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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



Introduction

Metal transport in hydrothermal fluids (XAS)

Autoclave technology

More *in situ* techniques

## Introduction

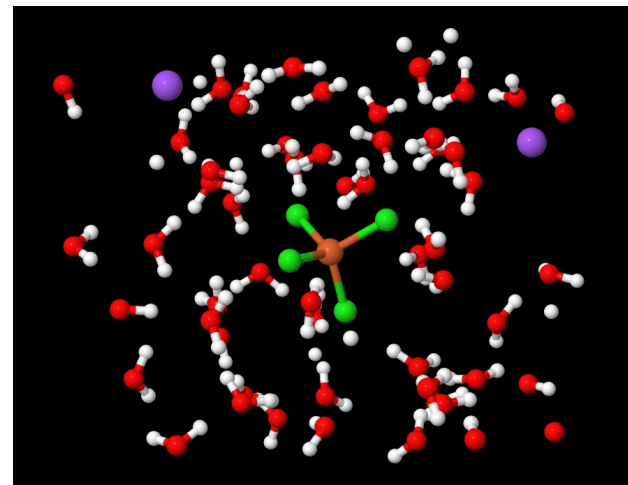
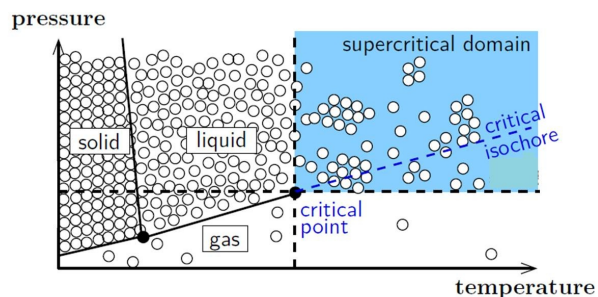
Metal transport in hydrothermal fluids (XAS)

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)*

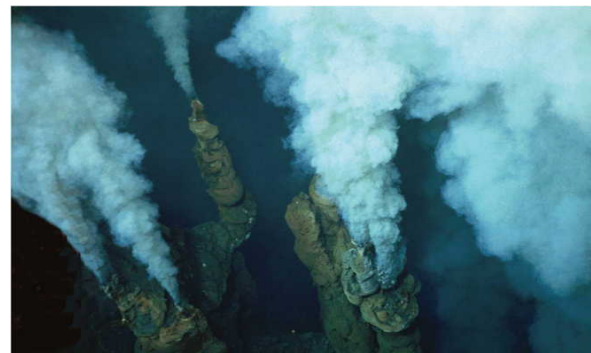


*Hellisheidi geothermal power plant, Iceland*

# Hydrothermal fluids

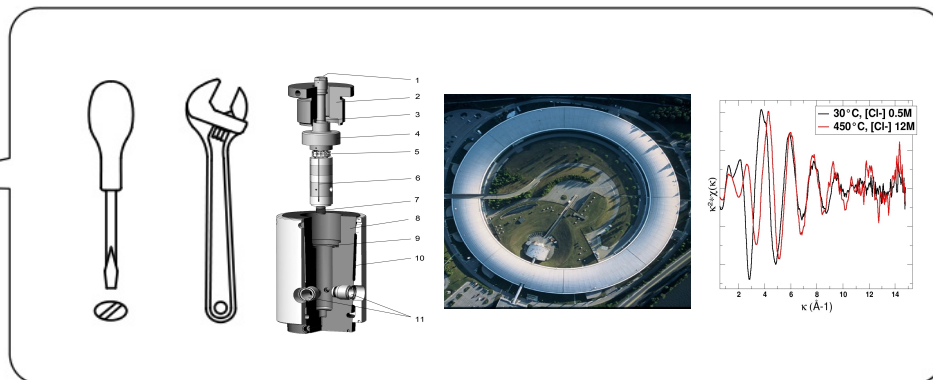
→ **Properties** of hydrothermal fluids:

- $T < 1000^\circ\text{C}$ ,  $P < 5000$  bar
- $0.04 < \text{density} < 1 \text{ g.cm}^{-3}$
- $\text{H}_2\text{O}-\text{NaCl} \pm \text{CO}_2, \text{S}, \text{F}, \text{P}$
- Unquenchable



→ **Characterization** of hydrothermal fluids:

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



Introduction

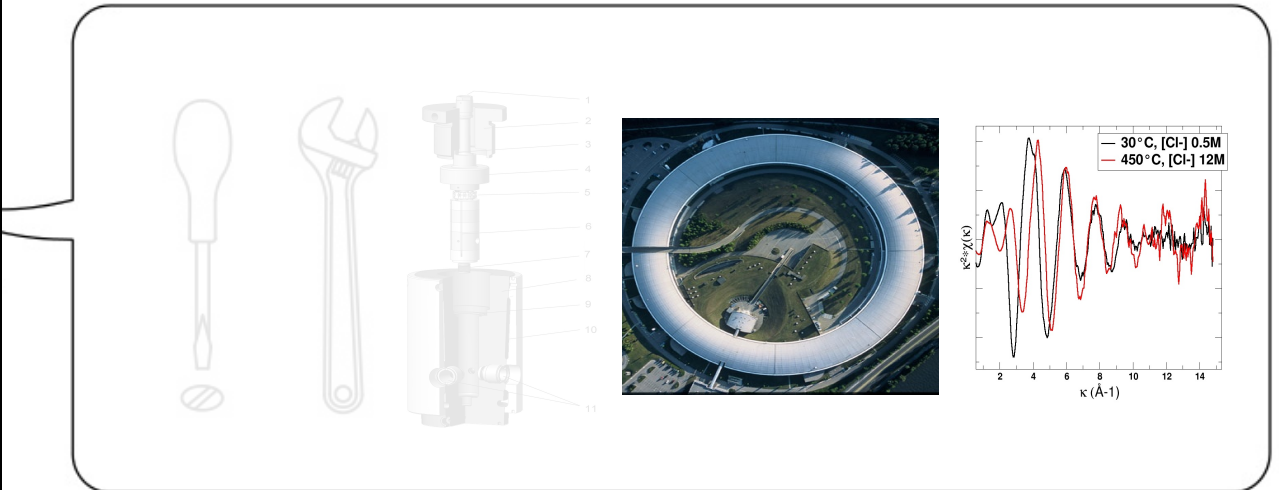
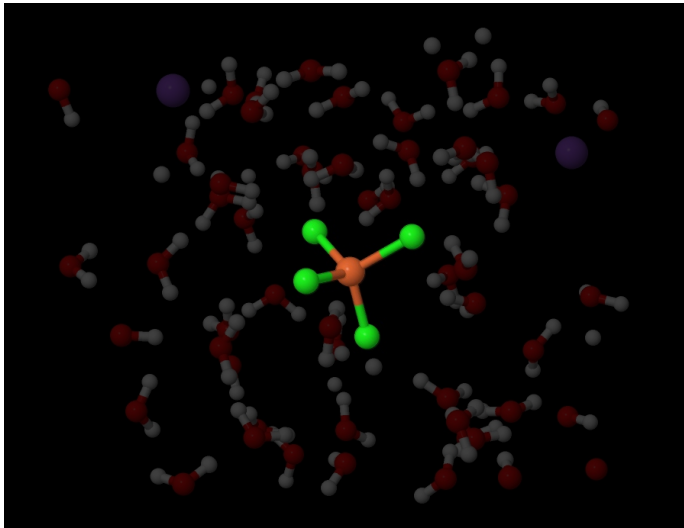
Metal transport in hydrothermal fluids → XAS methods

Autoclave technology

More *in situ* techniques

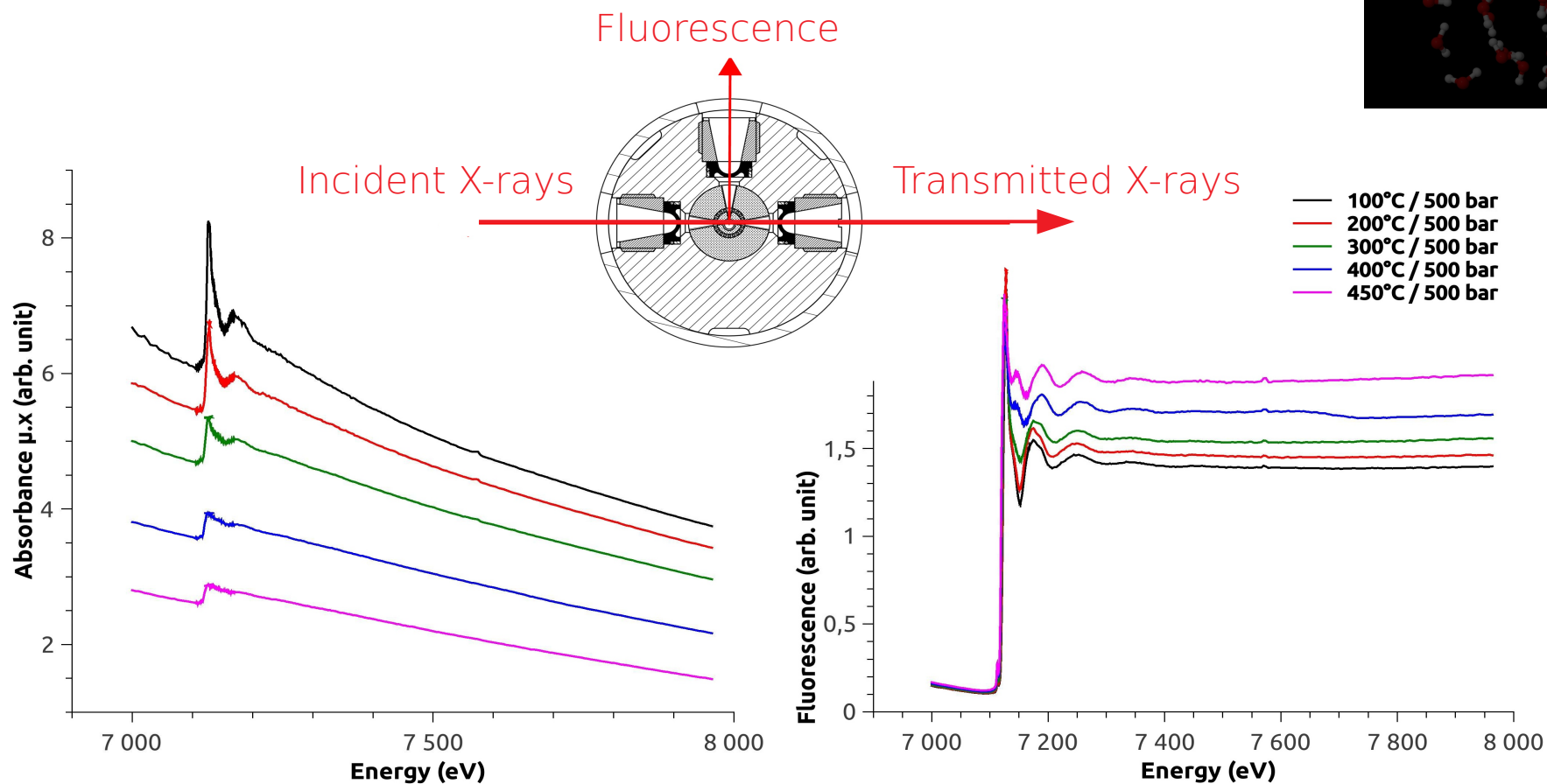
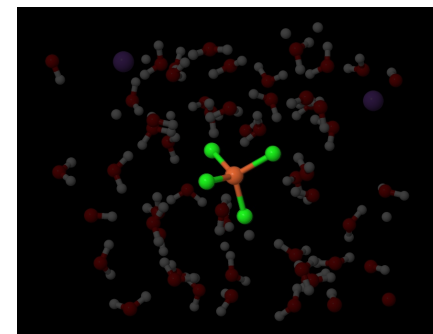
# Transport of iron in hydrothermal fluids

- 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.

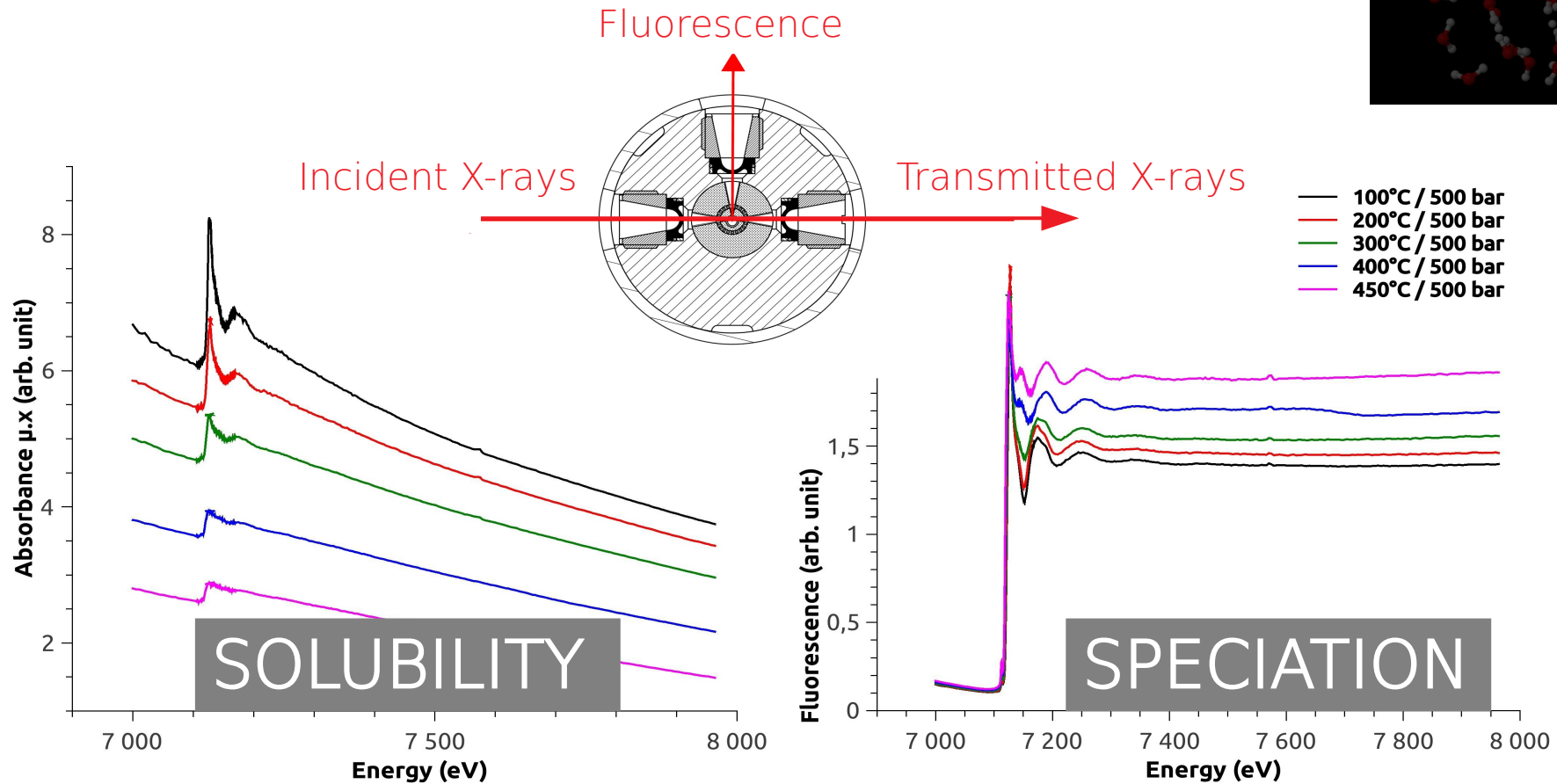
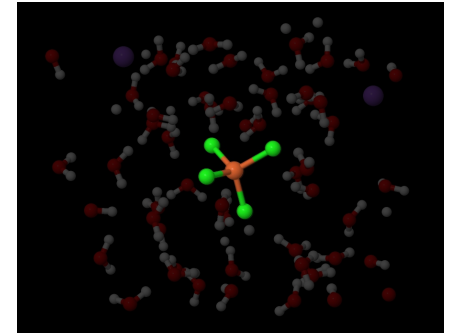




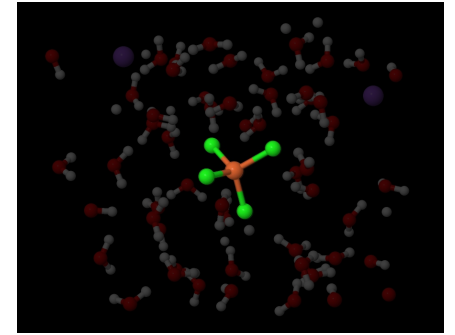
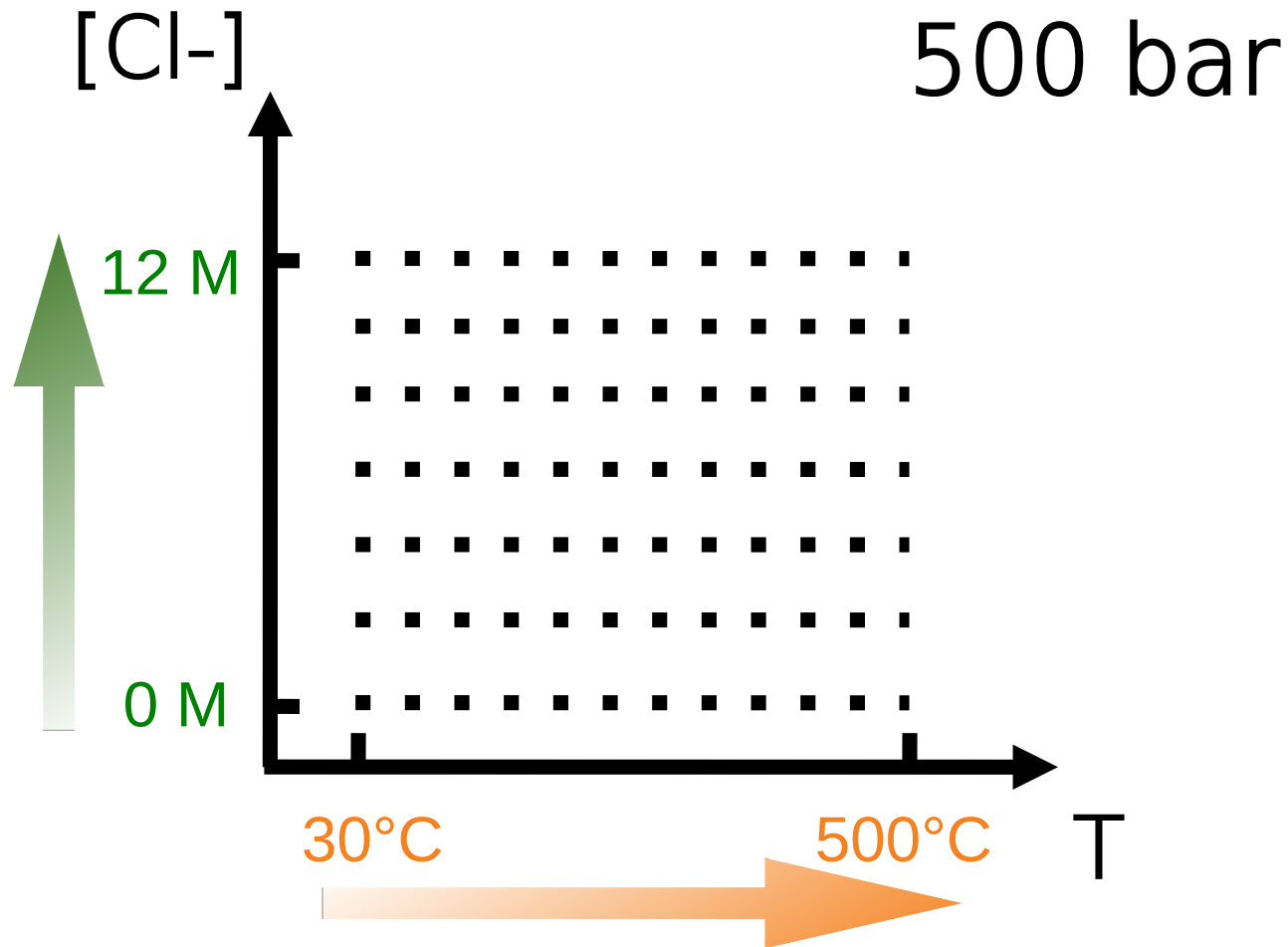
# Transport of iron in hydrothermal fluids



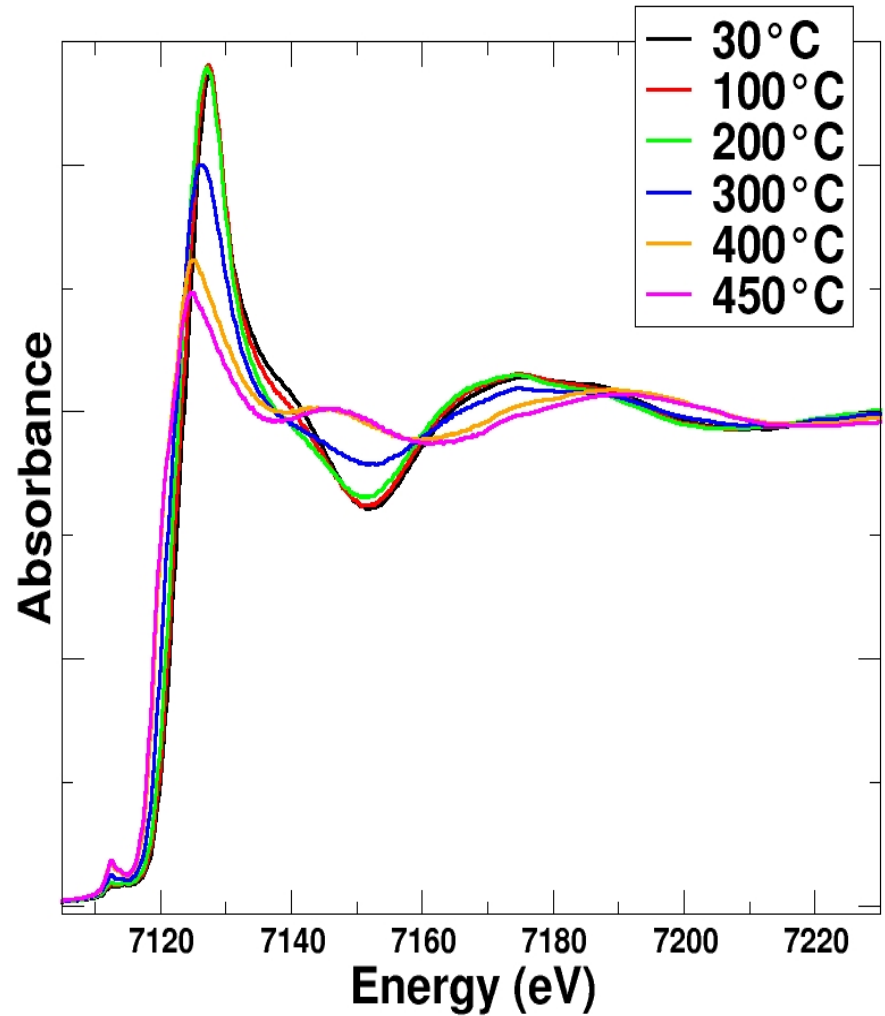
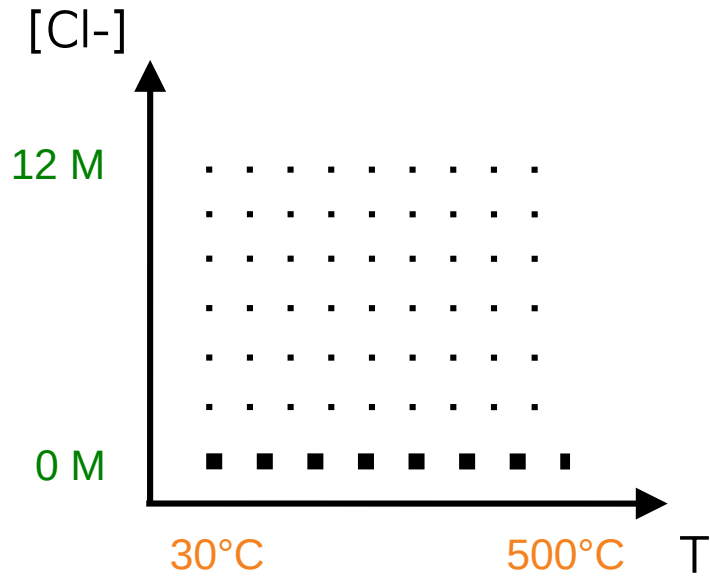
# Transport of iron in hydrothermal fluids



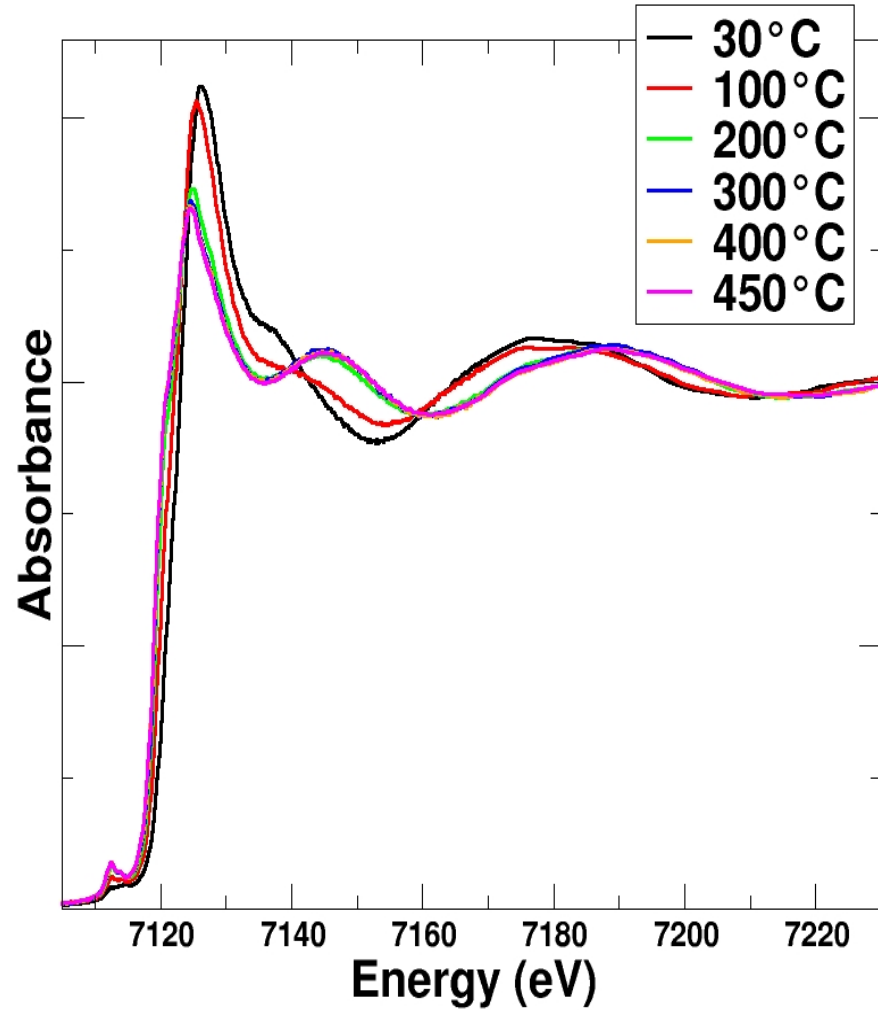
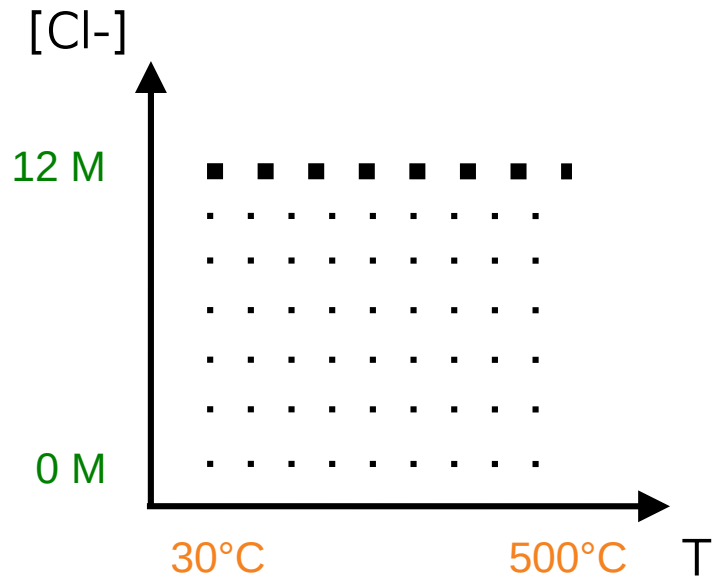
# Speciation of $\text{Fe}^{\text{II}}$



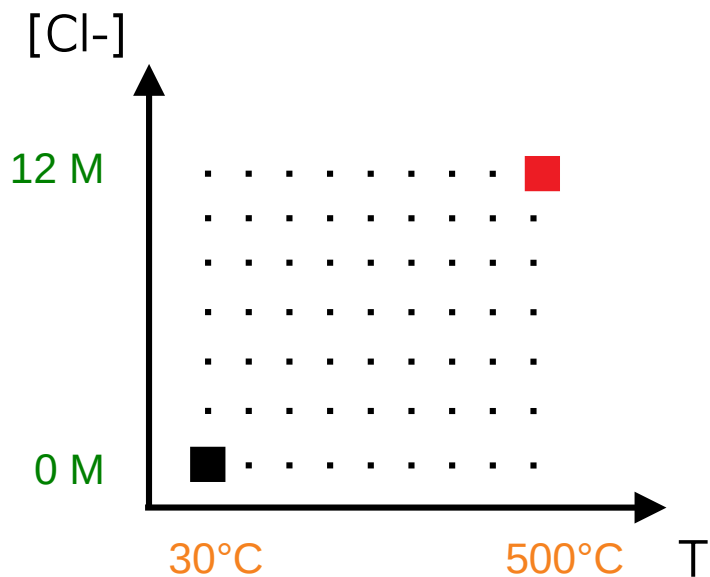
# Speciation of Fe<sup>II</sup>



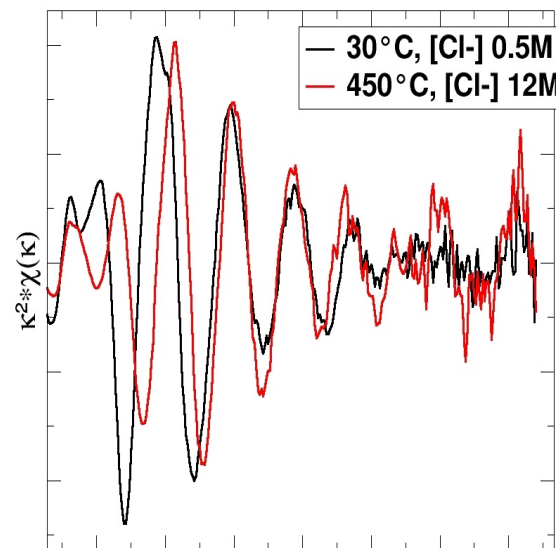
# Speciation of Fe<sup>II</sup>



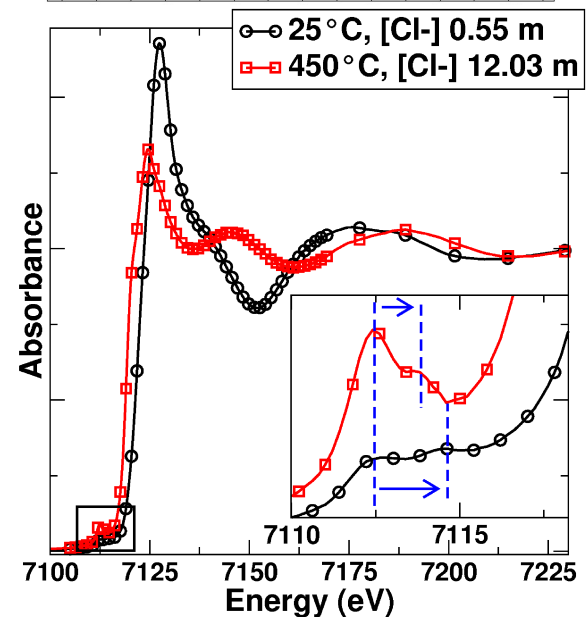
# Speciation of Fe<sup>II</sup>: end-members



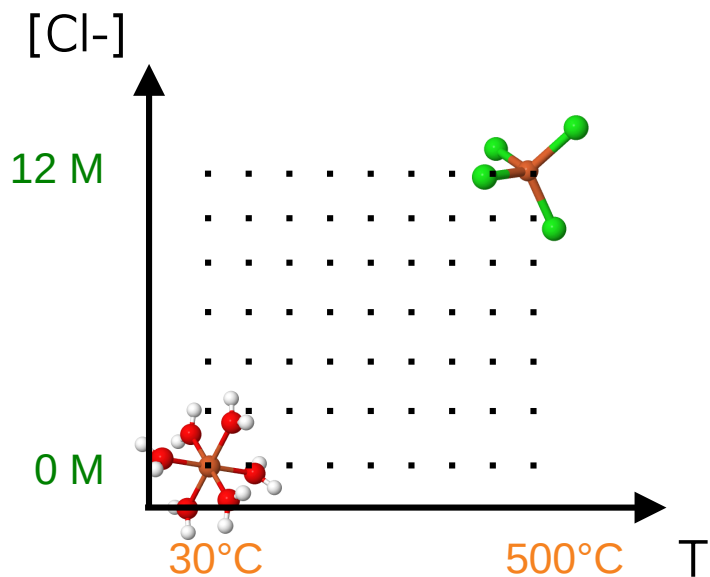
EXAFS:



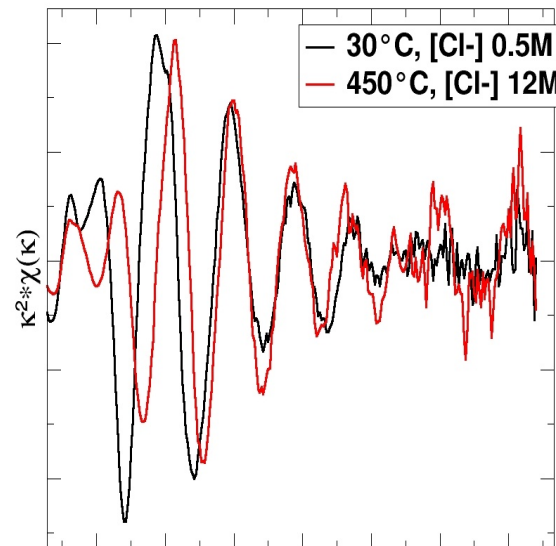
XANES:



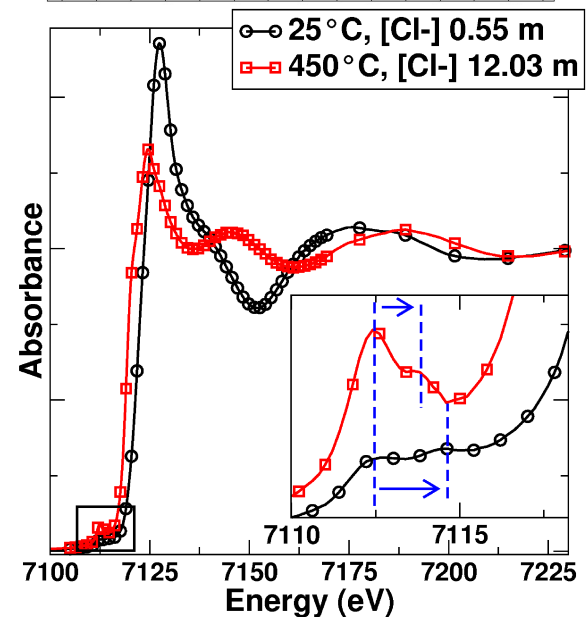
# Speciation of Fe<sup>II</sup>: end-members



EXAFS:



XANES:

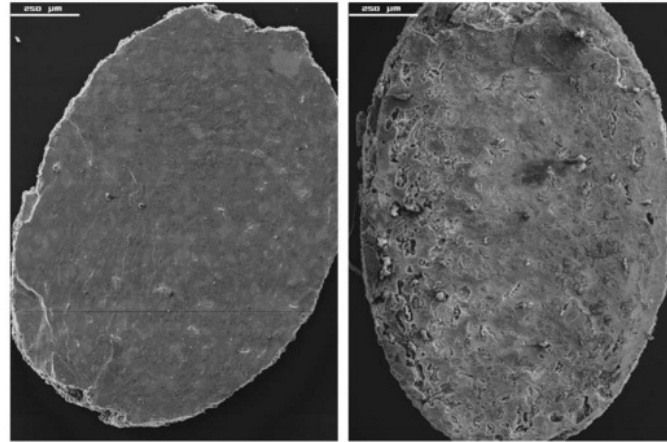
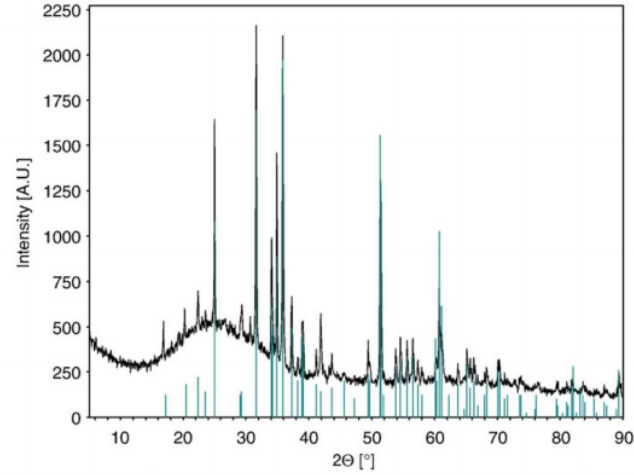
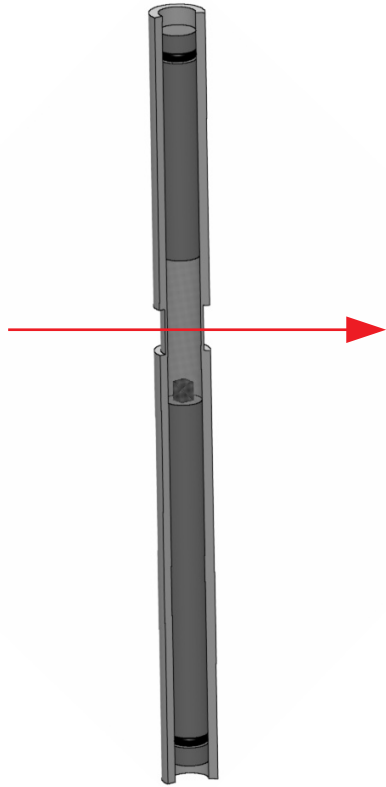


# Solubility of Fe<sup>II</sup>: **Fayalite** dissolution

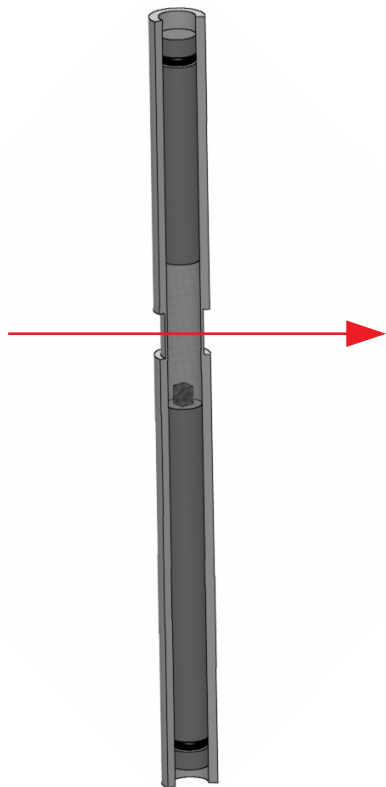
- Global context **CO<sub>2</sub> storage** (and H<sub>2</sub> generation): availability of dissolved ferrous iron.
- But **reaction rates** are poorly constrained: dissolution kinetics data needed.
- **Moderate P/T**: 300 bar/100°C



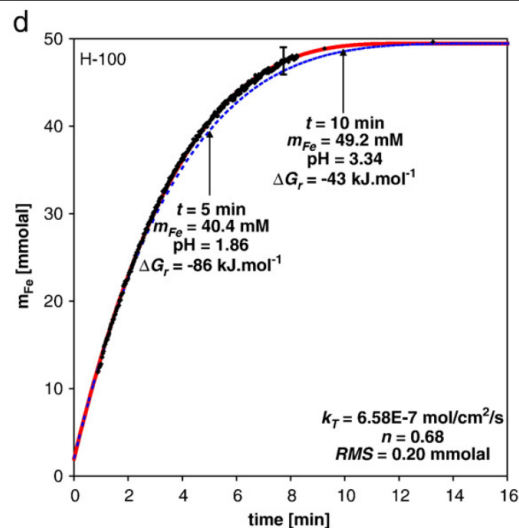
# Solubility of $\text{Fe}^{\text{II}}$ : Fayalite dissolution



# Solubility of Fe<sup>II</sup>: Fayalite dissolution



Solubility



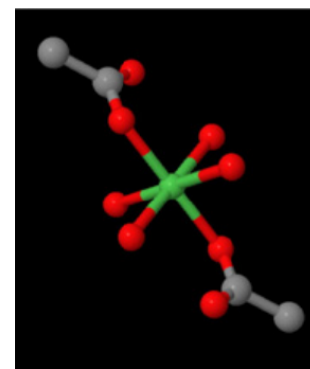
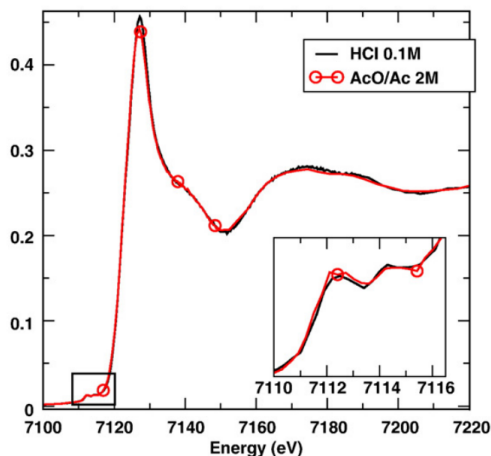
$$R_{\text{net}} = k_0 \exp(-E_a / RT) a_{\text{H}^+}^n$$

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

$$E_a = 45100 \pm 4200 \text{ J.mol}^{-1}$$

$$N = 0.74 \pm 0.15$$

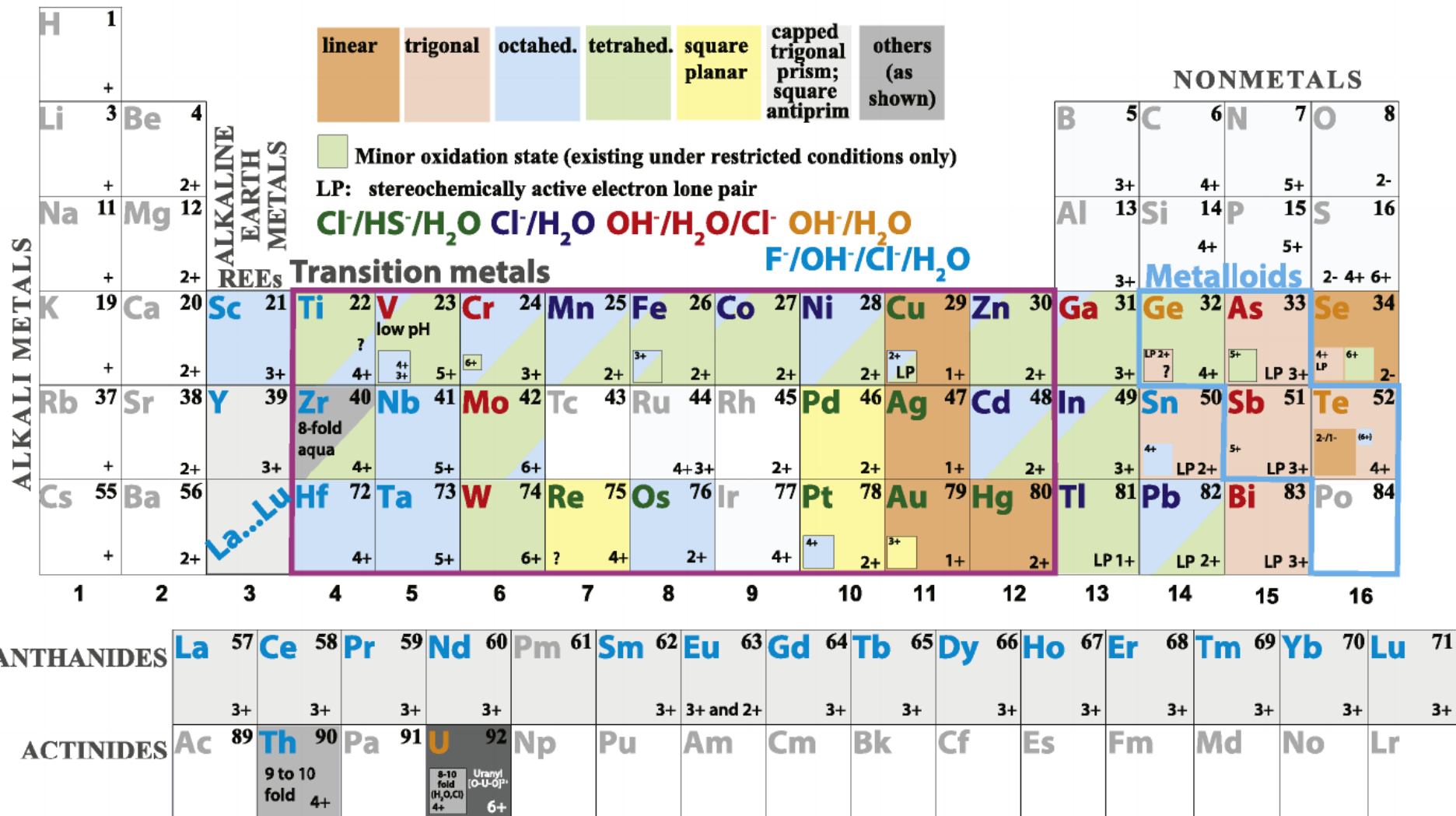
Speciation



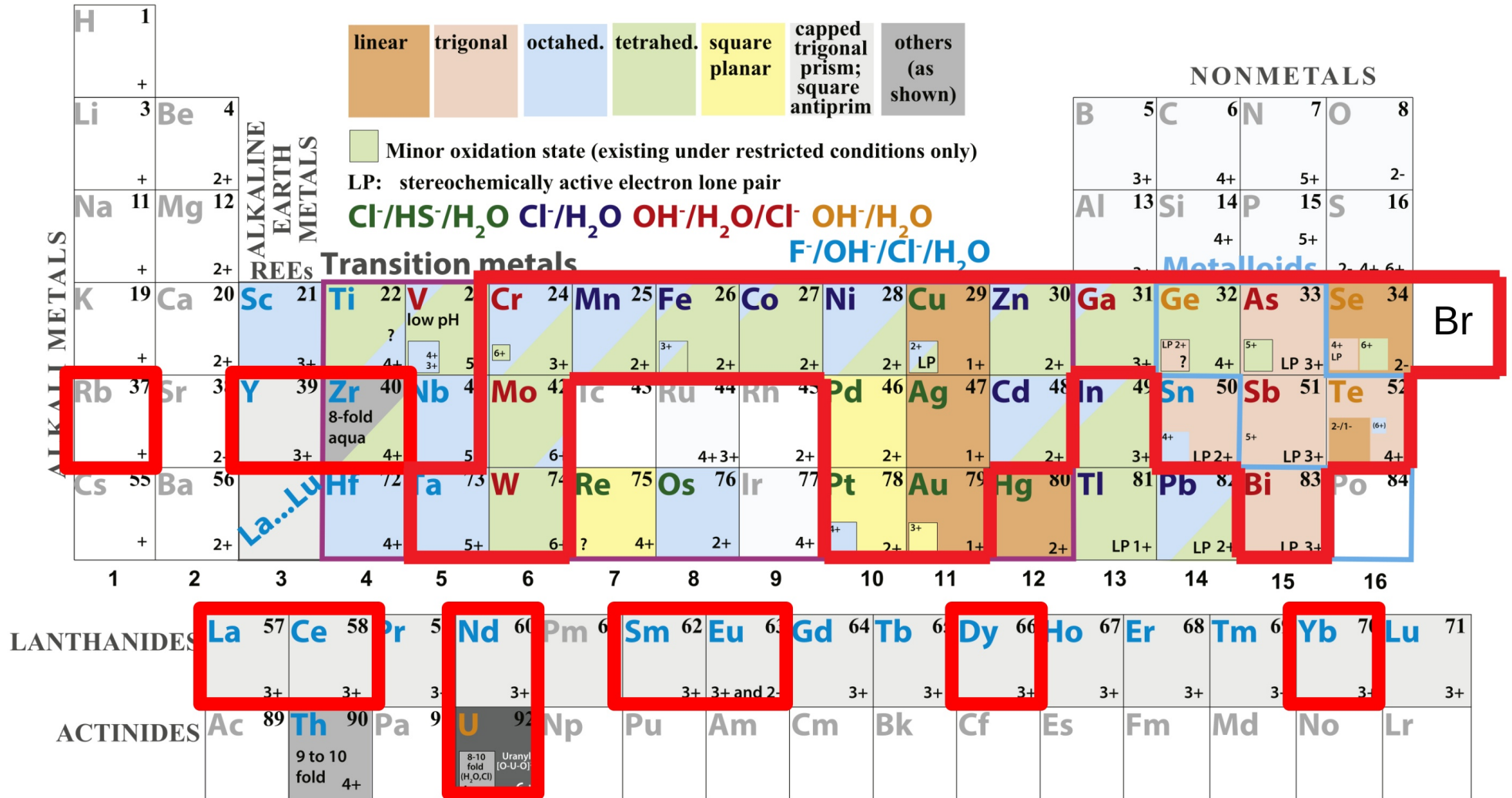
# Transport of **metals** in hydrothermal fluids

- 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



# Transport of metals in hydrothermal fluids



FAME/ Néel setup

# Outline

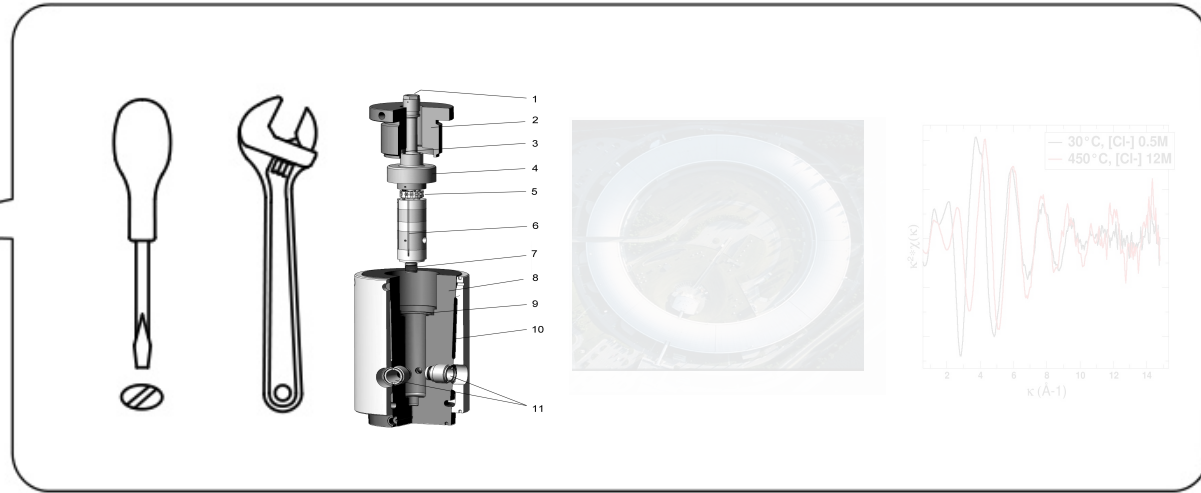
Introduction

Metal transport in hydrothermal fluids

Autoclave technology

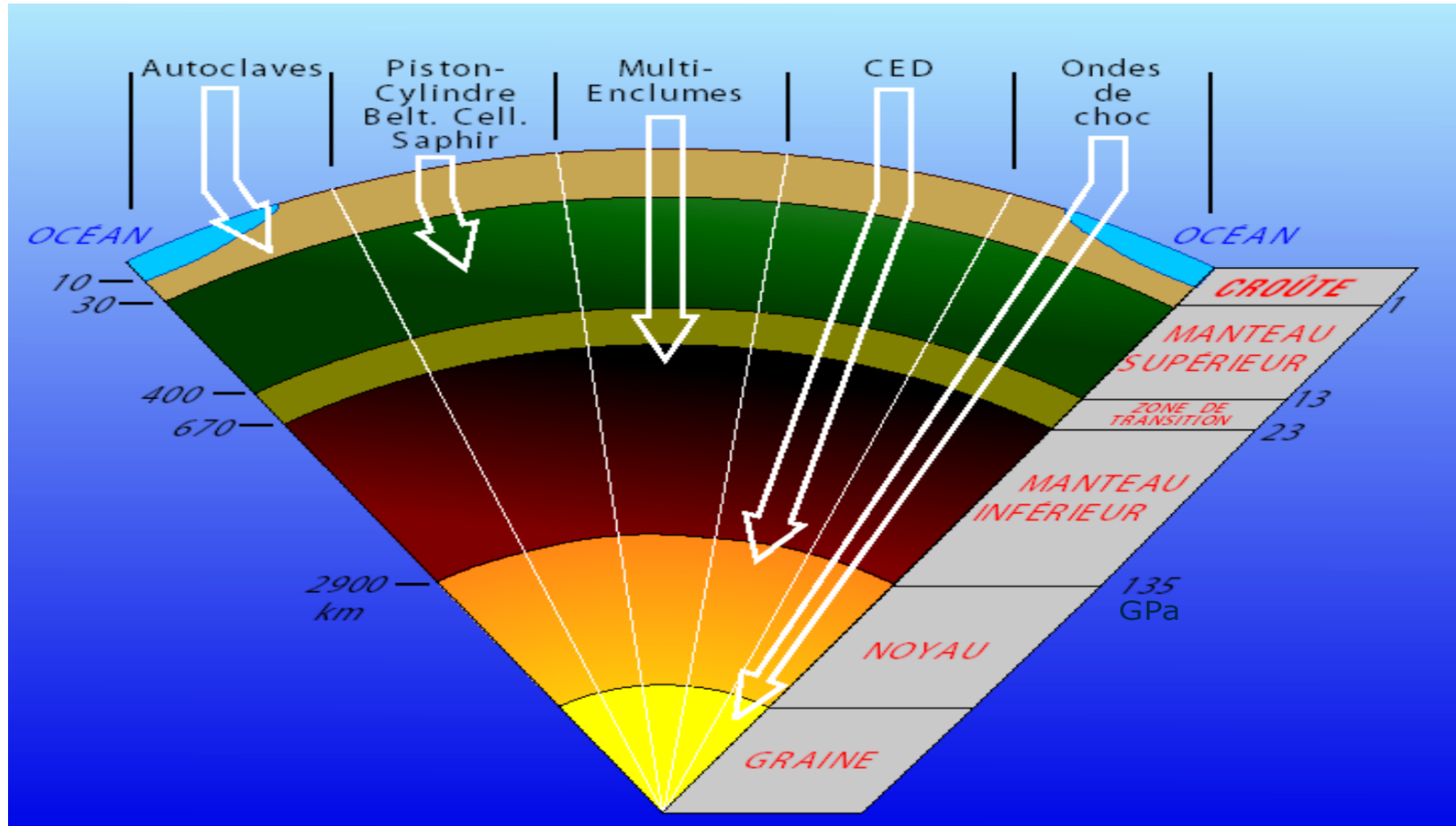
What's next?

# Autoclave technology - Context



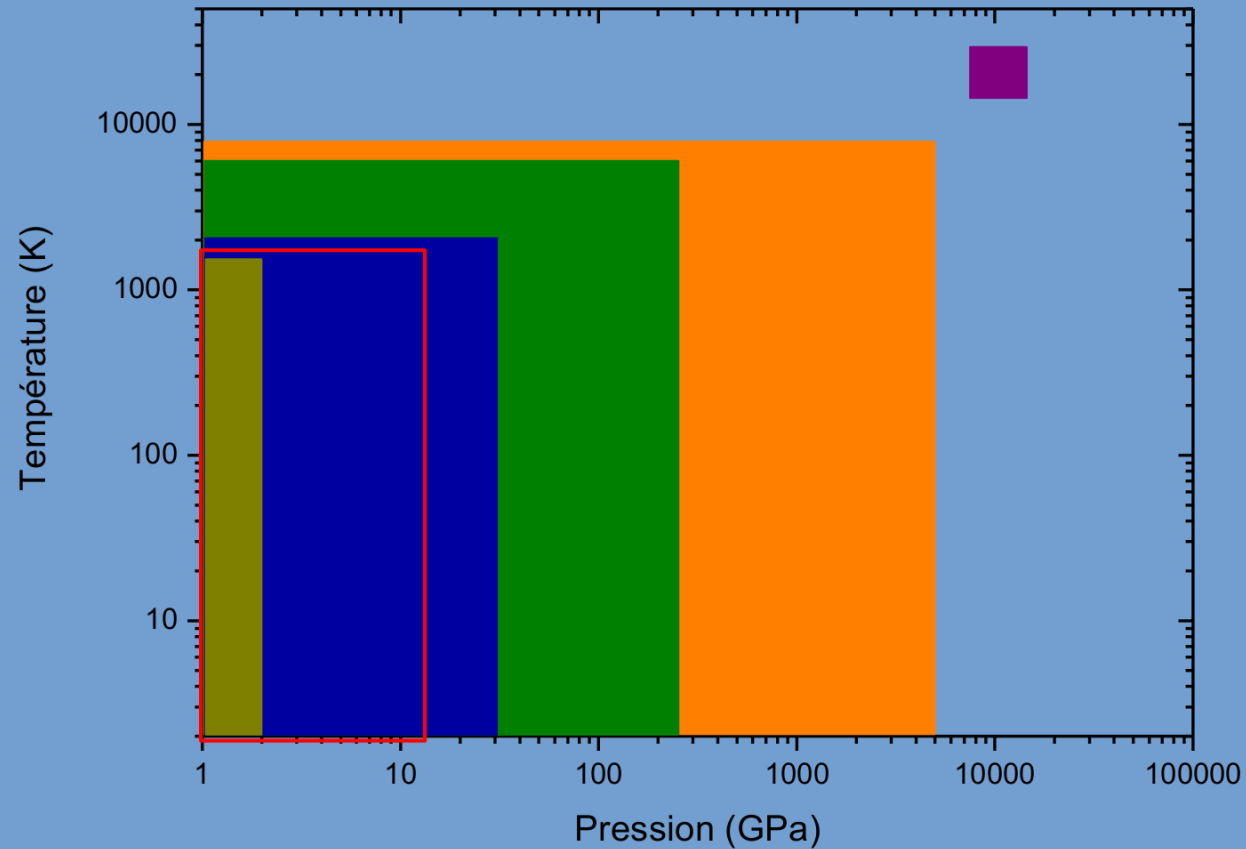
- Hydrothermal
- Spectroscopies
- *In situ*

# Autoclave technology - Context



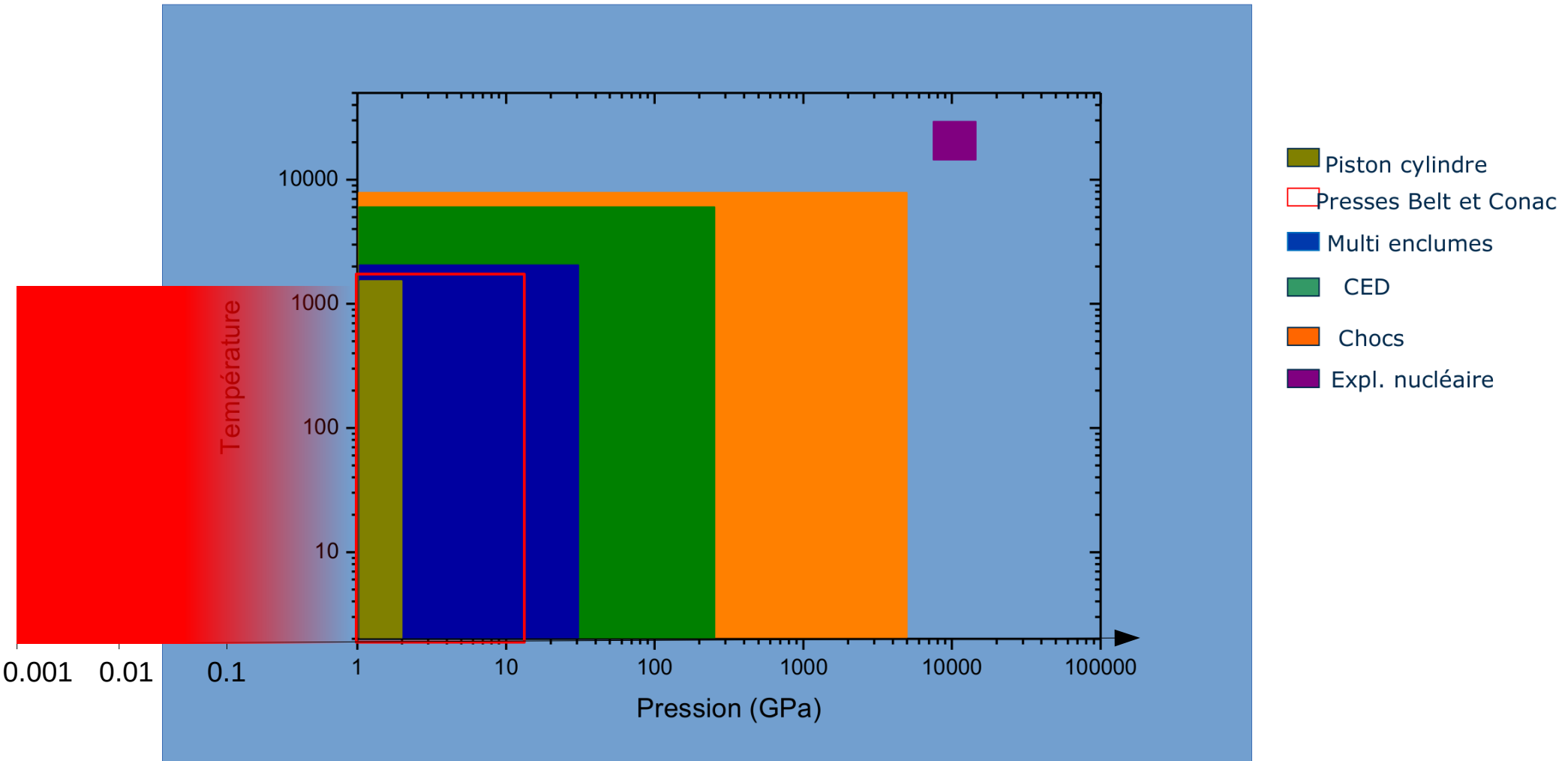


# Autoclave technology - Context

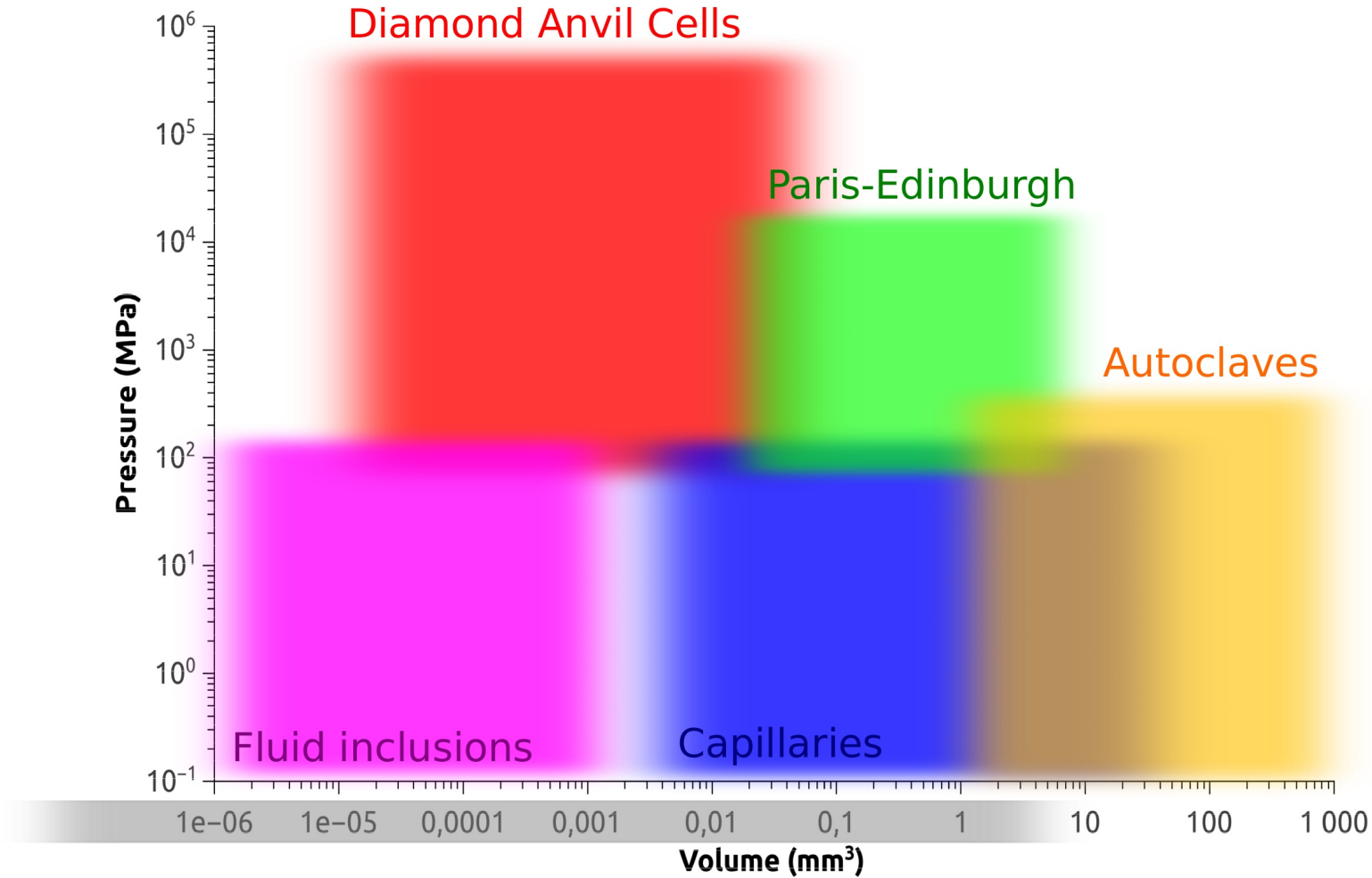


-  Piston cylindre
-  Presses Belt et Conac
-  Multi enclumes
-  CED
-  Chocs
-  Expl. nucléaire

# Autoclave technology - Context

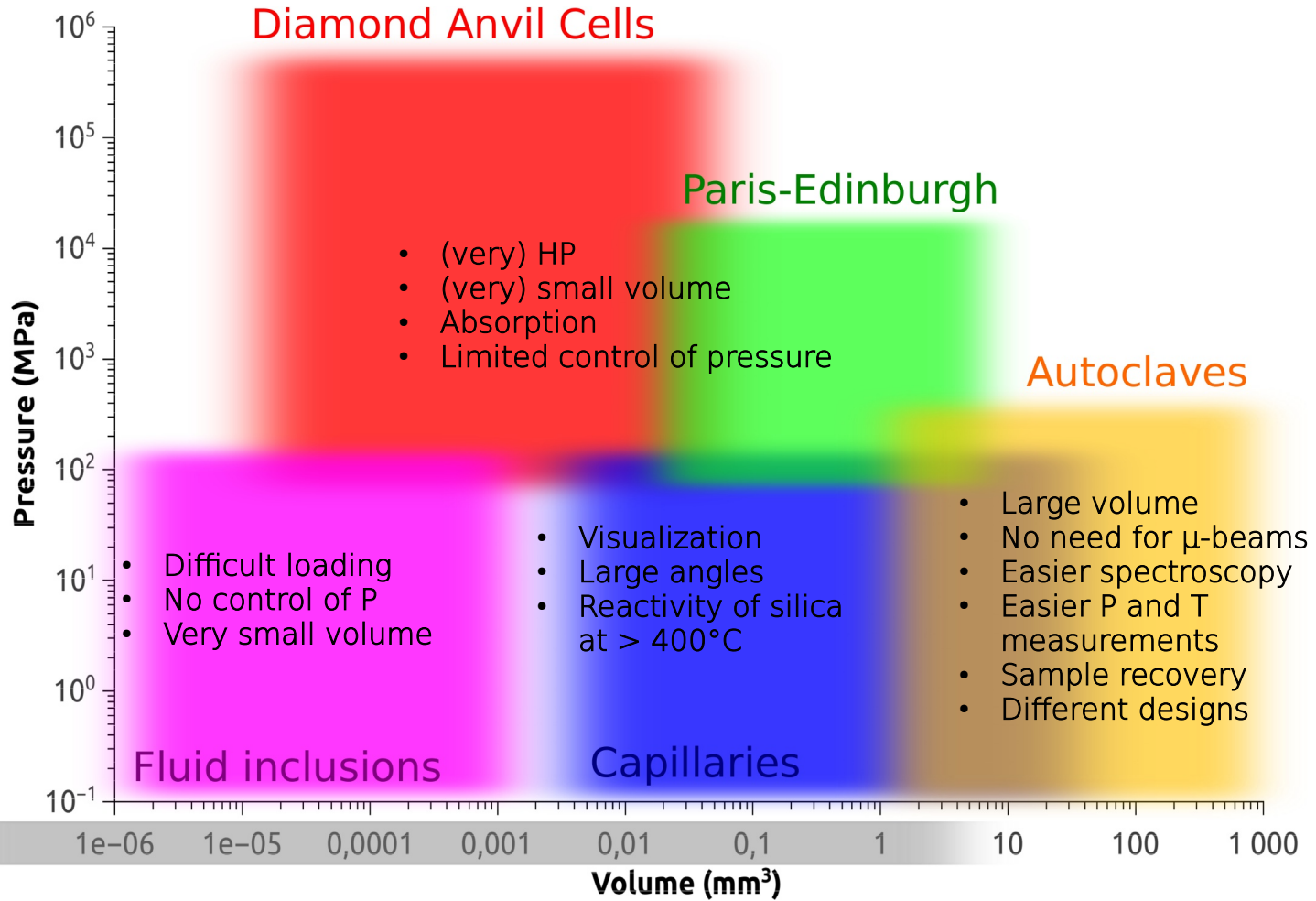


# Autoclave technology - Context



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

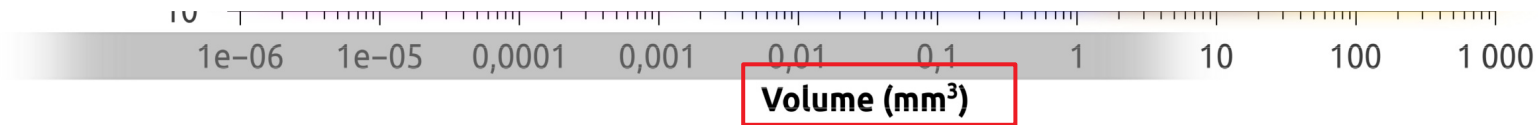
# Autoclave technology - Context



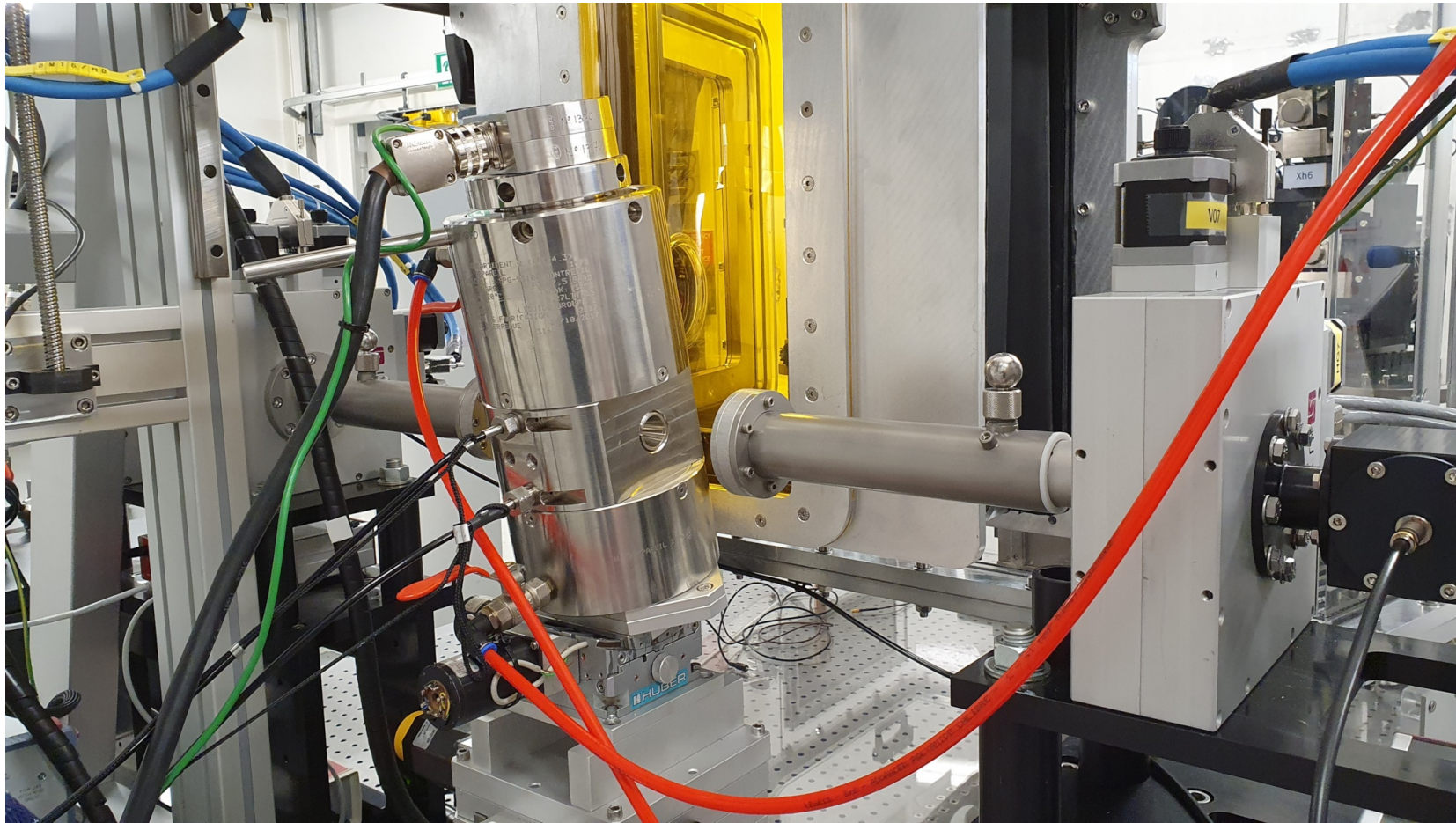
# Autoclave technology - Context

## Sample volume:

- Loading and recovery of samples
- Beam damage
  - radiolytic species
  - sample vol./beam vol. ratio
  - uncontrolled redox

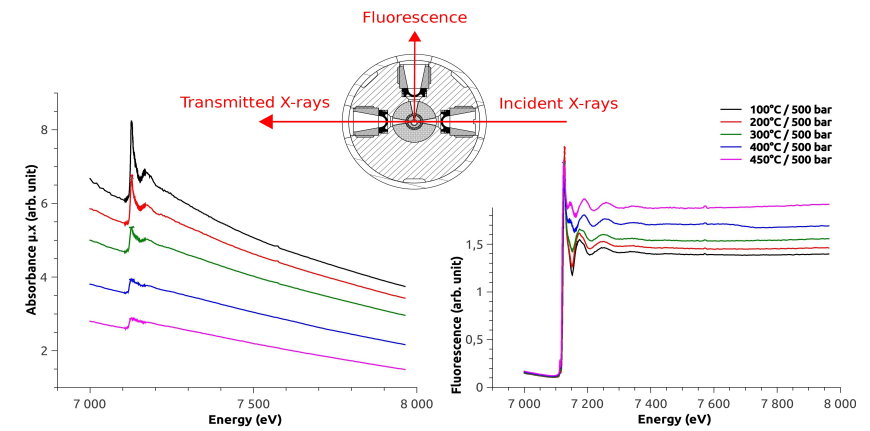
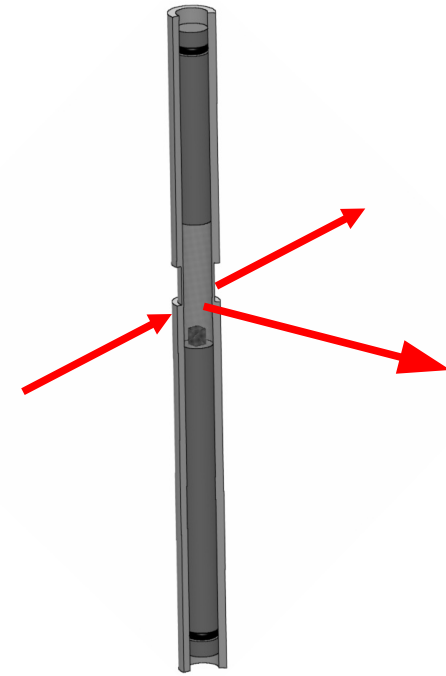
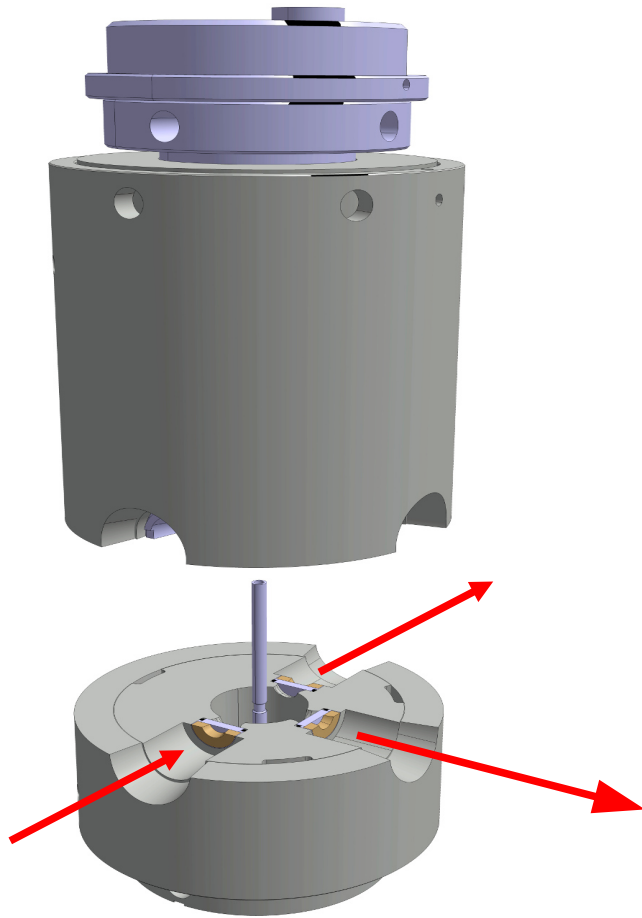


# Autoclave technology – The Néel autoclave



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

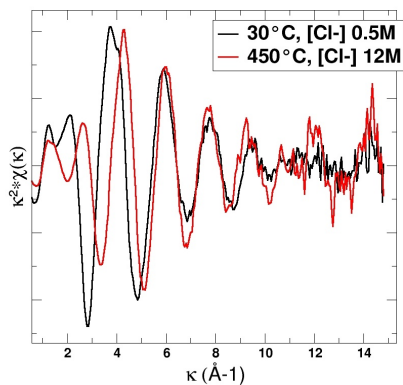
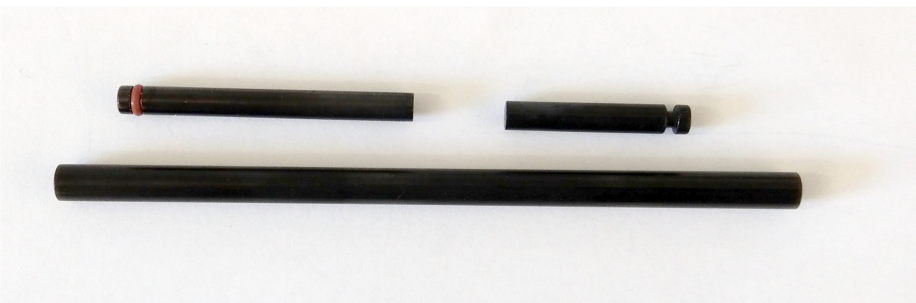
# Autoclave technology – The Néel autoclave



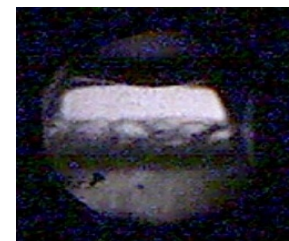
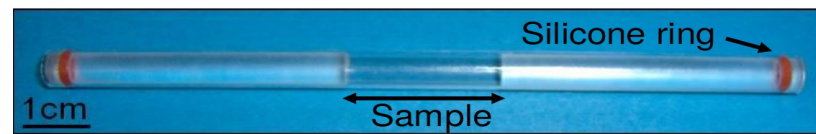
*Testemale et al., Rev. Sci. Instrum. (2005)*  
*Testemale et al., Rev. Sci. Instrum. (2016)*  
*Bruyère et al., J. Phys.: Conf. Series (2008)*

# Autoclave technology – The Néel autoclave

## X-rays (XAS, absorption)



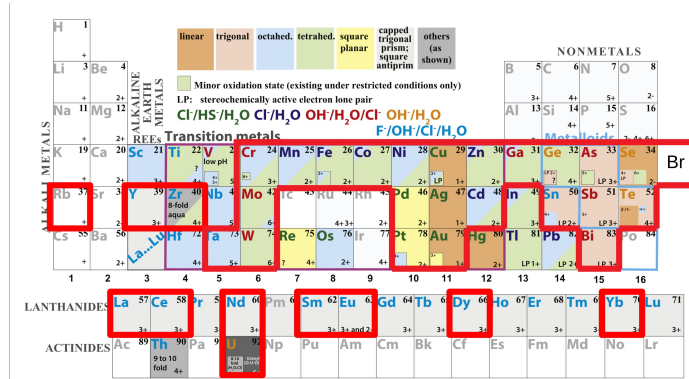
## Visible (Raman, observation)



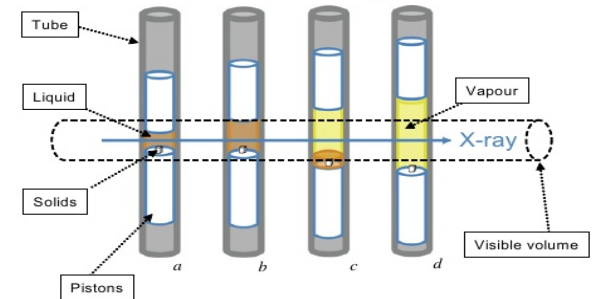


# Autoclave technology – The Néel autoclave

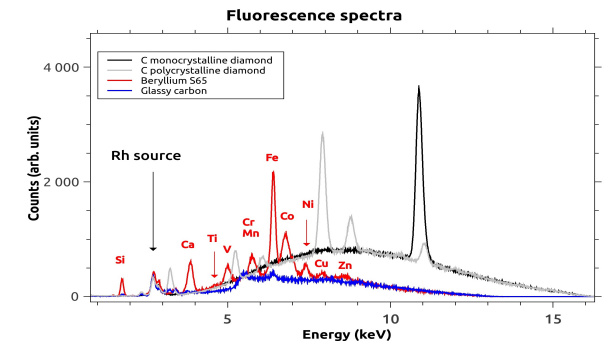
- Temperature/pressure :  
[1-2000 bar]  $\pm$  0.2 bar  
[30-1000°C]  $\pm$  0.05°C
- XAS : which elements ?
  - 5-40 keV
  - Glass-like carbon for photons <12keV (~Ga)



- Which phase ?  
Gas, liquid or solid  
Density > 0.05 g.cm<sup>-3</sup>



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

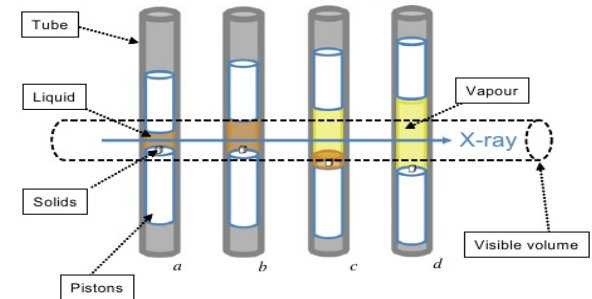


# Autoclave technology – The Néel autoclave

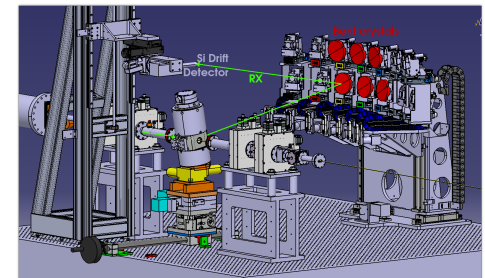
- Temperature/pressure :  
[1-2000 bar]  $\pm$  0.2 bar  
[30-1000°C]  $\pm$  0.05°C
- XAS : which elements ?
  - 5-40 keV
  - Glass-like carbon for photons <12keV (~Ga)

Periodic table showing oxidation states and coordination geometries. Key elements highlighted in red boxes include Rb, Sr, Y, Zr, Nb, Mo, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Th, Pa, U, Np, Pu, Am, Cm, Bk, Cf, Es, Fm, Md, No, Lr.

- Which phase ?  
Gas, liquid or solid  
Density > 0.05 g.cm<sup>-3</sup>

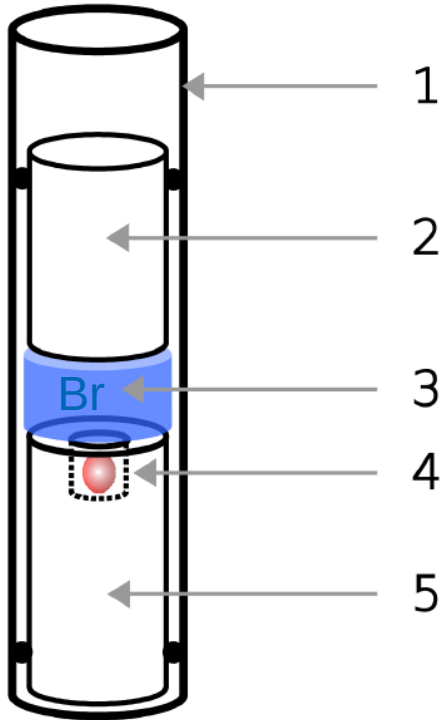


- Which concentrations ?
  - > 10 ppm for solubility and XANES
  - > 10<sup>0</sup> ppm for EXAFS
  - Beryllium impurities (carbon windows)



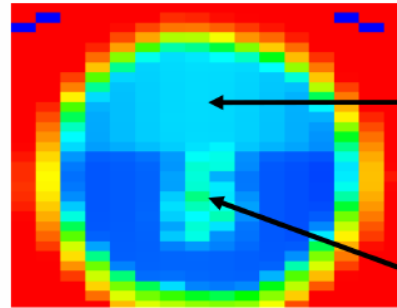
# Autoclave technology – Higher temperatures

- Melts ? Up to 700°C / 1300 bar.



25 °C – 1kbar

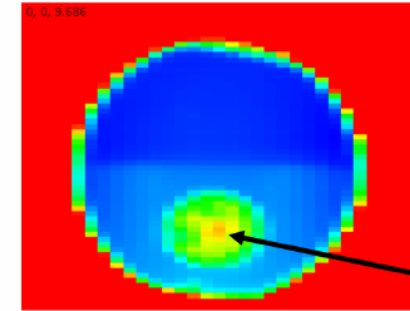
Transmission  
(density contrast)



Solution

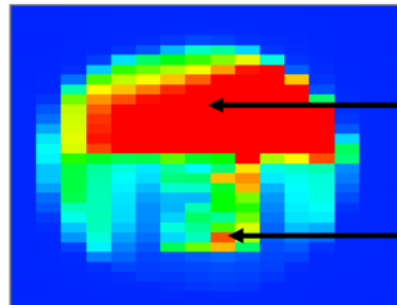
Chunks of glass

650 °C – 1kbar



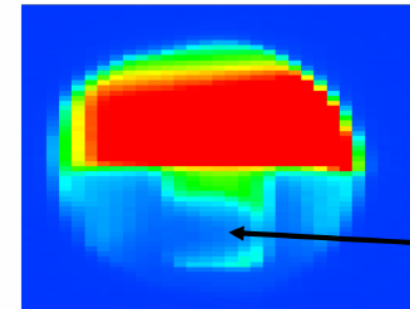
Melted globule

Br Fluorescence



Br in solution

Br signal from  
solution in voids



No Br?

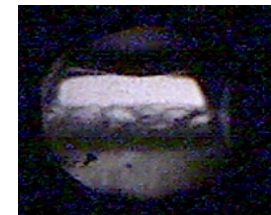
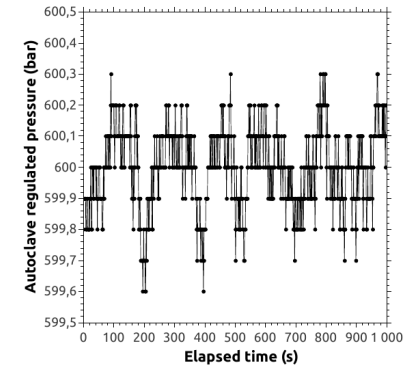
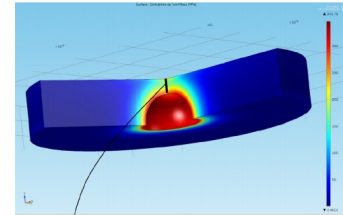
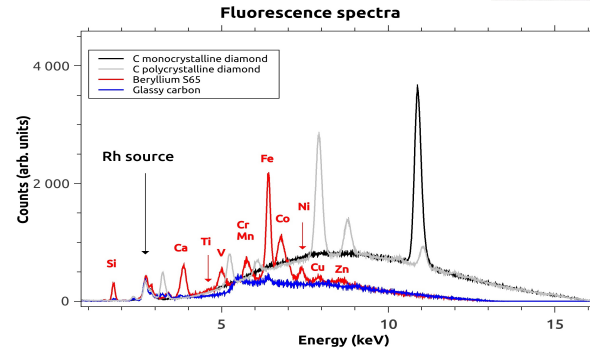
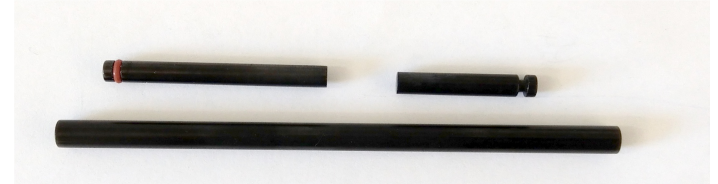
# Autoclave technology – Higher temperatures

- Melts ? Up to 900°C / 1300 bar.



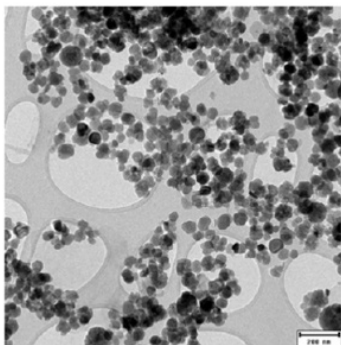
# Autoclave technology – Design and usage highlights

- Glass-like carbon internal cells
- HP windows material
- Beam damage and sample volume
- HP and HT stability
- Visual observation

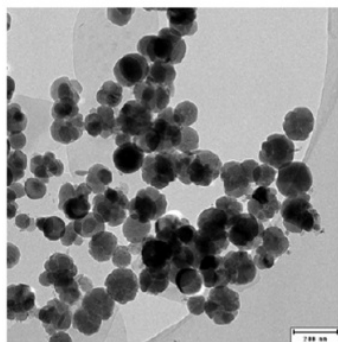


# Autoclave technology – Example

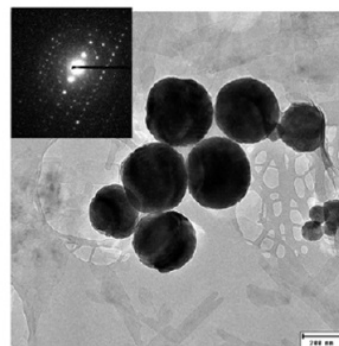
Solvothermal synthesis of YAG nanocrystals (G. Dantelle)



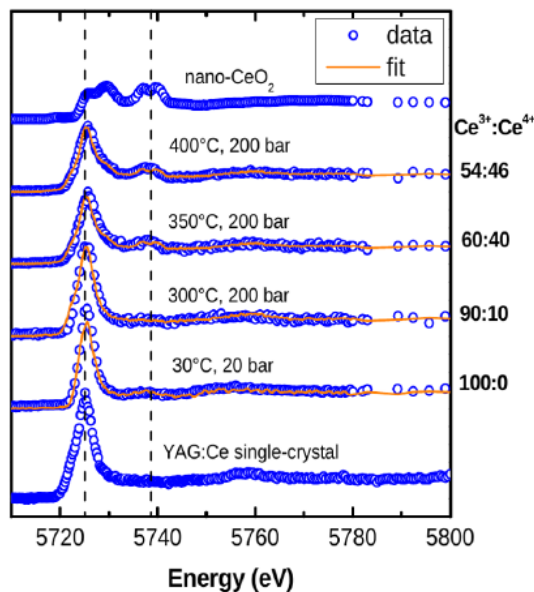
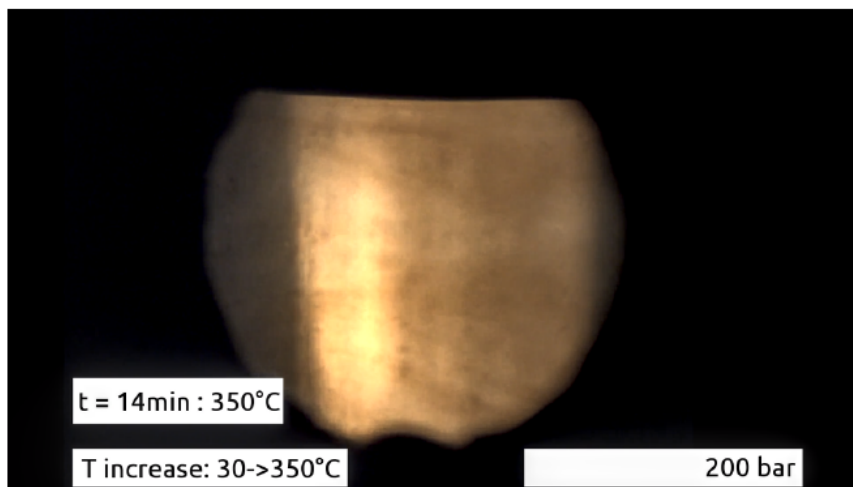
~ 30 nm



~ 100 nm



> 200 nm



# Outline

Introduction

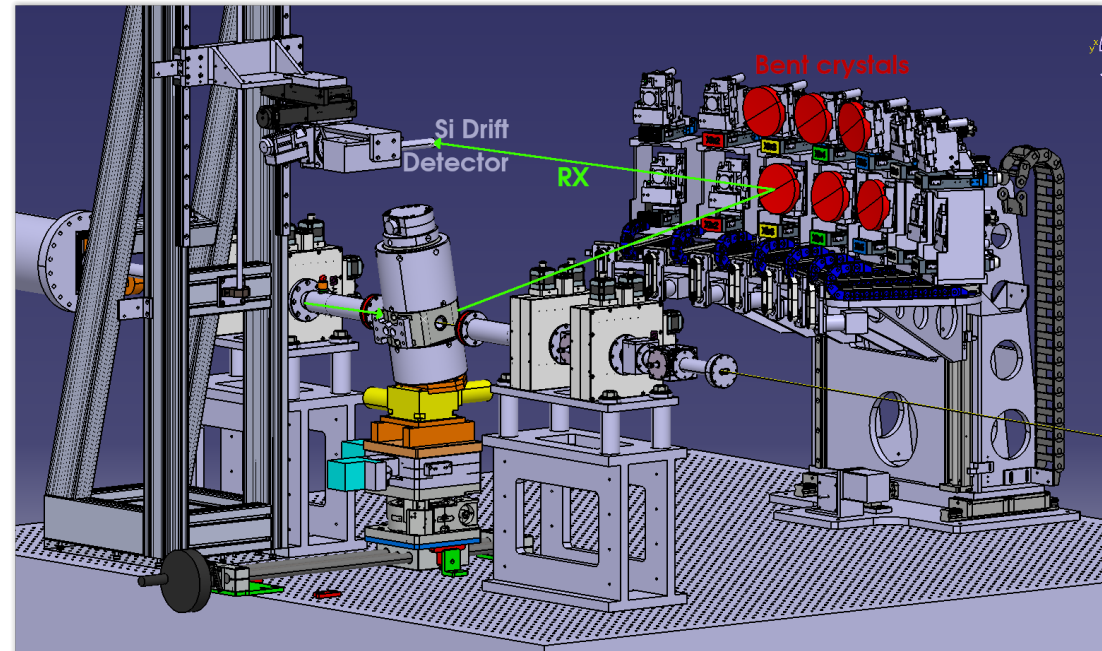
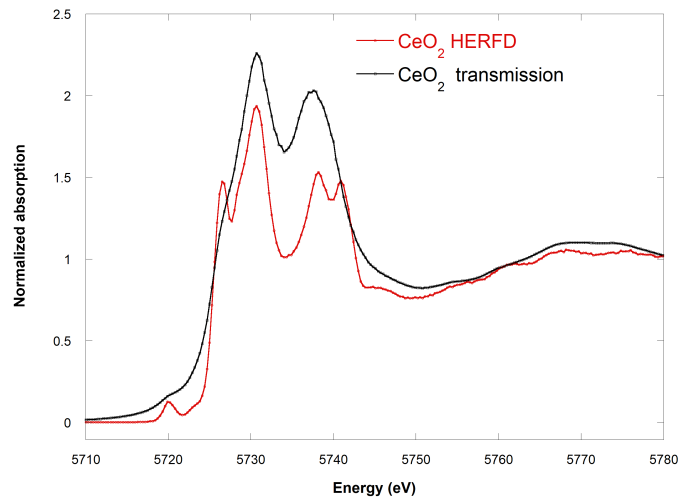
Metal transport in hydrothermal fluids

Autoclave technology

More *in situ* techniques

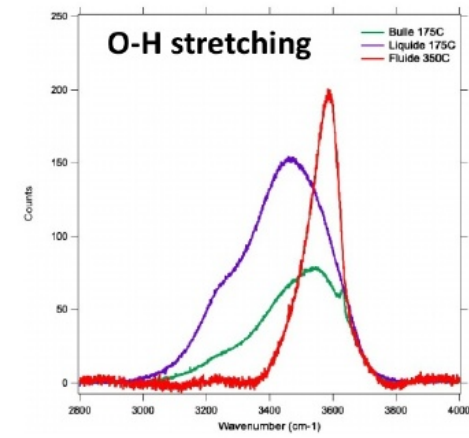
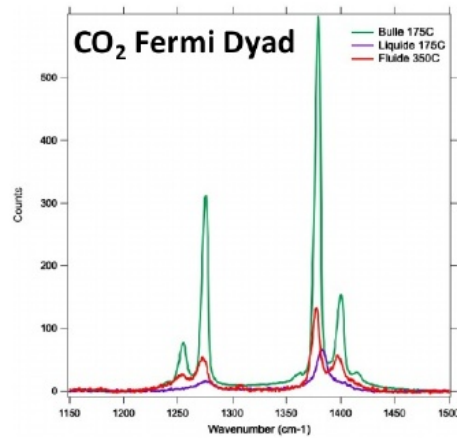
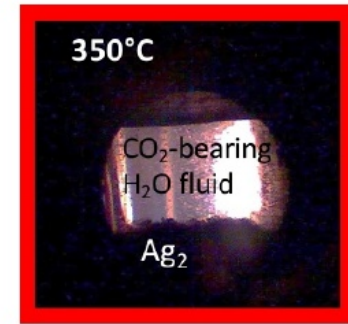
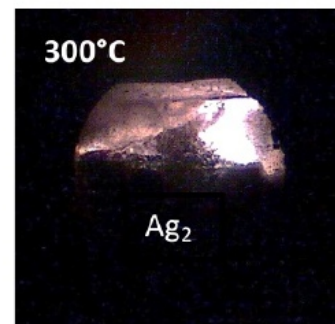
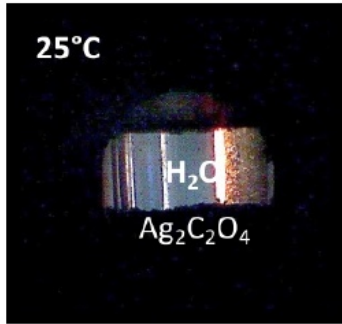
# High Energy Resolution Fluorescence Detection HERFD

- Better selection of fluorescence photons:
  - Lower XAS detection limits ( $\sim$ ppm)
  - Better spectral quality
- Finer spectral resolution :
  - XANES features
  - Fluorescence selection
  - Emission spectroscopy

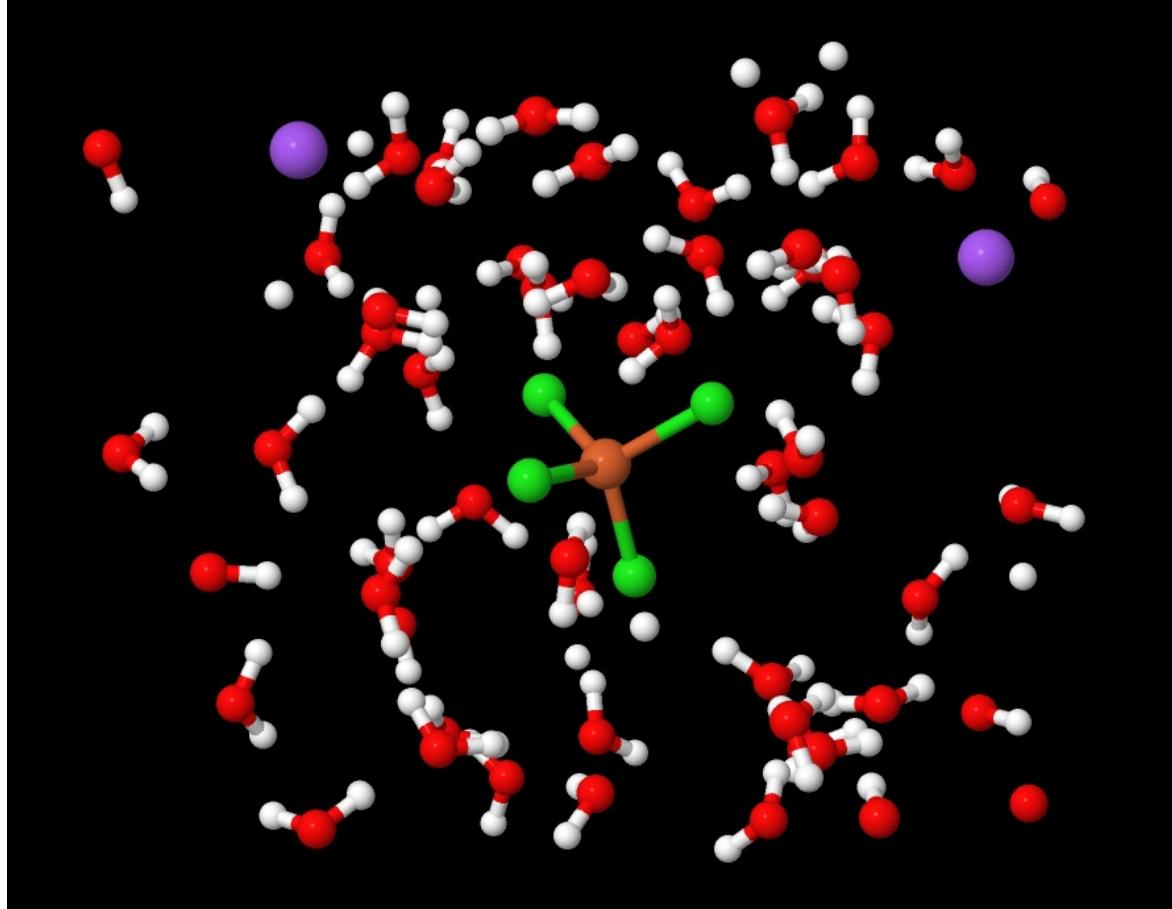




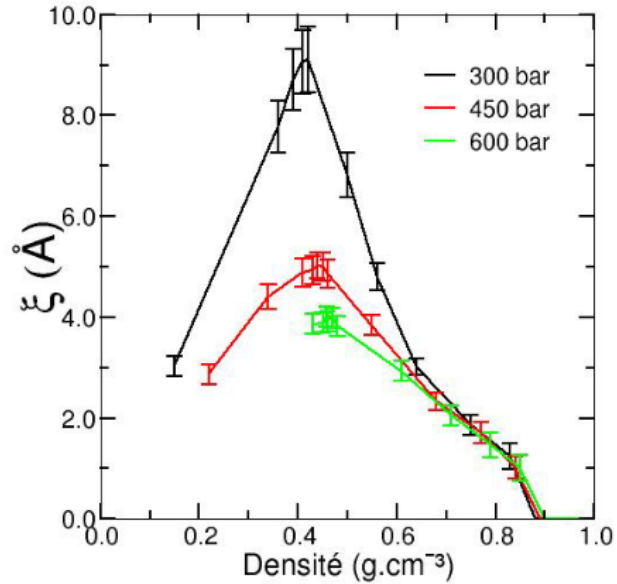
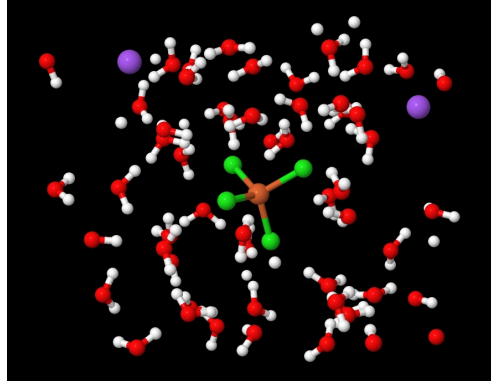
# Supercritical fluids – Raman of H<sub>2</sub>O-CO<sub>2</sub> supercritical solvents



# Structure of supercritical water

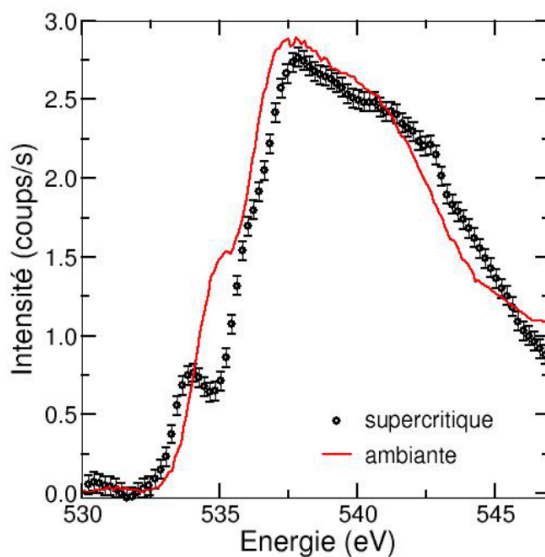
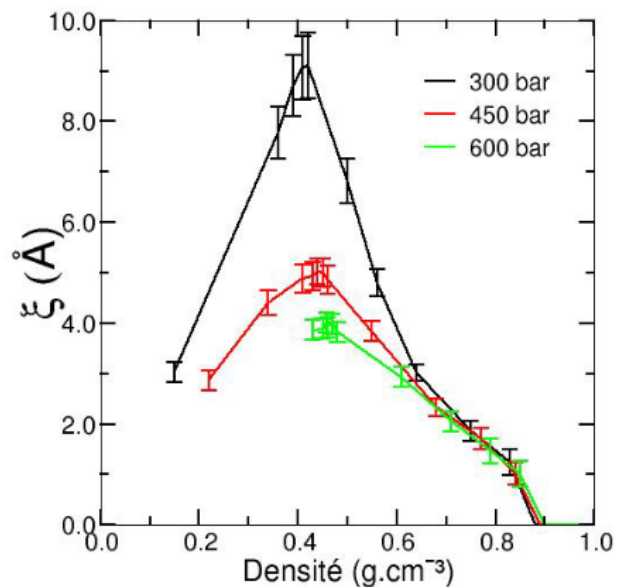
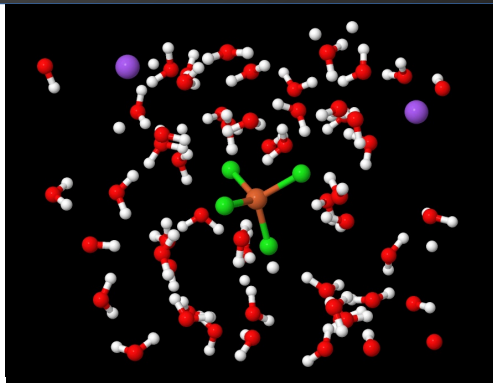


# Structure of supercritical water



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

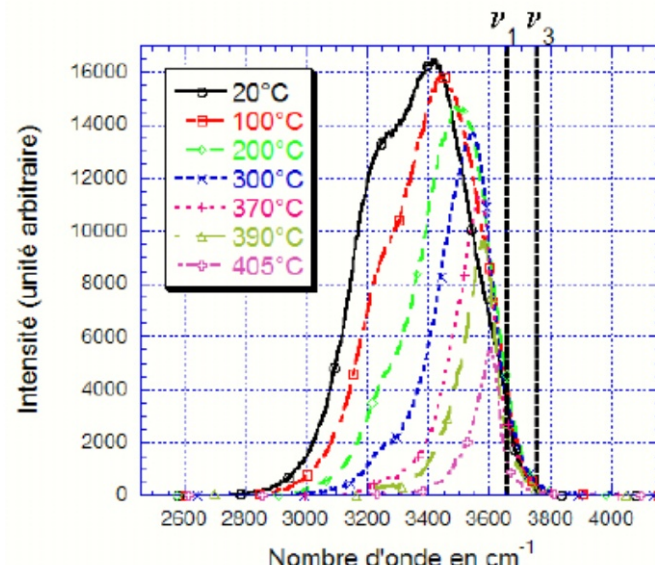
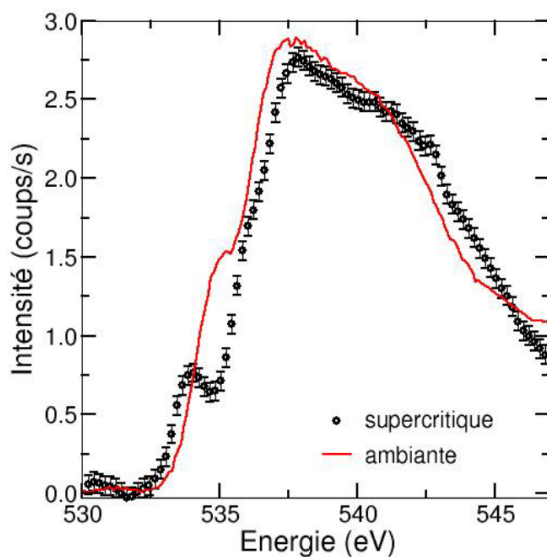
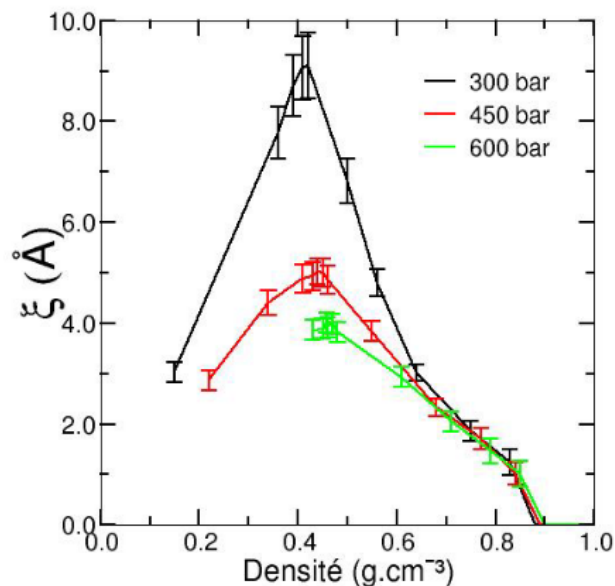
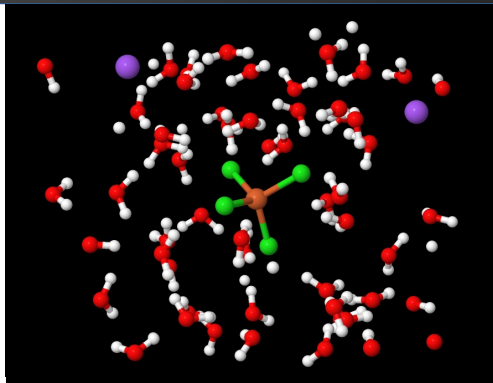
# Structure of supercritical water



SAXS: correlation length  
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*Testemale et al., J. Chem. Phys. (2005)*

IXS: oxygen K-edge  
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*Wernet et al., J. Chem. Phys. (2005)*

# Structure of supercritical water



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

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!

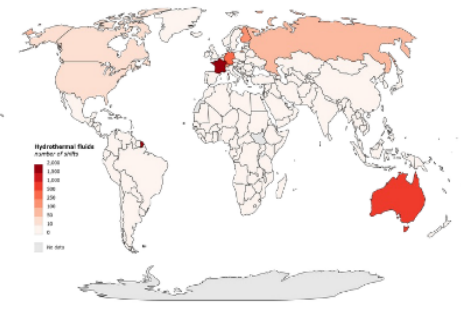
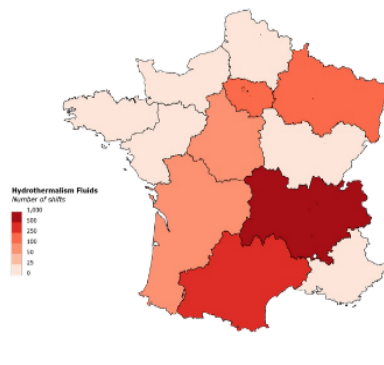


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