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In situ spectroscopy of hydrothermal fluids: What can we learn with autoclaves and photons?

Denis Testemale

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In situ spectroscopy of hydrothermal fluids: What can we learn with autoclaves and photons?

D. Testemale
Institut Néel, Grenoble
FAME/FAME-UHD CRG beamlines

CLS Supercritical fluid workshop April 12th 2022

Outline

Introduction

Metal transport in hydrothermal fluids (XAS)

Autoclave technology

More *in situ* techniques

Outline

Introduction

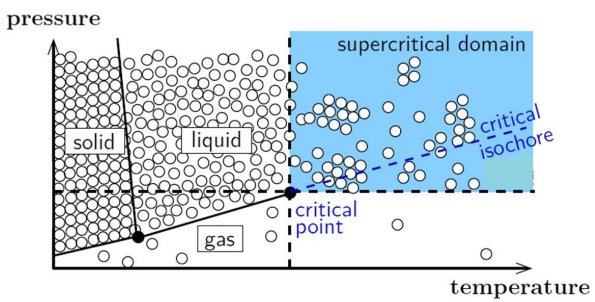
Metal transport in hydrothermal fluids (XAS)

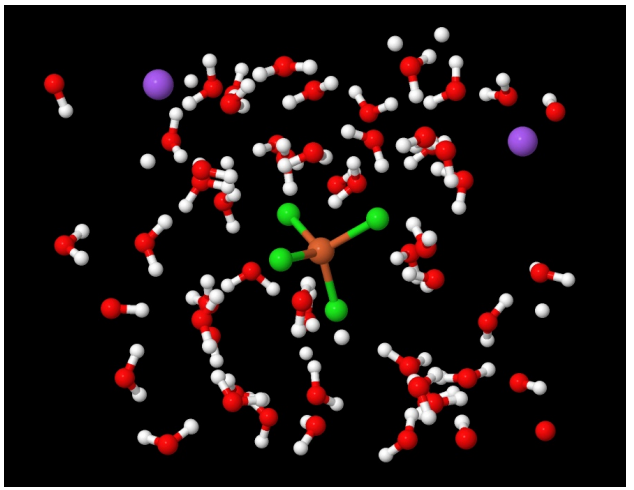
Autoclave technology

More *in situ* techniques

Hydrothermal fluids

- Physical-chemistry of supercritical fluids





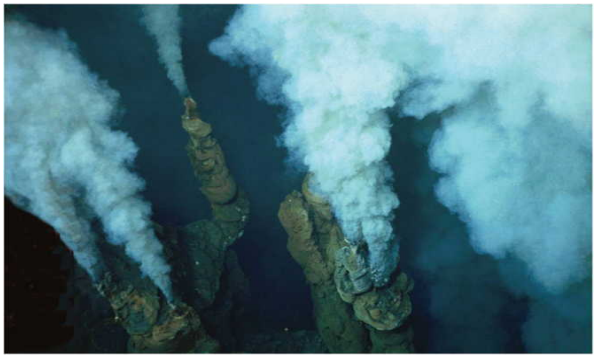
- Hydrothermal geochemistry

Pinatubo 1991 eruption, Indonesia

Bingham, USA (Cu-Au-Mo porphyry)

Hellisheidi geothermal power plant, Iceland

Hydrothermal fluids

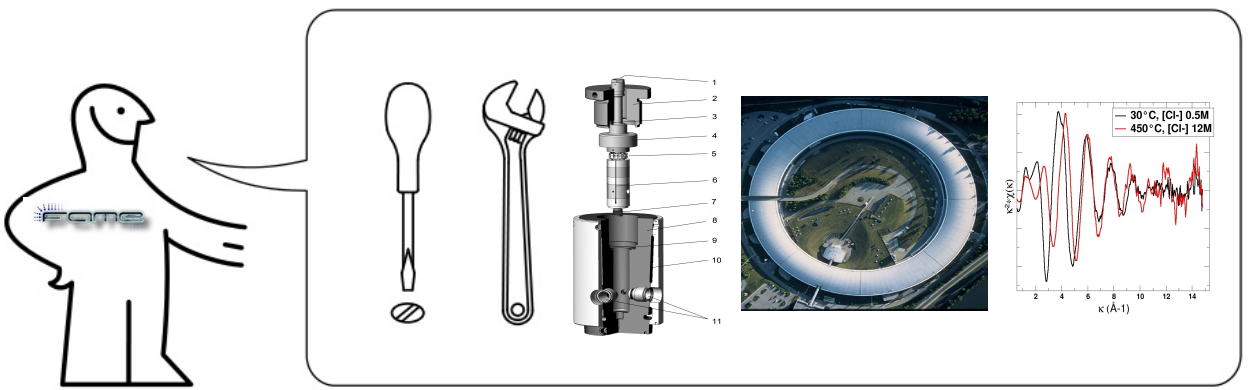


→ **Properties** of hydrothermal fluids:

- T<1000°C, P<5000 bar
- 0.04<density<1 g.cm^{-3}
- H_2O-NaCl ± CO_2, S, F, P
- Unquenchable

→ **Characterization** of hydrothermal fluids:

- Local structure, speciation, redox, etc.
- In aqueous solutions
- Has to be *in situ*



Outline

Introduction

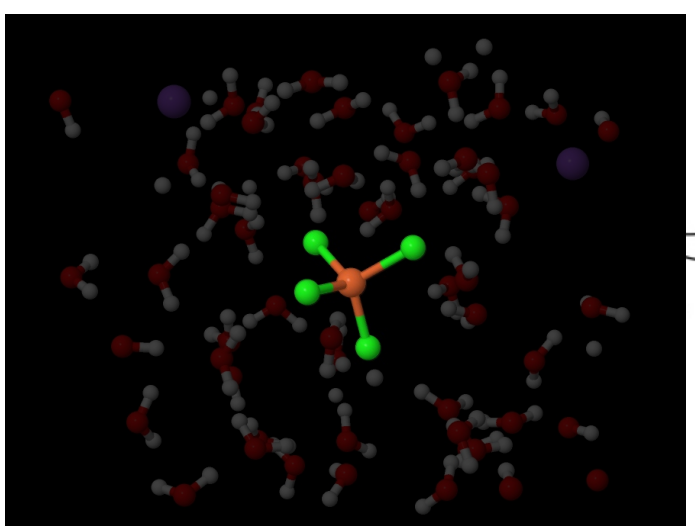
Metal transport in hydrothermal fluids → XAS methods

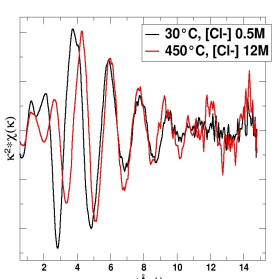
Autoclave technology

More *in situ* techniques

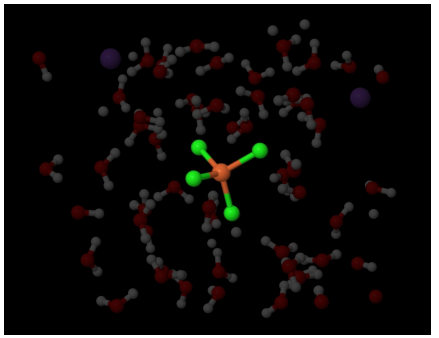
Transport of iron in hydrothermal fluids

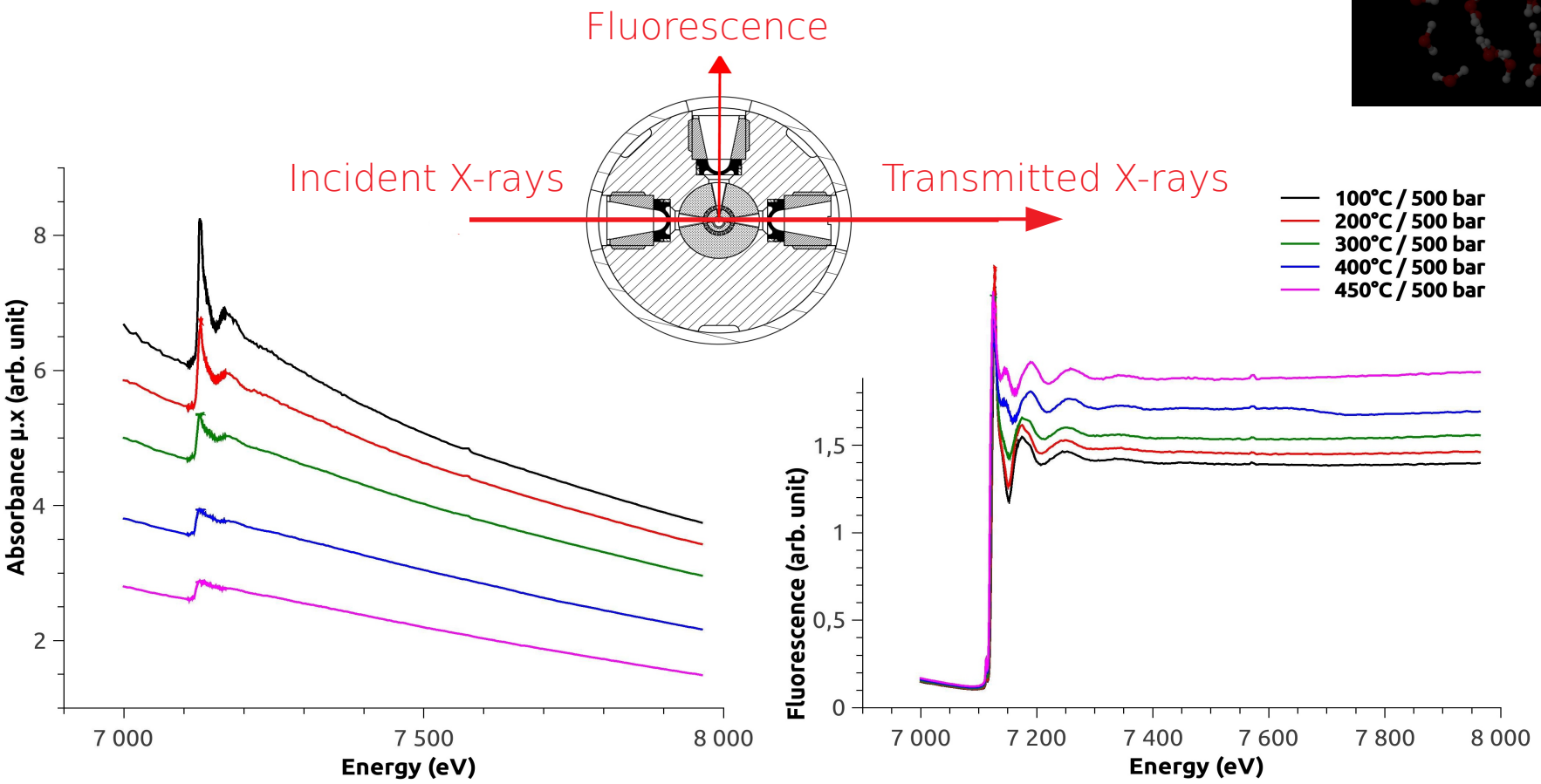
- Iron is among most abundant elements in Earth's crust + ubiquitous of many natural and industrial hydrothermal environments…
- … but HP/HT **speciation, redox and thermodynamic** data are still lacking.



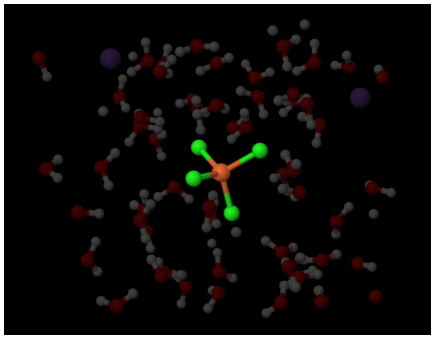


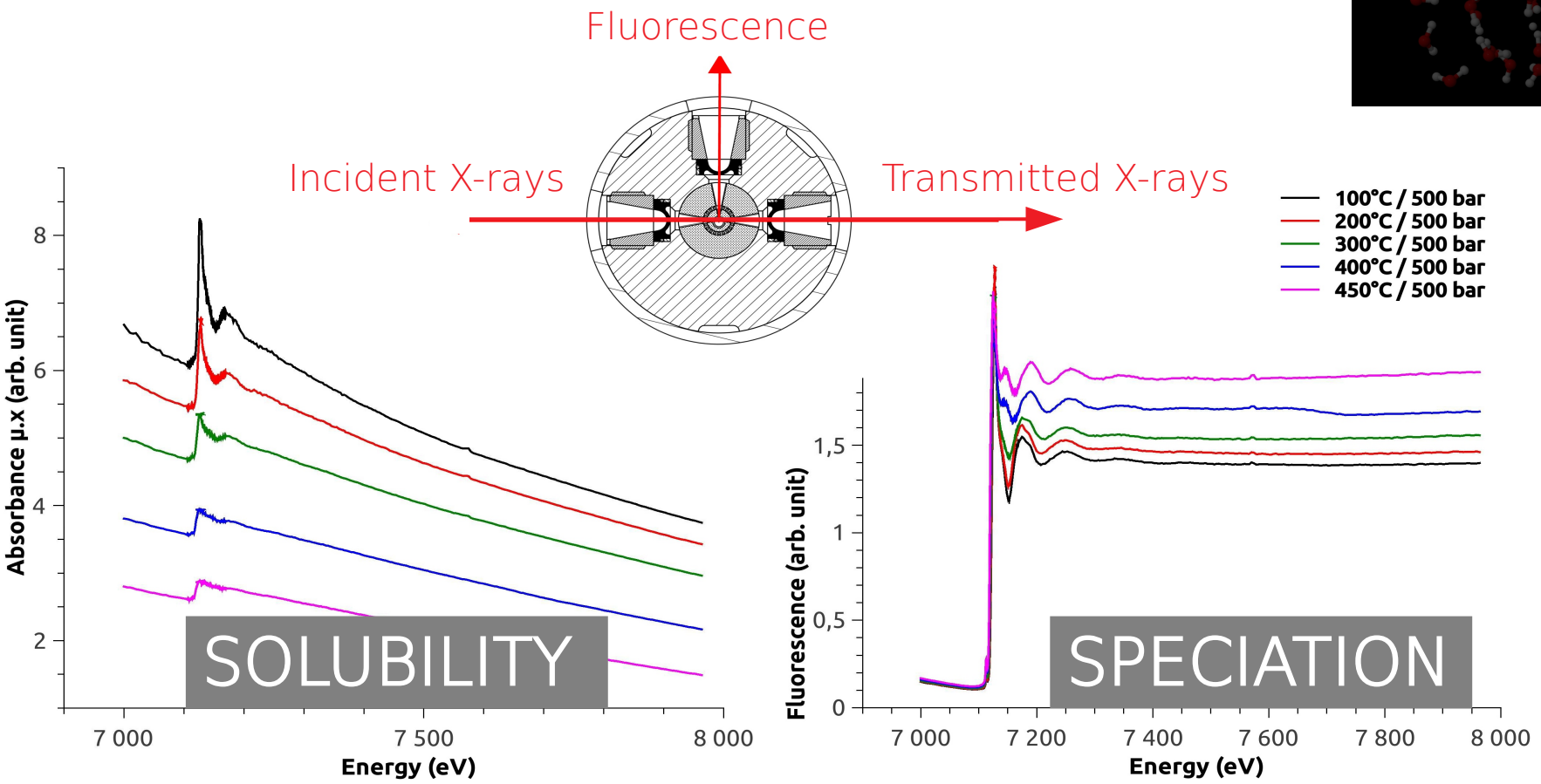
Transport of iron in hydrothermal fluids



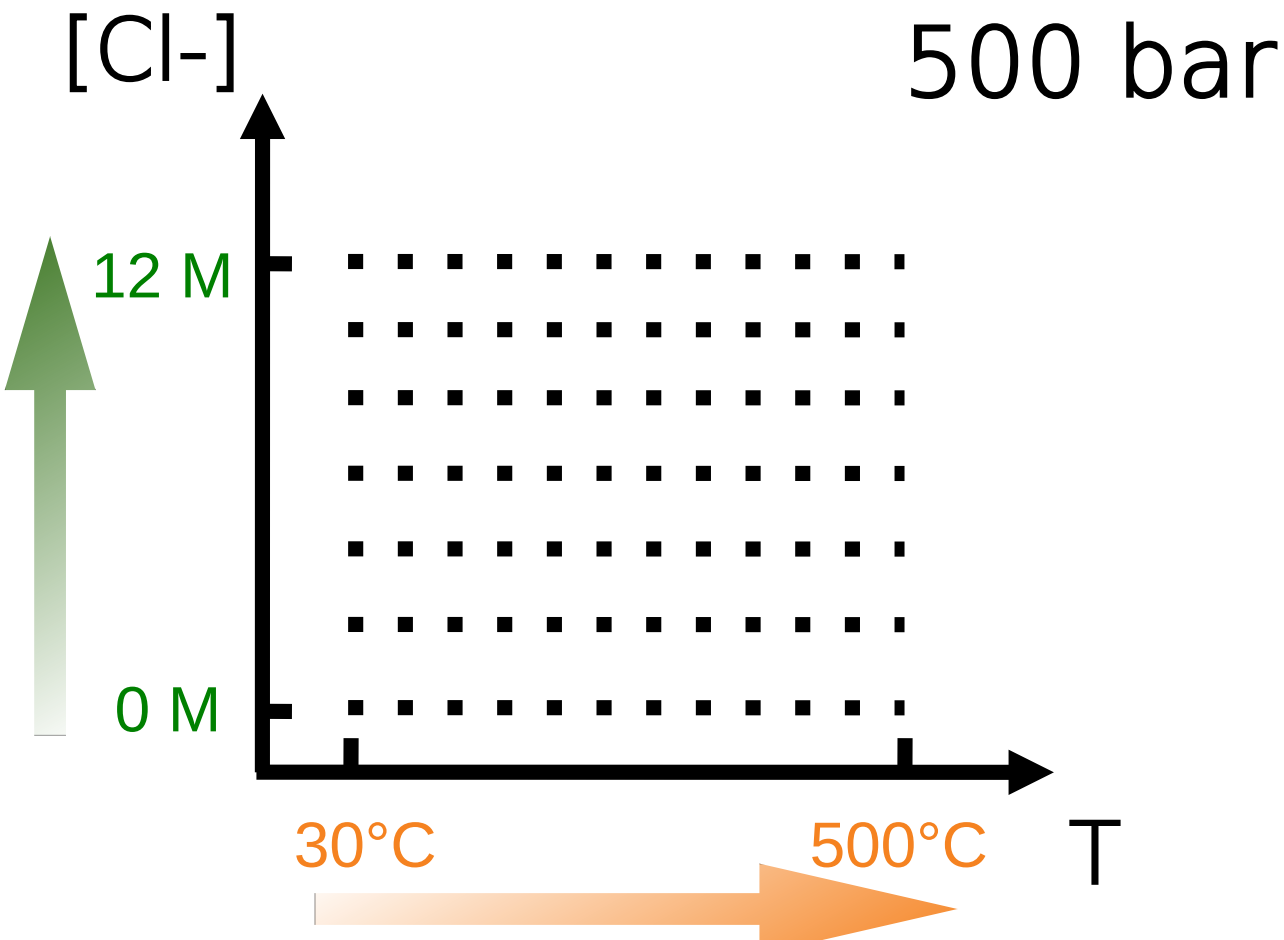


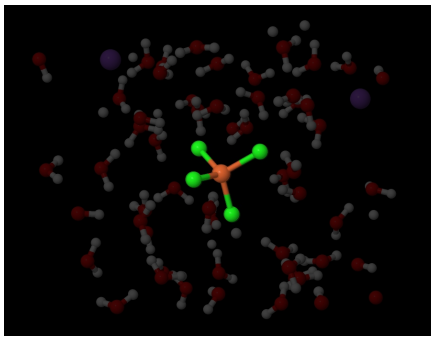
Transport of iron in hydrothermal fluids





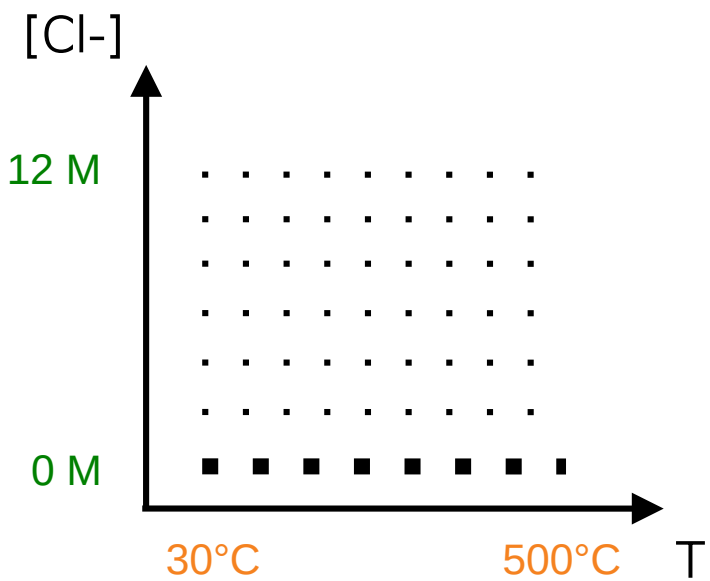
Speciation of Fe^{II}

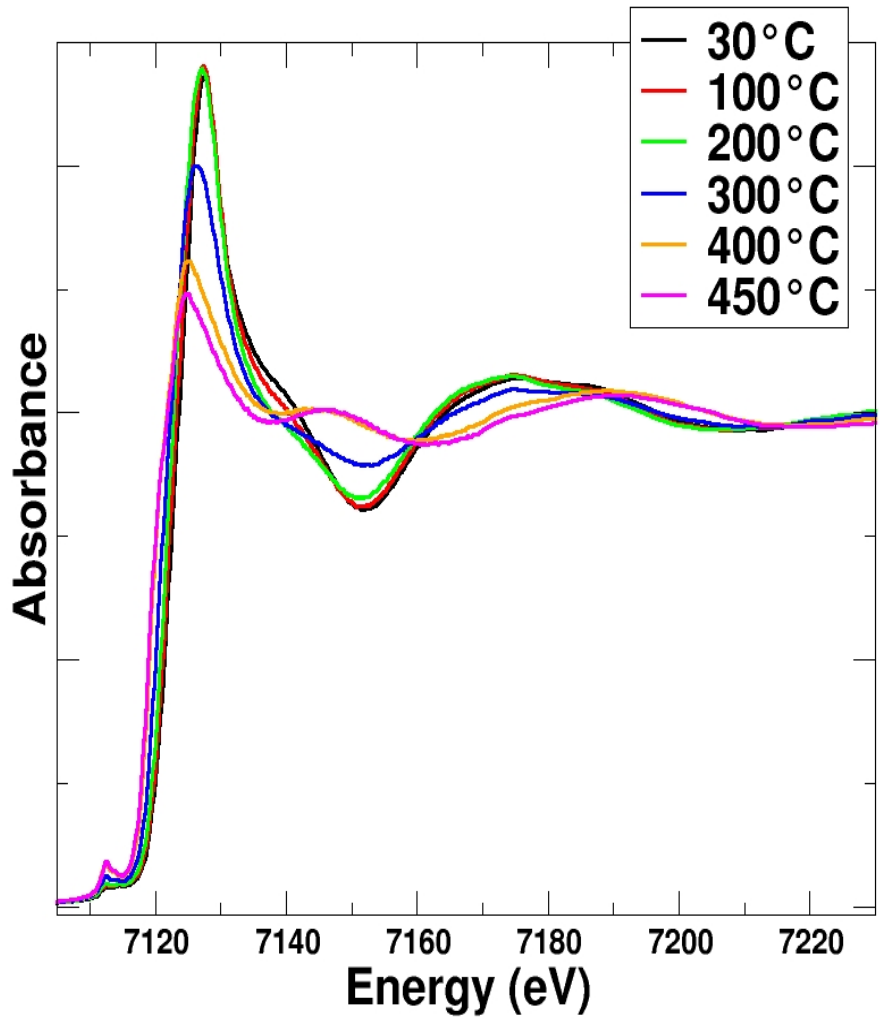




Testemale et al., *Chem. Geol.* 264 (2009)

Speciation of Fe^{II}





Testemale et al., *Chem. Geol.* 264 (2009)

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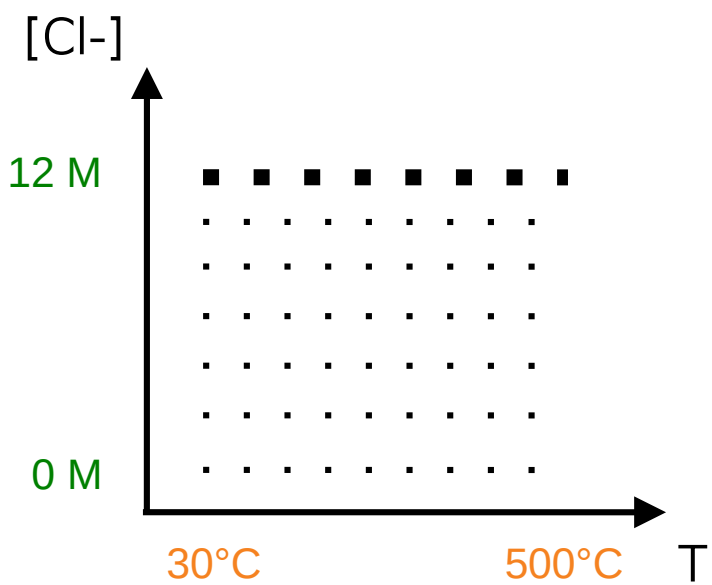
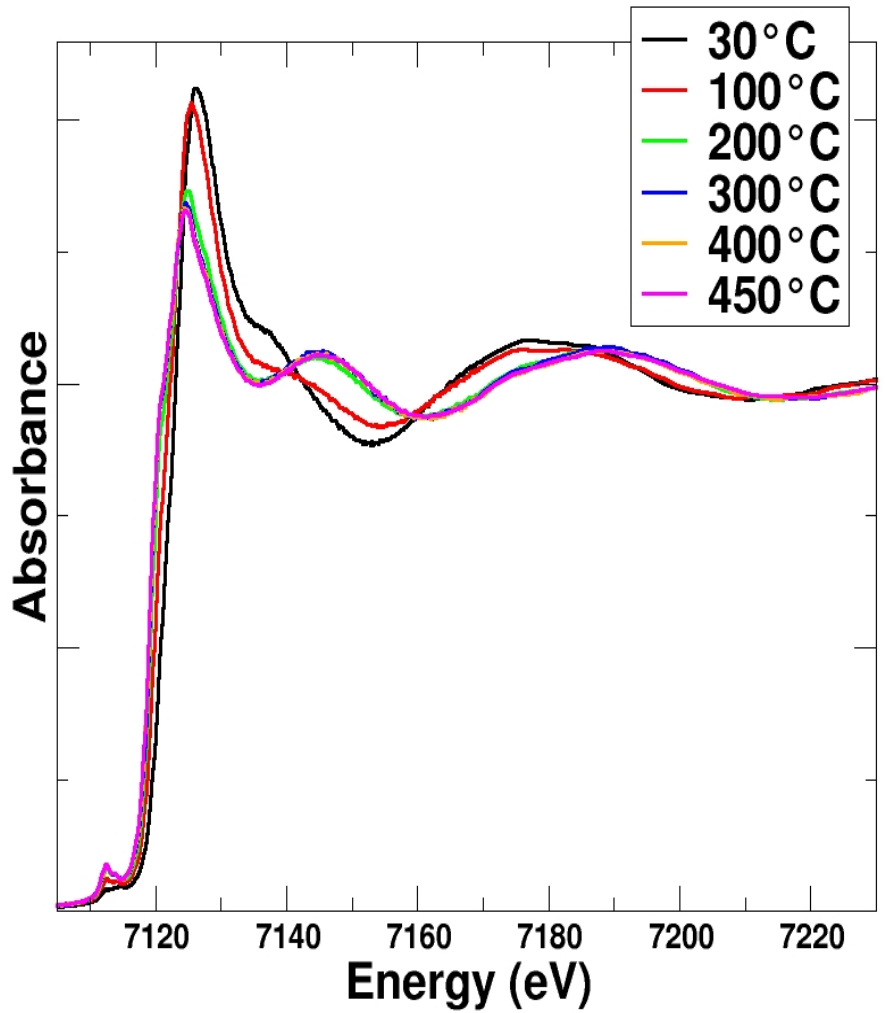
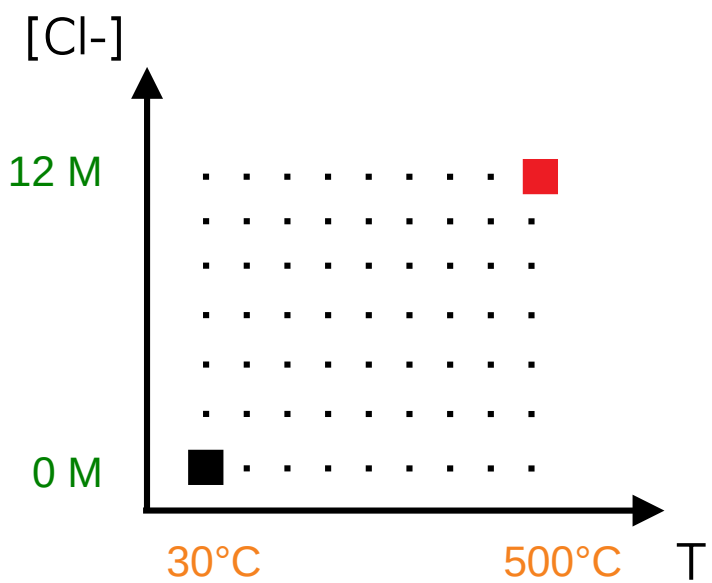




Testemale et al., *Chem. Geol.* 264 (2009)

Speciation of Fe^{II}: end-members



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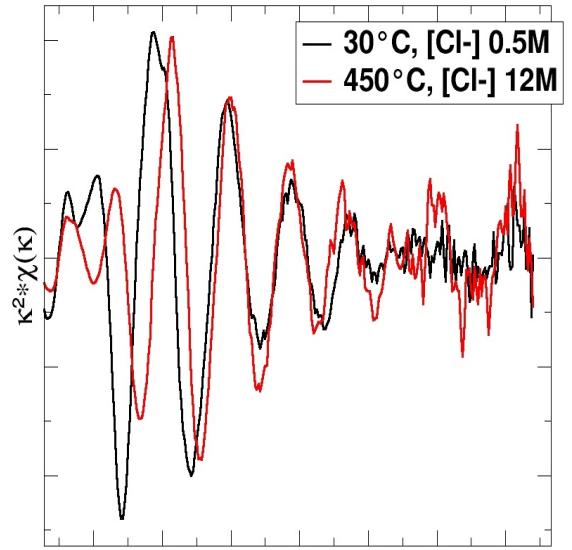

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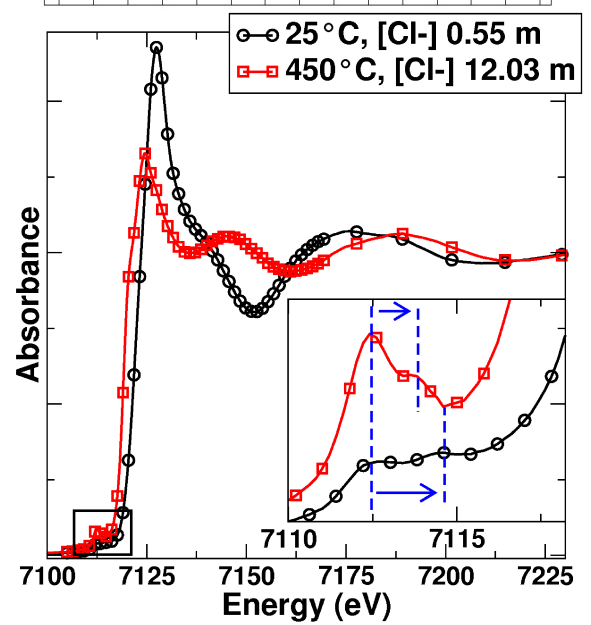
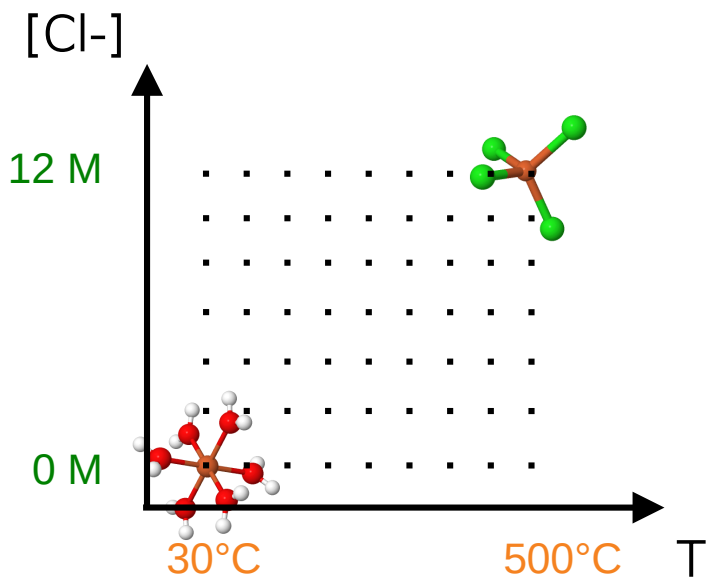


Testemale et al., *Chem. Geol.* 264 (2009)

Speciation of Fe^{II}: end-members



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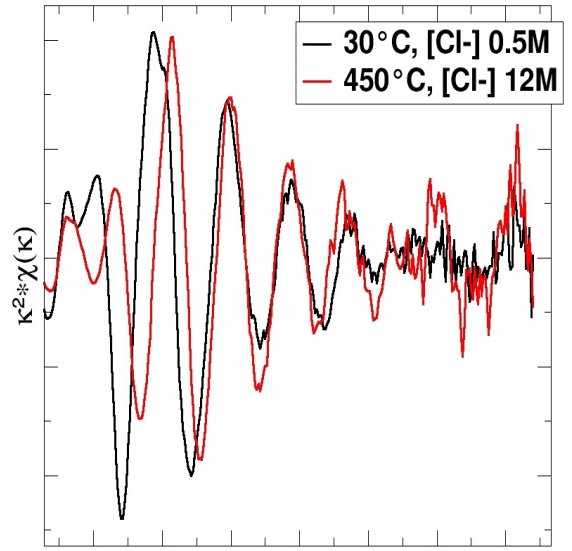

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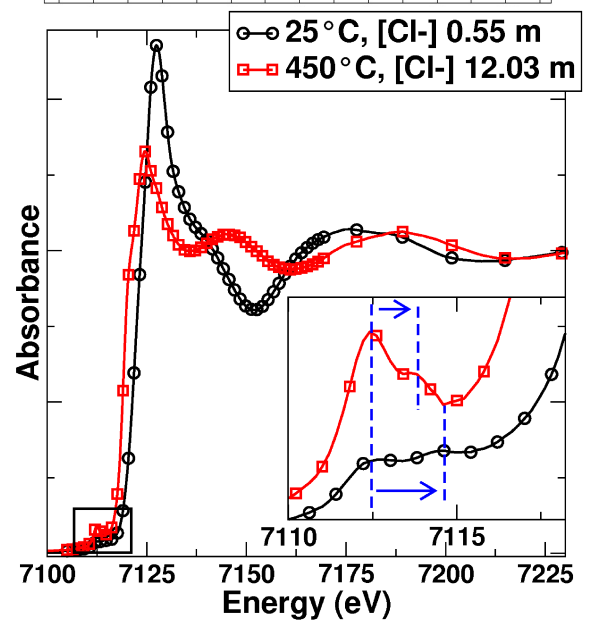


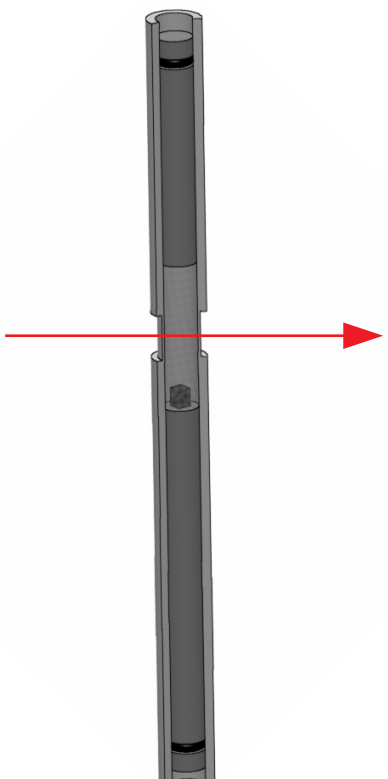
Testemale et al., *Chem. Geol.* 264 (2009)

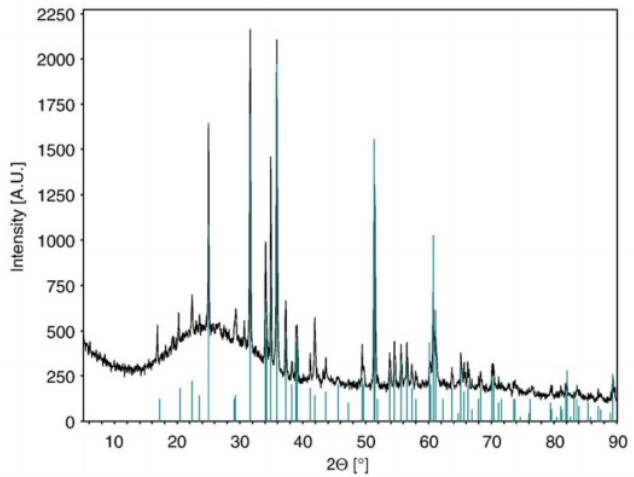
Solubility of Fe^{II}: **Fayalite** dissolution

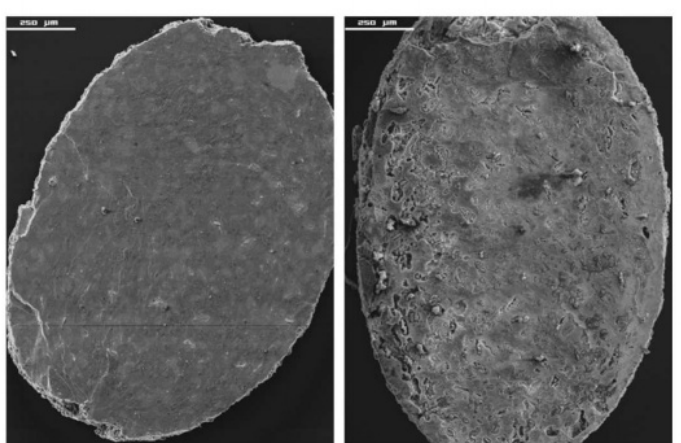
- Global context **CO_2 storage** (and H_2 generation): availability of dissolved ferrous iron.
- But **reaction rates** are poorly constrained: dissolution kinetics data needed.
- **Moderate P/T**: 300 bar/100°C

Daval et al., *Chem. Geol.* 275 (2010)

Solubility of Fe^{II}: Fayalite dissolution

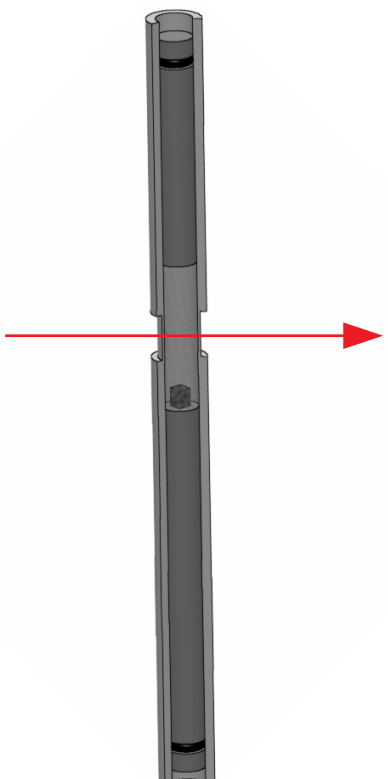




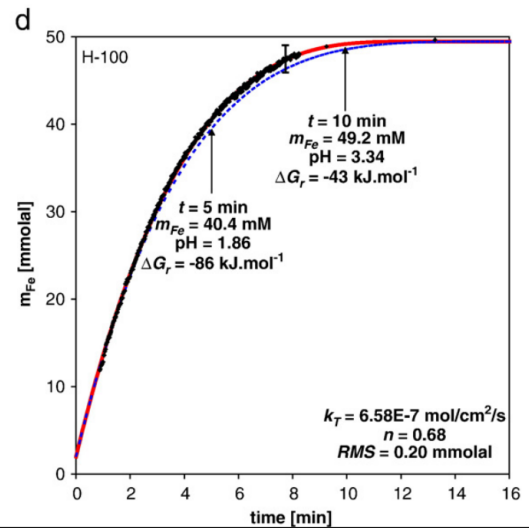


Daval et al., *Chem. Geol.* 275 (2010)

Solubility of Fe^{II}: Fayalite dissolution



Solubility



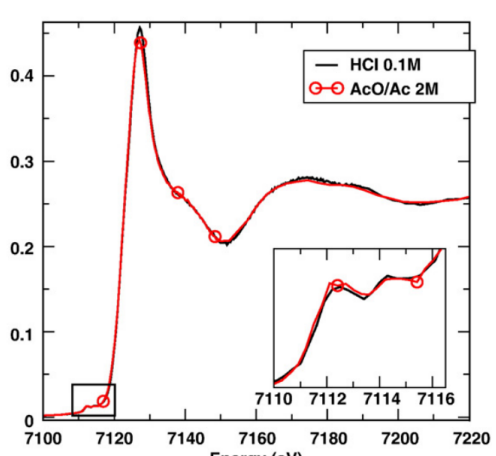
$$R_{\text{net}} = k_0 \exp\left(-E_a / RT\right) a_{H^+}^n$$

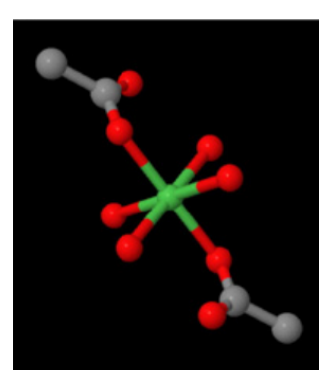
$\log(k_0) = 0.17 \pm 0.63$ mol.cm^{-2}.s^{-1}

Ea = 45100 ± 4200 J.mol^{-1}

N = 0.74 ± 0.15

Speciation



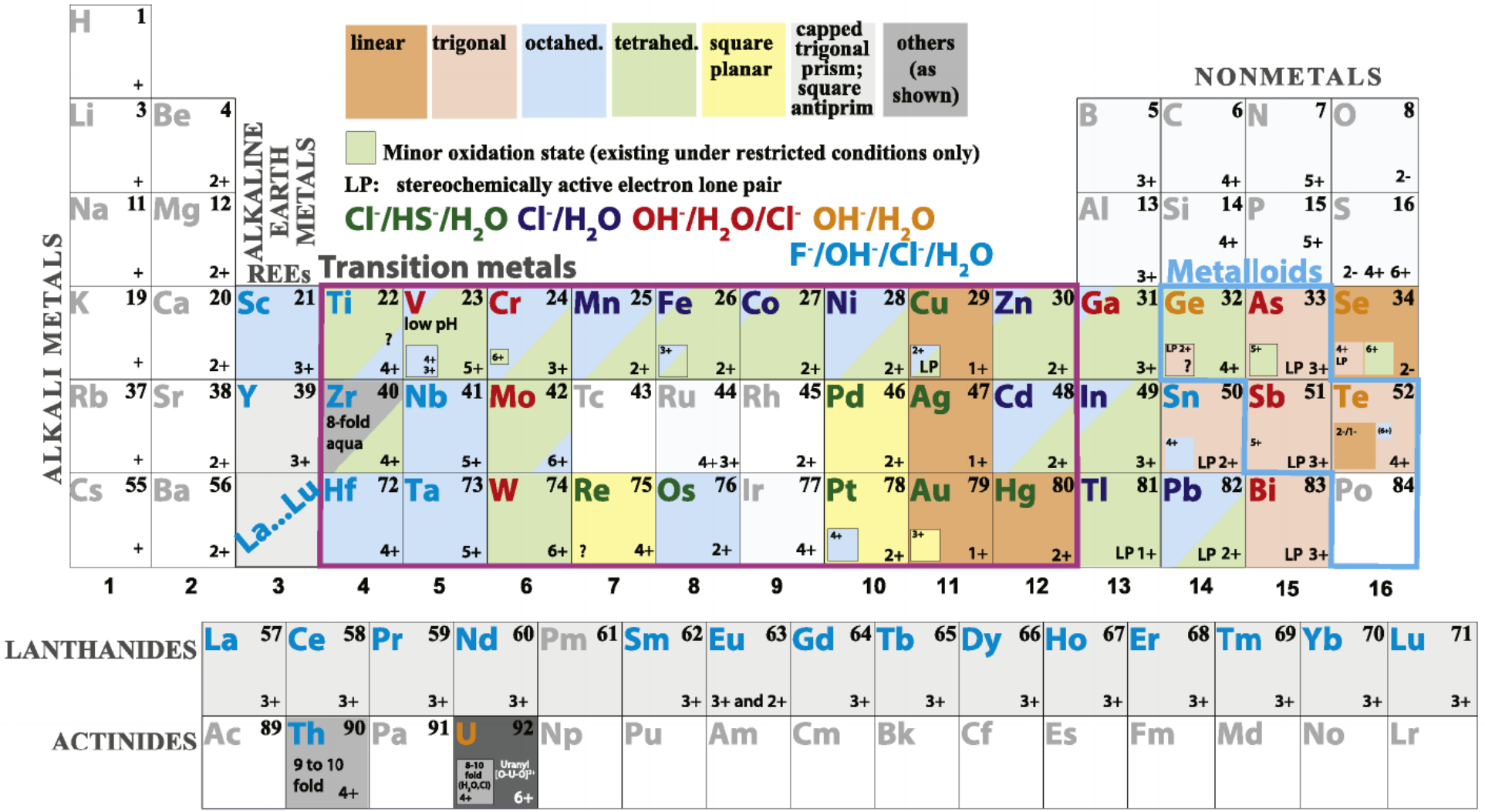


Daval et al., *Chem. Geol.* 275 (2010)

Transport of **metals** in hydrothermal fluids

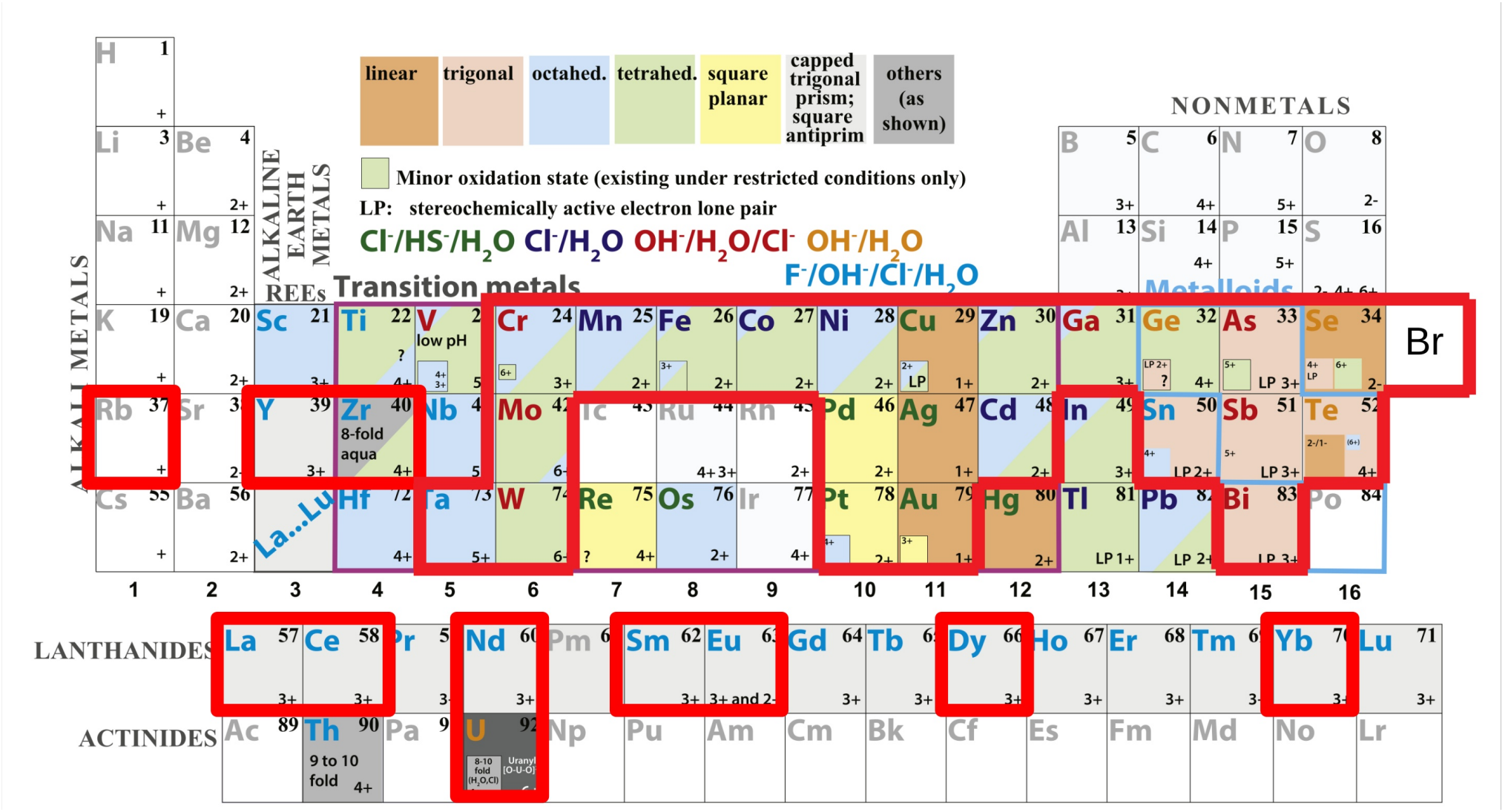
- Collection of high-quality **spectroscopic/speciation** data
- Collection of reliable **solubility and redox** data:
  micro-batch reactor for thermodynamics data
- … in **challenging experimental conditions**:
  low densities, low concentrations, low X-ray energies.

Transport of metals in hydrothermal fluids



Brugger et al., *Chem. Geol.* 447 (2016)

Transport of metals in hydrothermal fluids



FAME/ Néel setup

Brugger et al., *Chem. Geol.* 447 (2016)

Outline

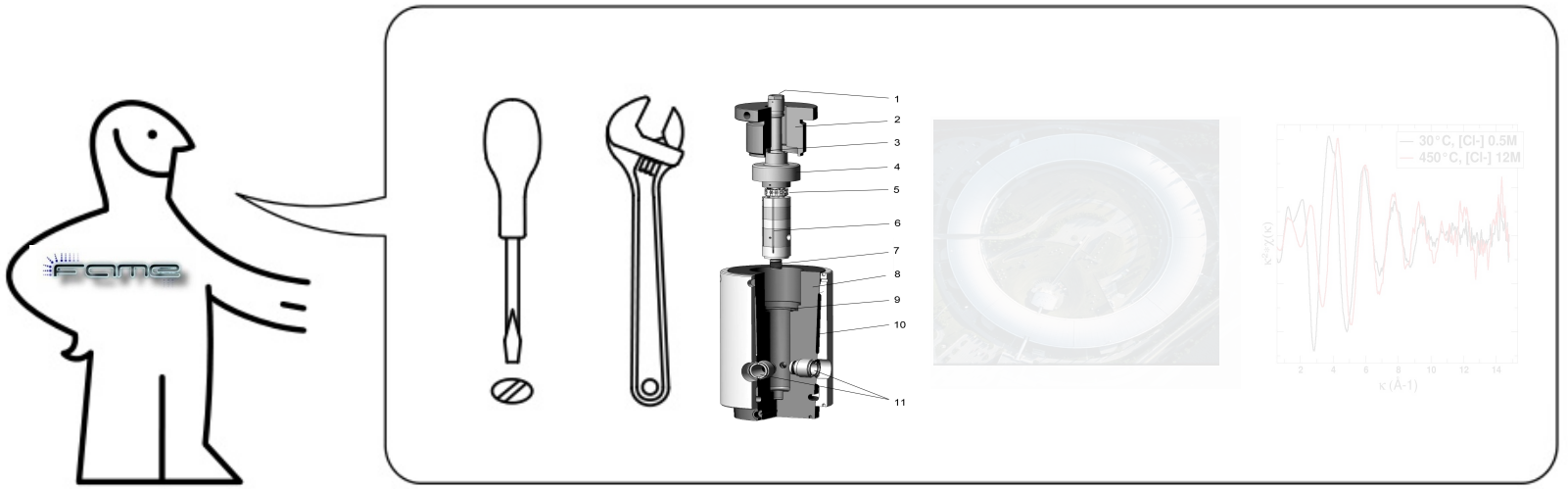
Introduction

Metal transport in hydrothermal fluids

Autoclave technology

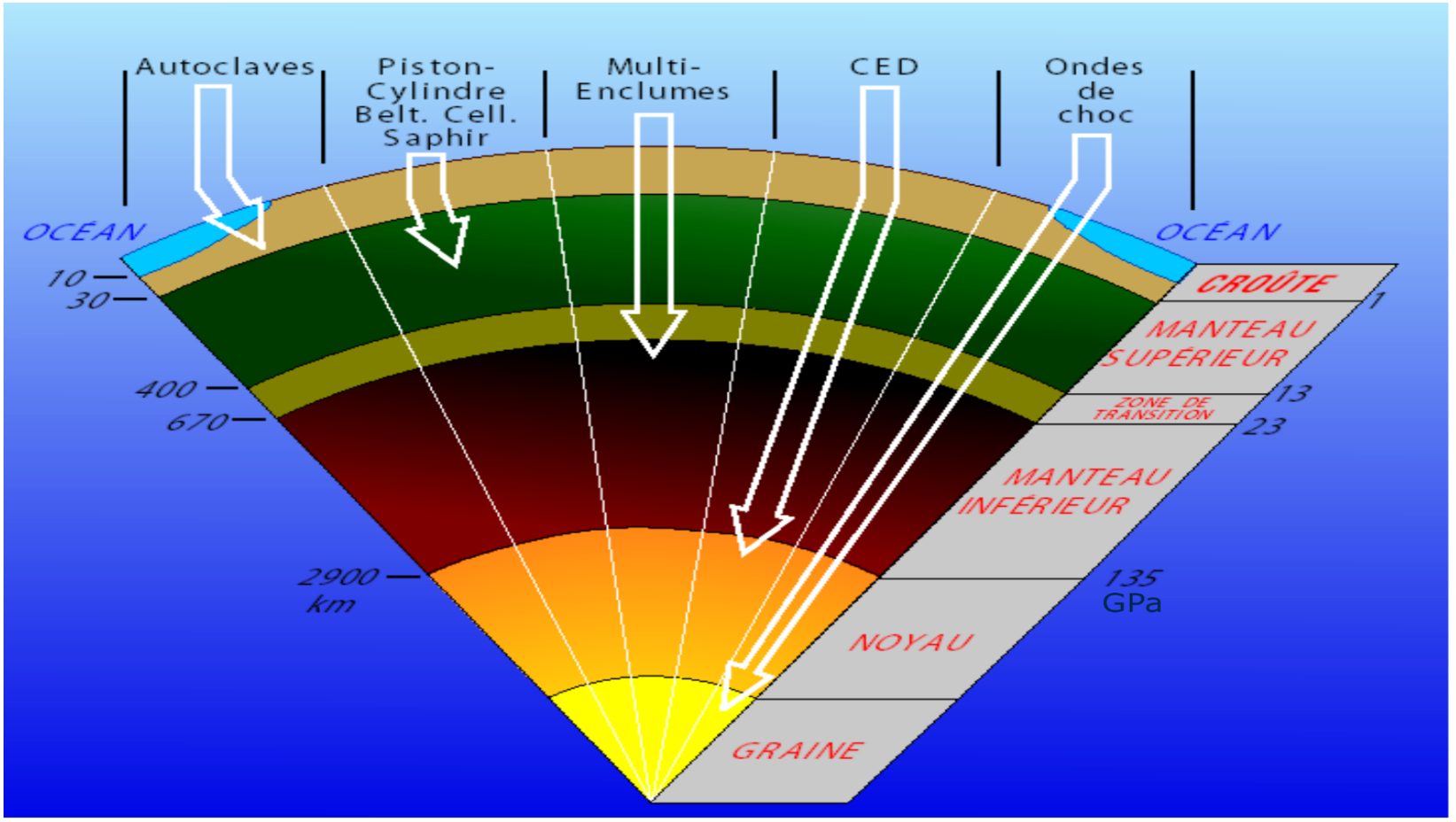
What's next?

Autoclave technology - **Context**



- Hydrothermal
- Spectroscopies
- *In situ*

Autoclave technology - **Context**



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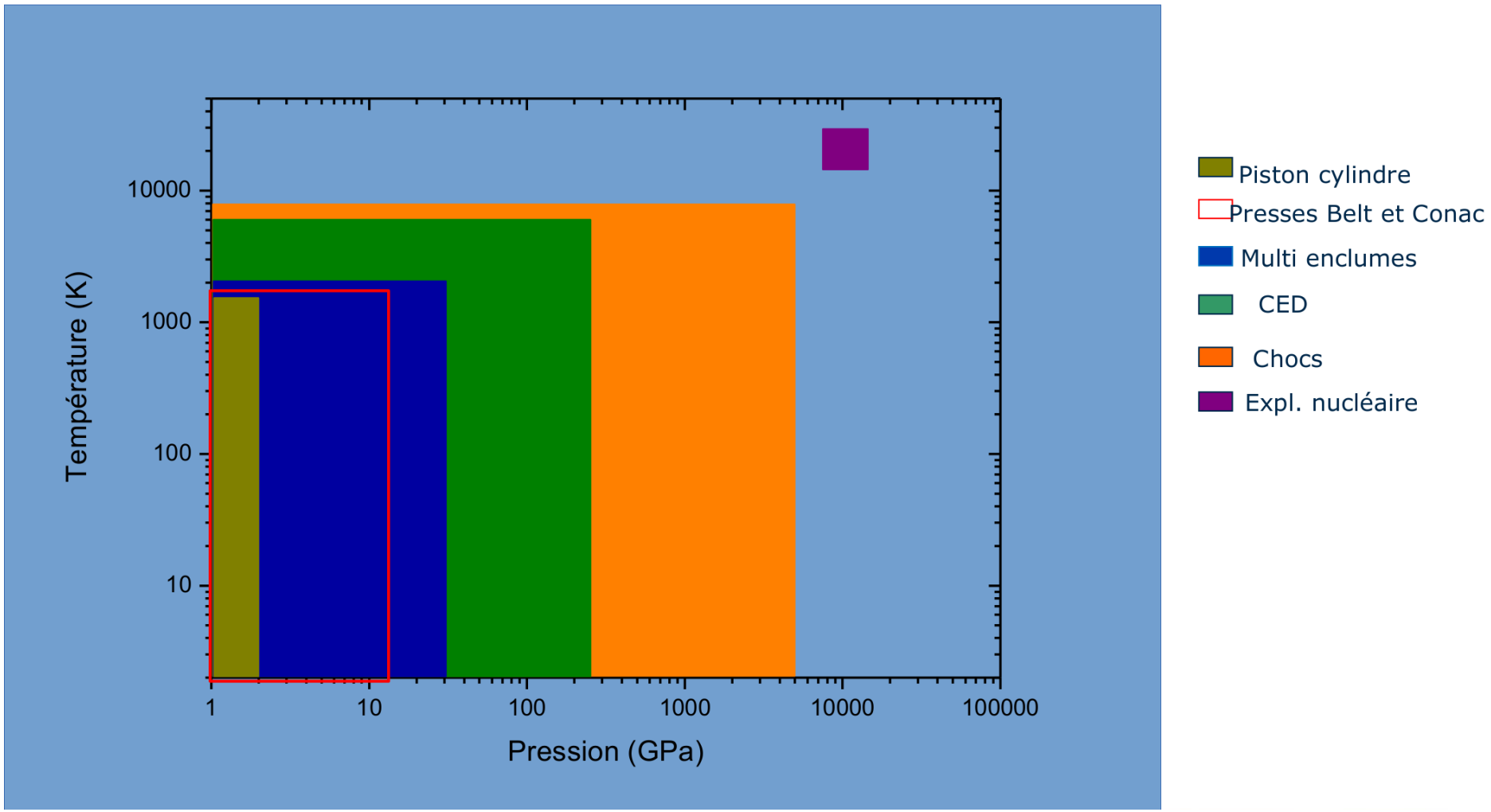
Autoclave technology - **Context**



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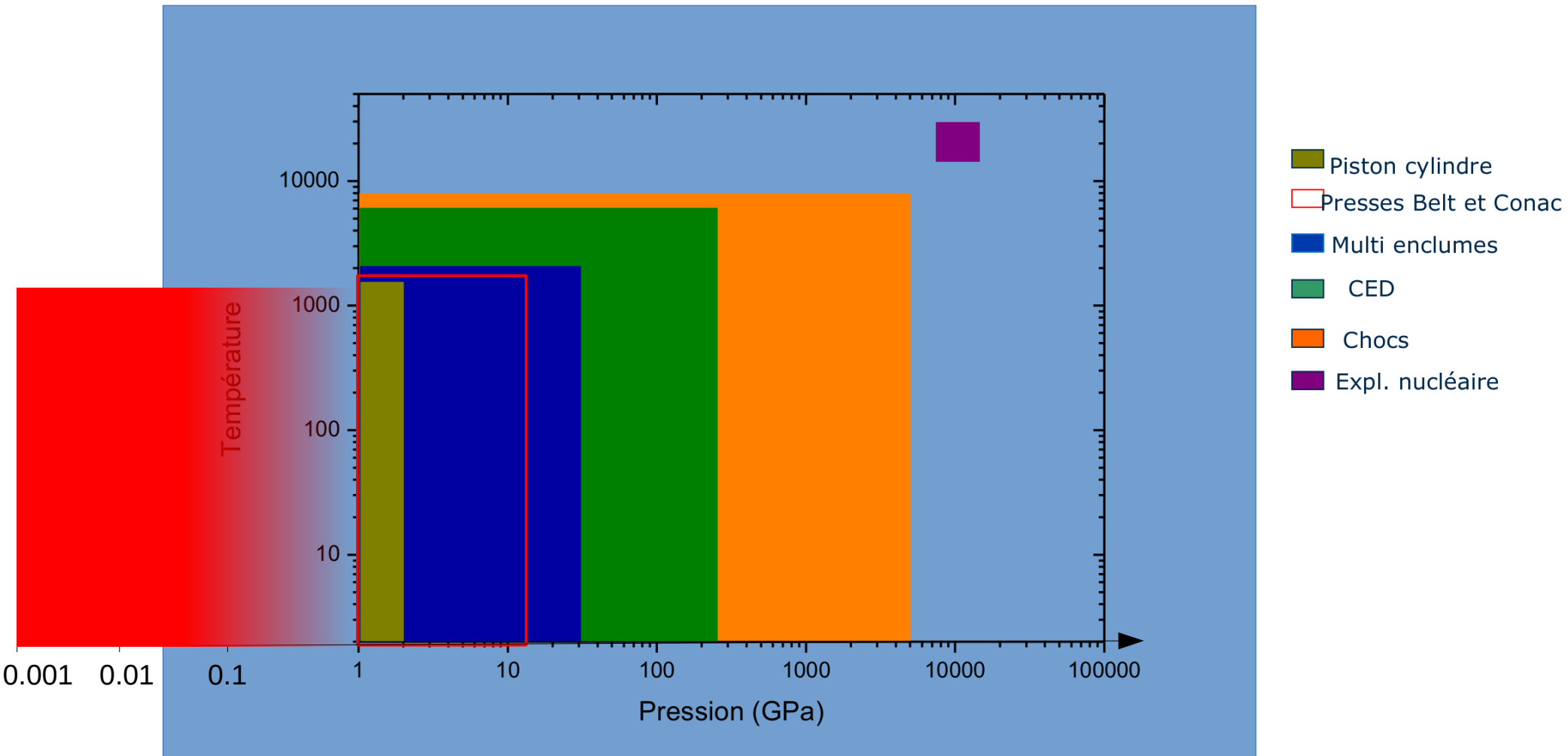
Autoclave technology - **Context**



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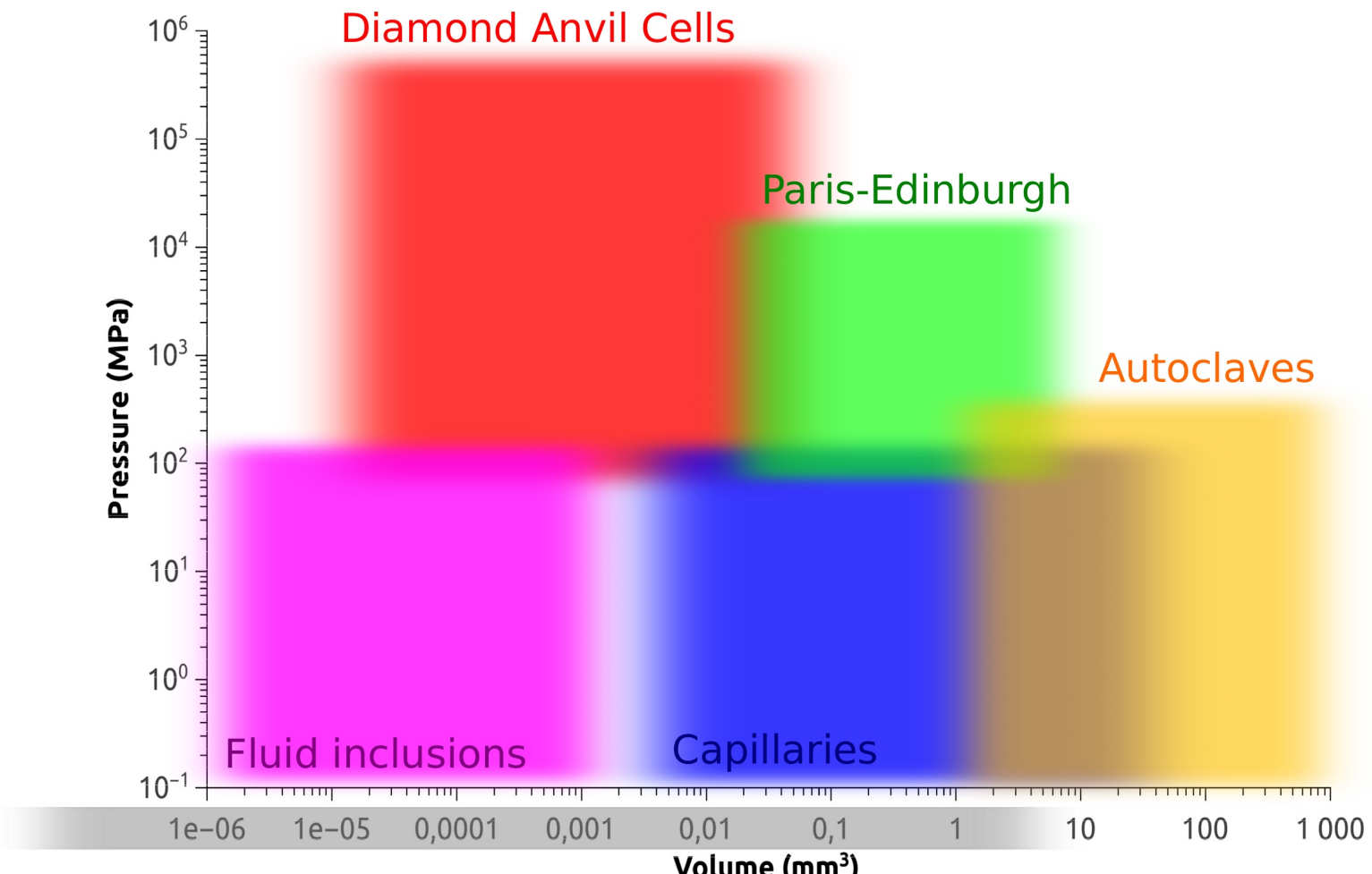
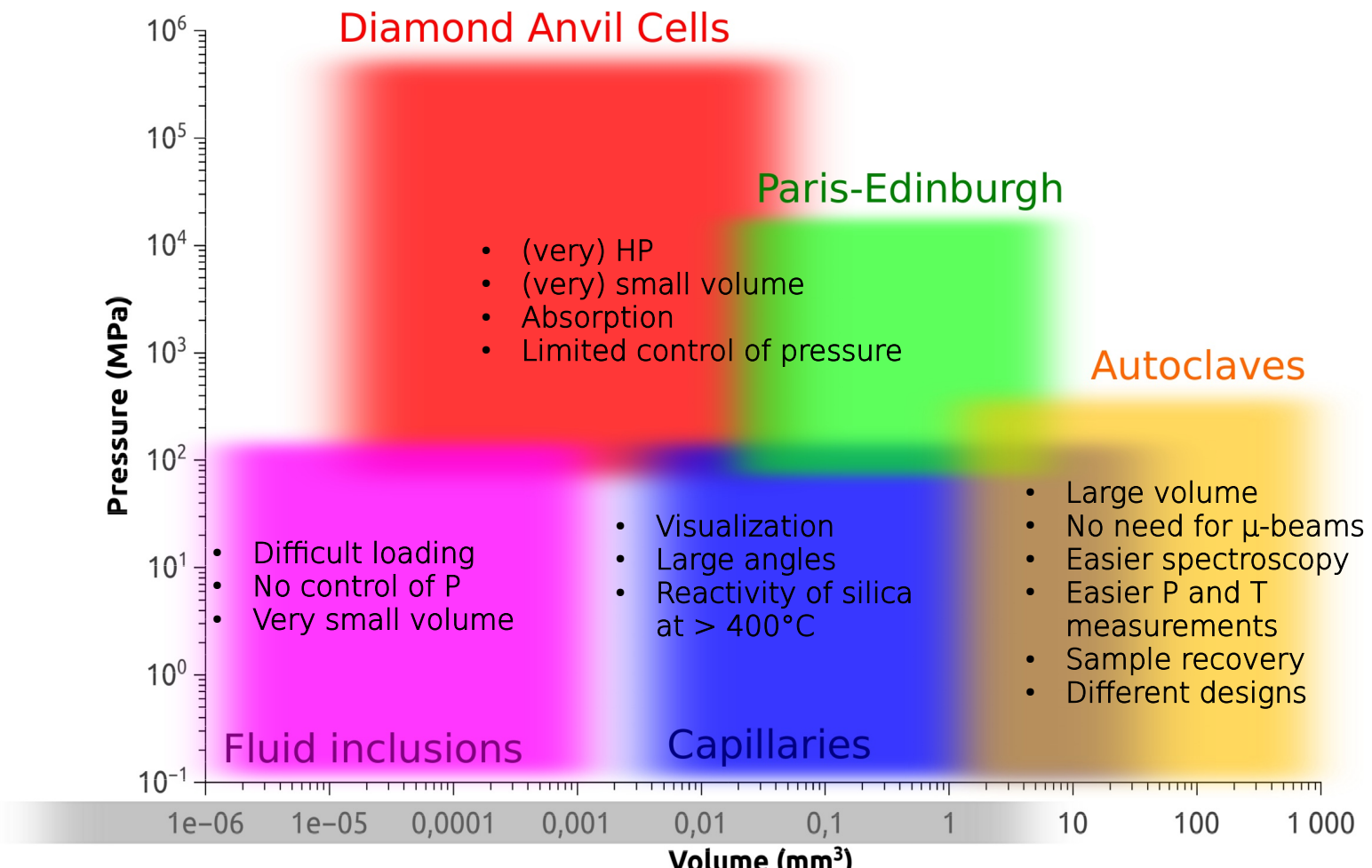
Autoclave technology - Context



D. Testemale, J. Brugger, *International Tables for Crystallography: Volume I, X-ray Absorption Spectroscopy and Related Techniques*; Cells for spectroscopy of fluids at elevated pressure and temperature

Autoclave technology - Context



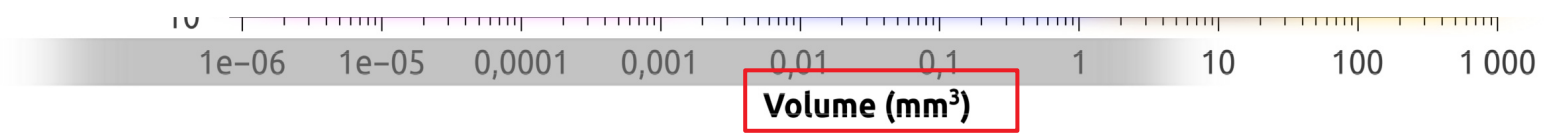
D. Testemale, J. Brugger, *International Tables for Crystallography: Volume I, X-ray Absorption Spectroscopy and Related Techniques*; Cells for spectroscopy of fluids at elevated pressure and temperature

Autoclave technology - **Context**

Sample volume:

- Loading and recovery of samples

- Beam damage
  - radiolytic species
  - sample vol./beam vol. ratio
  - uncontrolled redox



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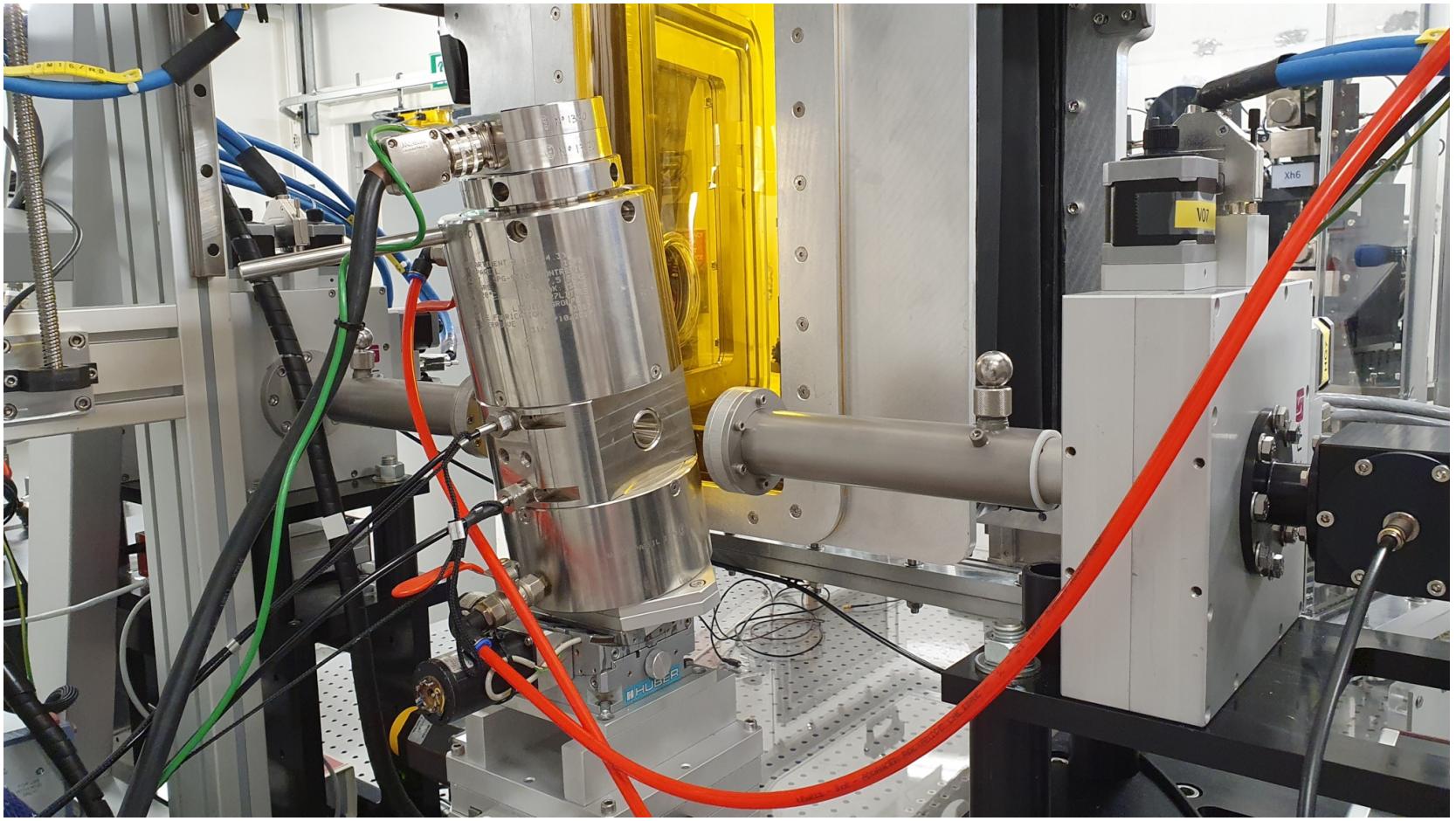
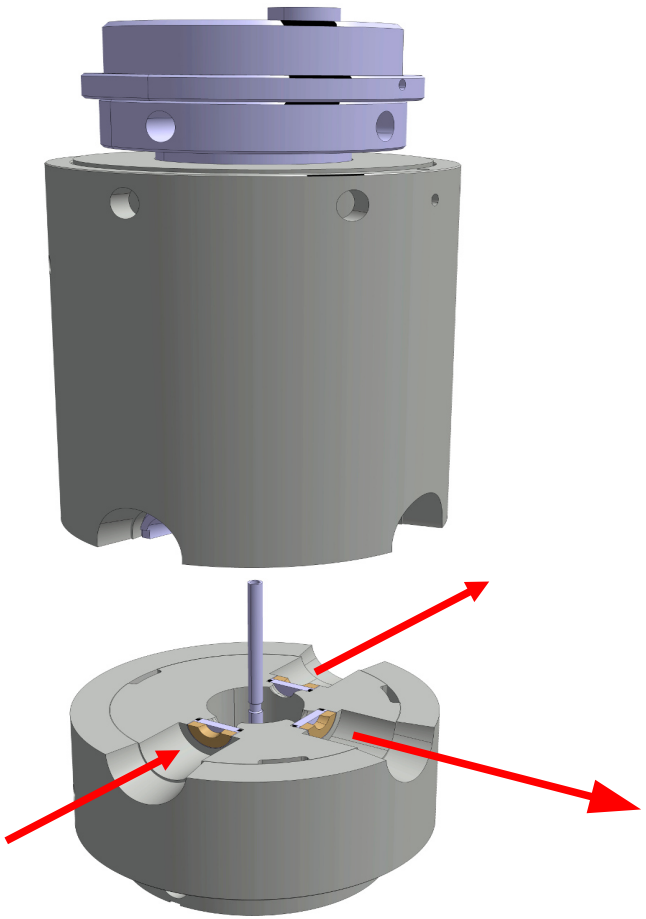
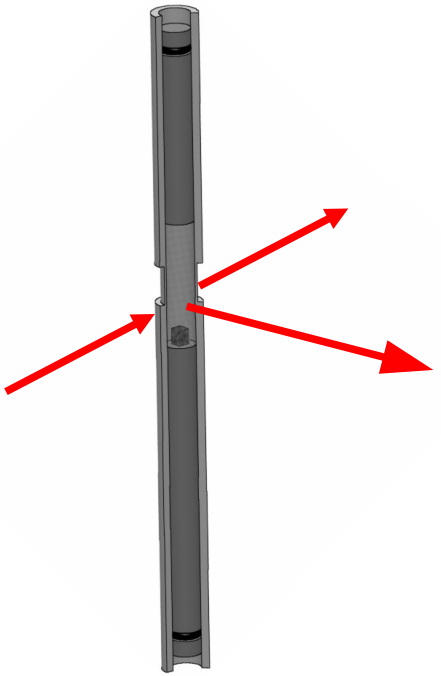
Autoclave technology – The Néel autoclave

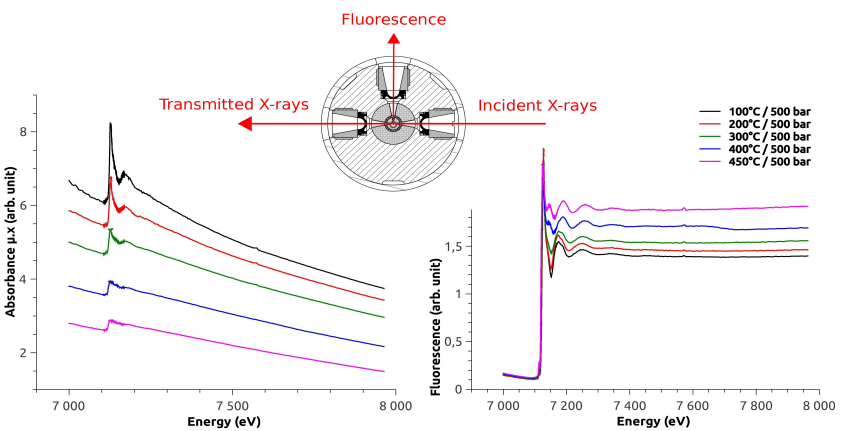


Testemale et al., Rev. Sci. Instrum. (2005)
Testemale et al., Rev. Sci. Instrum. (2016)
Bruyère et al., J. Phys.: Conf. Series (2008)

Autoclave technology – The Néel autoclave







Testemale et al., Rev. Sci. Instrum. (2005)
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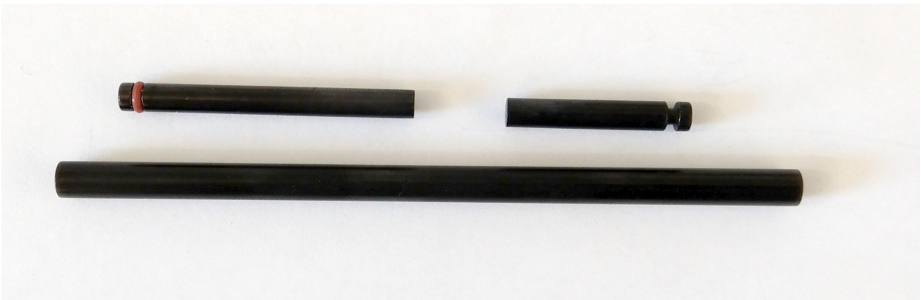
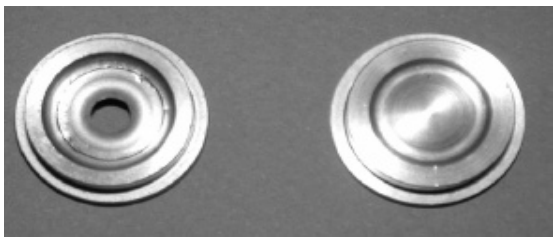
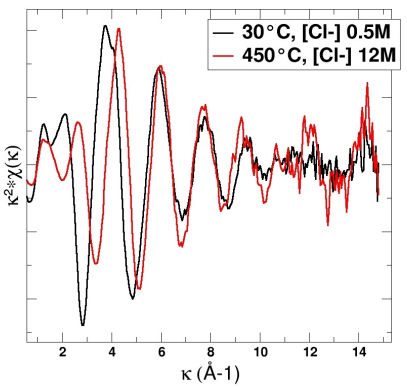
Autoclave technology – The Néel autoclave

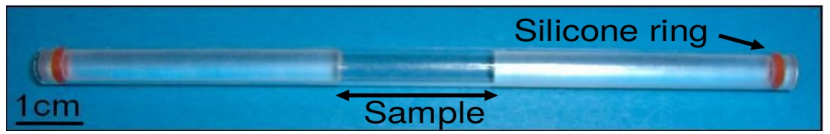
X-rays (XAS, absorption)







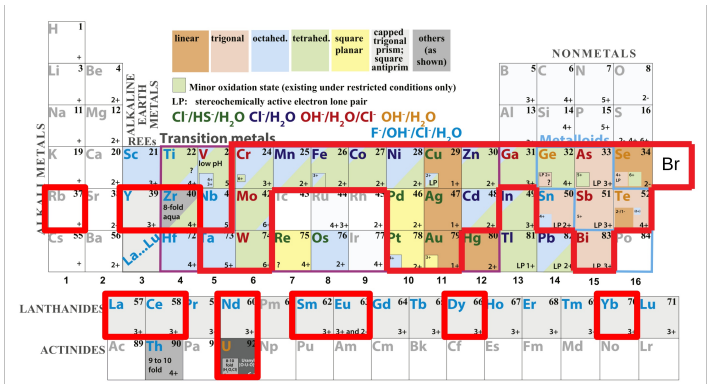
Visible (Raman, observation)



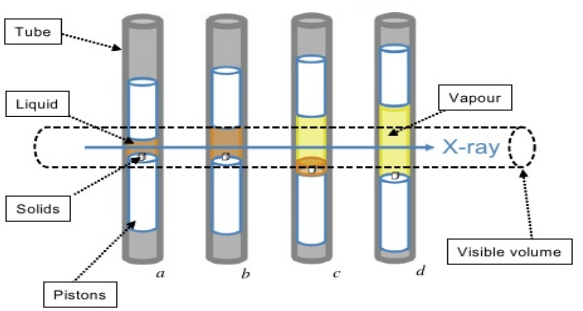
Autoclave technology – The Néel autoclave

- Temperature/pressure :
  [1-2000 bar] ± 0.2 bar
  [30-1000°C] ± 0.05°C

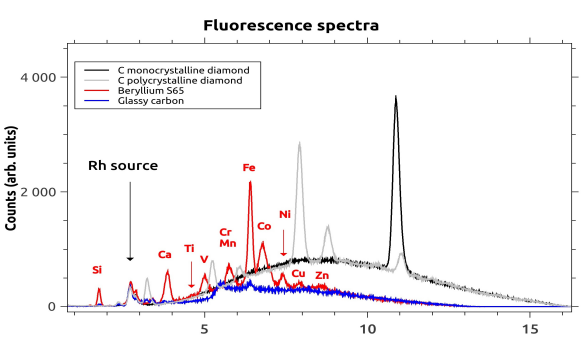
- XAS : which elements ?
  - 5-40 keV
  - Glass-like carbon for photons <12keV (~Ga)



- Which phase ?
Gas, liquid or solid
Density > 0.05 g.cm^{-3}



- Which concentrations ?
  - > 10 ppm for solubility and XANES
  - > 100 ppm for EXAFS
  - Beryllium impurities (carbon windows)



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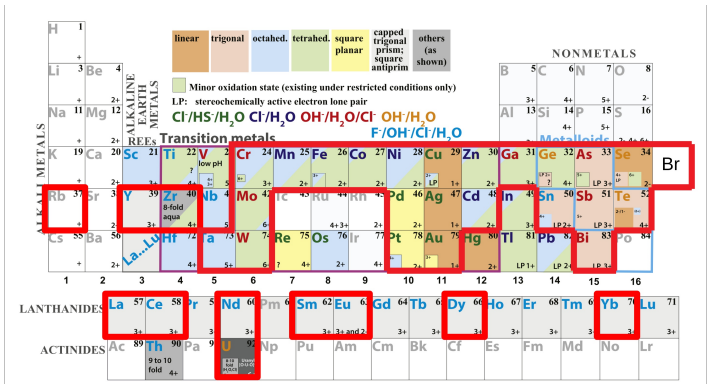

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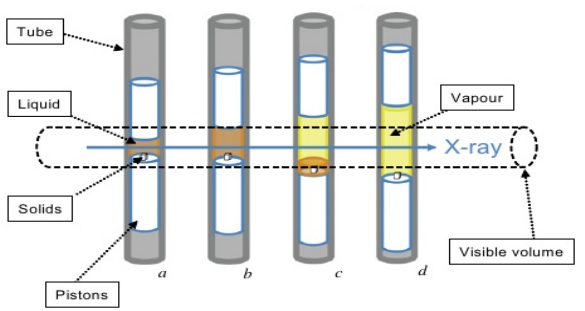

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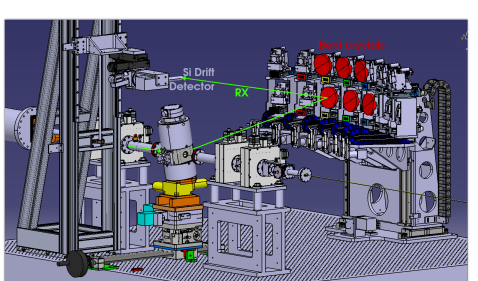
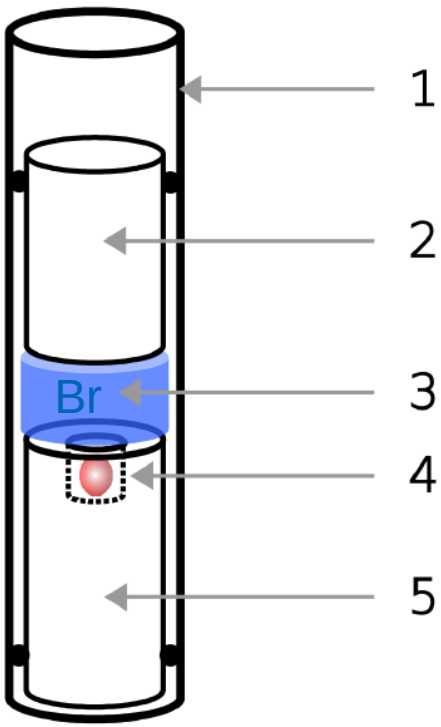
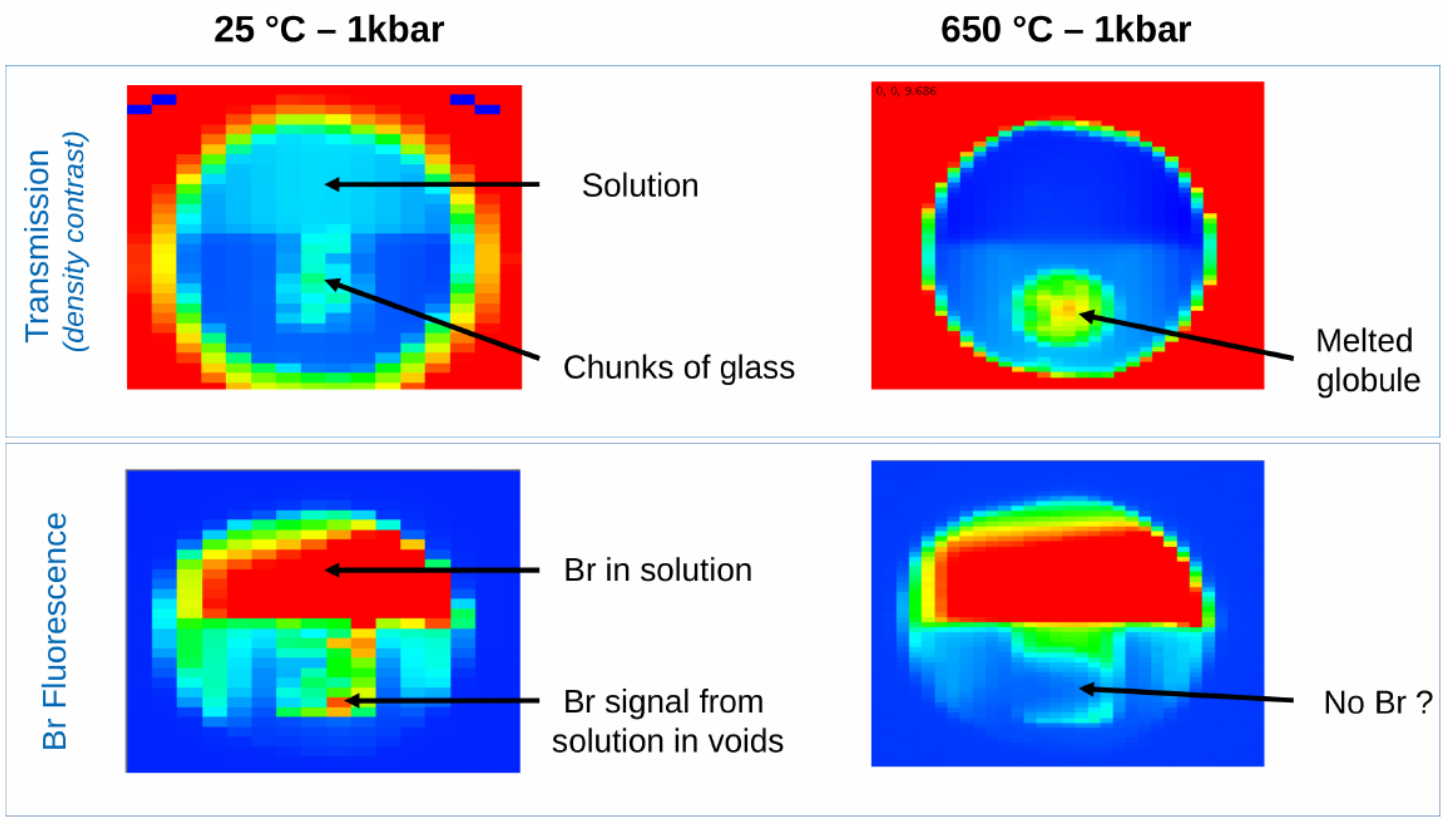


Autoclave technology – Higher temperatures

- **Melts ?** Up to 700°C / 1300 bar.





Louvel et al.

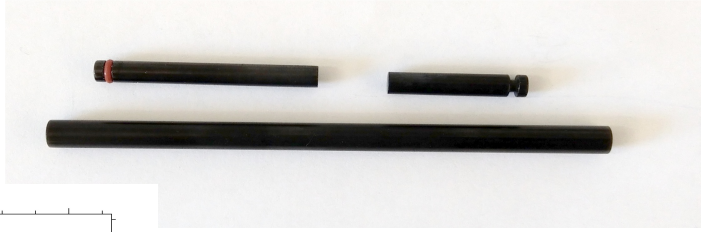
Autoclave technology – **Higher temperatures**

- **Melts ?** Up to **900°C** / 1300 bar.

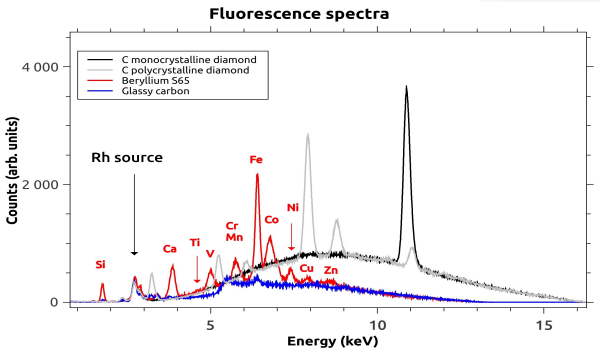
Louvel et al.

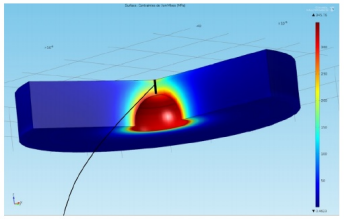
Autoclave technology – Design and usage highlights

- Glass-like carbon internal cells



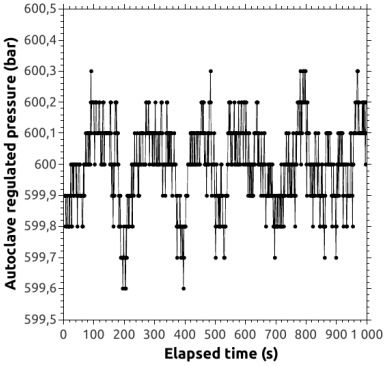
- HP windows material



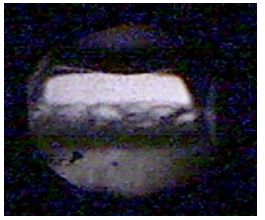


- Beam damage and sample volume

- HP and HT stability

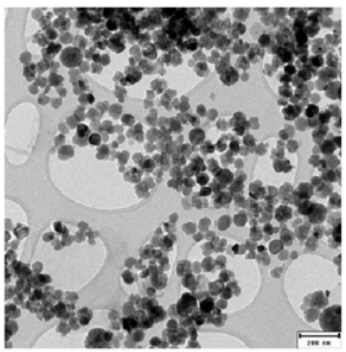


- Visual observation

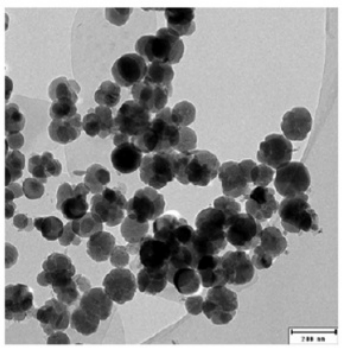


Autoclave technology – Example

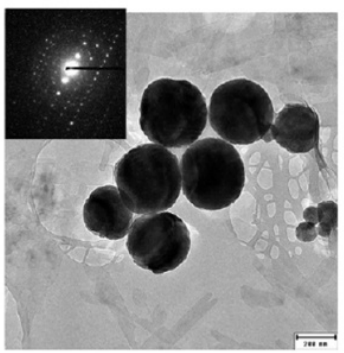
Solvothermal synthesis of **YAG nanocrystals** (G. Dantelle)



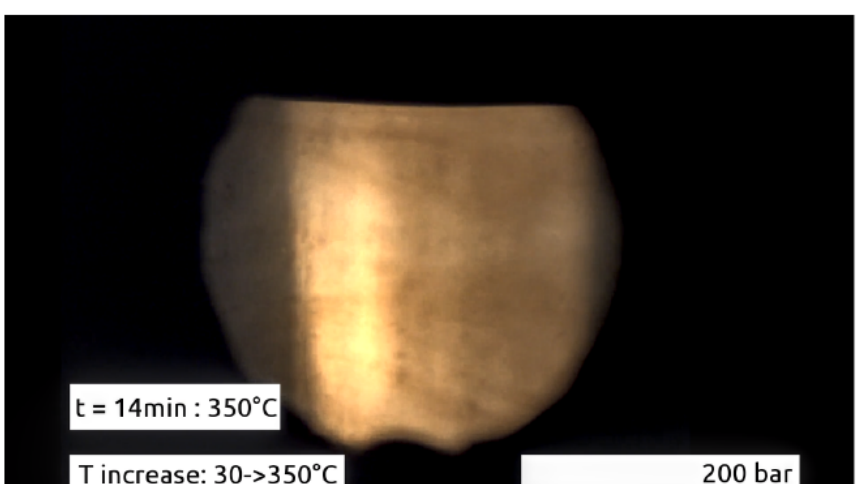
~ 30 nm

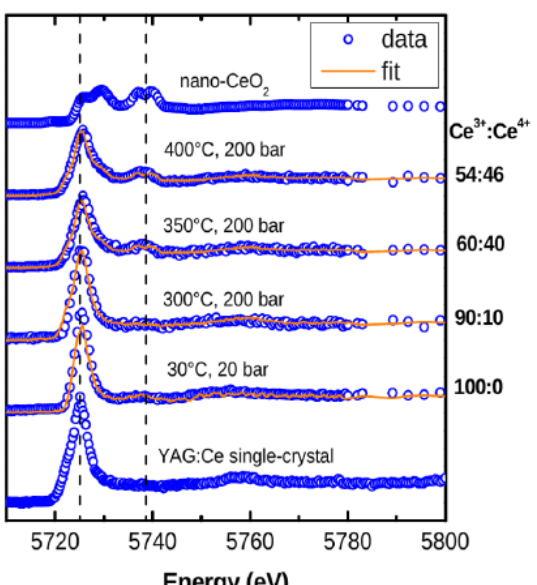


~ 100 nm



> 200 nm





Dantelle et al.
RSC Advances 8 (2018)

Outline

Introduction

Metal transport in hydrothermal fluids

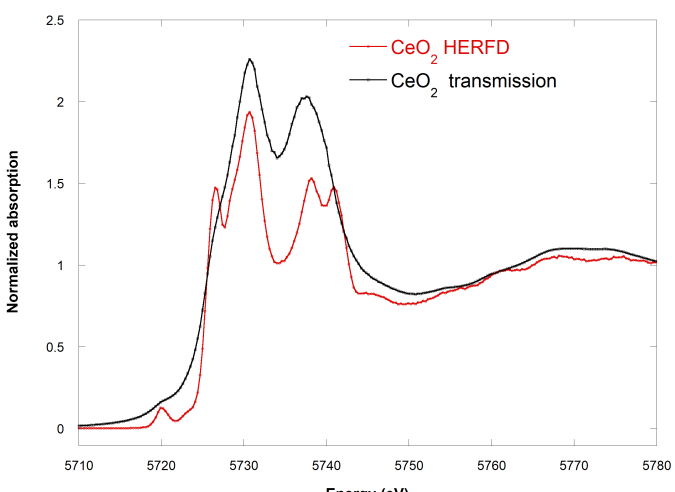
Autoclave technology

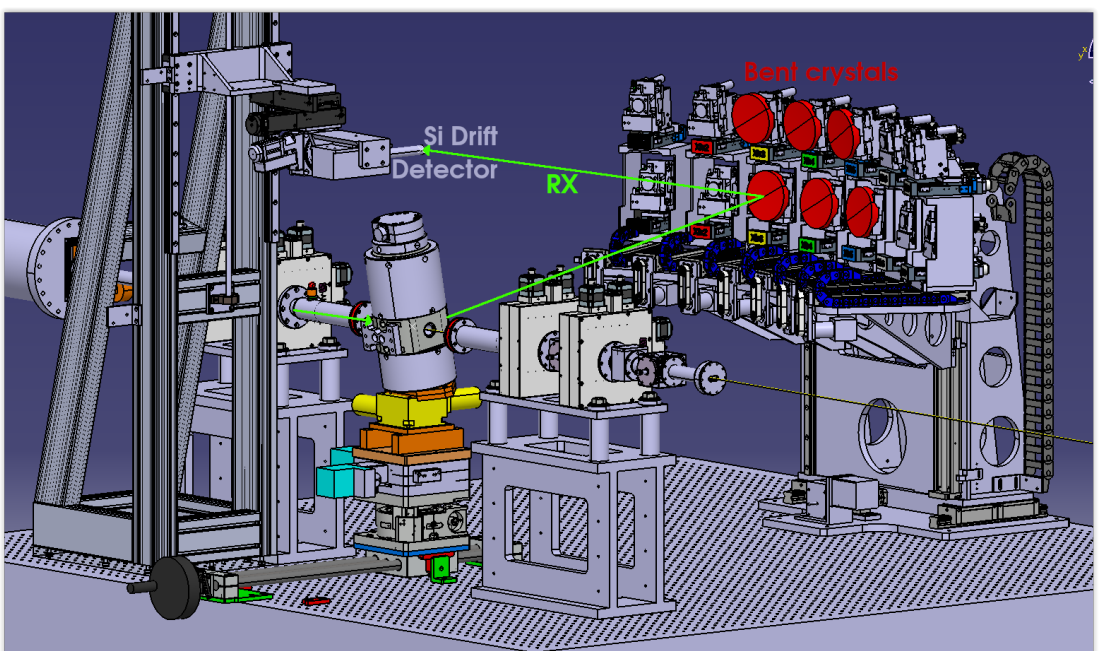
More *in situ* techniques

High Energy Resolution Fluorescence Detection HERFD

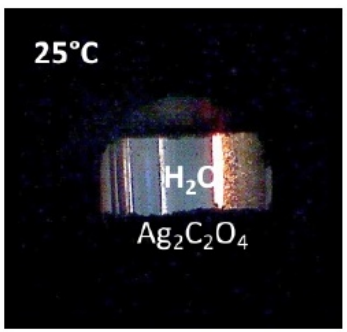
- Better selection of fluorescence photons:
  - Lower XAS detection limits (~ppm)
  - Better spectral quality

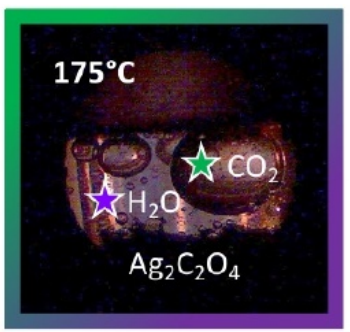
- Finer spectral resolution :
  - XANES features
  - Fluorescence selection
  - Emission spectroscopy

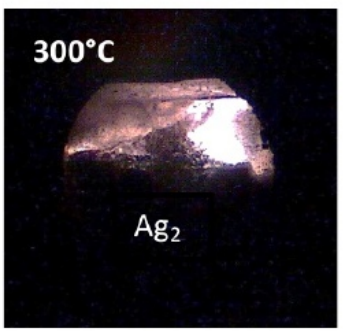


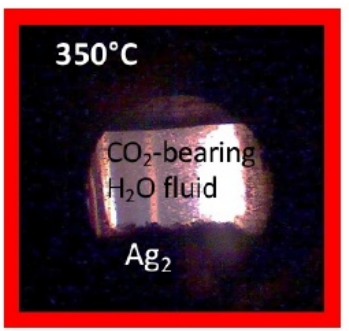


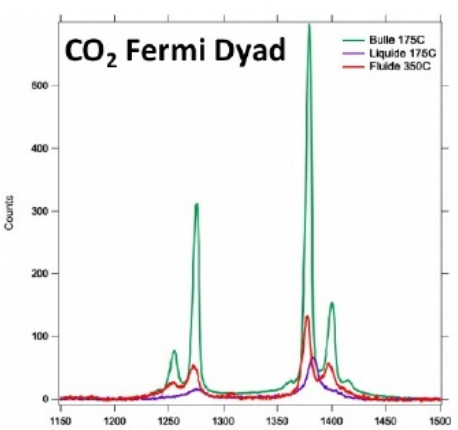
Supercritical fluids – Raman of H_2O-CO_2 supercritical solvents

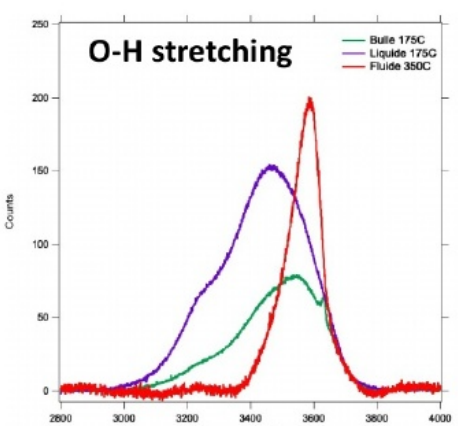






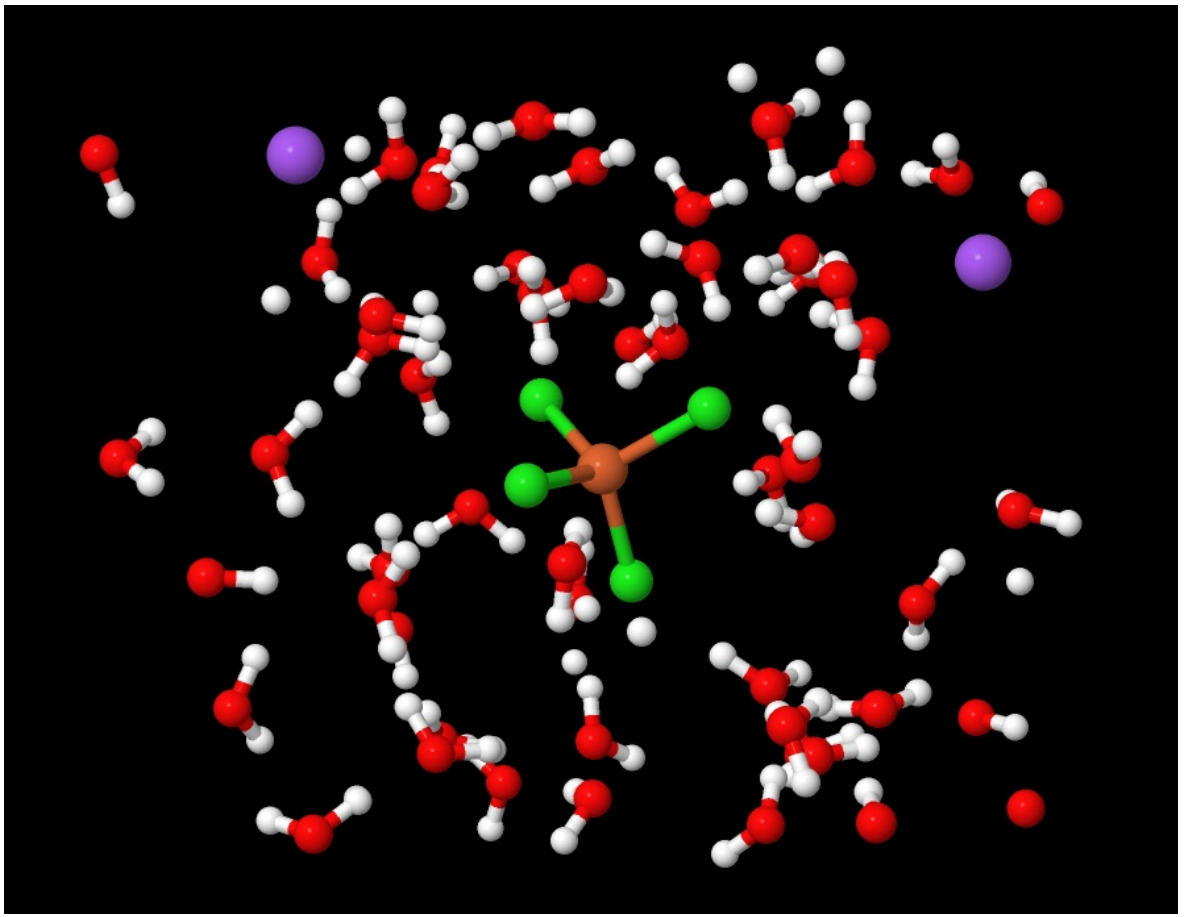






Louvel et al., J.Mol. Liquids 205 (2015)

Structure of supercritical water



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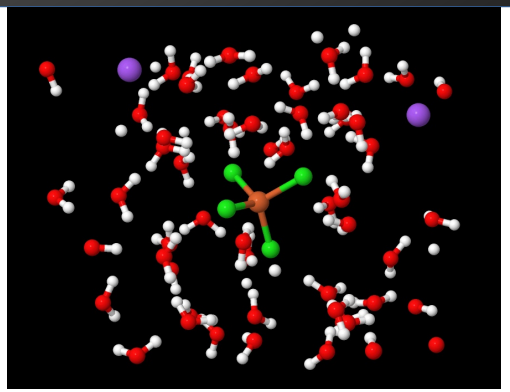

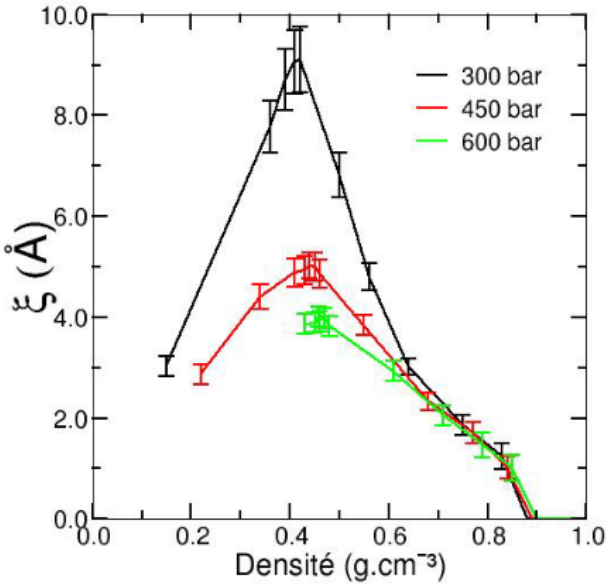

SAXS: correlation length
= size of density fluctuations
Testemale et al., J. Chem. Phys. (2005)

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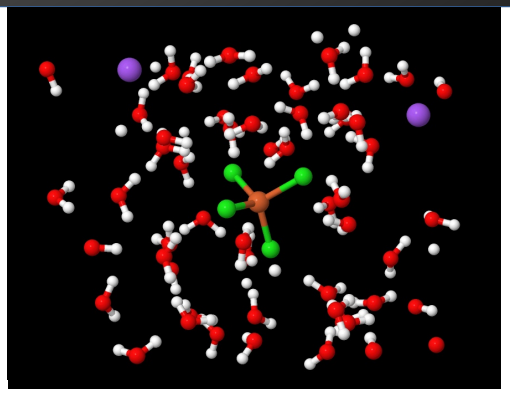

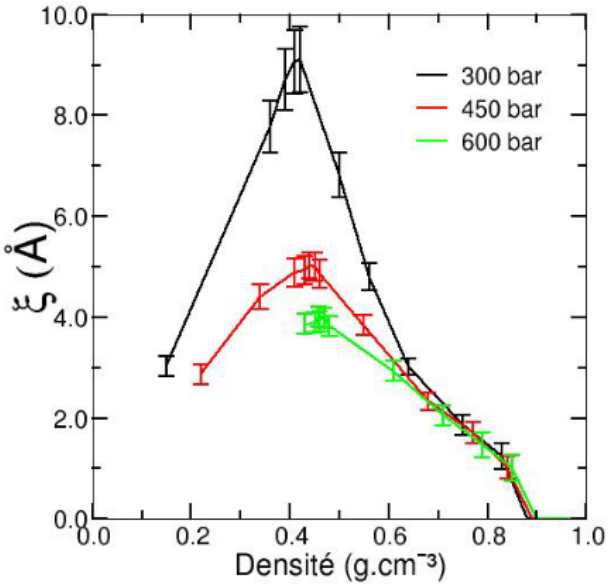

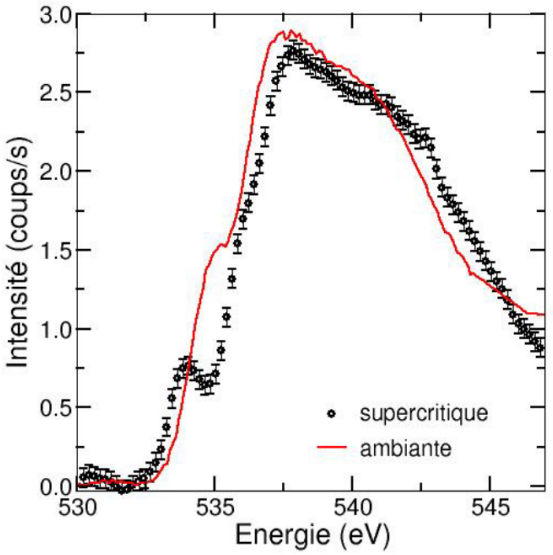

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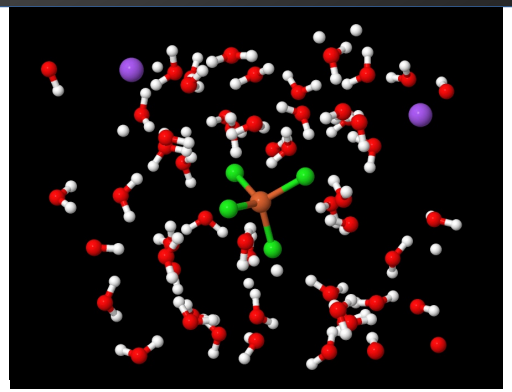

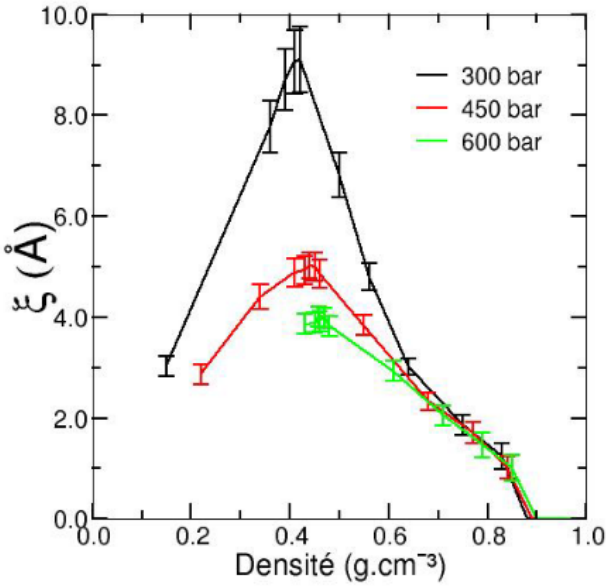

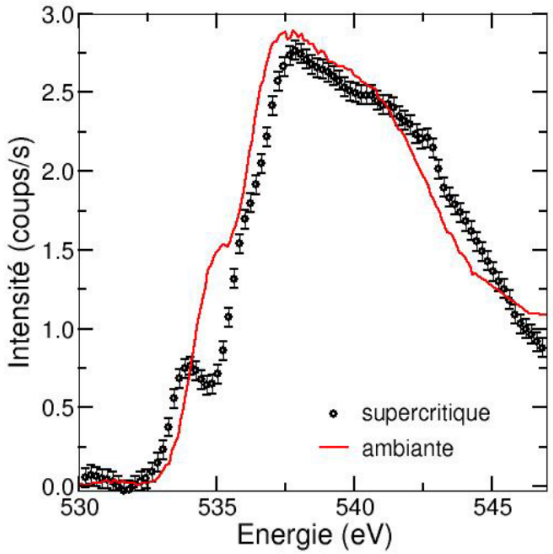

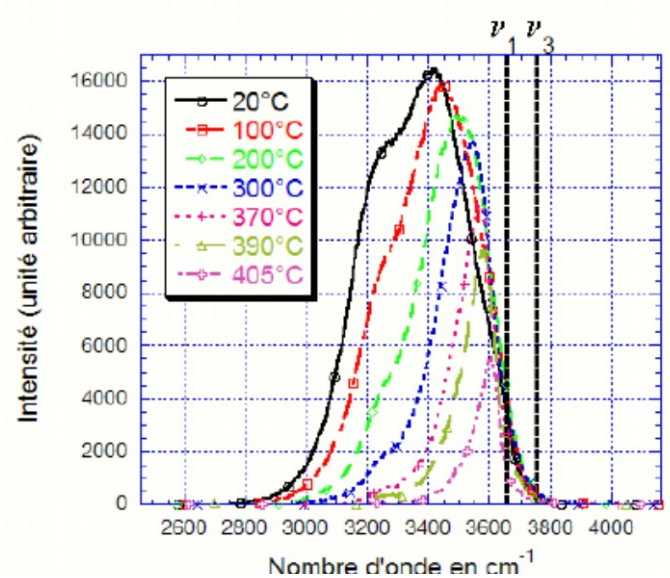

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IXS: oxygen K-edge
= structure of density fluctuations
Wernet et al., J. Chem. Phys. (2005)

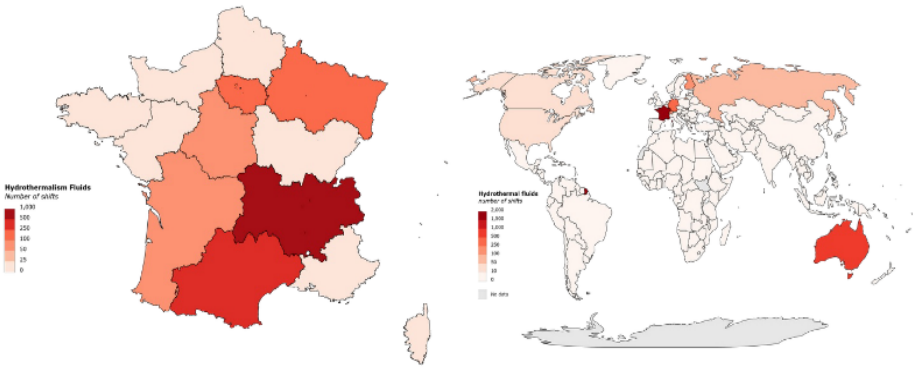
Raman: OH vibration
= solvation shell of water molecule
unpublished

Thanks!

- J.-L. Hazemann
- X'Press group (HP)
  (Alain, Céline, Rémy, Christophe, Murielle)
- R. Argoud
- P. Bouvier (Raman)
- C. Felix
- G. Dantelle

- E. Lahera
- O. Proux
- I. Kieffer
- W. Delnet

- G. Pokrovski
- J. Brugger, W. Liu, B. Etschmann
- F. Guyot, D. Daval
- All **FAME users** !



- Réseau technologique des hautes pressions (MI-CNRS)