Alligator Rivers (Koongarra, Australia)

Description: The Koongarra site is located in the north east of Australia in the Northern Territories. The site consists of a primary uranium ore body in a layered Proterozoic sequence which was metamorphosed to schist and dolomite 1870-1800 Ma ago. In a later period of uplift, accompanied by weathering and erosion, a new land surface was formed with the subsequent deposition of thick layers of sandstone comprising the Kombolgie formation. During the Phanerozoic, the Kombolgie sandstone was removed to expose the Cahill schist surface, which subsequently was lowered by more than 100 m, resulting in the weathering of part of the uranium ore body. From the range of surface lowering/erosion rates that were established for the Koongarra region, it seems likely that the weathering of the ore body has occurred within the last 1 to 6 Ma.

Today, the uranium mineralisation persists down to a depth of 100 m. The primary ore body is composed of uraninite and pitchblende-bearing veins within a zone of steeply dipping, sheared quartz-chlorite schists and a fault, which brings the ore body in contact with the Kombolgie sandstone. In the primary ore zone a uranyl silicate zone was formed by *in-situ* alteration of the primary ore. In the so-called ‘weathered zone’, which extends from the surface down to 25-30 m, carbonate rich oxidising waters have caused mobilisation and transport of uranium from the ore, forming a dispersion fan, today extending about 100 m in a south-easterly direction. Above the primary ore the uranium mineralisation is characterised by uranyl phosphates, i.e. saleeite, metatobernite, and renardite, which are found up to 50 m downstream from the ore body and are currently being leached. In the upstream part of the dispersion fan uranium appears to be dispersed in the weathered schists and is apparently sorbed onto clay and iron oxide mineral surfaces. In the weathered zone chlorite has been weathered to kaolinite, which now represents the dominant clay mineral. A simplified geological cross section is shown in Figure 1.

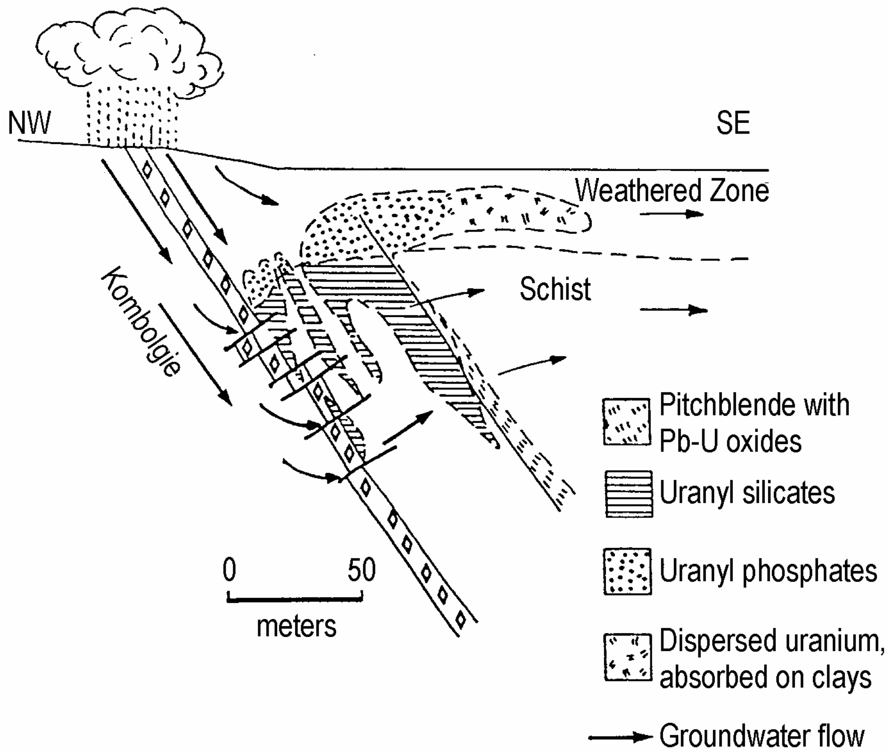

Figure 1: Simplified cross section of the Koongarra formation

The site has been investigated as an analogue for the geological disposal of radioactive wastes since 1981. The investigations have comprised detailed studies of the geology, geomorphology, mineralogy, hydrology, geochemistry and climate. With regard to radionuclide transport, the main emphasis was placed on the characterisation of uranium in the different mineral phases, the identification of mobilisation and immobilisation processes, and the application of geochemical and transport models. Most important have been the “International Alligator Rivers Analogue Project” (ARAP) from 1987-1992 and “Analogue Studies in the Alligator Rivers Region” (ASARR) from 1995-1998 coordinated by OECD-NEA and managed by ANSTO (Australia).

Characterisation of uranium in the primary ore zone and in the weathered zone.
A number of analytical methods have been applied to characterise uranium in the different immobile phases. Uranium series disequilibria, with particular interest in ^{238}U, ^{234}U, and ^{230}Th, have been extensively examined to understand the mobilisation and immobilisation processes. Activity ratios have been determined in both sediment and groundwater samples.

In the primary ore zone, secular equilibrium is observed in the uranium ore, confirming that no chemical weathering process occurred, whereas the groundwater shows $^{234}U/^{238}U$ activity ratios >1 as a consequence of the α–recoil process. In the weathered rock above the primary mineralised zone, high $^{230}Th/^{234}U$ activity ratios indicate strong recent leaching of uranium. The groundwater data suggest that the main uranium mobilisation occurred in the lower section of the weathered zone where groundwater chemistry is characterised by high levels of bicarbonate-forming uranium complexes. The weathering processes affecting the chlorite are indicated by high Mg contents in the groundwater.

Downstream in the dispersion fan, uranium is correlated with iron oxides and clays. The retardation mechanisms for uranium were investigated by a combination of sequential extraction methods combined with uranium series disequilibria analysis. A special sequential extraction procedure with regard to the relevance of iron oxides in the uranium fixation was developed and applied to natural samples from the dispersion fan. The results show that part of the uranium is adsorbed or accompanied by amorphous iron oxides and part accompanied by crystalline iron oxides. In the adsorbed phase the $^{234}U/^{238}U$ activity ratios are about 0.6 to 0.8 which are similar to the groundwater in this area, whereas the $^{234}U/^{238}U$ activity ratio in the crystalline iron oxide phases is about 1, indicating that uranium is not easily accessible and fixation of uranium occurred over a longer time period.

Amorphous iron oxides were formed by the weathering of chlorites; these generated iron oxides which subsequently underwent crystallisation, probably incorporating the uranium which initially was sorbed on the amorphous iron oxides. Such a process was demonstrated by integrated laboratory experiments and further insight was achieved by the application of high resolution microprobe (SHRIMP) analysis. Due to the high spatial resolution of this method the $^{234}U/^{238}U$ activity ratio in iron nodules could be determined separately. The measured ratio of 0.8–1.3 is in good agreement with the values measured by sequential extraction on the crystalline iron oxide phase and confirms that the crystalline phases, occurring in the form of iron nodules, do indeed fix part of the uranium no longer accessible to the groundwater.

Development and application of surface complexation models
In order better to understand the sorption processes of uranium on the natural samples, considerable work was undertaken on the uptake of uranium on single minerals, binary systems and natural materials. The objective was to understand the sorption properties of natural materials by investigating their major mineralogical components. Consequently a large number of batch experiments on the adsorption of uranium on ferrihydrite, imogolite, quartz, kaolinite and montmorillonite, as well as on natural sediment samples from Koongarra site, have been performed. The effects of iron oxide on U(VI) adsorption by quartz was investigated as a binary system. Parameters such as pH, ionic strength, bicarbonate and uranium concentrations, have been varied. On the basis of these experiments surface complexation models relating to distinct pure mineral systems have been developed.

Besides the so-called component addition approach, a simpler, generalised, composite approach was developed and applied to uranium sorption on single minerals and on natural sediments. For this approach the sample is regarded as a whole and the electrostatic layer is not considered. It is especially useful to describe sorption independent of geochemical conditions in rather complex systems. This generalised composite approach has been applied in reactive transport modelling by the USGS who demonstrated the utility of the SCM approach in modelling adsorbing inorganic solutes, such as uranium, under variable chemical conditions.

<u>Colloids</u>
Groundwater samples taken from boreholes were studied with respect to their colloidal contents, with samples collected closest to faults having the greatest variety of colloids. The colloids mostly consist of iron oxides and clay minerals with iron-rich particles dominating; uranium was only found in these iron-rich species. It could be shown by ultrafiltration experiments, however, that most of the uranium exists as dissolved species and not in colloidal form, whereas the majority of thorium and actinium is associated with larger particles of >1mm in size which are immobile and probably resulted from excessive pumping in the boreholes. Only a very small part of the thorium was associated with colloids <1µm. Low colloid concentrations (about 10^6 particles per litre or less) and the absence of radionuclides in colloids outside the centre of the ore body, indicate that colloids are relatively unimportant for uranium transport in the Koongarra groundwaters.

<u>Transport modelling</u>
Radionuclide transport modelling was performed in the ARAP-Project, as well as in the International Intraval Project, where one and two dimensional models were applied. In the Intraval Project the applicability of the rather simple models that are generally used in performance assessment, was tested. Advection-dispersion models with linear sorption and, in some cases, including chain decay, alpha-recoil and phase transfer, were applied. The calculations were based on hydrogeological work and derived data from the ARAP project. Kd-values were derived by considering only the accessible uranium from the solid phases (determined by sequential extraction). Using these reasonably selected parameter values, the calculated results were in fairly good agreement with the observed migration distance and concentration levels, although extensive simplification of the system was made. The uranium calculation was based on the time interval of a half million up to a few million years, which conforms with geomorphological evidence that the weathering process of the primary ore, and thereby the formation of the dispersion fan, commenced during the last 1-6 Ma.

In the ARAP-Project, more complex multi phase models were applied which were able to describe observed uranium concentrations and activity ratios in different mineral phases.

Relevance: The main relevance of the study lies in the illustration of uranium transport in natural systems over a million years, including processes of uranium retardation by sorption on Fe-oxy-hydroxides and subsequent fixation in crystalline iron minerals. A large number of integrated experiments allowed the development of surface complexation models, important for performance assessment, which have supported the range of Kd-values expected due to variations in geochemical conditions and mineral phases in the host rock. Furthermore, the study was suitable for the application and testing of transport models which are used for modelling far field radionuclide transport in repository environments.

Position(s) in the matrix tables: In the matrix table the study illustrates far field radionuclide sorption and precipitation/co-precipitation at low temperatures (<100°C) and the impact of colloids on such processes in mudrocks.

Limitations: The geochemical conditions at the Koongarra site, which are rather oxidising and slightly acidic, do not compare with typical conditions in the near field and far field environments expected to prevail in deep underground repositories. The process of uranium fixation in crystalline iron oxide phases occurred after significant alteration of the rock and formation of iron phases. This will probably not happen in host rocks where reducing conditions are expected.

The relatively near surface chlorite schists at Koongarra are fractured and therefore ,not fully comparable to expected repository host rocks such as clay or clay stone formations.

The uranium source is not comparable to spent fuel. The primary uranium ore (pitchblende or uraninite) has been mobilised and subsequently immobilised through the formation of uranyl silicates, which comprise the uranium source in the weathered zone.

Quantitative information: The Alligator Rivers site is well characterised. Groundwater data from more than one hundred boreholes are available and the extension of the uranium dispersion fan is well characterised in terms of:

- Natural isotope data: $\delta^{2}H$, $\delta^{18}O$, $\delta^{13}C$, and ^{14}C
- Uranium series disequilibrium data from rock and groundwater
- *In-situ* partitioning coefficients for uranium
- Sorption data of uranium on individual mineral phases and on natural sediment samples
- Variation of pH, ionic strength, uranium concentration, HCO_3-concentration, phosphate concentration and solid/liquid ratio.

Uncertainties: In general most data are of good quality. The main uncertainties are associated with the hydrogeological boundary conditions of the site and the age of the weathering process. With respect to the former, uncertainties appear in groundwater patterns and flow rate over geological time scales. Due to climate variations, the water levels could have significantly changed in the past. With respect to the latter, the region, in particular the weathered zone, is very heterogeneous with a wide range of material types and fracturing on several scales. Thus, the starting point of the weathering process of the primary uranium ore can only be estimated by assumptions concerning the original thickness of the Cahill formation and the nature of the surface lowering/erosion processes. The range given varies from 1 to 6 Ma ago.

Time-scale: The time scale addressed by the study is geological. The process of uranium weathering and transport commenced about 1-6 Ma ago.

PA/safety case applications: Due to the limitations outlined above, quantitative information has not been used as direct input into existing safety assessments for deep geological repositories.

In the Japanese H-12 PA, the Alligator Rivers Analogue was mentioned as one example showing the stability of the geological environment and it's ability to retain uranium and thorium over geological time periods. In the Swedish SR-97 PA, the Alligator Rivers Analogue is mentioned as offering the opportunity for improved process understanding. In the TSPA for Yucca Mountain, the Alligator Rivers Analogue is used to exemplify uranium transport in the saturated zone. Furthermore, it is mentioned as a site where colloidal transport has had little impact on uranium transport.

USNRC has applied coupled codes (surface complexation model, non electrostatic or generalised composite approach) to estimate the impact of uranium and other pollutants in near surface contaminated sites (Cape Cod, Naturita).

The Analogue has had a strong impact on the development of surface complexation models which are usually applied to support ranges of Kd-values used in Performance Assessment. The data for uranium sorption on a natural sample from Koongarra was referred to in the OECD/NEA Sorption Project Phase 2 as a well described test case for benchmark calculations using surface complexation models to compare component additivity and generalised composite approaches.

Communication applications:

The study was used in the Second AKEnd Workshop in Germany in 2001, to illustrate the strong barrier effect, high retardation potential and long-term stability of hydrochemical conditions in natural systems. It is also included in the CEC coordinated natural analogue video (Traces of the Future).

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Added value comments: The study represents a good example of uranium transport under natural conditions. Although the formation is not a typical host rock and a number of uncertainties exist which limit the testing of PA transport models, the source is rather well known, the immobile uranium phases are well characterised and, within some limits, the time frame of weathering is known. The time frame over which transport has occurred in the weathered zone at the Koongarra site (1-6 Ma) covers the typical time scale usually considered in PA and safety cases. Therefore the study is very suitable for illustration of uranium transport over such a time scale and the limitation of the uranium plume due to the barrier effect of the geological formation. This should be more emphasised in communication than has been done so far.

Potential follow-up work: Nothing planned

Keywords: Uranium, disequilibrium series, weathering, transport, sorption, surface complexation, iron oxides,

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