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.

	Experiment title: La speciation in high P-T fluids: Implications for the remobilization of REE by hydrothermal fluids and the formation of rare metals deposits.	Experiment number: 30-02-1130
Beamline: BM-30B	Date of experiment: from: 23 Jan 18 to: 30 Jan 18	Date of report: 08 Feb 18
Shifts: 15	Local contact(s): Denis Testemale, Elena Bazarkina	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Marion Louvel*, Cambridge University

Joel Brugger* and Barbara Etschmann*, Monash University

Aim

Accurate knowledge of rare earths (REE: La-Lu, +Y, Sc) speciation in high P-T fluids is of critical importance to understand and better model the role of fluids in formation of rare earths deposits. The aim of this experiment was to investigate La speciation and solubility in high temperature fluids involving different complexing ligands and pH, conducting in situ XAS measurements. These experiments will extend the experimental dataset on REE aqueous chemistry that has been developed since 2014 and enable the development of new depositional models for the REE.

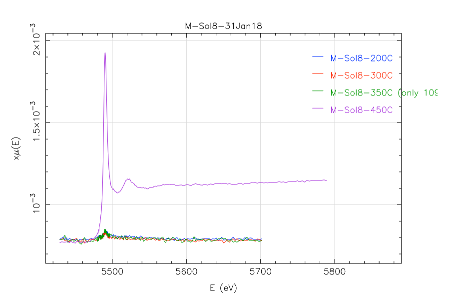
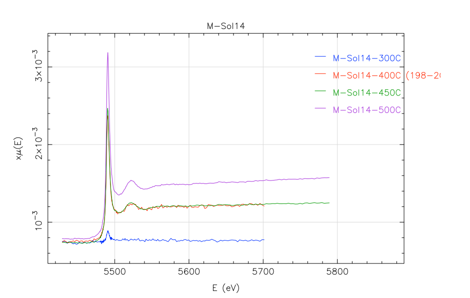
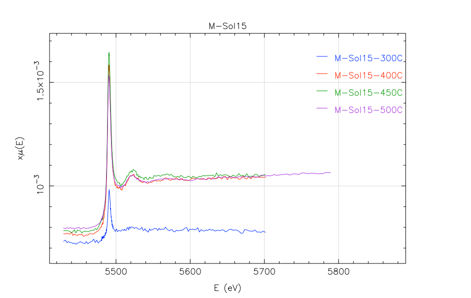
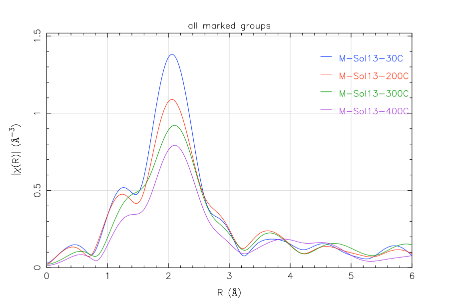
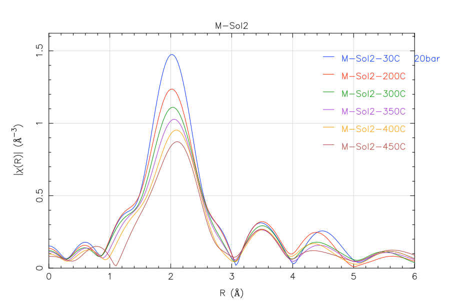
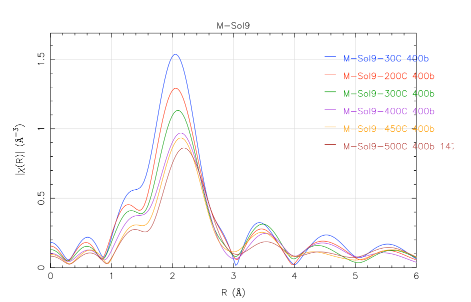
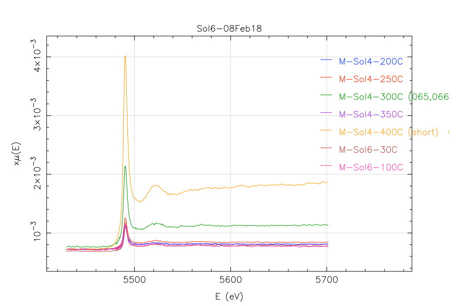
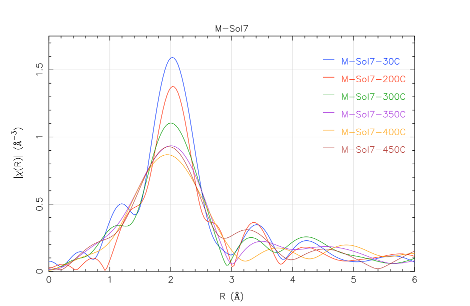
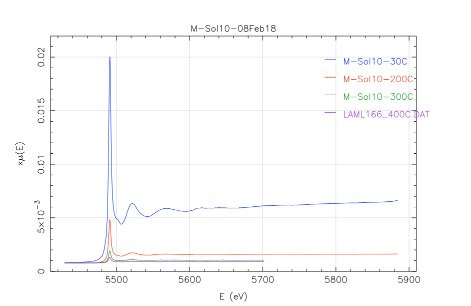
Experimental

Data were collected at the La L_3-edge (5483 eV) at the BM-30B (FAME) beamline, using the high T-P autoclave developed by the Institut Neel.

Sample	Conditions	Sample	Conditions
La_2O_3	Pellet	Sol7: $La_2O_3 + H_2SO_4$	30-450 ^oC, 400 bar
La_2CO_3F	Pellet	Sol8: $La_2O_3 + Na_2CO_3$	200-450 ^oC, 400 bar
$LaCl_3$	Pellet	Sol9: $LaCl_3$ + 4.5m LiCl	30-550 ^oC, 400 bar
LaF_3	Pellet	Sol10: $La(NO_3)_3 + Li_2SO_4 + H_2SO_4$	30-400 ^oC, 400 bar
Sol2: La_2O_3 + 1 m HCl	30-450 ^oC, 400 bar	Sol11: $La(CH_3COO)_3 + CH_3COOH$	30-400 ^oC, 400 bar
Sol3: $La(NO_3)_3$	30-400 ^oC, 400 bar	Sol13: La in 0.3m Cl	30-450 ^oC, 400 bar
Sol4: $La_2O_3 + Na_2SO_4$	200-400 ^oC, 400 bar	Sol14: La_2O_3 + 0.7 m Na_2CO_3 + 0.35 m NaF	300-500 ^oC, 400 bar
Sol6: $La_2O_3 + Na_2SO_4 + H_2SO_4$	30-100 ^oC, 400 bar	Sol15: La_2O_3 + 0.67 m Na_2CO_3 + 0.6 m NaF	30-500 ^oC, 400 bar

General observations

1. La follows 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.
2. Even in rather salty solutions, the uptake of Cl into the first coordination sphere is limited. Preliminary results suggest 1.5(4) Cl + 3.5(9) O are coordinated to La in a 4.5 m LiCl solution at 550 ^oC (Sol 9).
3. Observations in nature by Migdisov et al. (2016) indicate that some metal transport should occur under basic conditions. We tested this observation by measuring La_2O_3 in Na_2CO_3 ± NaF solutions and the results were astonishing – XANES with a demonstable step were observed at 300 ^oC and nice XANES could be obtained at 400 ^oC. The EXAFS are short range (La L_2 edge is 408 eV above the La L_3 edge) and rather noisy, but a rough "qualitative fit" may be obtainable.
4. La-SO_4 solutions - the solubility decreased quite dramatically with increasing temperature. The only solution with refinable EXAFS is Sol7 (highly acidic).

<table>
<tr><td colspan="3">Effect of $Na_2CO_3 \pm NaF$.</td></tr>
<tr><td>
</td><td>
</td><td>
</td></tr>
<tr><td>Sol8: Na_2CO_3</td><td>Sol14: 0.7 m Na_2CO_3 + 0.35 m NaF</td><td>Sol15: 0.67 m Na_2CO_3 + 0.6 m NaF</td></tr>
<tr><td colspan="3">Effect of adding salt</td></tr>
<tr><td>
</td><td>
</td><td>
</td></tr>
<tr><td>Sol13: 0.3 m Cl</td><td>Sol2: 1 m HCl</td><td>Sol9: 4.5 m LiCl</td></tr>
<tr><td colspan="3">Effect of SO_4^{2-}: difficult to determine bidentate La-S bond, due to high noise in spectra, eg see effect of salt above.</td></tr>
<tr><td>
</td><td>
</td><td>
</td></tr>
<tr><td>Sol4 & Sol6: La is not very soluble in these solutions</td><td>Sol7: solubility decreases with increasing T</td><td>Sol10 – solubility > than for Sol4 and Sol6, but not much, and decreases with T.</td></tr>
</table>

Impact

These measurements at the La edge complement previous efforts by M. Louvel (Experimental reports 30-02-1089 and 30-02-1096 – Louvel et al., 2015*), Brugger and Etschmann (Experimental report 30-02 1088, Liu et al. 2017*) and Louvel, Brugger and Etschmann (Experimental report 30-03 1102, ES-550) 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).

A number of publications are expected from this work: (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, (3) a short communication on metal transport in basic conditions and (4) the data will be used to ground-proof up-coming molecular dynamics calculations (Y, La).

*Louvel & Mavrogenes, 2015, 'Hydrothermal controls on the genesis of REE deposits: Insights from an in situ XAS study of Yb solubility and speciation in high temperature fluids (T<400C)'. *Chemical Geology*, vol 417., pp. 228-237

*Liu, Etschmann, Hazemann, Testemale, Migdisov and Brugger, 2017. Revisiting the hydrothermal geochemistry of europium(II/III) in light of new in-situ XAS spectroscopy results. *Chemical Geology*, 459, 61–74.