

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: An XAS study of europium speciation and redox reactions in hydrothermal solutions	Experiment number: 30-02-1088
Beamline: 30-BM-B	Date of experiment: from: 15 July 15 to: 21 July 15	Date of report: 23 Aug 15
Shifts: 18	Local contact(s): Jean-Louis Hazeman	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Joel Brugger* and Barbara Etschmann*, Monash University Weihua Liu*, CSIRO Art Migdisov* and Hakim Boukhalfa*, Los Alamos NL		

Report: Aim

This project aimed to identify and determine the structures of important Eu(II) and Eu(III) chloride and hydroxide species up to magmatic-hydrothermal conditions (600 bar, 500°C)

Experimental

Data were collected at the Eu L₂-edge (7617 eV) at the BM-30B (FAME) beam line, using the high T-P autoclave developed by the CNRS. Initial measurements were collected at the Eu L₃-edge (6977 eV), however there was enough Fe in the Be windows of the autoclave to have a measurable Fe edge, which added substantial noise to the Eu-EXAFS. This was eliminated by collecting data at the L₂ edge. An added bonus was that there appeared to be no discernable signal from multi-electron excitations which have given previous experimenters some headaches when collecting data at the L₃ edge. For comparison, 3 Gd solutions were measured at 0 and 2 m NaCl and 10 m LiCl.

Sample	Conditions	Sample	Conditions
EuCl ₃ ·6H ₂ O	Pellet		
Eu(II) in 0 m NaCl	35, 400 °C, 600 bar	Eu(II) in 1 m NaBr	35, 300-400 °C, 600 bar
Eu(II) in 1 m NaCl	35, 400 °C, 600 bar	Eu(II) in 10 m LiBr	400 °C, 600 bar
Eu(II) in 5 m NaCl	300-400 °C, 600 bar	Eu(III) in 5 m NaBr	35-400 °C, 600 bar
Eu(II) in 10 m LiCl	Insoluble (couldn't measure)	Eu(III) in 10 m LiBr	35-400 °C, 600 bar
Eu(III) in H ₂ O ₂	35-400 °C, 600 bar	Gd(III) in 0 m NaCl	35-400 °C, 600 bar
Eu(III) in HNO ₃	35, 300-400 °C, 600 bar	Gd(III) in 2 m NaCl	35-400 °C, 600 bar
Eu(III) in H ₂ SO ₄	35-400 °C, 600 bar	Gd(III) in 10 m LiCl	35-400 °C, 600 bar
Eu(III) in 5 m NaCl	35-400 °C, 600 bar		
Eu(III) in 16 m LiCl	35-400 °C, 600 bar		

General observations/preliminary fits

- At room temperature Eu prefers to be Eu(III), at 300-400 °C Eu prefers to be Eu(II).
- The dehydration effect (decrease of the total number of ligands with temperature) is more pronounced for Eu(III) than Eu(II) (Fig. 1).
- Preliminary fits** indicate that Eu(III) can be fitted with a maximum of 3 Cl (Fig. 2), while Eu(II) has less (still wrestling the data). However, this is using a single Debye-Waller factor (ie ssCl is constrained to be the same as ssO). When this constraint is released it is possible to get rather a lot more Cl into the first coordination shell, with rather large Debye-Waller factors. Still playing with the system to determine the best/most realistic model. Attempts to fit multiple-scattering peaks will hopefully pin down the coordination number.

4. The same dilemma, that the number of Cl increased when the number of constraints were loosed, was observed with the **preliminary fits** of the Gd data. However, it appears that at 400 °C, there are about 7 ligands around the Gd (consistent with the dehydration effect observed by eg. [Mayanovic et al. 2002, 2003](#)). When the data were fitted as GdO_nCl_m with $n=0-7$ and $m=7-0$, $n+m=7$, the best fit was with GdO_3Cl_4 ; however the fits with O ranging from 1 to 4 with Cl ranging from 6 to 3 were virtually (statistically) equally good.

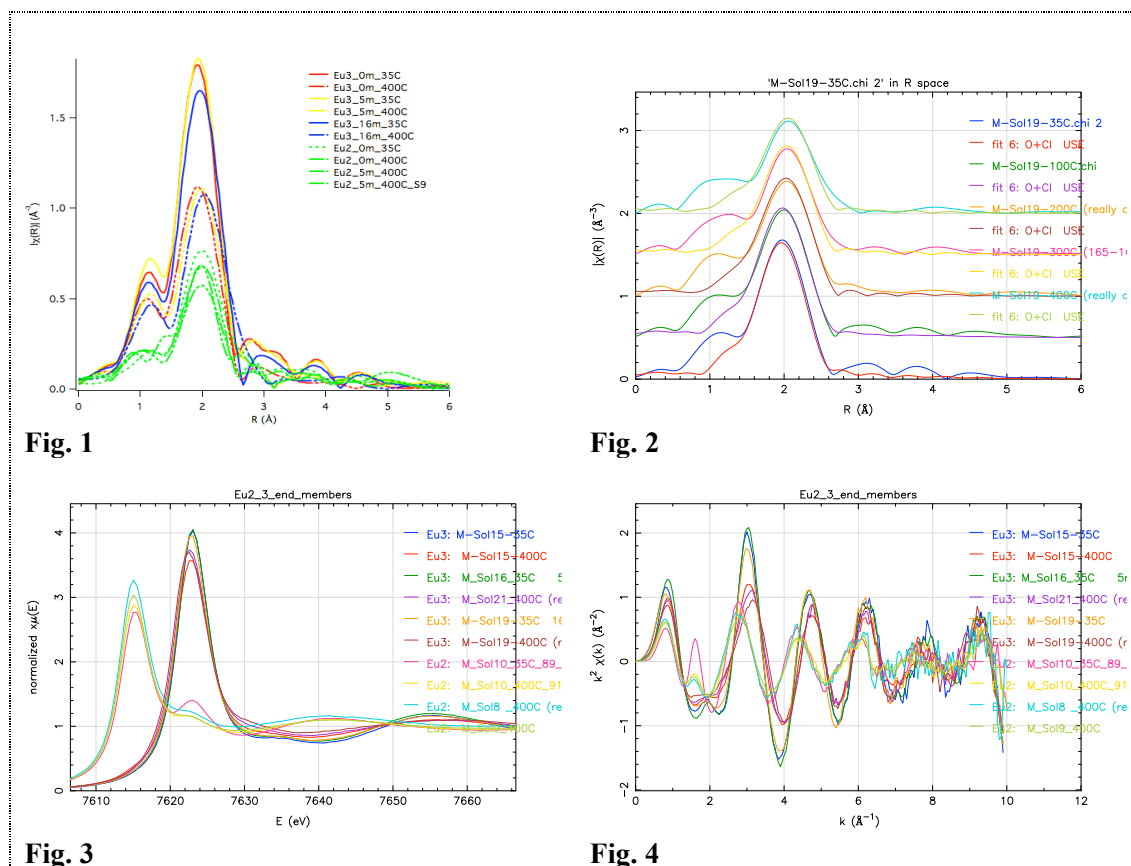


Fig. 1 R-space plot showing end-member salinities and temperature data collected for Eu(II) and Eu(III). The dehydration effect with temperature is more pronounced for Eu(III) than Eu(II).

Fig. 2 Preliminary fits for Eu(III) in 16 m LiCl, results given below.

Fig. 3 Eu(II) and Eu(III) E-space spectra, oxidation of Eu(II) at 35 °C is evident.

Fig. 4 Eu(II) and Eu(III) k-space spectra. The peak at 1.6 Å⁻¹ is related to the Eu(II) oxidation; this peak is shifted slightly for Eu(III) solutions (1.9 Å⁻¹) and decreases with increasing temperature. There is no (obvious) evidence for the multi-electron excitation peak (between 6-8 Å⁻¹) discussed by eg. [Moreau et al. \(2002\)](#) and [D'Angelo et al. \(1996\)](#).

Eu(III)		nO*	RO Å	nCl*	RCl Å	ss**	χ ² _{red}
HNO ₃	35 °C	9.000(6)*	2.43(2)	na	na	0.008(2)	486
	400 °C	5.3(6)	2.41(2)	0.7(6)	2.77 (fix)	0.008(2)	486
5 m NaCl	35 °C	9.000(8)	2.44(1)	na	na	0.008(1)	687
	400 °C	4.2(10)	2.44(3)	1.7(10)	2.69(6)	0.008(1)	687
16 m LiCl	35 °C	7.4(8)	2.44(3)	1.5(8)	2.74(5)	0.008(2)	333
	400 °C	2.8(9)	2.43(5)	3.1(10)	2.69(3)	0.008(2)	333
Eu(II)		nO ₁ *	RO ₁ Å	nO ₂ *	RO ₂ Å	ss**	χ ² _{red}
0 m NaCl	35 °C	6.6(8)	2.58(2)	2.4(8)	2.89(6)	0.016(5)	109
	400 °C	6.0(7)	2.54(3)	3.0(7)	2.86(5)	0.017(5)	324

* the total number of ligands was constrained to be between 4 and 9

** NB only 1 Debye-Waller factor was refined - this was for both O and Cl at both 35 and 400 °C