EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

ESRF

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.

ESRF	**Experiment title:** In situ investigation of the hydration and ion pairing of yttrium in high P-T fluids: Implications for the formation of rare metals deposits and the 'yttrium anomaly'.	**Experiment number**: ES-550
Beamline: BM-30B	**Date of experiment**: from: 16 Feb 17 to: 21 Feb 17	**Date of report**: 02 Aug 16
Shifts: 15	**Local contact(s)**: Jean-Louis Hazeman	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Joel Brugger* and Barbara Etschmann*, Monash University

Marion Louvel*, University of Bristol

Report:

Aim

This project aimed to identify and determine the structures of important Y(III)-chloride species up to magmatic-hydrothermal conditions (800 bar, 500^{o}C). A few other ligands and different fluid pH were tested. We will improve our understanding of the that result in separation among REE in nature by contrasting Y^{3+} data with those recently obtained on Nd(III), Sm(III), Eu(II/III), Gd(III), Dy(III), Er(III) and Yb(III), as well as provide a sound molecular-level understanding of the origin of the 'Y-anomaly' to support its use as a tracer of hydrothermal processes.

Experimental

Data were collected at the Y K-edge (17038 eV) at the BM-30B (FAME) beamline, using the high T-P autoclave developed by the Institut Neel.

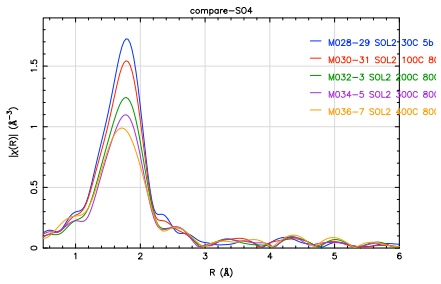
Sample	Conditions
Y_2O_3	Pellet
$Y_2(SO_4)_3$	Pellet
Water calibration	30-500 ^{o}C, 800 bar
Sol2: $Y_2(SO_4)_3$ + H_2SO_4 -> 0.3 m SO_4	30-450 ^{o}C, 800 bar
Sol3: 0.01m Y_2Cl_3	30-400 ^{o}C, 800 bar
Sol4: $Y_2(SO_4)_3$ + 0.3m H_2SO_4 + 0.7m Na_2SO_4	30-400 ^{o}C, 800 bar
Sol5: YCl_3 + 9.5m LiCl + 0.5m HCl	30-450 ^{o}C, 800 bar
Sol6: YCl_3 + 0.75m HCl	30-450 ^{o}C, 800 bar
Sol7: YCl_3 + 2m NaCl + 0.5m HCl	30-400 ^{o}C, 800 bar
Sol8: YCl_3 + 0.5m NaOH + 0.5m NaF	200-400 ^{o}C, 800 bar
Sol9: $Y_2(SO_4)_3$ + 2m H_2SO_4 + 2m NaCl	30-400 ^{o}C, 800 bar
Sol10: $Y_2(SO_4)_3$ + 0.3m Na_2SO_4	30-400 ^{o}C, 800 bar
Sol11: YCl_3 + 0.5m NaOH + 2m NaCl	200-400 ^{o}C, 800 bar
Sol12: 1m YCl_3	30-450 ^{o}C, 800 bar
Sol13: $Y_2(SO_4)_3$ + 0.3m Na_2SO_4 + 0.3m NaCl	200-400 ^{o}C, 800 bar
Sol14: $Y_2(SO_4)_3$ + 0.3m Na_2SO_4 + 1m NaCl	300-400 ^{o}C, 800 bar

General observations

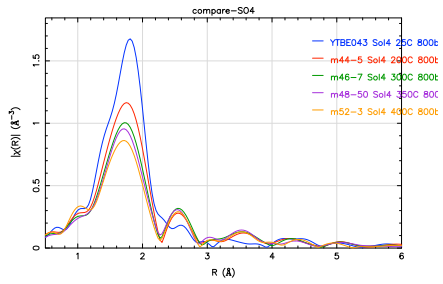
1. Y follows the same dehydration effect observed for other rare earths in that (i) the total number of ligands decreases and (ii) the number of Cl ligands increases. Though it should be noted that we could only observe a shift in the peak position in R-space for Sol5 (9.5 m LiCl+0.5 M HCl). Sol7 (2 m NaCl+0.5 m HCl) showed a very slight shift, indicating that the first coordination shell comprises predominantly of O (well water).

2. 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 YCl_3 in NaOH+NaF and NaOH+NaCl. A "peak" (well, a bump above the noise level) was observed at 400-450 ^oC.
3. Y-SO_4 solutions show bidentate-complexing peak with increasing T (<200 ^oC), but this peak only occurs with Na_2SO_4 and not if only have H_2SO_4. Addition of Cl appears to have little effect on this bidentate peak.

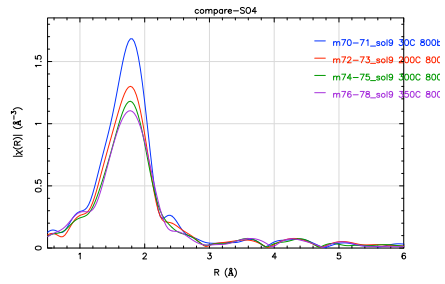
(1) Effect of SO_4 added as H_2SO_4 or Na_2SO_4. (2) Effect SO_4-Cl competition wrt to bidentate peak.



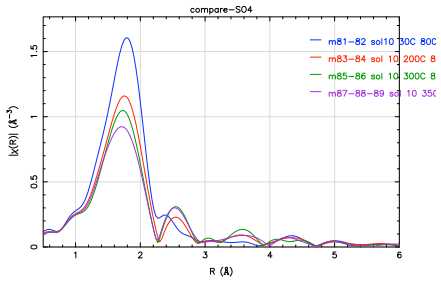
Sol2: 0.28 m H_2SO_4



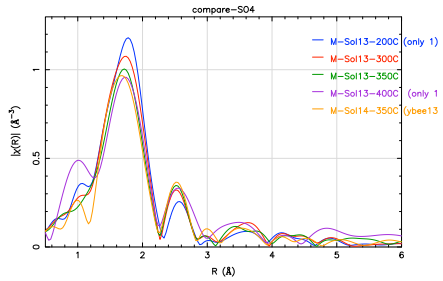
Sol4: 0.28 m H_2SO_4 + 1.7 m Na_2SO_4 = total ~2 m SO_4



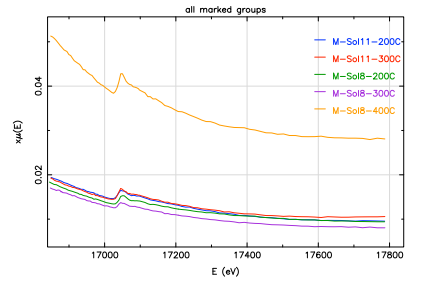
Sol9: 2.0 m H_2SO_4 + 2 m NaCl = total 2 m SO_4



Sol10: 0.28 m Na_2SO_4 + 0.01 m H_2SO_4 = total 0.29 m SO_4

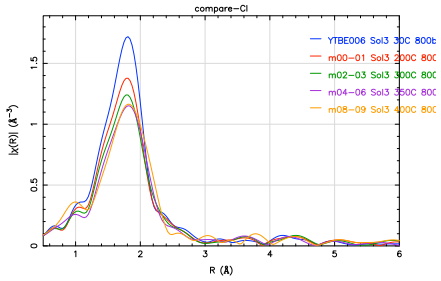


Sol13+Sol14
Sol13: 0.28 m Na_2SO_4 + 0.01 m H_2SO_4 + 0.3 m NaCl
Sol14: 0.28 m Na_2SO_4 + 0.01 m H_2SO_4 + 1.0 m NaCl

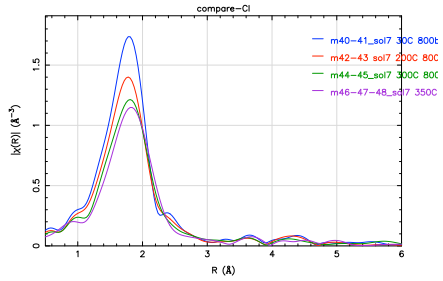


Compare Sol8 and 11 in mu(E). Sol8-400C has the largest step.

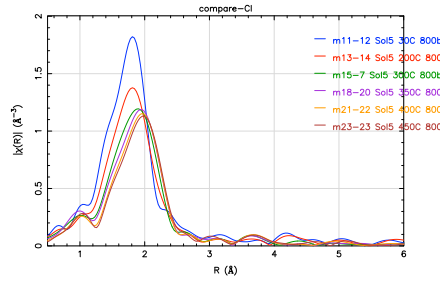
Effect of adding salt



Sol3: 0 m added NaCl



Sol7: 2 m NaCl



Sol5: 9.5 m LiCl

Impact

These measurements at the Y 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, manuscript in progress) and Louvel, Brugger and Etschmann (Experimental report 30-03 1102) 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).

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.