Standard Project

Experimental Report template

Proposal title: REEs speciation and monazite/xenotime solubility in fluids up to 800 °C and 7 GPa: Towards an improved understanding of subduction zone REE signatures		**Proposal number:** ES544
Beamline: BM23	**Date(s) of experiment:** from: 28/06/2017 to: 03/07/2017	**Date of report:** 10/02/2018
Shifts: 15	**Local contact(s):** Angelika Rosa	*Date of submission:* *10/02/2018*

Objective & expected results:

The initial objective of the experiments is to investigate the solubility of (REE+Y)-rich accessory phases (monazite, zircon or rutile) in high P-T fluids containing various amounts of Cl, S or F so as to assess their potential to mobilize these highly insoluble elements from the subducting slab to the mantle wedge. Such information on the high P-T hydrothermal transport of REE + Y are expected to help with the interpretation of REE signature recorded in volcanic arcs or exhumed high-pressure terranes.

As a first step, and in line with concomitant experiments conducted at lower P-T conditions on the BM30B beamline (report ES550), we decided to focus our efforts on determining the speciation of Y in Cl- and SO_4-rich fluids from 25 to 600 °C and 1 to 5 GPa. These two compositions are of particular interest as they have been shown to favor either enrichment in LREE or HREE [1] and we therefore wish to identify the complexes responsible for these different signatures. Furthermore, they enable high-concentration of Y in solution, hence facilitating high-quality XAS acquisition through the diamond-anvils.

Results and conclusions of the study:

The experiments were conducted from 25 to 430 °C and 0.3 to 2.6 GPa in the externally-heated DAC of the ESRF. XAS spectra were collected around the Y K-edge (17.047 keV). For the first time, our experimental set-up included an online Raman spectrometer to monitor the pressure-dependent $ZrSiO_4$ raman band [2] throughout the experiments (before and after XAS acquisition) (Fig. 1). This additional detector enabled us to determine the pressure with a precision of ±0.05 GPa, which constitute a considerable upgrade compare to previous technics relying on the EOS of pure water or Au that are either unadapted to our Cl and S-rich composition or lack sensibility at the moderate pressures we are interested in.

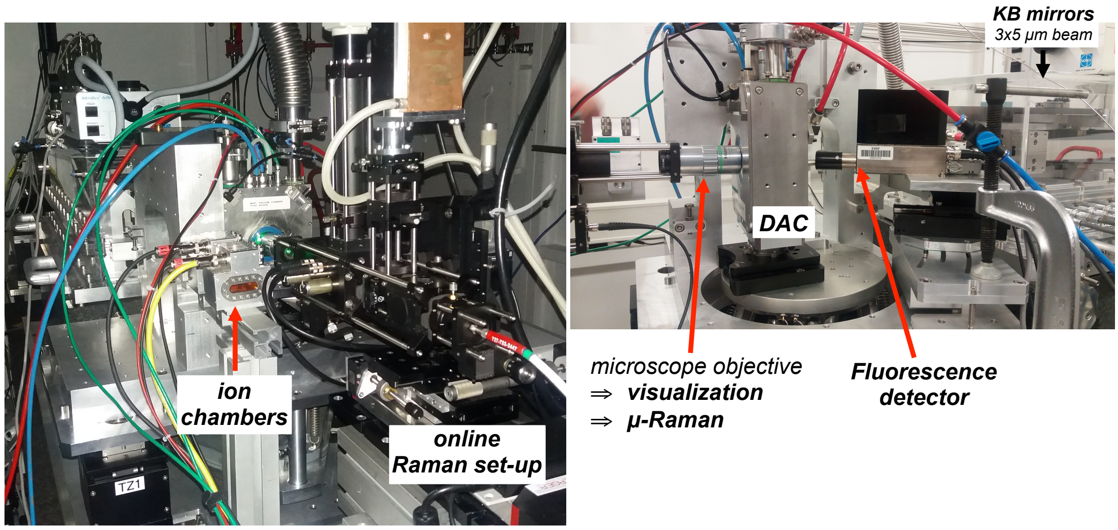

Fig. 1: Experimental XAS set-up at the BM23 beamline.

Four different Cl-bearing compositions were investigated, containing 5000 to 7500 ppm Y and 0.1-0.5-5-10 wt% NaCl (+HCl). One additional experiment involved a 1 wt% H_2SO_4 solution.

In fluids containing 0.1 to 0.5 wt% Cl, a significant reduction of Y solubility prevented the collection of analyzable XAS spectra. For higher Cl concentrations (5 and 10 wt%), the EXAFS spectra and their Fourier transforms suggest a significant reduction of Y-O bond length in comparison to spectra collected for same Cl concentration and temperature but low-pressure conditions (Fig. 2). EXAFS analysis and *Ab initio* MD simulations conducted by our collaborators at Monash University (J. Brugger and Y. Mei) are currently under way to assess if such structure with shorter bonds is thermodynamically stable.

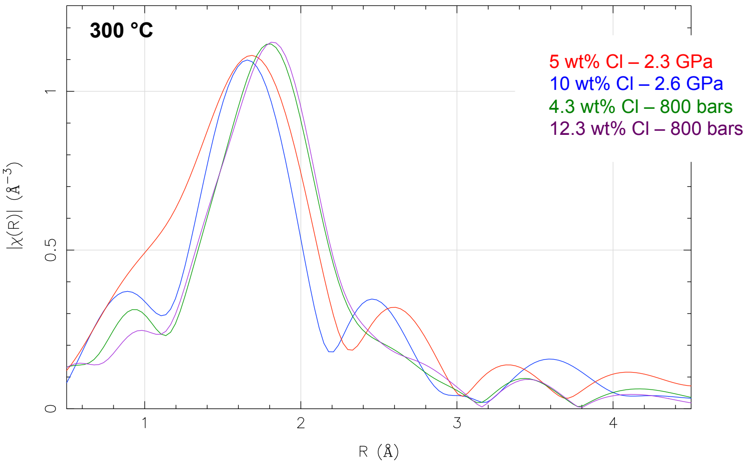

Fig. 2 : XAS Fourier transforms of Y in Cl-bearing solutions at 300 °C showing the reduction of the Y-O bond distance for low (report ES-550) versus high-pressure experiments.

Justification and comments about the use of beam time:

The success of this experiment results from efforts conducted over the last two-years with A. Rosa to enable optimal *in situ* SXRF and XAS analyses in high-temperature DAC on the BM23 beamline (cf. experimental reports for ES-370 and ES-494).

Together with experiments conducted at lower pressure on BM30B beamline (report ES-550) and MD simulations, the obtained dataset will enable to assess the effect of pressure (and hence fluid density) on the aqueous speciation of Y from crustal to deep earth conditions. Those data will be used to test the Deep Earth Water thermodynamic model (DEW) built to constrain geochemical exchange from the slab to the mantle wedge [3]. Over-all, this dataset is expected to improve our understanding of chemical transfer at subduction zones.

Publication(s):

[1] Tsay et al., 2014. EPSL 398, 101-112. [2] Schmidt et al., 2013. Am. Mineral. 98, 643-650. [3] Sverjenski et al., 2014. GCA 129, 125-145.