

XAS Studies Of Metal Transport In Hydrothermal Fluids : Autoclaves And Photons.

Denis Testemale^{1,2}, Eric Lahera^{2,3}, Alain Prat^{1,2†}, Isabelle Kieffer^{2,3}, Olivier Proux^{2,3}, William Del Net^{2,3}, Gleb Pokrovski⁴, Joël Brugger⁵, François Guyot⁶, Marion Louvel⁷, Jean-Louis Hazemann^{1,2}

1- Institut Néel, CNRS, Grenoble. 2-FAME-PIX and FAME-UHD beamlines, ESRF, Grenoble. 3- OSUG, Grenoble. 4- GET, Toulouse. 5-Monash University, Melbourne, Australia. 6-MNHN, Paris. 7- ISTO, Orléans.

ABSTRACT

Hydrothermal fluids, though minor in the Earth's lithosphere (~1%), play a pivotal role in forming economic metal deposits by extracting, transporting, and precipitating metals. Central to this process is the solubility and speciation of metals and volatiles in the fluid phase [1]. In situ synchrotron X-ray Absorption Spectroscopy is the method of choice to probe metal species, offering direct insights into their molecular structure and concentration. When combined with *ex situ* hydrothermal methods (e.g., batch and flow-through systems) and thermodynamic modeling, XAS has revolutionized our understanding of metal transport by geological fluids.

A key challenge lies in performing *in situ* XAS measurements under extreme conditions. This requires high-pressure, high-temperature experimental cells capable of withstanding the chemical reactivity of hydrothermal fluids while allowing X-ray access. Among the available technologies, autoclaves stand out for their versatility and robustness [2]. In this contribution, we present XAS methods developed using high-pressure, high-temperature autoclaves at the FAME and FAME-UHD french CRG beamlines at ESRF. These methods enable *in situ* acquisition of X-ray transmission and fluorescence spectra for hydrothermal fluids and silicate melts, providing both solubility and speciation data for metal complexes. Our autoclaves operate across a broad range of conditions, from liquid- to vapor-like hydrothermal fluids (metal concentrations: <1–10,000 ppm) to magmatic fluid-melt systems at 1000°C [3]. Scientific examples highlight the advantages of our spectroscopic "micro-batch" reactors, while integration with the FAME-UHD crystal analyzer spectrometer further enhances their capabilities.

During the last 25 years the FAME and FAME-UHD beamlines have pioneered the development of specialized XAS methods based on autoclaves, enabling unprecedented *in situ* studies of metal speciation and transport in hydrothermal systems [4]. These advancements allow for the calibration of solubility constants and quantitative predictions of metal transport, bridging the gap between laboratory experiments and natural processes.

REFERENCES

1. J. Brugger et al., A review of the coordination chemistry of hydrothermal systems, or do coordination changes make ore deposits?, *Chemical Geology* **447**, 219–253 (2016).
2. D. Testemale et al., In situ X-ray absorption spectroscopy using the FAME autoclave: a window into fluid-mineral-melt interactions in the Earth's crust, *High Pressure Research* **44**, 277–293 (2024).
3. M. Louvel et al., A transparent IHPV for the in-situ geochemical characterization of magmatic volatile phases and melts, *Journal of Volcanology and Geothermal Research* **466**, 108381 (2025).
4. von der Heyden B. P. Shedding light on ore deposits: A review of synchrotron X-ray radiation use in ore geology research. *Ore Geology Reviews* **117**, 103328 (2020).