

Report of ID: HD 259

Beamline: ID24

Title: QUANTITATIVE DETERMINATION OF THE KINETICS OF IRON REDOX REACTIONS IN SILICATE MELTS: THE EFFECTS OF ALUMINUM

The aim of this experiment was to obtain quantitative information on the kinetic of iron redox reactions in oxide glasses and melts. X-ray absorption spectroscopy (XAS) is a well suited technique to determine the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio in function of time by analysing the pre-edge feature and the position of the edge. The knowledge of redox reactions is necessary to control the vitrification processes and to predict the structural changes intervening in temperature within glasses and melts.

We have spent 6 days on ID24 beamline between Mai 07 and Mai 13 to investigate XANES at the Fe K-edge on alumino- boro-silicate glasses and melts (18 shifts allocated, 16 used, 2 loosed due to beam problems and/or beamline defect components; see below). Several compositions with different redox states (well characterized by chemical and electron microprobe analysis) were investigated during these experiments. The set of composition started from NS2Fe5 (63 mol% SiO_2 ; 31 mol% Na_2O ; 5 mol% FeO) to which different amounts of boron or alumina were added until the compositions NBF5 (64 mol% SiO_2 ; 13 mol% Na_2O ; 5 mol% FeO ; 18 mol % B_2O_3) or NAF5 (64 mol% SiO_2 ; 13 mol% Na_2O ; 5 mol% FeO ; 18 mol % Al_2O_3). To obtain various $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ratio, the glass samples were prepared under controlled atmosphere. These experiments are complementary of the work made by Magnien et al (2004, 2006, 2008) where they investigate the kinetics and mechanisms of redox reactions for simple silicate system (Si, Na, Mg, Ca, Fe, O). These experiments were devoted to have a better knowledge of the redox reactions in boro- and alumino-silicate glasses and melts where boron and alumina can play an important role as network formers in tetrahedral coordination similar at those observed for Fe^{3+} . Our objectives were thus to compare the results obtained from different compositions.

Samples were heated in our furnace, developed by Richet et al. (1993) and already used at the LURE D44 beamline, ESRF ID24 beamline (Magnien et al., 2004, 2006, 2008), SOLEIL ODE beamline and SLS LUCIA beamline (Neuville et al. 2007). This set-up consists of a Pt-10%Ir wire with a hole in which the sample is loaded. With this furnace, samples can be heated up to 1900°C. For each temperature stage, several XANES spectra were recorded according to time, in order to follow kinetics of redox reactions.

The two first shifts were used to align the beamline and set-up the experiment. At some times, several problems have emerged during the experiment preventing us to obtain good XANES spectra:

- 1) Due to the small beam size, sample homogeneity is a crucial parameter that we had first to solve. Using powder does not allow the acquisition of a good enough signal resolving the Fe^{2+} and Fe^{3+} contributions in the pre-edge. This was solved by melting and quenching the sample rapidly to have a glass with a homogeneous surface within the furnace hole.
- 2) The sample loading in the wire hole was extremely difficult due to the complicated control of the sample thickness in order to optimize the absorption condition
- 3) Due to defects in the Si220 mirror, some of the recorded XANES spectra contains glitches that prevent us to determine the evolution of the redox ratio, especially when the glitches were situated on the pre-edge feature (see figure 1).

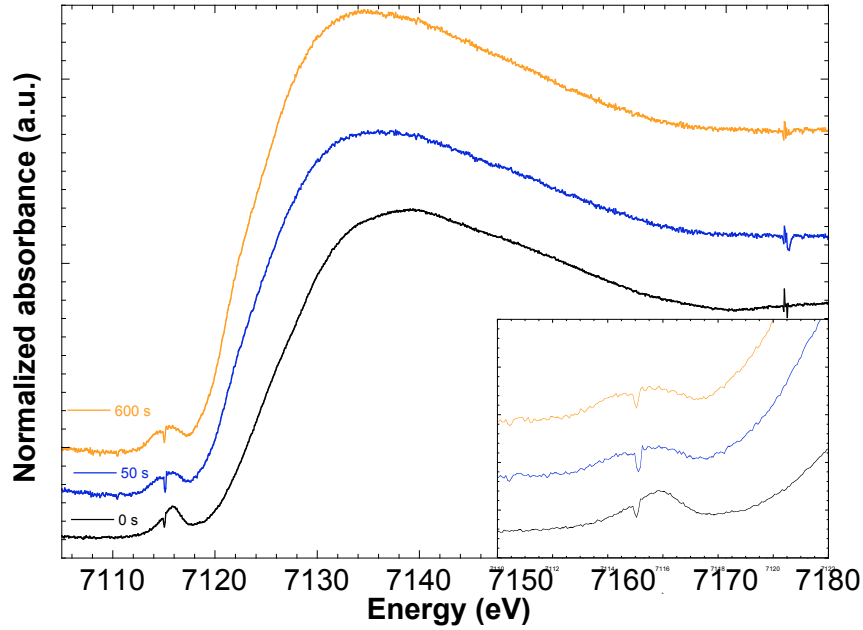


Fig 1. Xanes spectra that contains glitches

In spite of those problems and of the two shifts loosed due to a beam stop and to a failure in the cooling system of the mirrors beamline, we obtained some encouraging results.

Results:

For the silicate and aluminosilicate compositions some interesting and promising results could be extracted from the XANES spectra obtained at Fe K-edge. In figure 2, XANES spectra obtained at 1273K at different time for NAFe5 illustrate our results.

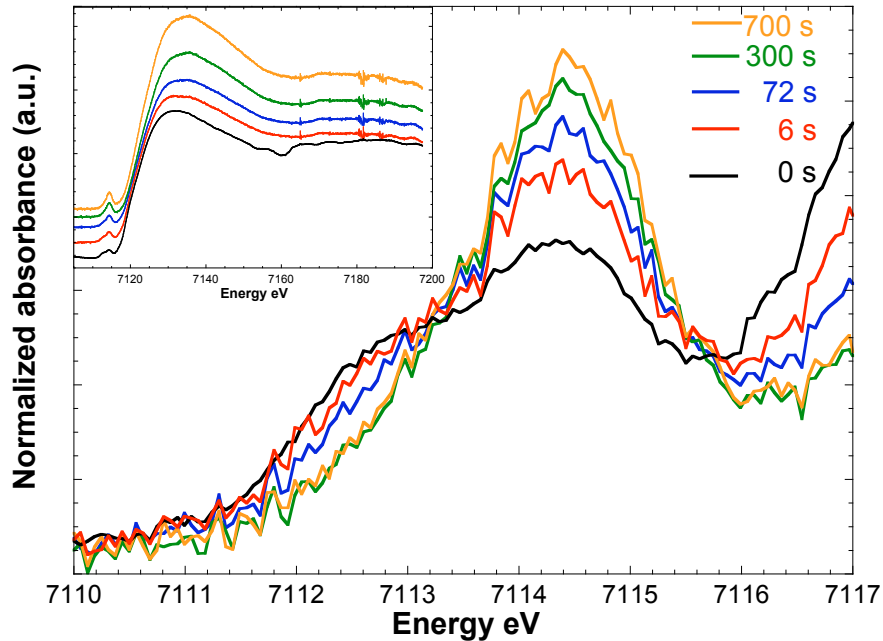


Fig 2. Evolution of the pre-edge of XANES spectra with time for a reduced NAFe5 melt heated at 1273 K in air; experiments made on the ID24 beamline at ESRF. (In the insert are shown entire XANES spectra)

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. It was possible to determine the evolution of the redox ratio over the time. Similar findings can be observed for the other silicate and aluminosilicate samples. These observations indicate the evolution of redox ratios with time. Whereas we observe progressive changes in the pre-edge feature of the XANES spectra as a function of time for silicate and aluminosilicate compositions, similar changes were hardly seen for the borosilicate compositions. It seems that boron play a particular role in the redox kinetics: they seem to be faster and in a shorter redox range. But the lack of time prevents us to obtain results leading to the characterization of the redox ratio evolution similar as for the silicate and the aluminosilicate glasses. We need further experiments to understand better the redox reactions in boron containing glasses. In particular, a new set of experiment with glasses containing different amount of boron will allow us to determine the role playing by the boron.

Conclusion

During these experiments, we observe that the sample chemical composition influences the iron redox kinetics (all our sample are 5 mol% of iron), in particular the ratio Si/Al. The results would be valuable to determine the influence on the redox kinetics of the network forming (Si vs Al) or network modifying (Na vs Ca) elements constituting the glass and melt structure. The results obtained during this experiment are very promising and the data are currently under treatment to extract information. The experiment feasibility was demonstrated successfully. The identified difficulties were or will be fixed. The present results give us some experimental reaction time required for oxidation process control in silicate and aluminosilicate glasses. However, due to the rapidity of some of the experiments, an exact determination of the process has not been obtained at the highest temperatures and also for boron containing composition. To pursue these kinetic X-ray absorption spectroscopy investigations and to obtain needed insights on the redox reaction in boron containing glasses as well as in chemically more complex silicate, we will ask for new shifts on ID24 beamline at the next proposal submission.

References:

- Magnien V., Neuville D. R., Cormier L., O. M., Pinet O., Briois V., Belin S., and Richet P. (2004) Kinetics of iron oxidation in silicate melts: A preliminary XANES study. *Chem. Geol.* 213, 253-263.
- Magnien V., Neuville D. R., Cormier L., Roux J., Pinet O., and Richet P. (2006) Kinetics of iron redox reactions: A high-temperature XANES and Raman spectroscopy study. *J. Nucl. Mater.*
- Neuville D.R. Cormier L., Flank AM, de Ligny D., Roux J. and Lagarde P. (2007) Local environment of light element in melts : a XANES spectroscopy study. *Amer. Mineral.*, sous presse.
- Richet, P., Gillet, P., Pierre, A., Bouhifd, A., Daniel, I., and Fiquet, G. (1993) Raman spectroscopy, X-ray diffraction, and phase relationship determinations with a versatile heating cell for measurements up to 3600 K (or 2700 K in air). *J. Appl. Phys.*, 74, 5451-5456.