



## 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 using the **Electronic Report Submission Application:**

*<http://193.49.43.2:8080/smis/servlet/UserUtils?start>*

### ***Reports supporting requests for additional beam time***

Reports can now 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.



<b>Experiment title:</b> In situ investigation of the stability of high-order REE-Cl complexes in high P-T fluids: Implications for the formation of rare metals deposits.		<b>Experiment number:</b> 30-02-1102
<b>Beamline:</b> BM-30B	<b>Date of experiment:</b> from: 25 July 16                      to: 1 August 16	<b>Date of report:</b> 02 Aug 16  <i>Received at ESRF:</i>
<b>Shifts:</b> 18	<b>Local contact(s):</b> Denis Testemale	
<b>Names and affiliations of applicants (* indicates experimentalists):</b> Marion Louvel*, University of Bristol Joel Brugger* and Barbara Etschmann*, Monash University Anthony Williams-Jones*, Magill University		

## Report: Aim

This project aimed to identify and determine the structures of important Sm(III) and Nd(III)-chloride species up to magmatic-hydrothermal conditions (800 bar, 500°C). A few other ligands and different fluid pH were tested. The XAS data were also used to study the evolution of Sm<sub>2</sub>O<sub>3</sub> solubility with increasing temperature in different fluid compositions.

## Experimental

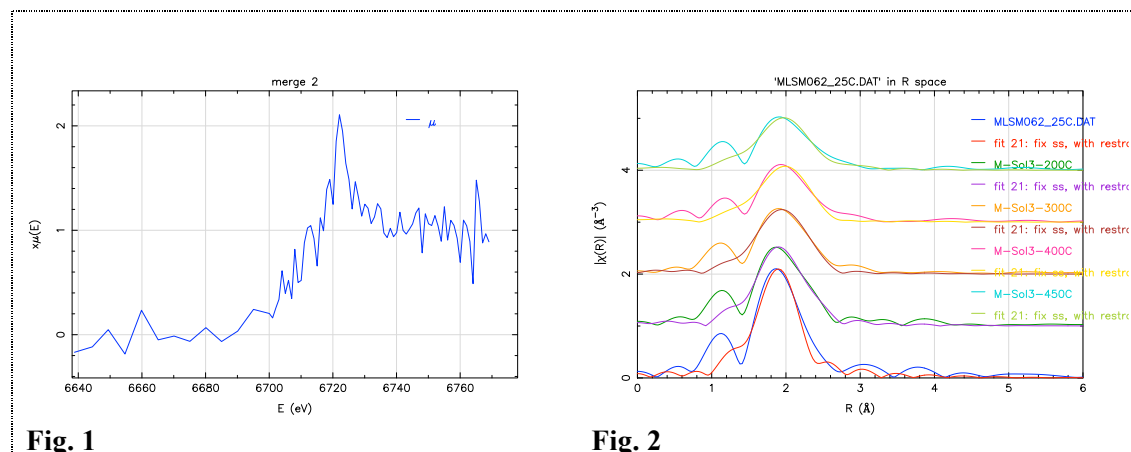
Data were collected at the Sm L<sub>3</sub>-edge (6716 eV) and the Nd L<sub>2</sub>-edge (6722 eV) at the BM-30B (FAME) beamline, using the high T-P autoclave developed by the Institut Neel. Initial measurements at the Nd L<sub>3</sub>-edge (6208 eV) were hampered by the incident beam being close to falling off the mirror, subsequent measurements at the L<sub>2</sub> edge resulted in more measurable photons.

Sample	Conditions
Sm <sub>2</sub> O <sub>3</sub>	Pellet
Water calibration	30-500 °C, 800 bar
Sm <sub>2</sub> O <sub>3</sub> in 0.5 m HCl	30-450 °C, 800 bar
Sm <sub>2</sub> O <sub>3</sub> in 2 m NaCl + 0.5m HCl	30-450 °C, 800 bar
Sm <sub>2</sub> O <sub>3</sub> in 9.5 m LiCl + 0.5 m HCl	30-450 °C, 800 bar
Sm <sub>2</sub> O <sub>3</sub> in 0.2 m H <sub>2</sub> SO <sub>4</sub>	30-400 °C, 800 bar
Sm <sub>2</sub> O <sub>3</sub> in 0.05 m HCl	30-500 °C, 800 bar
Sm <sub>2</sub> O <sub>3</sub> in 1 m NaOH	30-450 °C, 800 bar
Sm <sub>2</sub> O <sub>3</sub> in 4 m NaOH	200-450 °C, 800 bar
Nd <sub>2</sub> O <sub>3</sub> in 2 m NaCl + 0.5 m HCl	30-500 °C, 800 bar
Nd <sub>2</sub> O <sub>3</sub> in 9.5 m NaCl + 0.5 m HCl	30-500 °C, 800 bar
Nd <sub>2</sub> O <sub>3</sub> in 0.2 m H <sub>2</sub> SO <sub>4</sub>	30-400 °C, 800 bar
Calibration solutions for solubility measurements: 1000, 500, 200, 10 ppm Sm <sub>2</sub> O <sub>3</sub> in 1 wt% HNO <sub>3</sub>	Varying limiting T

## General observations/preliminary fits

- Sm and Nd follow the same dehydration effect observed for other rare earths in that (i) the total number of ligands decreases and (ii) the number of Cl ligands increases.
- Observations in nature by Williams-Jones et al. (2016) indicate that some metal transport should occur under basic conditions. We tested this observation by measuring Sm<sub>2</sub>O<sub>3</sub> in NaOH. A “peak” (well, a bump above the noise level) was observed at 400-450 °C (Fig. 1).

3. **Preliminary fits** indicate that Sm(III) in 9.5 m LiCl + 0.5 m HCl can be fitted with ~3 Cl ligands at 400-450 °C (Fig. 2).



**Fig 1.** Big excitement: a bump above the noise! This was with Sm<sub>2</sub>O<sub>3</sub> in 4 m NaOH at 400-450 °C. The concentration of Sm(III) in solution was estimated to be ~15 ppm.

**Fig. 2** Preliminary fits for Sm(III) in 9.5 m LiCl + 0.5 m HCl, results given below. The large peak between ~1<R<1.4 Å is most likely due to noise. Attempts to fit this peak resulted in un-physically short Sm-O bond lengths.

### Some preliminary fit results

Sm(III)	T (°C)	nO1*	R(O1) Å	nO2*	R(O2) Å	nCl*	R(Cl) Å	σ <sup>2**</sup>	χ <sup>2</sup> <sub>red</sub>
Sol3	25	3 (fix)	2.33(12)	7.500(5)	2.42(2)	0.5 (fix)	2.81(16)	0.003 (fix)	287
9.5m LiCl+ 5mHCl	200			5.7(4)	2.40(1)	1.8(4)	2.79(2)	0.003 (fix)	
	300			4.5(4)	2.40(1)	1.7(4)	2.77(2)	0.003 (fix)	
	400			3.9(6)	2.40(2)	2.1(4)	2.73(2)	0.007(2)	
	450			4.0(1)	2.41(2)	2+1 (fix)	2.71(2) 3.30(7)	0.008(2)	

\* the total number of ligands was constrained to be between 6 and 9

\*\* NB only 1 Debye-Waller factor was refined at each temperature.

### Impact and follow-up experiment

These measurements at the Sm and Nd edges complement previous efforts by M. Louvel (Experimental reports 30-02-1089 and 30-02-1096 – Louvel et al., 2015) and Brugger and Etschmann (Experimental report 30-02 1088, manuscript in progress) to improve the characterization of REE aqueous compounds in high temperature fluids that resemble those involved in the formation of economic rare earth ore deposits (e.g., Bayan Obo, China; Strange Lake, Canada). The new results on Sm and Nd suggest that LREE-Cl complexes are more stable than HREE-Cl complexes and hence confirm that LREE may be more easily mobilized by Cl-rich fluids in magmatic-hydrothermal environments (Migdisov et al., 2016).

The experiments test the speciation of Sm and Nd in S-bearing acidic fluids and basic solutions, which had not been done for the MREE and HREE previously analyzed (Gd, Er and Yb). Additional measurements will soon be conducted to cover this gap (November 2016). Two review publications presenting 1) the structure of REE complexes with OH, Cl and S ligands in high P-T fluids and 2) the influence of P-T conditions and fluid composition on the solubility, transport and deposition of the REEs in geological environments should come out of these two years work.

Louvel et al., 2015. *Chemical Geology*. 417, 228-237

Migdisov, A., Williams-Jones, A.E., Brugger, J. and Caporuscio, F., 2016. Hydrothermal transport, deposition, and fractionation of REE: Experimental data and thermodynamic calculations *Chemical Geology* 439, 13–42.