



HAL
open science

In situ X-ray absorption spectroscopy using the FAME autoclave: a window into fluid-mineral-melt interactions in the Earth's crust

Denis Testemale, G.S Pokrovski, E Lahera, A Prat, I Kieffer, W Delnet, O Proux, Marion Louvel, C Sanchez-Valle, Jean-Louis F Hazemann

► To cite this version:

Denis Testemale, G.S Pokrovski, E Lahera, A Prat, I Kieffer, 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, 2024, 44 (3), pp.277-293. 10.1080/08957959.2024.2380916 . hal-04678499

HAL Id: hal-04678499

<https://hal.science/hal-04678499v1>

Submitted on 17 Oct 2024

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



In situ X-ray absorption spectroscopy using the FAME autoclave: a window into fluid-mineral-melt interactions in the Earth's crust

D. Testemale, G. S. Pokrovski, E. Lahera, A. Prat, I. Kieffer, W. Delnet, O. Proux, M. Louvel, C. Sanchez-Valle & J. L. Hazemann

To cite this article: D. Testemale, G. S. Pokrovski, E. Lahera, A. Prat, I. Kieffer, W. Delnet, O. Proux, M. Louvel, C. Sanchez-Valle & J. L. Hazemann (2024) *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, 44:3, 277-293, DOI: [10.1080/08957959.2024.2380916](https://doi.org/10.1080/08957959.2024.2380916)

To link to this article: <https://doi.org/10.1080/08957959.2024.2380916>



Published online: 22 Jul 2024.



Submit your article to this journal [↗](#)



Article views: 30



View related articles [↗](#)



View Crossmark data [↗](#)



In situ X-ray absorption spectroscopy using the FAME autoclave: a window into fluid-mineral-melt interactions in the Earth's crust

D. Testemale^{a,b}, G. S. Pokrovski^c, E. Lahera^{b,d}, A. Prat^a, I. Kieffer^{b,d}, W. Delnet^e, O. Proux^{b,d}, M. Louvel^f, C. Sanchez-Valle^g and J. L. Hazemann^{a,b}

^aUniversité Grenoble Alpes, CNRS, Grenoble INP, Institut Néel, Grenoble, France; ^bFAME and FAME-UHD Beamlines, European Synchrotron Radiation Facility, Grenoble, France; ^cGéosciences Environnement Toulouse, Université Toulouse III, GET-CNRS-OMP-UPS-IRD-CNES, Toulouse, France; ^dObservatoire des Sciences de l'Univers de Grenoble, CNRS-Université Grenoble Alpes, Saint Martin d'Hères, France; ^eLaboratoire de Physique Subatomique et Cosmologie, Grenoble, France; ^fInstitut des Sciences de la Terre d'Orléans CNRS-UMR7327, Orléans, France; ^gInstitute of Mineralogy, University of Münster, Münster, Germany

ABSTRACT

We discuss the X-ray absorption spectroscopy (XAS) methods elaborated using the high pressure and high-temperature autoclaves installed at FAME and FAME-UHD beamlines. These methods are based on the *in situ* acquisition of X-ray transmission and fluorescence spectra of hydrothermal fluids and silicate melts and enable the derivation of both solubility and speciation information about metal complexes. The technological assets of our autoclaves are described across a wide range of experimental conditions spanning from different types of hydrothermal fluids, from liquid-like to vapor-like densities having metal concentrations of <1–10,000 ppm, to magmatic fluid-melt systems at 1000°C. Scientific examples are presented to illustrate the use and the advantages of our spectroscopic 'micro-batch' reactors. Finally, the integration of our autoclave setups on the FAME-UHD crystal analyzer spectrometer and the benefits of this technique are demonstrated.

ARTICLE HISTORY

Received 21 March 2024
Accepted 12 July 2024

KEYWORDS

X-ray absorption spectroscopy; high pressure autoclave; hydrothermal fluid; silicate melt; mineral deposit; metal speciation; metal solubility; *in situ* studies

Introduction

Although water represents only a tiny fraction of the terrestrial lithosphere (~1%), hydrothermal fluids are indispensable to the formation of economic metal concentrations in the Earth's crust. This is because it is impossible to imagine a process without a fluid phase which would allow extracting metals present in low concentrations from a large volume of rock or magma, massively transporting them through the crust, and precipitating them in a much focused fashion in the right place at the right moment to form a mineral deposit. In this complex process of ore deposit formation that yields enrichment

factors typically from 100 to 100,000 for metals compared to their abundance in common rocks, the fundamental thing to know is the solubility of ore minerals and the speciation of metals and major volatile elements such as sulfur, carbon or halogens in the fluid phase. Similar knowledge is required for the use of hydrothermal fluids in engineering applications such as geothermal energy, supercritical water as a green chemistry solvent, or hot fluids in power plants, to name a few [1].

In situ synchrotron X-ray absorption spectroscopy (XAS) is the method of choice to obtain identity, molecular structure, stoichiometry, and concentration of metal complexes with Cl-S-C-F ligands common in natural hydrothermal fluids. Combined with more routinely used *ex situ* hydrothermal methods (e.g. batch and flow-through autoclaves, synthetic fluid inclusions) and molecular and thermodynamic modeling, these approaches have enabled in the last decade unprecedented advances in our understanding of the speciation and transport of noble (Au, Ag), base (Cu, Ni, Co, Fe, Zn, Pb) and critical (e.g. Rare Earth Elements, REE, Platinum-Group Elements, PGE) metals by geological fluids [2]. These data allowed calibration of solubility constants and other thermodynamic parameters for describing the solubility of the metal-bearing minerals thereby enabling quantitative predictions of hydrothermal fluid evolution and metal transport and deposition.

Such *in situ* XAS measurements of hydrothermal samples are conducted in high pressure and high-temperature experimental cells that must both withstand the chemical reactivity of these fluids and allow X-ray access through windows. Different technologies can be used for this purpose and were reviewed recently (e.g. [1,3]), such as diamond anvil cells, fused silica glass capillary capsules, flow-through reactors and batch autoclaves. Each type conveys its own benefits and may be the tool of choice in specific conditions (such as very high pressure, low X-ray energy, highly reactive and unstable samples). The present manuscript focuses on the autoclaves developed at FAME and FAME-UHD (French Absorption beamlines for Material and Environmental sciences and Ultra-High Dilution) XAS beamlines at the ESRF [4,5].

The FAME and FAME-UHD XAS beamlines at ESRF

FAME [4] and FAME-UHD [5] are the French beamlines at the ESRF dedicated to X-ray Absorption Spectroscopy and High-Energy Resolution Fluorescence Detection XAS (HERFD-XAS), respectively. The experiments carried out at these two beamlines cover a wide variety of common applications of XAS, mainly in environmental and geochemical sciences, and also in material science, biophysics and chemistry. We aim at providing the highest possible photon flux on the sample, with a very spatially stable beam necessary to probe heterogeneous samples, combined with an efficient fluorescence detection. Both beamlines provide a sub-millimetric beam ($\sim 100 * 200 \mu\text{m}^2$ vertical * horizontal FWHM) and share a very similar optical design:

- since the ESRF EBS upgrade both beamlines use a Short Bending Magnet with 2 mrad horizontal divergence and a 0.85 T field;
- a first mirror for harmonic rejection and vertical collimation. It is a bendable Rh-coated silicon mirror cooled by water;

- a Si[220] 2-crystal monochromator. The first crystal is flat and nitrogen cooled, the second crystal is bendable for sagittal focussing and not cooled;
- a second mirror for harmonic rejection and vertical focussing. It is also a bendable Rh-coated silicon mirror, not cooled;
- several pairs of vertical and horizontal slits between optical elements;
- the experimental table that supports both the sample and the detectors follows the movement of the beam during an energy scan (monochromator is not fixed exit) with a sub-micrometric precision;
- incident and transmitted photon intensities are measured with silicon diodes that collect the scattered X-ray beam from a kapton foil.

The main differences between FAME and FAME-UHD lie in the fluorescence detection systems. FAME is equipped with a Mirion HPGe 16-element solid state detector (SSD) cooled with a CP5 cryocooler and associated with an XGLab electronics. Energy bandwidth of the SSD is around 130–250 eV, depending on the counting rate. The detection limit for XAS measurements at FAME is estimated to be ~ 10 ppm in the best case. FAME-UHD allows high resolution fluorescence detection with a 14-crystal Crystal Analyzer Spectrometer (CAS) in 1 m Rowland geometry placed in a helium box. The photons are counted by a Ketek single-element silicon drift diode (SDD) detector. Energy bandwidth of the CAS is around 1 eV. The detection limit for XAS measurements at FAME-UHD is then ~ 0.5 ppm at best.

The technology of the autoclave setup at FAME and FAME-UHD beamlines

The technological challenges raised by the development of autoclaves for *in situ* XAS measurements of hydrothermal fluids are manifold. First, the fluids are under high pressure and high-temperature which require the use of specific materials; the fluids can be chemically reactive with the sample holder; their densities should cover a wide range [0.1–1] g.cm⁻³ spanning from liquid-like to vapor-like fluids in a single experimental run during which the temperature is increased; the metal concentration relevant to natural fluids can be relatively low (a few ppm). Then, high pressure windows need to be used in the autoclave so that X-rays can reach the samples and be collected after their interaction with the sample; for XAS studies X-rays energies can be as low as 5 keV, *i.e.* energies at which the absorption of the high pressure and high-temperature (HP/HT) materials is very strong. Finally, *in situ* XAS measurements can last hours to days (to obtain sufficient data quality, reach fluid-mineral equilibrium, or study dissolution or precipitation rates), and as such they necessitate a precise and stable control of pressure and temperature.

The autoclaves installed at our beamlines [6–8] have been constantly improved in the last 20 years to enable more and more demanding experiments. They can be used routinely for aqueous solutions below 2000 bar and 600°C, but can also reach higher temperatures, up to 1200°C for specific experiments. A detailed description of their components is given elsewhere [6], a simplified diagram is shown in Figure 1. We highlight here some of their design and usage specificities and how they can impact the measurements. A selection of studies that benefited from this technique is described in the following sections.

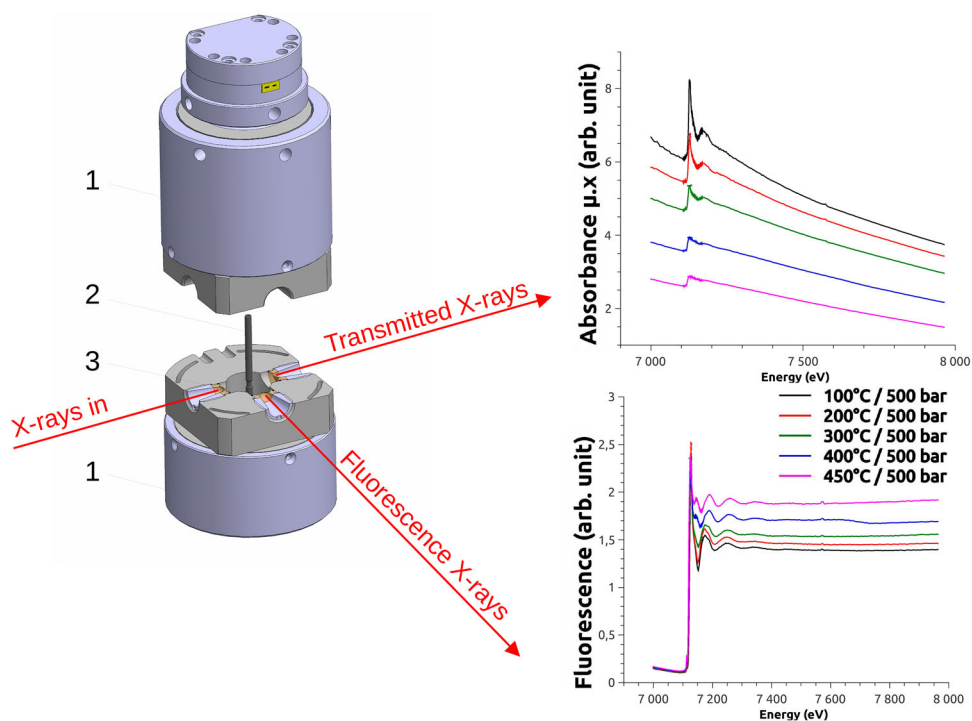


Figure 1. Left: rendering of the autoclave, with its body (1) cut in two halves at X-ray beam level. For clarity the heating elements (heater and ceramics) were removed so that the internal cell can be seen (2). The high pressure beryllium windows are also visible (3). The red arrows represent the X-ray beams: incoming, transmitted and fluorescence. Right: transmission (top) and fluorescence (bottom) spectra at the indicated T and P. The data come from [31] and correspond to an aqueous solution containing 0.045 m Fe^{2+} , 0.35 m NaCl and 0.1 m HCl (where m is the molality). Both set of spectra were measured simultaneously: the transmitted spectra are used to quantify iron concentration and the fluorescence spectra to determine iron speciation (see text for details). Note that the variation of absorption over the edge (eH, see text), in the transmission signal, decreases with temperature following the decrease of the fluid density. Adapted from [1] with permission from the International Union of Crystallography.

Internal cells made of glass-like carbon

The use of glass-like (glassy) carbon as a material for the internal cell that contains the sample opened the possibility for low X-ray energy spectroscopy (but still in the hard X-rays range, one example is the study of manganese complexation in hydrothermal fluids [9]). Glassy carbon is a low density material (density of $\sim 1.5 \text{ g.cm}^{-3}$), and as such is well transparent to X-rays. Figure 2 shows the X-ray transmission of glassy carbon, which is significantly higher at low X-ray energies compared to other typical materials used in HP research. Glassy carbon is also cheap, easy to machine, almost chemically inert, and has no significant impurities that could hinder the spectroscopic signal. The main drawback of glassy carbon in the context of hydrothermal geochemistry is its partial dissolution in aqueous solution at elevated temperatures ($>600\text{--}700^\circ\text{C}$), the degree of this reaction strongly depending on the redox conditions of the system and experimental duration.

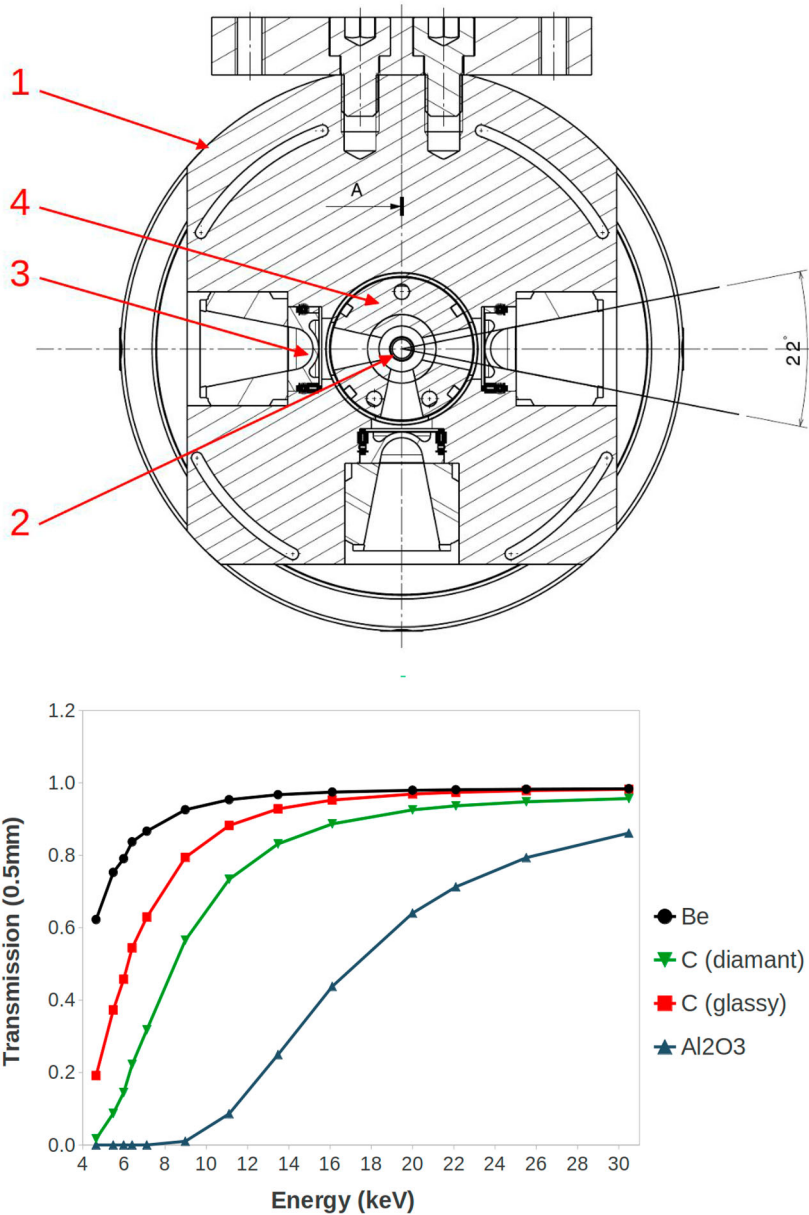


Figure 2. *Top:* Cross section view of the autoclave (see Figure 1) at the level of the X-ray beam, with labels on the body of the autoclave (1), the glassy carbon internal cell (2), three HP beryllium windows (3) and heater + ceramics (4). The angular aperture of these windows is 22°. *Bottom:* X-ray transmission of typical materials employed for HP windows and sample containers, calculated for a thickness of 0.5 mm, as a function of X-ray photon energy.

High pressure windows

The high pressure windows (see Figure 2) of the autoclave are made of beryllium to take advantage of the low X-ray absorption and high mechanical resistance of the metal. However, in the context of the study of metal solubility and speciation, high content of

other metallic impurities (Fe, Ni, Cu, Ti, Zr, Zn, Mn, Ag, Co, Pb, Mo [7]) in beryllium may add parasitic signals and thus prevent from studying fluids with low metal concentrations when these elements are present in the beryllium as impurities. For example, iron impurities inhibited solubility measurements at the iron K-edge below ~ 200 ppm Fe in the case of the study of siderite dissolution. [10] For this reason some pure glassy carbon high pressure windows, with no impurities, were built [7] and they can be used in these situations where a very low metal concentration in the fluids is expected. Figure 2 shows that glassy carbon displays higher absorbance than beryllium, albeit it remains advantageous compared to typical HP windows materials such as diamond or sapphire.

Sample volume and beam damage

The sample volume in our autoclave is large, in the range [0.05–1.00] mL. It allows us to easily load and unload the samples, such as mm-size solid phases (for dissolution experiments or pH and O₂ buffering using mineral assemblages), and to recover liquid and solid samples for *post mortem* analysis. Some examples are given below. The large sample volume also ensures that the sample/beam size ratio is large. This large ratio in the context of XAS hydrothermal measurements is essential to avoid beam damage and/or redox reactions of dissolved metals, and is a strength of autoclave experiments, as it was discussed elsewhere [1–3].

Pressure and temperature control and stability

Temperature and pressure are controlled independently in order to have the possibility to navigate across the water phase diagram over a large range of P-T. The temperature is easily and reliably regulated within 0.1°C with the use of a resistive heater and Eurotherm™ 3504 controllers. In order to ensure also a very good pressure stability over the duration of XAS measurements (at least several hours), specific high pressure valves and a regulation apparatus were developed [8]. They consist of high pressure (2000 bar) isolation valves operated by a low pressure compressed air circuit and electrovalves which are regulated by Eurotherm™ 3504 controllers. This system enables a very fine control of the pressure within ± 0.2 bar. This stability is particularly critical in the case of experiments where the sample density strongly varies with small changes of P and T, such as hydrothermal fluids in the region of the critical isochore (0.3–0.4 g.cm⁻³). As an illustration, for a measurement made at 300 bar/400°C on an aqueous sample, a variation of 0.2 bar translates to a fluid density variation of 0.001 g.cm⁻³, which is at the limit of detection on FAME beamlines. As a consequence, an oscillatory regulation of pressure with an amplitude larger than 0.2 bar would create oscillations in the XAS measurement over the acquisition time, and thus might interfere with the inherent oscillatory pattern of XAS spectra.

Versatility

As described in the original publication [6], the versatility relies on the possibility to swap the materials of the HP windows and internal cell. Two configurations are currently available: an 'X-ray configuration' that consists of beryllium windows and glassy carbon

internal cells, an 'optical configuration' that consists of sapphire windows and cells. The latter is dedicated to measurements with visible light such as Raman spectroscopy [11], visual observation [11], *in situ* photoluminescence and dynamic light scattering measurements [12,13].

The XAS methodology to derive metal solubility and speciation

In this section we will explain through scientific examples the methodology put in place by FAME and FAME-UHD users to derive solubility and speciation information from *in situ* XAS measurements conducted on hydrothermal fluids. By speciation we mean the local solvation and ligation structure around the metal ion of interest and its redox state.

The autoclave as a micro-batch reactor

The basis of our method is to combine transmission and fluorescence measurements to obtain solubility values and speciation information respectively [1]. Figure 1 is an illustration of the autoclave geometry that enables simultaneous acquisition of transmitted and fluorescence (at 90°) signals. To determine metal solubility, the abrupt variation of absorbance (the so-called edge height, eH) over the absorption edge of the transmitted XAS spectra is used, following equation (1):

$$eH = \Delta \left(\frac{\mu}{\rho} \right)_{metal} \cdot M_{metal} \cdot m_{metal} \cdot \rho \cdot x \quad (1)$$

where $\Delta \left(\frac{\mu}{\rho} \right)_{metal}$ is the difference in specific mass absorption ($\text{cm}^2 \cdot \text{g}^{-1}$) of the metal element, below and above the metal absorption edge (these values are known and tabulated), M_{metal} is the atomic mass ($\text{g} \cdot \text{mol}^{-1}$), m_{metal} is the molality of the dissolved metal ($\text{mol} \cdot \text{kg}^{-1}$), ρ is the fluid density ($\text{kg} \cdot \text{cm}^{-3}$) and x is the length of the X-ray path (cm) [14]. Note that this method is based on transmission measurements, is direct and does not require calibrations as a function of metal concentration as for most other analytical methods. In complement, it is worth mentioning that the transmitted signal can also be used to calculate the density of a sample with a high precision following equation (2):

$$\ln \left(\frac{I_0}{I_1} \right) = \mu \cdot x = \left(\frac{\mu}{\rho} \right)_{sample} \cdot \rho_{sample} \cdot x \quad (2)$$

where I_0 and I_1 are the incident and transmitted X-ray intensities, μ is the linear absorption coefficient (cm^{-1}), $\left(\frac{\mu}{\rho} \right)_{sample}$ is the specific mass absorption ($\text{cm}^2 \cdot \text{g}^{-1}$), ρ_{sample} is the sample density ($\text{g} \cdot \text{cm}^{-3}$) and x is the thickness of the sample (cm). When applied to fluids, this formula enables to determine their densities with a high accuracy ($\pm 0.001 \text{ g} \cdot \text{cm}^{-3}$). As a result, this method is applied to calibrate the temperature gradients in the autoclave between the heater and the position of the X-ray probed region: the method is based on loading pure water, calculating its density with equation (2) and comparing it to water density databases [15] to determine the temperature at the sample position. Metal concentrations down to a few mmol/L (*i.e.* ~ 100 ppm) are routinely measured with transmission measurements. Much lower concentration values are attainable using

fluorescence instead of transmission spectra. The method is less direct, however, because one needs to measure the signal from calibration solutions with known metal concentrations at similar conditions if possible (e.g. distance to the fluorescence detector, density of the solution, total fluid absorbance). Its advantage is that concentrations down to ~ 1 ppm can be quantified; some methodological details can be found elsewhere [16,17].

We describe our autoclave as a ‘micro-batch reactor’ as a reference to classical laboratory measurements where large volume batch reactors are used and fluid aliquots are sampled and analyzed *ex situ* (typically with mass spectrometry) to determine metal concentrations. These values are then exploited to establish thermodynamic models of metal complex stability and mineral solubility [14,18]. In this context, the strength of the methodology with our autoclaves is that these concentrations can be determined *in situ* and are complemented by speciation information, which is key to evaluate the relevance of such models and optimize them.

As an example, the work of Pokrovski et al. can be cited. They studied the dissolution of senarmontite (Sb_2O_3) in pure water and NaCl-HCl solutions and the nature of antimony complexes in hydrothermal fluids to 450°C and 600 bar [18,19]. Depending on the temperature, chloride concentration and pH, Sb(III) speciation is found to be dominated by $\text{Sb}(\text{OH})_3$ complexes, mixed Sb-hydroxy-chloride species, and Sb-chloride species, with increasing salinity and acidity. Also, P-T conditions of vapor-liquid separation (fluid unmixing) were investigated because this process plays a significant role in the transport of metals in the Earth’s crust. It was found that the same hydroxy-chloride species are dominant both in the brine and vapor phase, and the corresponding partition coefficient could be calculated from the determination of the respective concentrations using the absorption edge step (Figure 3 and equation [1]). Figure 3a shows that the Sb solubility determined through XAS transmission measurements is in excellent agreement with the values obtained using laboratory batch-reactor techniques and subsequent analysis of quenched fluids for Sb concentration. This agreement validates the relevance of this ‘micro-batch’ methodology for determining metal concentrations in hydrothermal fluids. The sensitivity of this method depends on several factors such as the X-ray energy, fluid density, or the presence of impurities in the autoclave materials (see the remark about beryllium above). For this reason, no general uncertainty value can be given and each experiment has its own constraints. Figure 3(b) illustrates a clear spatial separation of vapor and brine phases that enables the acquisition of spectra from both phases without interferences. At the same time, despite the lower spectral quality due to the very low density and low Sb concentration of the vapor phase ($0.17 \text{ g}\cdot\text{cm}^{-3}$), XAS can be used to derive speciation information. It can be seen that the spectra are very similar and the analysis demonstrated that the trigonal $\text{Sb}(\text{OH})_2\text{Cl}$ species is dominant and controls Sb transport in acidic saline hydrothermal fluids.

Another example is the study of the dissolution of magnetite (Fe_3O_4) in 3 molal (m) HCl solutions in the presence of SiO_2 silica (unpublished data). Although such highly acidic conditions are not geochemically relevant (m HCl < 0.1 m in most natural brines), this experiment can be considered as a proof of concept. Figure 4(a) shows the iron concentrations as a function of time at 300 bar and 100, 200 and 250°C. Compared to laboratory batch sampling experiments, these data illustrate another

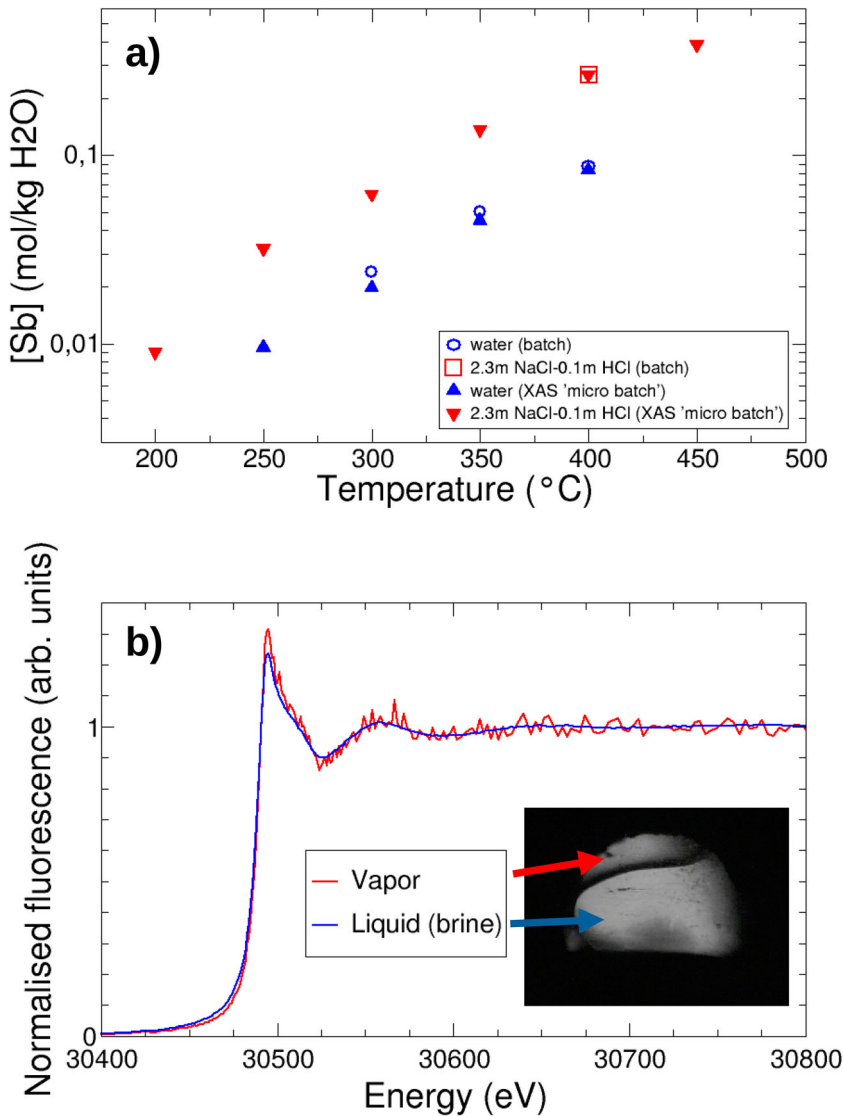


Figure 3. Figure adapted from studies of senarmonite (Sb_2O_3) dissolution in pure water and NaCl-HCl solutions at hydrothermal conditions. [18,19] (a) Antimony molal concentration measured in pure water and 2.3 m NaCl-0.1 m HCl solutions, at 600 bar as a function of temperature. The solubility data were obtained either from weight loss of the solid phase recovered from batch reactors on quench or by fluid sampling, as compared with *in situ* XAS transmission measurements. The values are in very good agreement. (b) Normalized fluorescence spectra collected *in situ* at the Sb K-edge (30,491 eV) at 271 bar and 400°C where liquid and vapor phases coexist in the reactor. The two spectra are similar and are interpreted by the $\text{Sb}(\text{OH})_2\text{Cl}$ complex of trigonal pyramidal geometry (see text). The inset picture is a view from a different experiment where a phase separation was observed in 1 m NaCl solution at 400 bar and 350°C and acquired with sapphire windows and sapphire internal cell: the purpose of this picture is to illustrate the geometry of a phase separation phenomenon in the autoclave and the two locations where the X-ray beam is focused to measure the fluorescence spectra.

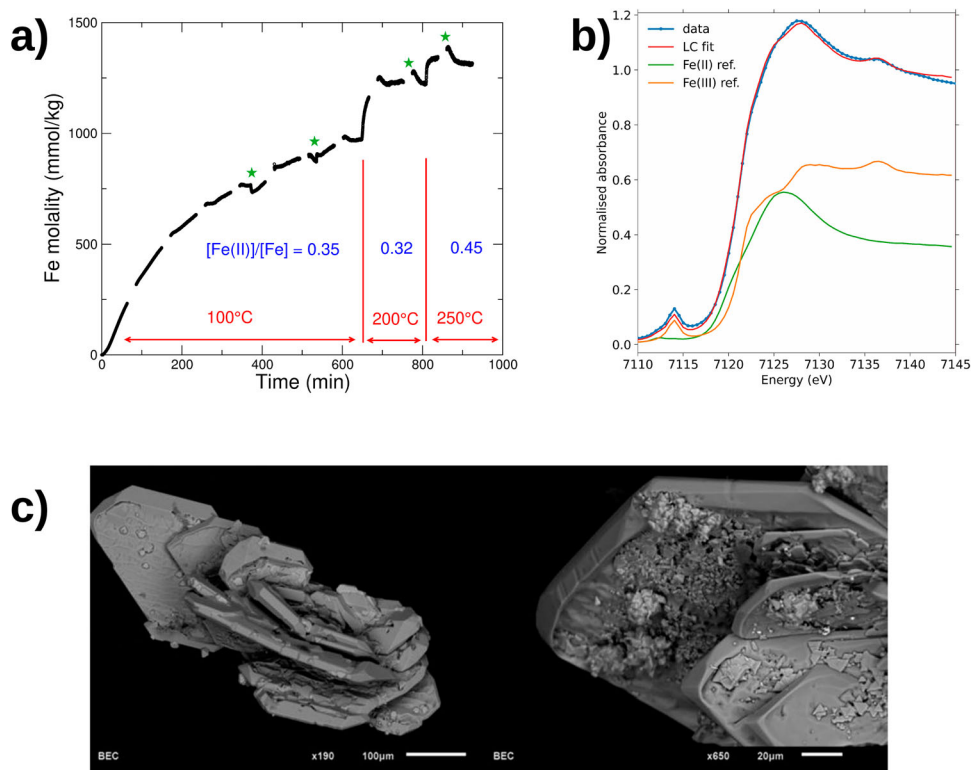


Figure 4. *In situ* XAS study of the dissolution of magnetite in quartz SiO_2 – saturated 3 m HCl, at 300 bar as a function of temperature. (a) Fe molality derived from XAS measurements is shown as a function of time. The temperature was raised to 200°C and 250°C during the experimental run. The kinks in the signal (green stars) are due to ESRF storage ring or monochromator liquid nitrogen cooling system refills. The blue numbers are the ratio of Fe(II) over total Fe concentrations, derived from linear combination (LC) fits of the fluorescence XANES spectra. (b) Fluorescence XANES spectrum acquired during the dissolution of magnetite at 250°C (blue), the corresponding LC fit (red) and relative LC contributions of the Fe(II) (green) and Fe(III) (orange) reference spectra. The reference spectra were acquired during other experimental runs where Fe(II) (and Fe(III) respectively) was dissolved in the same conditions (3 m HCl and 300 bar/250°C). See [32] for an overview of the LC method. (c) Scanning Electron Microprobe (SEM) images of recovered fragments of magnetite after the run of (a) and (b). Fayalite overgrowths are visible on the surface of mm-sized magnetite crystals, resulting from the precipitation of Fe and Si at high temperature.

advantage of *in situ* XAS measurements of metal concentration as they can be conducted as a function of time with a very fine precision allowing derivation of dissolution kinetics parameters [16]. Furthermore, in the case of the magnetite dissolution, the fluorescence spectra were used to determine *in situ* the redox ratio of iron in the solution by linear combination of spectra of Fe(II) and Fe(III) standards (Figure 4(b)). The molar concentration values of $[\text{Fe(II)}]/[\text{total Fe}]$ close to 0.33 (Figure 4(a)) are a direct demonstration that magnetite dissolution was congruent up to 200°C. Above this temperature, the solution stoichiometry changed as Fe(III) was reduced to Fe(II). This sensitivity to the dissolved metal redox state is a great asset that helps understanding the fluid-mineral interactions. The reduction of aqueous Fe(III) to Fe(II) at high temperature

is confirmed by the overgrown fayalite crystals (Fe(II)SiO_4) observed by Scanning Electron Microprobe (SEM) at the surface of magnetite recovered from the run (Figure 4 (c)). The SEM images also illustrate the large sample volume and the possibility to easily load mm-size solids. It is very useful for studies of fluid-rock interactions where *post mortem* analysis of recovered solids or fluids are important, but also for the possibility to load complex buffer mineral assemblages. This independent control of pH and $f\text{O}_2$ with mineral assemblages is essential when deriving metal speciation and thermodynamic constants of solubility reactions. Nevertheless, the exact influence of the glassy carbon sample container still needs to be investigated in details to rule out any experimental artifacts that would bias the redox interpretation.

Higher *T* and *P* for the study of hydrous melts

Recent versions of our autoclaves have been modified for better thermal behavior through the reduction of the temperature gradients and the optimization of materials for better thermal insulation. One of the ideas behind these modifications was to reach higher temperatures in order to investigate aqueous fluid-silicate melt interactions, including fluid exsolution (*i.e.* degassing) from magmas and fluid-rock interactions close to magma chambers. These processes are critical in the genesis of ore deposits as they condition the metal budget of magmatic fluids. However, natural samples prone to such studies are very scarce or do not preserve records of such phenomena. Furthermore, in terms of experimentation, quenching such high-temperature fluids might be doable but, at the very best, only enables to evaluate the bulk concentrations of species in the different coexisting phases. In most cases, the information about the nature of the complexes at high-temperature and their redox state is often lost during quenching or cooling. These limitations of *ex situ* techniques further highlight the necessity of *in situ* spectroscopic studies of such environments.

Figure 5 shows a proof-of-concept experiment to study the melting of Sr-doped hydrous haplogranite glass in 1 molal NaBr solution. The goal was to investigate, once the glass is melted above 600°C, the mechanisms of the transfer of Br and Sr between the coexisting vapor and melt phases. The elemental concentrations in the phases were measured via transmission XAS data complemented by Electron Probe Micro analysis (EPMA) of the initial glasses and recovered quenched melts, while their speciation was determined from fluorescence analysis. Pressures and temperatures up to 1300 bar and 900°C were reached during the experiment and no leak was observed over several hours. The quantitative results, *i.e.* concentrations and corresponding partition coefficient of Br between melts and fluid, and the conclusions about the speciation of Br and Sr will be detailed in a future publication. In the context of this review, this preliminary experiment shows that the methods developed for aqueous solutions can be extended to the study of fluid-melt interactions, with a geometry where both phases are clearly distinguished. The large sample volume and internal cell dimensions, combined with the possibility of easily machining glassy carbon, were an asset to shape a small crucible that held the melt (Figure 5). In terms of pressure and temperature conditions, the limit was imposed by the stability of glassy carbon in contact with an aqueous fluid at 900°C; other internal cell materials should be employed for higher temperatures.

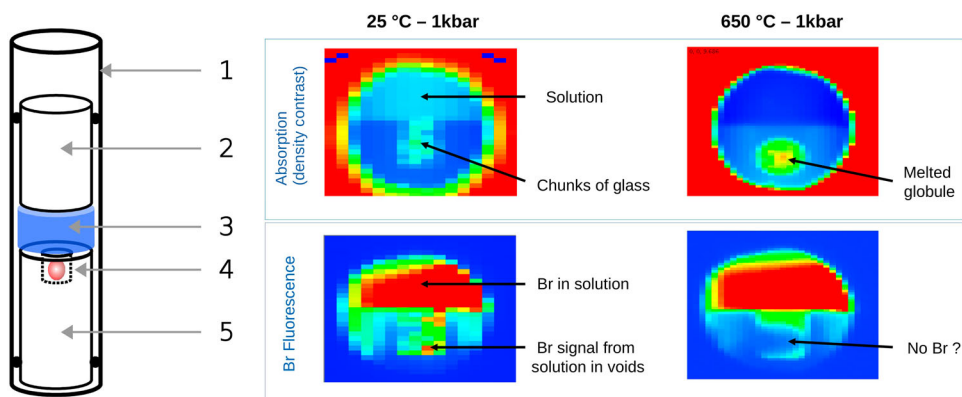


Figure 5. Graphical summary of an experiment to study Br and Sr speciation and partitioning in silicate melts and fluids. *Left:* schematic drawing of the internal cell assembly. 1: glassy carbon internal cell; 2: top piston; 3: sample NaBr-rich aqueous fluid; 4: crucible machined in the bottom piston, with a spherical chunk of haplogranite glass sample inside; 5: bottom piston. *Right:* 2D mappings of the sample at 1000 bar/250°C (left) and 1000 bar/650°C (right). The circular shape corresponds to the entrance HP window accessible to the X-rays: the top half of this shape shows the fluid, the bottom half shows the top part of the bottom piston, with the crucible fully visible. The maps are obtained by scanning the sample in the X-ray beam and by collecting either transmission signal (density contrast, top row), or Br fluorescence signal (bottom row). The color scale ranges from blue (low values) to red (high values). High absorption values (red) correspond to an area where the X-rays cannot pass through, low absorption values (blue) are where the sample and pistons are located. High fluorescence intensities (red) come from Br in solution, low fluorescence intensities (blue) correspond to areas where no Br is present or detected.

High energy resolution for a better sensitivity

FAME-UHD beamline (BM16 at ESRF) is a XAS beamline based on a spectrometer equipped with 14 analyzer crystals [5] for High Energy Resolution Fluorescence Detection (HERFD) spectroscopy. This technique is characterized by ~ 1 eV energy resolution energy and has two major benefits over classical solid-state fluorescence detection [3,5]. The first one is the removal of background radiation that sometimes saturates a solid-state detector: the signal-to-noise ratio is then largely improved, parasitic signals are erased and samples with much lower concentrations can be analyzed (below 1 ppm at FAME-UHD). The second one is the much improved spectral resolution, which provides better resolved XANES features. We installed an autoclave setup at FAME-UHD beamline to take advantage of those improvements over classical XAS (Figure 6). The objective is twofold: (i) to improve the detection limit for solubility measurements, and (ii) to use the better spectral resolution to derive more information from the XANES analysis. Indeed, *ab initio* XANES calculations, sometimes even combined with molecular dynamics (MD) simulations, are very informative to study the local solvation structures of metals in hydrothermal fluids [2] and greatly benefit from having more detailed experimental XANES spectra to be compared with. It is worth mentioning that the high pressure beryllium windows of the autoclaves were designed with the largest aperture angle possible (22°, see Figure 2) to improve the signal intensity. Thanks to this aperture 6 crystals (among the 14 available) are illuminated by the outgoing fluorescence photons.

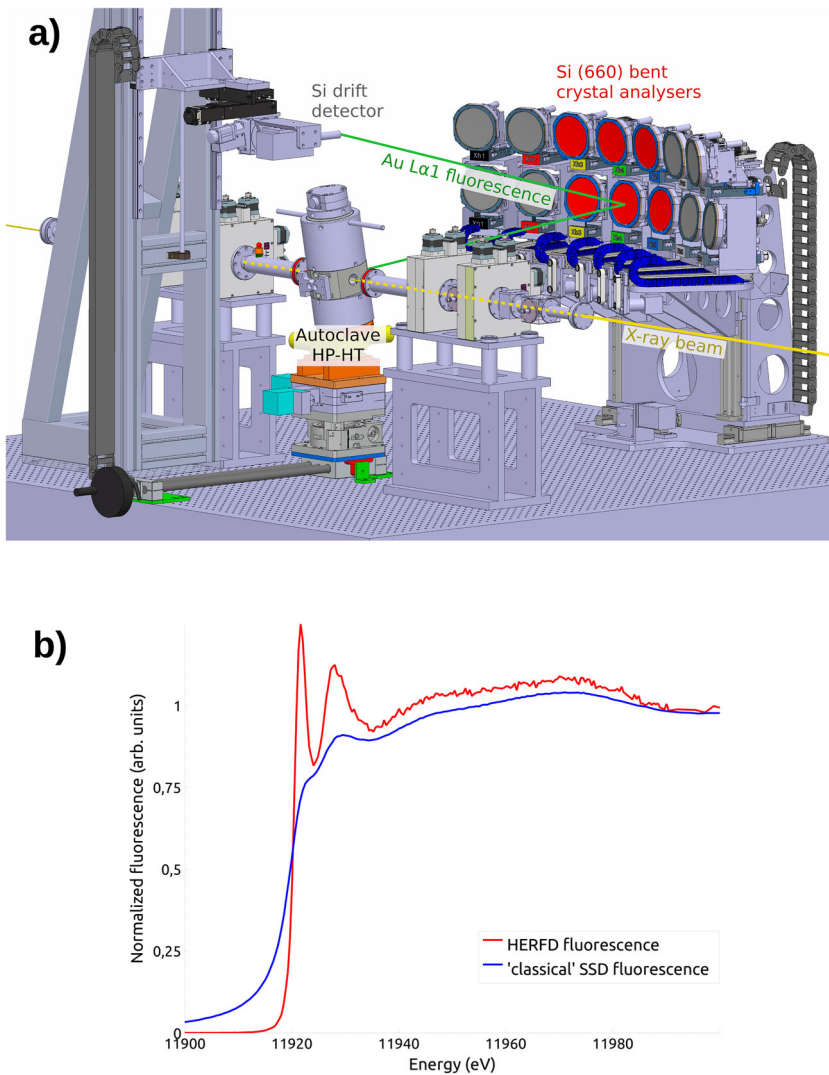


Figure 6. Gold speciation in sulfur-rich hydrothermal solutions up to 350°C and 600 bar (adapted from [20]). *Top:* HERFD-XAS setup at FAME-UHD beamline combining a high-resolution crystal analyzer spectrometer with the autoclave for *in situ* measurements of HERFD spectra. The autoclave is tilted from the vertical axis to match the required Bragg angle of the crystals to selectively probe the Au $L\alpha_1$ fluorescence line. Among the 14 crystals available, 6 are lit by the fluorescence photons, thanks to the large angular aperture of the high pressure windows of the autoclave. *Bottom:* Normalized fluorescence spectra collected *in situ* at the Au absorption L_{III} -edge (11,919 eV) at 600 bar and 350°C from an aqueous $K_2S_2O_3$ -KOH solution containing 1420 ppm of Au. The spectra were acquired either at FAME beamline with a 'classical' solid-state detector or at FAME-UHD beamline with the crystal analyzer spectrometer visible in (a). Even if the signal-to-noise ratio of the HERFD data is lower, the much better resolution of spectral features makes the XANES analysis and subsequent conclusions (*i.e.* predominance of the $Au(HS)_2^-$ species in this particular solution) much more robust.

In a recent study [20], Pokrovski et al. investigated the structure and stability of Au-bearing species in sulfur-rich solutions, at typical hydrothermal conditions of gold deposit formation (up to 350°C and 600 bar). Specifically, the objective was to understand

the role of sulfide HS^- and trisulfur S_3^- ligands in the transport of gold by hydrothermal fluids. This experiment really benefited from the improved spectral resolution of HERFD spectroscopy. Indeed, the XAS spectra in Figure 6 shows a dramatic improvement of the HERFD data compared to classical XAS data that were collected previously at FAME beamline with a solid state detector [21]. Au(I) (poly)sulfide and chloride complexes have a linear symmetry that results in quite 'featureless' XANES spectra [22], similarly to linear Cu(I) chloride and sulfide complexes [23]. In both cases, conclusions about the structure of these complexes drawn from small variations of weak XANES features have always been tentative. In contrast, in the present case, HERFD spectra contain much better resolved features, which can be interpreted far more convincingly. To do so, *ab initio* XANES calculations are conducted with the FDMNES code [24], based on MD structures for different complexes. The interplay between these three techniques (HERFD data, MD simulations and XANES calculations) enabled to clearly detect variations in the structure of Au-bearing complexes, thereby distinguishing $\text{Au}(\text{HS})_2^-$ and $\text{Au}(\text{HS})\text{S}_3^-$ whose XAS spectroscopic signals in normal resolution mode are virtually identical. Such resolution capabilities offered by the autoclave at FAME-UHD beamline are crucial for accurate thermodynamic interpretation of bulk solubility measurements.

Conclusions and perspectives

This overview illustrates with recent studies the technological and methodological developments conducted over the last 25 years in the field of hydrothermal geochemistry using *in situ* experimental approaches. They offer the possibility to collect *in situ* high-quality XAS data at hydrothermal conditions to determine metal speciation as well as mineral solubilities down to a few ppm that are essential to build robust thermodynamic models and interpret fluid-melt-rock interactions. These datasets can also be collected in very challenging experimental conditions relevant for hydrothermal metal transport: down to very low fluid densities ($\sim 0.1 \text{ g}\cdot\text{cm}^{-3}$), in the context of vapor-brine phase separation, and down to low X-ray energies (5 keV) where the more traditional high pressure materials hinder the measurements. All these autoclave tools and methods are routinely implemented at FAME and FAME-UHD beamlines, and are available for the synchrotron users community, whether it be for geochemical applications (*e.g.* as reviewed in [2,25]), or for other related scientific fields where the samples, experimental conditions and the relevance of XAS are similar (*e.g.* hydrothermal synthesis of nanoparticles [12]). Based on our pioneering design, two analogous autoclave setups have been installed at XAS beamlines worldwide: at the Australian synchrotron (Melbourne, Australia) [26,27] and at DESY (Germany) [28].

There are still a number of experimental challenges to optimize the setup and make it even more reliable. The main one is common to all *in situ* experimental cells: the necessity to control the oxygen fugacity, *i.e.* the redox environments of the sample container. Recently Cheng et al. [29] investigated the effect of rhenium gaskets of diamond anvil cells on the redox control of samples; in some cases, the effect may not be negligible and should be taken into account. In the case of the FAME autoclave, the material of the sample holder (internal cell) should always be considered. In most cases, glassy carbon does not significantly react with the fluid samples; if in doubt, mineral assemblages or mixed redox state solutions (*e.g.* sulfate and sulfide [20,21]) can be loaded to

buffer fO_2 (as well as pH). However, at temperatures higher than $\sim 600^\circ\text{C}$, carbon reaction with aqueous samples may be too strong to overcome the buffering capacities of the experimental system. Finally it is worth noting that the combination of the large volume of the sample holder in the autoclave and the low photon intensity at FAME and FAME-UHD bending magnet beamlines (as compared to insertion devices beamlines with much higher X-ray flux) are actually very favorable for the *in situ* XAS study of aqueous samples because beam-induced redox reactions are rather limited [30].

Acknowledgements

We acknowledge the European Synchrotron Radiation Facility for provision of synchrotron radiation facilities and we would like to thank the FAME and FAME-UHD staff for assistance. DT thanks François Guyot for fruitful discussions along those years.

Disclosure statement

No potential conflict of interest was reported by the author(s).

Funding

The HP/HT autoclave was financially supported by the French ‘grand emprunt’ EquipEx (PlanEx, ANR-11-EQPX-36). The FAME-UHD project is financially supported by the French ‘grand emprunt’ EquipEx (MAGNIFIX, ANR-21-ESRE-0011), the French ‘Programmes et équipements prioritaires de recherche (DIADEM), the CEA-CNRS CRG consortium and the INSU CNRS institute.

References

- [1] Testemale D, Brugger J. Cells for spectroscopy of fluids at elevated pressure and temperature. In International tables for crystallography. I: X-ray absorption spectroscopy and related techniques; 2023. doi:10.1107/S1574870722003238
- [2] Brugger J, Liu W, Etschmann B, et al. A review of the coordination chemistry of hydrothermal systems, or do coordination changes make ore deposits? Chem Geol. 2016;447:219–253. doi:10.1016/j.chemgeo.2016.10.021
- [3] Anderson AJ, Mayanovic RA. X-ray absorption spectroscopy studies in supercritical aqueous solutions. High Press Res. 2016;36:458–470. doi:10.1080/08957959.2016.1203431
- [4] Proux O, Biquard X, Lahera E, et al. FAME a new beamline for X-ray absorption investigations of very diluted systems of environmental, material and biological interests. Phys Scr. 2005; T115:970–973. doi:10.1238/Physica.Topical.115a00970
- [5] Proux O, Lahera E, Del Net W, et al. High-energy resolution fluorescence detected X-ray absorption spectroscopy: a powerful new structural tool in environmental biogeochemistry sciences. J Environ Qual. 2017;46:1146–1157. doi:10.2134/jeq2017.01.0023
- [6] Testemale D, Argoud R, Geaymond O, et al. High pressure/high temperature cell for x-ray absorption and scattering techniques. Rev Sci Instrum. 2005;76:043905. doi:10.1063/1.1884188
- [7] Testemale D, Prat A, Lahera E, et al. Novel high-pressure windows made of glass-like carbon for X-ray analysis. Rev Sci Instrum. 2016;87:075115. doi:10.1063/1.4959110
- [8] Bruyère R, Prat A, Goujon C, et al. A new pressure regulation device using high pressure isolation valves. J Phys: Conf Ser. 2008;121:122003. doi:10.1088/1742-6596/121/12/122003
- [9] Tian Y, Etschmann B, Mei Y, et al. Speciation and thermodynamic properties of manganese(II) chloride complexes in hydrothermal fluids: In situ XAS study. Geochim Cosmochim Acta. 2014;129:77–95. doi:10.1016/j.gca.2013.12.003

- [10] Testemale D, Dufaud F, Martinez I, et al. An X-ray absorption study of the dissolution of siderite at 300 bar between 50 °C and 100 °C. *Chem Geol.* 2009;259:8–16. doi:10.1016/j.chemgeo.2008.08.019
- [11] Louvel M, Bordage A, Da Silva-Cadoux C, et al. A high-pressure high-temperature setup for in situ Raman spectroscopy of supercritical fluids. *J Mol Liq.* 2015;205:54–60. doi:10.1016/j.molliq.2014.09.032
- [12] Dantelle G, Testemale D, Homeyer E, et al. A new solvothermal method for the synthesis of size-controlled YAG:Ce single-nanocrystals. *RSC Adv.* 2018;8:26857–26870. doi:10.1039/C8RA05914D
- [13] Cantarano A, Testemale D, de Sousa Nobre S, et al. Twofold advantage of gas bubbling for the advanced solvothermal preparation of efficient YAG:Ce nanophosphors. *J Mater Chem C.* 2020;8:9382–9390. doi:10.1039/D0TC02347G
- [14] Pokrovski GS, Roux J, Hazemann JL, et al. An X-ray absorption spectroscopy study of argutite solubility and aqueous Ge(IV) speciation in hydrothermal fluids to 500°C and 400 bar. *Chem Geol.* 2005;217:127–145. doi:10.1016/j.chemgeo.2005.01.006
- [15] Wagner W, Pruß A. The IAPWS formulation 1995 for the thermodynamic properties of ordinary water substance for general and scientific use. *J Phys Chem Ref Data.* 2002;31:387–535. doi:10.1063/1.1461829
- [16] Daval D, Testemale D, Recham N, et al. Fayalite (Fe₂SiO₄) dissolution kinetics determined by X-ray absorption spectroscopy. *Chem Geol.* 2010;275:161–175. doi:10.1016/j.chemgeo.2010.05.005
- [17] Laskar C, Bazarkina EF, Kokh MA, et al. Stability and structure of platinum sulfide complexes in hydrothermal fluids. *Geochim Cosmochim Acta.* 2022;336:407–422. doi:10.1016/j.gca.2022.08.015
- [18] Pokrovski GS, Borisova AY, Roux J, et al. Antimony speciation in saline hydrothermal fluids: a combined X-ray absorption fine structure spectroscopy and solubility study. *Geochim Cosmochim Acta.* 2006;70:4196–4214. doi:10.1016/j.gca.2006.06.1549
- [19] Pokrovski GS, Roux J, Hazemann J-L, et al. In situ X-ray absorption spectroscopy measurement of vapour-brine fractionation of antimony at hydrothermal conditions. *Mineral Mag.* 2008;72:667–681. doi:10.1180/minmag.2008.072.2.667
- [20] Pokrovski GS, Desmaele E, Laskar C, et al. Gold speciation in hydrothermal fluids revealed by in situ high energy resolution X-ray absorption spectroscopy. *Am Mineral.* 2022;107:369–376. doi:10.2138/am-2022-8008
- [21] Pokrovski GS, Tagirov BR, Schott J, et al. A new view on gold speciation in sulfur-bearing hydrothermal fluids from in situ X-ray absorption spectroscopy and quantum-chemical modeling. *Geochim Cosmochim Acta.* 2009;73:5406–5427. doi:10.1016/j.gca.2009.06.007
- [22] Pokrovski GS, Tagirov BR, Schott J, et al. An in situ X-ray absorption spectroscopy study of gold-chloride complexing in hydrothermal fluids. *Chem Geol.* 2009;259:17–29. doi:10.1016/j.chemgeo.2008.09.007
- [23] Etschmann BE, Liu W, Testemale D, et al. An in situ XAS study of copper(I) transport as hydro-sulfide complexes in hydrothermal solutions (25–592°C, 180–600 bar): speciation and solubility in vapor and liquid phases. *Geochim Cosmochim Acta.* 2010;74:4723–4739. doi:10.1016/j.gca.2010.05.013
- [24] Joly Y. X-ray absorption near-edge structure calculations beyond the muffin-tin approximation. *Phys Rev B [Internet].* 2001 [cited 2013 Feb 14]; 63. Available from: doi:10.1103/PhysRevB.63.125120
- [25] von der Heyden BP. Shedding light on ore deposits: a review of synchrotron X-ray radiation use in ore geology research. *Ore Geol Rev.* 2020;117:103328. doi:10.1016/j.oregeorev.2020.103328
- [26] Tian Y, Etschmann B, Liu W, et al. Speciation of nickel (II) chloride complexes in hydrothermal fluids: in situ XAS study. *Chem Geol.* 2012;334:345–363. doi:10.1016/j.chemgeo.2012.10.010
- [27] Tian Y, Brugger J, Liu W, et al. High-temperature and pressure spectroscopic cell for in situ XAS study of supercritical fluids at the Australian synchrotron. *Chemeca 2010: Engineering at the Edge*; 26–29 September 2010, Hilton Adelaide, South Australia. 2010; 3425.

- [28] Klemme S, Feldhaus M, Potapkin V, et al. A hydrothermal apparatus for x-ray absorption spectroscopy of hydrothermal fluids at DESY. *Rev Sci Instrum.* 2021;92:063903. doi:[10.1063/5.0044767](https://doi.org/10.1063/5.0044767)
- [29] Cheng N, Chou I-M, Wan Y, et al. The intrinsic effects of using rhenium gaskets in hydrothermal diamond anvil cell experiments on background fluorescence, contamination, and redox control. *Chem Geol.* 2023;632:121535. doi:[10.1016/j.chemgeo.2023.121535](https://doi.org/10.1016/j.chemgeo.2023.121535)
- [30] Picard A, Daniel I, Testemale D, et al. Monitoring microbial redox transformations of metal and metalloid elements under high pressure using in situ X-ray absorption spectroscopy: XANES on microbes under pressure. *Geobiology.* 2011;9:196–204. doi:[10.1111/j.1472-4669.2010.00270.x](https://doi.org/10.1111/j.1472-4669.2010.00270.x)
- [31] Testemale D, Brugger J, Liu W, et al. In-situ X-ray absorption study of iron(II) speciation in brines up to supercritical conditions. *Chem. Geol.* 2009;264:295–310. doi:[10.1016/j.chemgeo.2009.03.014](https://doi.org/10.1016/j.chemgeo.2009.03.014)
- [32] Berry AJ, O'Neill H, Jayasuriya KD, et al. XANES calibrations for the oxidation state of iron in a silicate glass. *Am Mineral.* 2003;88:967–977. doi:[10.2138/am-2003-0704](https://doi.org/10.2138/am-2003-0704)