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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⇒ Petroleum reservoirs
⇒ Geothermal energy and CO2 storage

Other (non-geological) applications:
Supercritical solvents for synthesis, extraction, etc…
Vapor-liquid, liquid-liquid equilibria

Pinatubo 1991 eruption, Indonesia
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$_2$O-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 H₂O loss (e.g. 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!

**Batch-reactor / Autoclave**

\[ T < 600 \, ^\circ\text{C} \quad \text{P} < 200 \, \text{MPa} \]

**Synthetic fluid inclusions**

\[ 600 < T < 1000 \, ^\circ\text{C} \quad \text{P} < 500 \, \text{MPa} \]

**Diamond-trap/weight loss exp.**

\[ 600 < T < 1400 \, ^\circ\text{C} \quad 0.5 < \text{P} < 6 \, \text{GPa} \]

**References:** 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*)
Challenging studies….

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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 – 0.1-2 kbar

**Si fused capillaries**

~ 500 °C - Psat

**HDAC**

900 °C – 5-30 kbar

Mineralizing fluids

CO₂ storage

Deep Earth fluids

Deep Earth fluids

P (kbar)

T (°C)

depth

10 km

50 km

80 km

10 km
In-situ spectroscopy on high T fluids

**Autoclave HT**
600 °C – 0.1-2 kbar

**Si fused capillaries**
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**HDAC**
900 °C – 5-30 kbar

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

- Visualization images:
  - Vapor
  - Brine
  - Melt
In-situ spectroscopy on high T fluids

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1. **Visualization**
   - phase separation, homogenization, melting

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

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**Increasing temperature**

REE(H₂O)₈³⁺

REECl₃(H₂O)₄
**In-situ spectroscopy on high T fluids**

**Autoclave HT**  
600 °C – 0.1-2 kbar

**Si fused capillaries**  
~ 500 °C - Psat

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

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

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

**HDAC**  
900 °C – 5-30 kbar

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**Mineralizing fluids**  
**CO₂ storage**

**Deep Earth fluids**

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**Pokrovski et al., 2011-2015**

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

- X-ray beam
- Raman
- Fluo. X-ray
- Visu

**Transm. X-ray**

- 5 cm

**Pressure ±0.4 bars**

**Temperature ±0.1 °C**

**He pressure**

**100mm sample cell**

**5mm window**

**Solution**

**Mo resistive heater**

**Mineral**

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

- **Heater**: Cu or Mo
- **X-ray beam**
- **Raman**
- **Fluo. X-ray**
- **Visu**
- **Transm. X-ray**

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

**Heater**: Cu or Mo

**X-ray beam**

**Fluo. X-ray**

**Visu**

**Transm. X-ray**

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*

![Image of autoclave setup with labeled components: X-ray beam, fluo, transmitted I₁, Canberra 30 elm detector.](image-url)
The autoclave: Concept and set-up for \textit{in-situ} spectroscopy

\textbf{\textit{in-situ} XAS}

\begin{itemize}
\item X-ray beam
\item transmitted $I_1$
\item fluo
\item Canberra 30 elmt detector
\item Be or C windows
\item Vitreous C sample container
\end{itemize}

References: Testemale et al., 2005, 2016
The autoclave: Concept and set-up for *in-situ* spectroscopy

**in-situ XAS**

- **Experimental Conditions:**
  
  Beam $\sim$ 200x100 $\mu$m HxV (FWHM)
  
  $P$ is known and $T$ calibrated to water EOS
  
  $6 < E < 25$ keV (Mn K-edge/La L$_3$-edge; Sb K-edge)
The autoclave: Concept and set-up for *in-situ* spectroscopy

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

![Diagram of X-ray setup and spectrum](image)
The autoclave: Concept and set-up for *in-situ* spectroscopy

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

![Graph showing absorption spectra and temperature increments]

- **Results**:
  - 25°C, [Cl-] 0.55 m
  - 450°C, [Cl-] 12.03 m

![Diagram showing Gd complexes at different temperatures]

**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

![Image of autoclave](image)

Transmission spectra at As K-edge

\[
C_{As} = \frac{Dm \cdot Ds \cdot As \times M_{As} \times x \cdot r}{4000 \text{ ppm}}
\]

X-ray beam

Transmitted \( I_1 \)
in-situ XAS: Solubility

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

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

0.05 m HCl
0.15 m HCl
0.82 m HCl
The autoclave: Concept and set-up for *in-situ* spectroscopy

- *in-situ* XAS: Density measurements

### Transmission spectra at As K-edge

Transmission spectra at As K-edge.

Transmission spectra at As K-edge.

Beer-Lambert law:

\[
\ln \left( \frac{I_0}{I_{\text{trans}}} \right) = -\mu(E)x \rho \]

\( \mu(E) = 4.4 \)

\( \rho = 1.11 \text{ g.cm}^{-3} \)
The autoclave: Concept and set-up for \textit{in-situ} spectroscopy

\textbf{\textit{in-situ} XAS: Density measurements}

\begin{itemize}
\item 2m NaCl – 1000 bars
\item 4m NaCl – 800 bars
\item 1m NaCl – 800 bars
\end{itemize}

Deviation to EOS (Driesner, 2007) 6%
The autoclave: Concept and set-up for *in-situ* spectroscopy

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

©Celine Goujon
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$_2$O – CO$_2$ (500 bars)

(A) C piston, H$_2$O, Ox. Ac. at 25 °C
(B) V, L at 250 °C
(C) V at 300 °C
(D) V, L at 355 °C

$X_{CO_2}^*=0.071$

$T=250 °C$

References: Louvel et al., 2015
Some perspectives and future developments
The autoclave: Advantages and Limitations

- **Pressure and temperature control** (± 1-2 bars, while it is ± 0.3-0.5 GPa for hydrothermal DAC)
The autoclave: Advantages and Limitations

- **Pressure and temperature control** (± 1-2 bars, while it is ± 0.3-0.5 GPa for hydrothermal DAC)
- **Fluid composition at high P-T** (*Raman: Volatiles speciation - CO₂, CH₄, SO₂, S₃⁻, etc...*)
The autoclave: Advantages and Limitations

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- fO₂ control

Mineral buffers:
- IW
- MnO/Mn₃O₄
- HM
- CuO/Cu₂O
The autoclave: Advantages and Limitations

- Pressure and temperature control (± 1-2 bars, while it is ± 0.3-0.5 GPa for hydrothermal DAC)
- Fluid composition at high P-T (Raman: Volatiles speciation - CO₂, CH₄, SO₂, S₃⁻, etc…)
- fO₂ control

![Diagram showing autoclave components and fluid composition](image)

Formation of CH-CO species in H₂O-Ox.Acid mixture at the IW buffer

- Mineral buffers: IW, MnO/Mn₃O₄, HM, CuO/Cu₂O
- Formation of CH-CO species in the 1000-1600 cm⁻¹ range
- δCH₂, (CH₂)₄, rCH₃-CO
- ZOOM on CH-CO species in the 1000-1600 cm⁻¹ range
- δCH₂, (CH₂)₄, rCH₃-CO
- Formation of CH-CO species in H₂O-Ox.Acid mixture at the IW buffer

- 8 mol% CO₂
- IW buffer
- 600 C
- 400 C
- 8.3 mol% CO₂
- CCO buffer
- 400 C

Wavenumber (cm⁻¹)
The autoclave: Advantages and Limitations

- **Pressure and temperature control** (± 1-2 bars, while it is ± 0.3-0.5 GPa for hydrothermal DAC)

- **Fluid composition at high P-T** (*Raman: Volatiles speciation* - \(\text{CO}_2\), \(\text{CH}_4\), \(\text{SO}_2\), \(\text{S}_3^-\), etc…)

- **\(fO_2\) control**

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

Mineral buffers
- *IW*
- *MnO/Mn_3O_4*
- *HM*
- *CuO/Cu_2O*
The autoclave: Advantages and Limitations

- **Detection limits**
  - ~10-100 ppm for quantification (solubility)
  - ~1000 ppm for ‘correct’ EXAFS
The autoclave: Advantages and Limitations

- **Detection limits**
  - \(\sim 10-100\) ppm for quantification (solubility)
  - \(\sim 1000\) ppm for ‘correct’ EXAFS

- **P-T limitations**
  - only enable moderate P-T

![Diagram showing different regions for different conditions](image)

- **DACs for Deep Earth**
  - Magmatic melts, fluids, and gases
  - Hydrothermal fluids

![Image of an autoclave](image)
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!

- Fixed piston with ‘internal crucible’ to contain high T melt
- X-ray window
- Pre-melted sphere of glass
The autoclave: Advantages and Limitations

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

![Image of autoclave with X-ray window, fixed piston, and pre-melted sphere of glass.]

- Fixed piston with 'internal crucible' to contain high T melt
- X-ray window

- 800 °C – 1.5 kbar
- H$_2$O$_{\text{gas}}$
- Haplogranite melt
The autoclave: Advantages and Limitations

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

- Fixed piston with 'internal crucible' to contain high T melt

- X-ray window

- Pre-melted sphere of glass

- Haplogranite + NaBr sol
  - 650 °C – 1kbar

- Melted globule
  - Transmission (density contrast)

- Br-rich gas

- Br-poor melt

- Fluorescence (Br concentrations)