

## 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> XANES and EXAFS of Lanthanide-bearing silicate glasses	<b>Experiment number:</b> 08-01-702
<b>Beamline:</b> BM08	<b>Date of experiment:</b> <b>from: 16-APR-05 to: 19-APR-05</b>	<b>Date of report:</b> 24.10.05
<b>Shifts:</b> 9	<b>Local contact(s):</b> Chiara Battocchio, Chiara Maurizio	<i>Received at ESRF:</i>

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**Report:**

In order to model the magmatic processes and to obtain phase diagrams for lanthanide host phases the accurate determination of the configurational role of lanthanides in silicate melts is required. In magmatic systems, lanthanides can be found in bivalent, trivalent and tetravalent oxidation states whereas little is known about their coordination environments and their structural configuration in general. Naturally, both coordination number and oxidation state of these elements can influence the physical properties of magmatic liquids, even at the low concentrations pertaining to silicate melts.

We measured in our experiment XANES spectra on synthetic glasses, containing different lanthanide sesquioxides, either synthesized under normal atmospheric conditions or, in case of Eu, under controlled oxygen fugacity in order to vary its oxidation state. The synthetic glass compositions were chosen to represent a simplified basaltic melt and a strongly depolymerized alkali-enriched composition. Lanthanide sesquioxides (i.e., Ce<sub>2</sub>O<sub>3</sub>, Pr<sub>2</sub>O<sub>3</sub>, Nd<sub>2</sub>O<sub>3</sub>, Sm<sub>2</sub>O<sub>3</sub>, Eu<sub>2</sub>O<sub>3</sub>, Gd<sub>2</sub>O<sub>3</sub>, Tb<sub>2</sub>O<sub>3</sub>, Dy<sub>2</sub>O<sub>3</sub>, Ho<sub>2</sub>O<sub>3</sub>, Er<sub>2</sub>O<sub>3</sub>, Tm<sub>2</sub>O<sub>3</sub> and Yb<sub>2</sub>O<sub>3</sub>) were present in concentrations ranging from 1 to 25 wt% of the basic compositions and at different oxygen fugacities.

Together with the XANES spectroscopy at the L<sub>I-III</sub> thresholds of the lanthanide element, we also obtained good quality EXAFS data in order to be able to better distinguish different coordination polyhedra by modelling the lanthanide-O pair distribution function.

Even for the lowest lanthanide content glasses and the relatively low beam current, we observed good signal to noise ratio in the spectra due to the multichannel fluorescence detector utilized at the beamline.

Results for the Eu bearing samples are reported below.

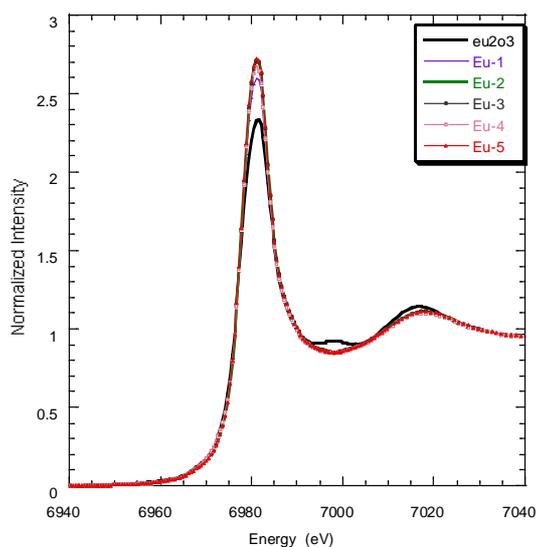


Fig 1. XANES spectra acquired on Eu-bearing glasses, synthesized at different oxygen fugacities.

For the Eu synthesised under different oxygen fugacities conditions, we did not observe a clear variation in energy position of the L-edge peak as an indicator of different oxidation states. The Eu II+ white line should indeed be present at -8eV respect to the Eu III+ white line maximum.

However, the difference spectra taken respect to the n.5 sample (fig. 2) show that a small Eu<sup>2+</sup> contribution should be present, and the difference in concentration respect to the sample 5 is detectable and less than 2% and 1% for the samples n.4 and 5 respectively.

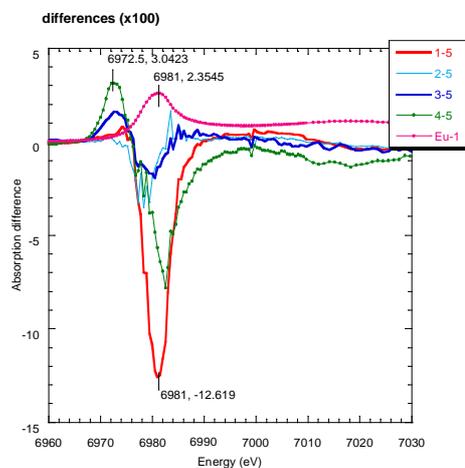
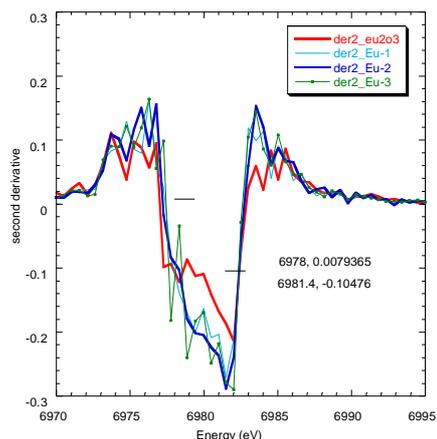


Fig. 2 Eu LIII-edge XANES difference spectra.



*Fig. 3. The Eu LIII-edge spectra second derivative.*

The white line analysis is compatible with the framework of an octahedral coordination for all Eu glasses. The spectra second derivative shows for all samples a clear two minima structure in the region around the white line, separated by 3.4 eV. This value confirm the result and is consistent with the value reported from Antonio et al., (J. Alloys and Compounds, 250 (1997) 536 ) in the case of octahedrally-coordinated NaEuSi<sub>3</sub>O<sub>8</sub> silicate glasses.

From the energy position of the XANES spectra for the other lanthanide elements for all the concentrations and for the two different base compositions we can infer a trivalent oxidation state. Accurate EXAFS analysis is now under process.

The results obtained in this study will be compared with the partial molar volumes of these glasses in order to develop a model of lanthanide-bearing silicate melt structure over a wide compositional range relevant to a variety of geological environments and technical applications.

