



Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:

<https://www.esrf.fr/misapps/SMISWebClient/protected/welcome.do>

Reports supporting requests for additional beam time

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



Experiment title: In situ study of rare earth (REE) speciation and partitioning in high PT supercritical fluids and melts: Implications for REE transport and fractionation in subduction zones

Experiment number:
ES-370

Beamline: BM23	Date of experiment: from: 07/06/2016 to:13/06/2016	Date of report: 30/08/2016
Shifts: 18	Local contact(s): Dr. Angelika Rosa	<i>Received at ESRF:</i>

Names and affiliations of applicants (* indicates experimentalists):

***Dr. Marion Louvel**

Dr. John Mavrogenes

Dr. Stefanie Luginbuehl

Report:

Objective & expected results:

The main aim of the experiments was to provide new *in situ* constraints on the behavior of the rare earth elements (REEs) in high P-T subduction zone fluids. Especially, we proposed to determine the speciation and partitioning of selected light and heavy REE (Nd and Yb) in pure H₂O, Cl-rich fluids and haplogranite melts so as to assess how those elements may be recycled up from the subducting slab to the source of arc magmas, and if particular fluid or melt composition could help to explain the LREE/HREE fractionation recorded in arc magmas.

Comments about the beamline, results and the conclusions of the study:

The proposed experiments required collecting μ XAS data on high P-T fluids/melts contained in a resistively-heated diamond-anvil cell (RH-DAC) at low energy (< 9 keV) and the L-edges of the elements as well as at low concentrations of elements down to 500 ppm. The RH-DAC was equipped on the backscattering side with one fully perforated single-crystal diamond anvil (hole size at the culet of 100 micron) sealed with a nano-crystalline diamond window of 150 micron thickness. This setup was tested previously during a commissioning experiment at the Ni K-edge down to concentrations of 1000 ppm, showing that high-quality μ XRF and XAS spectra can be obtained due to the minimization of the diamond anvil absorption. The beam was focused down to 5x4 μ m, an optimal size for μ XAS measurements in the 100 μ m sample chamber of the RH-DAC.

In a first step we have acquired XAS spectra for standard solutions of La, Gd, Nd or Yb ranging from 500 – 7500 ppm. Examples of XANES spectra from 1000 ppm Yb solution with increasing temperature are presented in Fig. 1. The data resolution appears too poor for the detailed analysis of XANES features and hence the determination of precise REE coordination structures. Especially, the low signal intensity of L₁ or L₃-edges in the present setup are mostly due to the signal absorption from the air. While the X-ray beam-path up to the exit of the KB-focusing system was either under vacuum or flushed with He, the incoming and emitted X-ray beam were traveling through a portion of air of 10 cm located between the focusing KB mirrors, the RH-DAC and the Vortex detector. The implementation of a bag flushed with He mounted around the experimental equipment (including the RH-DAC and the Vortex detector) should avoid the absorption of the air at energies below 8 keV. Such a modification was not feasible during the allocated beamtime but it is foreseen for future experiments in order to improve the EXAFS data quality and acquisition time for high P-T conditions (*ie.*, <3-4 h at a given P-T).

Similarly, uXRF spectra collected on Nd and Yb standard solutions (500-1000 ppm) at the weak L-shell emission lines showed very low intensity due to the absorption of the air. At this low count rate the noise signal coming from the excitation of the Vortex detector shielding superimposed the sample signal. This rather low noise signal is negligible for strong K-edge lines above 8 keV (as for Ni) and could be easily suppressed using a Mo-collimator mounted in front of the detector. The collimator however further reduces the signal intensity towards the Vortex detector. It remains therefore to be tested if the signal intensity of Nb- and Y-standard solutions down to 500 ppm are measurable using a setup that involves a He bag and a Mo-collimator.

Due to the difficulties encountered for measurements on Nb and Yb in solution, we investigate the solubility of LaPO_4 and GdPO_4 in 1m HCl. Indeed, the La, Gd and Ho L-emission-lines are the sole REE falling in between the detector shielding noise signals (Fe, Cr, Ni K-emission-lines) thus allowing proper uXRF data collection. Two experiments were performed using the externally heated DAC up to 200-300 °C and ~1 GPa. The experiments suggest that both LaPO_4 and GdPO_4 readily dissolved in 1m HCl, in agreement with previous studies on monazite/xenotime solubility [2,3,4]. Figure 2 shows a finely meshed uXRF map in which the precipitation of new La-crystals (La-L_α emission line in red) on the Re gasket edges (Re-L_α emission line in blue) can be seen. However, in both experiments the fluid was lost upon P/T increase most likely due to the rough surface of the nano-crystalline diamond window that preventing correct sealing of the sample chamber.

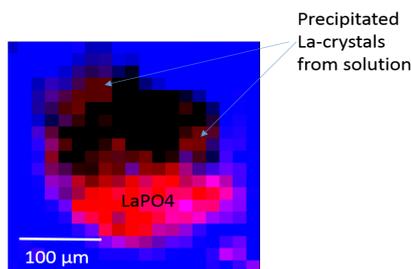


Fig. 2 uXRF map taken @ 9 keV from a LaPO_4 crystal loaded together with a 1ml HCl solution at 1 GPa and 300 °C. Red and blue represents counts at the La-L_α - and Re-L_α -emission lines, respectively.

One run on GdPO_4 was conducted up to 650 °C and 7 GPa using a single-crystal diamond window to avoid fluid loss during P/T increase. The first results from this experiment suggests that Gd completely dissolves at 5 GPa and 200 °C. At higher P/T conditions we observed the precipitation of a Gd compound, and hence a possible retrograde solubility of GdPO_4 at extreme conditions. In addition, the acquired XAS spectra might suggest a change of the local coordination of Gd in solution with increasing P/T conditions (Fig. 1.2).

Summary and outlook

In comparison to previous studies, the use of the RH-DAC enabled a significant increase of the investigated pressure range to conditions more relevant for the dehydration of the top of the slab in cold or warm subduction zones (eg., from 200 C – 2.5 GPa to 800 C - 7 GPa). Indeed the single-crystal diamond windows employed in the experiment pertained up to temperature of ~700 °C and pressure of 7 GPa, while enabling also visual monitoring of the sample chamber during heating. Furthermore, acquired XAS data at the Gd L_3 -edge were free of diamond Bragg peaks at least from ~7.24 to 8.33 keV, which opens opportunities for future high-quality EXAFS measurements in this detection geometry and at those low energies.

Although we could not modify the analytical set-up during beamtime to improve the XAS and uXRF signal to noise ratio, we are planning to employ a He bag between the KB mirrors and the RH-DAC for next experiments so as to reduce the significant absorption from air observed below 8 keV and enable optimal excitation at the REEs L_3 -edges. A new proposal, building on this experiments and the advice from the BM23 staff will be submitted in September 2016 to test the effect of pressure, temperature and different fluid compositions (eg., 2m NaCl-0.25mHCl or Si-Na rich fluids resembling supercritical fluids) on the solubility of LaPO_4 and HoPO_4 .

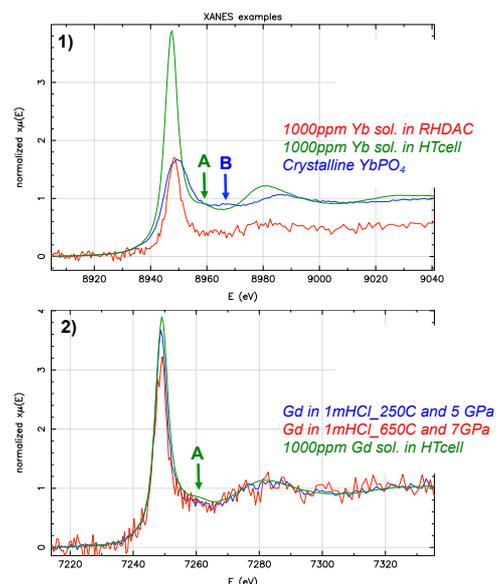


Fig. 1: XANES spectra collected at the Yb (1) and Gd (2) L_3 -edges. In (1) the experimental Yb (500 ppm) spectra in RHDAC is of poor resolution and does not enable to distinguish key features of aqueous (A) vs. solid (B) Yb compounds that were previously identified from measurements in a HTCell dedicated to low pressure analyses ($P < 0.2$ GPa – see [1]). In (2) the aqueous Gd feature (A) previously observed at high T and low P appears to be reproduced at 250 °C, but disappears at 650 °C.