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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: Fe K-edge XANES and EXAFS of natural and synthetic iron-bearing glasses	**Experiment number**: 08-01-691

Beamline: BM08	**Date of experiment**: from: 02-Oct-2004 to: 08-Oct-2004	**Date of report**: 29.10.2004
Shifts:	**Local contact(s)**: Francesco D'Acapito, Chiara Maurizio	*Received at ESRF:*

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Report:

Iron is the most abundant transition metal in the Earth's interior, even excluding the iron-rich core. Due to the lack of long-range order or symmetry constraints in molten silicate systems, Fe can be found in a variety of coordination environments ranging from tetrahedral, to pentahedral to octahedral and in both its bivalent and trivalent oxidation states. Naturally, both coordination number and oxidation state of iron can strongly influence the physical properties of magmatic liquids, even at low Fe concentrations, and thus it is important to characterize its structural environment in order to assess its influence on these properties.

While the Fe K-edge XANES pre-edge peak is considered the most indicative XAS feature describing the local environment surrounding iron as its energy position and intensity are correlated to oxidation state and coordination number, respectively, we also obtained excellent quality EXAFS data in order to be able to better distinguish different coordination polyhedra by modelling the Fe-O pair distribution function. The glasses were crushed and ground to powder form and mechanically mixed with celluose in an appropriate amount based on a rudimentary absorption calculation for both Fe K-edge XANES and EXAFS spectroscopy. We required no special sample environment such as controlled atmosphere or high (or low) temperature or high pressure conditions.

The glasses measured in our experiment covered a wide range of chemical composition. Synthetic glasses were either synthesized under normal atmospheric conditions or under controlled oxygen fugacity in order to vary the oxidation state of Fe. These glasses ranged from a moderately polymerized basaltic analog to a strongly depolymerized alkali-rich composition with varying amounts of Fe2O3 added. In addition, the effect of both the type and amount of halogen (F, Cl, Br, I) was investigated in a different suite of glasses in order to detect the possible presence of Fe-X (X=halogen) clusters, which are expected to strongly affect physical properties such as viscosity and density. In Fig. 1 below we show that the pre-edge peak is slightly affected by

the amount of Br added to the glass, as the proportion of Fe^{3+} appears to increase with increasing Br concentration, evident by the more intense peak near 7115 eV and the lack of a shoulder near 7113 eV, while more notable is the energy position of the main it exhibits a strong blue shift with increasing amounts of Br.

Fig. 1
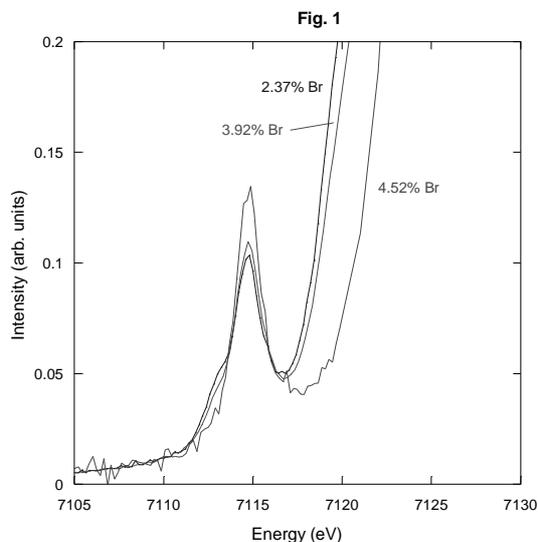
Several natural glass samples were also analyzed in this experiment, ranging from basanitic to phonolitic to trachyitic and rhyolitic compositions. Fe contents in these samples ranged from as low as 1 wt% Fe_2O_3 up to 13 wt%. Even for the lowest Fe content glasses and the relatively low beam current, we observed good signal to noise ratio in the spectra due to the multichannel fluorescence detector utilized at the beamline. This allowed us, for example, to characterize the Fe environment in a trachyitic glass (AMS) as a function of its dissolved water content (Fig 2). The anhydrous glass is characterized by a substantial proportion of Fe^{3+}, whereas, with increasing water content, the proportion of Fe^{2+} increases. This observation suggests that not only does the amount of water in the melt influence viscosity, but also the amount of iron as it becomes more ferrous and takes on a role as a network-modifying rather than network-forming type cation. Thus, viscosity models must take into account how iron oxidation state (and thus coordination environment) is affected by the presence of water.

Fig. 2