



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:
Kinetics of oxydoreduction of iron in silicate glasses and liquids.

Experiment number:
HS2411

Beamline: ID24	Date of experiment: from: 11 March 2003 to: 16 march 2003	Date of report: <i>Received at ESRF:</i>
Shifts: 21	Local contact(s): Dr. Manuel Munoz, ID24, ESRF	

Names and affiliations of applicants (* indicates experimentalists):

*Daniel Neuville, Physique des Minéraux et des Magmas, IPGP-CNRS, Paris

*Véronique Magnien, Physique des Minéraux et des Magmas, IPGP-CNRS, Paris

*Laurent Cormier, LMCP, Paris

*Pascal Richet, Physique des Minéraux et des Magmas, IPGP-CNRS, Paris

*Jacques Roux, Physique des Minéraux et des Magmas, IPGP-CNRS, Paris

Report:

The aim of this experiment was to obtain quantitative information on the kinetic of iron redox reactions in silicate glasses and melts. For this purpose, X-ray absorption spectroscopy (XAS) is well suited because it allows the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio to be determined as a function of time through analysis of the pre-peak feature and of the position of the edge. Understanding of redox reactions is in particular required to control the vitrification processes and the temperature-induced structural changes in glasses and melts.

The first 5 shifts were used to align the beamline and set-up the experiment. The sample was heated in the microfurnace developed by Richet et al. (1993) and already used at the ESRF. This set-up consists of a Pt wire with a hole in which the sample is loaded. With this furnace, samples can be heated up to 1900°C. The glass samples had been prepared in Paris under controlled atmosphere to ensure initially different $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratios, and were characterized using wet chemical analyses, Mössbauer spectroscopy, electron microprobe and XANES spectroscopy made on the D44 at LURE (Magnien et al., 2004). As a matter of fact, several problems have emerged during these experiment and had to be solved before good XANES spectra could be recorded :

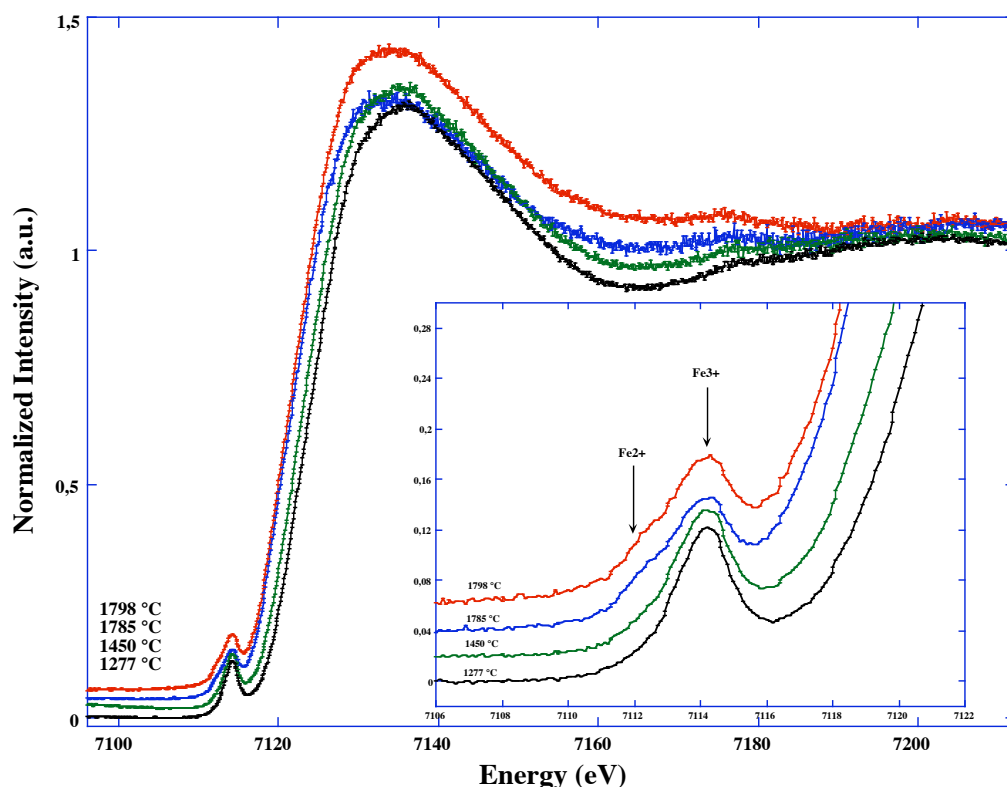
- i) on this beam line, and a very small beam, the homogeneity of the sample is a very important parameter. Use of powder did not allow us to obtain a signal of good quality to discriminate the Fe^{2+} and Fe^{3+} contributions in the prepeak. This was solved by melting the sample and quenching it rapidly to have a glass with an homogeneous surface.
- ii) the loading of the sample in the hole of the Pt wire has been extremely difficult due to the difficulty to control the thickness of the sample
- iii) during the XANES acquisition at high temperature, the thickness of the sample evolved, which also affected the quality of absorption edges. The stability of the Pt wire had also to be improved.

We had previously made measurements on other synchrotron beamlines (D44 and D11 at LURE). Due to the great focus of the beam on ID24, we had to modify our experimental conditions for loading and acquisition. Compared with our previous measurements, the XANES spectra on ID24 show an improvement in the acquisition time and on the resolution of pre-edge feature.

Finally, we have found a good procedure to charge the cell, and control the thickness of the sample during the experiments. For two different glasses (Pyrox = 50% mole SiO₂, 10% FeO, 20%CaO, 20%MgO, and PyroxNa = 50% mole SiO₂, 10%, 5% Na₂O, FeO, 17,5%CaO, 17,5%MgO,) we were able to follow the kinetic of the reduction and of the oxidation.

Results:

The results obtained during this experiment are very promising and the data are currently under treatment to extract quantitative information. In the following figure, we present, four XANES spectra obtained at high temperature, 1277, 1450, 1785 and 1798°C during kinetics measurements.



From these first results, we observe a rapid change in the pre-edge of the XANES spectra as a function of temperature. When the temperature increases, the kinetics of reduction is faster than 100 ms at 1785 and 1798°C. In contrast, the kinetics of oxidation takes a longer time, close to 20 and 15 minutes when the temperature is decreased to 1277 and 1450°C, respectively.

In summary, we have overcome the main difficulties and proven the feasibility of the experiment. The present results give us first estimates of the time required for the oxidation process of the sample. However, due to the rapid time for reduction, an exact determination of the process has not been obtained. To pursue these kinetic X-ray absorption spectroscopy measurements at high temperature, we asked for a continuation of 18 shifts in order to complete and obtain complementary information. We plan to modify the furnace to minimize the displacement of the Pt wire at high temperature. Due to the rapid reduction kinetics, we will modify the heating set-up to synchronize it with the acquisition of the XANES spectra. The ID24 beam line, with its small beam and good time resolution is a good tool to study this oxydoreduction kinetics.