Introduction to autoclave technics

In-situ studies of high-temperature fluids and melts (P < 2 kbar)
and their application to Geosciences

@ BM16, BM30B and Institut Néel

Marion Louvel

Hands on ! High-pressure techniques at the ESRF-EBS – June 21st, 2019

Introduction : High-temperature fluids and associated challenges

Why studying high-temperature fluids?

High T fluids (100 < T < 800 °C) play a key role in geological processes and have important impact on our societies

⇒ *Volcanic degassing (Explosive vs. Passive ; Climatic impact)*
⇒ *Ore deposit formation*
⇒ *Petroleum reservoirs*
⇒ *Geothermal energy and CO2 storage*

Pinatubo 1991 eruption, Indonesia

Kawah-Ijen, Indonesia (S deposit)
Bingham, USA (Cu-Au-Mo porphyry)

Hellisheidi geothermal power plant
Carbfix CO2 storage project, Iceland

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Pinatubo 1991 eruption, Indonesia

<u>Other (non-geological) applications:</u>
Supercritical solvents for synthesis, extraction, *etc…*
Vapor-liquid, liquid-liquid equilibria

What we want to know

Composition

depends on nature of protolith and P-T

- Solubility of volatile-rich minerals in fluids
- Nature of volatiles species as a function of P-T (HCO_3^- or CO_3^{2-}?)
- Phase diagram for complex fluids involving H_2O-CO_2-NaCl-F, S, P, *etc…*

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Effect of fluid-rock-magma interactions on composition

- Solubility of metals and minerals
- Nature of metal complexation (e.g. $Cu(II)Cl^{2-}$ or $Cu(I)Cl_2^-$)

Circulation in rocks/magmas

- Physical properties (density, viscosity)

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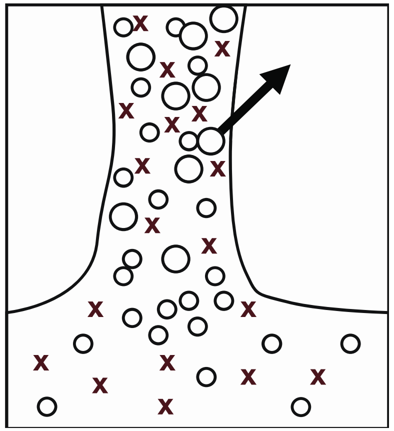
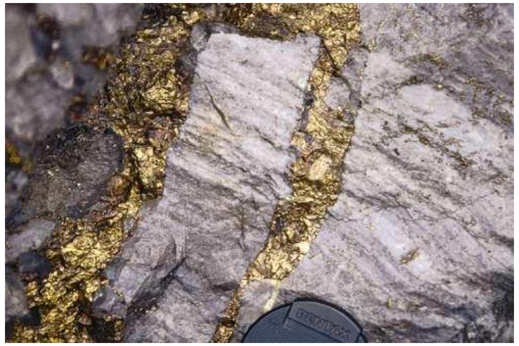
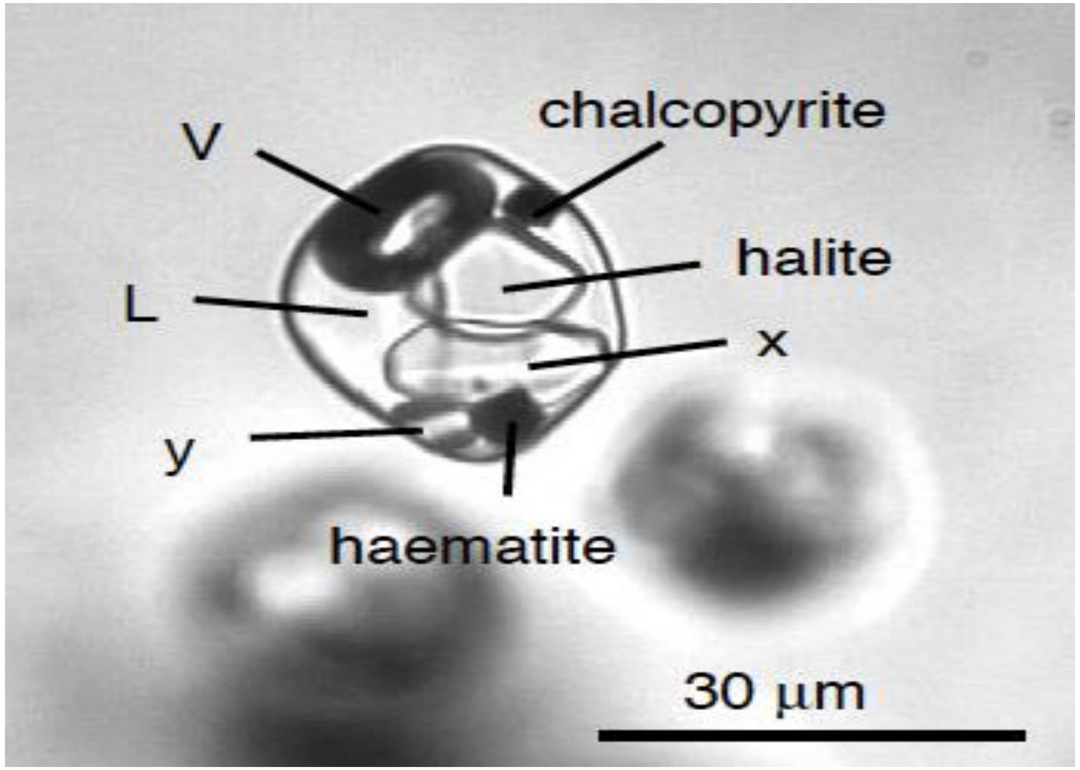




Challenging studies….

Fluids are difficult/impossible to sample….



Fluid inclusions

✗ **Post-entrapment modification**

Fast H_2O loss *(eg. Bakker and Doppler, 2016)*

Cu, Au diffusion *(Lerchbaumer and Audetat, 2012; Guo and Audetat, 2017)*

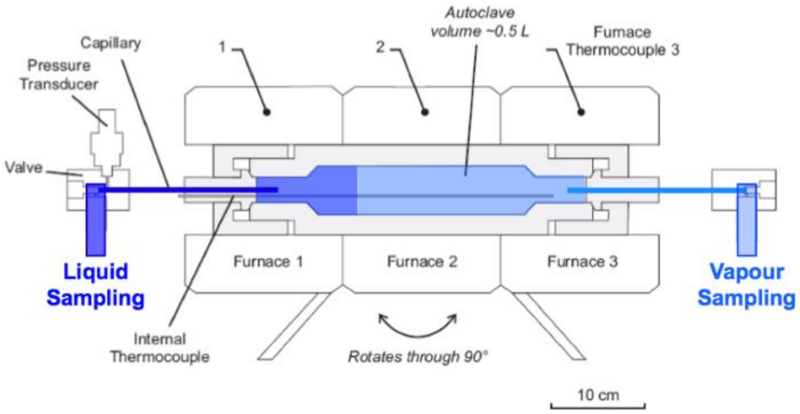
Volcanic gases

✗ **Do not represent 'deep' composition**

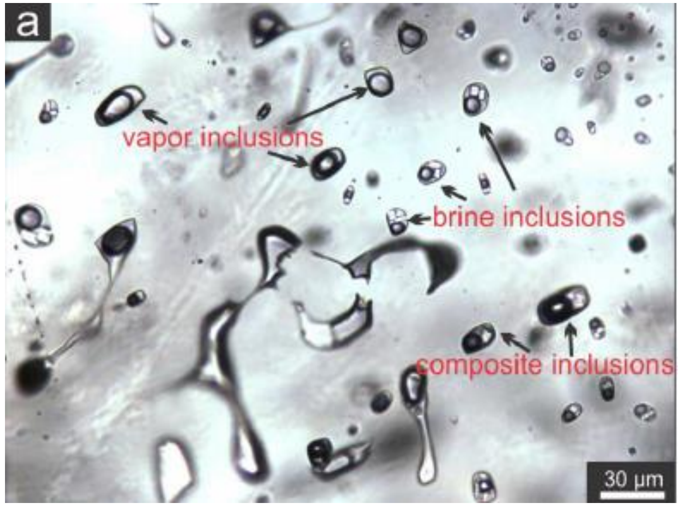
Challenging studies….

=> Experimental constraints are required !

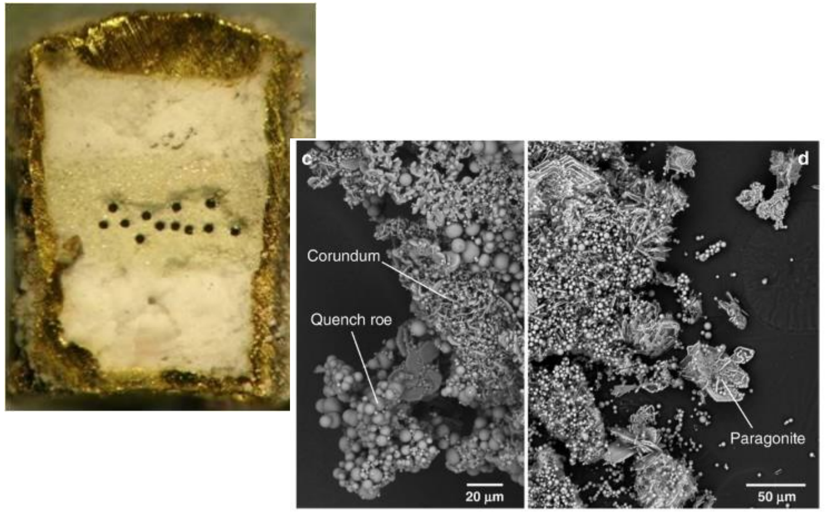
<u>Batch-reactor / Autoclave</u>
T < 600 °C – P < 200 MPa



<u>Synthetic fluid inclusions</u>
600 < T < 1000 °C – P < 500 MPa



<u>Diamond-trap/weight loss exp.</u>
600 < T < 1400 °C – 0.5 < P < 6 GPa



<u>References:</u> Antignano and Manning, 2008; Kessel et al., 2005; Dvir and Kessel, 2017 *(deep fluids equilibrated with eclogites)*; Loges et al., 2013 *(YF3 solubility); Pokrovski et al., 2005-2008 (fluid-vapor partitioning of metals); Zajacz et al., 2009-2017 (Cu-Au-S solubility and fluid-melt-vapor partitioning)*

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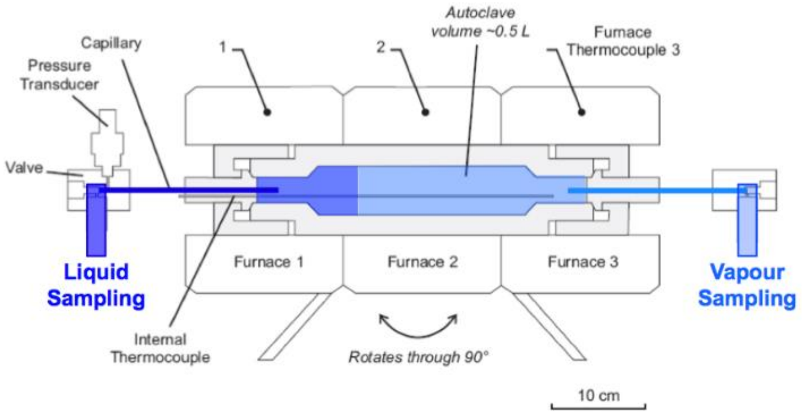

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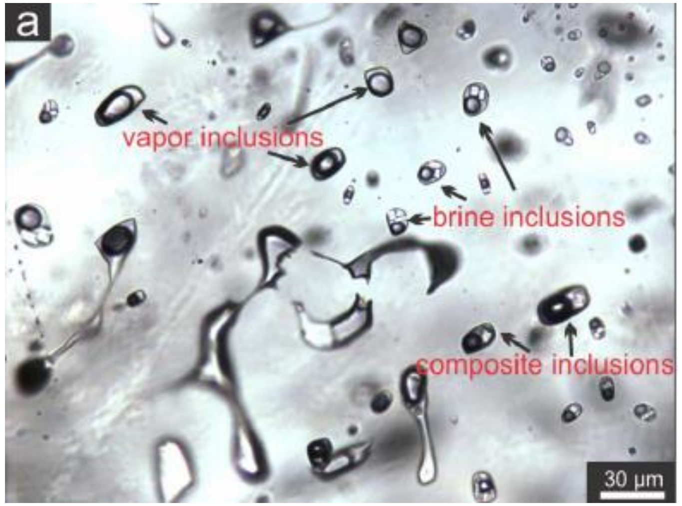

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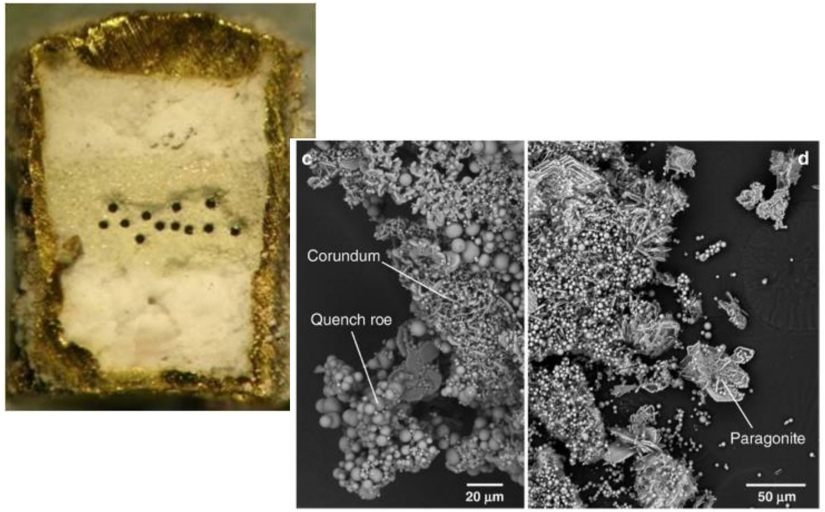

✓ **Great for quantification**

Challenging studies….

=> Experimental constraints are required !

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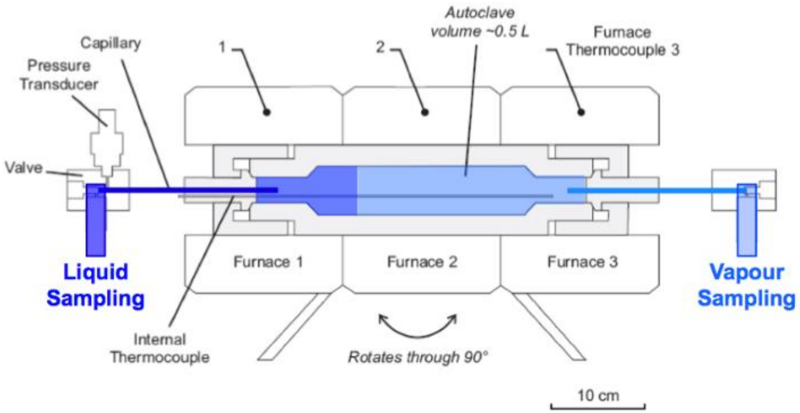

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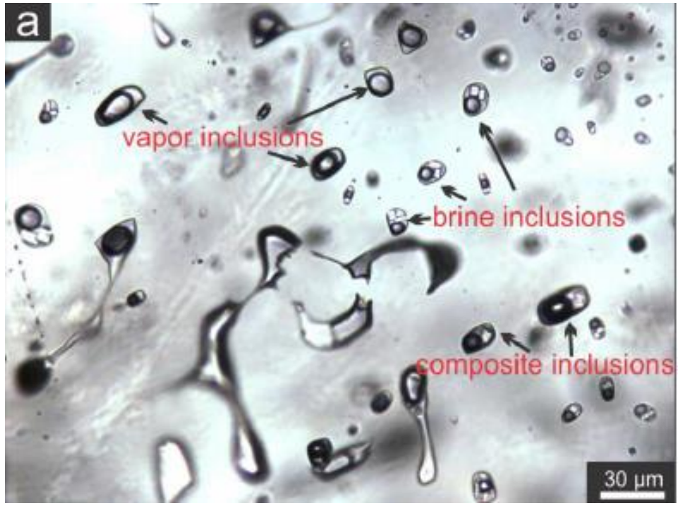

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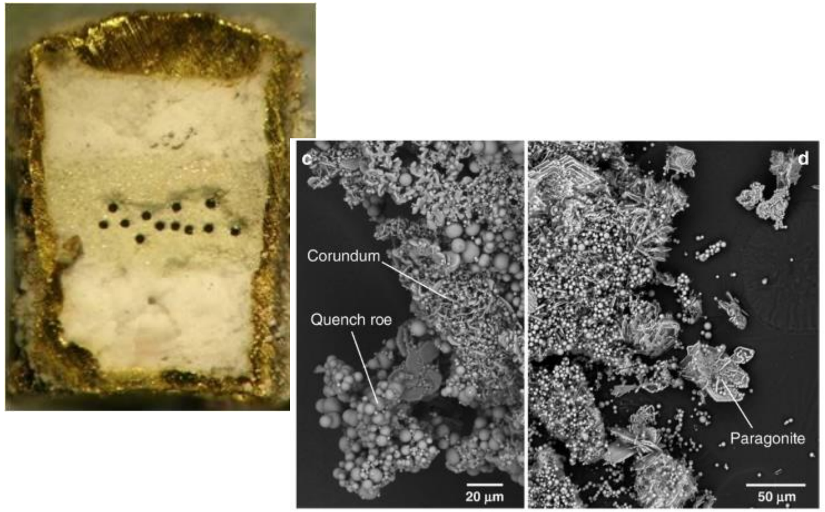


✓ Great for quantification
✗ High P-T species unknown
✗ Nature of high T fluids (brine, gas)?

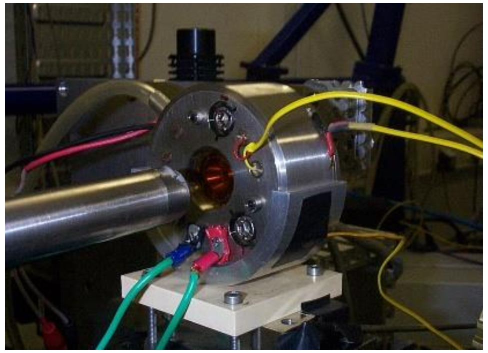
In-situ spectroscopy on high T fluids

Autoclave HT

600 °C – 0.1-2kbar

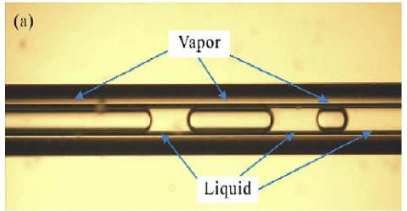
HDAC

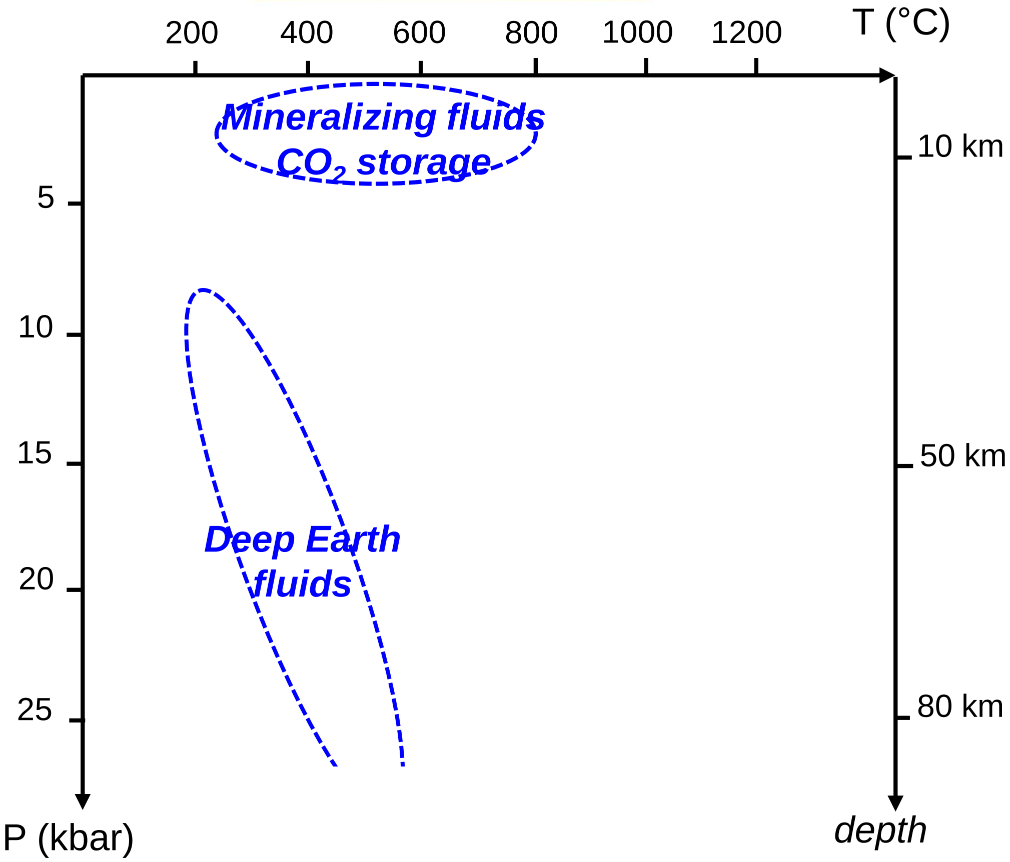
900 °C – 5-30 kbar



Si fused capillaries

~ 500 °C - *Psat*





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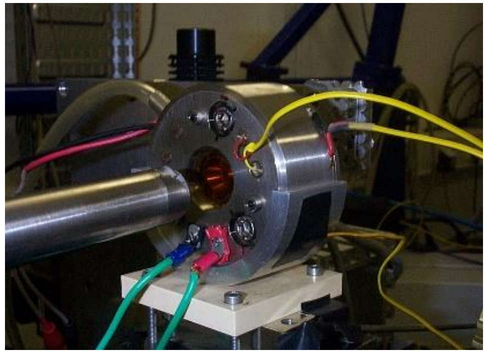

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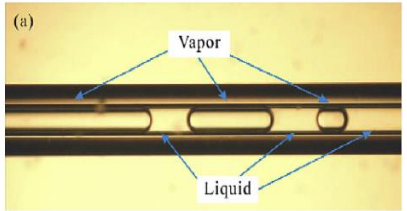
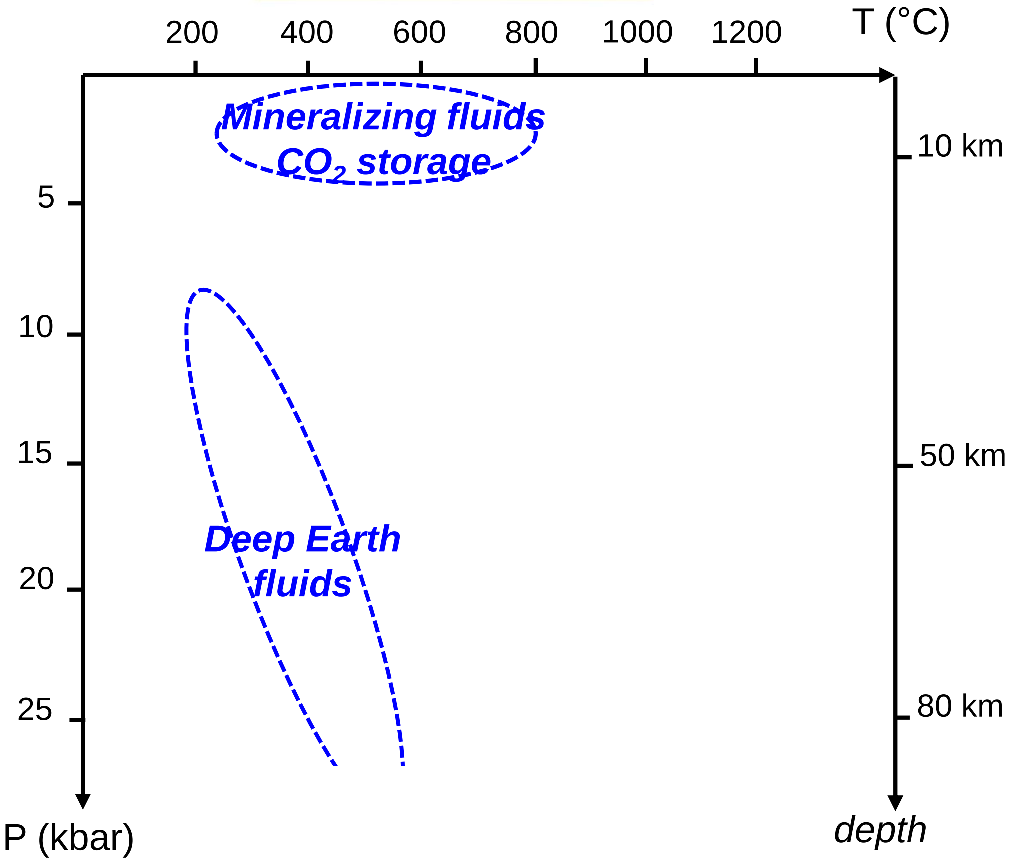
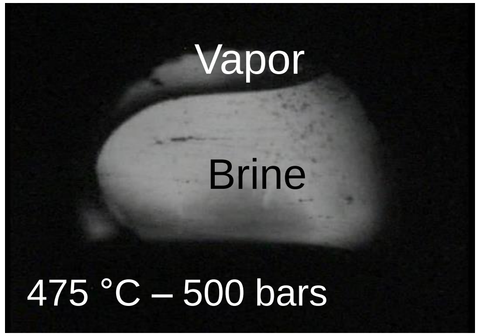
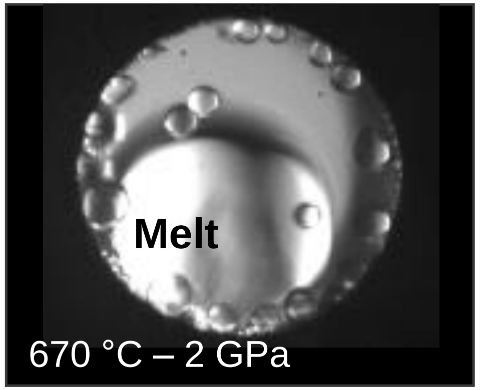




1. **Visualization**

phase separation, homogeneization, melting





In-situ spectroscopy on high T fluids

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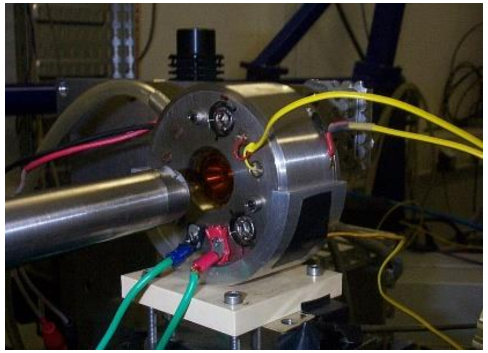

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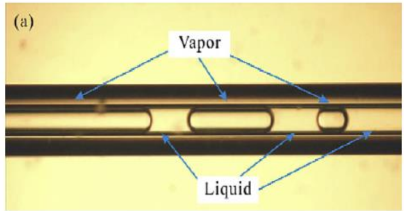
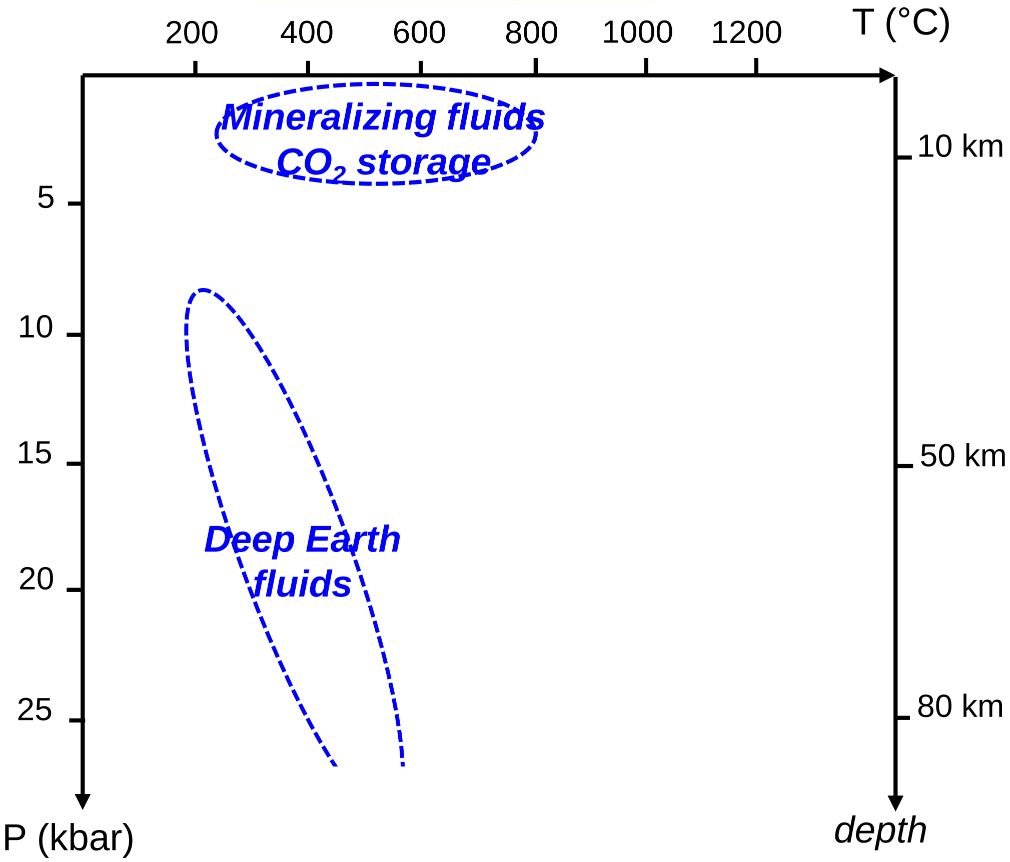
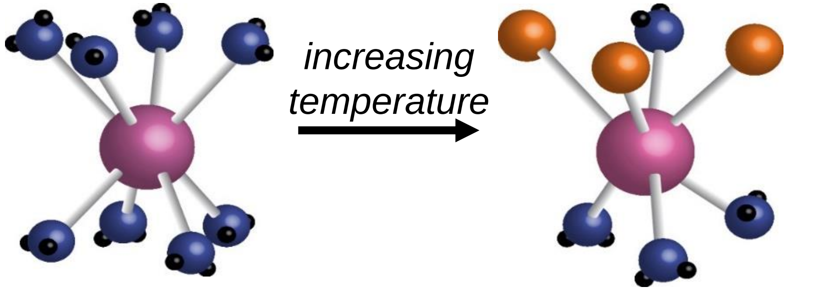




1. Visualization
phase separation, homogeneization, melting

2. X-ray absorption/fluorescence
solubility, speciation, density



$REE(H_2O)_8^{3+}$ **$REECl_3(H_2O)_4$**

In-situ spectroscopy on high T fluids

Autoclave HT

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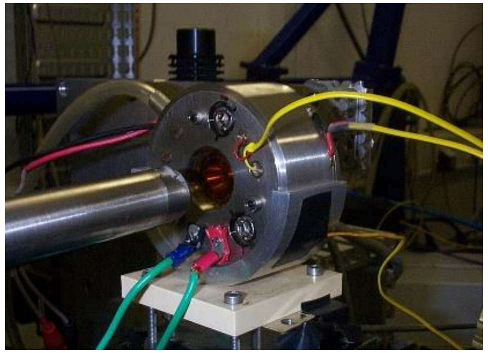

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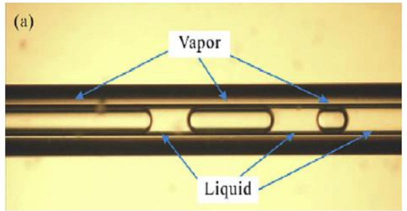
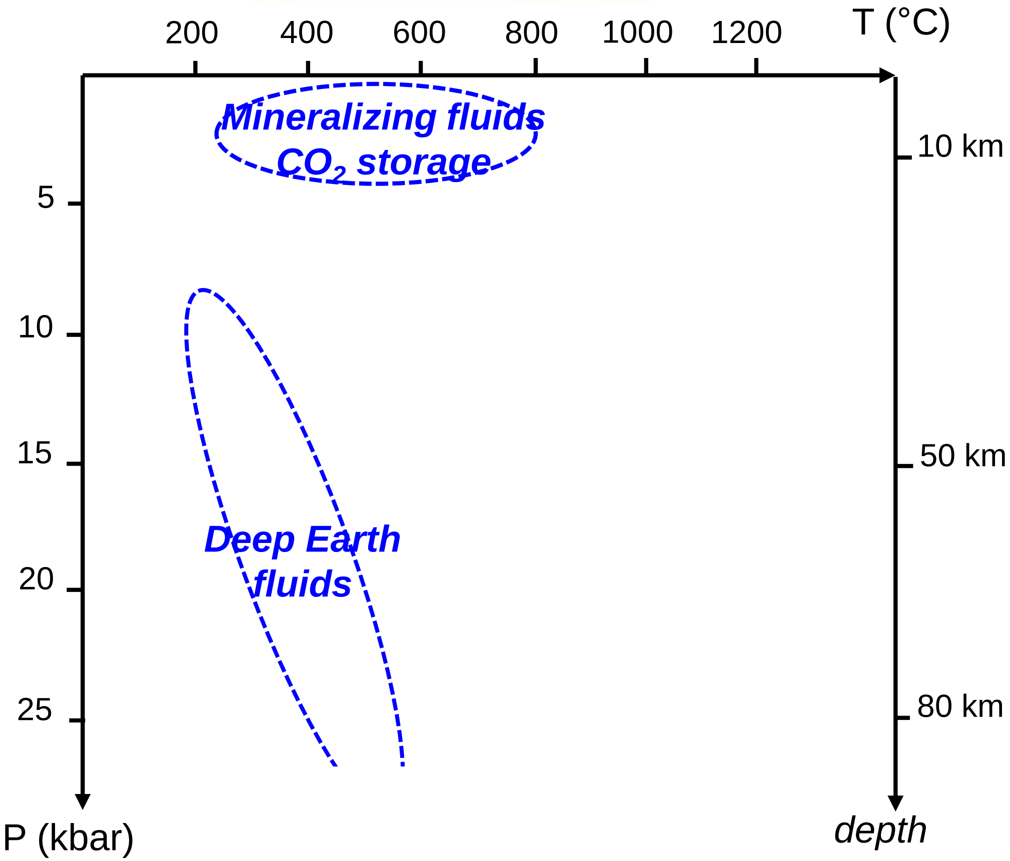
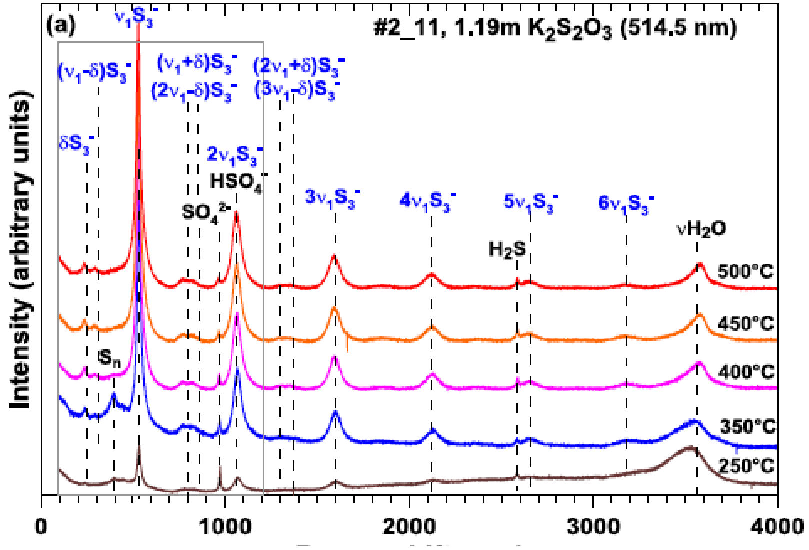




1. **Visualization**
   phase separation, homogeneization, melting

2. **X-ray absorption/fluorescence**
   solubility, speciation, density

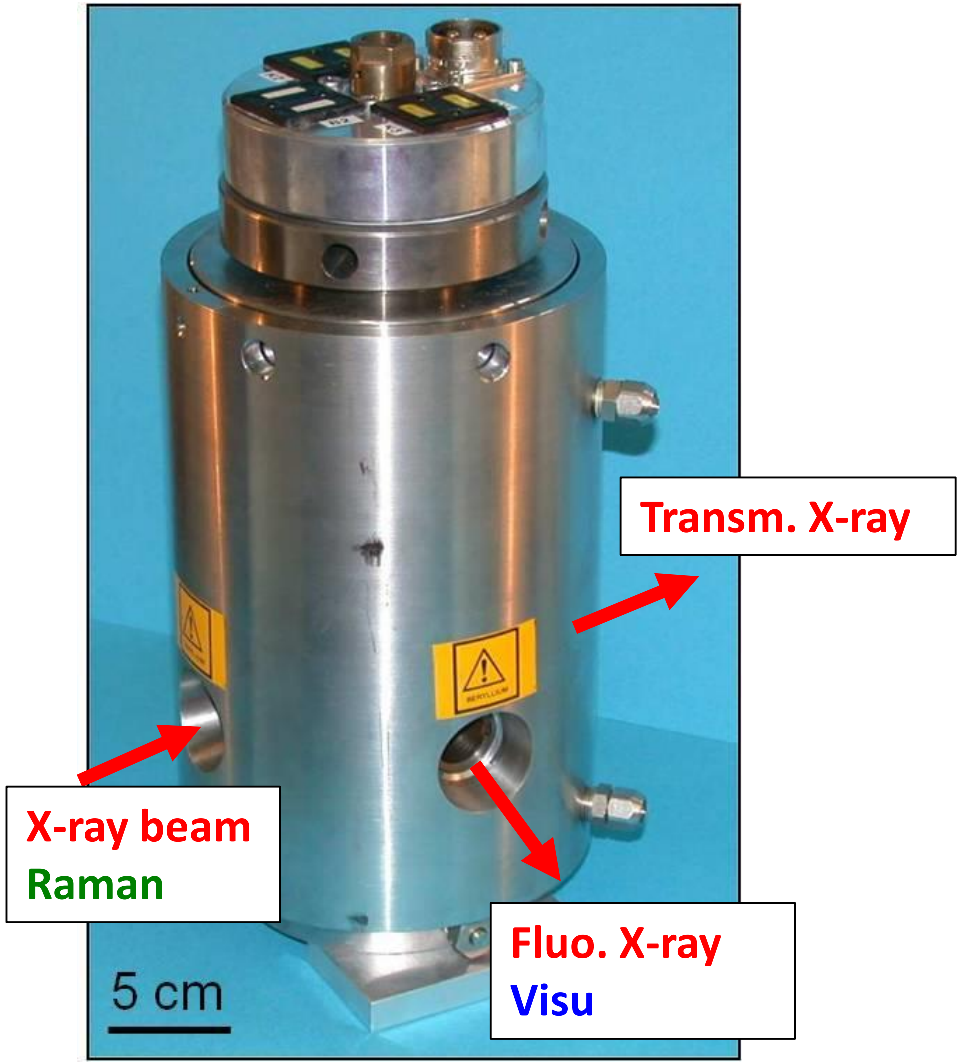
3. **Raman**
   volatile species, structure of solvent

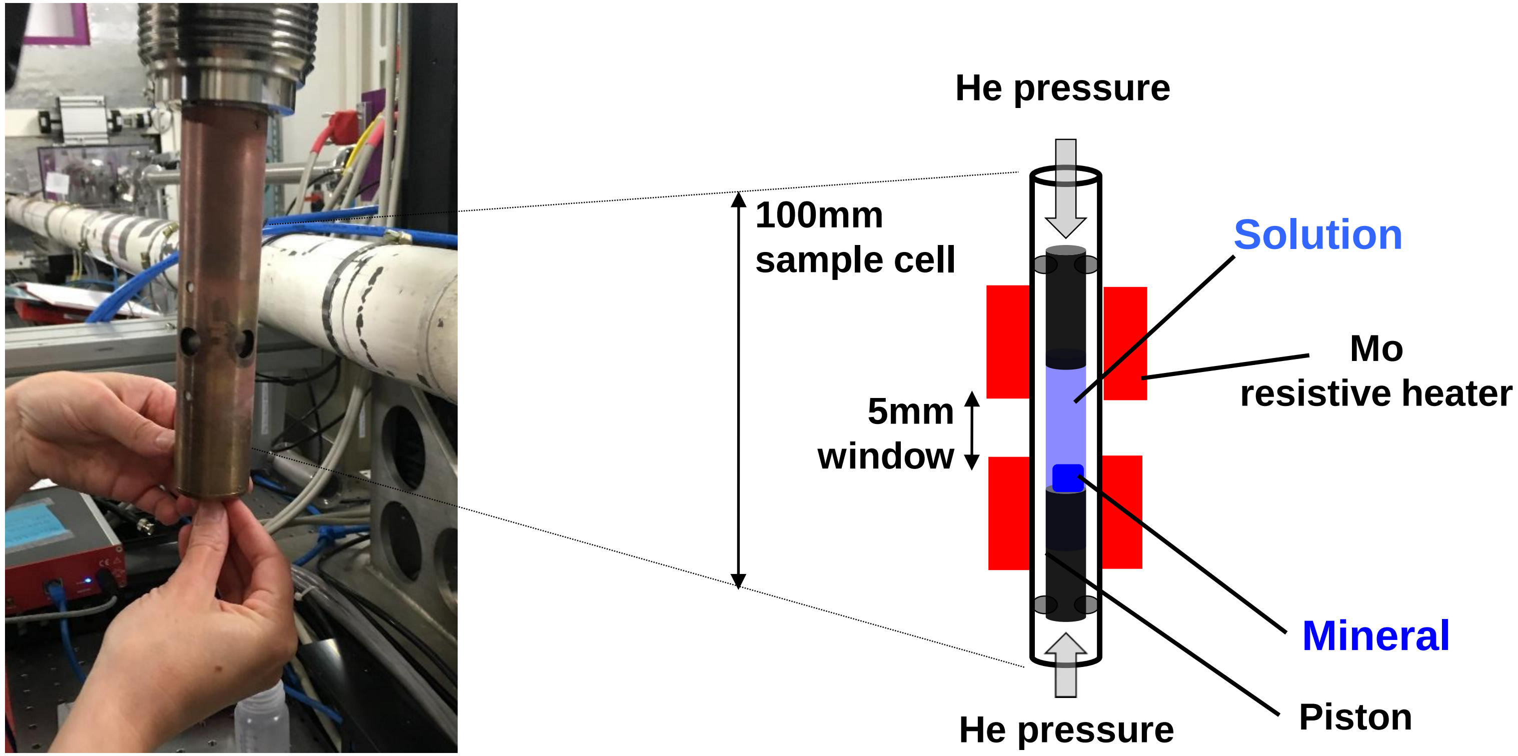


Pokrovski et al., 2011-2015

The autoclave

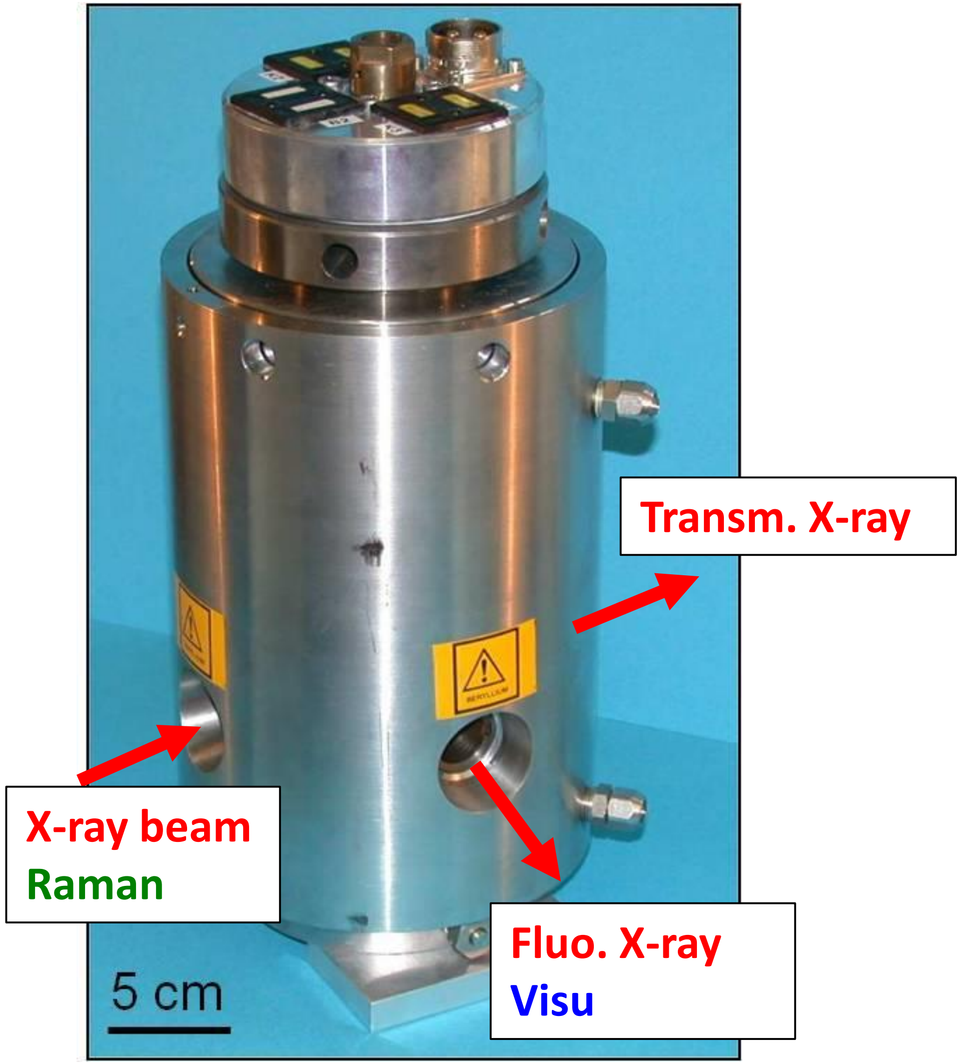
The autoclave : Concept and set-up for *in-situ* spectroscopy

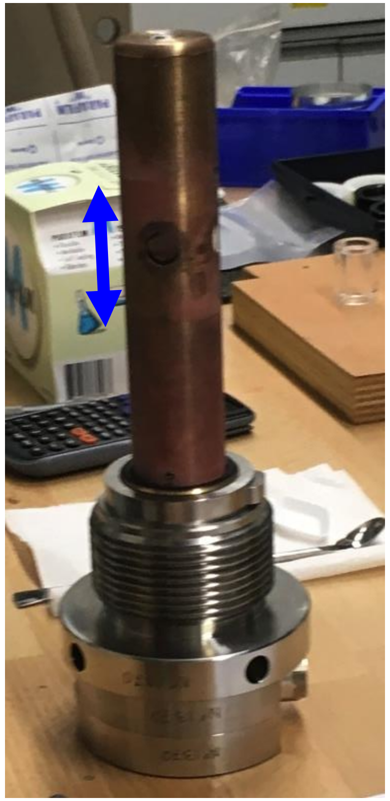




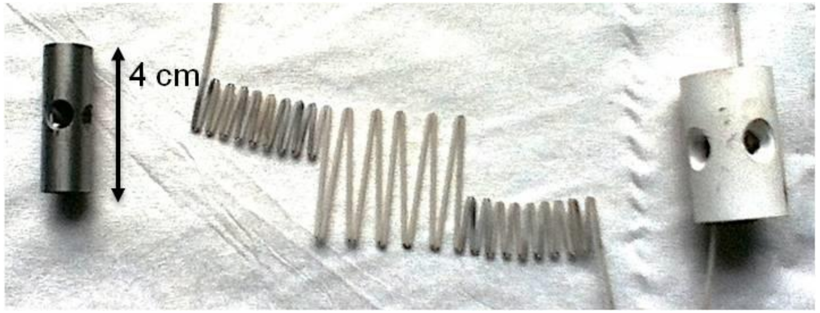
Pressure ±0.4 bars
Temperature ±0.1 °C

The autoclave : Concept and set-up for *in-situ* spectroscopy

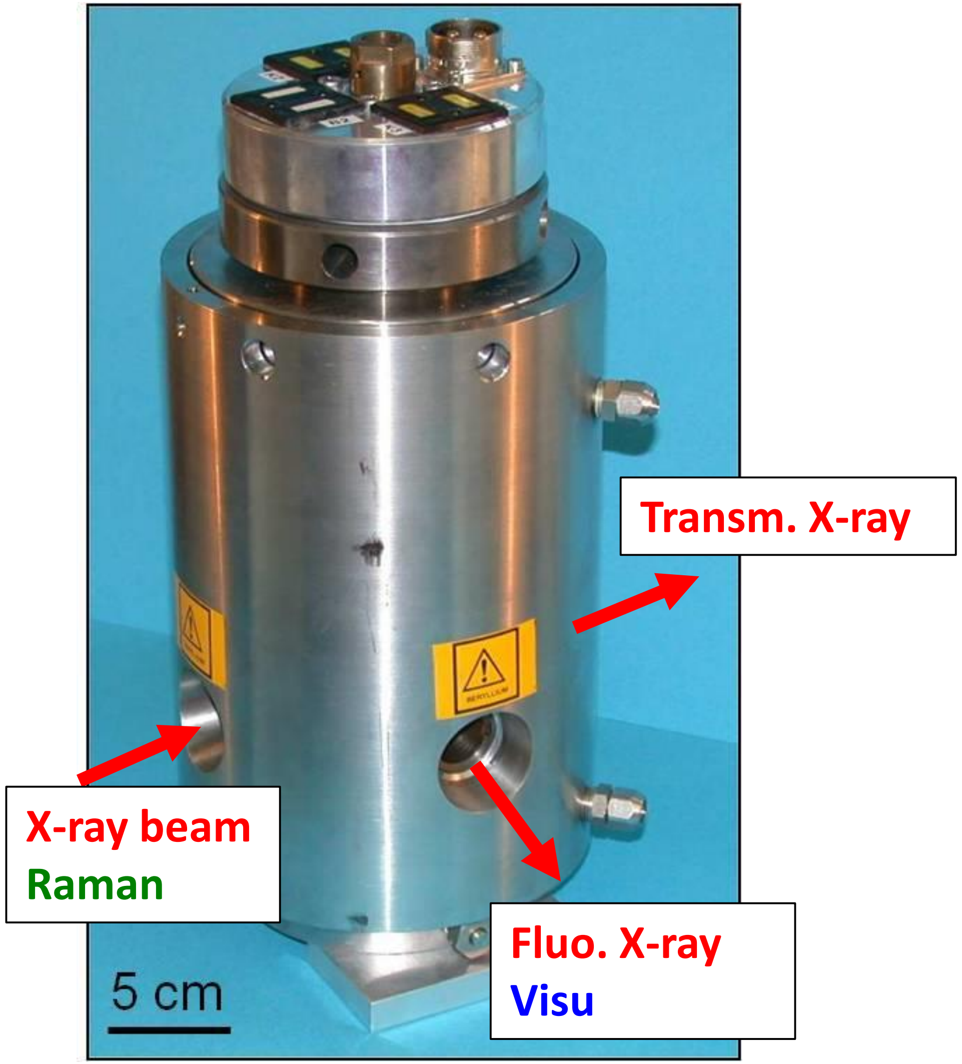


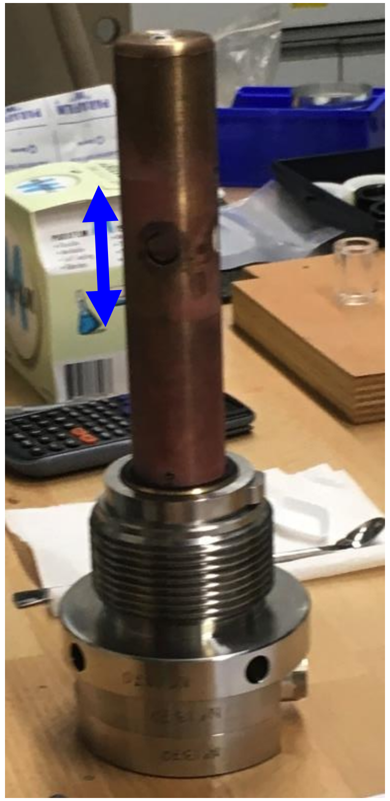


Heater : Cu or Mo



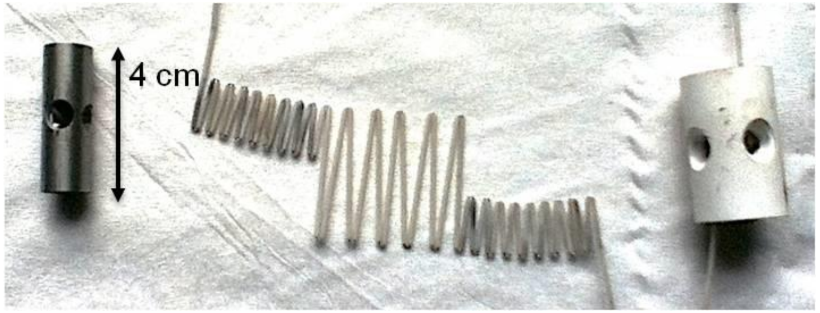
The autoclave : Concept and set-up for *in-situ* spectroscopy





50-100 µm Be screen prevents heat loss

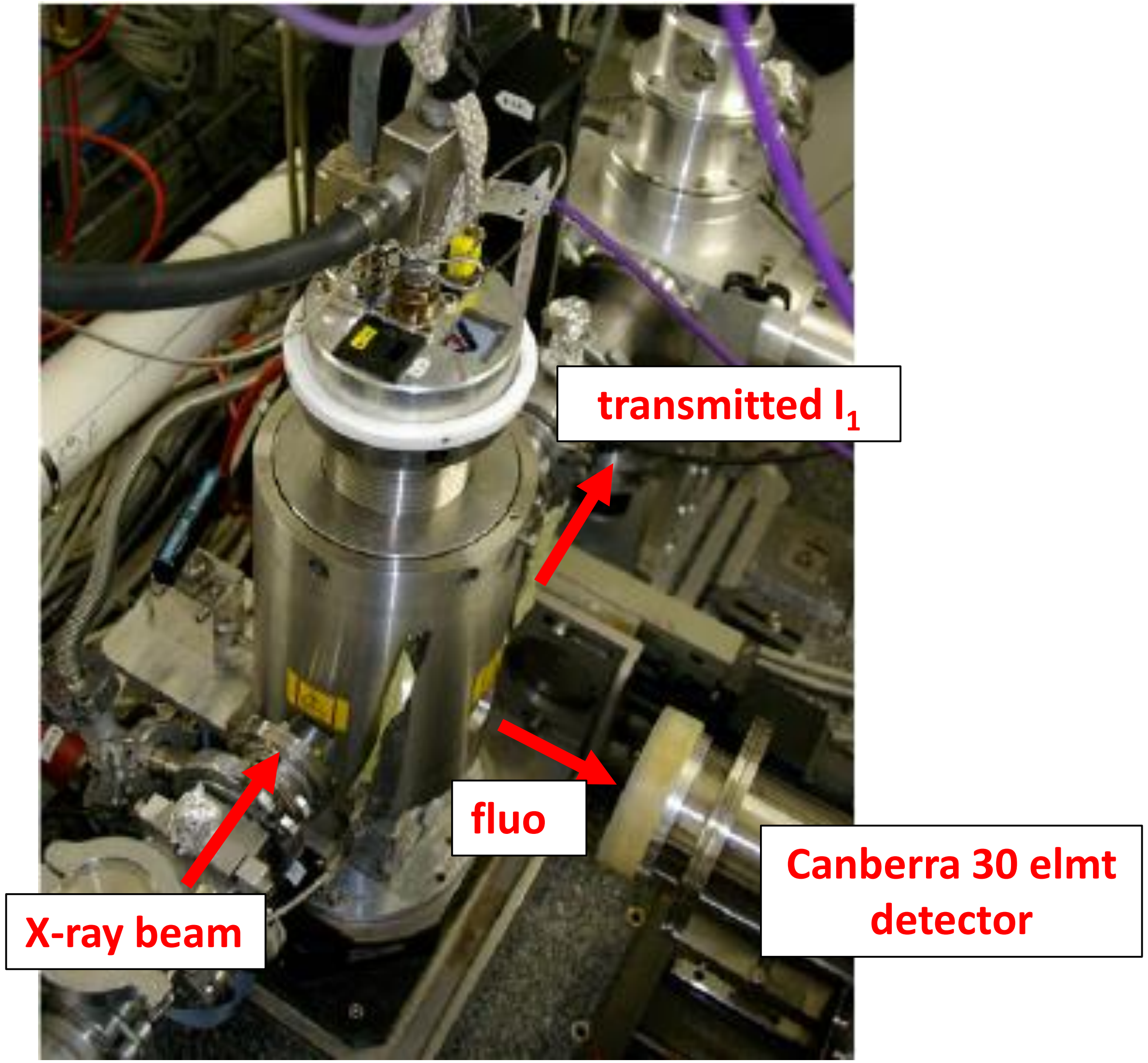
Heater : Cu or Mo



Autoclave I : in-situ X-ray absorption

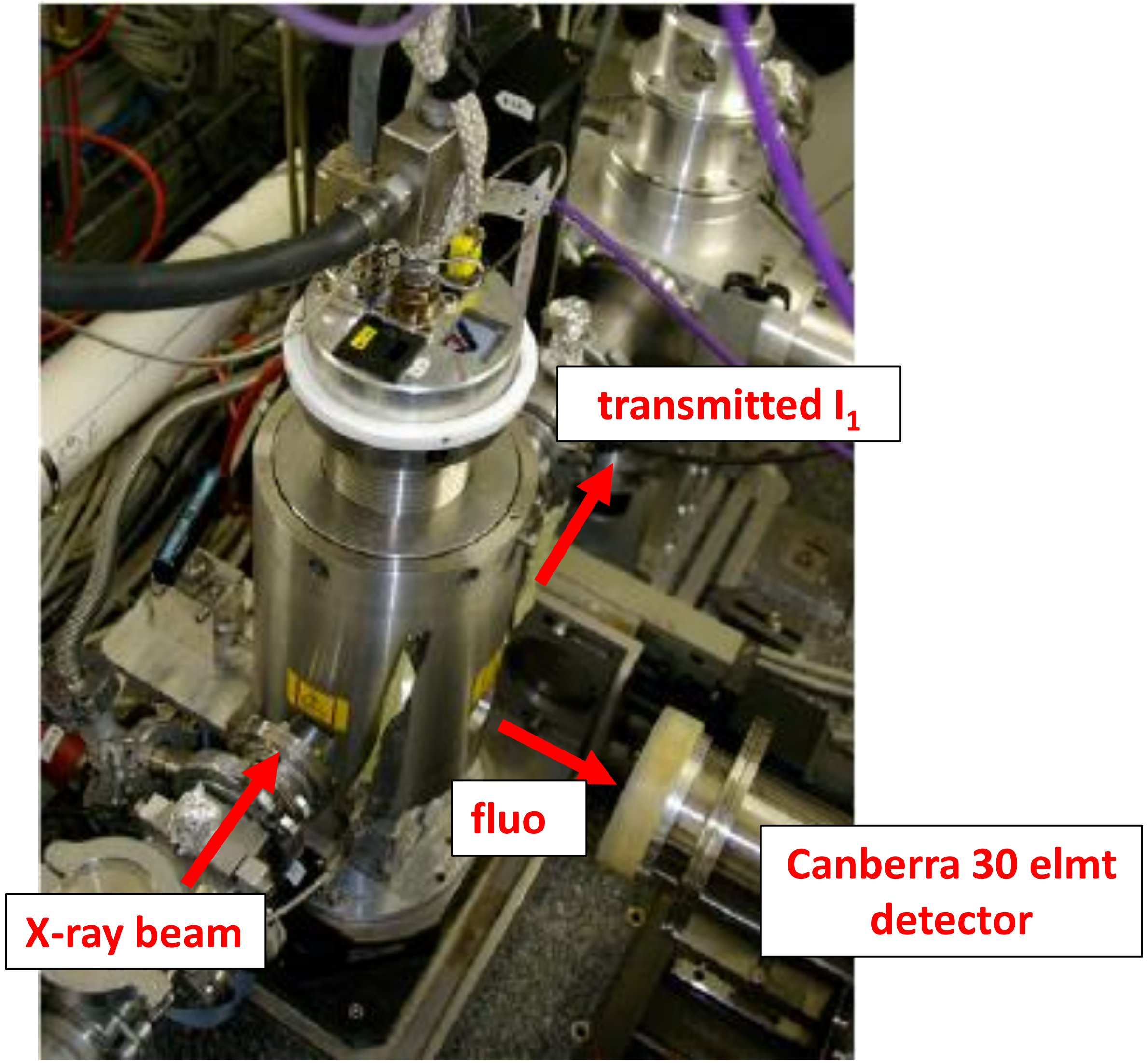
The autoclave : Concept and set-up for *in-situ* spectroscopy

- *in-situ* XAS

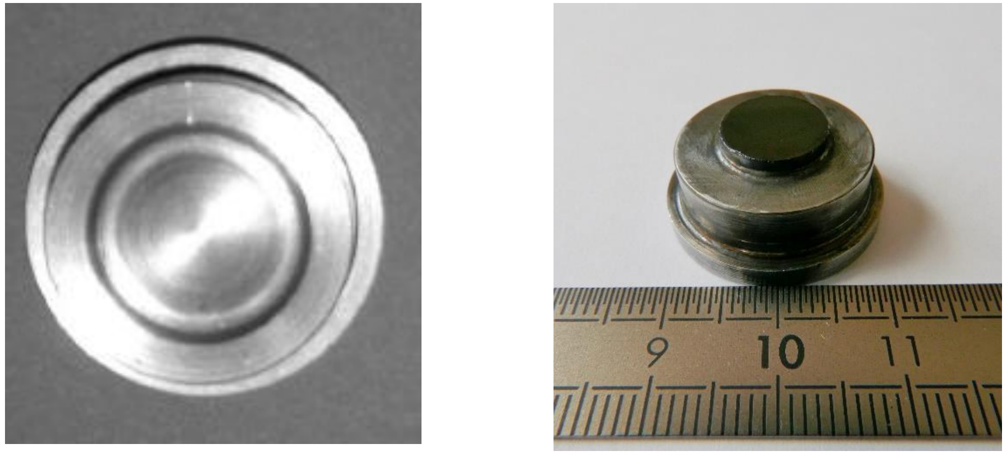


The autoclave : Concept and set-up for *in-situ* spectroscopy

- *in-situ* XAS



Be or C windows

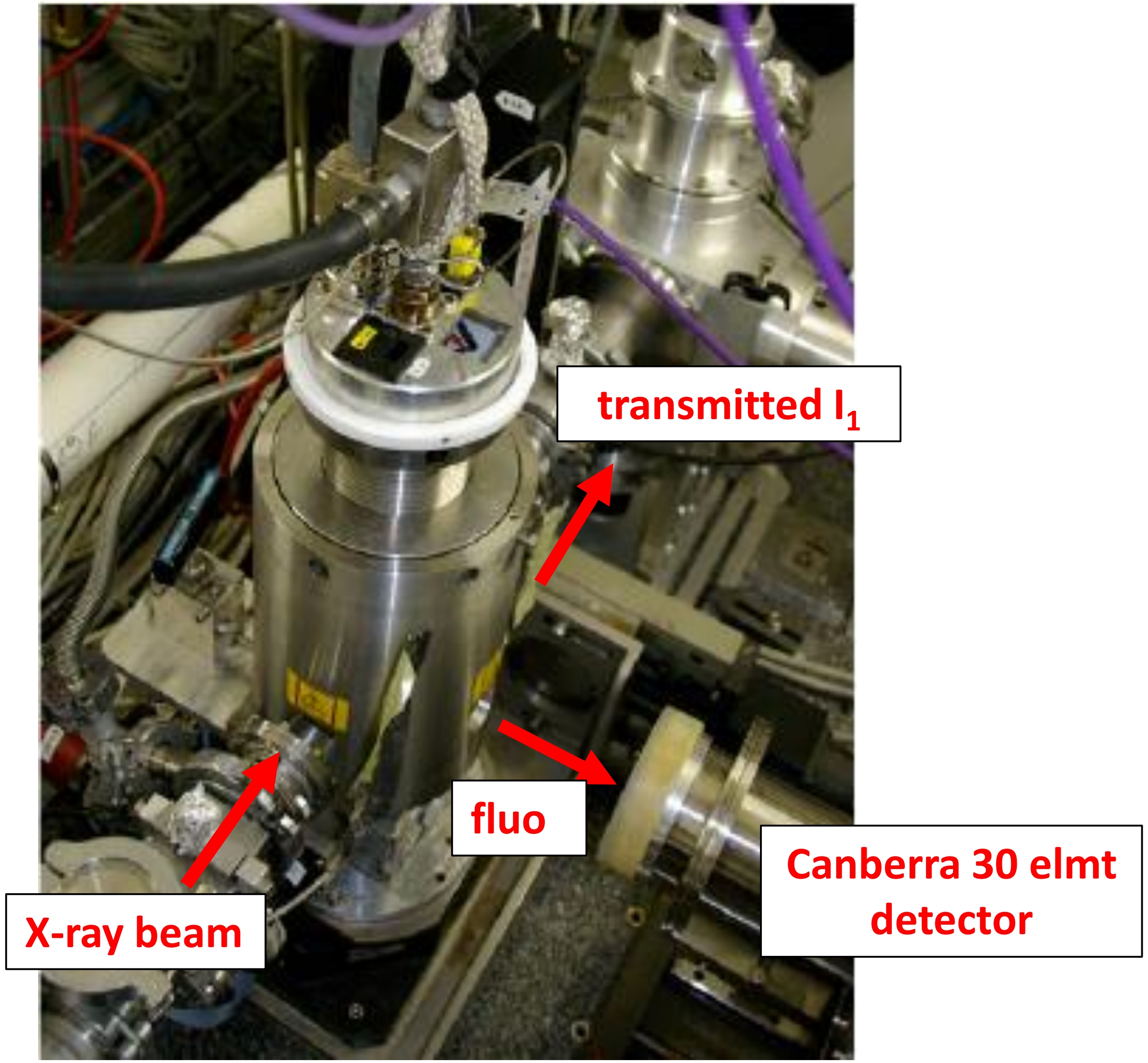


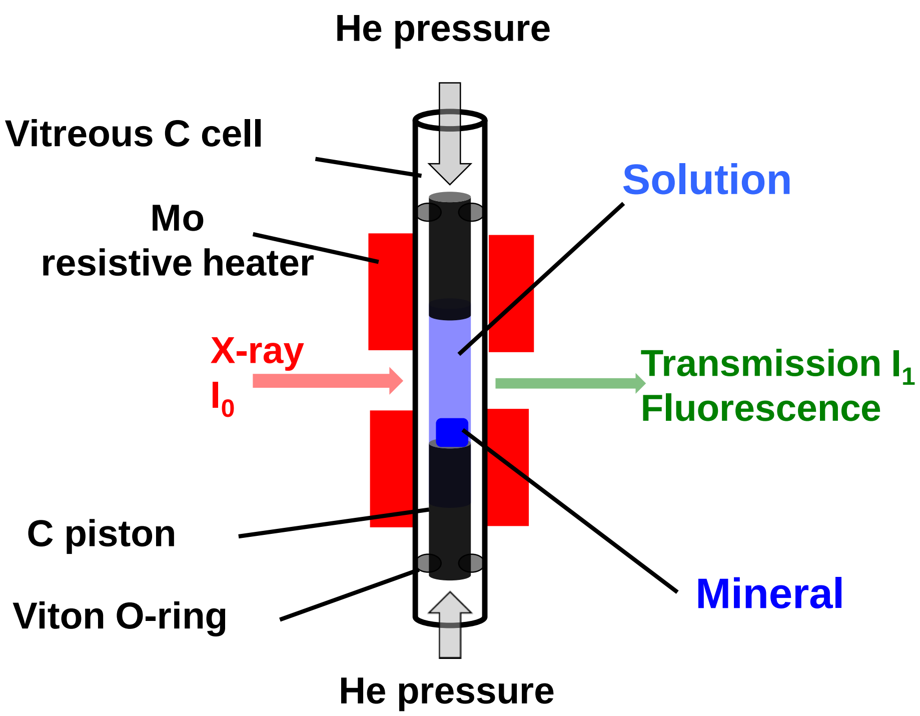
Vitreous C sample container

References: Testemale et al., 2005, 2016

The autoclave : Concept and set-up for *in-situ* spectroscopy

➢ ***in-situ* XAS**





➢ **Experimental Conditions:**

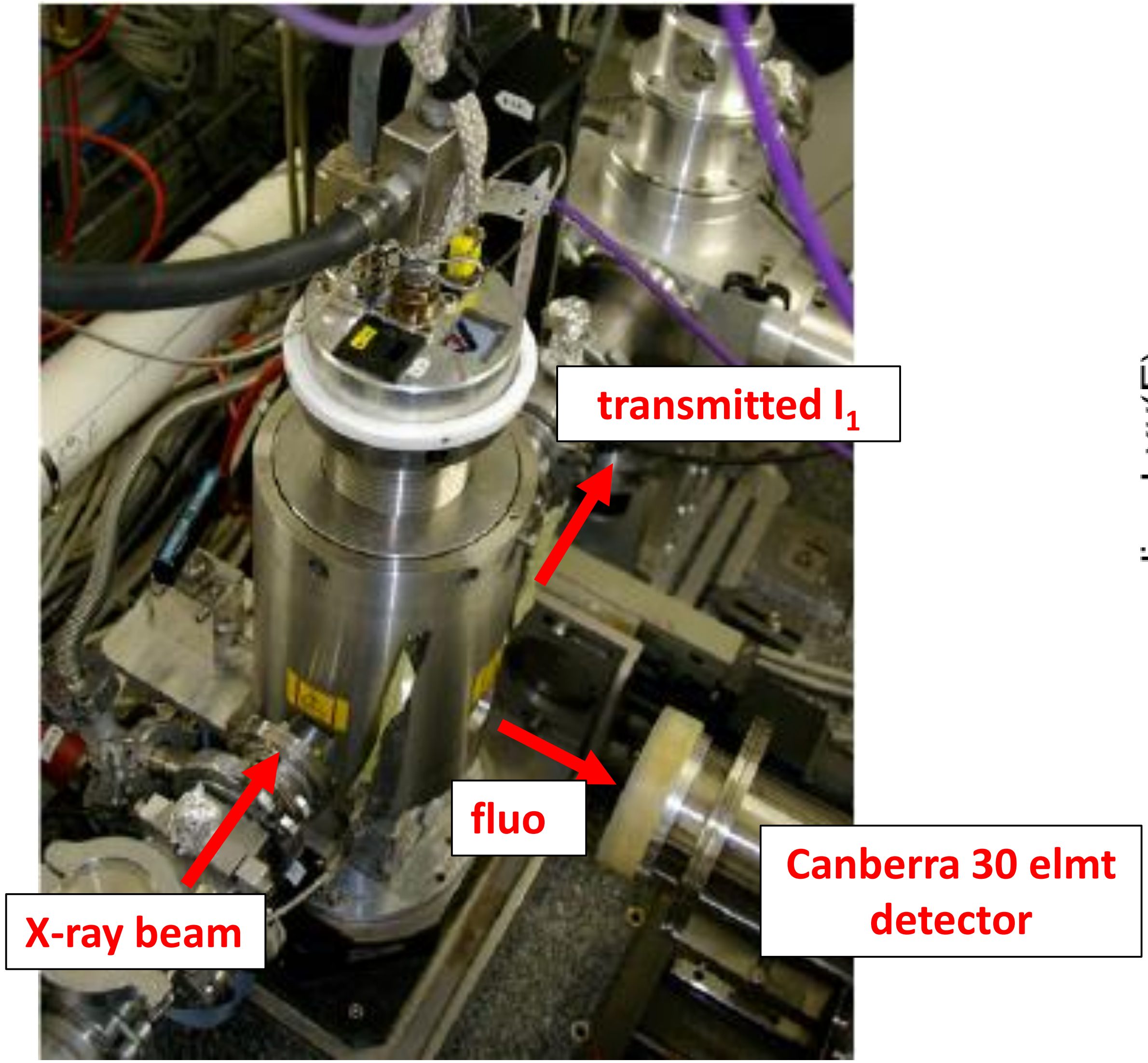
Beam ~ 200x100 µm HxV (FWHM)

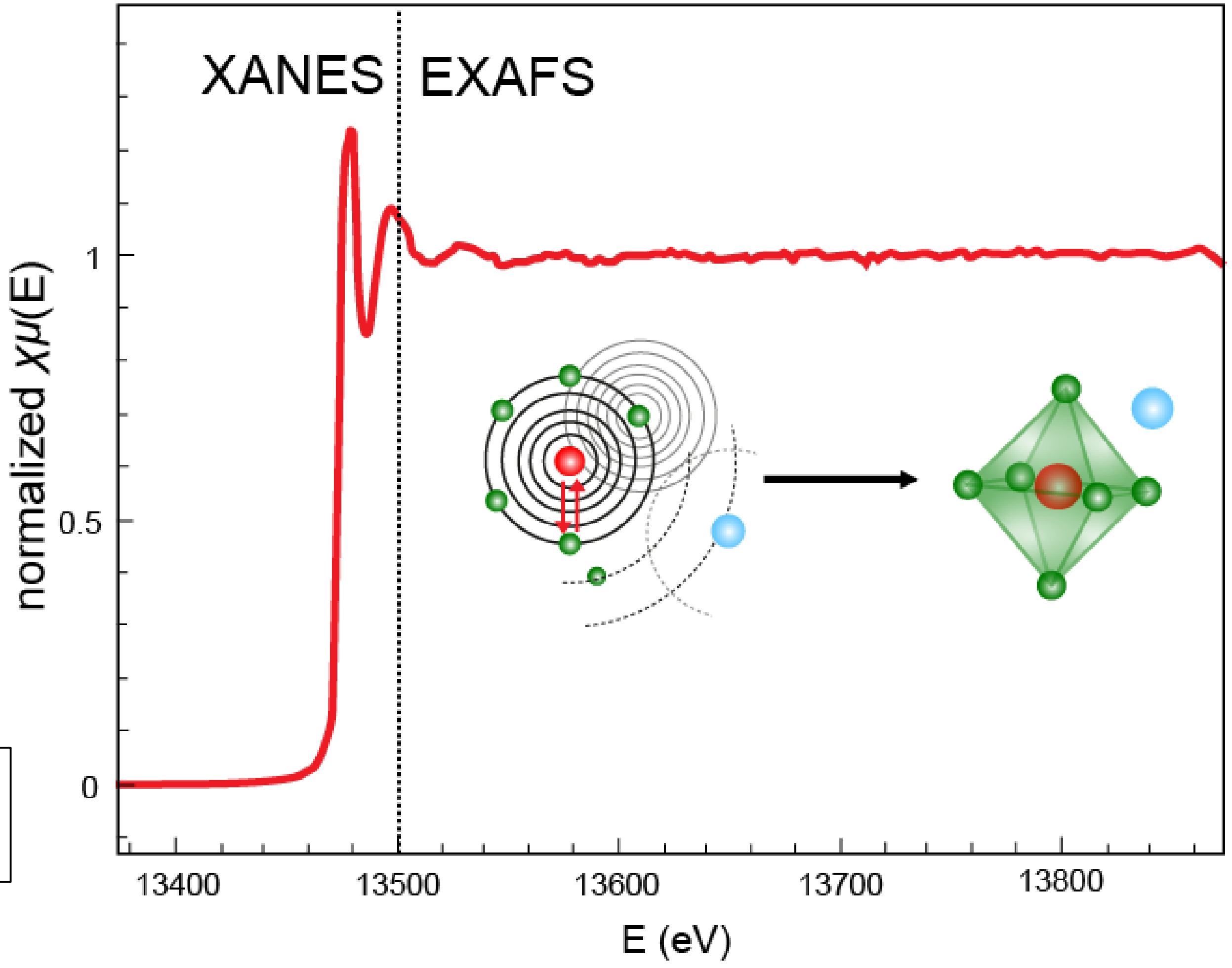
P is known and T calibrated to water EOS

6 < E < 25 keV (Mn K-edge/La L3-edge ; Sb K-edge)

The autoclave : Concept and set-up for *in-situ* spectroscopy

- ***in-situ*** **XAS : Speciation (XANES + EXAFS)**





The autoclave : Concept and set-up for *in-situ* spectroscopy

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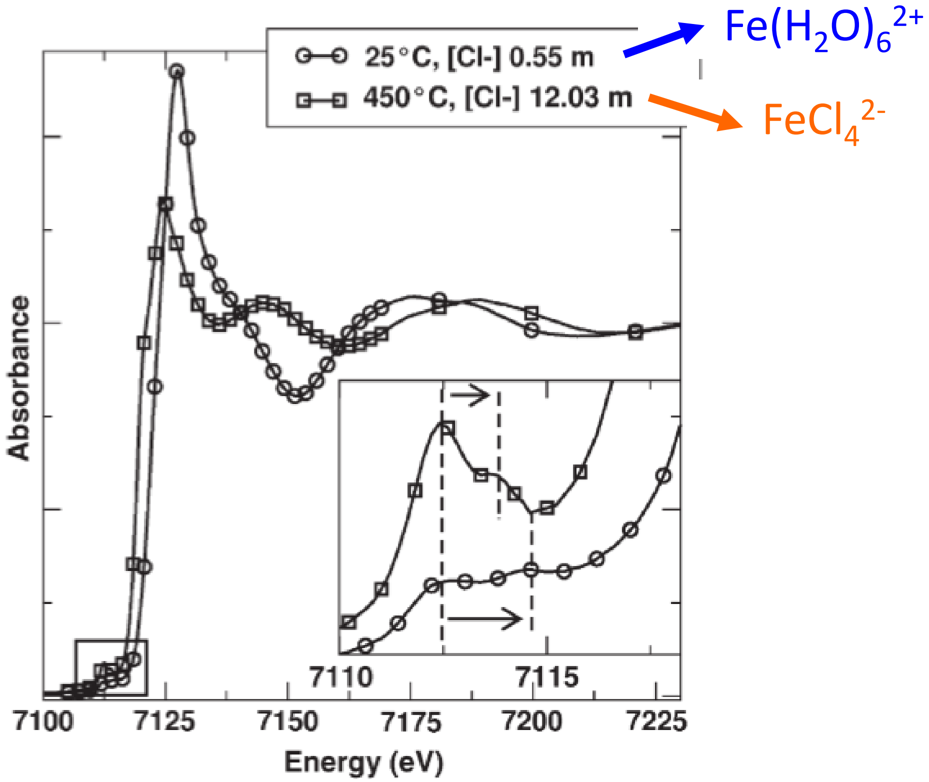
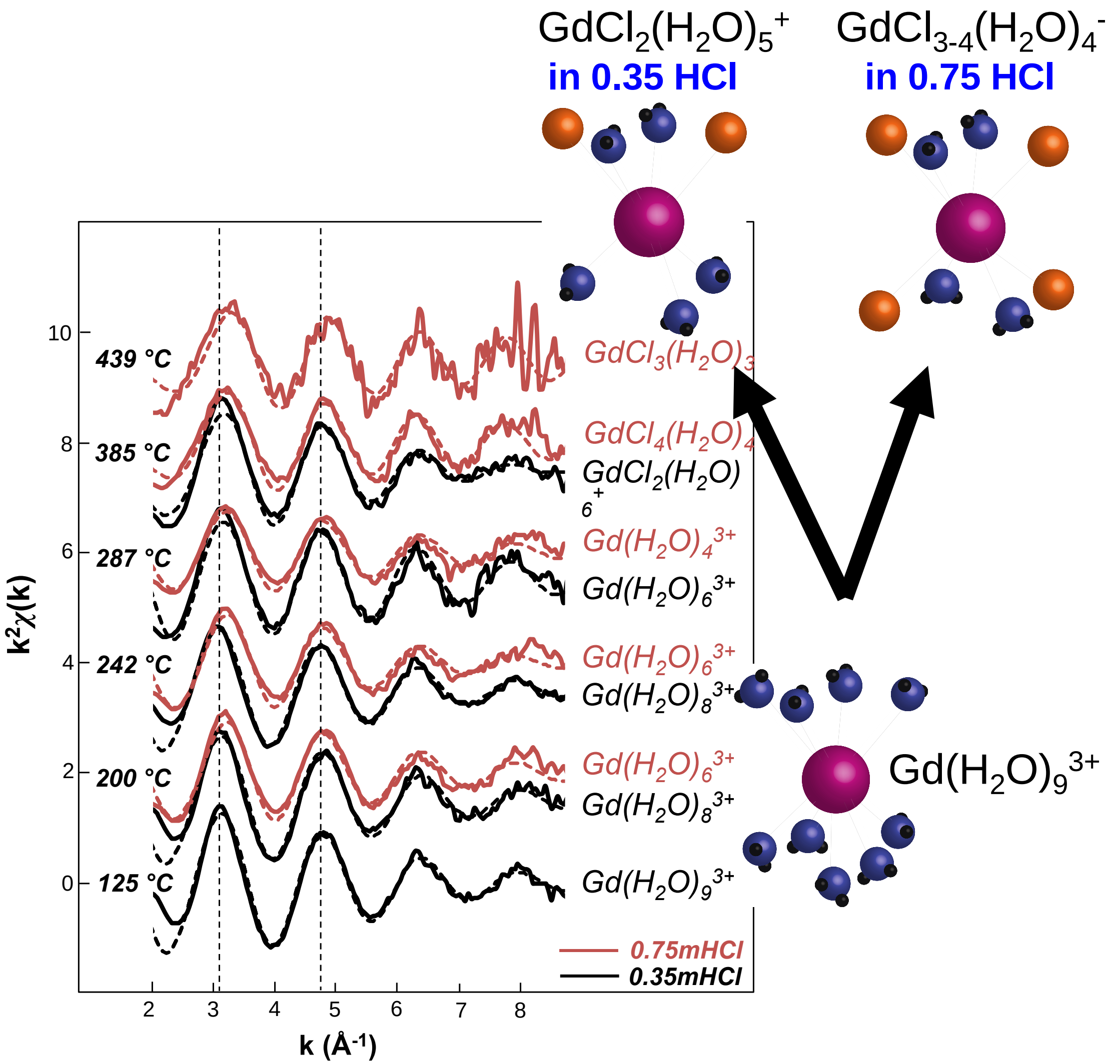


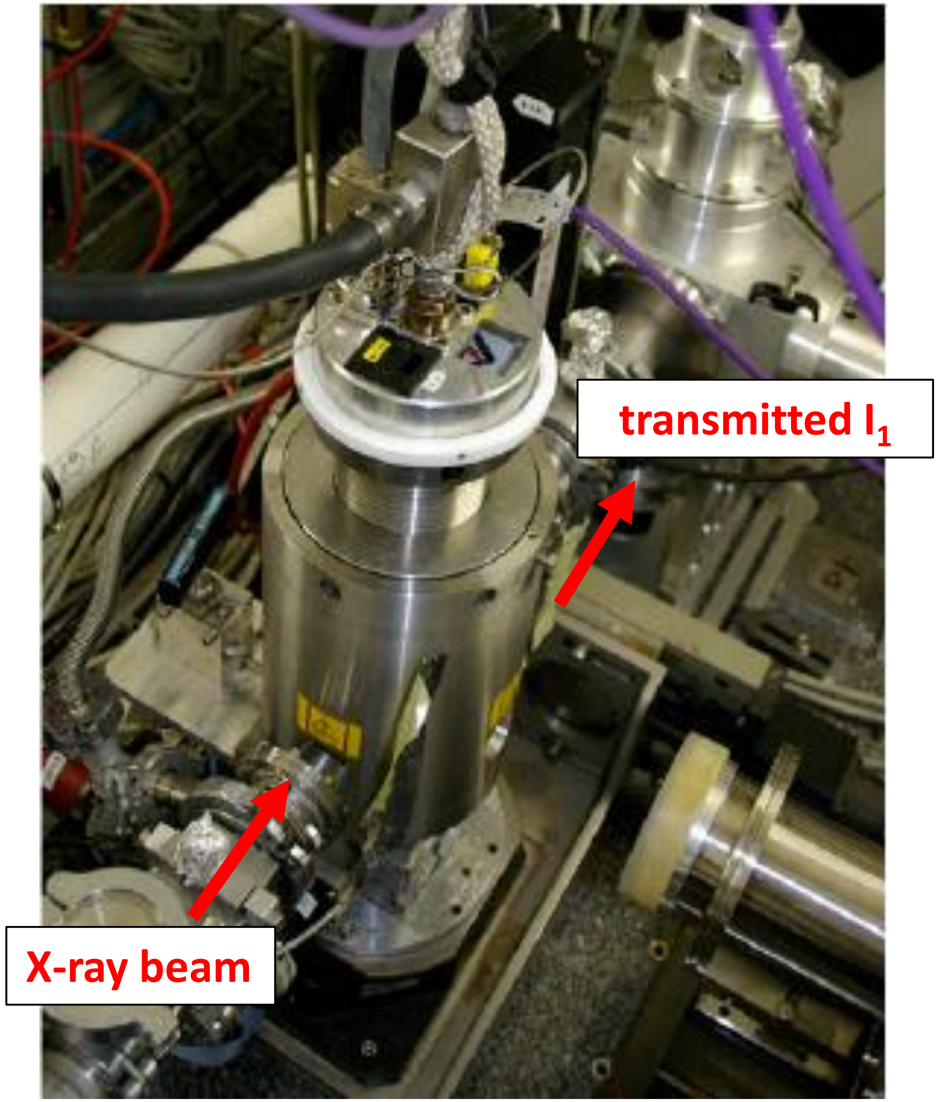
Testemale et al., 2009

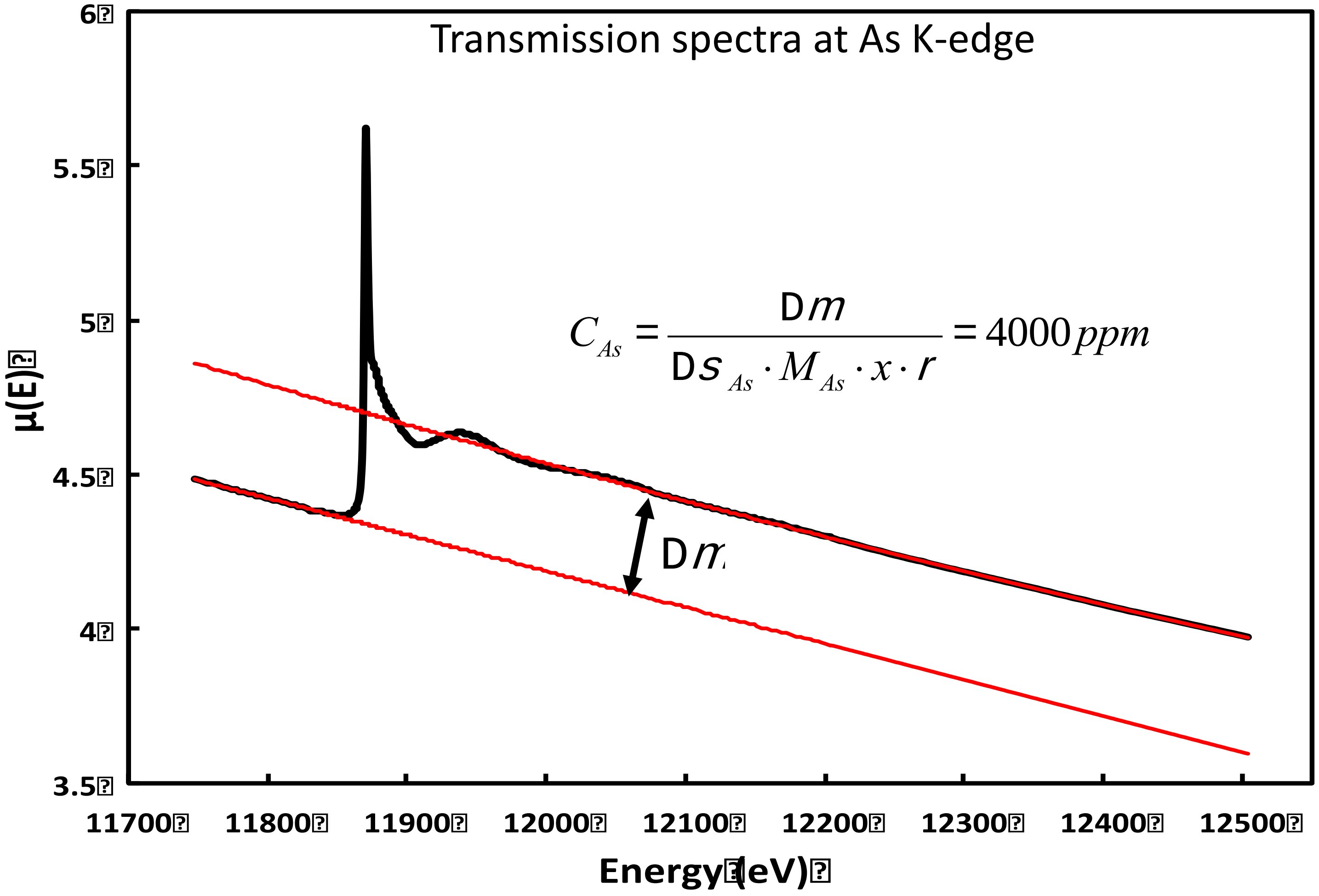


References: Pokrovski et al, 2005, 2009,2013 (Ag, Au, As, Ge) Brugger, Etschmann, Liu et al., 2008, 2011, 2013, 2016, 2018 (Cu, Au, Zn, Co, Pb, Bi, Eu); Bazarkina et al., 2010, 2014 (Cd, Pd); Dargent et al, 2013 (U); Louvel et al., 2015, 2017 (Cu, Yb); Testemale et al., 2009 (Fe)

The autoclave : Concept and set-up for *in-situ* spectroscopy

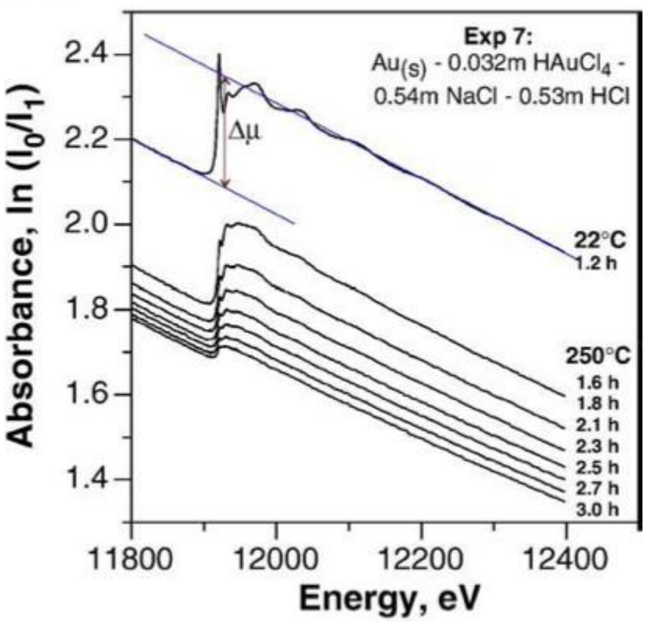
- ***in-situ*** **XAS : Solubility**



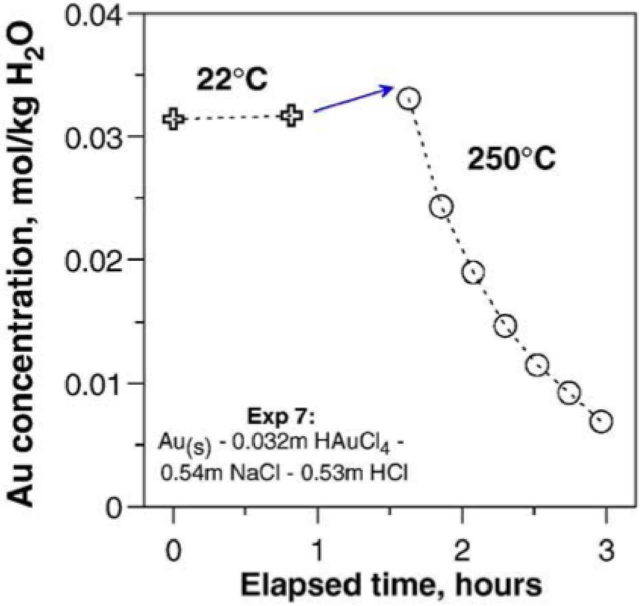


The autoclave : Concept and set-up for *in-situ* spectroscopy

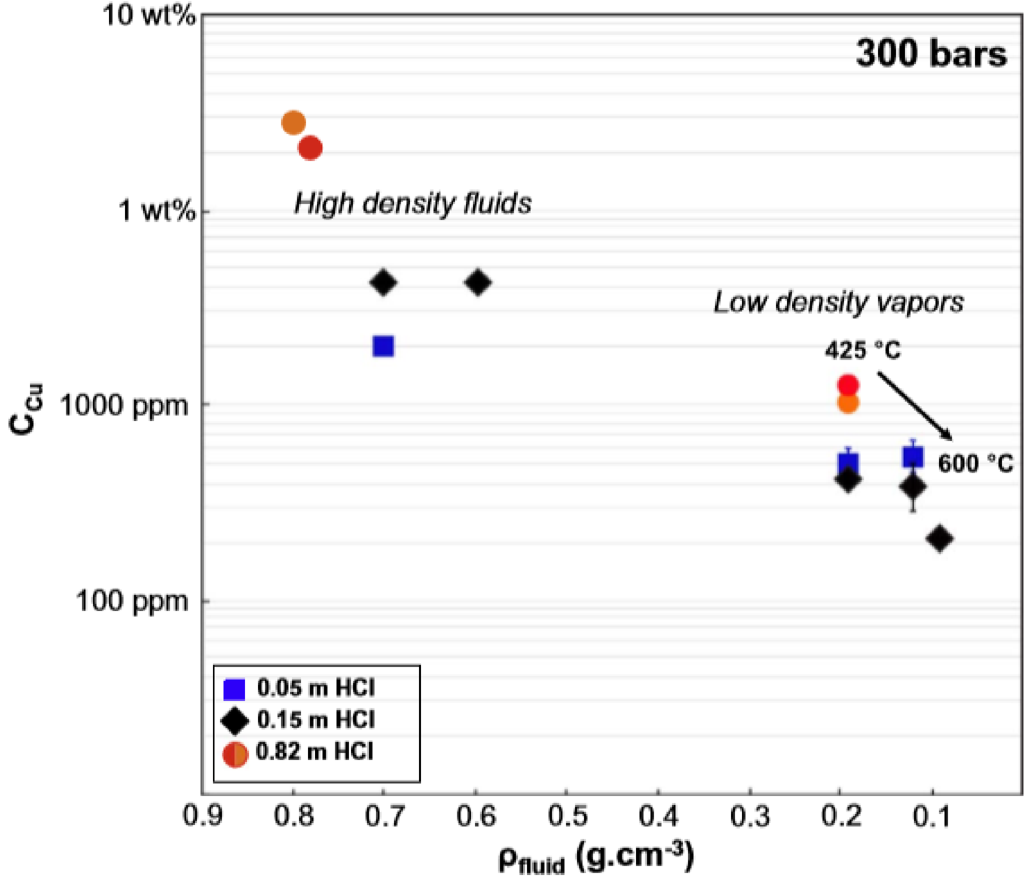
- ***in-situ* XAS : Solubility**



Au precipitation
in Au-NaCl-HCl fluids
Pokrovski et al., 2009

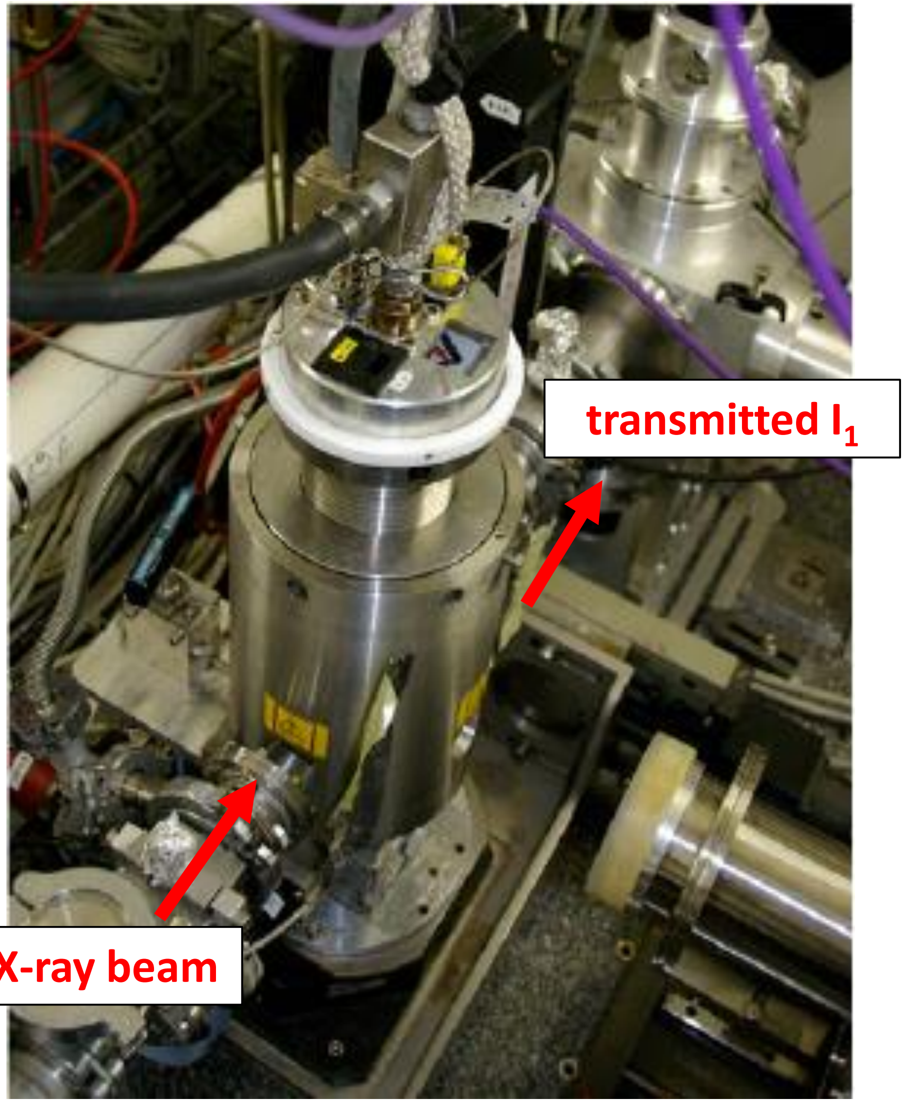


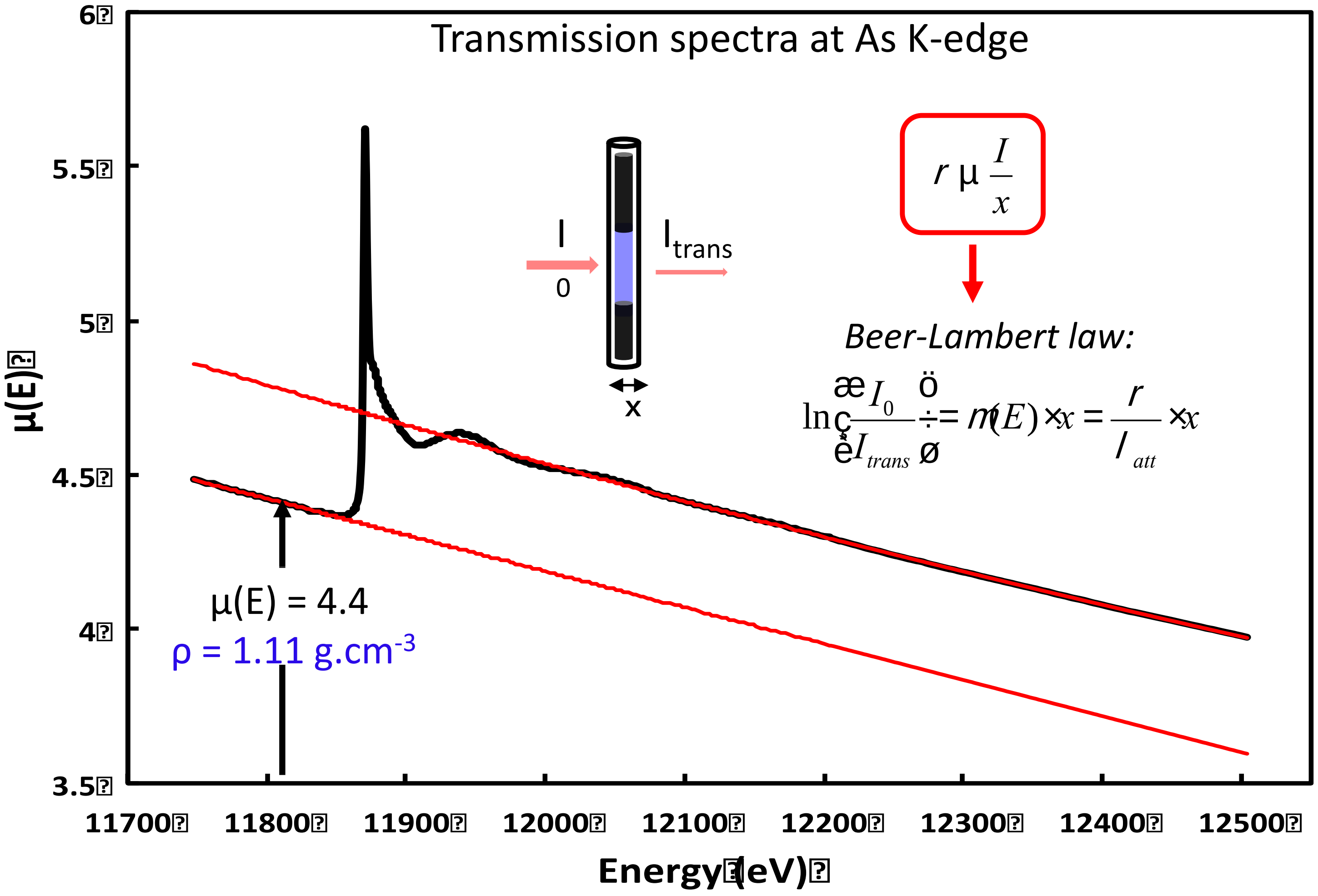
Cu solubility in HCl fluids and 'gas'
Louvel et al., 2017



The autoclave : Concept and set-up for *in-situ* spectroscopy

- ***in-situ* XAS : Density measurements**





The autoclave : Concept and set-up for *in-situ* spectroscopy

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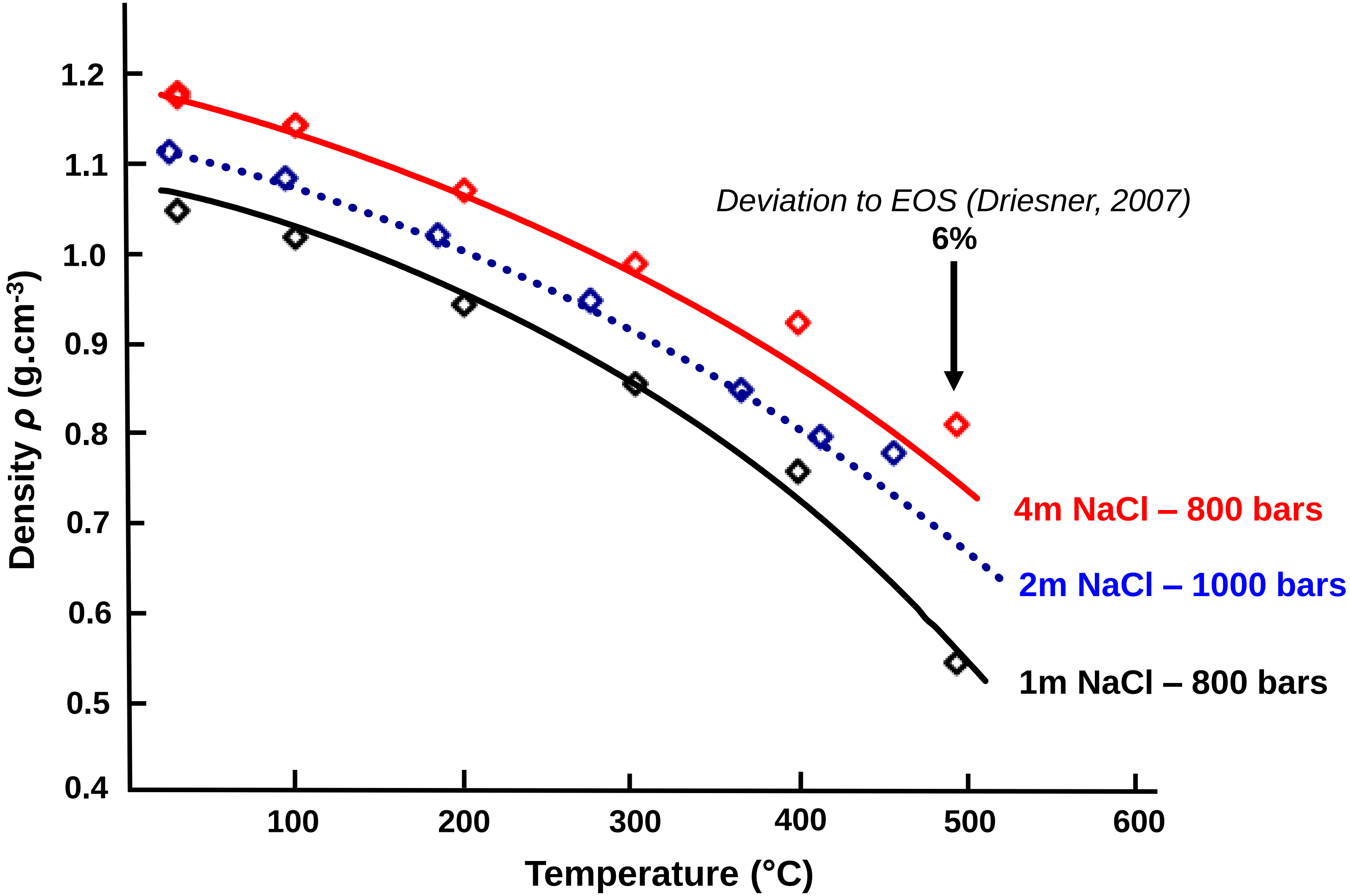
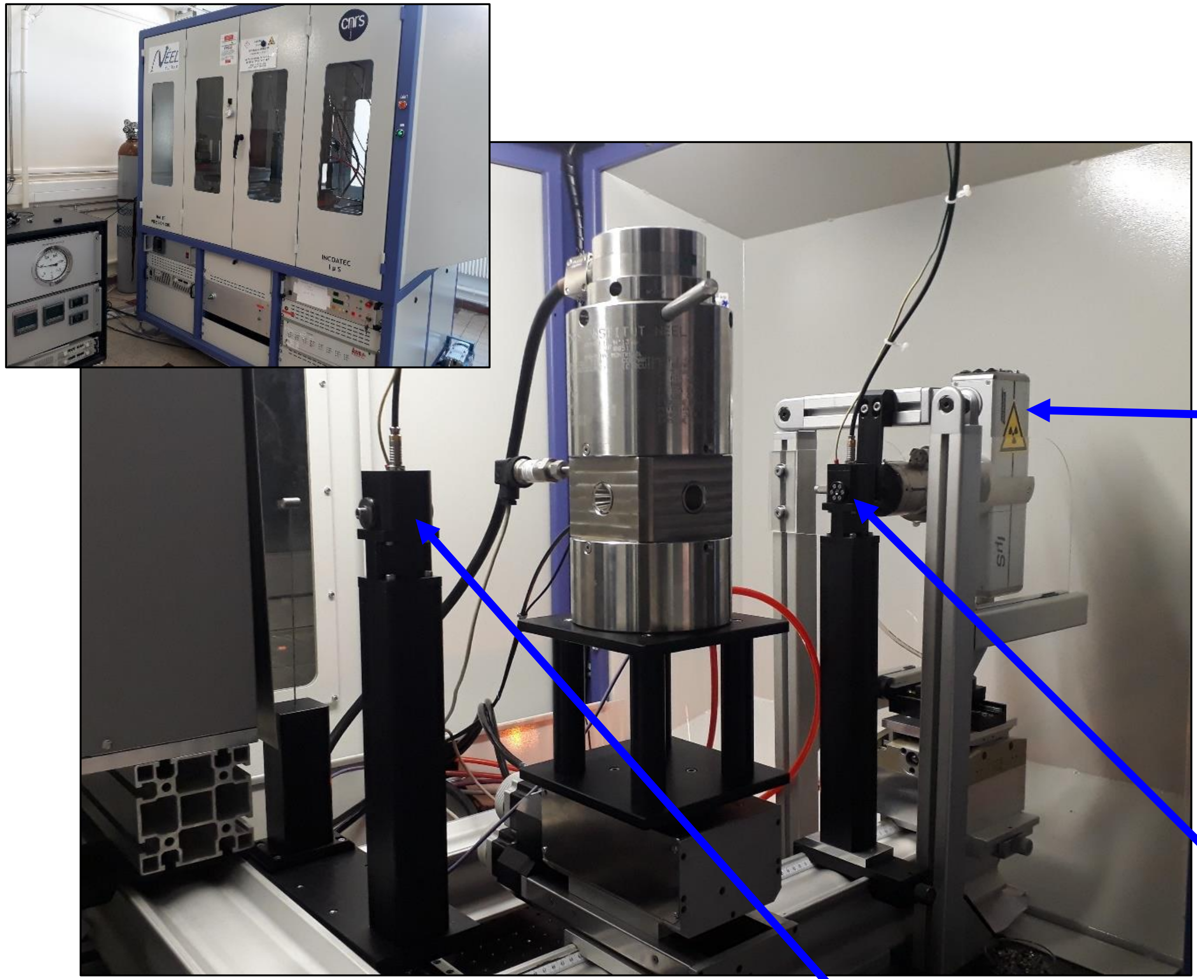


The autoclave : Concept and set-up for *in-situ* spectroscopy

- ***in-situ* XAS : Density measurements without synchrotron at Institut Néel**



RX Incoatec Ag Source
22 keV
≈ 160 µm²

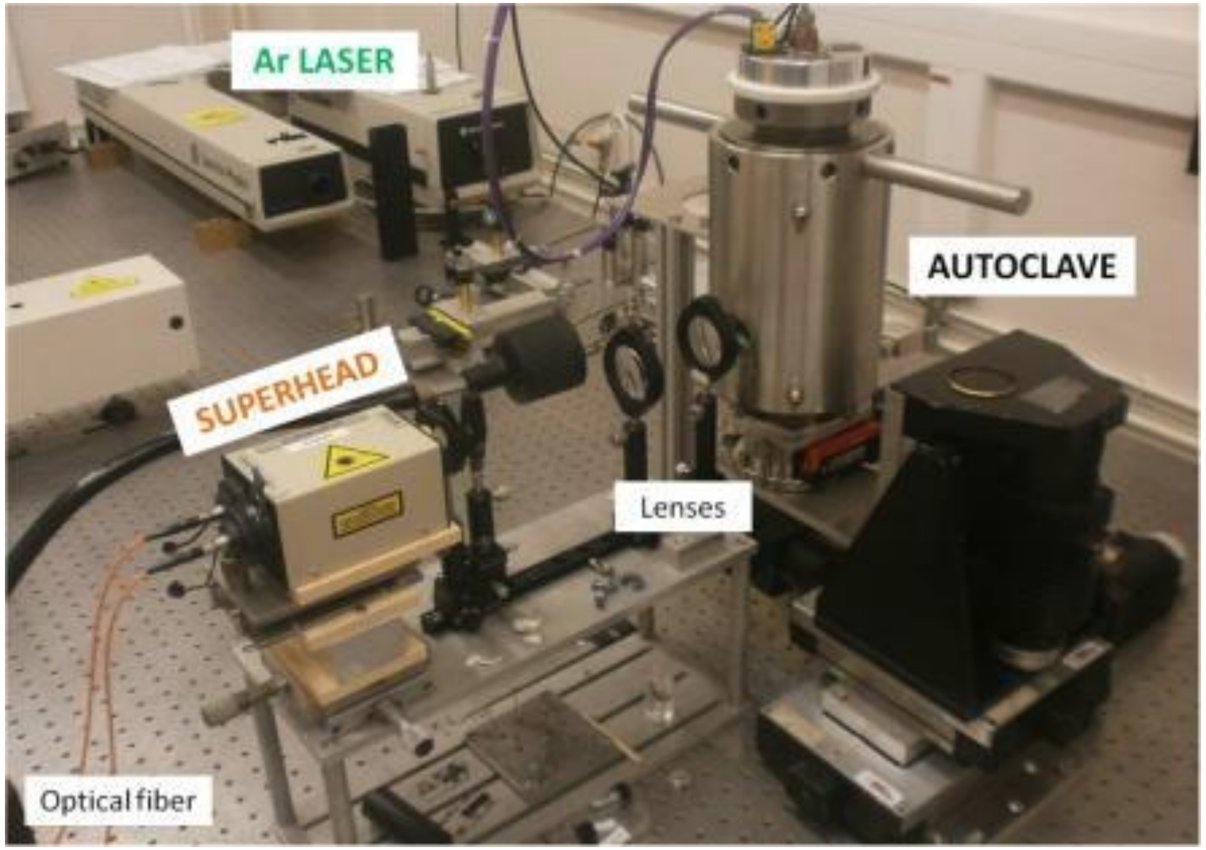
Beam I_0

Transmission I_1

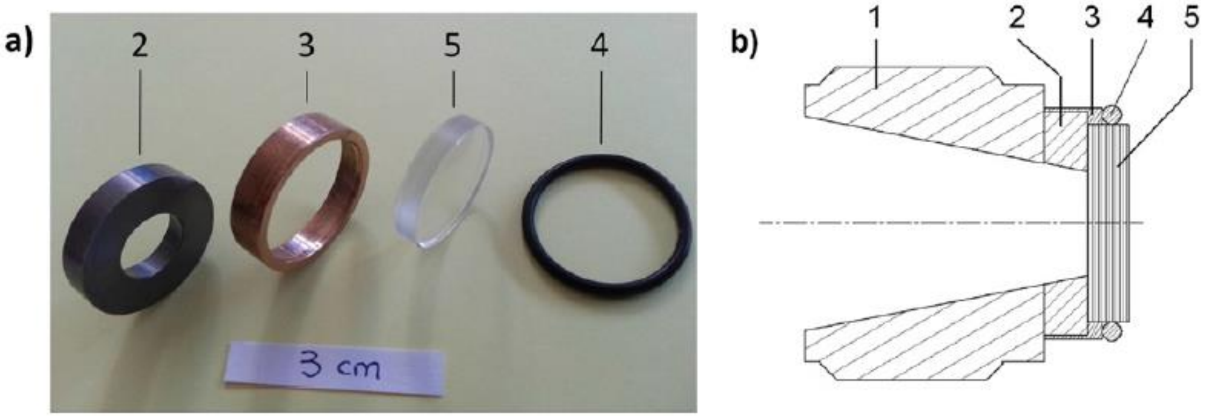
Autoclave II : in-situ Raman

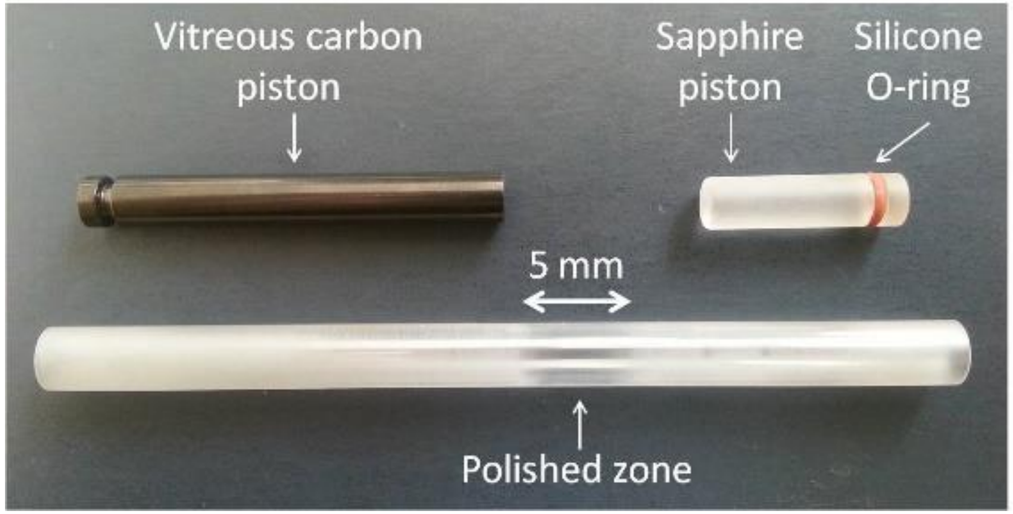
The autoclave : Concept and set-up for *in-situ* spectroscopy

➢ ***in-situ* Raman**



Sapphire windows and cells:



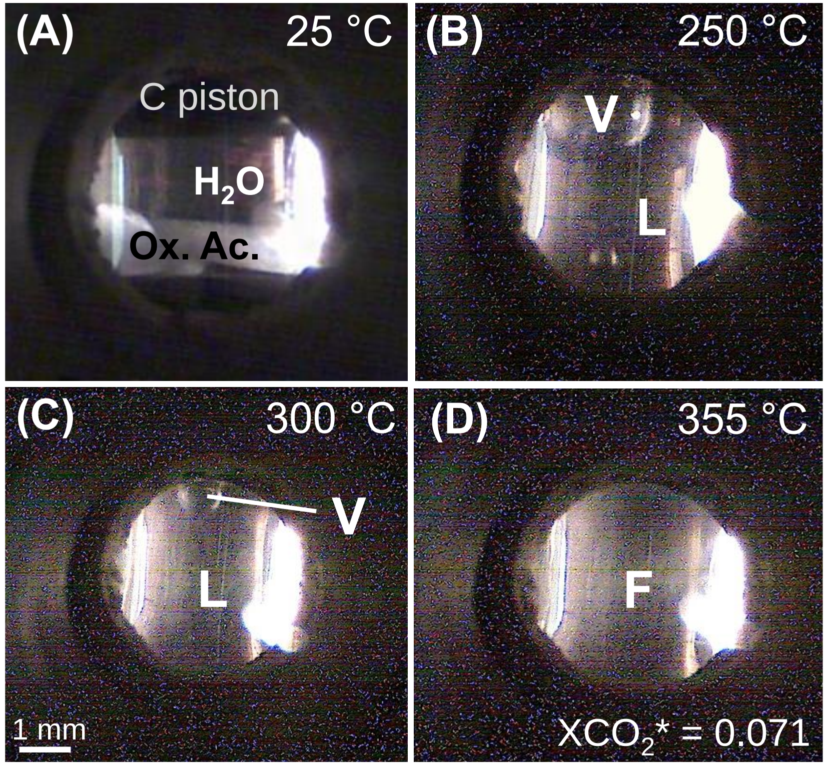


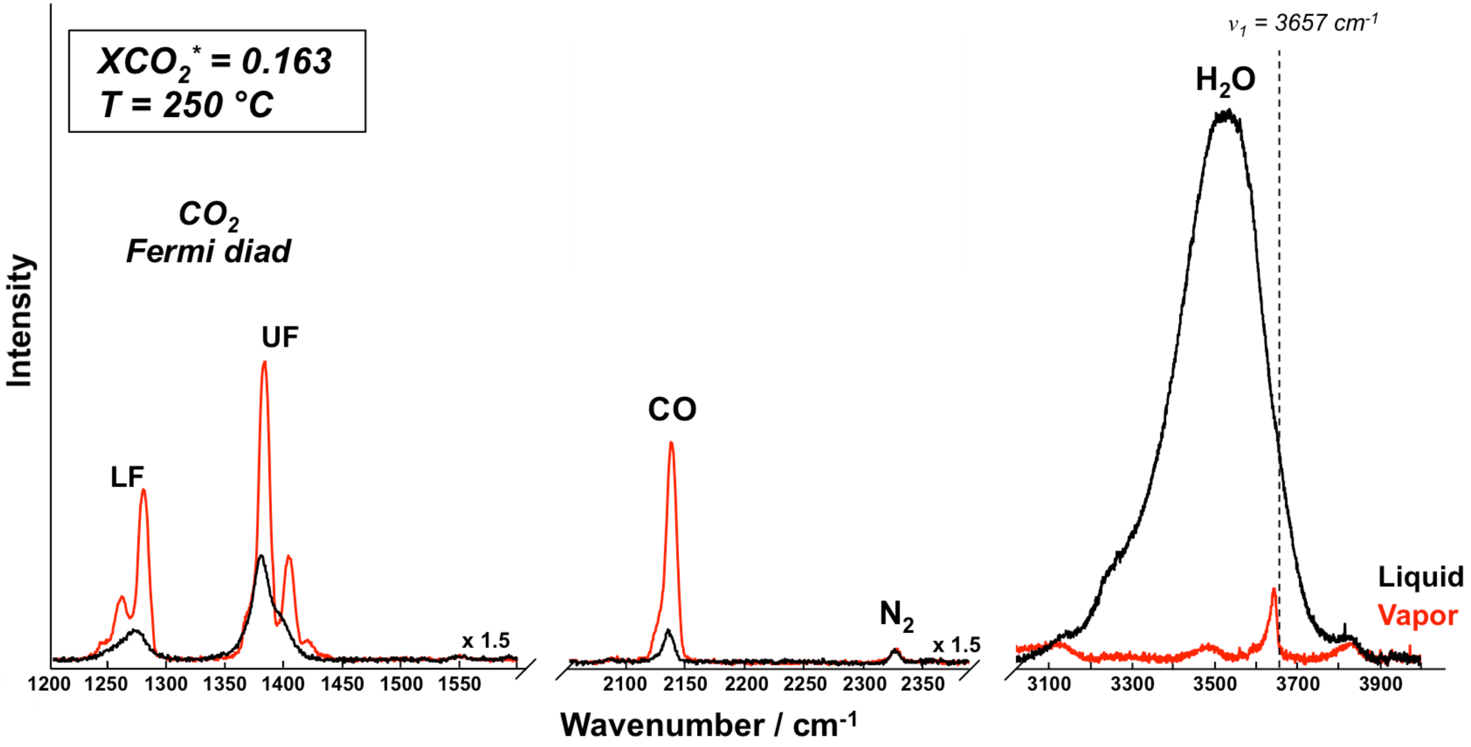
References : Louvel et al., 2015

The autoclave : Concept and set-up for *in-situ* spectroscopy

- ***in-situ* Raman**

H_2O – CO_2 (500 bars)





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Some perspectives and future developments

The autoclave : Advantages and Limitations

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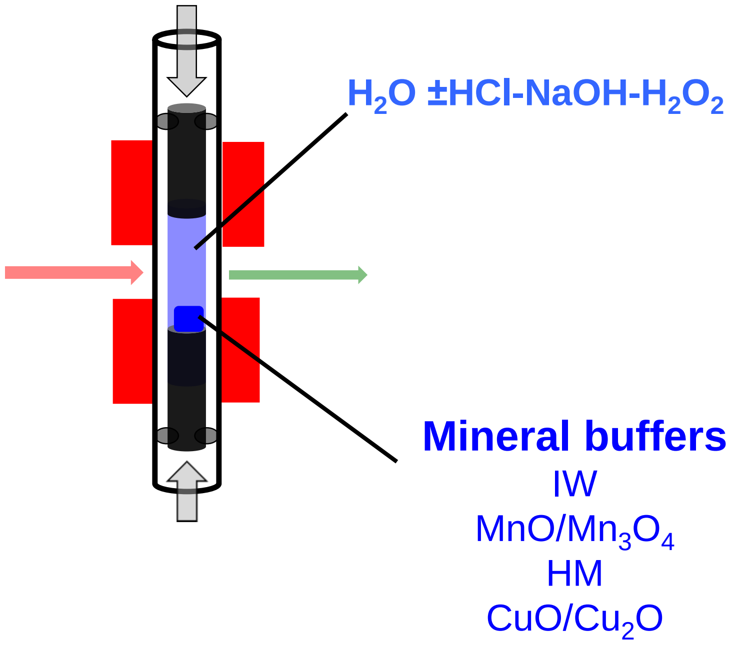

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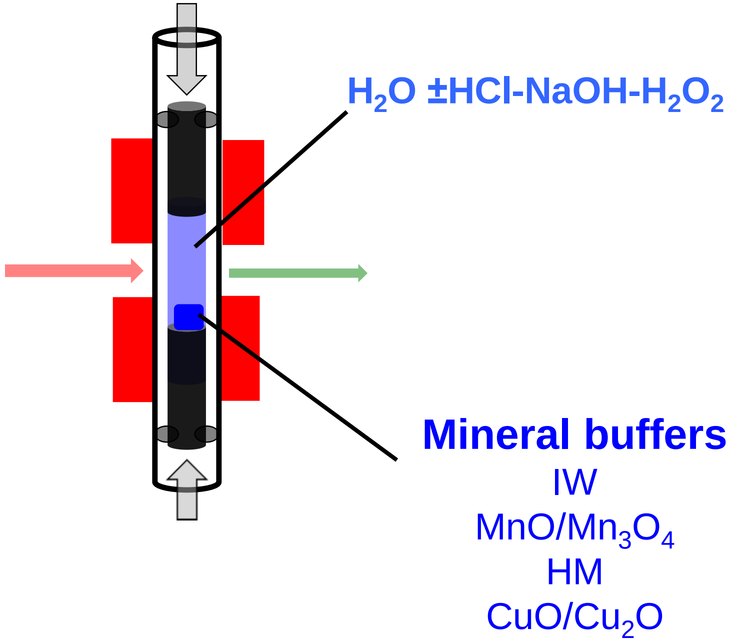
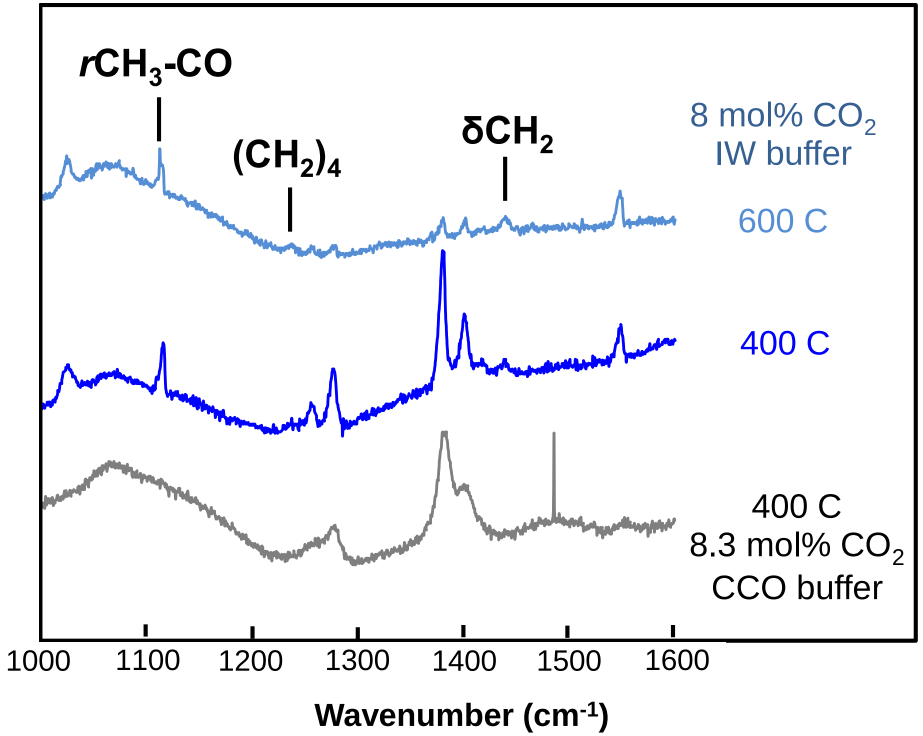


Formation of CH-CO species in H_2O-Ox.Acid mixture at the IW buffer



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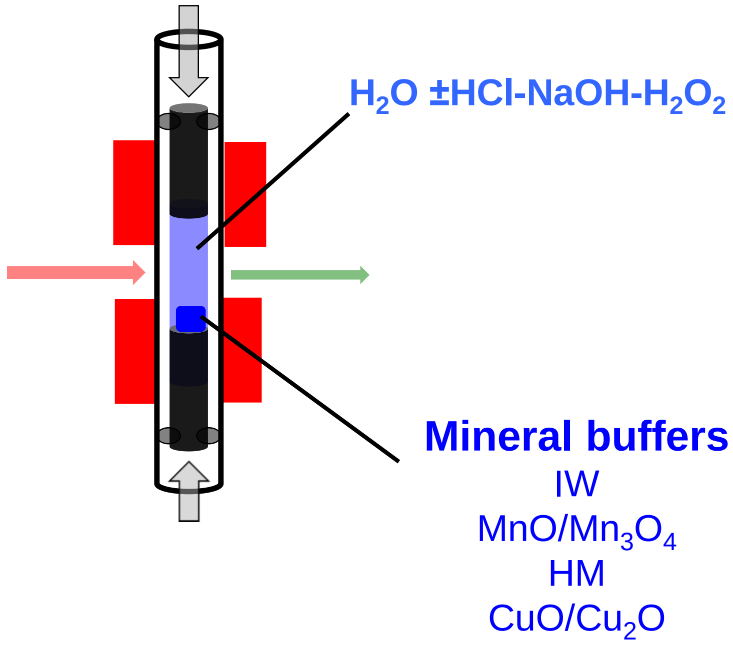
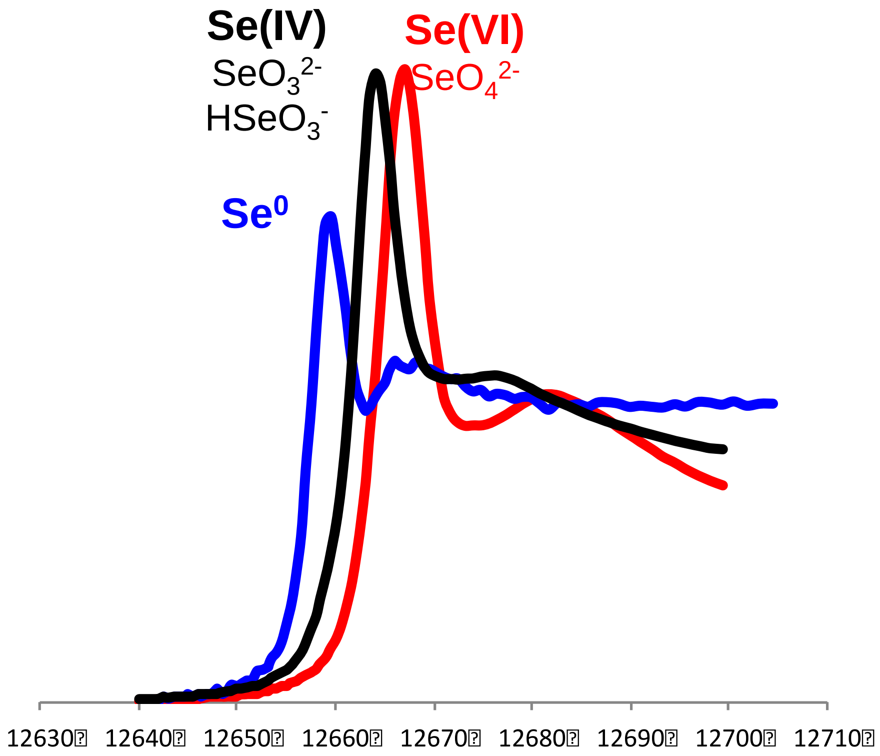


Se oxidation at CuO/Cu_2O buffer with increasing T (100-350 °C)



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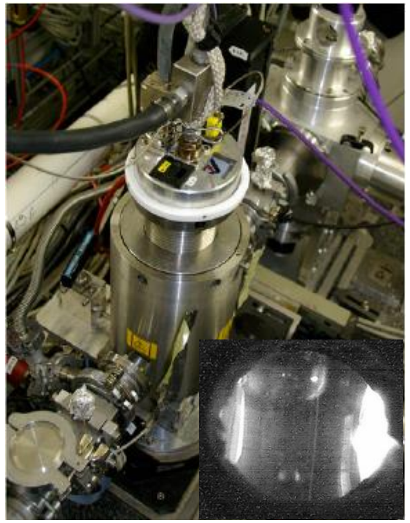
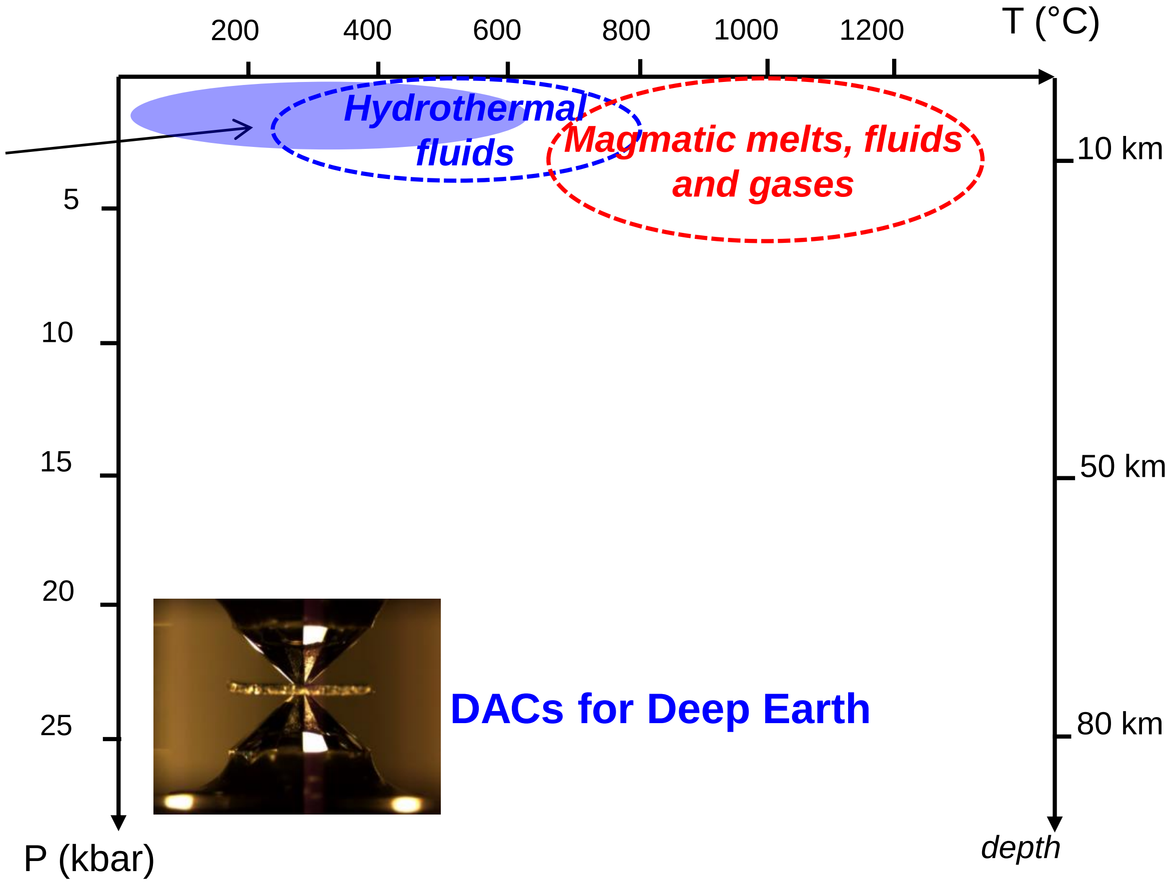




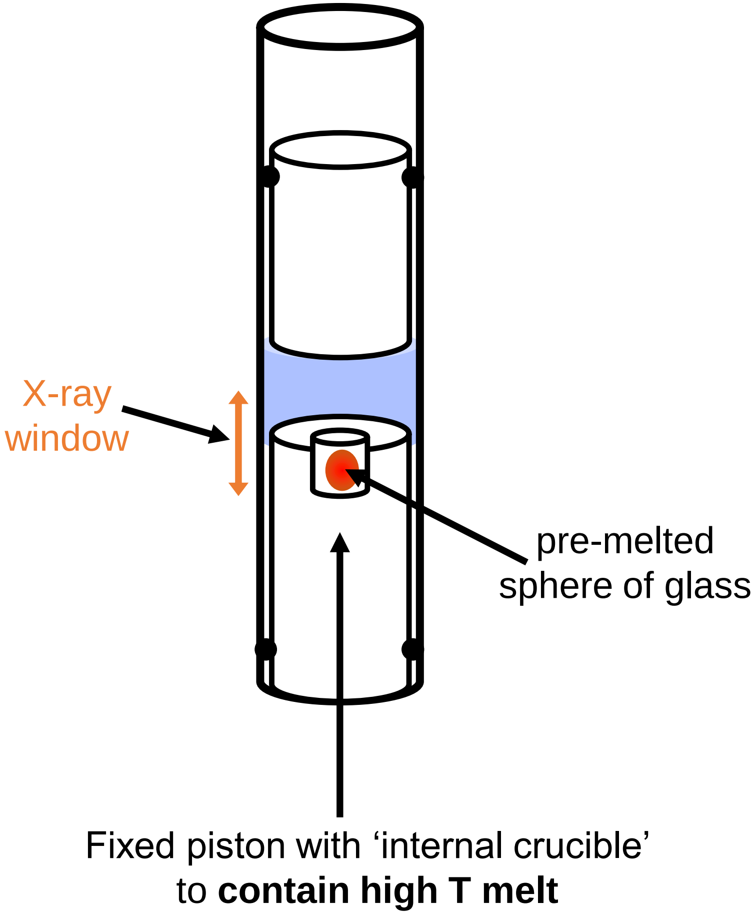
The autoclave : Advantages and Limitations

- **Detection limits**

✓ **EBS => Improved flux**
✓ **BM16 => HERFD –XAS**
Ask D.Testemale and E.Bazarkina!

The autoclave : Advantages and Limitations

- **P-T limitations** *new Autoclave that can reach 1200 °C !*



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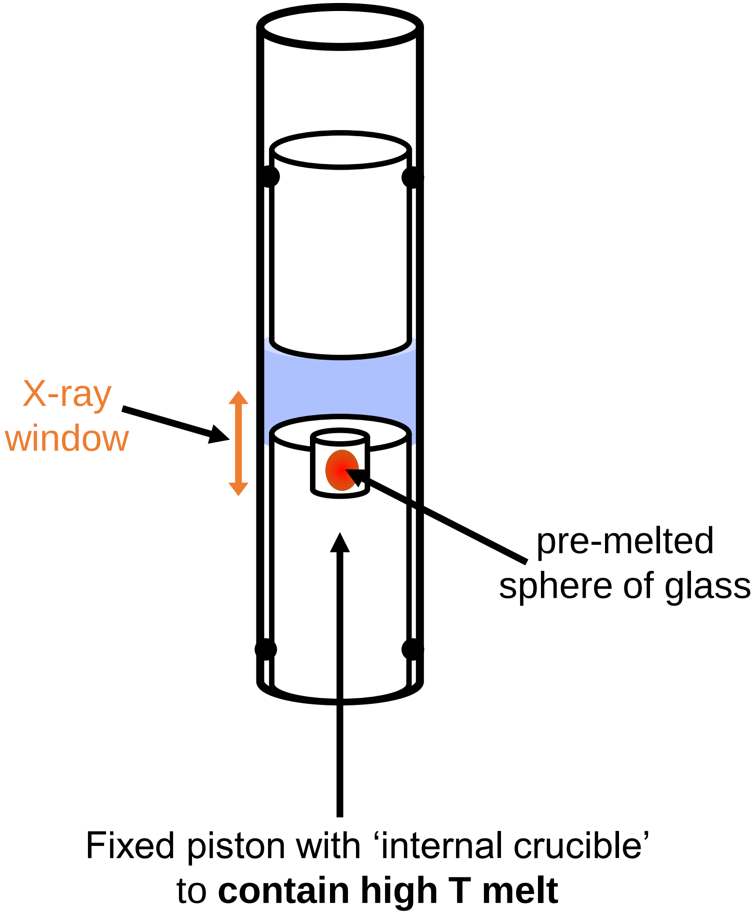

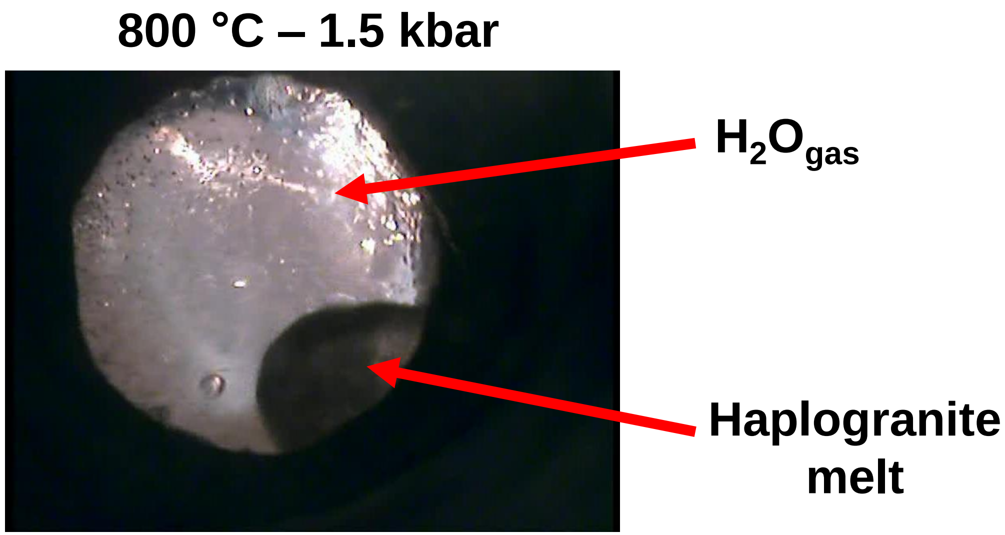

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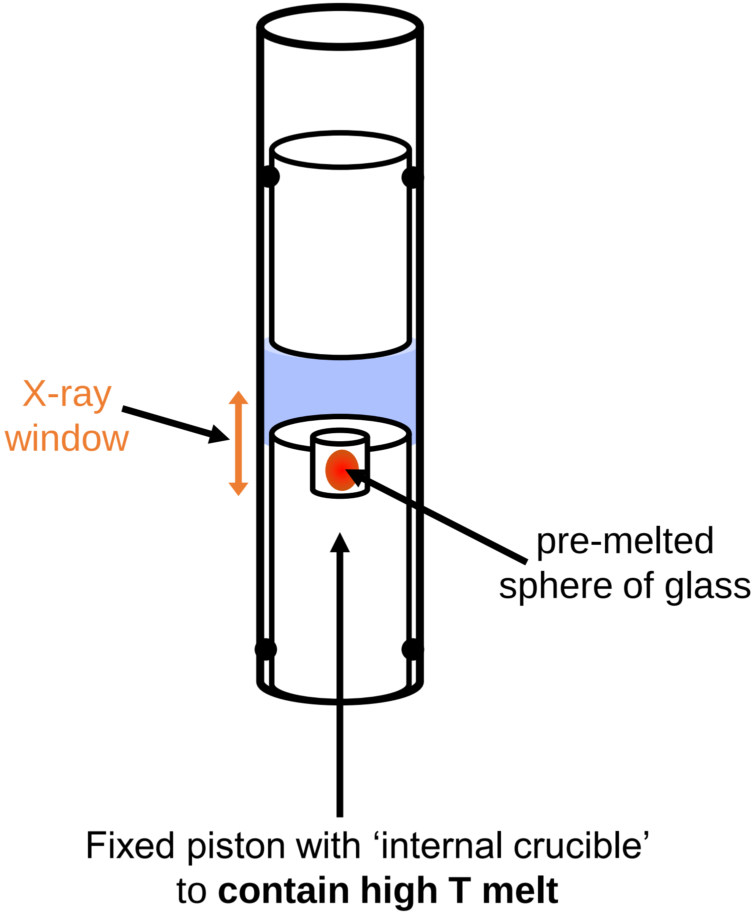

Haplogranite + NaBr sol
650 °C – 1kbar