Multiscale and isotopic analyses to understand the corrosion mechanisms of 400 years archaeological iron analogues

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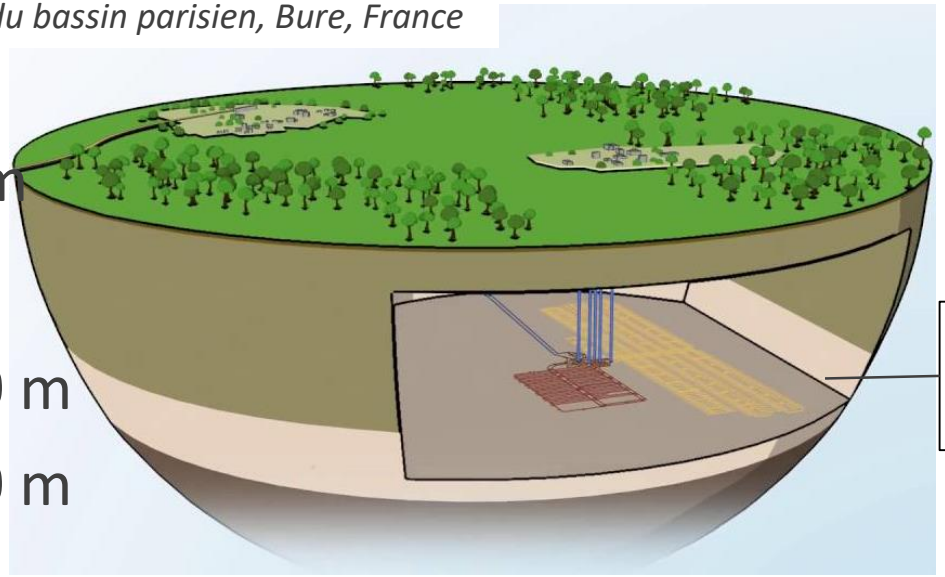
Scientific context: nuclear waste storage

ANDRA
Agence nationale pour la gestion des déchets radioactifs

Cigéo
Centre industriel de stockage géologique

Est du bassin parisien, Bure, France

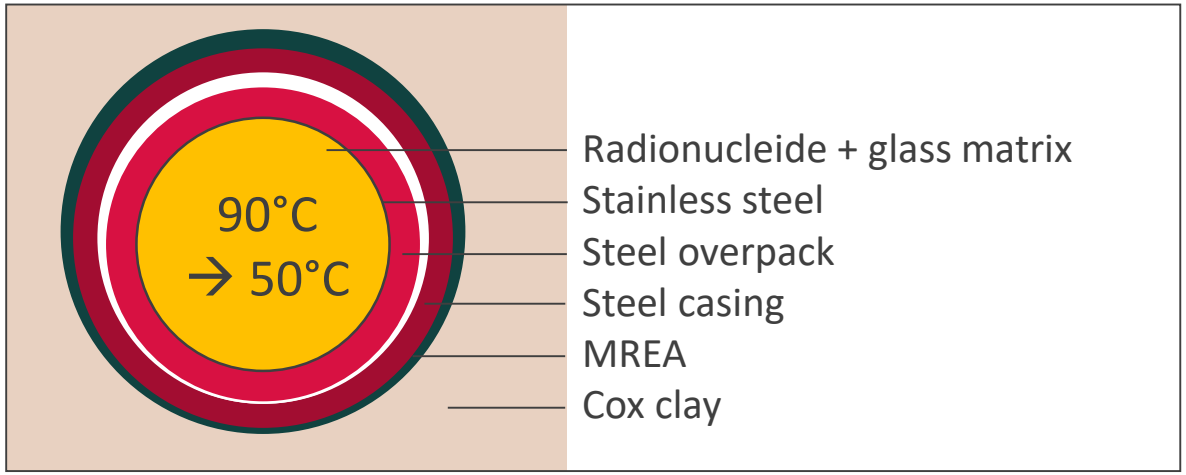


- Callovo-oxfordian : clayey medium
- Bure porewater : carbonated water

Scientific context: nuclear waste storage

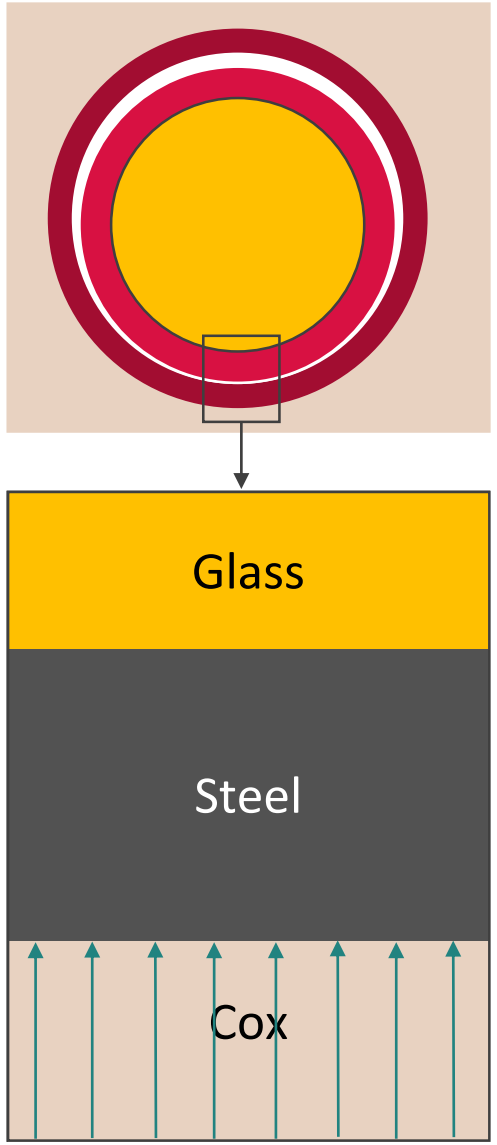
HAVL overpack

Schematic diagram

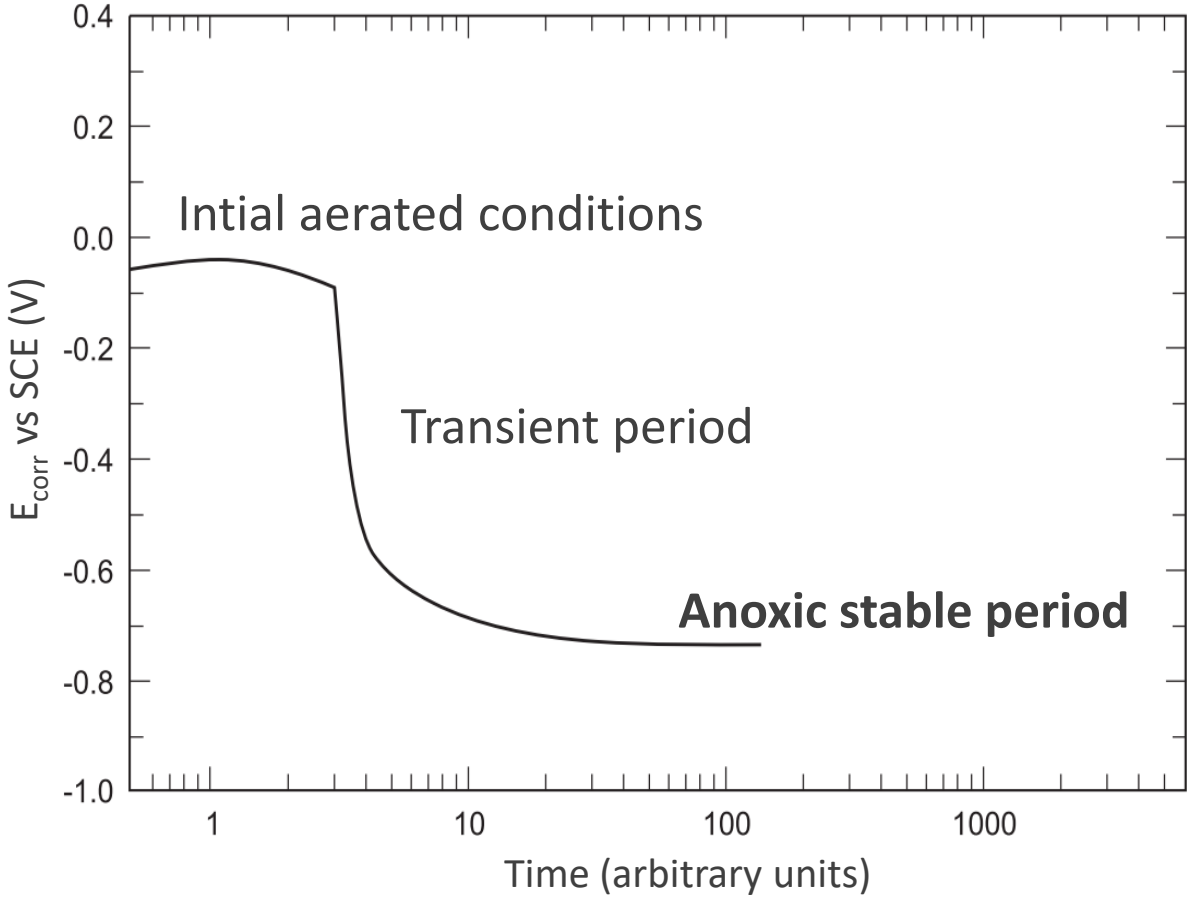


Over 1000 years

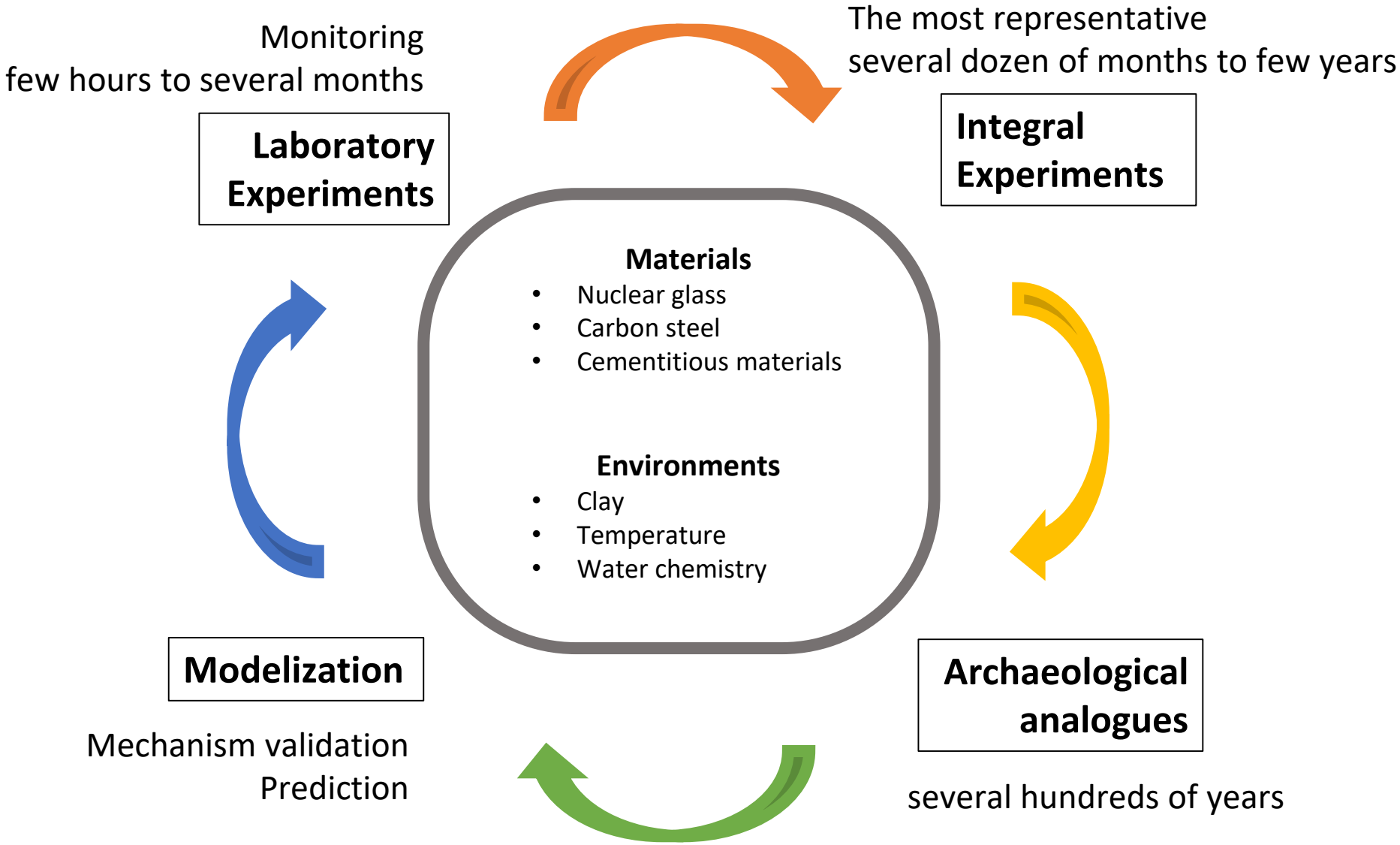
Storage context



Saturation by Cox porewater
Corrosion in anoxic carbonated solution

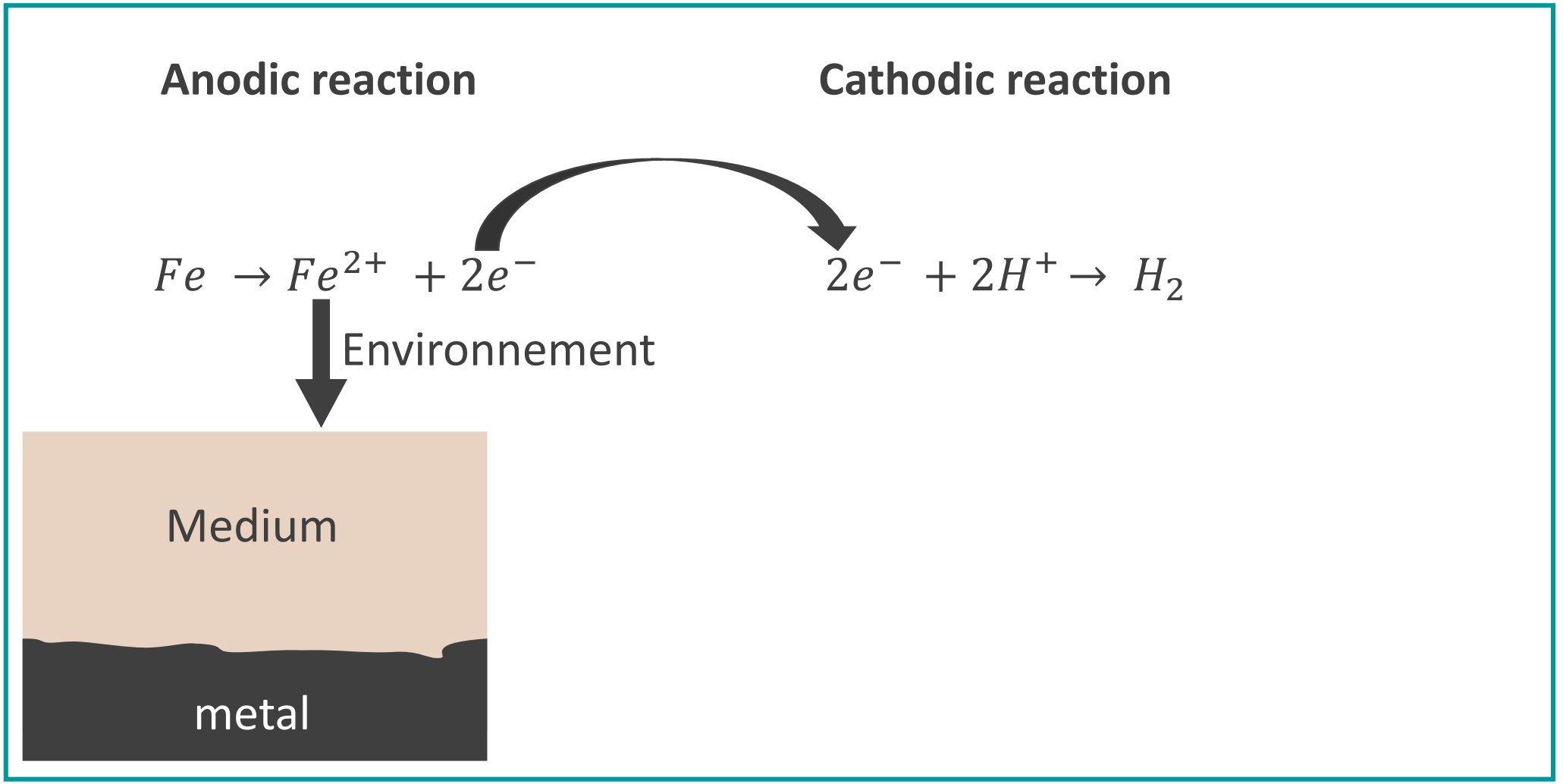


Long term corrosion study: general methodology



Long term corrosion of steel

Anoxic saturated medium



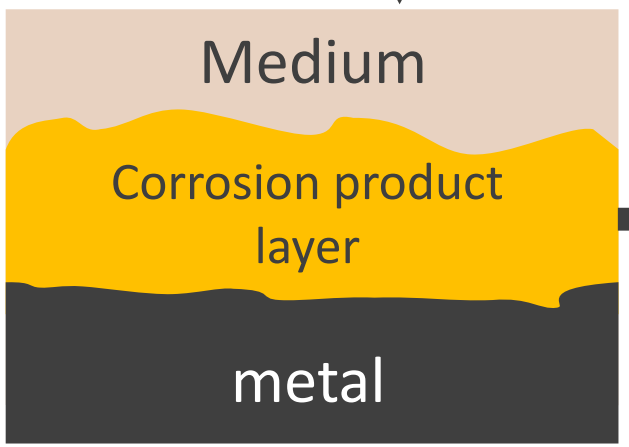
Long term corrosion of steel

Anoxic saturated medium

Anodic reaction **Cathodic reaction**

$Fe \rightarrow Fe^{2+} + 2e^-$ $2e^- + 2H^+ \rightarrow H_2$

Environnement

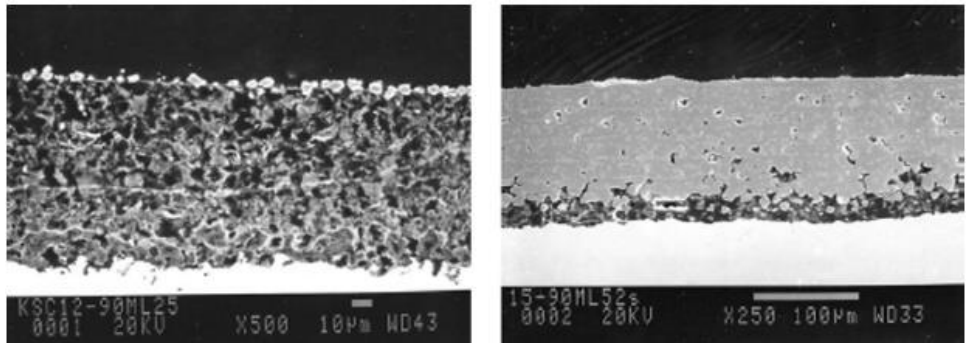


Modification of iron/medium interaction
Physico-chemical properties of the CPL

State of the art: corrosion mechanisms at the first steps
Passive layer formation

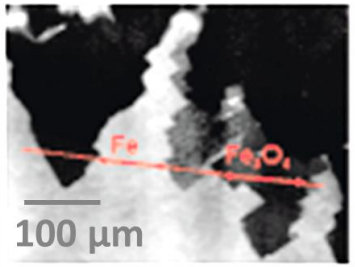
▶ Short term laboratory experiments (few hours to days)

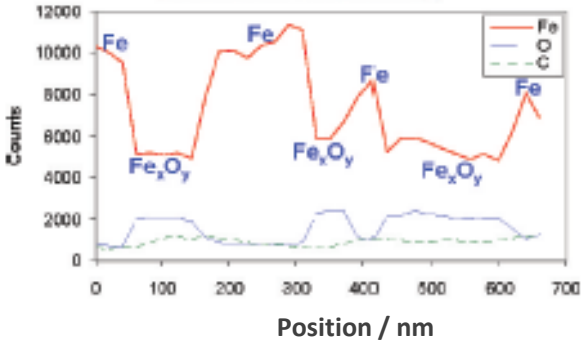
- In carbonate anoxic solution
  - **Siderite protective layer**
  - Protectiveness varies with T, P, P_{CO2}



Review: Barker et al 2018

- In carbonate anoxic solution
  - **TEM-EDS and GIXRD**
  - FexOy





Han et al, Ind. Eng. Chem. Res. 2010

- Metal sheet corroded in a clayey anoxic environment
  - **Electrochemical Impedance Spectroscopy**
  - **Conductive and compact submicronic layer at the metal interface**

Bataillon et al J Phys IV, 2001

State of the art : Oxide interfacial layer

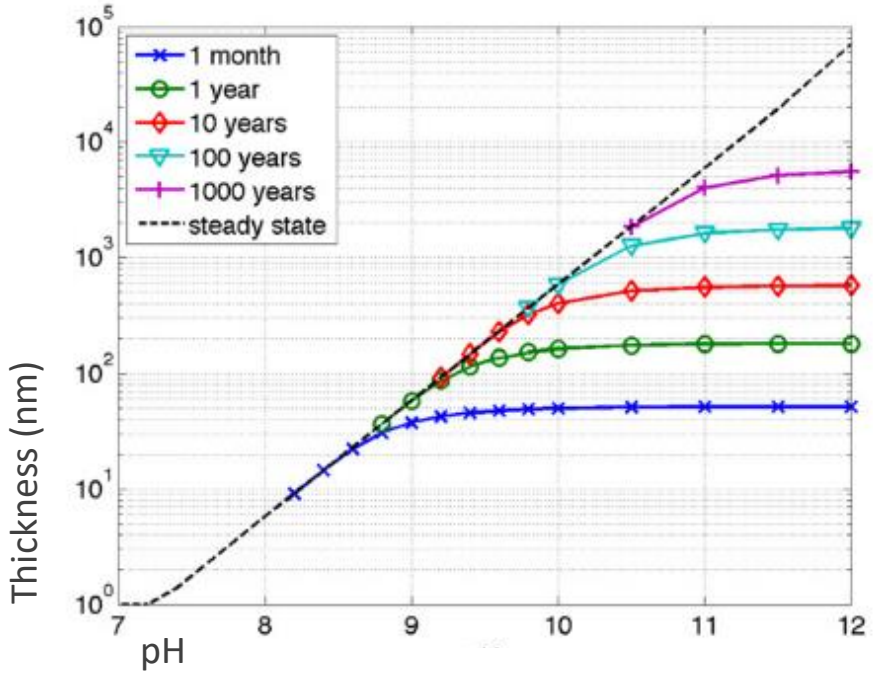
- Short term laboratory experiments (several months to years)

	Laboratory experiments	*Integral experiments*			
		Laboratory experiments		*URL experiments (Bure)*	
	BAT-X80	**ARCORR 2008**	**CORRIDA**	**EST44834 / MCO A139**	**EST4521 / MCO A143**
Parameters • Time • Type of substrate • Type of environment	48 months  Ferrite 0,0002%m. C - Argilite MX 80 (3%) - Synt. Bure water - 90°C	24 months  Ferrite 0,0002%m. C - Argilite COx-Bure-445m - Synt. Bure porewater - 90°C	40 months  Steel 0,12%m. C - Argilite COx-Bure - Synt. Bure water - 90°C	25 months Steel 0,16%m. C - COx clay formation - Bure pore water - 85°C	28 months  Steel 0,16%m. C - COx clay formation - Bure pore water - 85°C
Nanometric layer with variable thickness	Magnetite-Maghemite 400 - 1000 nm	Maghemite 100 – 400 nm	Maghemite ≥ 100 nm ?	Maghemite ≤ 100 nm	Maghemite ≤ 50 nm

Leon. Andra report 2013

State of the art : Oxide interfacial layer

- **Modelisation: Corrosion modelling (adapted from the Point Defect Model)**



Bataillon et al. Journal of Computational 2012

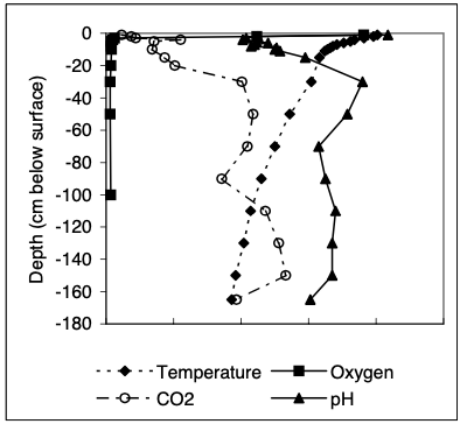
- *Oxide layer at the M/CPL interface that could impact the corrosion rate*
- *Size and impact on the corrosion rate depend on pH and time*

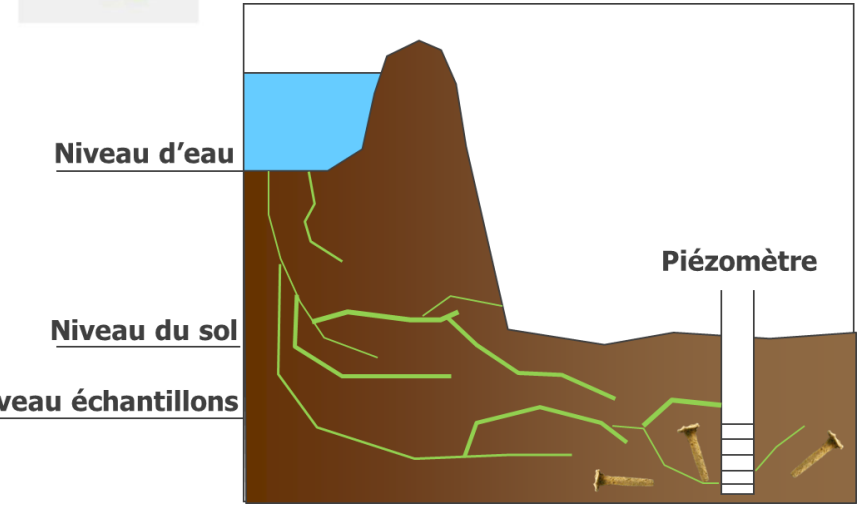
Methodology developped for archaeological analogue studies

Archaeological analogue sites: anoxic conditions

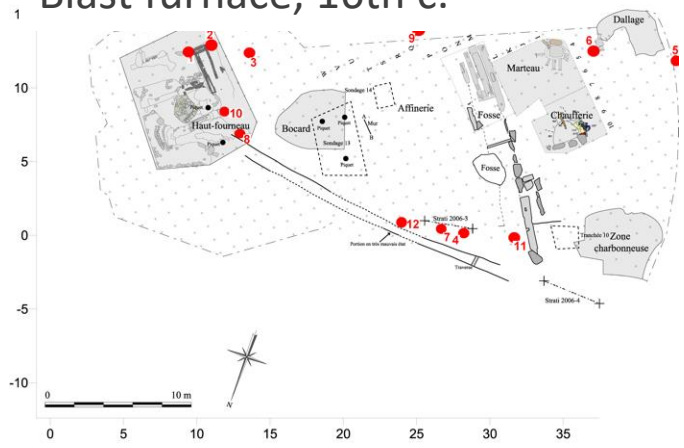
Archaeological site of Glinet, France (450 years)

Site of Nydam Mose (Denmark)
4th cent AD

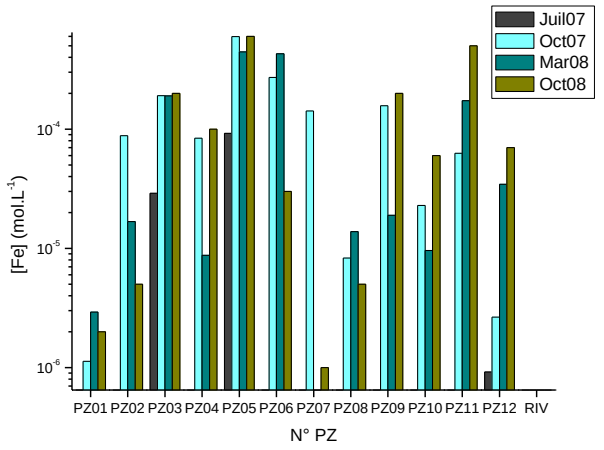




Blast furnace, 16th c.

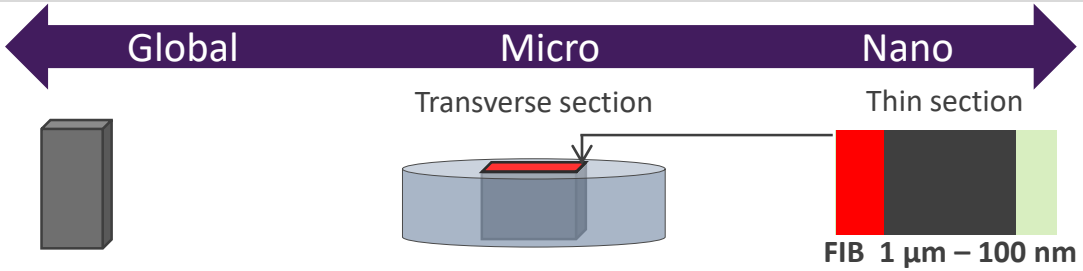


Saheb et al, Applied geochemistry, 2014

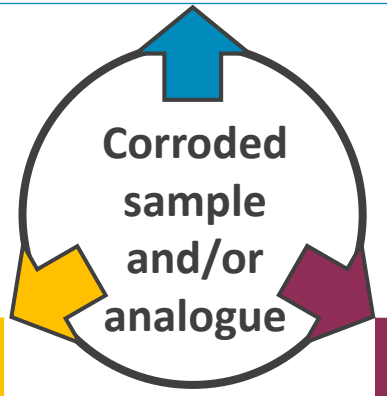


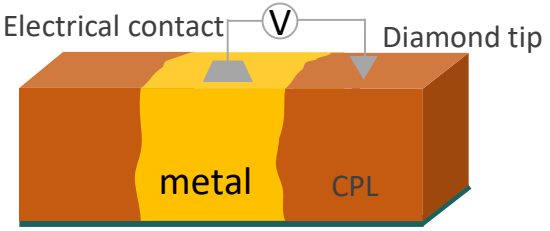
Collaboration National Museum of Denmark

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

Characterisation of the electronic transport M/CPL		
global	i/V	Conductivity
nano	**C-AFM**	

$$Fe \rightarrow Fe^{2+} + 2e^- \qquad 2e^- + 2H^+ \rightarrow H_2$$

Experimental protocols

1. Deuterated synthetic anoxic solution

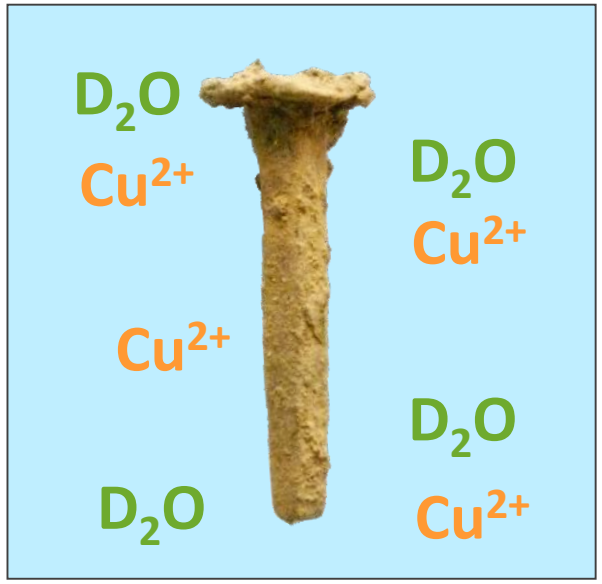
Water labeling

2. $CuCl_2$ anoxic solution

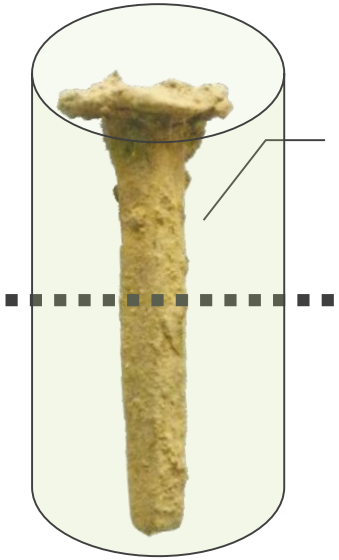
Electron marking

3. Amperometric analyses in anoxic solution

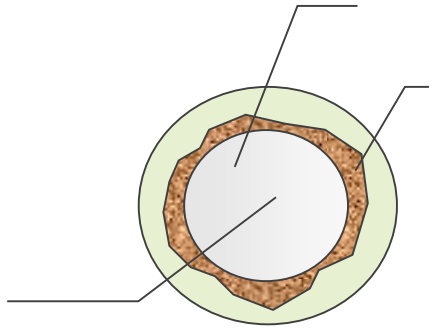
Rate limiting step of the cathodic reaction



Several weeks to several months



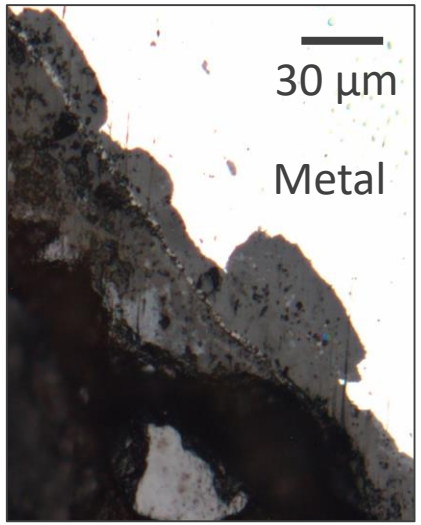
RESIN

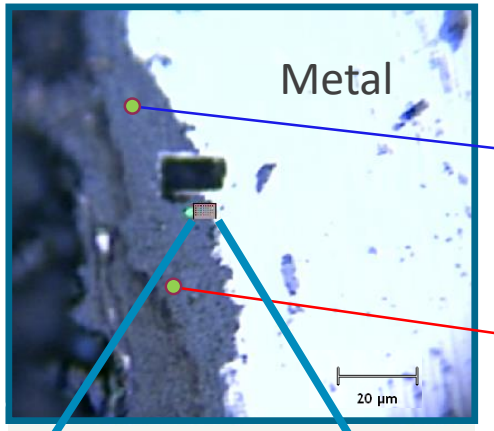


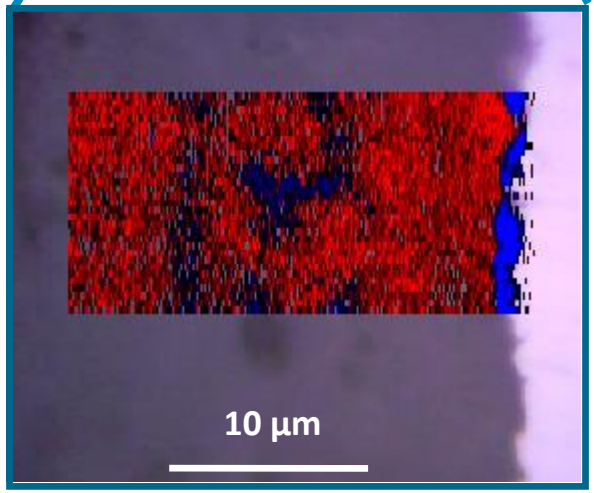
Results

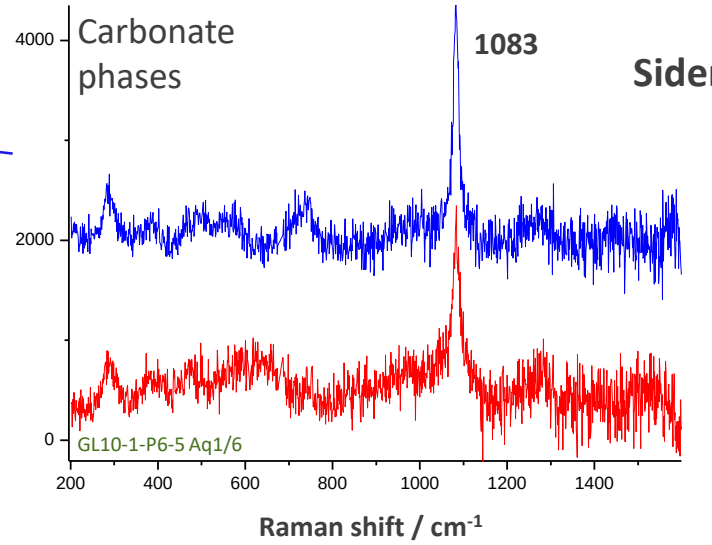
Corrosion scale characterisation: micrometric scale

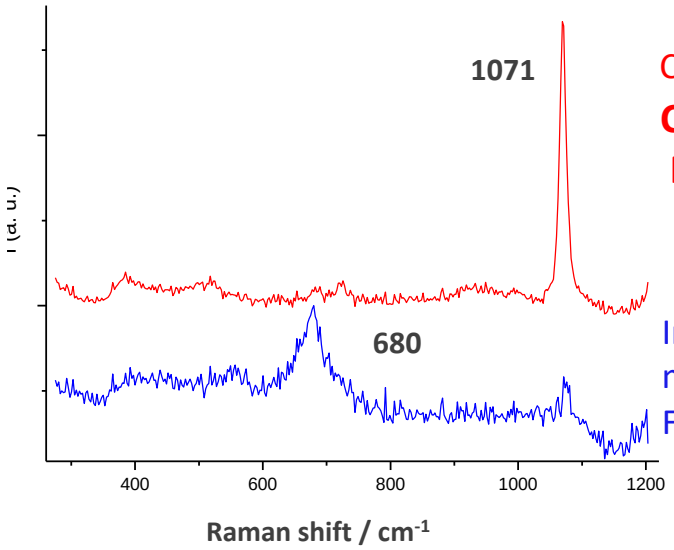
Archaeological site of Glinet (450 years)











Carbonates

Chukanovite

$Fe_2(OH)_2CO_3$

Iron oxides mix:

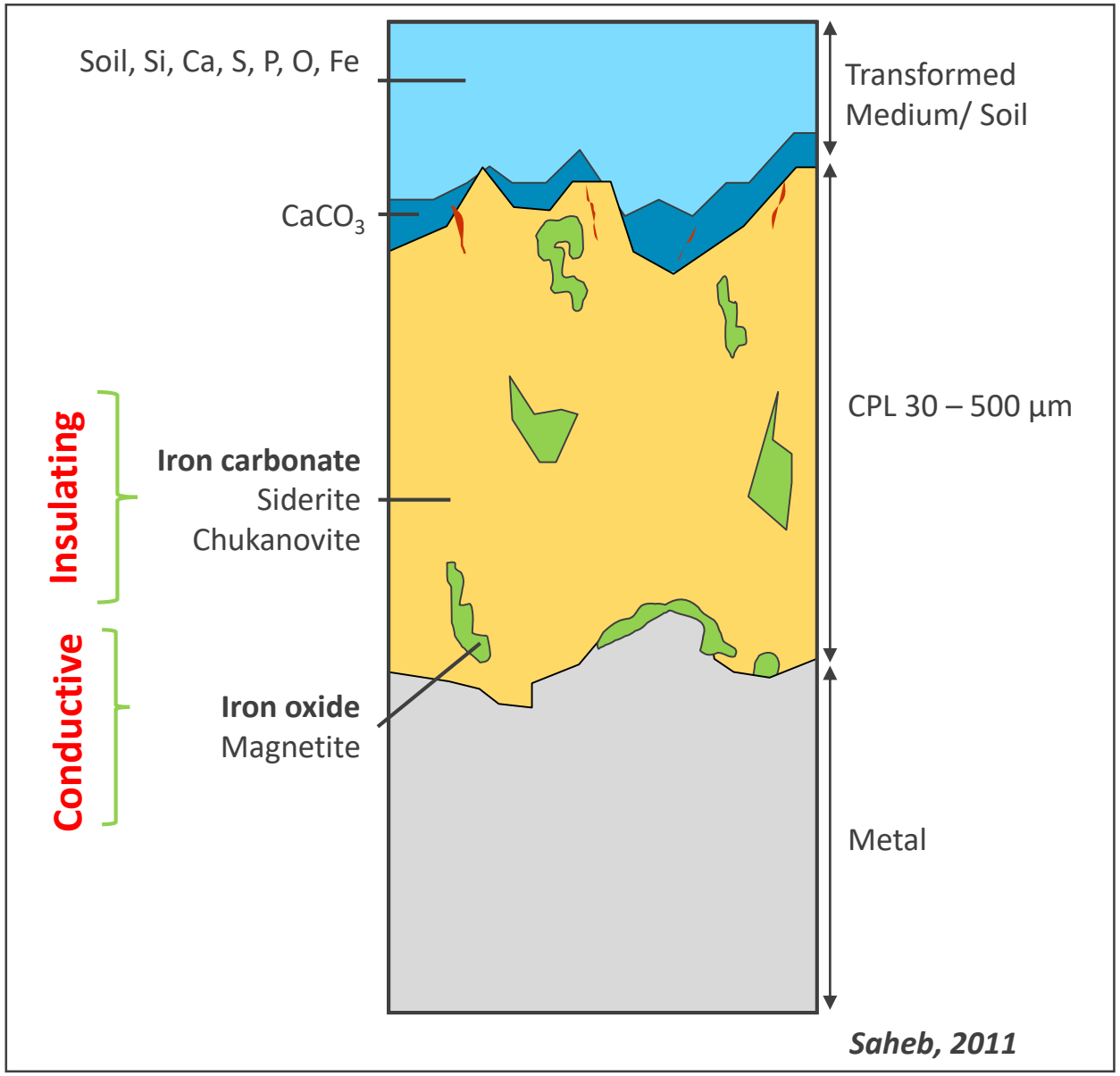
magnetite/maghemite

Fe_3O_4 / γ-Fe_2O_3

Raman spectroscopy HR
Ø 0.7 µm

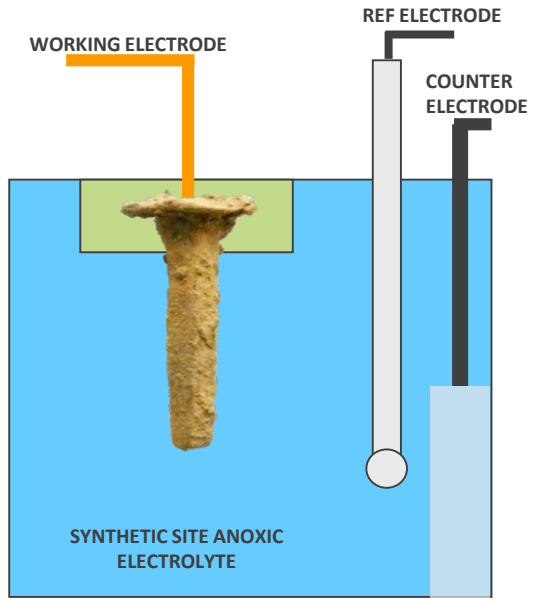
Morphology and nature of the CPL: micrometric scale

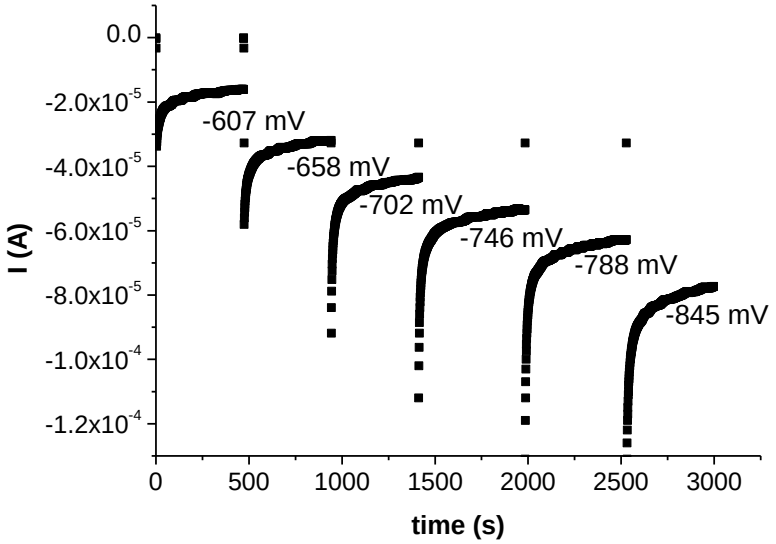
→ Influence of the CPL on the corrosion processes?

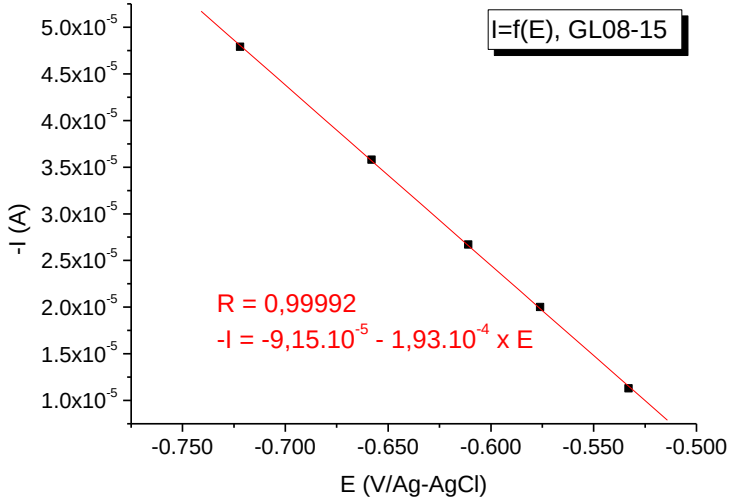


Rate limiting step of the cathodic reaction

- **Archaeological analogues, 450 years, anoxic carbonated medium**
  - Chronoamperometry: Ohmic behaviour, Electron flux controlled by a compact layer

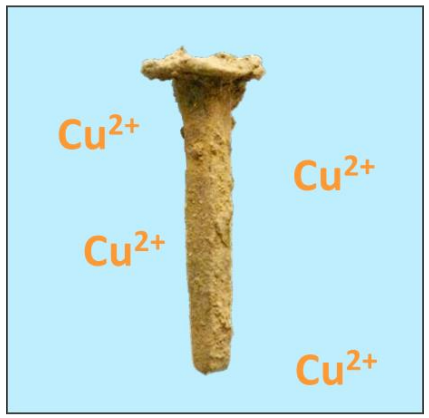






$$Fe \rightarrow Fe^{2+} + 2e^- \qquad 2e^- + 2H^+ \rightarrow H_2$$

Location of the cathodic reaction



- 2 weeks
- With or without E applied
- $CuCl_2$ 5.10^{-3} mol.L^{-1}

Anodic reaction

$$Fe \rightarrow Fe^{2+} + 2e^-$$

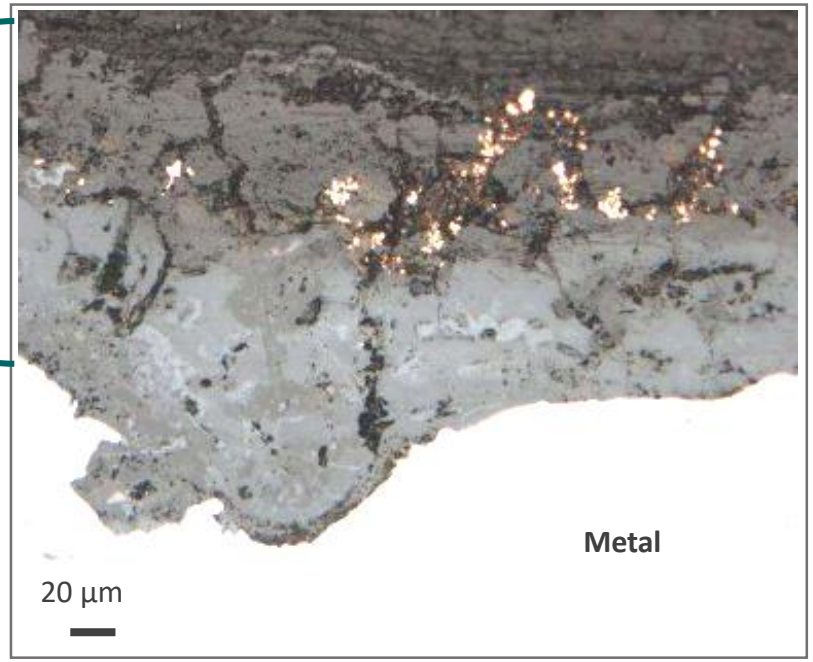
Cathodic reaction

$$2H^+ + e^- \rightarrow H_2$$

$$Cu^{2+} + 2e^- \rightarrow Cu$$

Location of the cathodic reaction thanks to copper tracing experiment

Cu^0 In the CPL



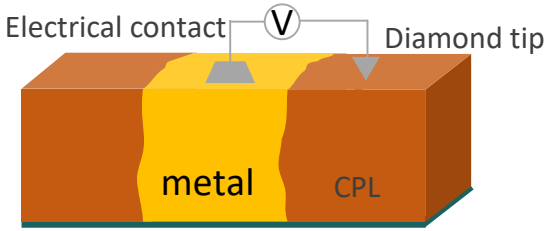
Electron consumption in the whole thickness of the CPL

Electron transfer in the whole thickness of the CPL

Saheb et al. Corrosion Science 2011

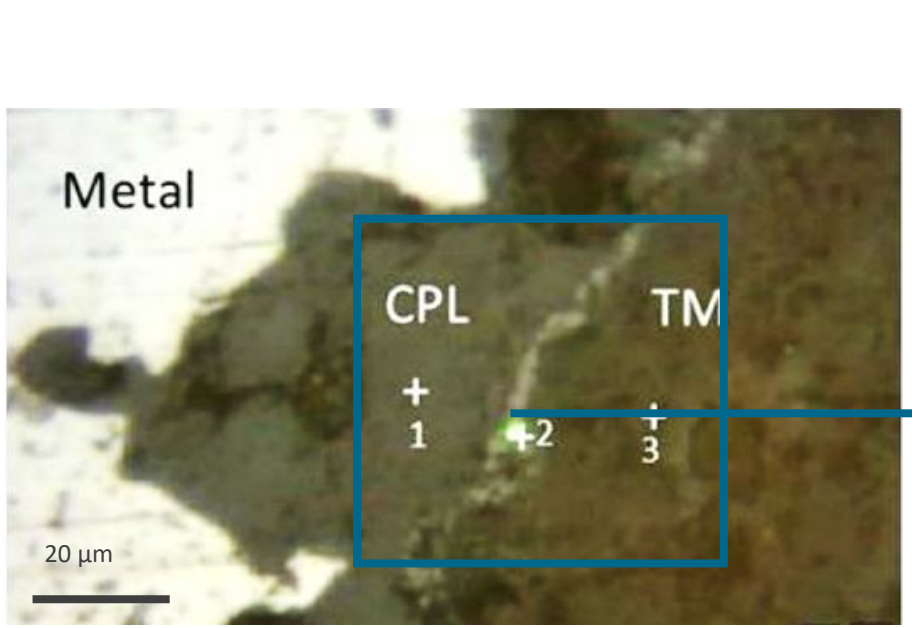
Location of the cathodic reaction

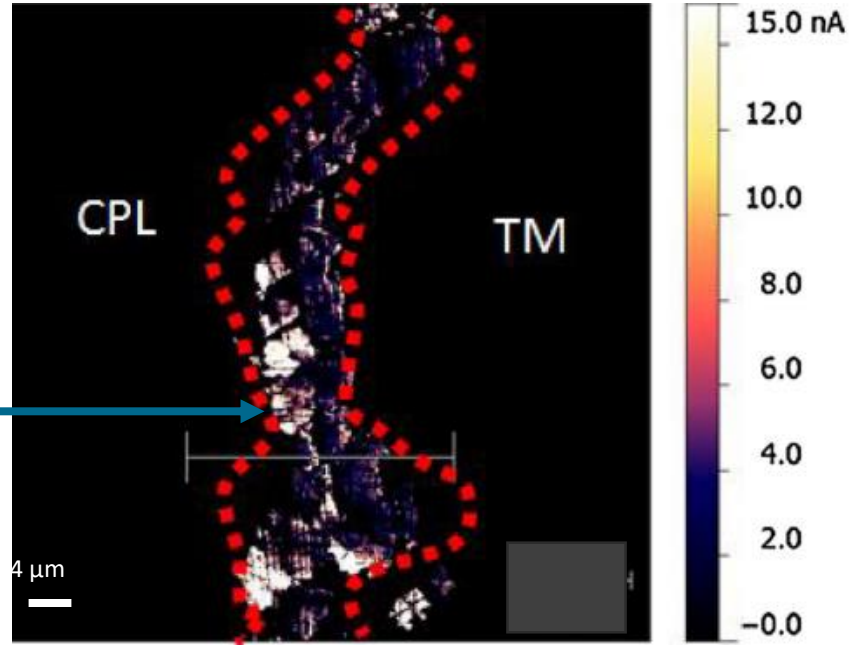
Current CPL mapping by CAFM



Mercier-Bion et al. Corrosion science 2018

Optical image and current image associated to a magnetite strip

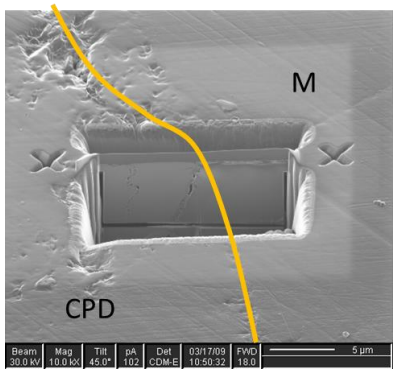




Conductive area in the insulating CPL

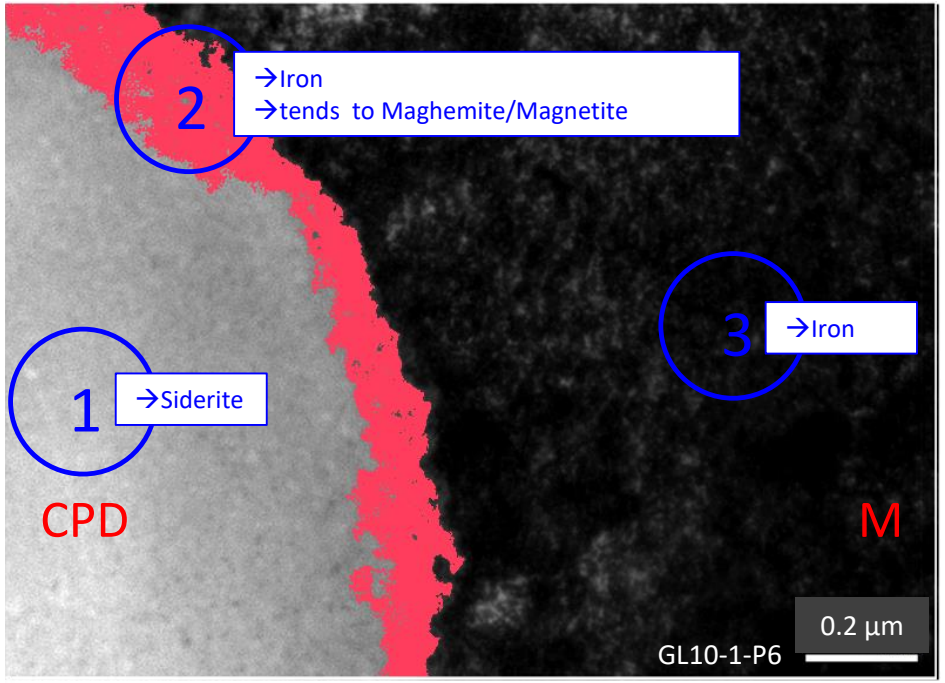
→ electrical connection to the metal

Nanometric investigation
TEM and electronic diffraction

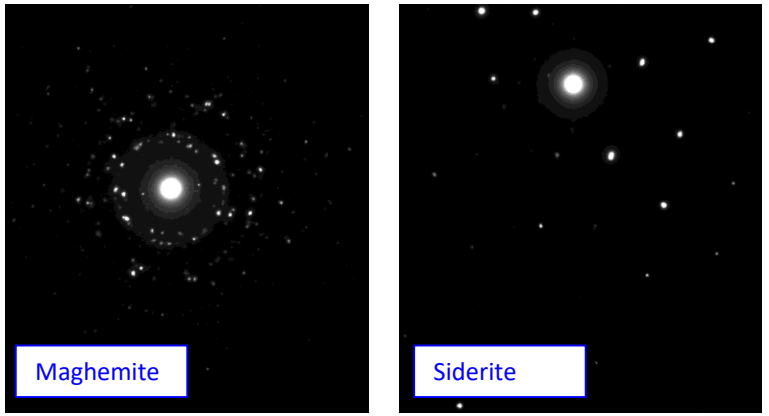


Thin section

FIB 1 µm – 100 nm



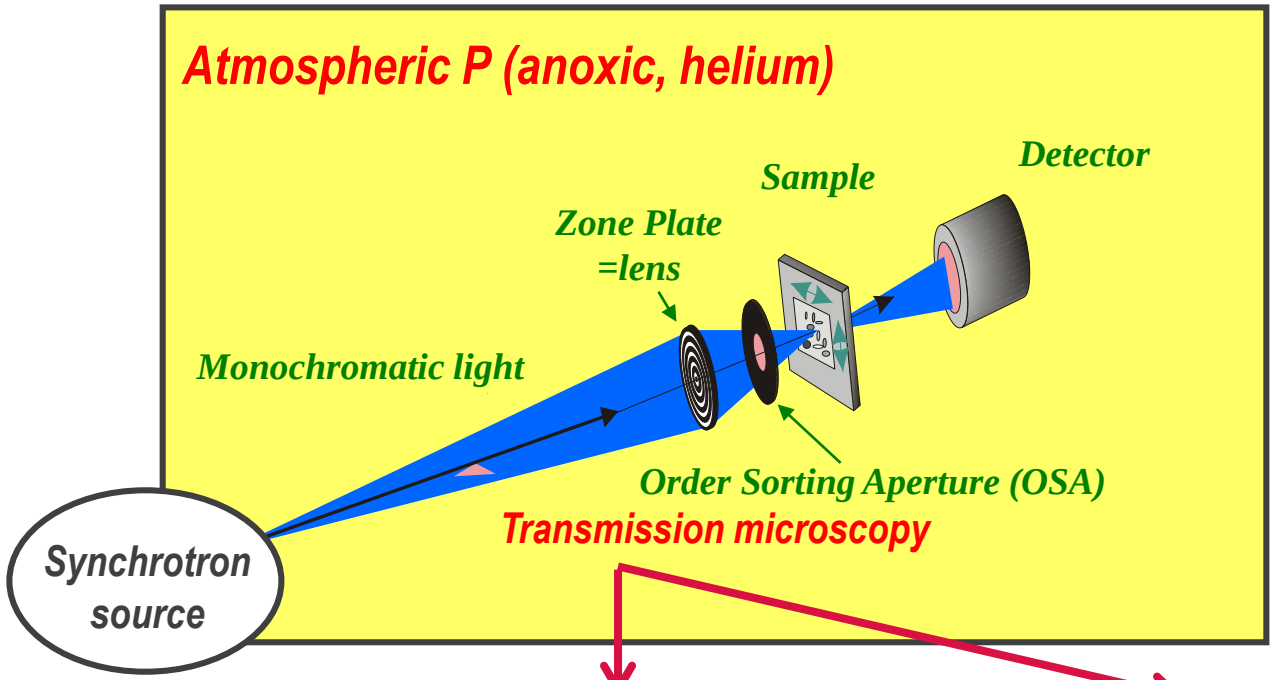
→ Indexation and comparison with references



→ Comparison with JCPDS files

Maghemite and magnetite difficult to distinguish by diffraction

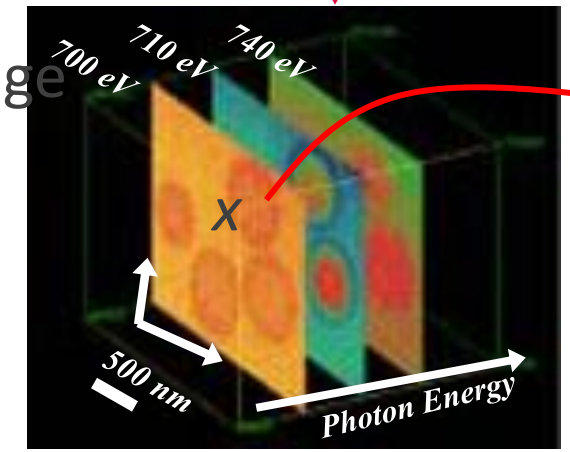
STXM analyses to determine the crystalline structure of the nanolayer



CLS (Saskatoon)
SLS (Villigen)

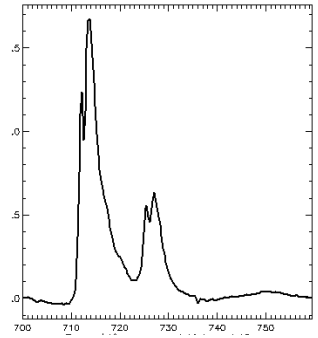
Spatial resolution : 30 nm

Fe : $L_{2,3}$ edge



Chemical Imaging

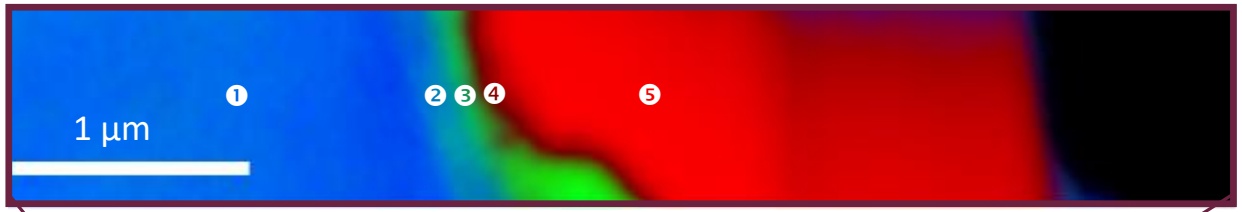
XANES spectroscopy



Photon energy (eV)

Fe speciation

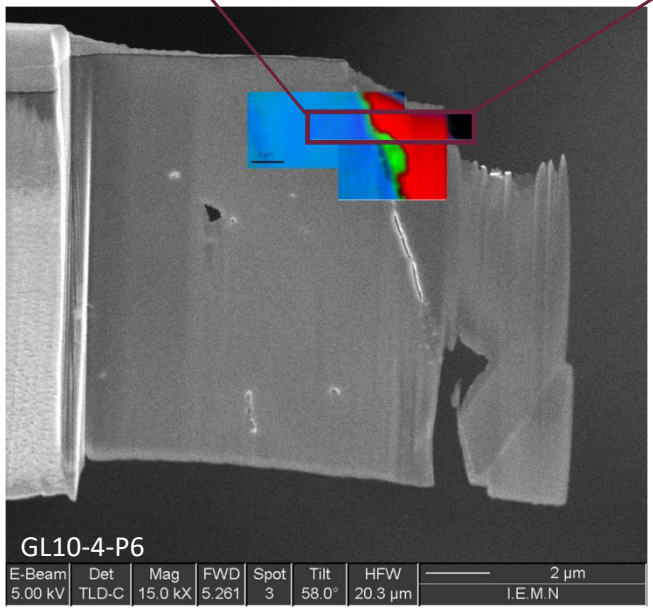
Presence of a nanometric layer



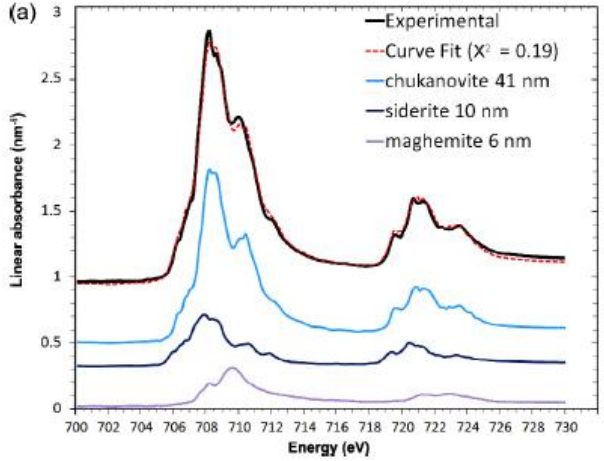
External corrosion layer Fe^{II}-rich

Interface Fe^{III}-rich

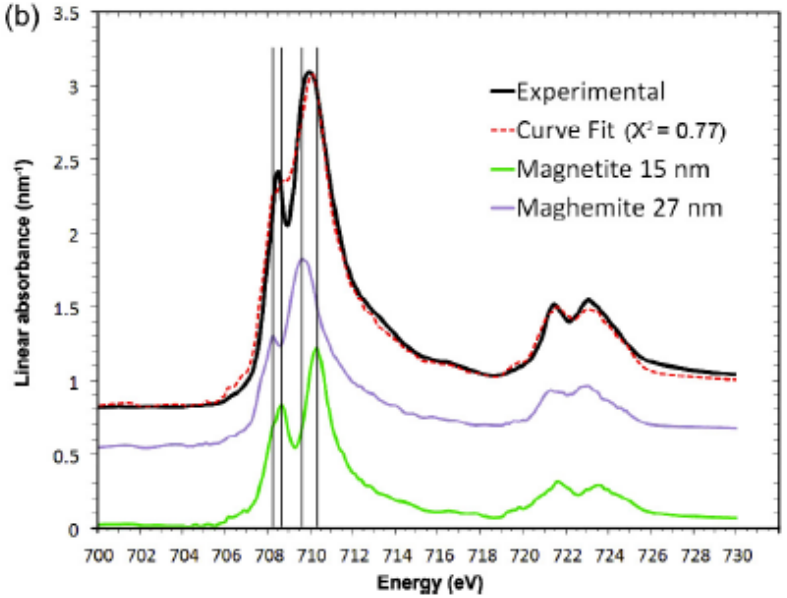
Metal



Sp 1: carbonate



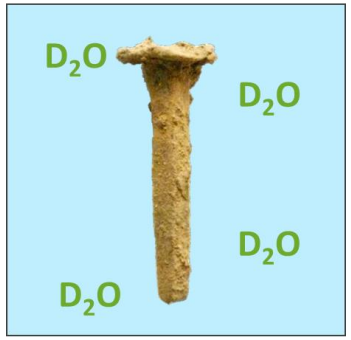
Sp 3: iron oxides



Leon et al. Corrosion science 2014

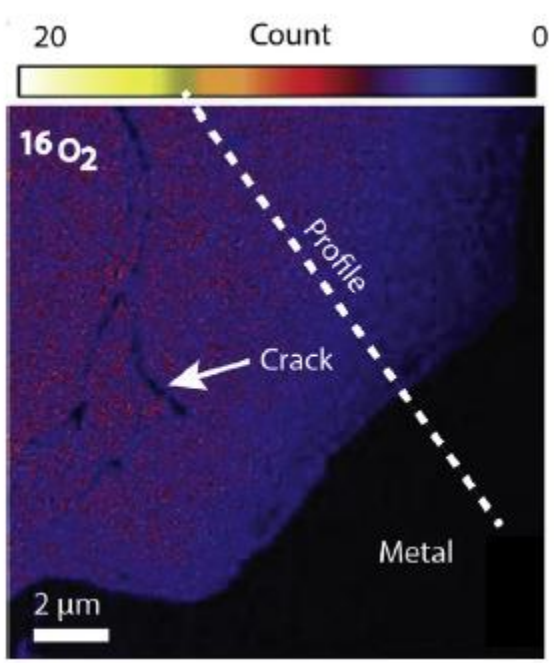
20-500 nm

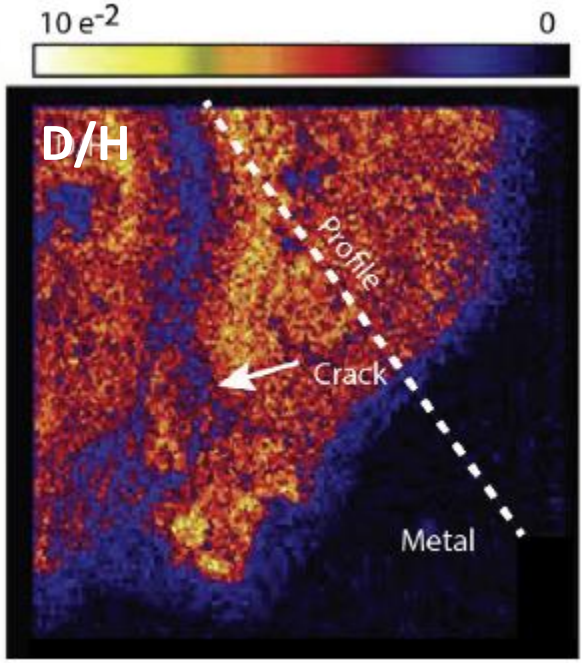
CPL permeability



Anodic reaction	Cathodic reaction
$Fe \rightarrow Fe^{2+} + 2e^-$	$2H^+ + e^- \rightarrow H_2$

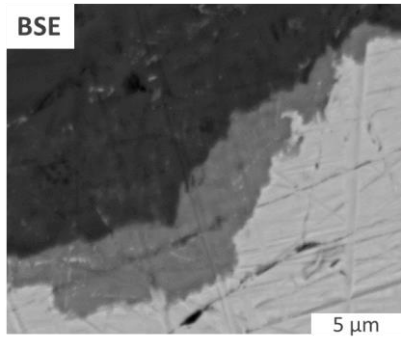
2 – 4 months
nanoSIMS

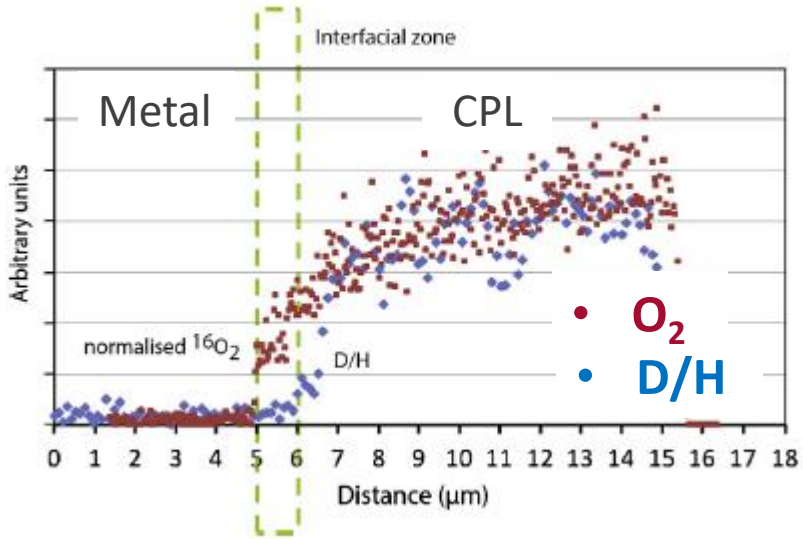




Archaeological analogues

At M/CPL interface





Leon et al. Corrosion science 2014

Impermeability of the internal layer

Conclusion

Refining the long term properties of long term corroded metals

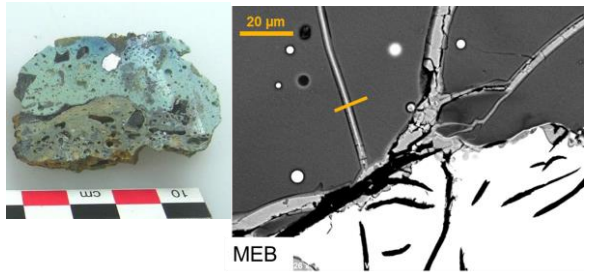
- **Chemical properties**
  - Heterogeneous distribution of the phases
- **Physical**
  - Permeability
- **Electrochemical**
  - Delocation of the cathodic reaction at the micro and nanometric scale

Towards Modeling of corrosion:

- Consolidation of the simulation obtained by the corrosion model
- Coupling of corrosion and geochemical models (transport of chemical species in the environment)

Analogue approach is adapted to study the properties of heterogenous samples at micro and nanoscales

- on laboratory samples (lab and Andra URL)
- on other analogues: glass, iron-glass, copper



Michelin et al 2012

Perspectives

Collaboration with Fraser King

▶ Potential applications to copper corrosion issues

- Specific question #1: Reactivity of Cu/Cu_2S surface
- Specific question #2: Competition between Cu and Fe for sulfide
- Specific question #3: Long-term stability of iron sulfide
- Specific question #4 : sulfur in grain boundaries Stress corrosion

General analogue approach on copper based artefacts

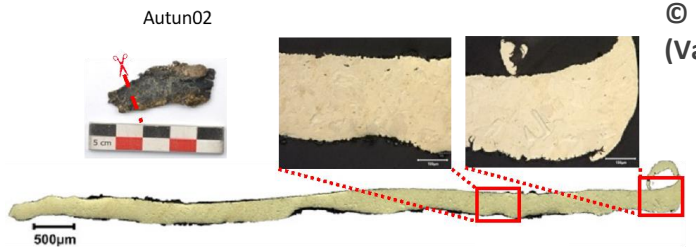
- First a general multiscale characterization of the corrosion products must be performed

- Then properties (transport, conductivity,…) of the phases under interest must be considered by specific techniques

Important to choose environments validated by the characterization of the corrosion system (presence of sulfides)

Nature of available samples

1. Artefacts already sampled but possibility to come back to the archaeological site to sample solution



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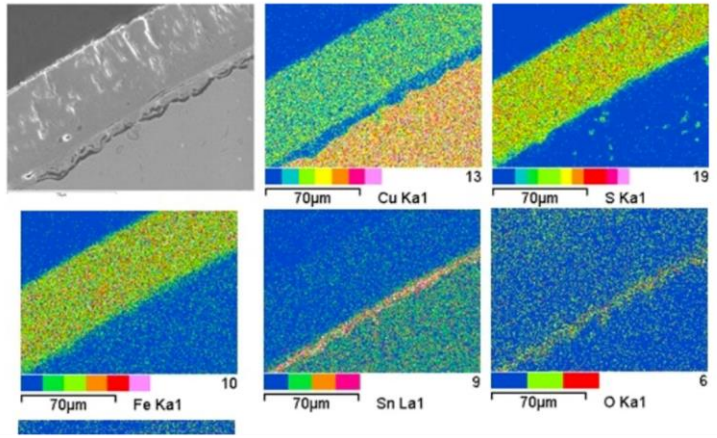
2. Already prepared cross-sections available for fine characterisation (nanoscale, conductivity, porosity etc)



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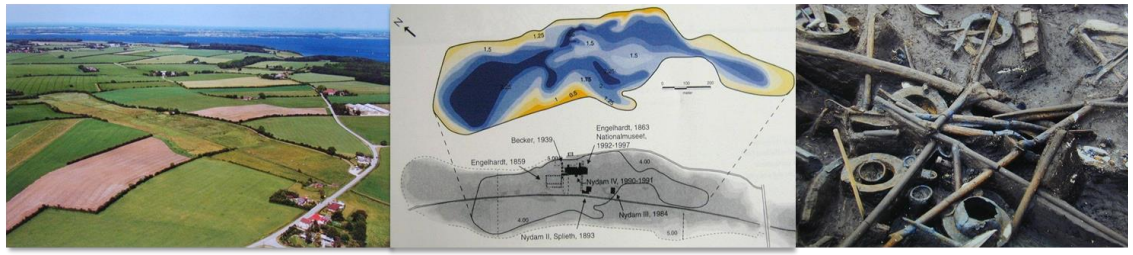
Master internship report, He-Arc Neuchâtel 2022

3. Samples put in a monitored waterlogged site 22 years ago (collab Nat Museum Denmark)



Nydam Mose, Denmark

Glass samples

Collaboration F. Angeli, S. Gin
CEA Marcoule

- 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 are available at CEA Marcoule.

- The study will focus on alteration products (nature, composition, thickness, porosity, transtion with fresh glass). Analytical tools : SEM, HR-TEM

- Comparison with litteraure data (natural samples and samples aged in laboratory under controlled conditions)
- Discussion on rate-limiting mechanisms

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