



## 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> <b>Variations des cinétiques d'oxydoréduction du fer dans les verres et liquides silicatés à faible teneur en fer.</b>	<b>Experiment number:</b> 30-02-730
<b>Beamline:</b> BM30B	<b>Date of experiment:</b> from: 15March2005 to:21March 2005	<b>Date of report:</b>  <i>Received at ESRF:</i>
<b>Shifts:</b> 15	<b>Local contact(s):</b> Dr. Olivier PROUX, BM30B, ESRF	
<b>Names and affiliations of applicants</b> (* indicates experimentalists): * Véronique Magnien, Physique des Minéraux et des Magmas, IPGP-CNRS, Paris * Daniel Neuville, 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 * Matthieu Roskosz, Physique des Minéraux et des Magmas, IPGP-CNRS, Paris		

## Report:

The aim of our experiment was to use X-ray absorption spectroscopy to determine the kinetics of iron redox reactions in silicate glasses and melts. Especially it is interesting for us to derive information concerning implied mechanisms in order to control vitrification processes and the temperature-induced structural changes in glass or nuclear industry. XANES techniques are well adapted to answer to this goal because they allow not only the determination of the redox coordination states of iron by resolving the pre-edge feature but also the realization of *in situ* measurements.

For this reason, we used a microfurnace set-up developed by Richet et al.(1993), which is made of a Pt wire with a hole which can be heated from ambient up to 2000K. A small amount of powder is placed in the hole (1 mm in diameter) and heated at different temperature stages. For each temperature stage, several XANES spectra were recorded according to time, in order to follow kinetics of oxidation reaction. Several compositions with different redox states (well characterized by chemical, Mössbauer spectroscopy and electron microprobe analyses) were investigated during these experiments, especially :

- PyroxNaFe3 : 50% mole SiO<sub>2</sub>, 3% FeO, 21% CaO, 21% MgO, 5% Na<sub>2</sub>O
- PyroxNaFe1 : 50% mole SiO<sub>2</sub>, 5% Na<sub>2</sub>O, 1% FeO, 22% CaO, 22% MgO
- PyroxNaFe0.5 : 50% mole SiO<sub>2</sub>, 5% Na<sub>2</sub>O, 0.5% FeO, 22.25% CaO, 22.25% MgO
- And anorthite compositions (aluminosilicate)

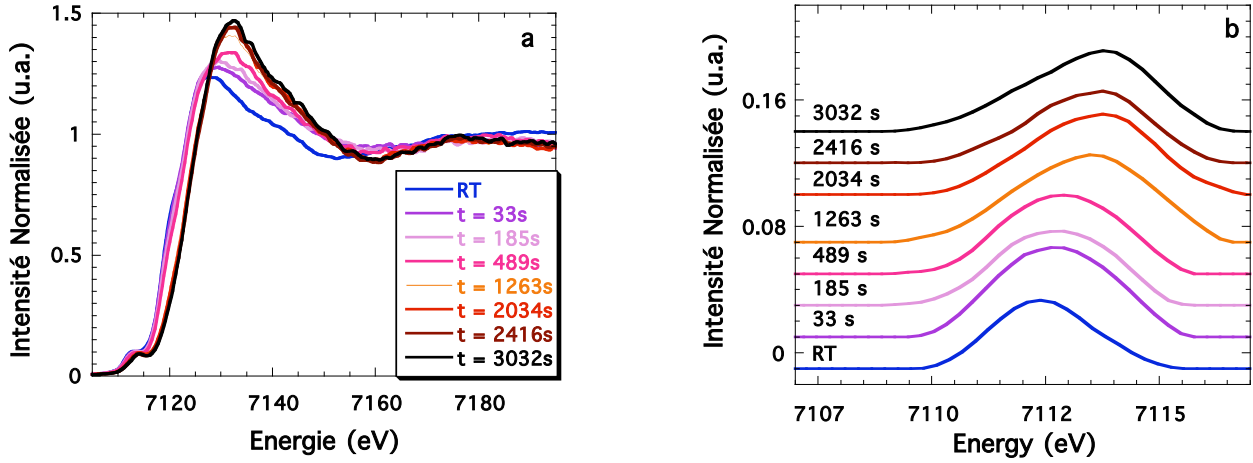
These experiments were complementary of those carried out on ID24 in March 2004 and on FAME in May 2004. Indeed, the studied compositions were in both cases Ca, Mg – bearing iron silicates, at high temperature and near the glass transition temperature. Interesting results were obtained to understand redox mechanisms near these two temperature ranges. Iron and alumina contents could have a significant influence on redox kinetics. Our objectives were thus to compare the results obtained from different compositions.

The two first shifts were used to align the beamline and set-up the experiment according to previous experiment. Some difficulties in the loading of the sample could be encountered due to the high content of iron in our glasses, so that a very small amount of powder should be introduced within the hole in the Pt wire.

To conclude, we have observed the oxidation of these compositions from 873K to 1123K.

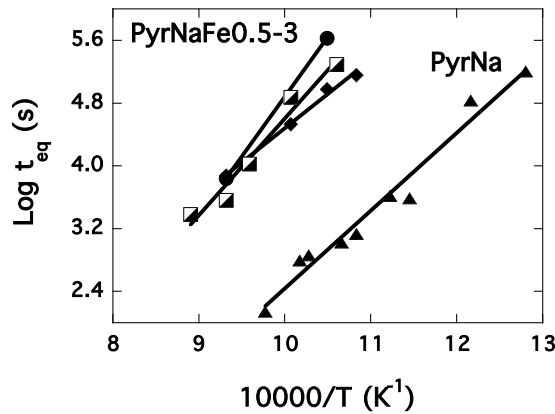
### Results:

Some interesting and promising results could be extracted from the XANES spectra obtained at Fe K-edge. In figure 1, XANES spectra obtained at 1123 K after different time for PyroxNaFe3 illustrate our results. By comparison, the spectrum at room temperature is shown too.



**Figure 1.** Left: Fe K-edge spectra obtained for the PyroxNaFe3 at 1123 K for different time until complete oxidation of Fe. Right: Zoom on the extracted pre-edge region showing the sensitivity in the position and intensity of the pre-edge, whose analysis allow the determination of iron redox and coordination state.

We observe modification of the pre-edge feature of the XANES spectra as a function of time, especially the progressive increase of a contribution at high energy (and a parallel decrease of the contribution at low energy), characterizing the oxidation state of our sample with time. Similar findings can be observed for the other samples and other temperatures. These observations indicate the evolution of redox ratios with time. Moreover slight differences between composition could be observed, indeed redox kinetics seem to be speed up by the increase of iron content.



**Figure 2.** Time required for the oxidation process upon the temperature for various compositions.

These promising results allow to derive some estimates for the time required for the oxidation process (figure 2) and to shed light on the interpretation for the implied mechanisms. Redox kinetics seem to be significantly fast near  $T_g$ , indicating probably a divalent cation diffusion as limiting mechanism. The same conclusion was obtained for redox kinetics in composition with 10 mol% of iron from previous experiments. A comparison with previous data and results obtained by other techniques should confirm this conclusion. Besides, these results illustrate also the suitability of BM30B beamline with its large beam for the study of redox kinetics, especially near  $T_g$ .

Some additional experiments near  $T_g$  are mandatory in order to investigate other compositions. Those information should be essential to complete the understanding of redox mechanisms and the influence of composition.