

Standard Project

Experimental Report template

Proposal title: Solubility and speciation of Niobium in high temperature fluids: Implications for the formation of rare metals ore deposits and HFSE fractionation in subduction zones		Proposal number: 20150033
Beamline: BM30-B	Date(s) of experiment: from: 23/09/2015 to: 29/09/2015	Date of report: 21/12/2015
Shifts: 18	Local contact(s): Jean-Louis Hazemann	Date of submission: 21/12/2015

Objective & expected results:

The increasing need of the green energy and high technology sectors for rare metals (REE are HFSE) requires a better understanding of the processes favoring the formation and controlling the grade of rare metal ore deposits. The main aim of our experiments is to provide 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**. While the proposal originally aimed at the study of a HFSE (Nb), we decided to investigate a REE so as to complement previous *in situ* XAS experiments investigating Yb and Gd solubility and speciation up to 500 °C (*Experimental Reports 20140566 and 20141167*). Therefore, we have now determined the solubility and speciation of Er in fluids containing Cl, carbonates or alkalis and silicates and of different pH (<1 to ~12) from 200 to 500 °C at 80 MPa. The experimental results confirm that heavy rare earth (HREE: Dy to Lu) may only be transported in low amounts in Cl-rich fluids, which provides an explanation for the preferential LREE enrichment observed in most magmatic-hydrothermal deposits (e.g., Bayan Obo, China), but also call for further investigation of HREE uptake by particular fluids to explain HREE enrichments reported in distinct environments (e.g., Strange Lake, Canada).

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 [1]. XAS spectra collected around the Er L_{III}-edge (8.358 keV) in transmission and fluorescence modes from 200 to 500 °C at 80 MPa were used to determine both the speciation and the solubility of Er in the high temperature fluids, using similar technique as described in [2].

The effect of Cl concentrations and fluid's pH on Er₂O₃ solubility were first investigated in the 0.05-0.75m HCl and 0.1 < pH < 1.3 range. The experimental data confirm the strong decrease of (M,H)REE solubility above 300-350 °C that was previously reported for Yb and Gd (Fig. 1). The most common view regarding the role of hydrothermal (re)mobilization of REE in the development of economic concentrations is that the mineralizing fluids are Cl-rich

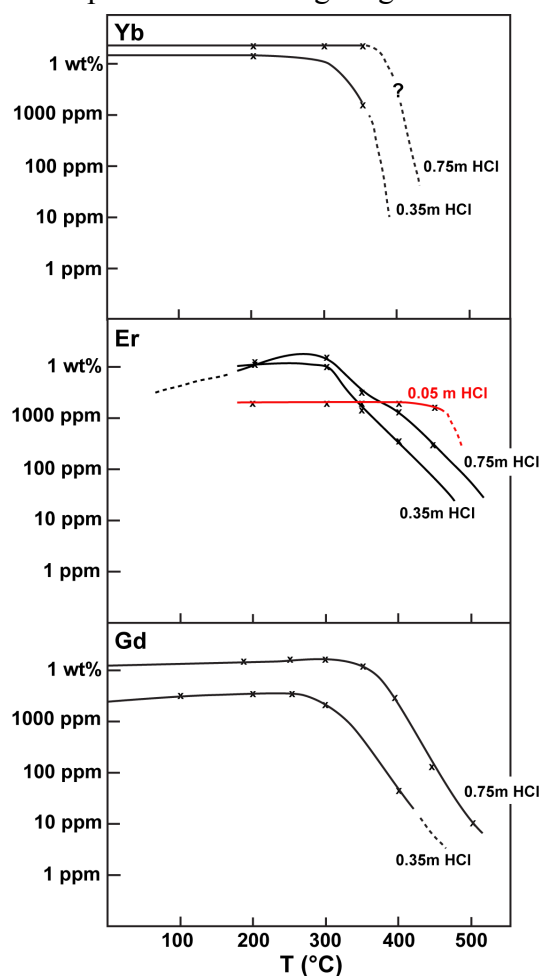


Fig. 1 : Yb, Er and Gd solubility with increasing temperature and different HCl concentrations as determined from the XAS spectra.

acidic high-temperature fluids ($\text{pH} < 2$ and $T > 400$ °C) [3]. While the stability of such acidic fluids upon continuous interaction with the host rocks is already highly questionable, the experimental dataset we have implemented since October 2014 (*Experimental Reports 20140566 and 20141167* – [2]) suggests that only small amounts ($< 1\text{-}10$ ppm) of MREE and HREE may be transported by such Cl-rich acidic fluids at $T > 400$ °C. Thus, other fluid compositions may be involved in the formation of (M,H)REE-enriched deposits. High-pressure studies such as that of [4] suggest that LREE (La to Sm) may be transported in significantly higher amounts in Cl-bearing fluids. Such differential uptake could provide an explanation for the LREE-enrichment reported in most rare metals deposits and a LREE (Sm) solubility and speciation should hence be tested during our next allocated beamtime (July-September 2016 - *Proposal 20150737*).

Furthermore, XANES and EXAFS analysis also suggests that Er is present as Er^{3+} aqua ion in all Cl-bearing compositions. The hydration shell around Er is found to slightly decrease from 9-10 water molecules at 200 °C to ~ 8 at 400 °C (Fig. 2). In comparison, we found that Yb was coordinated to 8 to 7 oxygens over similar P-T-mHCl range, while Gd tend to form complexes involving 2 to 3 Cl with increasing temperature and Cl contents (*Experimental Reports 20140566 and 20141167* – [2]). Thus, (slightly) different speciation may develop for each different (M,H)REE. The fitted speciation further contrasts with the expected high stability of REE-Cl complexes modeled from solubility experiments by [3], as well as previous XAS measurements in HDAC that suggested the formation of HREE aqua-chloro complexes involving one to two chlorine atoms with increasing temperature [5]. The discrepancies between those and our XAS study may arise from the use of different starting material (REE_2O_3 and REECl_3) or from the EXAFS analysis itself (*i.e.*, ‘forcing’ or not Cl atoms in the EXAFS fits – *although they could not be fitted, the slight shift of the EXAFS oscillations with increasing temperature underlined by the dashed line in Fig. 2. could be attributed to the incorporation of Cl atoms in Er first coordination shell*). Potential differences arising from starting material will be further investigated during our next allocated beamtime (July-September 2016 - *Proposal 20150737*).

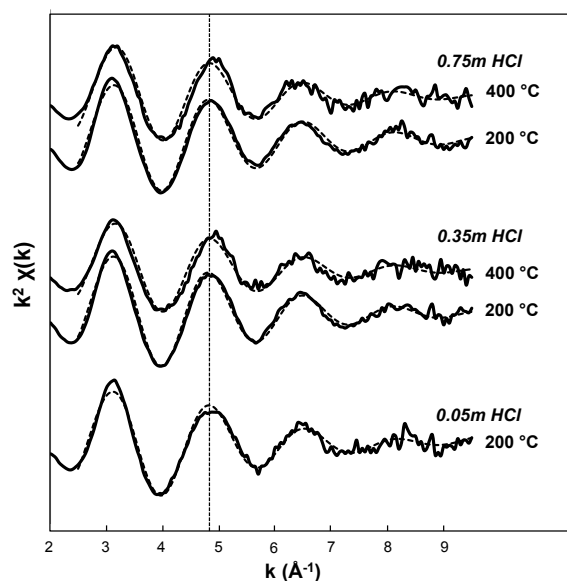


Fig. 2 : k^2 -weighted EXAFS oscillations of Er in 0.05, 0.35 and 0.75 m HCl solutions at 200 and 400 °C and 80 MPa. Least-square fits conducted with IFEFFIT are reported as dashed lines on top of the experimental spectra.

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 Yb and Gd 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. To complement the solubility data while refining our structural analysis, new XAS measurements will be conducted on REE doped Cl-rich solutions at the BM-30B beamline in July-September 2016 (*Proposal 20150737*). *Those data should enable the redaction of a manuscript comparing the solubility and speciation of LREE (Sm), MREE (Gd) and HREE (Er and Yb) in Cl-rich fluids, and for instance provide explanations for the selective transport of LREE or HREE in particular settings.*

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 and Williams-Jones, A.E. 2014. *Mineralium Deposita* 49, 987-997. [4] Tsay, A. et al., 2014. *EPSL* 398, 101-112. [5] Mayanovic, R.A. et al., 2009. *American Mineralogist* 94, 1487-1490.