

Standard Project

Experimental Report template

Proposal title: Investigation of Se melt/vapor partition and speciation by in situ XAS up to 1300 °C and 300 MPa: New constraints on chalcogenes (S, Se, Te) ancient and modern degassing		Proposal number: ES551
Beamline: BM30-B	Date(s) of experiment: from: 05/07/2017 to: 11/07/2017	Date of report: 08/09/2017
Shifts: 18	Local contact(s): Denis Testemale	Date of submission: 08/09/2017

Objective & expected results:

The initial aim of the experiments was to investigate Selenium high temperature partitioning between vapor and silicate melts to model chalcogenes (S, Se, Te) magmatic degassing. Unfortunately, the measurements required a new autoclave for *in situ* XAS measurements up to 1300 °C and 300 MPa that was not delivered in time for the experiments.

Instead, I decided to investigate the effect of pH, fO_2 and different metals (Fe, Cu, Mn) on the aqueous and gaseous speciation of Se up to 425 °C at 30 MPa. The experiments will constitute a theoretical framework for a future study of Se high-temperature partitioning between vapor and silicate melts.

Furthermore, while S/Se signature of magmatic sulfides (MS) are commonly used to assess the origin of sulfide saturation in Ni-Cu-PGE deposits (*ie.*, is S saturation due to mantellic pre-enrichment or input through crustal assimilation within the crust?), it has been suggested that the hydrothermal alteration of the MS by low-temperature ($T < 300$ °C) oxidizing fluids could significantly complicate the interpretation of the S/Se signature [1]. **Yet, little is known about the aqueous speciation of Selenium at $T > 25$ °C, and especially about the effect of pH and fO_2 .** Thermodynamic model by [2] suggests that at 300 °C reduced Se(-II) remains the dominant oxidation state of Se in aqueous fluids up to the CuO/Cu₂O buffer. Thus, hydroselenides complexes should dominate metal complexation. Our experimental results contradict those conclusions, pointing to a significant underestimation of the stability of Se(IV) species (SeO₃²⁻ or HSeO₃⁻) at high temperature.

Results and conclusions of the study:

The experiments were conducted in the high temperature autoclave dedicated to *in situ* X-Ray absorption spectroscopy of hydrothermal fluids available on the BM30-B beamline [3]. XAS spectra collected around the Se K-edge (12.6578 keV) in transmission and fluorescence modes from 25 to 425 °C at 30 MPa were

used to determine both the speciation and the solubility of Se in the high temperature fluids, using similar technique as described in [4]. The effect of increasing temperature on the speciation of a 0.1m Se solution were first investigated in pure H₂O, 0.1m HCl, 0.1m NaOH and 0.1m H₂O₂. Then, we used mineral fO_2 buffers to vary the redox conditions within the experimental load (Fe/FeO, MnO/Mn₃O₄, Fe₂O₃/Fe₃O₄ and CuO/Cu₂O – increasingly oxidizing).

All solutions have an initial speciation dominated by Se(IV). The XANES spectra have been used to fingerprint the oxidation state of Se at increasing temperature (E0 for Se0 and Se(IV) are 12658 and 12662 eV,

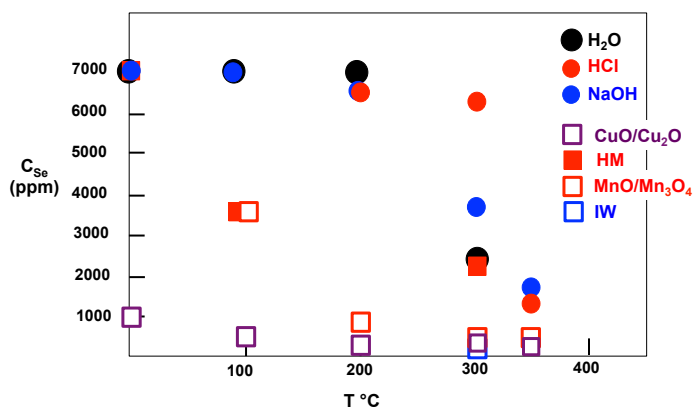


Fig. 1 : Se concentration in the high-temperature fluids with increasing temperature for different fluid compositions and mineral buffers. The Se concentration are determined from the amplitude of the absorption edge from transmitted spectra [4].

respectively). In unbuffered solutions, we observe a significant decrease of Se aqueous concentration at 300 °C (Fig. 1), which is related to the formation of Se^0 particles by reduction of the Se(IV). However, up to 1000 ppm Se is found to remain in solution as Se(IV) up to 350 °C (Fig. 2). Potential reduction of Se(IV) due to the beam was also investigated, leaving an 0.1m Se solution at 300 °C for ~ 4h with the shutter closed and then collecting a fast XANES. It appears the formation of Se^0 is solely due to temperature increase.

Under controlled redox conditions, the presence of metals buffer Se aqueous concentrations under 1000-500 ppm, probably due to adsorption of Se on the mineral buffers. Se(IV) however remains the dominant high-temperature specie from the $\text{MnO}/\text{Mn}_3\text{O}_4$ to the $\text{CuO}/\text{Cu}_2\text{O}$ buffer. At the reduced Fe/FeO buffer, only the precipitation of Se^0 is recorded. The most oxidized Se state (VI) is never observed. These results suggest that the stability field of Se(IV) can be extended to much

lower $f\text{O}_2$ conditions than predicted by previous thermodynamic model [2] and calls for revision of the thermodynamic database currently available to model metal-selenides precipitation.

Additionally, XAS spectra have been acquired in low-density ‘gas-like’ phase at 425 °C and 30 MPa ($\rho_{\text{H}_2\text{O}} = 0.188 \text{ g.cm}^{-3}$). At these conditions, the concentrations of Se in the gas were below our detection limit in transmission, $\ll 100$ ppm. Yet, XANES spectra collected in fluorescence mode (90 ° geometry) suggest that H_2Se is the dominant gaseous specie at all investigated conditions, except under the most oxidized conditions ($\text{CuO}/\text{Cu}_2\text{O}$ buffer) where Se is present as SeO_2 .

EXAFS analysis is currently being conducted to refine the aqueous structure at each P-T-X conditions.

Justification and comments about the use of beam time:

The BM30-B beamline provides a unique environment for the *in situ* study of aqueous fluids at the P-T relevant to the hydrothermal precipitation of economic minerals/metals in shallow crustal environments ($200 < T < 600$ °C and $P < 200$ MPa). *Those data will constitute an important database for new experiments that aim at determining the high temperature speciation and partitioning of Se between vapor and silicate melts and model chalcogenes (S,Se,Te) magmatic degassing (follow-up proposal to be submitted in September 2017).*

Publication(s):

[1] Prichard et al., 2013. *Miner. Deposita* 48, 767-786. [2] Akinfiyev and Tagirov, 2006. *Geol. Ore Deposits* 48, 402-413. [3] Testemale, D. et al., 2005. *Reviews of Scientific Instruments* 76, 043905-1-5. [4] Louvel, M. et al., 2015. *Chemical Geology* 417, 228-237.

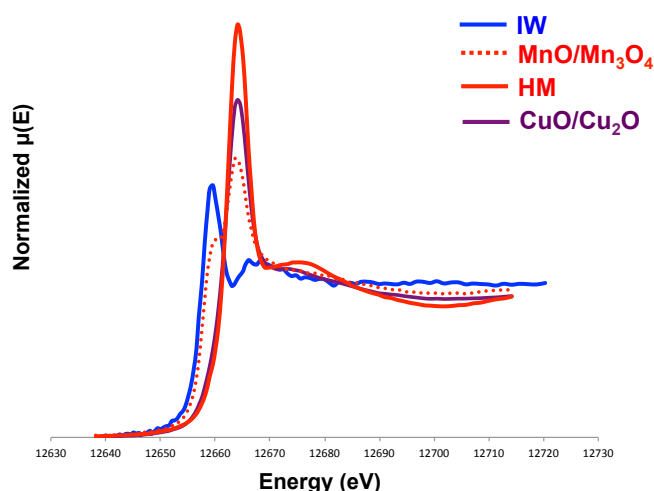


Fig. 2 : XANES spectra collected at 300 °C at the Fe/FeO (IW), $\text{MnO}/\text{Mn}_3\text{O}_4$, $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$ (HM) and $\text{CuO}/\text{Cu}_2\text{O}$ buffers. The low energy shoulder on the $\text{MnO}/\text{Mn}_3\text{O}_4$ spectrum is attributed to Se^0 particles ‘floating’ in the solution.