

Experimental Report template

Proposal title: Investigation of Se melt/vapor partitioning 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: 30-02-1115
Beamline: BM30-B	Date(s) of experiment: from: 26/10/2016 to: 01/11/2016	Date of report: 30/01/2017
Shifts: 18	Local contact(s): Denis Testemale	Date of submission: 30/01/2017

Objective & expected results:

The initial aim of the experiments was to investigate Se high temperature partitioning between vapor and silicate melts to model chalcogenes (S,Se,Te) magmatic degassing. Unfortunately, the experiments 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.

Consequently, I decided to resume previous work that aims at providing new constraints on the role of hydrothermal fluids in the formation of rare metals mineralization in large igneous provinces (*e.g.*, Bayan Obo, China/Thor Lake, Canada) by **studying the HFSE and REE high temperature aqueous chemistry using *in situ* XAS**. This study started in October 2014 and has seen my collaborators and me investigating the aqueous solubility and speciation of Sm, Eu, Gd, Er and Yb up to 500 °C and 80 MPa over 5x18 shifts of beamtime on the BM-30B beamline (*Experimental Reports* 30-02-1089; 30-02-1096; 30-02-1102). A full understanding of the compositional controls on the hydrothermal mobilization and concentration of REE in rare metals ore deposits yet needed to study the role of fluid's pH and complexation to S in the development of light (La to Eu) to heavy (Gd to Lu) REE fractionation reported in some mineralizing environments. Therefore, we have now determined the solubility and speciation of Nd in fluids containing Cl, carbonates or sulfates and of different pH (<1 to ~12) from 200 to 500 °C at 80 MPa.

Results and conclusions of the study:

The experiments were conducted from 200 to 500 °C at 80 MPa around the Nd L_{III}-edge (6.208 keV) in the high temperature autoclave dedicated to *in situ* X-Ray absorption spectroscopy of hydrothermal fluids available on the BM30-B beamline [1]. This is the lowest energy ever reached for *in situ* XAS measurements in the autoclave on BM-30B. The XAS spectra collected in fluorescence modes were used to determine both the speciation and the solubility of Nd in the high temperature fluids. Generally, we use the XAS spectra collected in transmission to determine the concentration of elements in the solution, *ie.*, the solubility of REE [2], but complete absorption of the X-ray beam by the aqueous solutions prevented their collection. Instead, the fluorescence signal was calibrated with solutions of 200, 1000 and 2000 ppm of Nd in H₂O and 0.5m HCl for solubility measurements.

Nd oxides and phosphates solubility and speciation was investigated over different

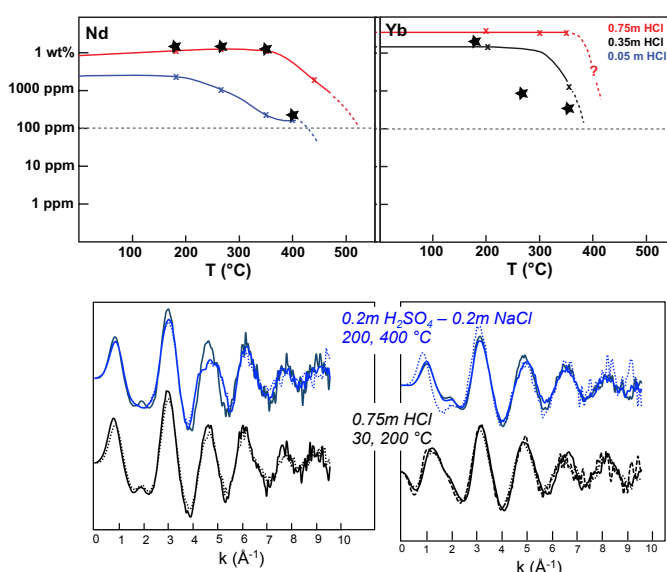


Fig. 1 : *On top* - Nd versus Yb oxides solubility in HCl (solid lines) and S-bearing solutions (stars). *Below* - k^2 -weighted EXAFS oscillations collected in 0.75m HCl and H₂SO₄-NaCl solutions from 30 to 400 °C and 80 MPa showing the change of Nd speciation with temperature increase from 200 to 400 °C in H₂SO₄-NaCl.

compositions with $2 < \text{pH} < 12$ including 0.05-0.75 m HCl, 0.2m H₃PO₄, 0.5 m NaHCO₃, mixed H₂SO₄-NaCl and mixed NaOH-NaCl solutions.

In Cl-rich fluids, the experimental results suggest that Nd oxides and phosphates are more soluble than Gd, Er or Yb compounds over similar P-T-X range. The experiments further show that Nd forms chloride complexes with 2-3 Cl atoms from 200 °C onwards in solutions with 0.05 to 0.75m HCl, confirming the higher stability of LREE- over HREE-Cl complexes in high-temperature fluids (same for Sm, as seen in Experimental Report 30-02-1102). These complexes are expected to account for the more efficient mobilization of LREE by Cl-rich fluids in magmatic-hydrothermal environments.

The same appears true for H₂SO₄-NaCl solution, where the solubility of Nd significantly exceeds that of Yb, at least up to 400 °C (Fig.1.). Besides, comparison of the EXAFS oscillations for these compositions suggest a significant change of speciation upon temperature increase for Nd, which is not observed for Yb. EXAFS analysis is currently underway, but we expect this different complex to involve sulfur atoms. Hence, these observations could be the first experimental ones supporting thermodynamic calculations that suggested an increased stability of sulfate over chloride complexes with increasing temperature [3]. Finally, as for the other REEs, Nd solubility is extremely low (at least $< 20\text{-}50$ ppm according to our calibration) in phosphoric acid, pure H₂O and alkaline solutions, which confirms the significant role of pH increase and P leaching in the rare earth ore precipitation [2, 3].

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). The present study confirms and complements previous measurements at the Sm, Eu, Gd, Er and Yb L_{III}-edges. In particular, the EXAFS analysis demonstrated that each REE might form different complexes in the same fluid compositions, which confirms the critical inputs of the *in situ* approach to provide new insights on the REE aqueous chemistry and the potential effect of fluid composition on the formation of rare metals ore deposits. In the next months, the entire dataset on Nd, Sm, Eu, Gd, Er and Yb will be summarized in two manuscripts: one describing in detail REE-Cl complexation in high-temperature fluids and the second one focusing on the compositional controls on the solubility of the different rare earth. Over-all, this dataset is expected to facilitate future modeling of REEs aqueous transport and deposition in mineralizing environments.

Publication(s):

[1] Testemale, D. et al., 2005. Reviews of Scientific Instruments 76, 043905-1-5. [2] Louvel, M. et al., 2015. Chemical Geology 417, 228-237. [3] Migdisov, A.A et al., 2016. Chemical Geology 439, 13-42.