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### **Fe K-edge XANES of synthetic silicate glasses**

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### **6 shifts from 11-07-2007 to 13-07-2007**

Beam quality good. No technical problems regarding data acquisition.

### **No other beamtime on other beamlines**

### **Introduction**

XANES spectroscopy has been demonstrated to be very effective in determining oxidation state and coordination number of Fe (and other transition elements) in amorphous materials [1-4], by careful analysis of both the pre-edge and main edge regions of the spectrum. Here we examine the XANES spectrum of several synthetic Fe-bearing silicate glasses of varying bulk chemical composition and formed over a range of different oxygen fugacities. Analysis of the pre-edge region of the spectrum shows that systematic variations in both centroid position and intensity of the pre-edge peak can be correlated to compositional parameters and oxygen fugacity. With respect to the spectral features observed for crystalline standard compounds, these correlations allow us to determine how both the  $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$  and average Fe coordination number varies with chemical composition and  $f\text{O}_2$  in multicomponent silicate liquids.

### **Experiment**

Synthetic glass samples ranged in both base chemical composition (sodium disilicate NS2, haplogranitic HPG8, anorthite-diopside AnDi) and total Fe content (between 5 to 20 % Fe oxide component). Samples were crushed and ground to powder form and placed on a flat plate for Fe K-edge XANES spectroscopy. No special sample environment such as controlled atmosphere or high (or low) temperature or high pressure conditions were required. Relatively low Fe concentrations in the samples required that the spectra be collected in fluorescence mode using the high-purity 13-element Ge detector. Spectra of several Fe-bearing crystalline standards with known structure and oxidation state were also acquired in order to calibrate the energy and to model the edge shape (edge energy, white line energy, intensity and width, pre-edge peak energy and intensity) according to Fe coordination number and oxidation state.

### **Results**

For each chemical composition, as many as four different samples ranging in oxygen fugacity at which the glass was formed was examined by Fe K-edge XANES spectroscopy. An example set of data showing baseline corrected and normalized intensities of the pre-edge region is shown in Fig. 1. With decreasing  $f\text{O}_2$ , the centroid position of the pre-edge shifts to lower energy and the intensity of the pre-edge peak also decreases. This behaviour is consistent regardless of chemical composition, and can be interpreted in general as both a decrease of the  $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$  and an increase in the average Fe coordination number. Using a distribution map of Fe species ranging between ferric and ferrous with coordination numbers ranging from [IV] to [V] to [VI] based on the centroid

positions and intensities of crystalline standards, we are able to model the local Fe environment in the multicomponent glasses (Fig. 2). As expected, with decreasing  $fO_2$ , the centroid positions shift to lower energies, indicating a greater abundance of ferrous iron. Using mixing curves generated from the numerical averaging of spectral parameters for each Fe species, we can estimate both the oxidation state and average coordination number of Fe for each series as a function of  $fO_2$ . Correlations between chemical parameter, as alkalis and alkaline earth content, and local iron environment have also been revealed.

Fig. 1. Pre-edge spectral region of anorthite-diopside glasses containing 5 wt%  $Fe_2O_3$ , synthesized at various oxygen fugacities. Decreasing  $fO_2$  is indicated as the color of the data goes from blue to red to green to violet.

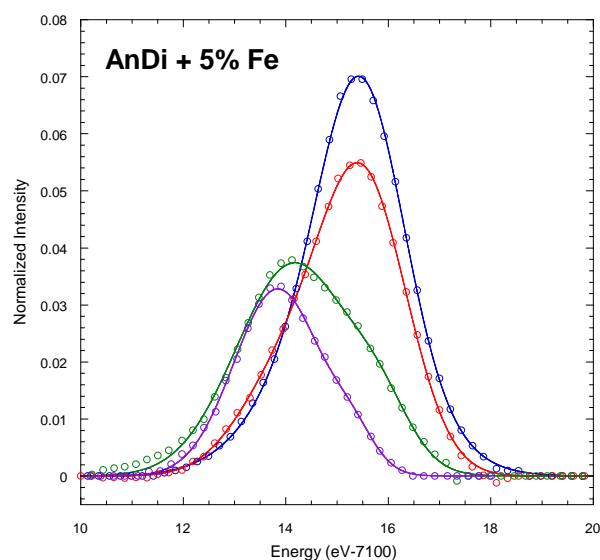
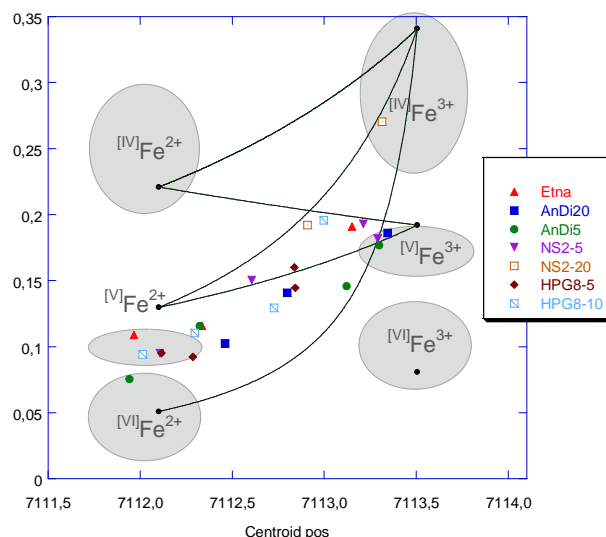


Fig. 2. Fit results of centroid positions and intensities of Fe K pre-edges for all glasses. Mixing lines (solid black lines) are shown between selected pairs of Fe species. The glass data indicate that at oxidizing conditions Fe has a high  $Fe^{3+}/Fe_{tot}$  and average coordination number near 5 (Fe-rich NS2 shows more tetrahedral character). With decreasing  $fO_2$ , as the concentration of ferrous iron increases, average Fe coordination also increases to ca. 5.5



## Future Perspectives

Additional XANES data over a wider range of chemical compositions would allow us to predict how Fe behaves in a variety of geochemical environments. A developing model for the characterization of the local structure surrounding Fe and other transition elements in amorphous materials complemented by independent Fe redox measurements would also allow us to predict the rheological and other physical properties of magmatic liquids in a range of volcanological settings, as these properties have been shown to be intimately correlated to the variability of the structural

environment of Fe. As Fe oxidation state and coordination are also linked to the presence and amount of dissolved H<sub>2</sub>O in silicate liquids, it is also important to characterize hydrous Fe-bearing glasses using XANES spectroscopy.

### **References**

1. Galois, L., Cals, G., Arrio, M.A., 2001. *Chemical Geology*, 174, 307-319.
2. Wilke, M., Partzsch, G.M., Bernhardt, R., Lattard, D., 2005. *Chem. Geol.* 220, 143–161.
3. Berry, A.J., O'Neill, H.S.C., Jayasuriya, K.D., Campbell, S.J., Foran, G.J., 2003. *Am. Min.* 88, 967–977.
4. Métrich, N., Susini, J., Foy, E., Farges, F., Massare, D., Sylla, L., Lequien, S., Bonnin-Mosbah, M., 2006. *Chemical Geology*, 231, 350-363.

### **Publications**

None currently

### **Conferences**

None currently