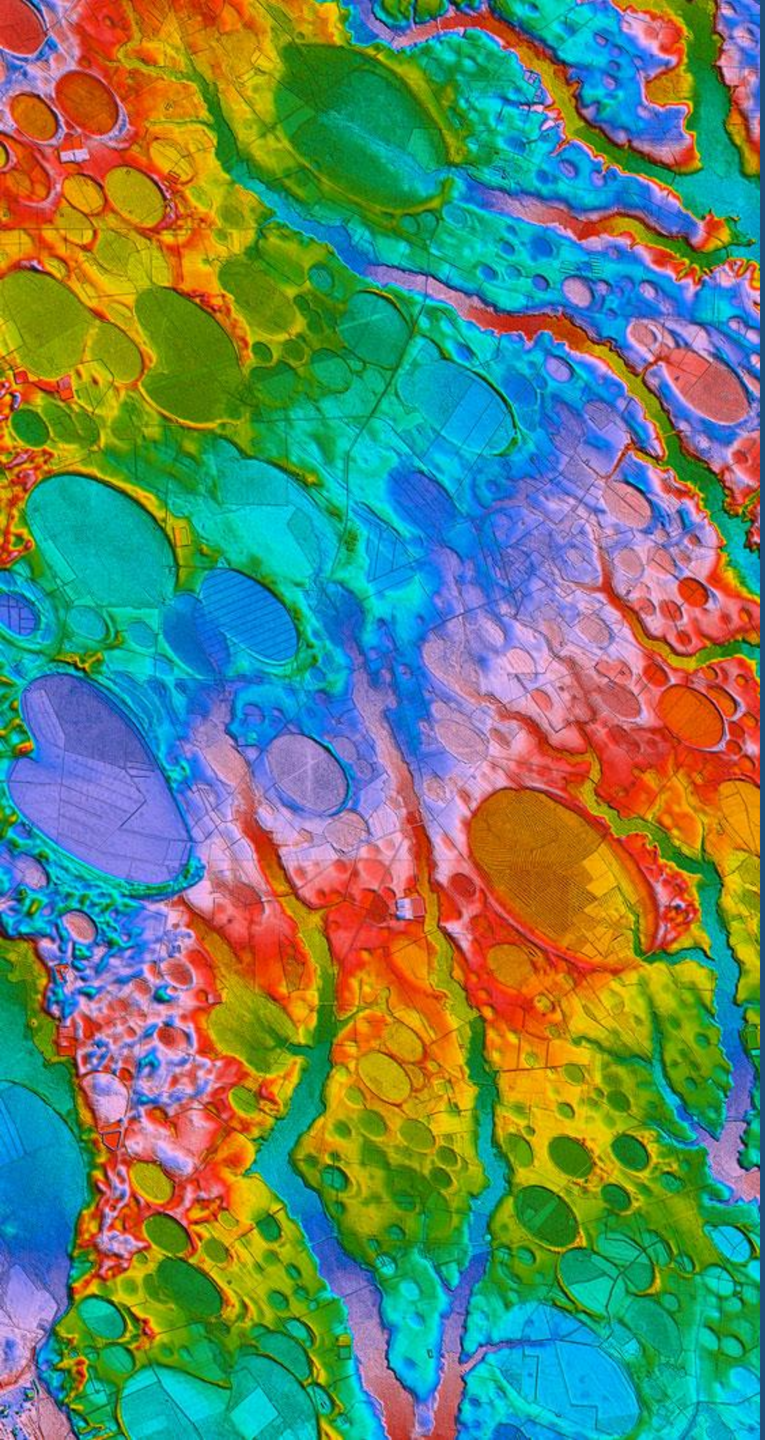

Geochemical pathways of onshore natural hydrogen generation & imaging based approach to quantify H_2 potential

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Research area: Fluid-rock interactions related to CO_2 storage in minerals, Natural H_2 (Thermodynamic, kinetics and interface processes)

UNIVERSITÉ DE PAU ET DES PAYS DE L'ADOUR

e2s UPPA energy environment solutions

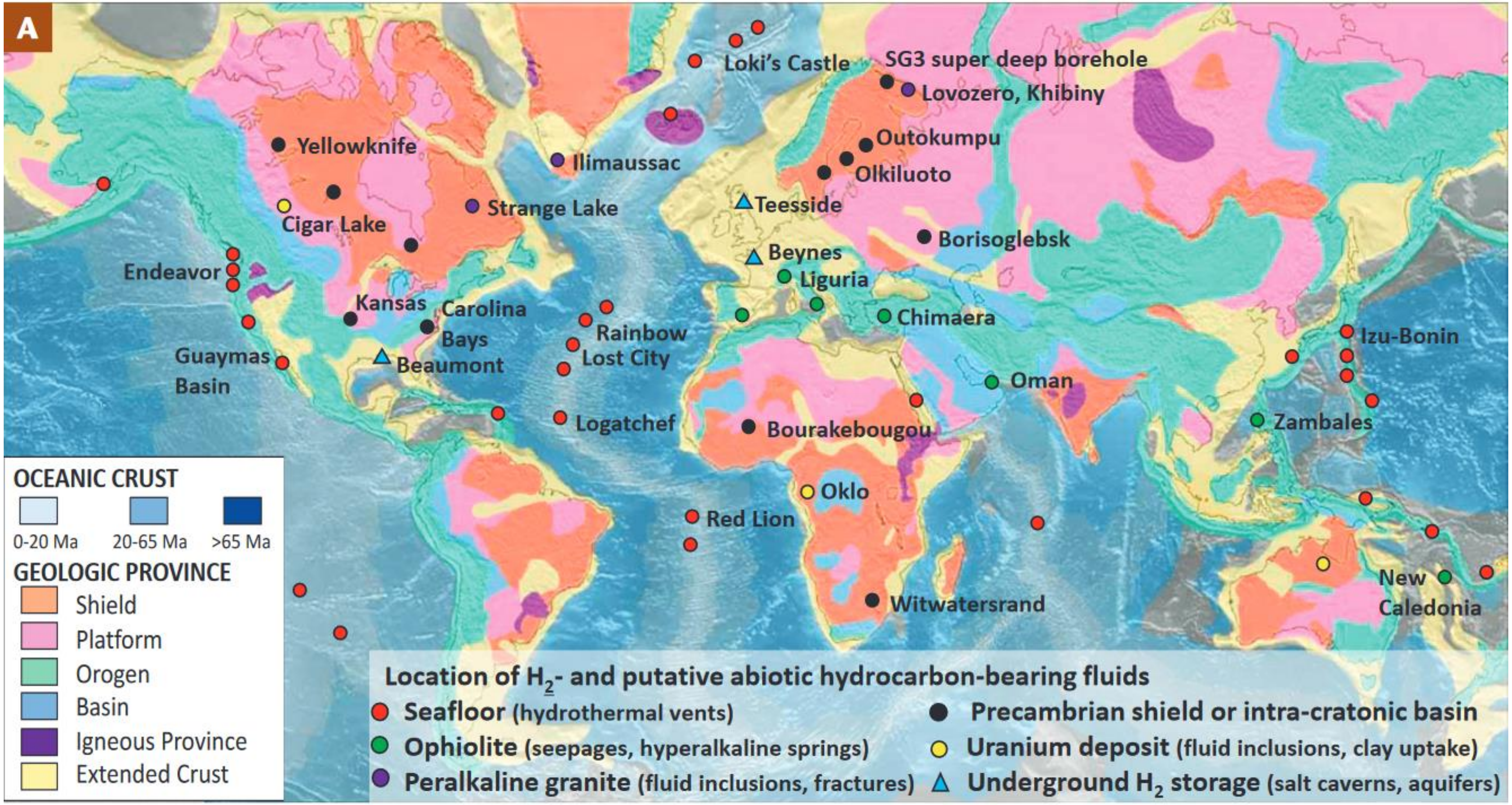
Natural hydrogen

- **Hydrogen formed by natural processes**
- Also called: **NATIVE H2, GEOLOGIC H2, GOLD H2**
- **WHITE H2** (Osselin et al., 2022, *Nature*)

Geological settings where Natural hydrogen is found

- Extension zones (Mid-ocean ridge, Iceland, African rift)
- Compression zones (eg. Ophiolites)
- Stable intracratonic basins

(Lévy, Moretti et al., 2023 "Natural H2 exploration: tools and workflows to characterize a play")



(Truche et al., 2020 "Hydrogen and Abiotic Hydrocarbons: Molecules that Change the World")

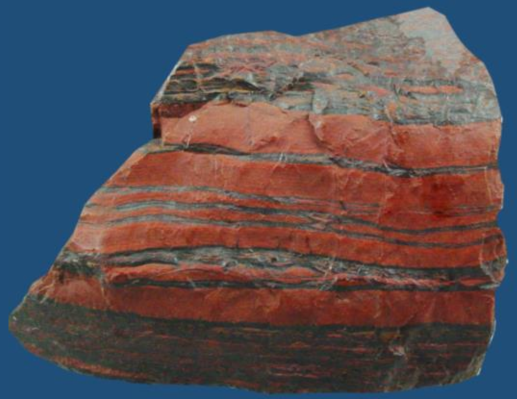
Geochemical processes leading to natural H2 generation

- Redox reaction between Fe^{2+} and water
- Radiolysis of water (U, Th, K)
- Organic maturation (pyrolysis)

(Lévy, Moretti et al., 2023 "Natural H2 exploration: tools and workflows to characterize a play")

Iron (Fe) rich rocks are the target!

Serpentinized rocks



Banded iron formation (BIF)

- Redox reaction between Fe^{2+} and H_2O

$$2Fe^{2+}_{(mineral)} + 2H_2O = 2Fe^{3+}_{(mineral)} + 2OH^- + H_2$$

- This is the simplest reaction (there are more…)
- Quantification of Fe^{2+} is important to know the H2 generation potential → H2(mol)/ rock mass (ton)

Geochemical pathways of natural H2 generation

Kularatne et al., 2024

$$Fe^{2+} + H_2O = Fe^{3+} + 2OH^- + H_2$$

Ophiolites/ ultramafic

Olivine + H_2O → Serpentine ± Brucite ± Magnetite + $H_{2(g)}$

Olivine + pyroxene+ H_2O → Serpentine + Magnetite + $H_{2(g)}$

$3Fe_2SiO_{4(fayalite)} + 2H_2O_{(l)} \rightarrow 2Fe_3O_{4(magnetite)} + 3SiO_{2(quartz)} + 2H_{2(g)}$

$3FeCO_{3(siderite)} + H_2O_{(l)} \rightarrow Fe_3O_{4(magnetite)} + 3CO_{2(g)} + H_{2(g)}$

$2Fe_3O_{4(magnetite)} + H_2O_{(l)} \rightarrow 3Fe_2O_{3(hematite)} + H_{2(g)}$

Sedimentary formations

$Fe_2O_{3(hematite)} + 4H_2S_{(g)} \rightarrow 2FeS_{2(pyrite)} + 3H_2O_{(l)} + H_{2(g)}$

$Fe_3O_{4(magnetite)} + 6H_2S_{(g)} \rightarrow 3FeS_{2(pyrite)} + 4H_2O_{(l)} + 2H_{2(g)}$

Granites

Biotite + H_2O → $Fe^{3+}{}_2O_{3(goethite/hematite)} + H_{2(g)}$

Biotite + H_2O → $Fe_3O_{4(magnetite)} + H_{2(g)}$

Arfvedsonite + H_2O → aegirine + $H_{2(g)}$

Banded iron formations

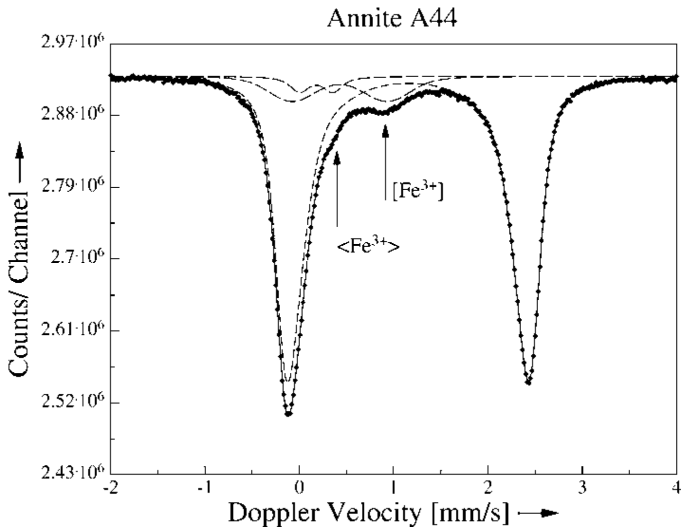
$2Fe^{2+}O_{(silicate)} + H_2O_{(g)} \rightarrow Fe^{3+}O_{3(goethite)} + H_{2(g)}$

$2Fe^{2+}O_{(magnetite)} + H_2O_{(g)} \rightarrow Fe^{3+}{}_2O_{3(goethite/hematite)} + H_{2(g)}$

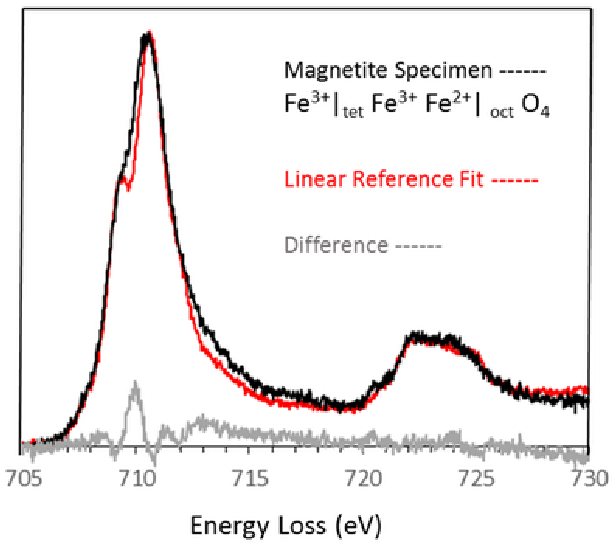
Methods to quantify Fe^{2+} in a rock

- Wet-chemical methods
- Mössbauer spectroscopy
- TEM EELS (electron energy-loss spectroscopy)

Mössbauer spectroscopy showing iron speciation in annite



EELS spectroscopy showing iron speciation in magnetite



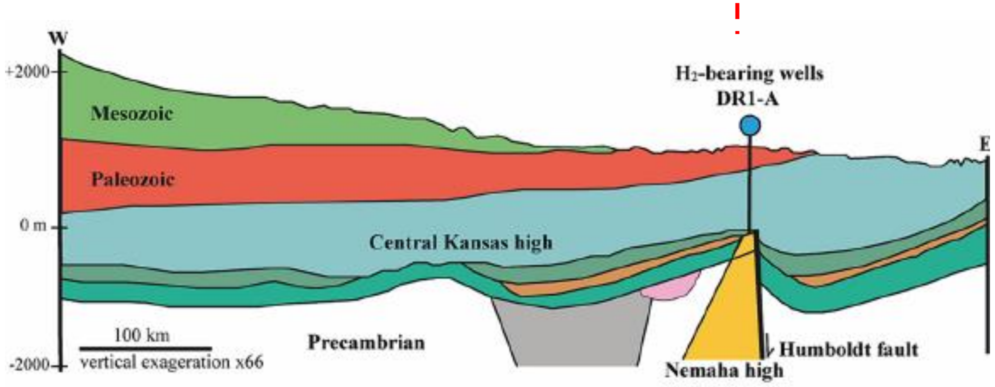
Limitations

- Destructive
- Small sample size

Imaging based approach to quantify Fe^{2+} : Case study of Kansas

Valentine Combaudon
IFPEN & DMEX
PhD thesis, 2023

Collaboration: Pascale Senechal, Valantine Combaudon, Stephen Centrella, Olivier Sissmann, Eric Deville, Othmane Darouich, Maria Angels Subirana, Dirk Schaumloffel, Caroline Delhaye, Arnaud Prioretti, Hannelore Derluyn



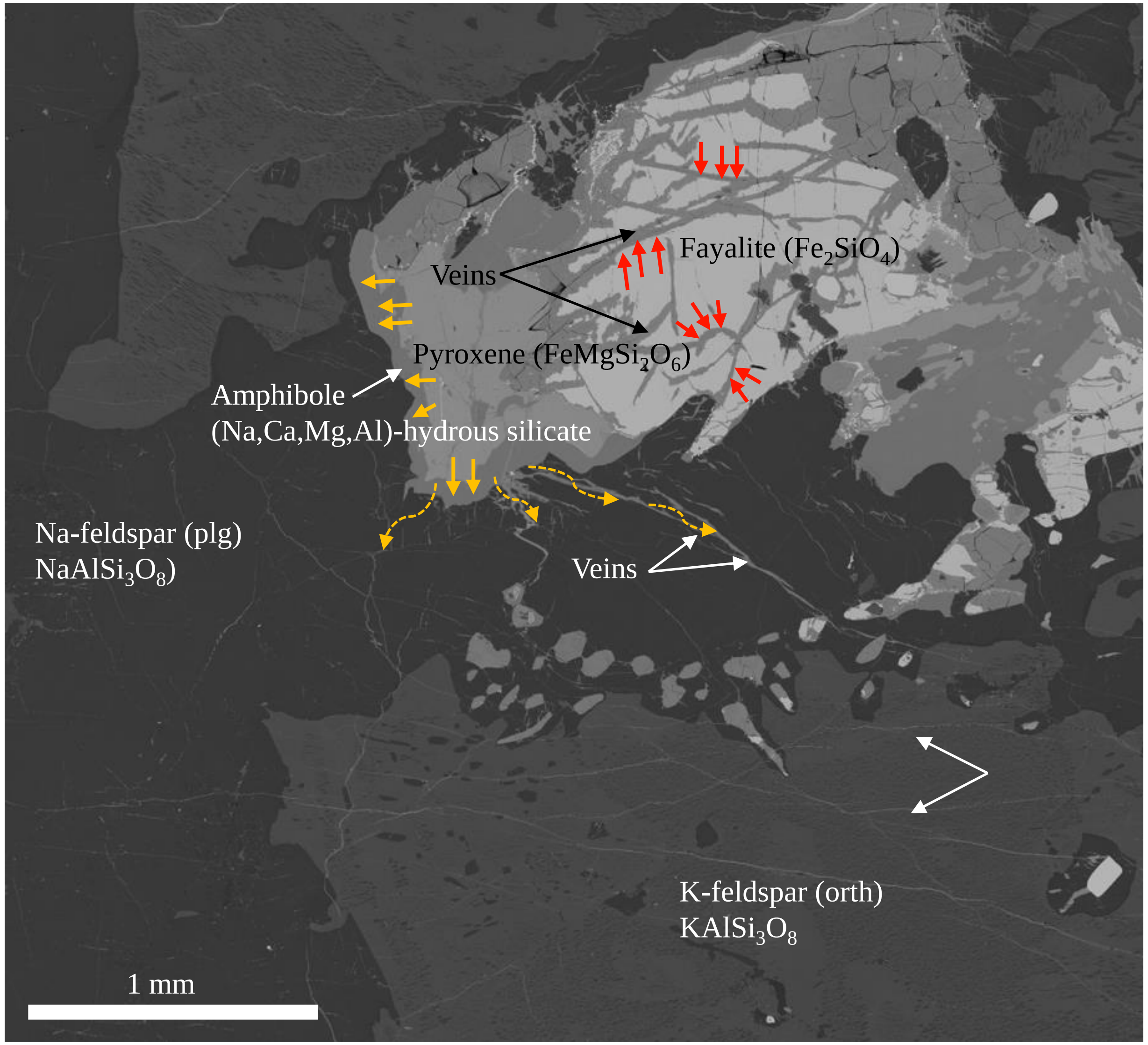
Core from DR1-A well
Monzo-diorite
H_2 (mol) / rock (ton) ???

(Combaudon et al., 2024 "Are the Fe-rich-clay veins in the igneous rock of the Kansas (USA) Precambrian crust of magmatic origin?")

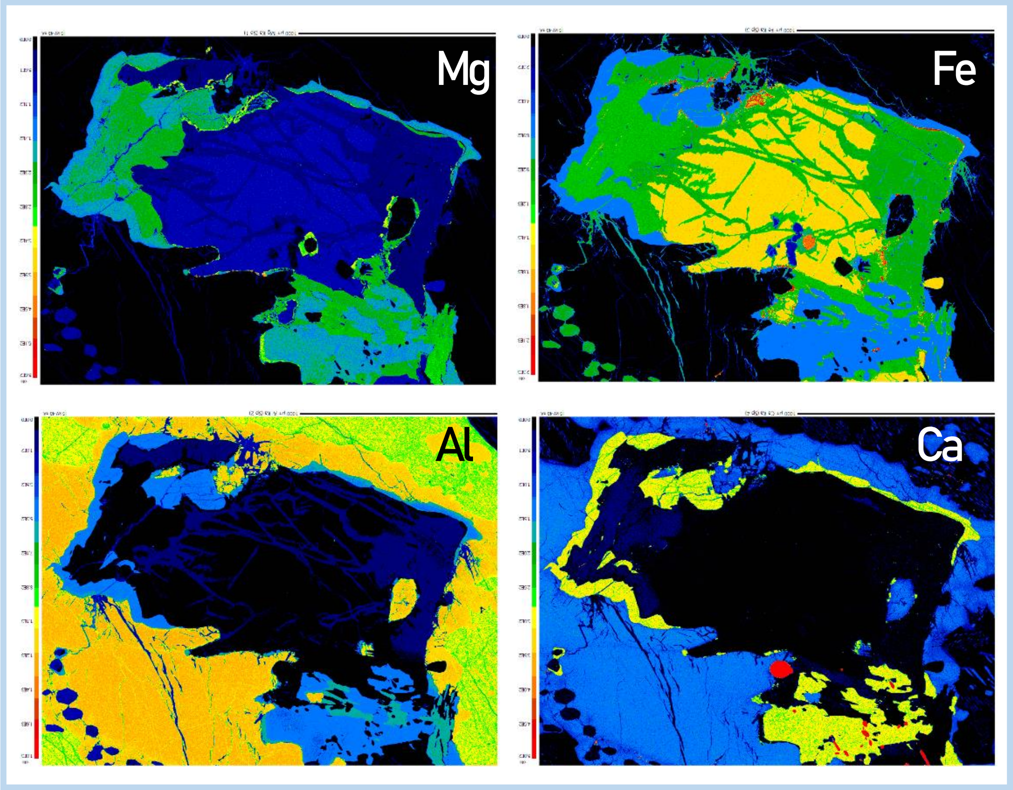
Two H_2 generating reactions identified:

- Pyroxene + H_2O → amphibole + H_2
- Fayalite + H_2O → serpentine + H_2

$$\text{Pyroxene} + H_2O \rightarrow \text{amphibole} + H_2$$
$$\text{Fayalite} + H_2O \rightarrow \text{serpentine} + H_2$$

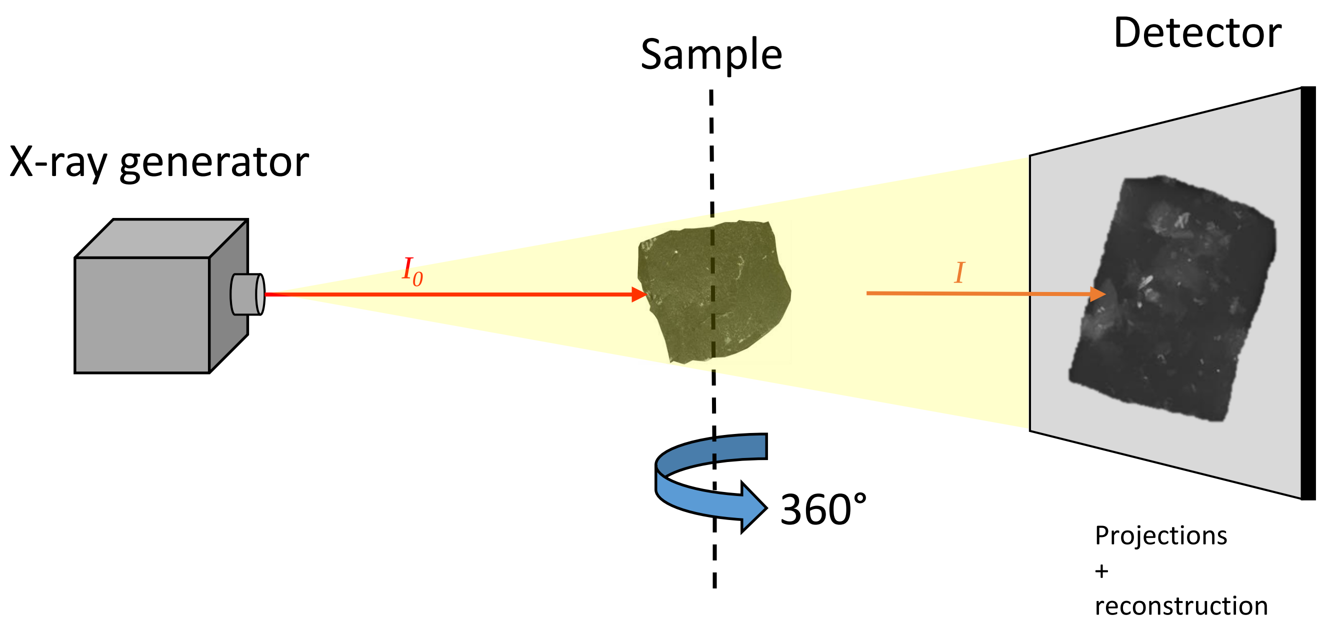


Quantitative element mapping using EMPA



Aim of the study is to quantify H_2 generation potential by the two reactions above and to quantify H_2 already generated

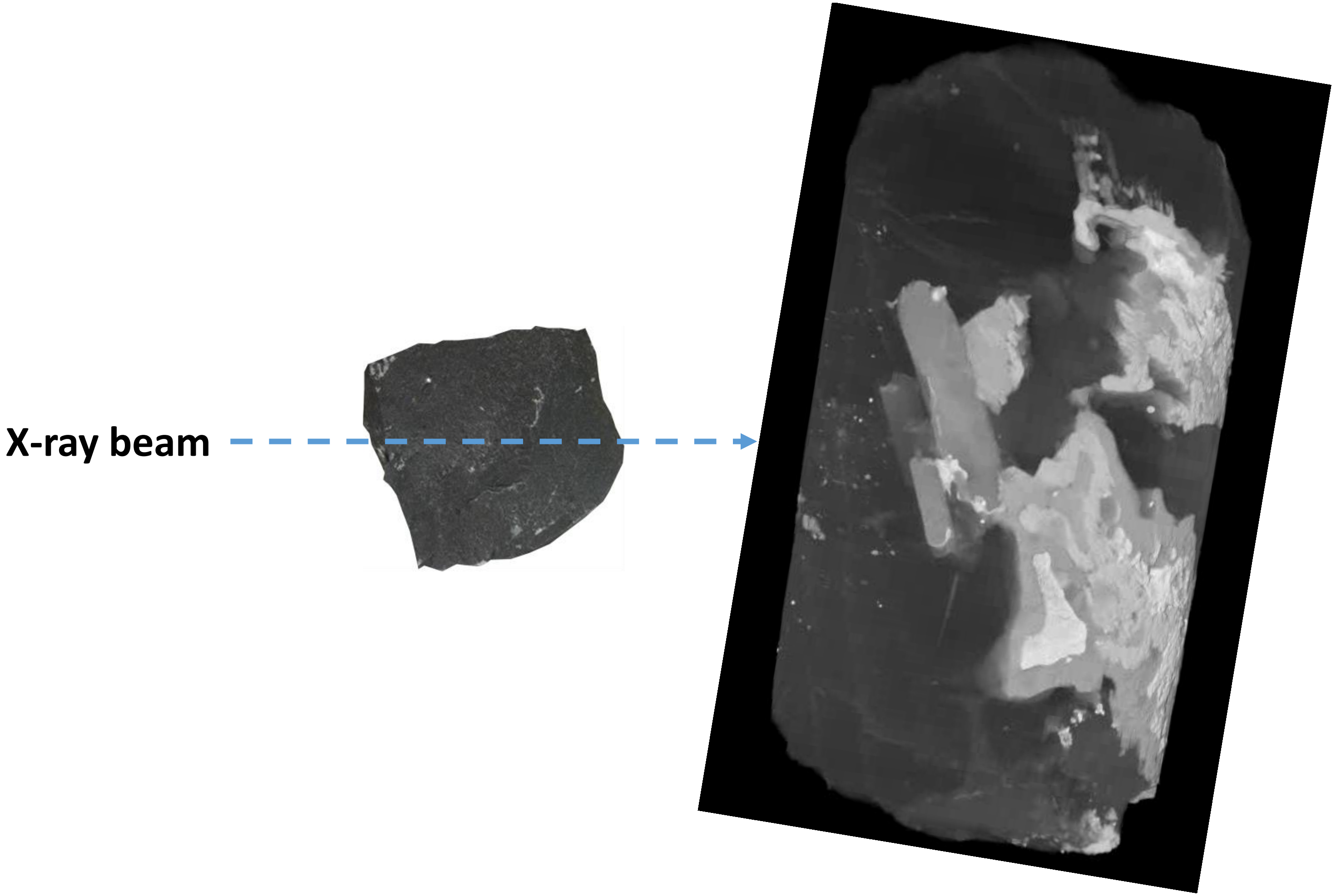
X-ray computed tomography (XCT)



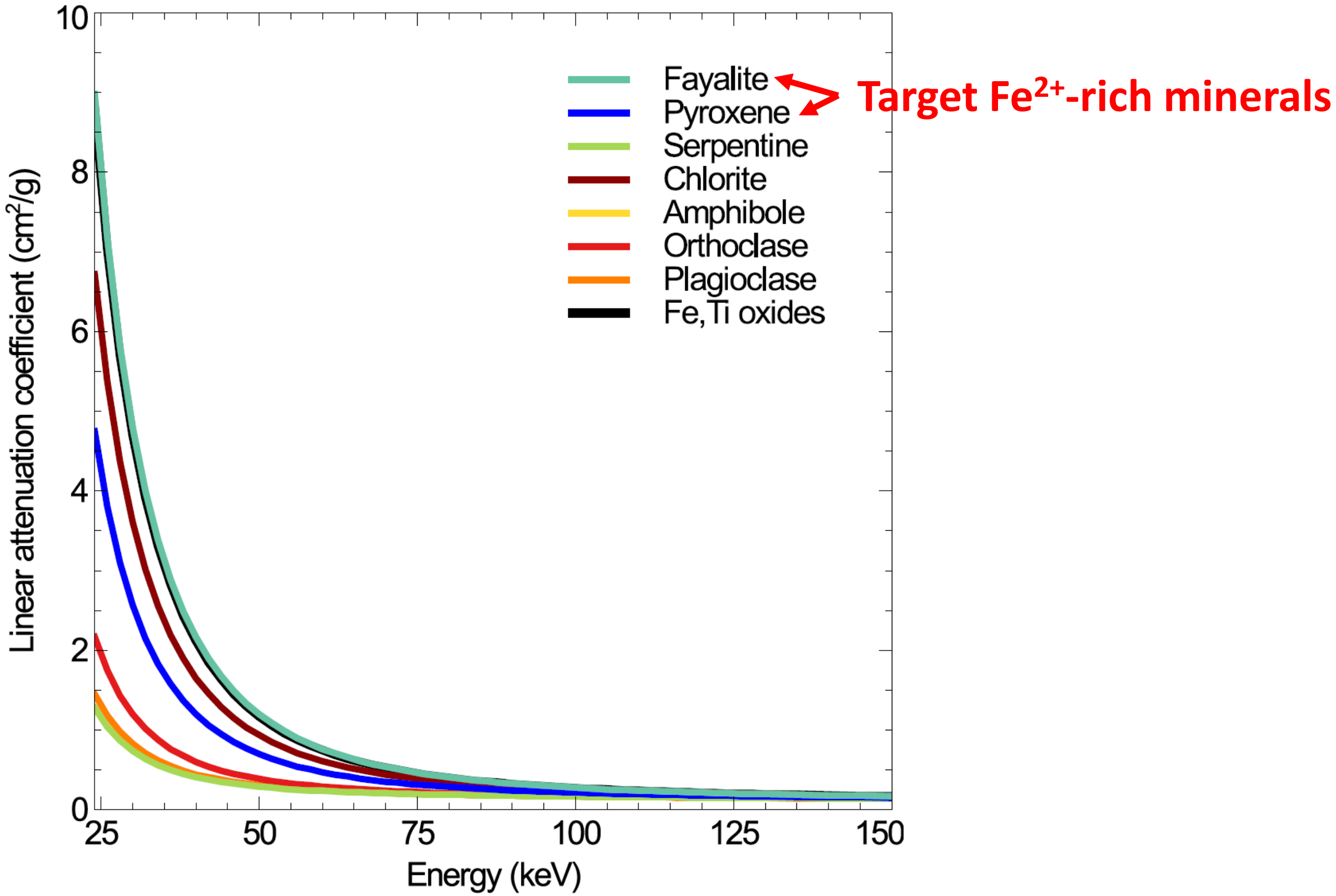
- Beer-Lambert law: $\frac{I}{I_0} = exp^{-\mu d}$
- µ = linear attenuation coefficient (LAC)
- d= distance between generator and sample

Advantages
- Non-destructive
- Large sample size
- 3D information

Imaging using XCT

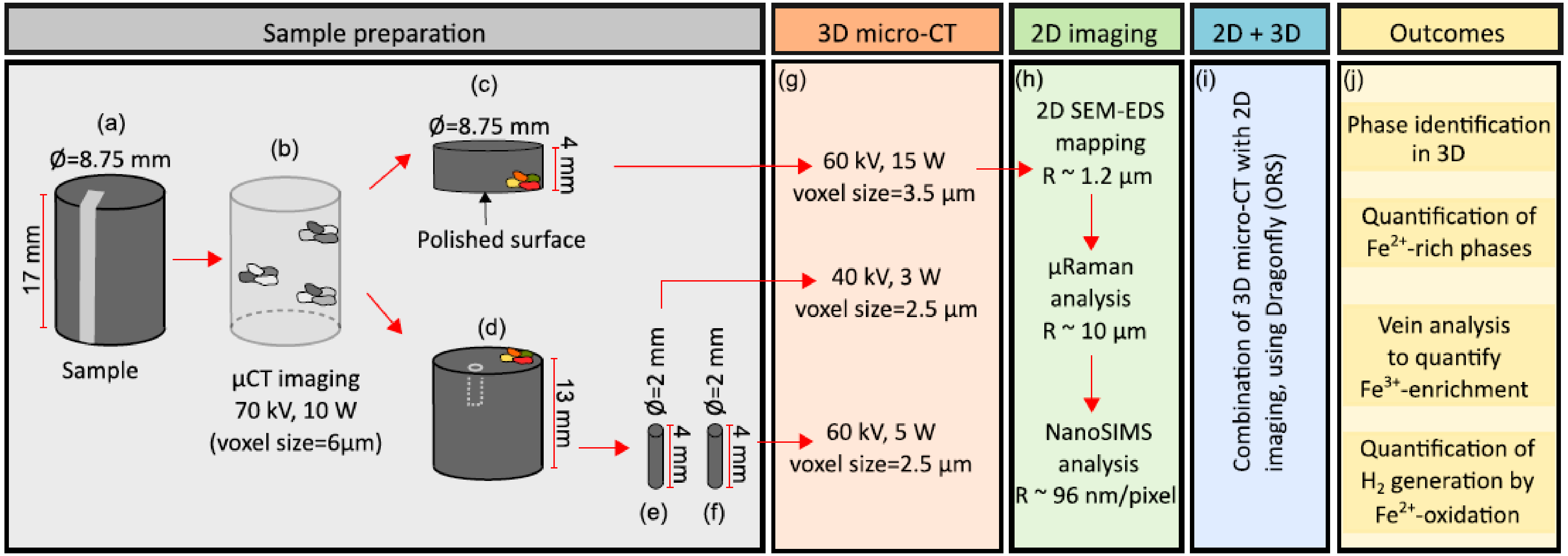


Theoretical LAC of minerals in the sample

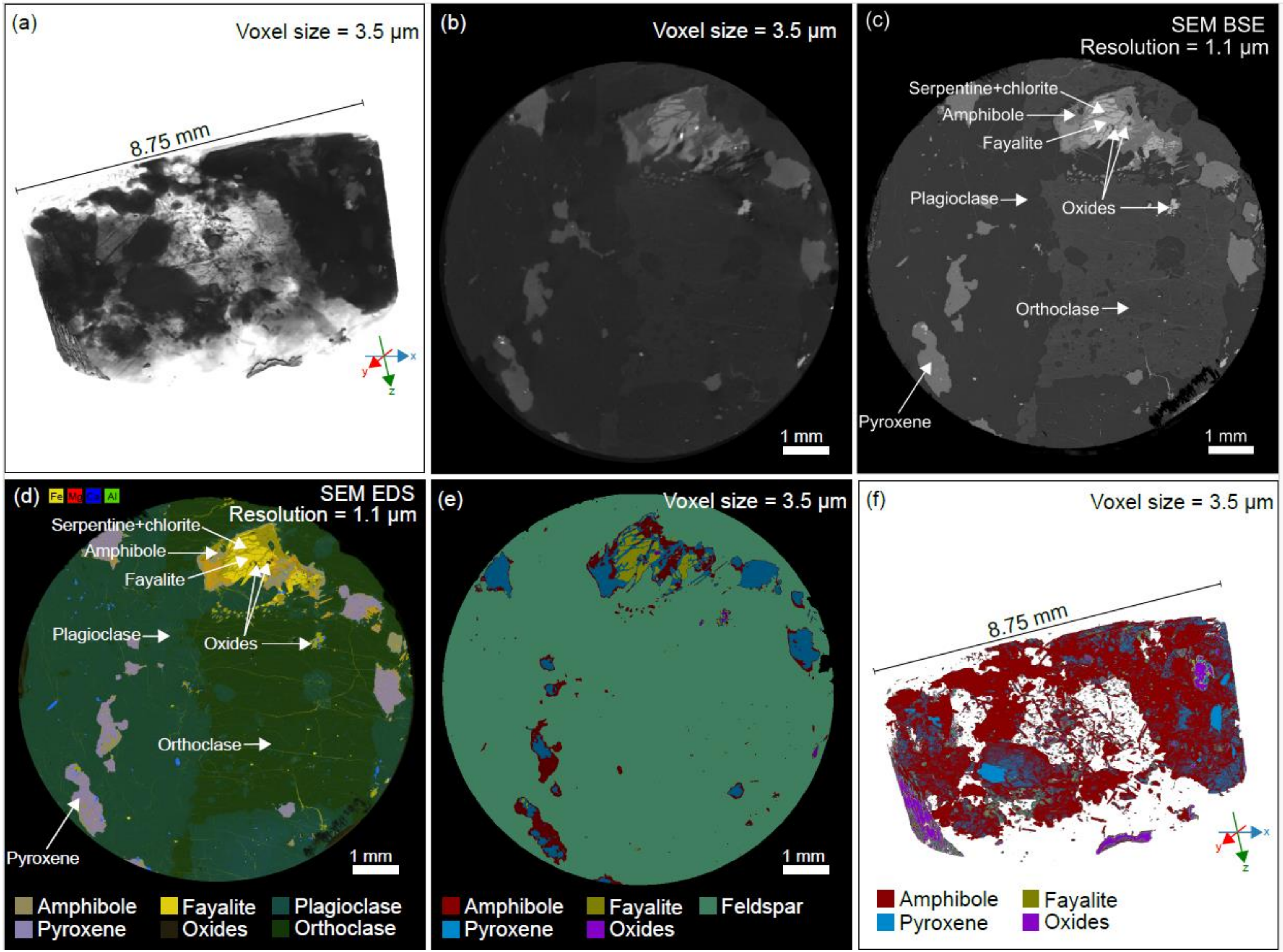


- LACs calcuated using Arion simulator (Dhaene et al., 2015)
- NIST XCOM Photon Cross Sections database

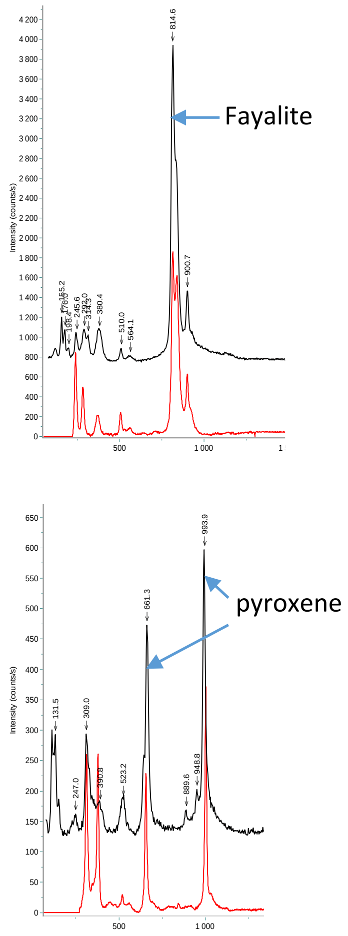
Correlative imaging workflow

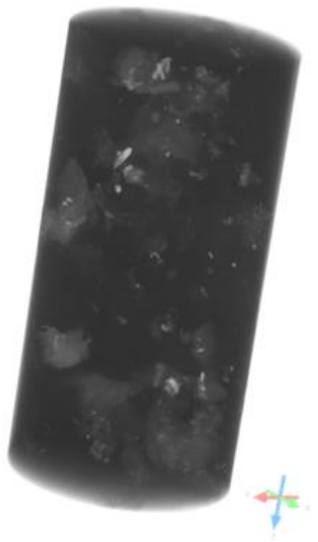


Kularatne et al., 2024 «X-ray micro-computed tomography-based approach to estimate the upper limit of natural H2 generation by Fe2+ oxidation in the intracratonic lithologies»

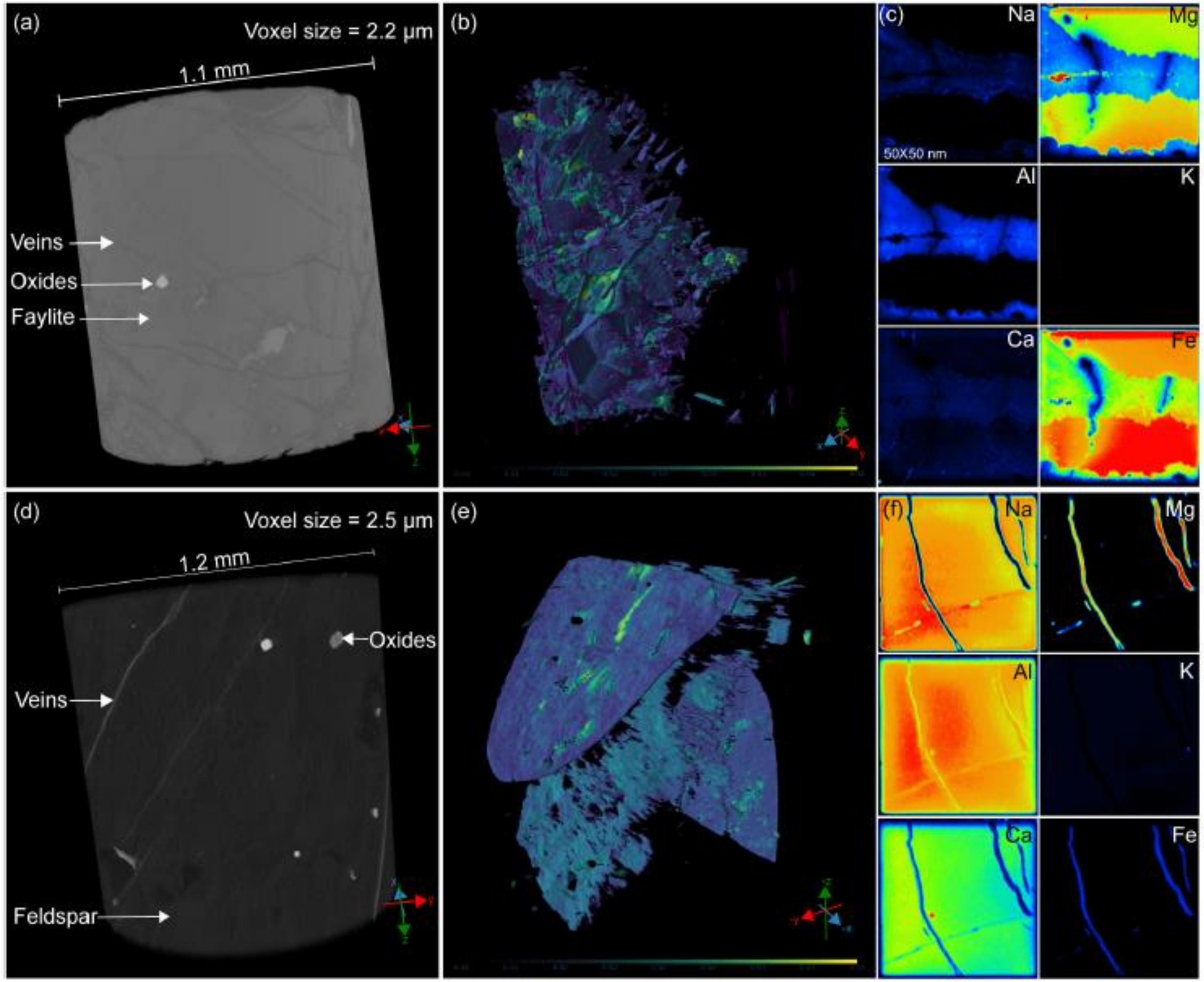


<u>µRaman spectroscopy</u>



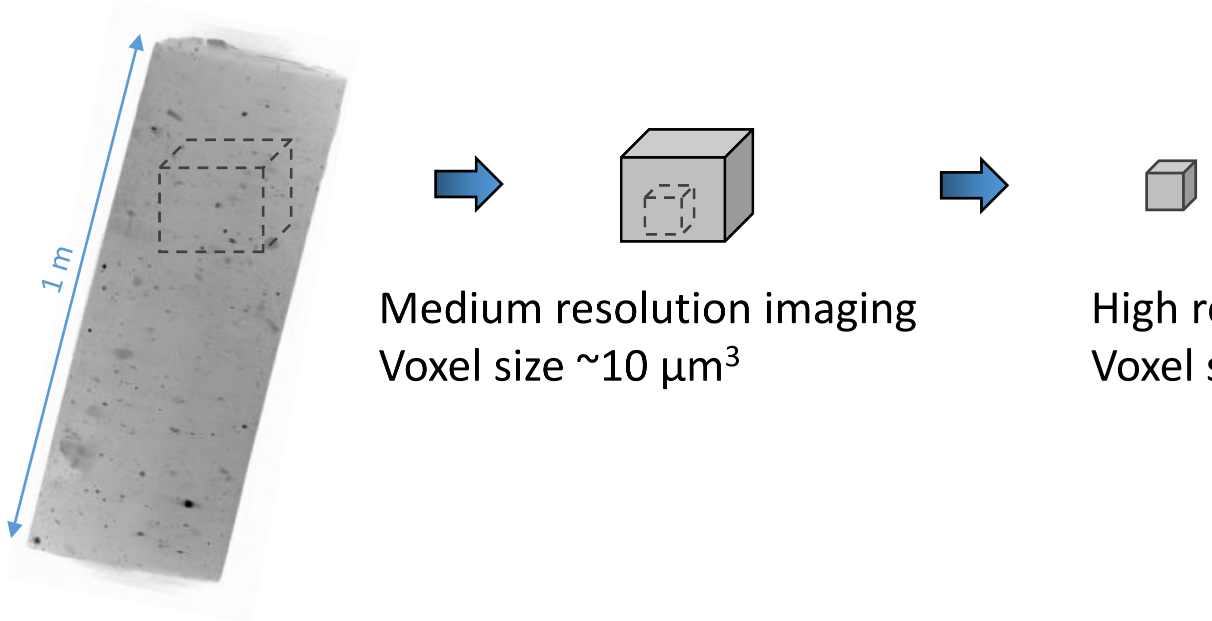
	Full sample	Pyroxene	Fayalite
			
Density	2.8 g/cm^3	3.95 g/cm^3	2.8 g/cm^3
Chemical formula	-	Fe1.6Mg0.5Mn0.1Si2O6	Fe1.8Mn0.1Mg0.1SiO4
Fe^{2+} content	-	0.43 g/mol	0.50 g/mol
XCT volume	100 mm^3	11.38 vol.%	1.3 vol.%
H2 mol / ton (rock)	-	615.03 ± 8.61	92.90 ± 27.26
Total H2 mol / ton (rock)	**707.93 ± 49.18** **Maximum H2 possible if all Fe^{2+} generates H_2 according to:** **$Fe^{2+} + H_2O = Fe^{3+} + 2OH^- + H_2$**		

*Reaction kinetics are not taken into account



- $[Fe^{3+}]/\Sigma Fe$ value from XANES
- The calculated Fe^{3+} content in 100 mm^3 volume of the rock is 1.35 ± 0.24 µmols.
- Assuming that all iron in both minerals are divalent (Fe^{2+}) and that they oxidize completely, generating H_2 (Eq. (1)), the fayalite alteration in the rock has generated 2.19 ± 0.39 mol (H_2)/ton (source rock).

Advantages



Low resolution imaging
Voxel size ~30 µm^3

Medium resolution imaging
Voxel size ~10 µm^3

High resolution imaging
Voxel size ~2-3 µm^3

- Large, representative samples → High accuracy
- Minimum sample destruction
- Cheap

Implications

$Fe^{2+} + H_2O = Fe^{3+} + 2OH^- + H_2$

Ophiolites/ ultramafic

Olivine + H_2O → Serpentine ± Brucite ± Magnetite + $H_{2(g)}$

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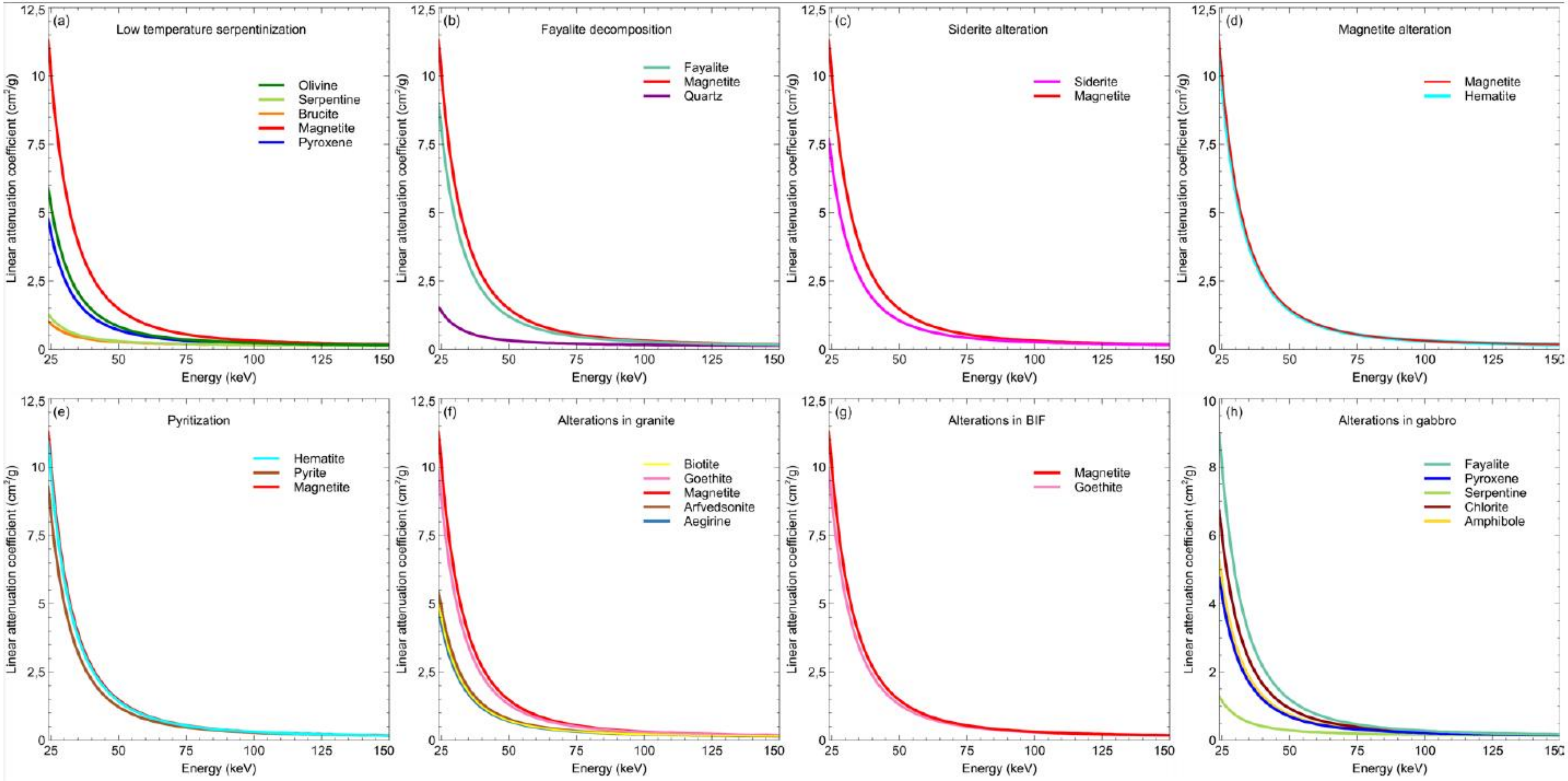
(a) Low temperature serpentinization
Olivine
Serpentine
Brucite
Magnetite
Pyroxene
(b) Fayalite decomposition
Fayalite
Magnetite
Quartz
(c) Siderite alteration
Siderite
Magnetite
(d) Magnetite alteration
Magnetite
Hematite
(e) Pyritization
Hematite
Pyrite
Magnetite
(f) Alterations in granite
Biotite
Goethite
Magnetite
Arfvedsonite
Aegirine
(g) Alterations in BIF
Magnetite
Goethite
(h) Alterations in gabbro
Fayalite
Pyroxene
Serpentine
Chlorite
Amphibole
Linear attenuation coefficient (cm²/g)
Energy (keV)

Conclusions & perspectives

1. Novel approach to estimate the upper limit of hydrogen (H_2) generation via Fe^{2+} oxidation in Fe-rich lithologies
2. Allows imaging larger samples (1 m drill cores)
3. Representative volumes of rock, therefore representative quantification
4. Minimum sample destruction
5. Implication to early exploration & enhanced H_2 generation
6. Perspectives : application of this method to other lithologies (two follow-up projects in UPPA), Quantitative EMPA mapping and mass balance equation (work in progress), use spectral tomography to resolve phases that are still inseparable by the current method (paper under review), add kinetic factor to the reactions

Thank you for your attention !

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