Natural and Anthropic Glass Analogues for Nuclear Waste Confinement Matrix

From Experiments to Modelling

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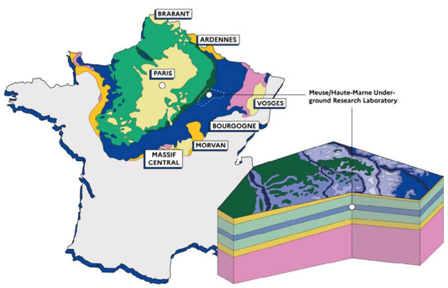
Focus on archaeological artefacts in this talk

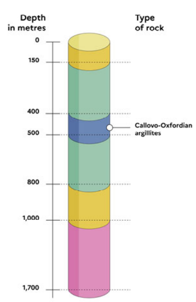
Context

ANDRA (French National Agency for Radioactive Waste Management)

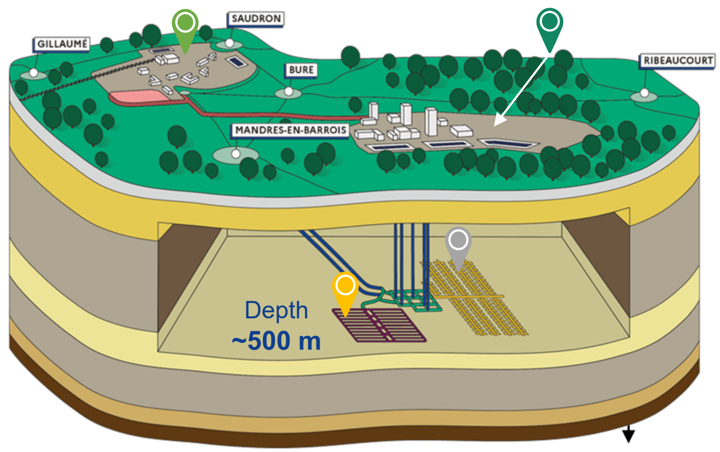
In charge of disposal facilities and waste management since 1979

Cigeo project



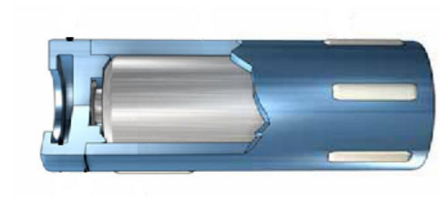


Location: *Bure (Haute Marne, France)*



Centre for Industrial Geological Disposal, Cigeo

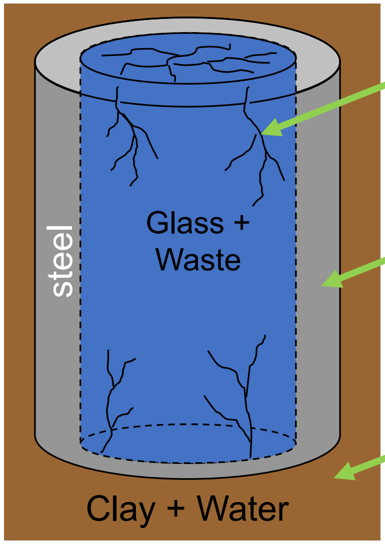
HLW Disposal cell, Bure underground laboratory



- HLW glass canisters stored at depth of 500 m
- Callovo-oxfordian claystone (Cox) ➔ low permeability: radionuclides confinement and sorption properties
- Disposal cell ~ 80 m long

HLW glass

Long duration confinement ➔ **Multi-layer** storage concept

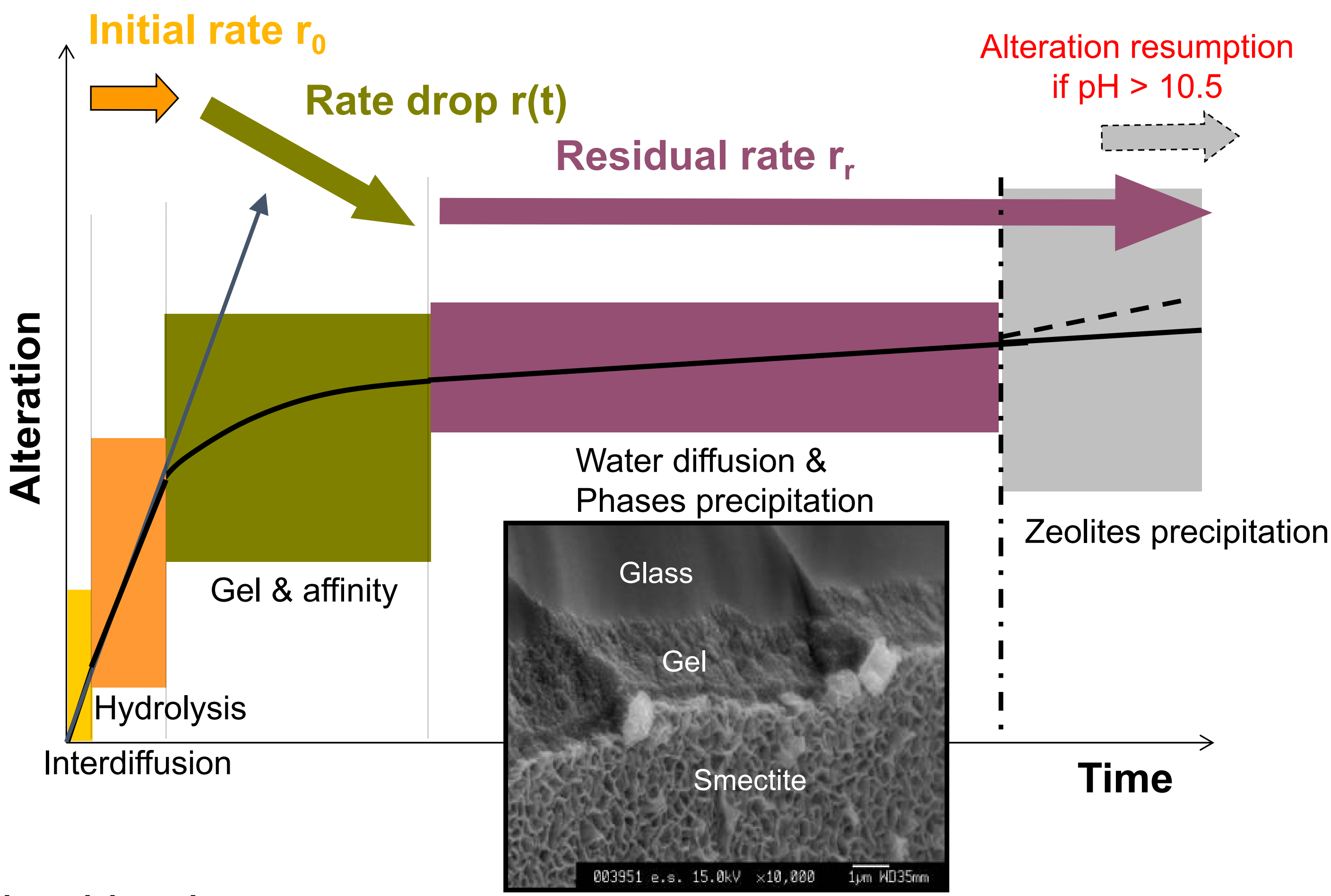


Glass fractured by rapid cooling,
→ Contact surface with the solution
→ Alteration surface

Metallic envelopes (primary canister and overpack)
→ **Fe**: main element near the glass
+ Iron release in porewater

Host rock: Callovo-Oxfordien (COx)
Clay minerals, anoxic, water saturated

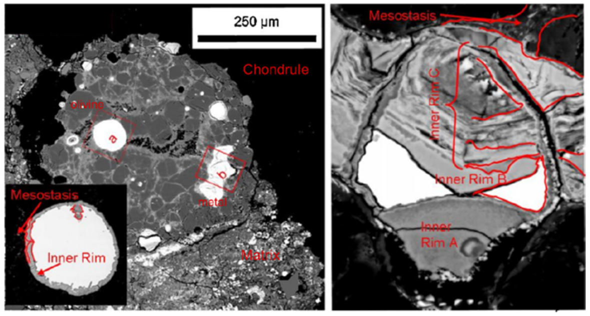
Glass alteration mechanisms



Glass dissolution kinetics

Types of glass for alteration analogy

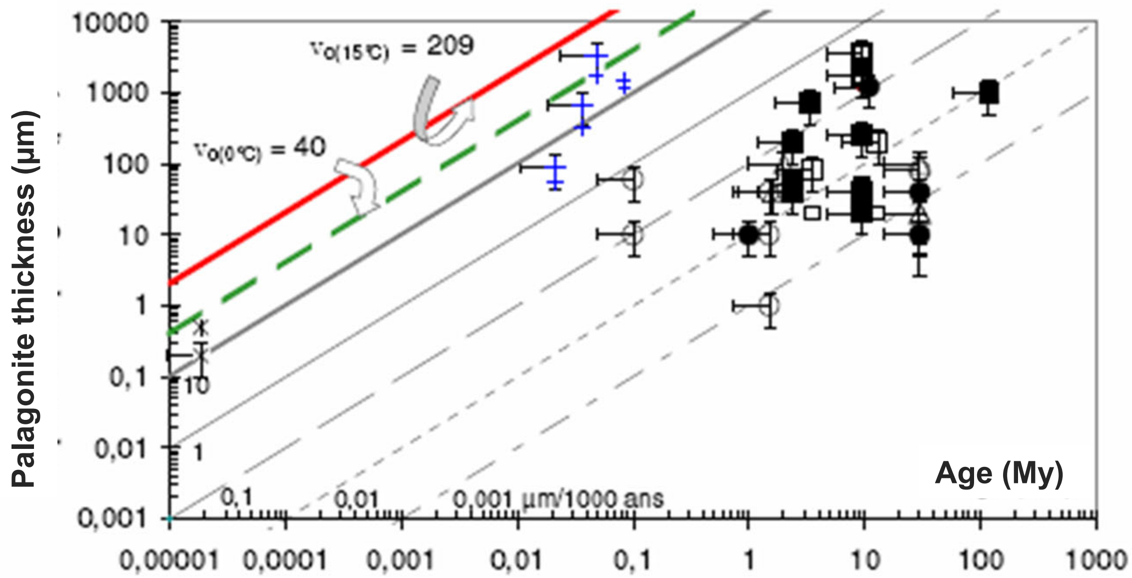
- Natural glass – up to 10^6 years
  - Basaltic glass: Alteration in various environments: marine, continental area (various climate conditions)
  - Obsidian
  - Meteorite glass



State of the art: basaltic glass

Natural analogues

- Basaltic glasses
- 1000 – 100 000 years



Techer et al, 2001

- **Alteration Products:**
  - Phyllosilicates and zeolites
- **Mechanisms:**
  - Ion exchange and interdiffusion
  - Dissolution by hydrolysis
- **Long-term Durability:**
  - Stability and alteration kinetics

Alteration conditions not well known

Types of glass for alteration analogy

- Natural glass – up to 10^6 years
  - Basaltic glass: Alteration in various environments: marine, continental area (various climate conditions)
  - Obsidian
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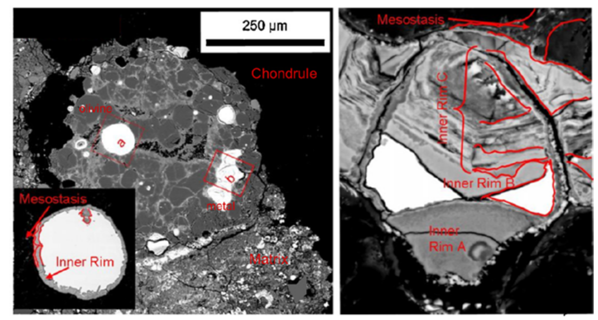


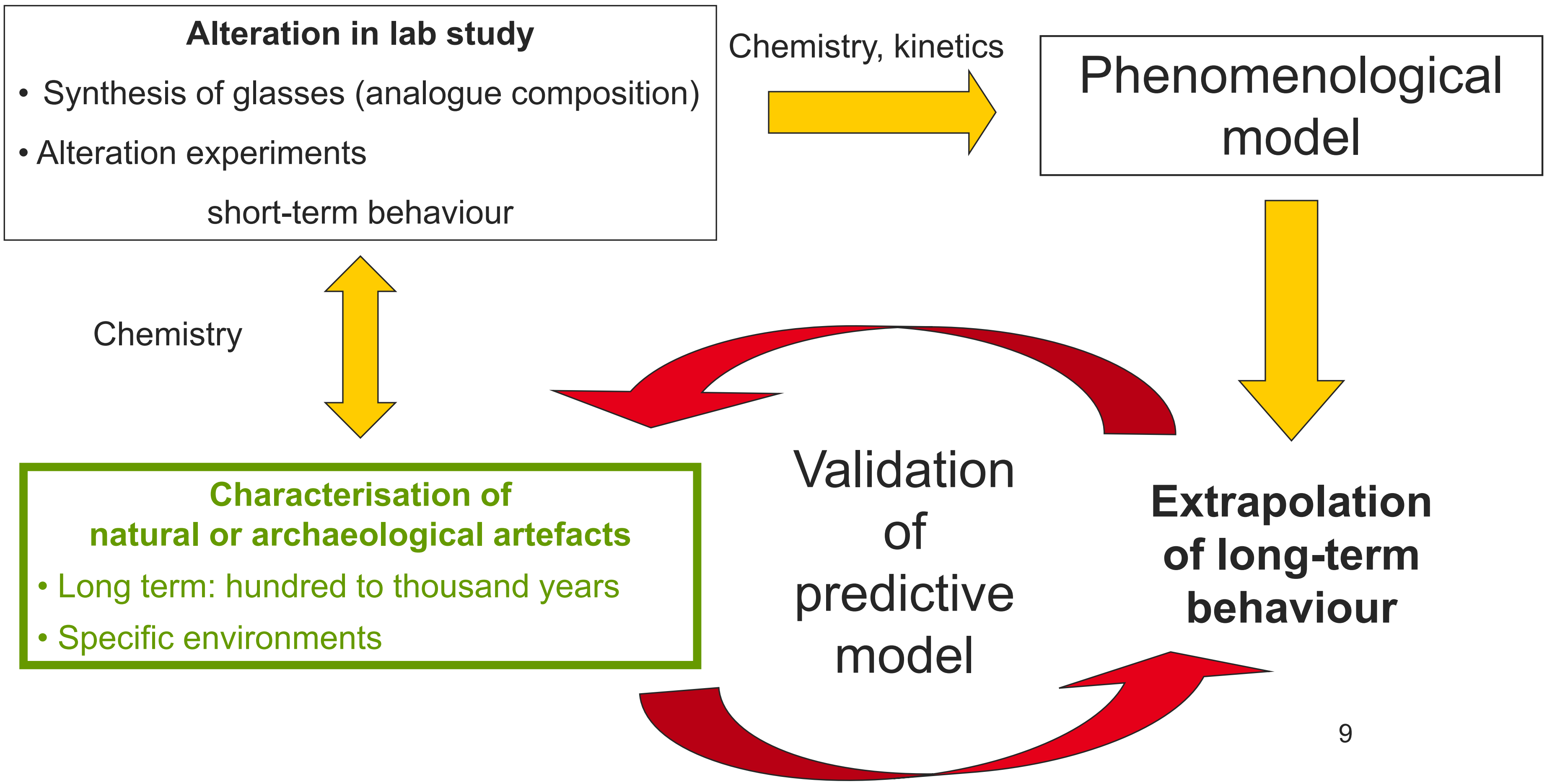
- Anthropogenic glass - 10^2 to 10^3 years
  - Roman glass: Les Embiez (France), Marine environment, fractured glass, influence of the secondary phases precipitation
  - Slag furnace glass: Glinet (France), soil

Objectives of the studies on glassy materials

Gather phenomenological data on systems that have evolved over hundreds to thousands of years	• Hundred to thousand years • Estimation of corrosion rates
Identify key phenomena controlling the long-term behavior of glass	• Glass alteration layers composition • Precipitation of secondary phases
Address specific questions related to nuclear glass in geological repositories	• Role of cracks within the glass • Impact of iron corrosion due to the presence of the carbon steel container
Local chemical conditions encountered at various stages of the repository timescale	• Aerated/ deaerated conditions • Iron release by metallic elements of the close environment

cea

Integration of analogues in the methodology for model validation



Archaeological artefacts

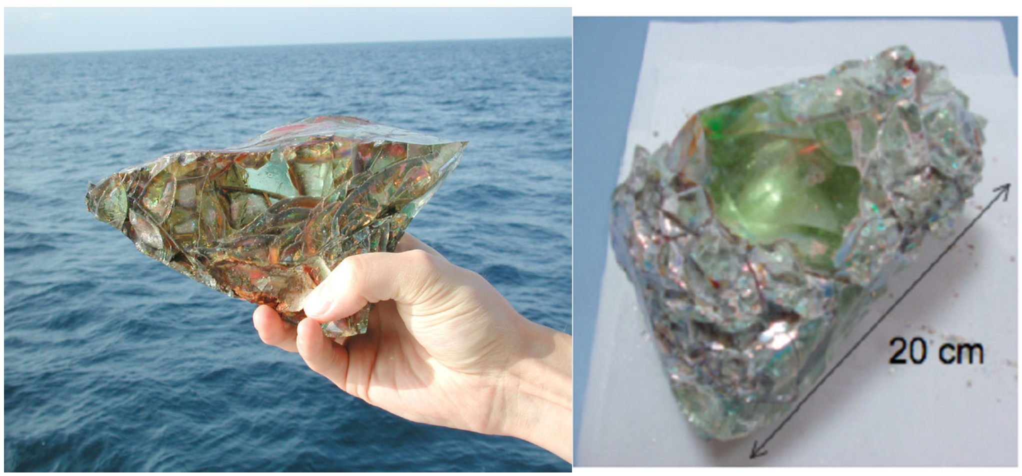
- Roman Glass
- Slag furnace glass

Roman glass

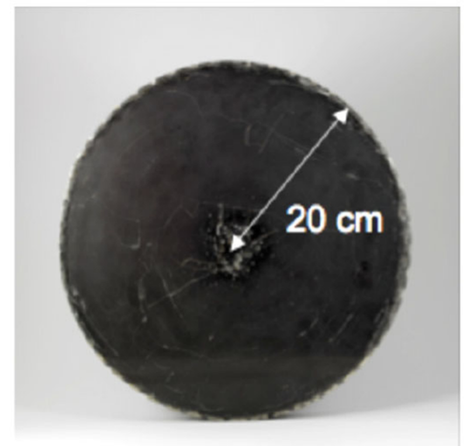
Archaeological analogue

- Sodo-calcic glass
- 1800 years

Comparable macroscopic morphology
with nuclear glass



Verney-Carron, 2009



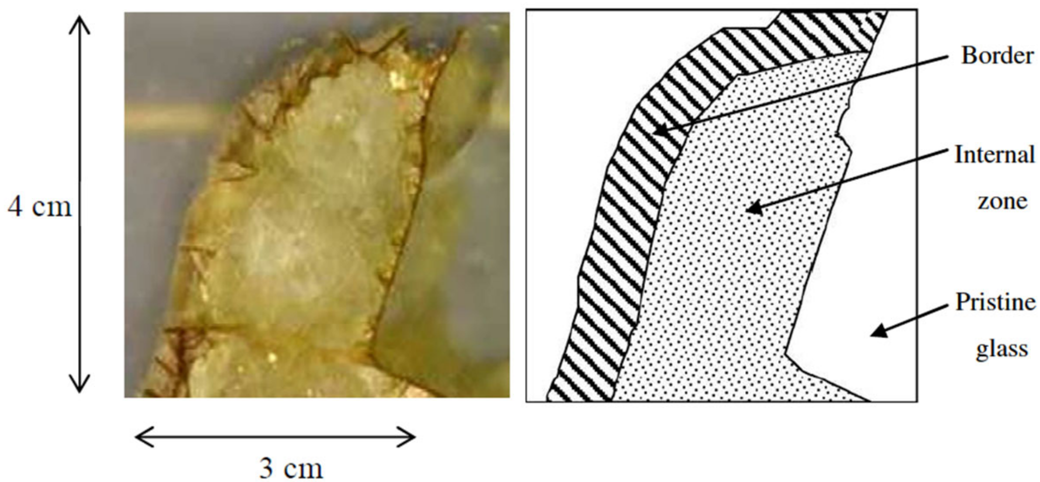
SON 68 glass

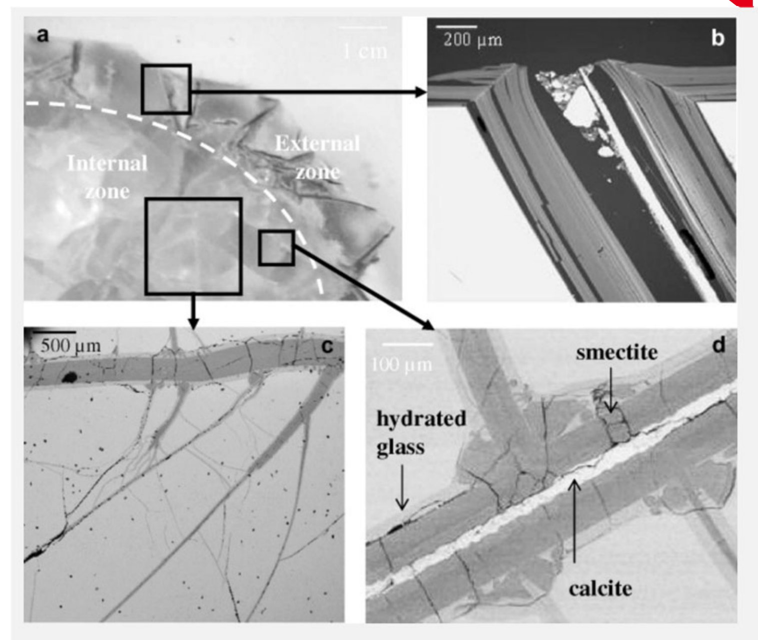
Objectives: testing the geochemical models

Aurélie Verney-Carron PhD thesis, Montpellier university 2009

Characterisation of the alteration facies in the fracture

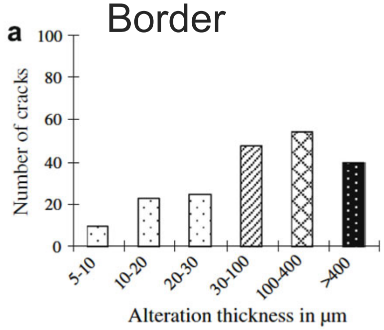
- Location in the sample



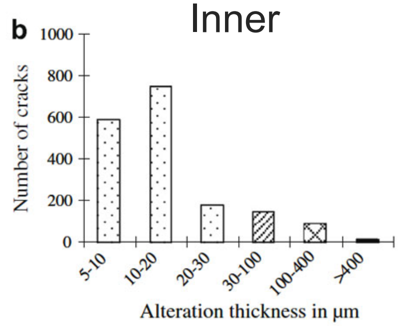


Verney-Carron et al., 2008

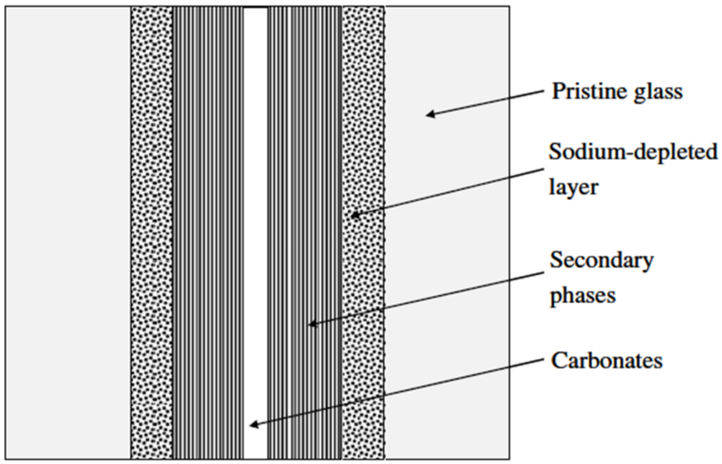
Border



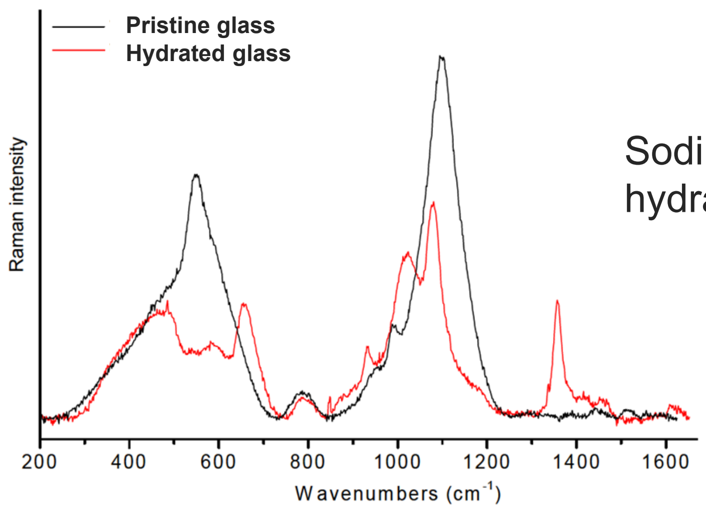
Inner



Alteration pattern of the cracks



	Pristine glass	Na depleted zone	Secondary phases
SiO_2	69.61	63.44	50.25
Na_2O	18.57	0.52	0.96
Al_2O_3	1.84	1.68	2.05
CaO	5.05	5.05	0.41
Fe_2O_3	0.34	0.26	2.09
K_2O	0.32	0.63	0.51
MgO	0.49	0.38	19.80
Sb_2O_3	0.70	0.83	
SO_3	0.37	0.25	
Cl	1.04	1.32	
MnO	0.03		
TiO_2	0.04		
P_2O_5	0.06		
Sr	±		
Ba	±		
Zr	±		
Total	98.47	74.36	76.50

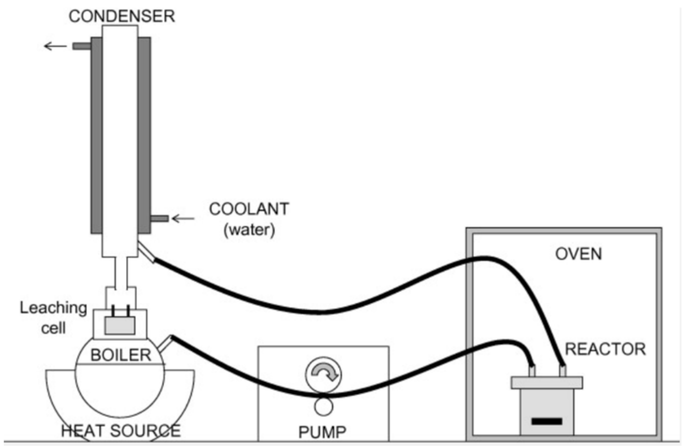


Sodium depleted zone: hydrated glass

Secondary phases: smectites (XRD)

Modelling

Leaching experiments for kinetic data



Wt.%	Archaeological glass	Synthetic glass VS5
SiO_2	70.70 ± 0.76[a]	69.48
Al_2O_3	1.78 ± 0.02	1.90
Na_2O	19.52 ± 0.55	19.65
CaO	4.94 ± 0.03	4.74
SO_3	0.26 ± 0.01	0.20
Sb_2O_3	0.83 ± 0.07	1.18
Fe_2O_3	0.30 ± 0.01	0.34
MgO	0.38 ± 0.02	0.42
K_2O	0.38 ± 0.01	0.37
Li_2O	–	1.00
Cl	1.00 ± 0.03	0.85

[a] The standard deviations correspond to variations for three different replicates.

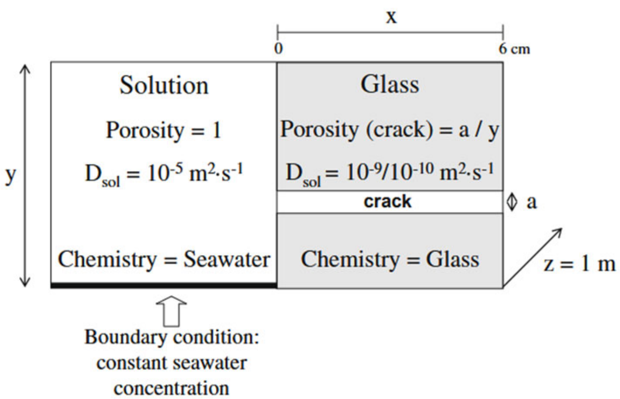
Reproducing the archaeological glass composition

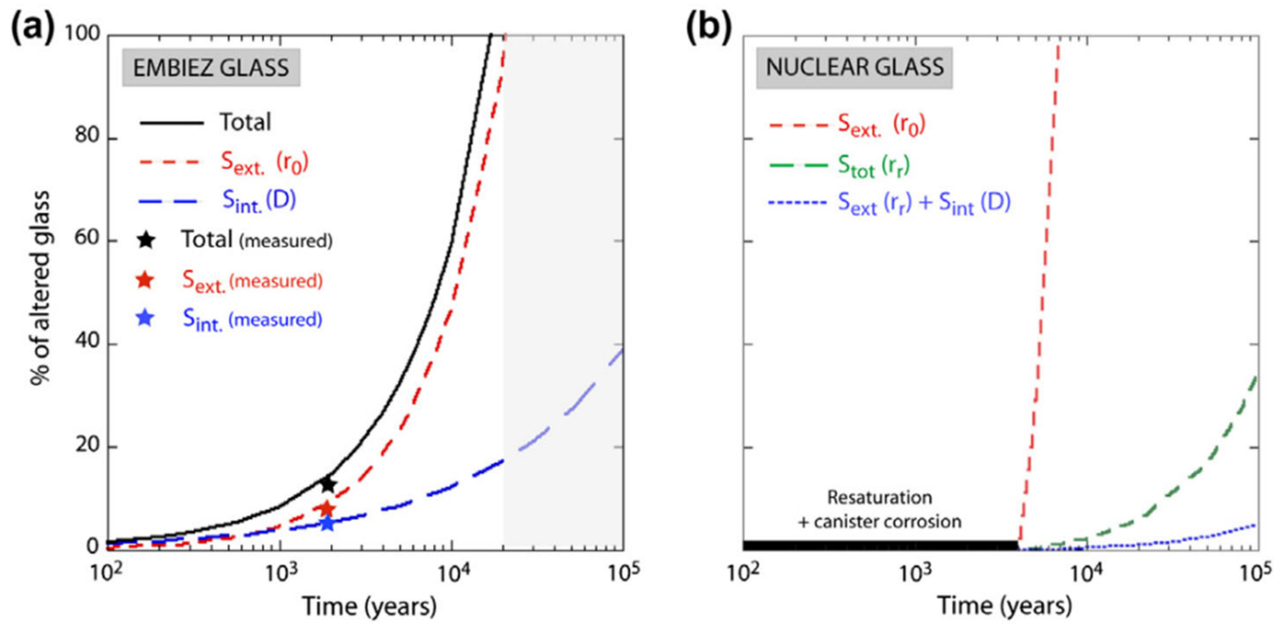
Several conditions from immersed conditions to repository conditions

- Pure water
- 0.044 M NaOH (pH 10.78 at 89°C)
- Seawater (pH 7.29 at 89 °C)

Verney-Carron et al, GCA 2010

1800 years analogue modeling





Consistent thickness values with the measured ones

Boundary conditions not favorable for the archaeological glass

Verney-Carron et al, J Nuc Mat 20

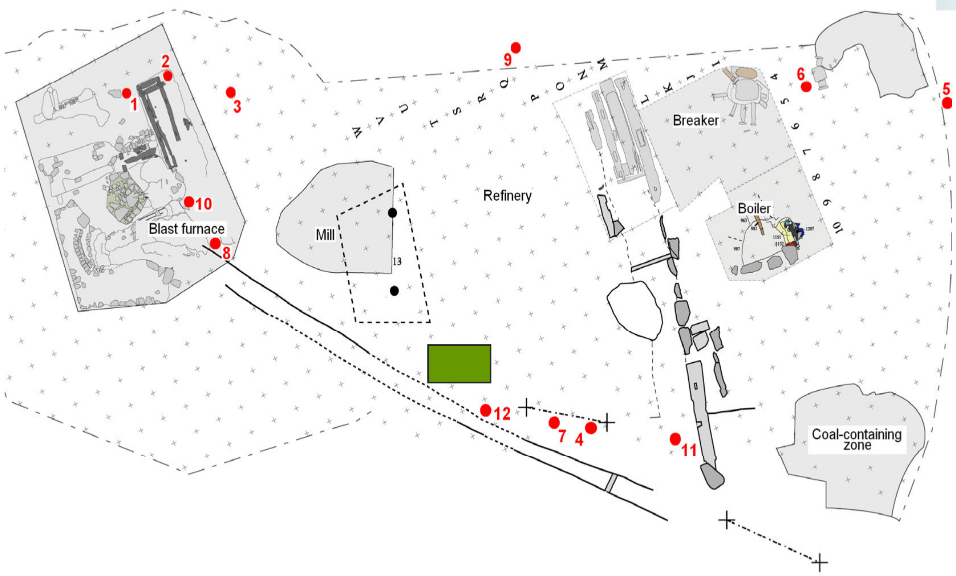
Archaelogical analogues studied: slags from Glinet site

Slag: waste vitreous material left after making steel in blast furnace

Waterlogged site: Anoxic conditions of burial

Sampling area

Piezometers

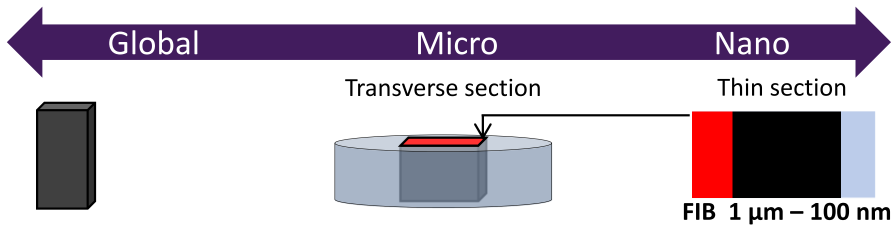


Glinet: 16th century ironmaking site, in Normandy, France

→ **Reference site:** characterization during several field investigations
Calco-carbonic solution

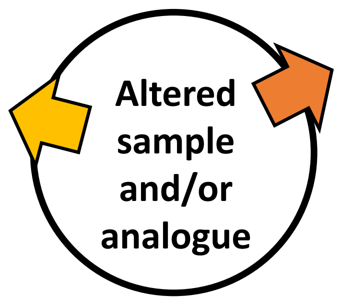
Anne Michelin PhD thesis, UPMC 2011

Analytical strategy

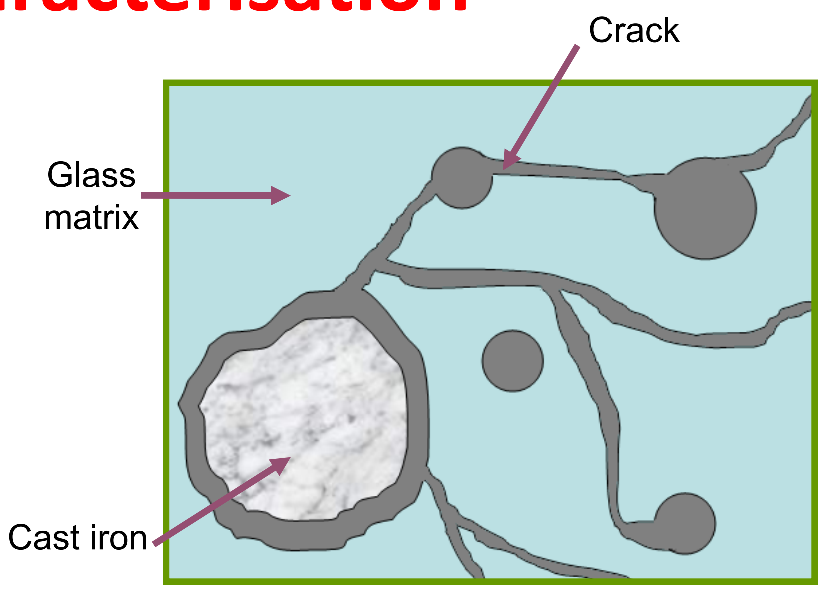


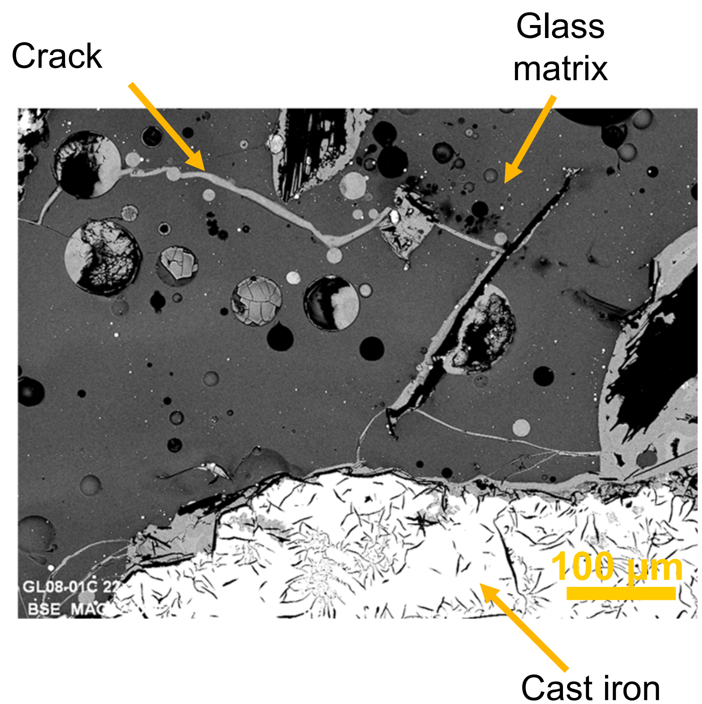
Chemical characterisation of the CPL		
Micro	OM/SEM	Morphology, thickness
	EDS	Elementary analyses
	µ-Raman	Structural analyses
Nano	STEM	Morphology
	STXM/XANES	Structural analyses
	TEM/SAED	

Species transport characterisation solution/CPL – Isotopic labeling		
Micro Nano	**ToF-SIMS** **nanoSIMS**	Permeability of the CPL
		Precipitation of siderite



Corrosion products/glass interface characterisation

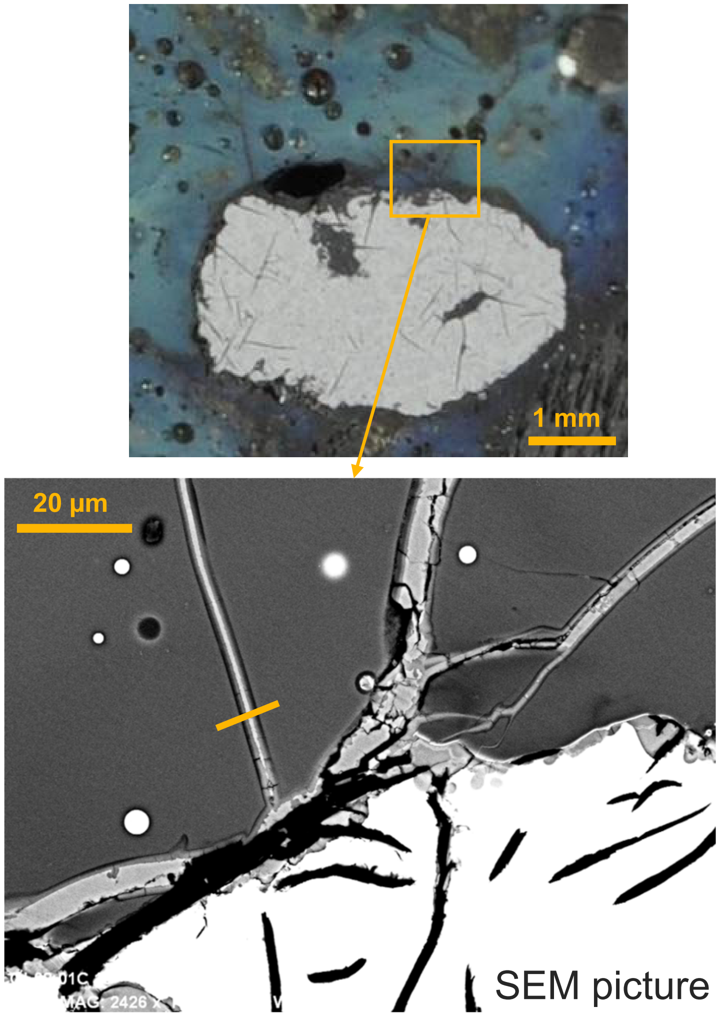




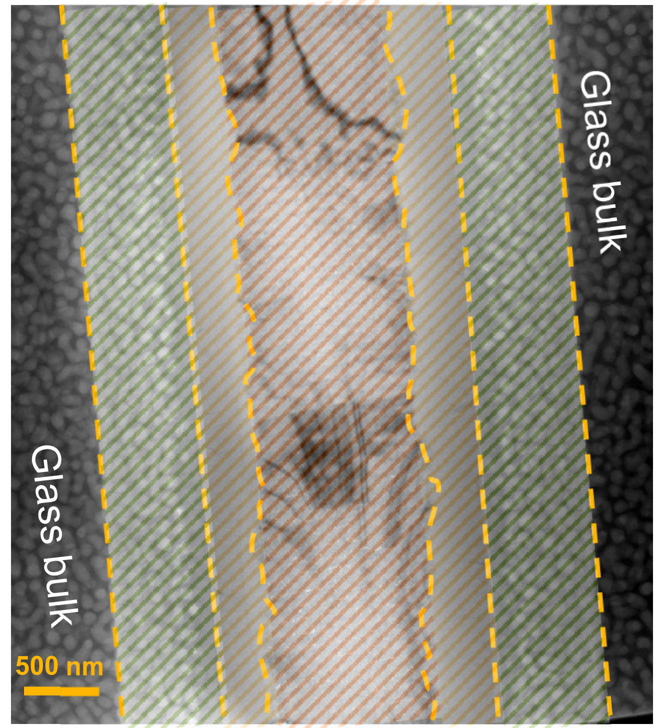
SEM-EDS (mass.%)
SiO_2: 61-68 %
CaO: 13-25 %
Al_2O_3: 5-9 %
FeO: 1-11 %

Cracks and cavities network filled with corrosion products

Typical crack



TEM picture



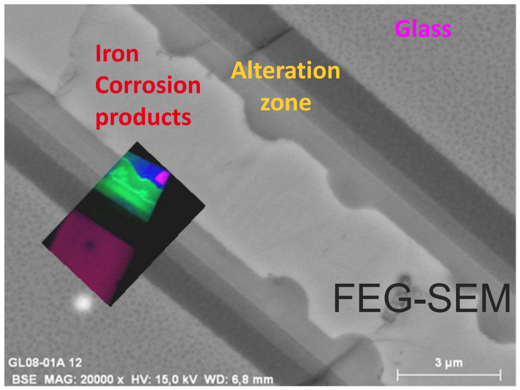
Siderite ($FeCO_3$)

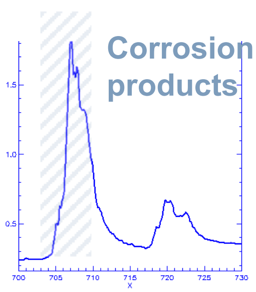
Glass alteration area

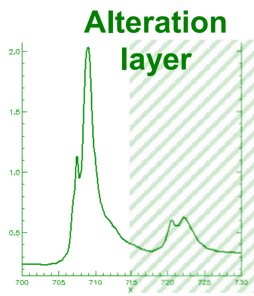
Iron silicate

Michelin et al, Chemical Geology 2015

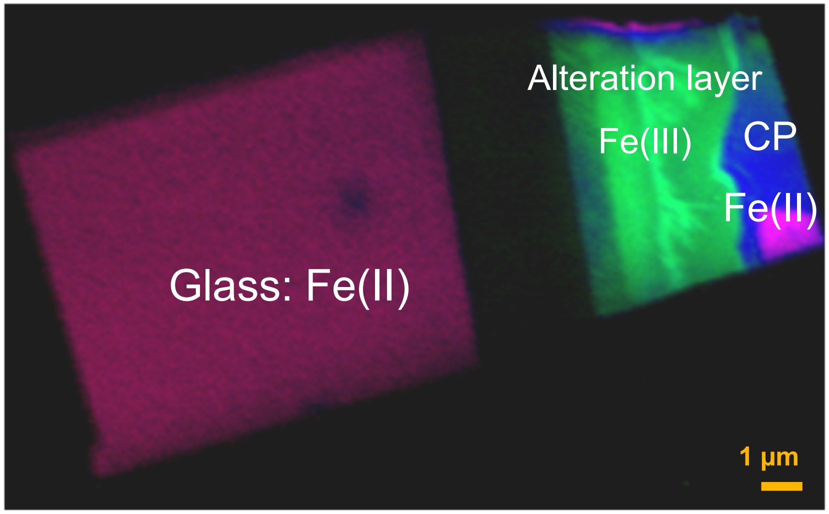
Long term alteration of glass in contact with iron







Oxidation state of Fe in the altered zones

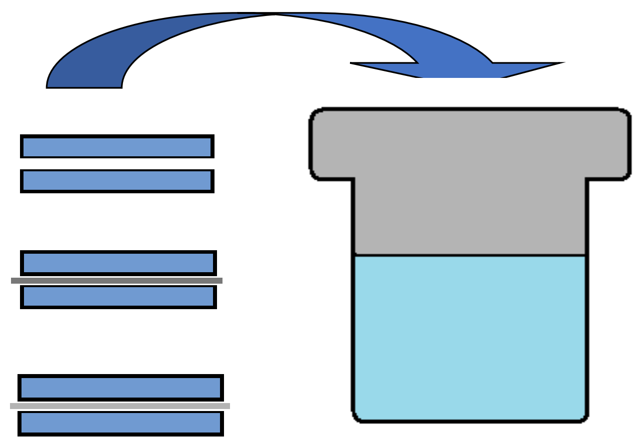


Michelin et al, Chemical Geology 2015

Lixiviation experiments on typical cracks

Objectives: determine alteration phenomenology and products

Experimental conditions
- Hermetic autoclave
- Water of the Glinet site
- T = 50°C
- Anoxic environment (CO_2/N_2)



2 glass monoliths

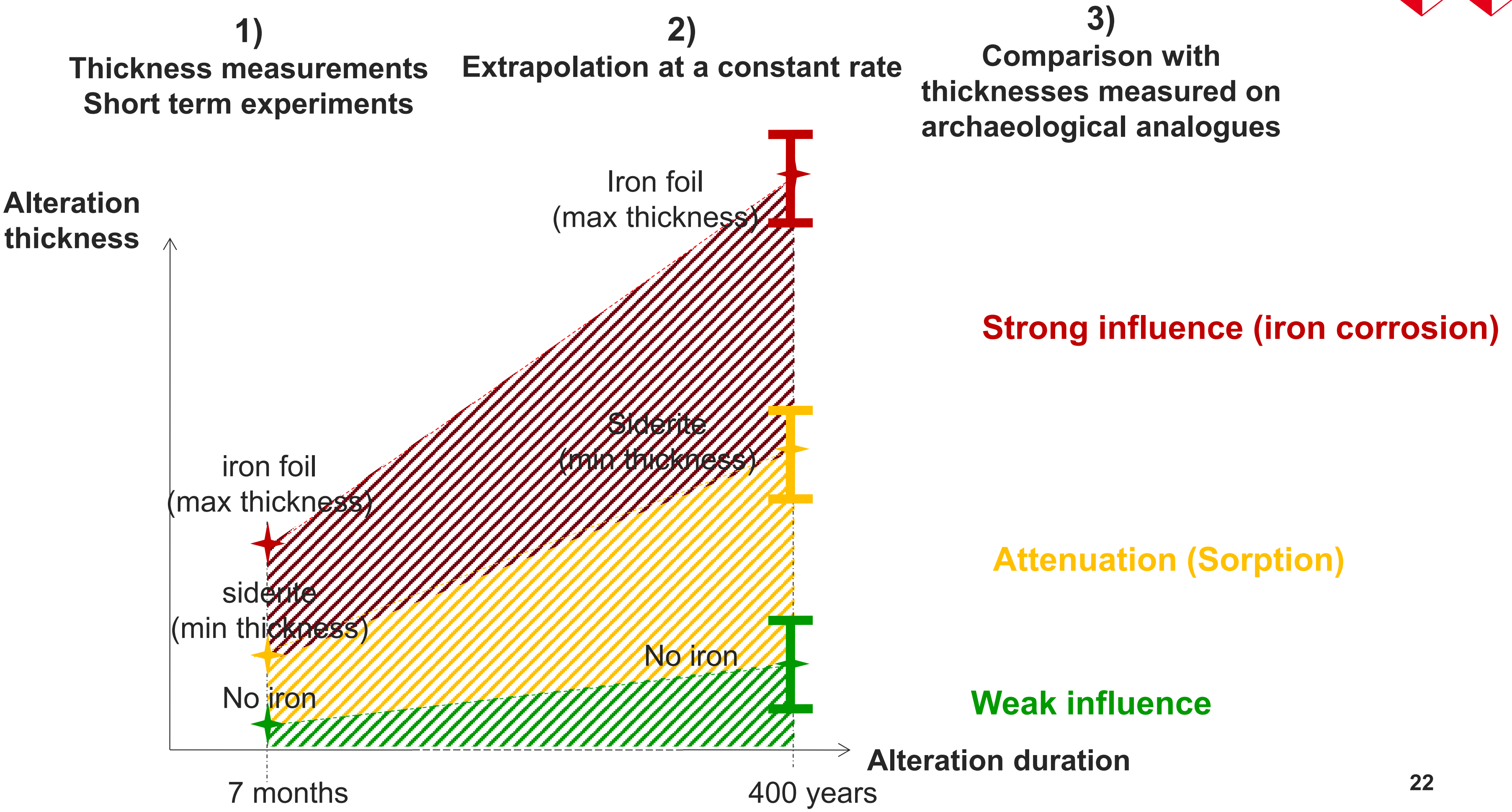
2 glass monoliths + iron foil — Iron corrosion

2 glass monoliths + siderite — Sorption

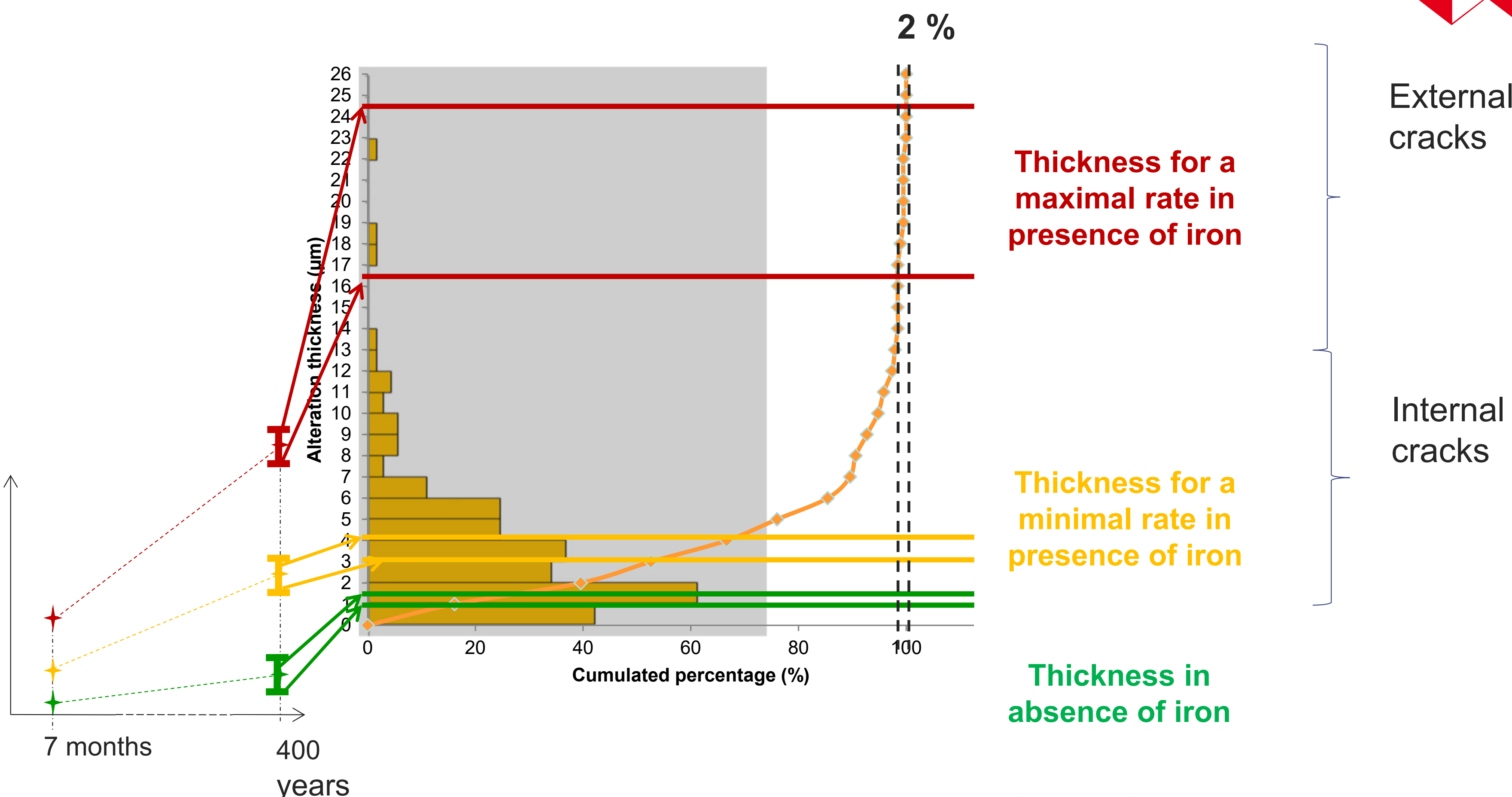
Michelin et al, Cor Sci 2013

Alteration Kinetic: long term

Prediction



Alteration Kinetic: long term



Michelin et al, Chemical Geology 2015

Perspectives

Literature survey

- Data available in the literature
  - glass stained windows studies from the literature
  - Archaeological Roman glass alteration: alteration in soil, in atmospheric conditions
- Synthesis of the data available in the experiments dedicated to analogy and in the literature to refine the prediction models

Characterisation of new analogues

- Basaltic glass samples from Iceland and Sicily aged from a few 10^3 yr to a few 10^6 yr in contact with fresh water (Iceland) and Ca-rich water (Sicily). Samples available at CEA Marcoule
- Alteration product characterisation (nature, composition, thickness, porosity, transtion with fresh glass).
  - SEM, HR-TEM
- Comparison with litteraure data (natural samples and samples aged in laboratory under controlled conditions)
- Discussion on rate-limiting mechanisms

Thank you for your attention

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Glass matrix characterisation

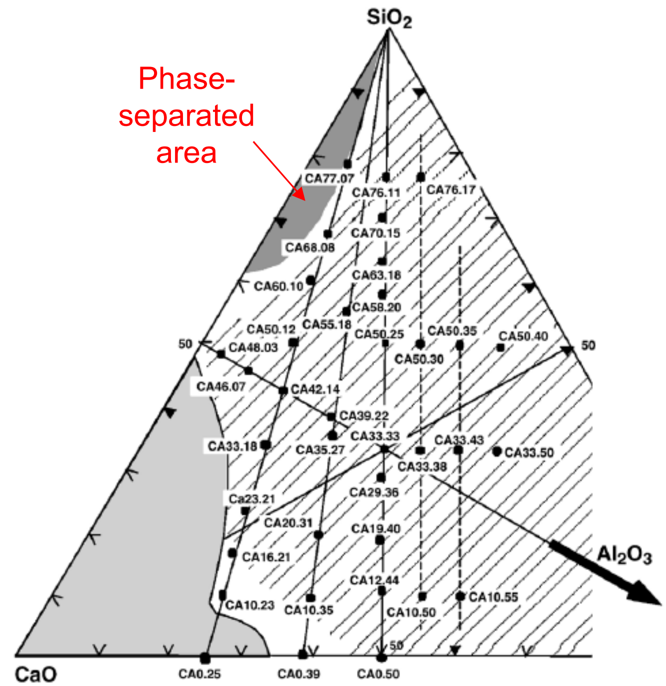
Glass composition

Opaque blue glasses

SEM-EDS analyses (wt%)

SiO_2 : 64-77 %
CaO : 13-21 %
Al_2O_3 : 5-9 %
Fe_2O_3/FeO : 1-8 %

• Globally homogeneous composition:
Calcium silicate glass rich in Fe



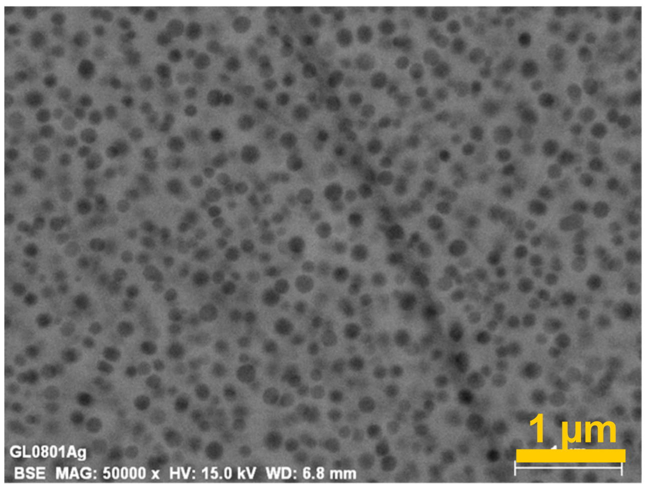
Slag composition reported in the ternary diagram

26

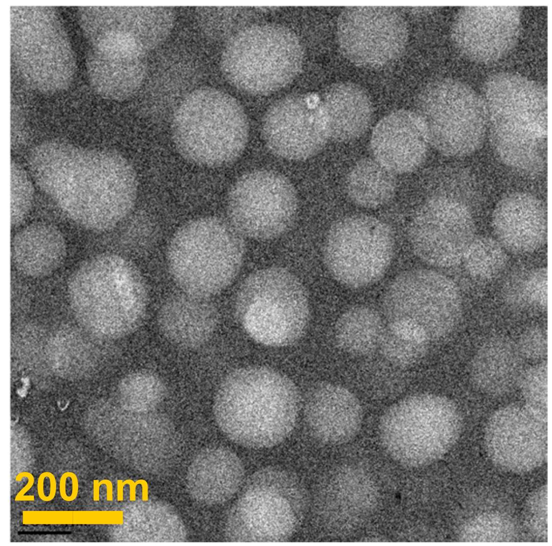
Glass matrix characterisation

Glass morphology

Phase-separated glass : 2 glass phases (with different composition) imbricated



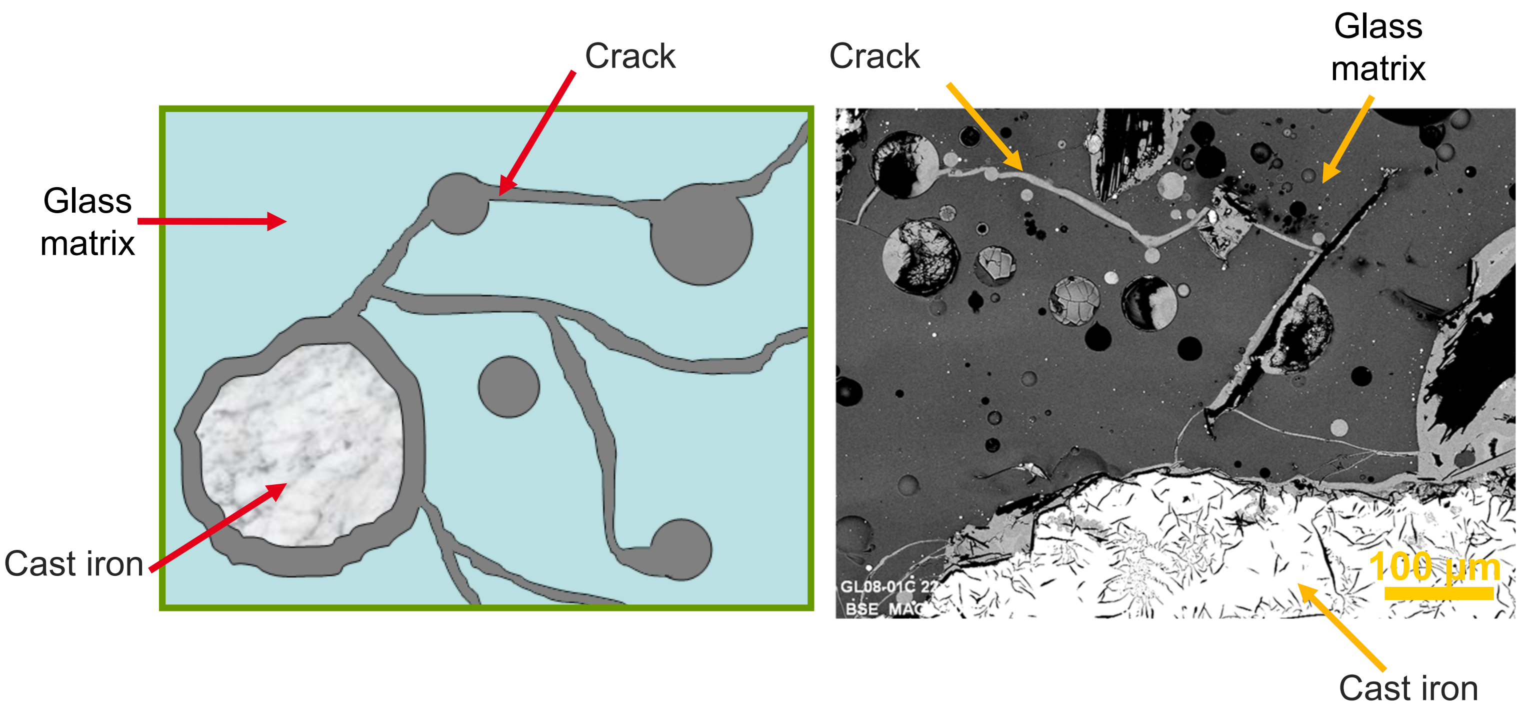
SEM-FEG picture



TEM picture

• Spheroids, Ø 100-200 nm, high in Si
• Glass matrix with Ca, Fe

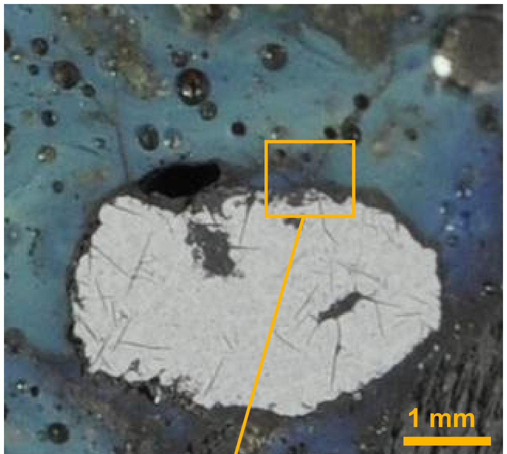
Corrosion products/glass interface characterisation

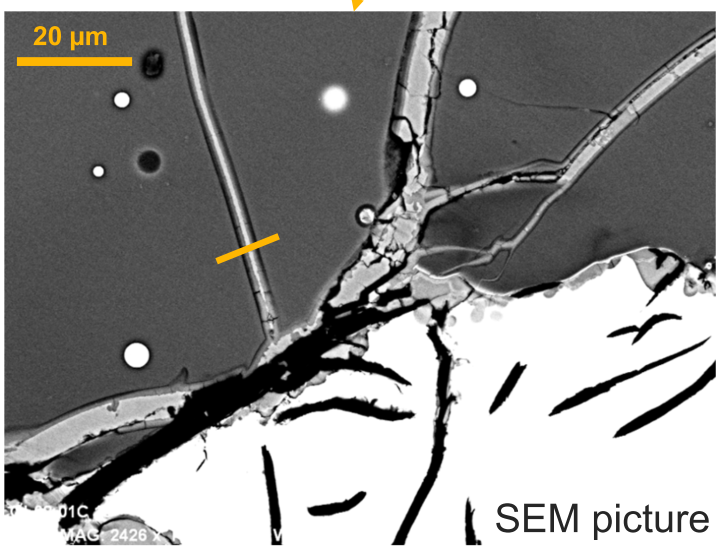


Cracks and cavities network filled with corrosion products

28

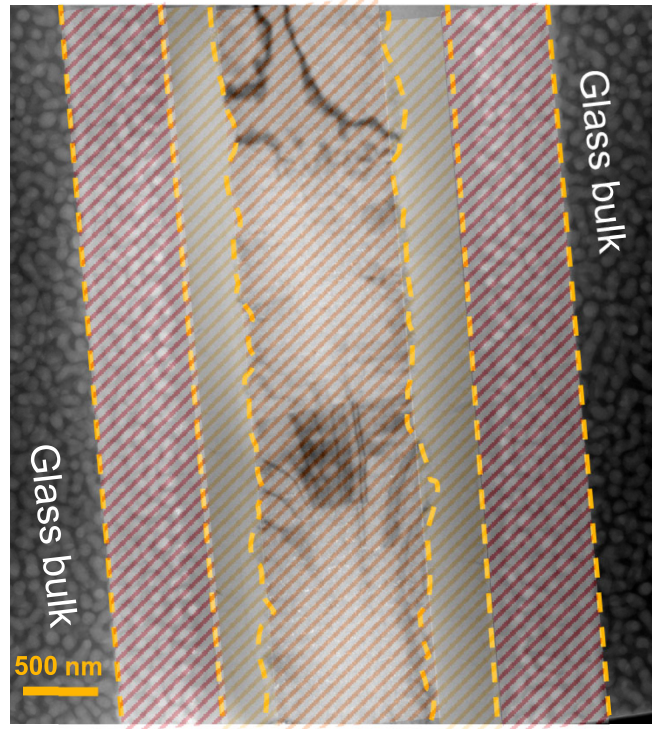
Typical crack





SEM picture

TEM picture

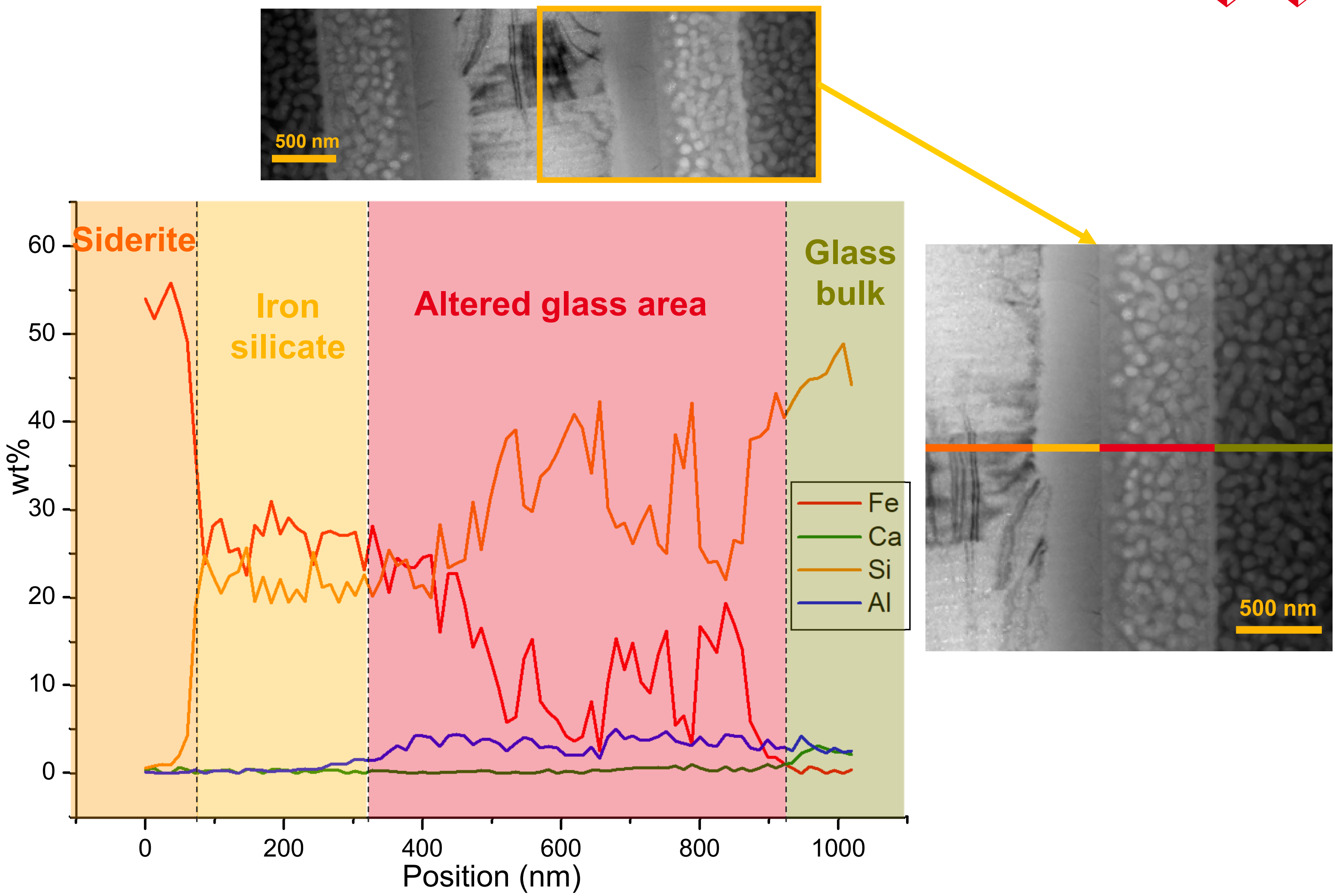


Siderite ($FeCO_3$)

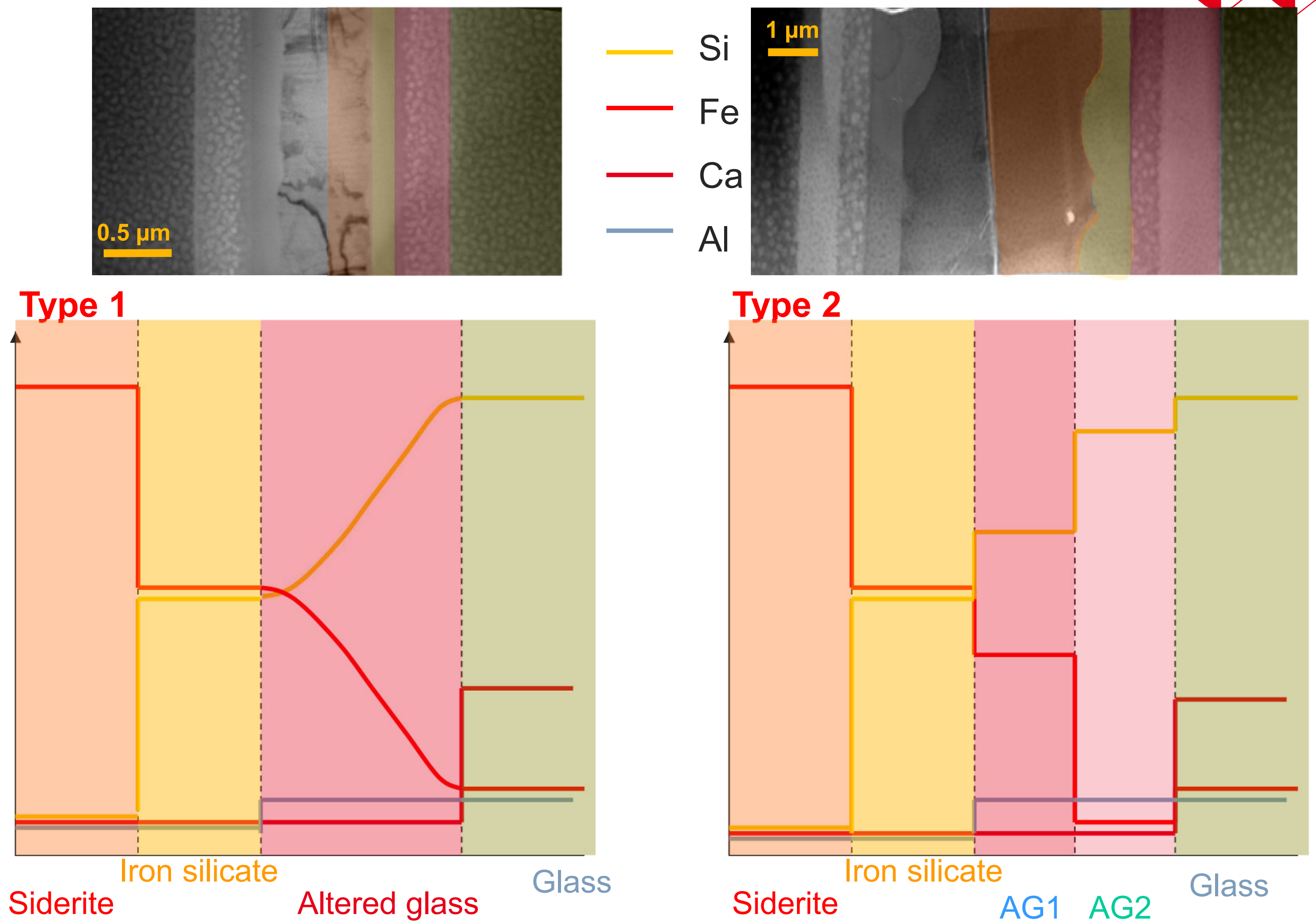
Glass alteration area

Iron silicate

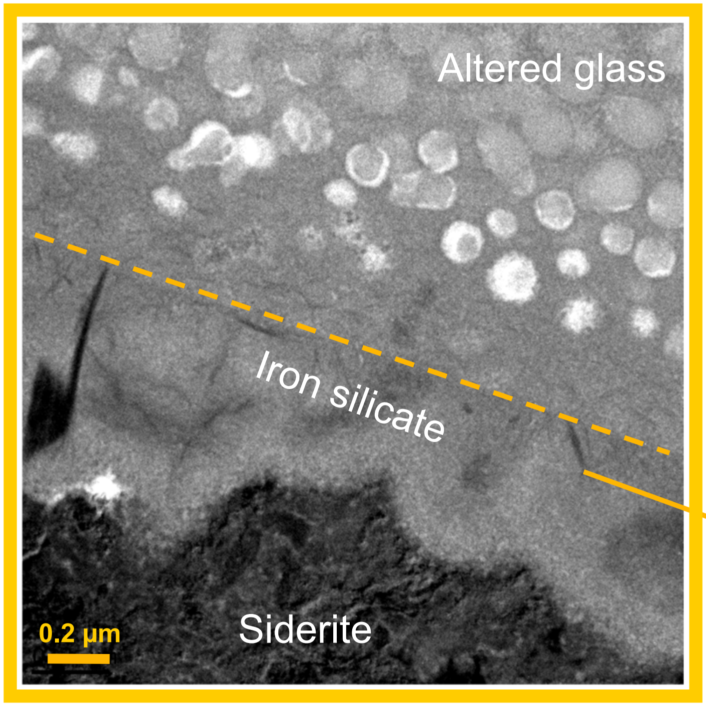
Composition profile

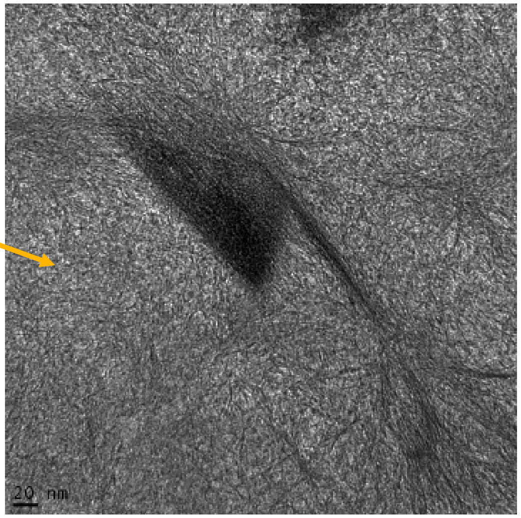


Several layout



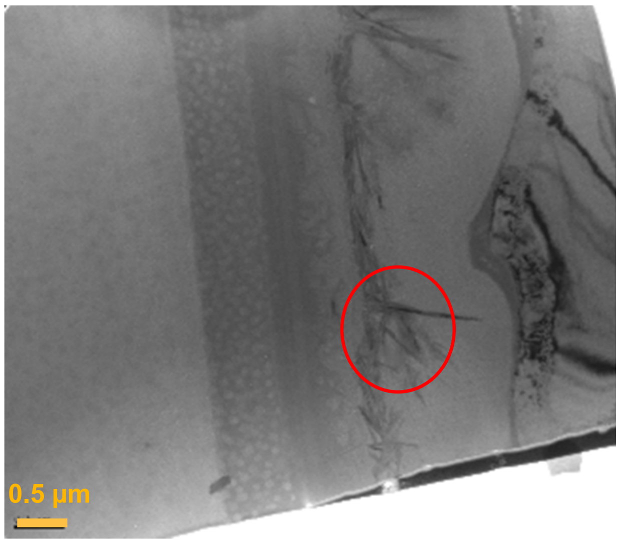
Fibrous area identification

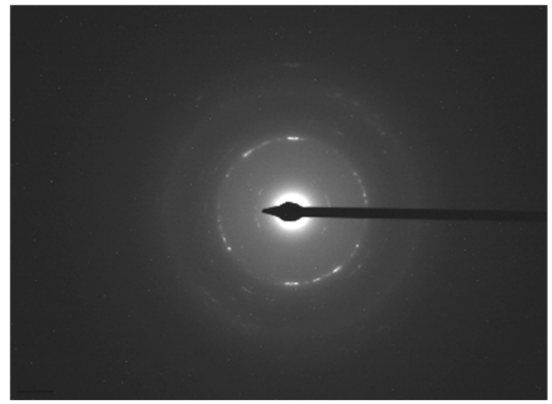


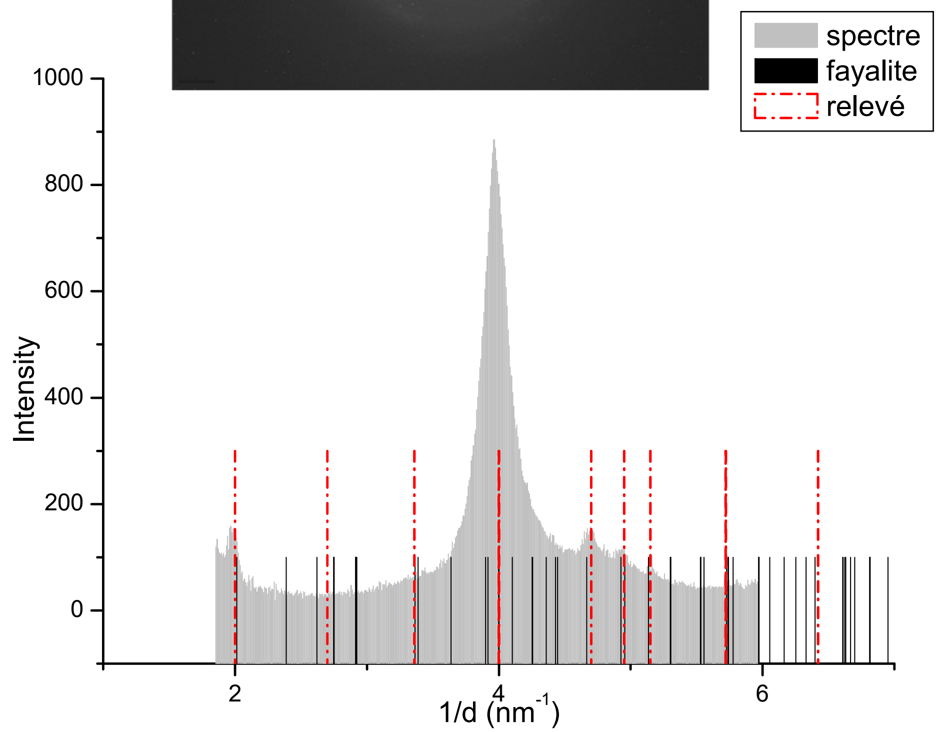


Dark crystallized fibrous area (Fe rich) : clay minerals ?

Fibrous area identification



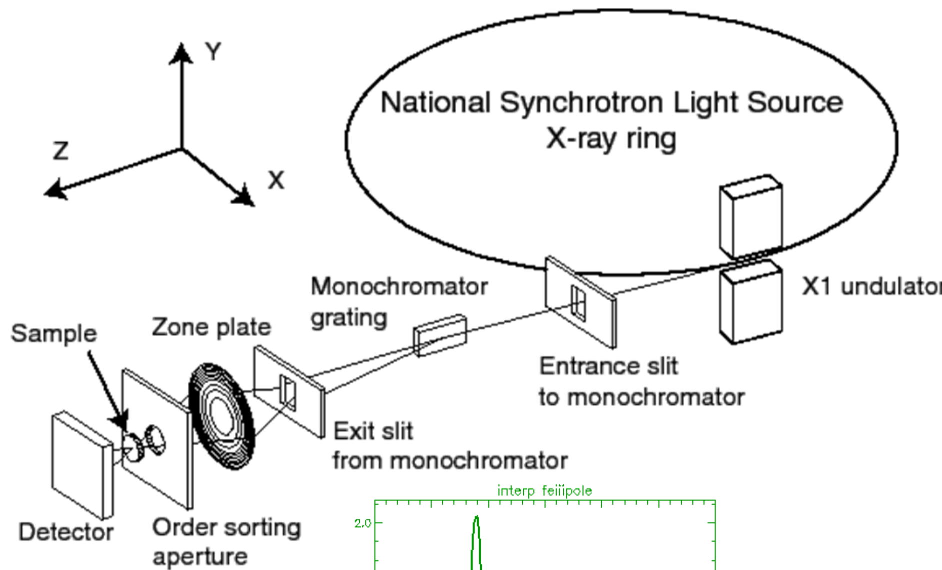


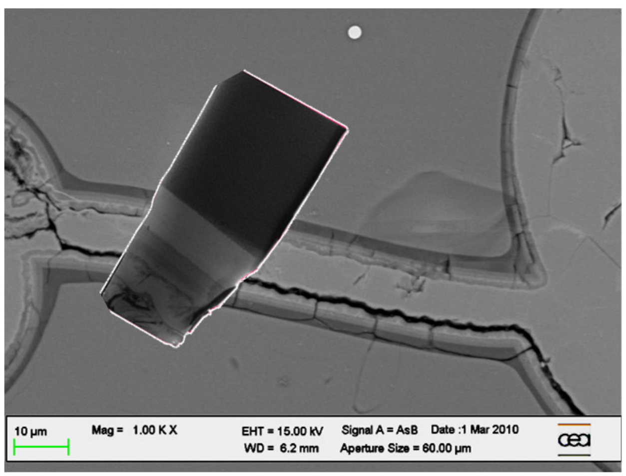


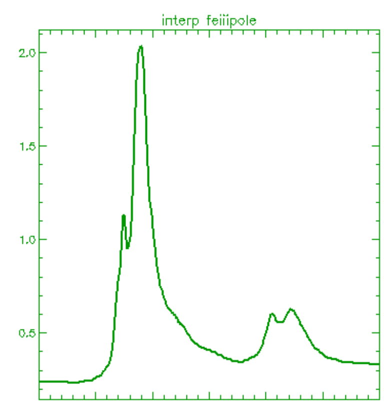
→ Fe_2SiO_4: Fayalite?

Scanning Transmission X-ray Microscope

Advanced Light Source (ALS), Lawrence Berkeley National Laboratory, USA

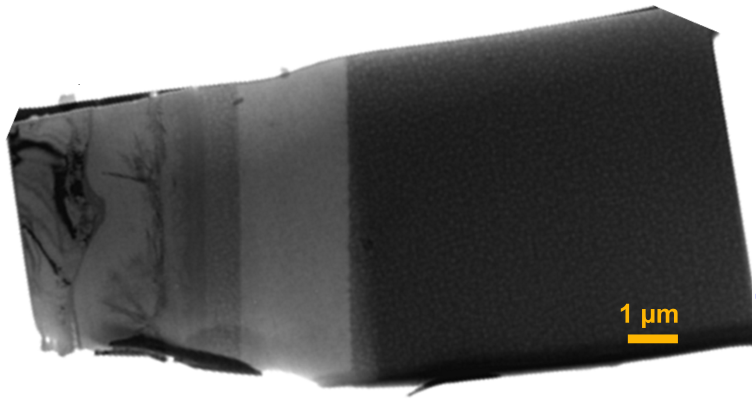


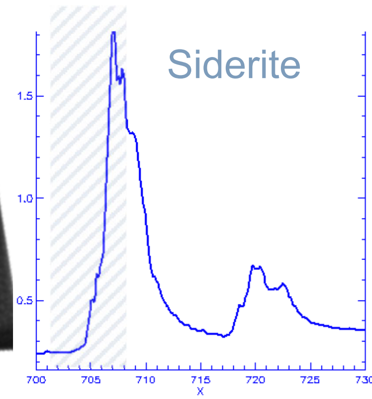


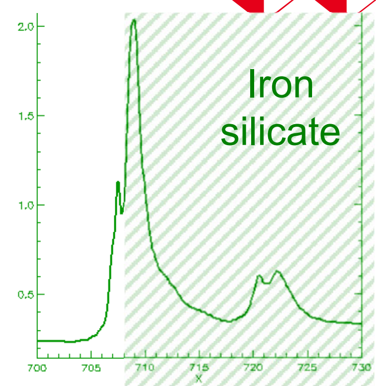


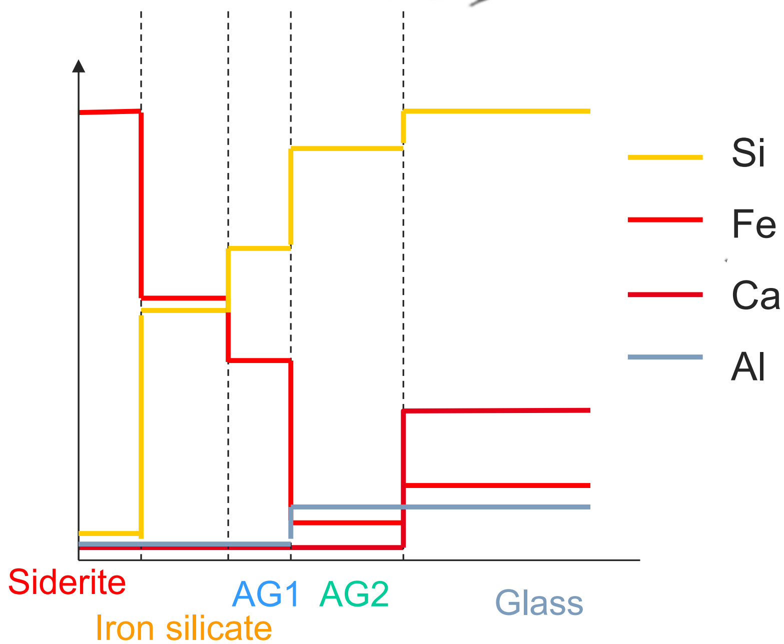
X-ray absorption spectrum on Fe $L_{2,3}$ edge

Fe III/Fe II mapping: first results





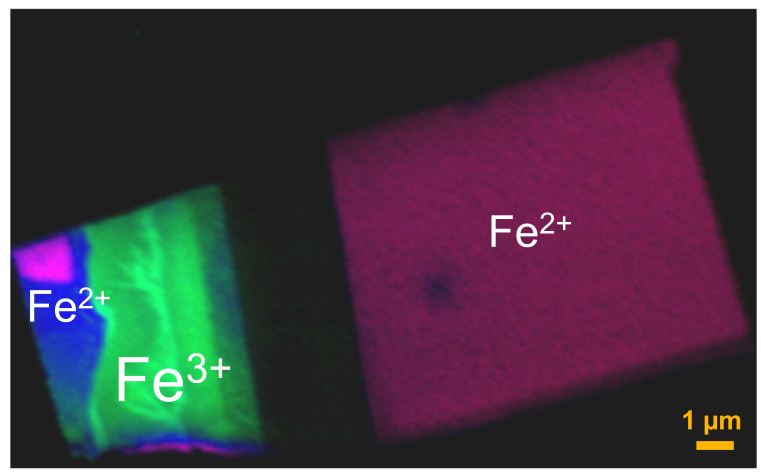




Red: 707.1-709 → Fe^{2+} in glass

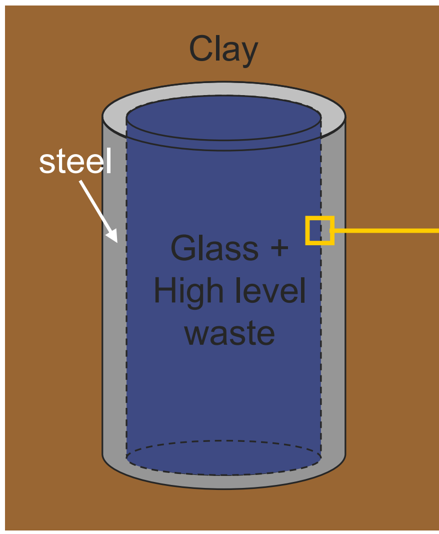
Green: 709-807.1 →Fe^{3+}

Blue: 707.1-700 → Fe^{2+} in siderite



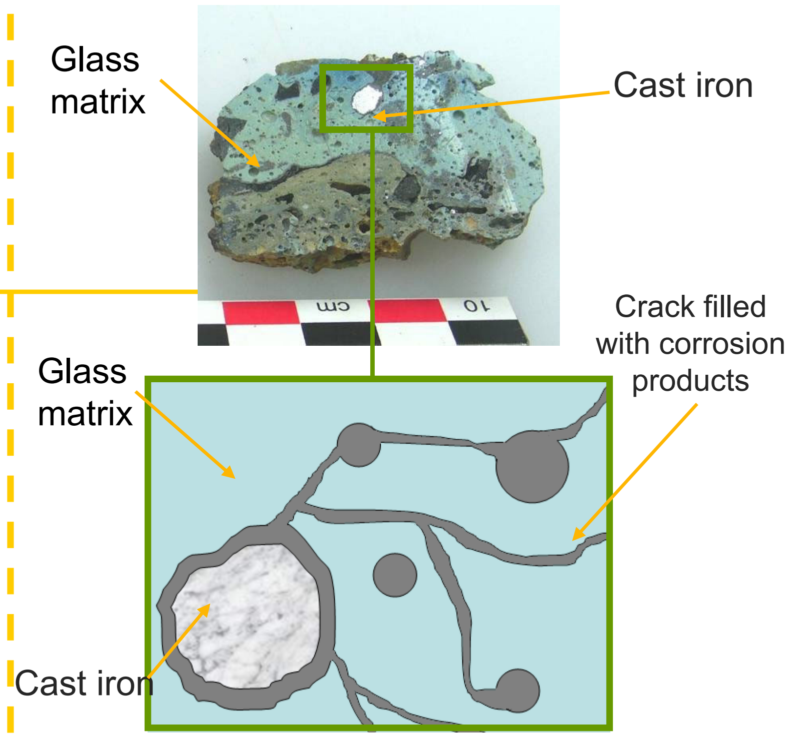
Slag: why an analogue of nuclear glass ?

Multi-barrier system for nuclear waste disposal



Long term alteration in anoxic medium

Archaeological analogues



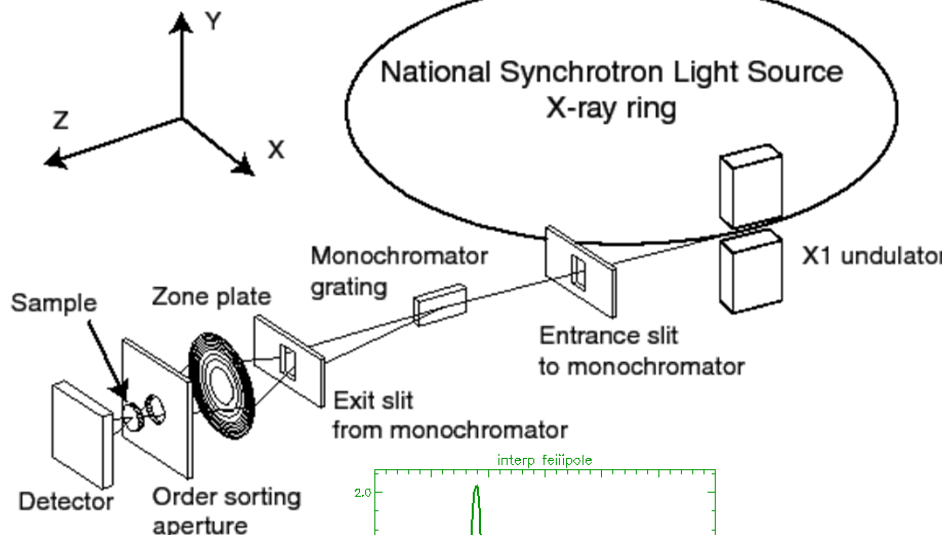
Altered 400 years, clay environment

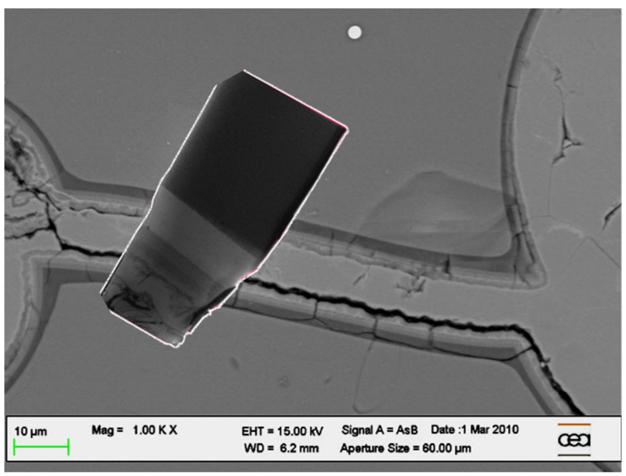
- Iron corrosion products in contact with glass
- Anoxic clay environment

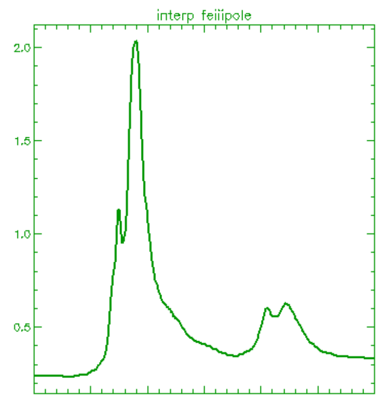
36

Scanning Transmission X-ray Microscope

Advanced Light Source (ALS), Lawrence Berkeley National Laboratory, USA

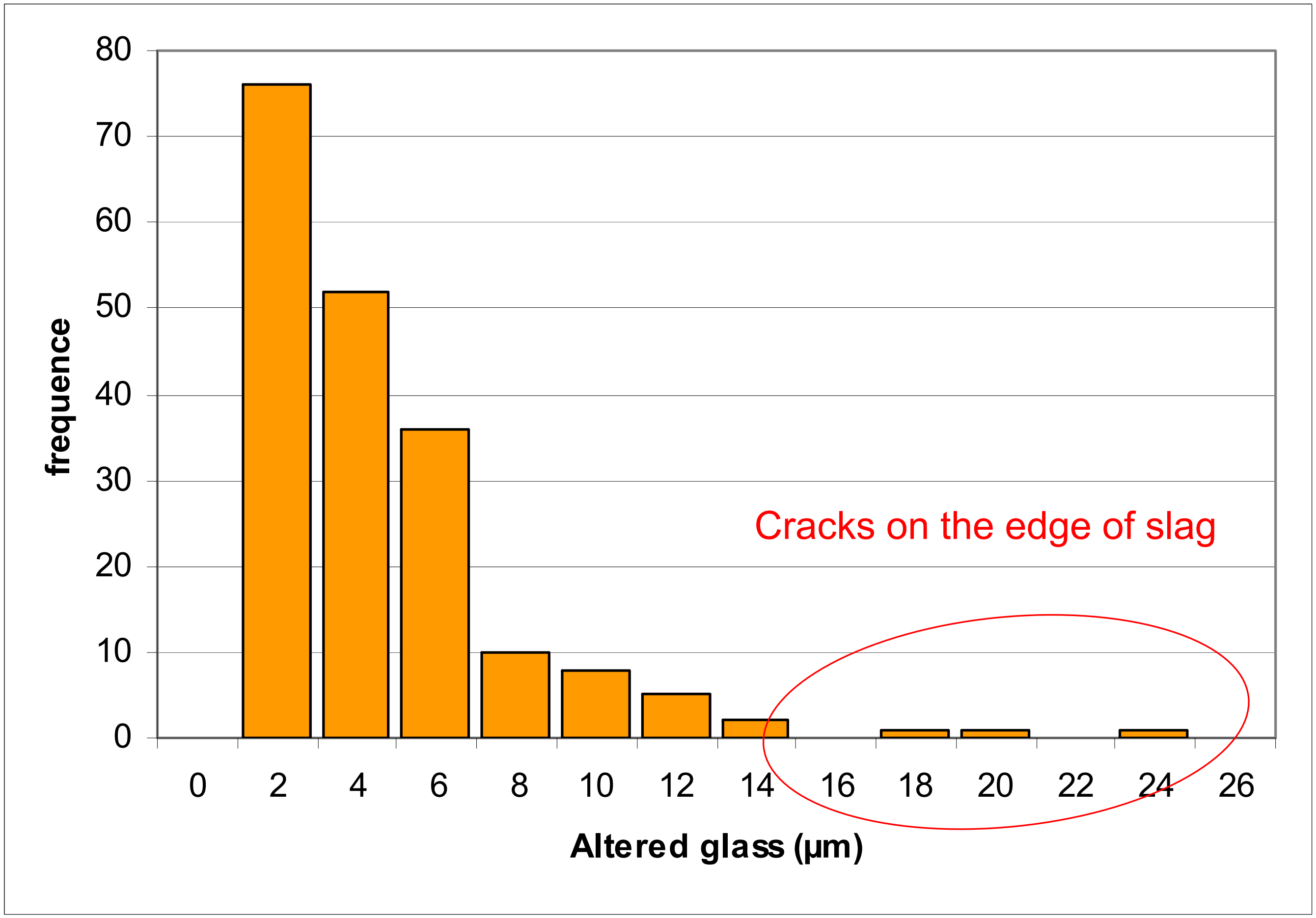






X-ray absorption spectrum on Fe $L_{2,3}$ edge

Altered glass thickness



Chemical modeling validation

Geochemical model coupled to transport

1. formation of a hydrated glass by interdiffusion, whose kinetics are controlled by a pH and temperature dependent diffusion coefficient;
2. the dissolution of the hydrated glass, whose kinetics are based on an affinity law;
3. the precipitation of secondary phases if thermodynamic saturation is reached.

Kinetic parameters were determined from experiments