| ESRF | **Experiment title:** Pre-edge spectroscopy of iron in natural and synthetic glasses | **Experiment number:** 32-1-164 |
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| **Beamline:** BM 32 | **Date of experiment:** from: 12/02/2000 to: 15/02/2000 | **Date of report:** 29/02/2000 |
| **Shifts:** 09 | **Local contact(s):** Dr. J.L. Hazemann | *Received at ESRF:* |

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**Report:**

Nine shifts were allocated by the program committee on beam line BM 32, and started on Sunday, Feb. 13th in the morning, extending to Tuesday, Feb. 15th in the evening. A specific requirement for performing pre-edge spectroscopy was to use a Si 311 monochromator to achieve spectral resolution able to resolve the various components of the pre-edge. Changing the monochromator from a Si 111 to a Si 311 crystal also implies a non-focusing character of the beam, with a subsequent change in the optics of the beam line. Such modifications are very infrequent on beam line 32 and more than one shift was needed to perform the adjustments.

On Sunday evening, we were able to resolve correctly the pre-edge of andradite, a mineral in which the pre-edge of octahedral ferric iron is split into two overlapping components, which gives a good estimate of the spectral resolution actually achieve on the experiment. All the spectra were recorded in the fluorescence mode because of the low Fe content of the glasses. The samples had been previously prepared in our laboratory as polished slabs, the thickness of which was adjusted to allow about 10 percent of the beam to be transmitted, in order to record simultaneously the absorption edge of a metallic Fe foil for spectral calibration.However, the flux delivered by the Si 311 monochromator is too low as compared to that given by the Si 111 monochromator and we were obliged to record a reference sample between each glass investigated. The last measurements were made before Tuesday noon, in order to allow themonochromator to be changed in order to come back to the Si 111 focusing geometry used for EXAFS experiments. We have then used two useful days, a little more than six shifts. All measurements were made at room temperature.

The first set of samples consisted of synthetic glasses and reference samples in which only one oxidation state was present. We have obtained pre-edge spectra with a very good resolution and spectral features very well resolved. The systematic checking with a reference spectrum has shown that there is no chemical shift for one oxidation state. By contrast, there is a positive shift of 1.5 eV from ferrous to ferriccompounds, in agreement with previous experiments (Galoisy et al.,2000). Reference samples consisted of ferrous and ferric-bearing minerals, in which iron is in 4-, 5-and 6-coordination. Although 5-coordinated iron is a possible surrounding in silicate glasses, the pre-edge spectra have not yet been published for this peculiar coordination state. After this first set of samples, which has given us a unique dataset of reference pre-edge spectra of Fe in minerals and glasses, we have recorded spectra of two kinds of mixed valence synthetic and natural glasses. Synthetic mixed valence iron-bearing glasses consisted of samples synthesized under contrasted redox conditions. The low Fe content, 1 wt. %, hindered to get accurate redox data on these samples using other spectroscopic methods such as Mössbauer spectroscopy. The excellent spectral resolution achieved on BM 32 enables to determine redox data with accuracy at low Fe contents.We have been able to investigate five synthetic glasses with increasing ferrous to ferric ratio. Natural mixed valence Fe-bearing glasses consisted of one impact glass and five different volcanic glasses with a low Fe content (less than 1 wt.%). The first examination of the raw data show that impact glasses (tektites) only contain ferrous iron. The volcanic glasses investigated consisted of obsidians from different locations. Pre-edge spectra indicate that Fe-bearing clusters play a dominant role in iron speciation in volcanic glasses, showing the importance of a magnetite-like surrounding in the samples investigated. Here too, the excellent quality of the data, as well as the spectral resolution and the good signal to noise ratio, will allow to recognize the various contributions from ferrous and ferric ions in the glass structure and from magnetite clusters.

In conclusion, the data obtained on BM 32 show that there is no continuous chemical shift of pre-edge spectra of mixed valence samples as a function of the redox ratio, by contrast to what has been published based on data obtained under lower resolution conditions on other synchrotron radiation sources. On the contrary, variations in the redox ratio give rise to a bimodal distribution between the two oxidation endmembers, which opens the possibility of a quantification by fitting the spectral data using the contribution of these endmembers.

Fig 1

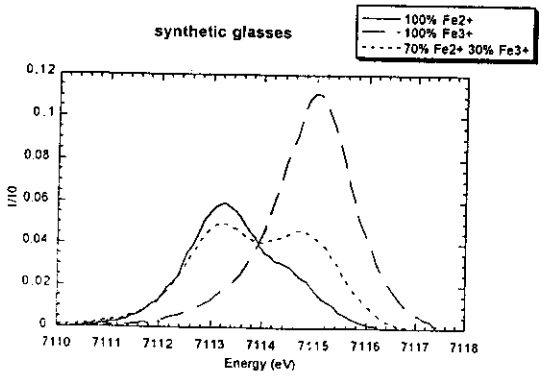


Fig 2

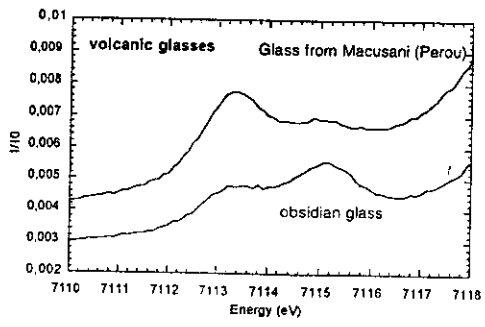


figure 1 : normalized pre-edge spectra of a synthetic glasses of the same composition but of different redox

figure 2 : Raw data for volcanic glasses