

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: 30-02-676
Beamline: BM30B	Date of experiment: from: 12May2004 to:17May 2004	Date of report:
Shifts: 15	Local contact(s): Dr. Jean-Louis HAZEMANN, BM30B, ESRF	<i>Received at ESRF:</i>
Names and affiliations of applicants (* 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		

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 present a two-fold advantage in that they allow not only to determine the redox coordination states of iron with the pre-edge feature but also to realize in situ measurements.

For this reason, we used a set-up of microfurnace 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 (1mm) and heated in different temperature stages. On each stages, several XANES were recorded according to time in order to follow oxidation reaction. Several compositions with different redox states (well characterized by chemical, Mössbauer spectroscopy and electron microprobe analyses) were investigated during these experiments, especially :

- Pyrox : 50% mole SiO₂, 10% FeO, 20%CaO, 20%MgO
- PyroxNa : 50% mole SiO₂, 5% Na₂O, 10% FeO, 17,5%CaO, 17,5%MgO
- PyroxLi : 50% mole SiO₂, 5% Li₂O, 10% FeO, 17,5%CaO, 17,5%MgO

Those experiments were complementary of those carried out on ID24 in March 2004. Indeed, the studied compositions were in both cases Ca, Mg – bearing iron silicates, but contrary to ID24, BM30 exhibits a relatively large spot, which offers the possibility to work on powder then to study redox kinetics for temperatures near glass transition (whereas the investigated temperature on ID24 were higher than 1273K).

The two first shifts were used to align the beamline and set-up the experiment. No significant problem have emerged during theses experiments. Nevertheless, we can note three remarks. At first, during the XANES acquisition, all the engines managing displacements of the table, monochromator or the detector must move

simultaneously. So some problems of synchronisation have been encountered which have deteriorated the quality of spectra. This was punctually solved by the change of temporization of some engines.

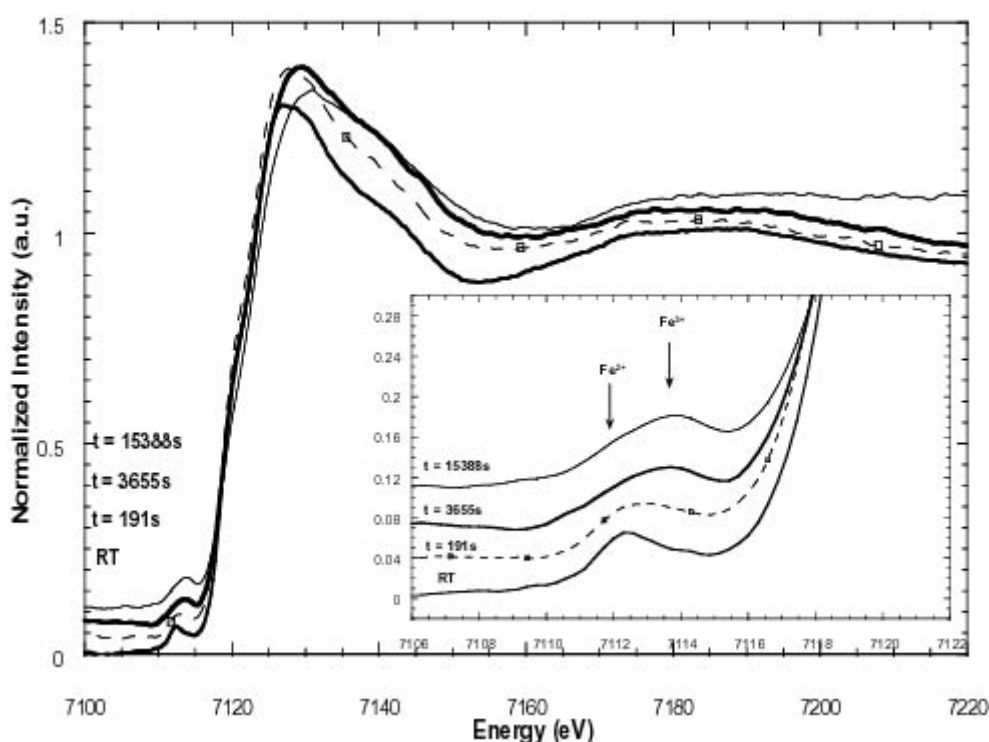
Moreover, some difficulties in the loading of the sample could be encountered due to the high amount of iron, then a very small amount of powder should be introduced.

Finally, for relatively high temperatures (above T_g) and very small granulometry, redox kinetics seem to be extremely fast and the set-up is not adapted for the following of fast reaction, acquisition time being too long. It could be improved by a change in the granulometry of our sample to slow down redox kinetics.

To conclude, we have observed the oxidation of these three compositions from 673K to 1073K.

Results:

Despite the fact that the major part of spectra was under treatment, some interesting and promising results could be extracted. In the following figure, three XANES spectra obtained at 781K according to time for PyroxNa could illustrate our results. By comparison, the spectra at room temperature is shown too.



Here we observe a change in the pre-edge of the XANES spectra as a function of time, especially the progressive increase of a contribution at high energy to the detriment of that at low energy, characterising the oxidation of our sample with time. Same features are observed for the majority of samples and temperatures. Moreover slight differences between composition could be observed, indeed redox kinetics in PyroxLi seem to be faster than in the others and those for Pyrox slower. Then those promising results let consider not only some estimates of the time required for the oxidation process and some interpretation on implied mechanisms, but a first basis of interpretation of the influence of composition on redox kinetics, especially the influence of the amount or the type of alumin element. Besides they illustrate also the use of BM30B beamline with this large beam for the study of redox kinetics, especially near glass transition.

Some additional experiments near glass transition are necessary in order to investigate other compositions, as alumin and borosilicate glasses. Those information should be essential to complete the understanding of redox mechanisms and the influence of composition.