unattainable goal. Science advances by testing the deduced consequences of theories and models, checking for logical consistency, applying skeptical criticism and peer review, and finally arriving at an informed judgement. Improvements to geochemical models of natural systems is an iterative procedure by which we gradually gain more accurate and more detailed understanding of water-rock interactions by collecting more field data of a higher quality. Inverse modeling techniques (e.g. Plummer, 1984, 1992) can contribute significantly to building this knowledge, especially when complemented with uncertainty analysis. Geochemical models are useful as a guide to our thinking and our understanding of the data, but attempts to validate them for regulatory purposes are inappropriate because this leads to misconceptions about scientific and technical capabilities.

1. Introduction

In the quest for safe disposal of both high-level and low-level radioactive waste, models have been developed and applied to quantify the processes affecting radionuclide migration through the subsurface to the surface. Many types of models are used, including hydrologic models, ecological models, generalized flux models, and geochemical models. Geochemical models were originally developed as tools to increase our understanding of water-rock interactions. The application of geochemical models to ground-water systems has generally been of two types: forward modeling (or simulation) and inverse modeling (or the field mass balance approach; Plummer, and others, 1983; Plummer, 1984; Plummer, 1992). There is a third approach to interpreting hydrogeochemical systems using statistics, especially factor analysis, without employing thermodynamic or kinetic data (Drever, 1988; Puckett and Bricker, 1992) but it does not allow a deterministic interpretation of geochemical systems. Forward modeling is often generic in nature and was developed to answer "what . . . if?" That is, what are the thermodynamic consequences if rock A reacts with fluid B? This approach was pioneered by Helgeson and co-workers for multicomponent, multiphase systems over a wide range of temperature and pressure. Numerous assumptions are used by forward modelers such as the extent to which reactions reach equilibrium, whether the correct reactions are specified, whether there are reliable data for the specified reactions, and whether relative or absolute reaction rates are correctly defined. Inverse modeling was developed in response to the need for a rational, deterministic strategy of interpreting ground water compositions. It attempts to answer the question: what does this set of data mean? Inverse modeling was pioneered by Garrels and Mackenzie and formalized by Plummer and co-workers. The focal point of the inverse approach is the mass balance calculation for water-mineral reactions using real water compositions and mineral occurrences. Forward modeling is largely unconstrained and simulates geochemical reactions with reaction progress and/or time whereas inverse modeling is constrained by the available water chemistry, mineralogy, and isotopic data. Both methods use a chemical model (speciation and equilibrium mass transfer techniques) that can be tested to demonstrate its reliability. Geochemical models used in radioactive waste research have often been expanded to include trace element radionuclides for which the thermodynamic data may contain significant uncertainties. Questions naturally arise: how credible is geochemical modeling? Do geochemical models provide realistic estimates of actual processes? How reliable does a geochemical model have to be to provide useful information for the performance assessment of a radioactive waste repository? How can geochemical models be calibrated, verified, and validated? How sensitive are models to errors in input and to our assumptions about how geochemical processes operate in natural systems (extent of equilibrium, etc.)?

The purpose of this paper is (1) to discuss the inherent difficulties with usage of the words verification and validation with respect to scientific theories and models, (2) to suggest a systematic procedure for the evaluation and application of geochemical models, (3) to recount why geochemical models cannot be validated by field data, and (4) to advocate that continued model testing with error propagation and sensitivity analysis using the inverse approach at specific sites holds the greatest possibility for increasing our knowledge of geochemical processes. Only by increasing our understanding can we hope to increase our confidence in our ability to safely dispose of high-level radioactive waste in the subsurface environment.

2. Definitions

This paper would serve no purpose if it did not begin with a set of definitions. Terms like "model," "chemical model," "geochemical model," and "validation" have been abused and overused to the point where definitions are essential. These particular definitions have been distilled from several sources including works on the philosophy of science (especially Strahler, 1992), dictionaries, published scientific documents, the author's own experience, and discussions with colleagues.

> model: a testable idea, hypothesis, theory or a combination of theories that provides new insight or a new interpretation of an old problem (author's original, distilled from numerous references).

Greenwood (1990) points out that scientific models begin as an idea. This idea is the "conceptual model" and as such it may be only a weak or preposterous "Cloud-9" model or it may be fruitful. The distinguishing characteristic is whether or not it has testable consequences and the amount of support from those testable consequences. A great many types of models could be described: numerical models, descriptive models, scale models, empirical models, probabilistic models, kinetic models, thermodynamic models, etc.

> chemical model: a theoretical construct that permits the calculation of physicochemical properties and processes of substances (such as the thermodynamic, kinetic, and quantum mechanic properties)

> geochemical (or hydrogeochemical) model: a chemical model developed for geologic systems; this paper focuses only on water-rock-gas interaction models for temperatures of 0 to 100°C.

> verification: the establishment or confirmation of the truth of a fact, theory, etc. (Webster's New World Dictionary, 1964).

The problem here is similar to that for validation. "Scientific fact" or "scientific theory" are not permanent truths about physical reality. Our understanding about our physical environment is always imperfect and inadequate. We improve our understanding by developing theories and testing them ("guess and test," Lehr, 1990) but when the results of a test are positive it does not mean that the theory is verified, it means only that the particular deduced consequence of the theory has been verified for the particular conditions of the test. A corollary is that negative test results do not necessarily disprove a theory, there may be additional factors or phenomena particular to the test conditions that affect the results more strongly or the test may be wrong. The ASTM proposed definition for verification of an environmental model is a test of a model to see that it calculates what it is supposed to calculate, i.e. code verification, to determine that the algorithm and code are correctly written, and that the code truly represents the conceptual model (ASTM, 1984). If "verification" is always used with adjectival qualifier "code" then such a definition could be helpful. These implications will be explored later in this paper.

> validation: a making or declaring valid; proof; confirmation (Webster's New World Dictionary, 1964).

Validation, unfortunately, implies a permanence of truth or falsity that science cannot guarantee. It also implies official confirmation of the validity of something. We can validate a will, or validate a parking ticket, but we cannot validate a scientific theory or model. We can only estimate the probability that a proposition may be judged true or false, a view advocated by the new epistemology (Strahler, 1992). The worst scenario that might arise from misusing the word "validation" is that a particular numerical code may receive validation through limited testing and thereafter become the officially accepted code for regulatory purposes. Such a move on the part of a regulatory agency would be a public declaration that all critical thinking had stopped and that the electro-mechanical chatter of a computer were sufficient to solve hazardous waste issues.

The ASTM proposed definition of validation of an environmental model is a test of a model to see that it truly reproduces experimental or observational data of the environment independently derived (ASTM, 1984). However, reproducing experimental or observational data is not really validation because it is not unusual to find several different models that can reproduce the same experimental data and yet they may give different answers on predictions that are as yet untested. Considerable caution is always justified when reaching conclusions based on model tests.

prediction: to state a consequence

Among all the words used with regard to the performance of models, probably no other ranks as high in causing confusion as "prediction." The confusion has been caused by the difference between scientific and common usage of the word (Strahler, 1992). Prediction in a scientific sense means ***logical prediction,*** i.e. predicting the deduced consequences of a theory or model. Common usage refers to ***temporal prediction***, predicting an event in the future. Science does not do temporal prediction *per se*. Predicting future events is only possible for regularly repeating or cyclic events. Such events are more commonly thought of as predictable because of deduced consequences, e.g. the orbits of the planets are predictable as a consequence of Newton's laws (and Einstein's theory of relativity for a proper accounting of Mercury's orbit). Probabilistic models can provide some help with estimating the likelihood of certain types of future events, however, their reliability is only as good as the data base upon which they are based. The fewer times some event has occurred in the past the greater the uncertainty on estimating future probabilities for recurrences.

internal consistency: for a network of interrelated thermodynamic properties of substances, the fundamental thermodynamic relationships are obeyed, common scales are used for temperature, pressure, energy, atomic mass, and fundamental physical constants, conflicts among measurements have been resolved, an appropriate chemical model has been adopted, an appropriate mathematical model for temperature and pressure dependence has been adopted, an appropriate choice of standard states has been made, and an appropriate starting point in the network sequence has been made (Nordstrom and Munoz, 1986).

One source of confusion is that the word "model" in geochemistry has been used with different meanings. Sometimes it is used for the chemical model, other times for the geochemical model. A chemical model incorporates one or more chemical principles and theories into an integrated computational scheme. For example, models for solving aqueous solution equilibria utilize the law of conservation of mass and energy, the law of mass action, and some form of Debye-Hückel theory. Such models are solution equilibrium models, a type of chemical model. In hydrogeochemistry, solution equilibrium models are combined with mineral reaction models and isotope models to produce a geochemical model. For example, Plummer, and others (1990) have made a geochemical model for the Madison regional aquifer that can be summarized by the following reactions:

Dedolomitization + sulfate reduction + ferric hydroxide dissolution + pyrite authigenesis + cation exchange + halite dissolution

based on ground-water compositions, mineralogy of the aquifers, and isotope data. Another example is from Lee and Strickland (1988) who found that the evolution of water composition between two wells in the Middendorf aquifer of the southeastern United States could be explained by the reaction:

$$(\text{solution}, \delta^{13}C = -18.3‰) + 0.182CaCO_3(\delta C = 0.0‰) + 0.058CaSO_4{\bullet}2H_2O +$$
$$0.368\text{Ca-Na exchange} + 0.745NaAlSi_3O_8 + 0.016FeOOH + 0.118CH_2O(\delta^{13}C = -22.0‰)$$

Speciation models and heterogeneous solution equilibrium models can be tested against known output for an identical set of input parameters to see that it performs correctly for code verification. For example, a surface seawater analysis is a well-established and nearly constant analysis world-wide that could be used along with an identical thermodynamic data set as one already in use to test the output. If all the input parameters are identical and the code has been correctly set up then the results should be identical. They can be further tested for reliability by reproducing evaluated experimental data on thermodynamic properties of minerals and aqueous solutions that are independent of the data base used in the model. For example, a model could be tested by simulating the solubility of gypsum in various solutes over a range of concentration (Harvie and Weare, 1980) or a model could be tested by simulating the solubility over a range of temperature. In this sense, the speciation model contained within geochemical models can be evaluated. The evaluation, however, applies only to the conditions that were modeled. For example, just because gypsum solubility might have been successfully reproduced as a function of sodium chloride concentration does not mean that it will work for all ground water compositions. In addition, there are hydrological, geological, thermal, and mechanical factors that can affect water chemistry. Hence, evaluation of a chemical model only means partial evaluation of a geochemical model.

Geochemical models only take on meaning above and beyond chemical models when they are applied to specific field sites. Therefore, they cannot be validated because of the considerable complexities of natural water-rock phenomena and because of the inherent nature of the problem (see section 5 on evaluation). Geochemical models are not unique. Many more processes are operative in natural environments than can determined from lab experiments.

A final word of caution on the use of the words "validation" and "validate." These words do not have unambiguous meanings. We usually think of validation of the process of proving something is true, demonstrating that it conforms to the known facts, or showing that it represents reality. Various evolving debates on the philosophy of science has brought considerable insight to the meaning of validation in a scientific framework (Lakatos and Musgrave, 1970; O'Hear, 1990). First, there are no immutable facts (Futuyma, 1982). Nothing can ever be proven in an absolute sense. The difference between fact and hypothesis or theory is a matter of degree, a matter of how much evidence there is (Futuyma, 1982). Second, a satisfactory comparison of a model or theory with observations is not enough to "prove" or demonstrate the correctness of it. "Empirical adequacy is no reason for thinking that the model advanced by a theory is true" (O'Hear, 1990). Third, we must always keep in mind that nature is far more complex and far more untidy than any model we may construct. The most far-reaching and fundamental laws of physics and chemistry tend to be abstractions in which both the observations and the equations have been simplified and fitted to each other (Cartwright, 1983; O'Hear, 1990). Appreciation of these points can only lead to a more honest approach to scientific investigations and a greater humility regarding whatever insights we might discover.

3. Code verification with uncertainty analysis

Code verification of chemical models is primarily an exercise to confirm that the computer code functions correctly. If verification is carried out with a sensitivity analysis for error propagation then considerable insight and confidence can be gained as to the limits and reliability of the model output with respect to the input data. Input errors are from two sources: errors in analytical determinations and errors in the thermodynamic/electrolyte data base. These two sets of errors can be systematically examined during the verification process. The uncertainties that result from error propagation can be determined and generalized for the purposes of geochemical modelling. An important consequence of identifying these uncertainties is that we learn how reliable thermodynamic parameters must be to do meaningful chemical modelling. These results can be quite helpful to those measuring or evaluating thermodynamic properties.

The following sequential procedure is suggested for verification of geochemical codes with error propagation.

- for different data bases in different codes, identify differences in thermodynamic and electrolyte properties (log K or ΔG_r , ΔH_r , $\gamma_\pm$, and temperature dependence)
- verify that for the same set of thermodynamic data, the same output are produced with the same set of water analyses (test cases)
- assign errors to the thermodynamic data and propagate them through the speciation analyses for the test cases used previously
- assign errors to the analytical data of the same test cases and propagate them
- establish output uncertainties for various combinations of selected input uncertainties

Data bases have been compared in the CHEMVAL project (Read and Broyd, 1991) but the emphasis has been on establishing a common reference point for interpreting and comparing model results. Differences due to activity coefficient expressions and temperature dependence have not been explored. "Internal consistency" within the CHEMVAL project has been used on occasion to refer to agreement between data bases and output, not the usual meaning in thermodynamics of that given in the definition above. Semantic differences such as these will lead to confusion and misrepresentation. Internal consistency as defined above can be achieved if a thorough evaluation is carried out. Examples include the work of Haas and Fisher (1976) using non-linear regression for fitting which has led to the evaluation of minerals in the basalt system (Robinson, and others, 1982) with an example for calcium aluminosilicates published by Haas, and others (1981). An alternative approach to achieving internally consistent data using linear programming has been published by Berman and Brown (1985), Berman, and others (1985), and Berman (1988).

Recent changes in the CHEMVAL program (CHEMVAL2) have included a critical examination of temperature effects, ionic strength effects, organic complexing, sorption processes, co-precipitation, and coupled modeling (von Maravic, written communication, 1993) but there is no clear connection with other leading research groups such as CODATA for peer review or comparison of strategies.

Similar output from models or data bases does not mean that models or data bases can be considered reliable. Similar model output usually means that the same source of thermodynamic data was used. The same invalid numbers might have been used. Furthermore, different model output may result from the same set of thermodynamic data because of differences in activity coefficients, temperature dependences, operator decisions, redox capabilities, and assumptions regarding equilibrium. Comparisons of data bases or code output cannot be used as a basis for determining "consistency" or "reliability" of models. Comparisons can be used, however, to point out the inconsistencies and unreliabilities of databases in models.

The next step in code verification involves taking the same set of water analyses and performing speciation calculations with the same set of thermodynamic data and confirming that the results are comparable. Verification of this type should begin by comparing output from the reference sea water test case and the reference river water test case from the first comparison paper published more than 13 years ago (Nordstrom, and others, 1979). Although any water analysis (or even a hypothetical solution) could be used, the average surface sea water is especially useful because the major ion and trace element concentrations are nearly constant world-wide, the numbers are well-established, and there are several independent estimates of speciation and mineral saturation. Two more test cases have been added in the recent update of the WATEQ program (Ball and Nordstrom, 1991), both real ground water analyses, one containing Se(IV/VI) determinations and the other containing a uranium concentration. These four test cases comprise a good starting point that can be expanded to include highly reliable water analyses from natural analogue sites where they exist. Possible candidates include ground waters from the Stripa site, the Poços de Caldas site, the Alligator River site, the Cigar Lake site, and the hyperalkaline sites. However, rational decisions must be made on how to handle redox and other parameters that might interfer with the comparison of code outputs.

4. **Sensitivity Analyses**

Parallel with the geochemical code verification, sensitivity analyses should be carried out to determine the sensitivity of critical output parameters to several input parameters. Two basic approaches are possible, the Monte Carlo technique or the brute force technique. Monte Carlo calculations are most appropriate for error propagations but they aren't practical to carry out on all elements or components in the system. A good example of this technique are the two papers of Schecher and Driscoll (1987, 1988) on aluminum speciation errors propagated from thermodynamic and analytical data for acidified surface waters. The brute force technique is more practical but less appealing statistically. The input data is simply changed by the assigned uncertainty and the speciation calculation repeated and compared to the unmodified speciated output. Of course, one must perform many modified speciation calculations to compare with Monte Carlo simulations, but the results should be the same. The Monte Carlo technique is well-suited for examining the output error distribution for a given input error distribution and in this sense it determines the effect of precision uncertainty. The brute force technique is more suitable for determining the effect of uncertainty due to inaccuracies.

A good example of the brute force technique is the study by Nordstrom and Ball (1989) who performed sensitivity analyses on a set of acid mine water analyses and a set of ground water analyses from the Stripa site. The sensitivity of mineral saturation indices for calcite, fluorite, barite, gibbsite, and ferrihydrite to errors in the appropriate thermodynamic and analytical data were determined to see if they accounted for the consistent supersaturation indices that were found. The conclusion was that they did not; kinetic factors were most likely responsible for the supersaturation results.

Errors from both thermodynamic and analytical sources should be propagated through speciation calculations in such a manner that general criteria for acceptable uncertainties can be developed. For propagating errors from analytical values, an uncertainty of 10% could be used along with a 0.1 pH uncertainty. By making numerous computer runs, the acceptable range of output uncertainty could be used in reverse to point out how accurate and precise the analyses must be for the modeling results to be meaningful. Similarly, acceptable uncertainties on speciation output could be used to determine acceptable errors from the thermodynamic data. This procedure is only practical if there is a criterion on what is acceptable uncertainty on the output. Output uncertainty could be developed with a chosen code and a chosen, reliable set of water analyses. For output consisting of saturation indices, these need to be normalized to the sum of the stoichiometric coefficients (Zhang and Nancollas, 1990). Next, random error distributions must be examined for given mineral saturation indices. The statistics of the distribution can then be converted to an uncertainty that can be used as a criterion for an acceptable range on thermodynamic properties. A rough idea of how this strategy might be implemented can be found in Nordstrom and Ball (1989).

5. **Evaluation**

Evaluation can be perormed on the chemical model part of the geochemical model to demonstrate that it can reasonably reproduce experimental data. The experimental data that should be reproducible includes mineral solubilities as a function of solute concentration and temperature, mean activity coefficients, titrations, and other potentiometric measurements. Again, there have been some limited examples of evaluation tests within the CHEMVAL project (Read and Broyd, 1991) and in a few references in the literature (Jenne and Krupka, 1984; Krupka, and others, 1983; Kerrisk, 1981; Kincaid and Morrey, 1984). The following procedure is suggested for the systematic evaluation of the chemical models within the geochemical model.

- reproduce mean activity coefficients as a function of concentration and temperature, defining the limits of applicability
- reproduce solubility data as a function of solute concentration, temperature, and particle properties such as grain size or surface area, ordering, solid-solution and impurity composition and defect structure where possible, and defining the limits of applicability
- reproduce acid-base and redox titrations, defining the limits of applicability
- reproduce potentiometric measurements such as redox potential measurements, defining the limits of applicability

The major ions and minerals that react in natural waters should be chosen for evaluation first and then extended to trace elements of interest to radionuclide migration. It is extremely important to test these geochemical models for the major species distribution before being concerned about the trace element distribution because a small error in a major species distribution can translate into a large error for the distribution of a trace element. It should also be kept in mind that this type of evaluation is really testing the chemical model part of the geochemical model and not the geochemical model itself.

6. **Field Testing**

A controversial aspect of model testing is whether or not field observations can be used to validate geochemical models. The difficulty here is that field observations do not constitute a set of robust variables that lead to a unique solution of geochemical processes. It is quite different from a lab experiment where the major variables are controlled and the phenomenon is usually well understood. The major variables and processes in the field must be deduced from the application of mineralogical, isotopic, and water compositional data, hydrogeological information, and the techniques of inverse modeling, forward modeling and statistics. The more data one has, the less dependence on forward modeling and statistics and *vice versa*. With more field data, the better chance one has of finding a unique set of processes that can explain all the observations. The geochemical model is arrived at by careful reasoning not by reformatting the output from a computer code and publishing it. If a geochemical model is sufficiently robust it might be used to predict what the isotopic signature of some critical part of the system should be and compare that with the actual measured values. For example, Plummer, and others (1990) tested the validity of their mass balance model for the Madison aquifer by comparing the modeled sulfur isotope compositions of anhydrite with the actual values determined later from core samples. Remarkably good agreement on a regional scale indicated the validity of their model. Such model testing has not been accomplished within the nuclear waste programs at natural analogue sites.

I agree with Konikow and Bredehoeft (1992) and with Anderson and Woessner (1992) that the definition for model validation as *a procedure demonstrating that a model adequately represents actual processes in the real world* is a regulatory one and not a scientific one. To validate means to prove the truth and accuracy of a model. The catch is we don't know what the truth is. We have no absolute reference point. We have no accurate and complete knowledge of any hydrogeochemical system, only approximations to them.

7. **Application of Geochemical Models**

Hydrogeochemical processes can be exceedingly complex and their interpretation requires a considerable amount of training. Mercer, and others (1982) point out that "Inappropriate model use is the major factor that contributes to a lack of credibility in model results. This misuse is usually related to the experience of the user." It cannot be overemphasized that the practical hydrogeochemical knowledge a person brings to bear on a problem is far more important than the sophistication of a computer code.

The idea of "blind prediction tests" inspired by performance assessment for radioactive waste management does not seem particularly relevant to the evaluation of geochemical codes. If the concept is to see what phase is computed to control the solubility of a trace element, it is telling one nothing about the actual processes occurring in natural systems. No real information is gained except what differences exist in the data bases among different codes. A better approach would be to apply the field mass balance approach to sites where the flow paths are well known and there is highly reliable water analyses for trace elements as well as major ions. Inverse modelling (Plummer, 1984) could be used along with information on flow rates to estimate the migration rate as well as the possible controls on trace element concentrations, especially if this approach was repeatedly used at different sites with different water compositions to cover the range of water types. The end result would be a much more quantitative picture of the geochemical behavior of trace element behavior in ground-water systems surrounding repositories. By continuing the scientific method of iterating between field data and the geochemical model, by applying the inverse modelling approach to more and more sites, by obtaining proper isotopic and mineralogic data in addition to carefully collected water samples, and by discarding hypotheses that are not supported by reliable field data, we should gradually develop an understanding of the main processes controlling trace element behavior during water-rock interactions.

8. Discussion and Conclusions

It is very disturbing that validation of geochemical models is being pursued within the nuclear-waste industry without a sound basis in either science or philosophy. Konikow and Bredehoeft (1992) have pointed out very clearly (as have many others before them) that validation is not generally accepted as part of the scientific method. Theories and hypotheses are not proven or validated, they are proposed and gradually accepted as more observations are found to be consistent with them. When a hypothesis is tested and invalidated then it is either rejected or altered to accommodate the new facts. Alternatively, the reliability of the new observations may be called into question. "Our understanding only increases when we falsify a hypothesis (model) and advance to a new, more encompassing, hypothesis (model)" (Konikow and Bredehoeft, 1992).

For field observations to validate a geochemical model, a complete and thorough understanding of all the physical and chemical processes at a site is required (Tsang, 1991). This prospect is not likely for two reasons: (1) no organization is likely to fund such a project (although more expensive projects with greater risk of failure have been funded) and (2) so many drillholes could be required that the hydrogeochemical system might be irretrievably perturbed from its original natural condition. The most important point is that field characterization is always inadequate. The uncertainty introduced from inadequate characterization results in an inadequate conceptual model and only through an iterative process of collecting more field data and making the necessary model improvements can the conceptual model be improved. "It is rare to find such a large commitment of time and money to a modeling effort" (Anderson and Woessner, 1992). The natural analogue studies are to be complimented in this regard for they come close to such a quest.

Models serve one valuable purpose: *they help guide our thinking*. They open up new possibilities, new insight, new hypotheses that might not have been possible before. They are stepping-stones to a better understanding of nature. They are ideas that advance our knowledge by finding the flaws in previous ideas, as they themselves will be invalidated by the next set of discoveries. If this spirit of the scientific method could be incorporated into the modeling efforts of the nuclear-waste industry, it should improve our progress towards finding a permanent solution to the nuclear waste disposal problem.

9. Acknowledgements

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References

Anderson, M.P. and Woessner, W.W. (1992) The role of the postaudit in model validation, Adv. Water Resour. **15**, 167-173.

A.S.T.M., American Society for Testing and Materials (1984) Standard practice for evaluating environmental fate models of chemicals, American Society for Testing and Materials, E 978-84, p.

Ball, J.W. and Nordstrom, D.K. (1991) User's manual for WATEQ4F with revised thermodynamic data base and test cases for calculating speciation of major, trace and redox elements in natural waters, U.S. Geological Survey Open-File Report 91-183, 189 pp.

Berman, R.G. and Brown, T.H. (1985) The heat capacity of minerals in the system K_2O-Na_2O-Cao-MgO-FeO-Fe_2O_3-Al_2O_3-SiO_2-TiO_2-H_2O-CO_2: representation, estimation, and high-temperature extrapolation, Contr. Mineral. Petrol. **89**, 168-183.

Berman, R.G., Brown, T.H., and Greenwood, H.J. (1985) An internally consistent data base for minerals in the system Na_2O-K_2O-CaO-MgO-FeO-Fe_2O_3-Al_2O_3-SiO_2-TiO_2-H_2O-CO_2, Atomic Energy of Canada Limited, Tech. Report TR-377, 62 pp.

Berman, R.G. (1988) Internally consistent data base for minerals in the system Na_2O-K_2O-CaO-MgO-FeO-Fe_2O_3-Al_2O_3-SiO_2-TiO_2-H_2O-CO_2, J. Petrol. **29**, 445-522.

Cartwright, Nancy (1983) How the Laws of Physics Lie, Clarendon Press, Oxford.

Drever, J.I. (1988) The Geochemistry of Natural Waters, 2nd edition, Prentice-Hall, New Jersey, 437 pp.

Futuyma, D. J. (1982) Science on Trial, The Case for Evolution, Pantheon Books, Random House, Inc., New York, 251 pp.

Greenwood, H.J. (1989) On models and modeling, Can. Miner. **27**, 1-14.

Haas, J.L., Jr. and Fisher, J.R. (1976) Simultaneous evaluation and correlation of thermodynamic data, Am. J. Sci. **276**, 525-545.

Haas, J.L., Jr., Robinson, G.R., Jr., and Hemingway, B.S. (1981) Thermodynamic tabulations for selected phases in the system CaO-Al_2O_3-SiO_2-H_2O at 101.325 kPa (1 atm) between 273.15 and 1800 K, J. Phys. Chem. Ref. Data **10**, 575-669.

Harvie, C.E. and Weare, J.H. (1980) The prediction of mineral solubilities in natural waters: the Na-K-Mg-Ca-Cl-SO_4-H_2O system from zero to high concentration at 25’, Geochim. Cosmochim. Acta **44**, 981-997.

Jenne, E.A. and Krupka, K.M. (1984) Validation of geochemical models, Battelle Pacific Northwest Laboratories, PNL-SA-12442, 9 pp.

Kerrisk, J.F. (1981) Chemical equilibrium calculations for aqueous geothermal brines, Los Alamos, New Mexico, LA-8851-MS, 21 pp.

Kincaid, C.T. and Morrey, J.R. (1984) Geohydrochemical models for solute migration. Volume 2: Preliminary evaluation of selected computer codes, EPRI Report EA-3417, 340 pp.

Konikow, L.F. and Bredehoeft, J.D. (1992) Ground-water models cannot be validated, Adv. Water Resour. **15**, 75-83.

Krupka, K.M., Jenne, E.A., and Deutsch, W.J. (1983) Validation of the WATEQ4 geochemical model for uranium, Battelle Pacific Northwest Laboratory, PNL-4333, 114 pp.

Lakatos, Imre and Musgrave, Alan (1970) Criticism and the Growth of Knowledge, Proceedings of the International Colloquium in the Philosophy of Science, London, 1965, **4**, Cambridge University Press, New York, 282 pp.

Lee, R.W. and Strickland, D.J. (1988) Geochemistry and groundwater in Tertiary and Cretaceous sediments of the southeastern coastal plain in eastern Georgia, South Carolina, and southeastern North Carolina, Water Resour. Res. **24**, 291-303.

Lehr, J.H. (1990) The scientific process - Part I: Do we understand it? Ground Water **28**, 658-663.

Mercer, J.W., Faust, C.R., Miller, W.J., and Pearson, F.J., Jr. (1982) Review of simulation techniques for Aquifer Thermal Energy Storage (ATES), Adv. Hydroscience **13**, V.T. Chow, ed., Academic Press, 1-129.

Nordstrom, D.K. and Ball, J.W. (1989) Mineral saturation states in natural waters and their sensitivity to thermodynamic and analytic errors, Sci. Geol., Bull. **42**, 269-280.

Nordstrom, D.K. and Munoz, J.L. (1986) Geochemical Thermodynamics, Blackwell Scientific Publications, 477 pp.

Nordstrom, D.K., Plummer, L.N., Wigley, T.M.L., Wolery, T.J., Ball, J.W., Jenne, E.A., Bassett, R.L., Crerar, D.A., Florence, T.M., Fritz, Bertrand, Hoffman, Michael, Holdren, G.R., Jr., Lafon, G.M., Mattigod, S.V., McDuff, R.E., Morel, Francois, Reddy, M.M., Sposito, Garrison, and Thrailkill, J. (1979) A comparison of computerized chemical models for equilibrium calculations in aqueous systems, In Chemical Modeling in Aqueous Systems, ed., E.A. Jenne, American Chemical Society Symposium Series **93**, 857-892.

O'Hear, Anthony (1990) An Introduction to the Philosophy of Science, Oxford University Press, New York, 239 pp.

Plummer, L.N. (1984) Geochemical modeling: a comparison of forward and inverse methods, In First Canadian/American Conference on Hydrogeology, ed. Brian Hitchon and E.I. Wallick, National Well Water Association, 149-177.

Plummer, L.N. (1992) Geochemical modeling of water-rock interaction: Past, present, future, Proceedings of the Seventh International Symposium on Water-Rock Interaction, A. A. Balkema, 23-33.

Plummer, L.N., Parkhurst, D.L., and Thorstenson, D.C. (1983) Development of reaction models for groundwater systems, Geochim. Cosmochim. Acta **47**, 665-685.

Plummer, L.N., Busby, J.F., Lee, R.W., and Hanshaw, B.B. (1990) Geochemical modeling of the Madison aquifer in parts of Montana, Wyoming, and South Dakota, Water Resour. Res. 26, 1981-2014.

Puckett, L.J. and Bricker, O.P. (1992) Factors controlling the major ion chemistry of streams in the Blue Ridge and valley and ridge physiographic provinces of Virginia and Maryland, Hydrol. Processes **6**, 79-98.

Read, David and Broyd, T.W. (1991) The CHEMVAL international exercise: a geochemical benchmark within the MIRAGE project - Second phase, Radioactive Waste Management and Disposal, CEC Publ., 574-584.

Robinson, G.R., Jr., Haas, J.L., Jr., Schafer, C.M., and Haselton, H.T., Jr. (1982) Thermodynamic and thermophysical properties of selected phases in the $MgO-SiO_2-H_2O-CO_2$, $CaO-Al_2O_3-SiO_2-H_2O-CO_2$, and $FeO-Fe_2O_3-SiO_2$ chemical system, with special emphasis on the properties of basalts and their mineral components, U.S. Geol. Survey Open-File Report 83-79, 429 pp.

Schecher, W.D. and Driscoll, C.T. (1987) An evaluation of uncertainty associated with aluminum equilibrium calculations, Water Resour. Res. **23**, 525-534.

Schecher, W.D. and Driscoll, C.T. (1988) An evaluation of the equilibrium calculations within acidification models: the effect of uncertainty in measured chemical components, Water Resour. Res. **24**, 533-540.

Strahler, A.N. (1992) Understanding Science, Prometheus Books, 409 pp.

Tsang, C.-F. (1991) The modeling process and model validation, Ground Water **29**, 825-831.

Zhang, J.-W. and Nancollas, G.H. (1990) Mechanisms of growth and dissolution of sparingly soluble salts, in Mineral-water Interface Geochemistry, M.F. Hochella, Jr. and A.F. White, editors, Rev. Mineral. **23**, Mineralogical Society of America, 365-396.

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This joint workshop combined the fifth meeting of the CEC Natural Analogue Working Group (NAWG) and the final workshop of the Alligator Rivers Analogue Project (ARAP), a project coordinated by the OECD/NEA and managed by the Australian Nuclear Science and Technology Organization (ANSTO).

Eighty-three specialists from six EC Member States (Belgium, Spain, France, Italy, the Netherlands and the United Kingdom) as well as from Australia, Finland, Japan, Sweden, Switzerland, the USA and international organizations (OECD/NEA and the CEC) attended the meeting which was hosted by Enresa (Spain).

About 40 papers and 10 posters presented during the five days aimed at:

(i) presenting the final results of the ARAP project on site characterization and measurements for geochemical and radionuclide transport models;

(ii) presenting the state-of-the-art of major analogue studies and their relevance to repository performance assessments;

(iii) discussing the concept of natural analogues in reflecting geochemical processes to include further processes of relevance to repository performance assessment;

(iv) debating in a panel session the respective role of the performance assessor and the analogue worker in performance assessment.

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