



Experiment Report Form



Experiment title:

Redox evolution with temperature and atmosphere for low iron content alkali and earth-alkali silicates

Experiment

number:

EC 828

<p>Beamline: DUBBLE- BM26A</p>	<p>Date of experiment: from: 15 July 2011 to 21 July 2011</p>	<p>Date of report: 31/08/2012</p>
<p>Shifts: 18</p>	<p>Local contact(s): Dr. Sergei Nikitenko, BM26, ESRF</p>	<p><i>Received at ESRF:</i></p>

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Rapport:

The aim of this experiment was to obtain quantitative information on the structure and oxidation state of iron in silicate glasses and melts at different PO₂ and temperatures, for low iron content systems. X-ray absorption spectroscopy (XAS) is well suited to measure the Fe²⁺/Fe³⁺ ratio in the glasses and the melts by analysis of the pre-peak feature and the position of the K edge. Oxidoreduction reactions which take place during the melting process due to the evolution of PO₂ environment and temperature are very important for the final properties of the material. Current knowledge of the kinetics and mechanism underlying oxidoreduction reactions when iron is present as a trace element is quite poor.

In this work we have used X-ray absorption spectroscopy to the K-edge of iron, in fluorescence mode, to study redox equilibrium and kinetics in alkali and earth-alkali silicates with an amount of Fe₂O₃ comprised between 150 ppm and 5000 ppm. Those systems are representative of the most common industrial soda lime silicate glasses

Two types of measurements were conducted:

1. Redox measurements at room temperature on samples, with different iron contents, previously equilibrated with different T and PO₂ conditions;
2. In situ kinetic measurements on the redox evolution with T and PO₂ of samples heated in our new micro furnace with controlled atmosphere. This set-up consists of a Pt wire, with a 1mm diameter hole approximately, where the sample is loaded and can be heated up to 1900°C by Joule effect. The system is then placed inside a closed enceinte in order to control the atmosphere. We have used Ar, Ar/H, N₂, and O₂. The first beam time shift was used to align the beam line and set-up the experiment.

During the room temperature experiments we have observed and quantified for the first time on a glass sample a photoreduction effect of iron by the X-ray beam:

On figure 1, we show the change on the pre-edge of the XANES spectra at the Fe K-edge as a function of time, at room temperature. It is clearly visible that this photoreduction effect by the beam is directly correlated with the total iron content of the sample.

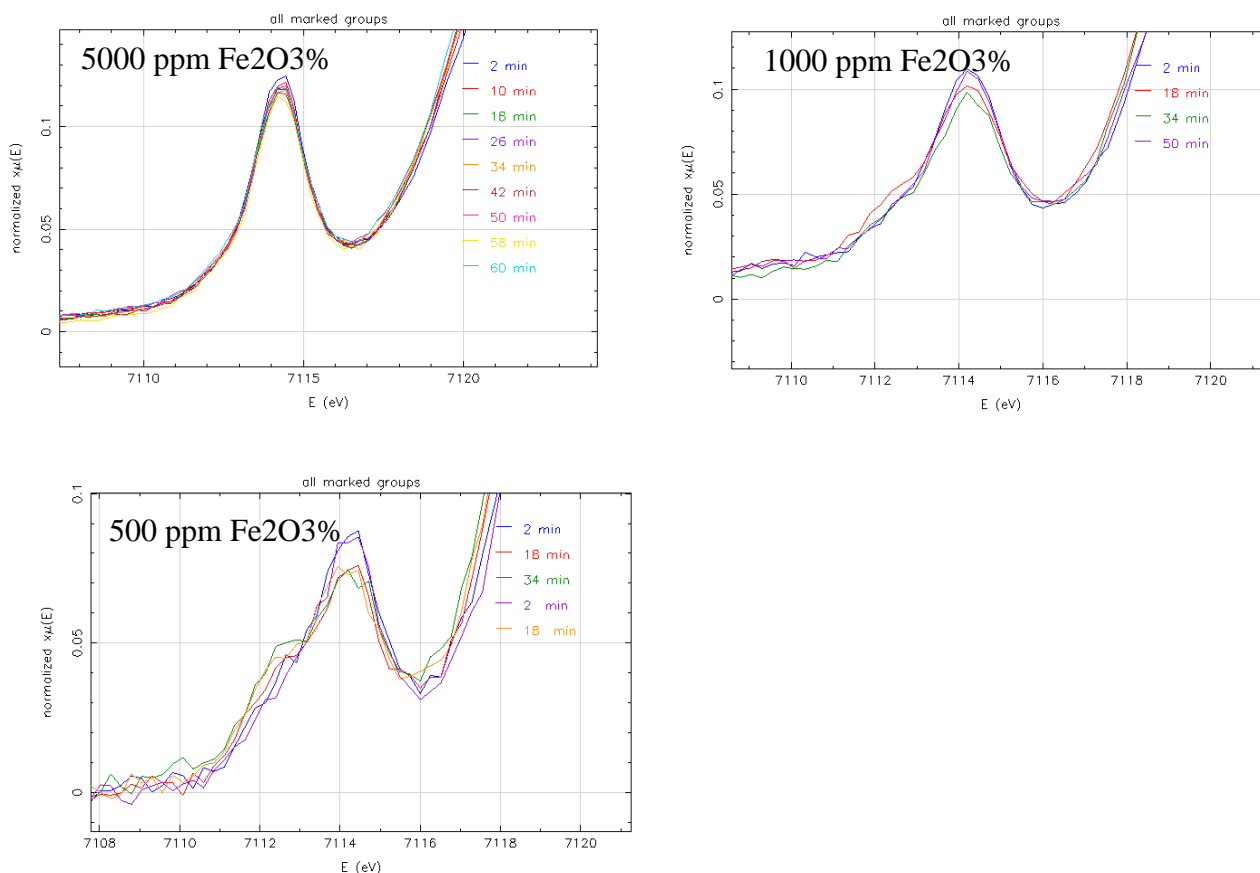


Figure 1 –Evolution of the pre-peak region and edge with acquisition time for the same glass with different iron content: a) 5000 ppm, b) 1000 ppm and c) 500 ppm. A reduction of iron is observed as time increases. This phenomenon becomes more pronounced when the iron content of the sample diminishes (Gonçalves Ferreira et al., 2012).

The kinetics of redox reduction by the beam for the three samples is shown in figure 2.

Redox values were computed using the ratio $A_{Fe^{2+}}/(A_{Fe^{2+}}+A_{Fe^{3+}})$ of the deconvoluted areas of Fe²⁺ and Fe³⁺ in the spectra. The redox is obtained from deconvolution of the XANES spectra following previous works (Magnien et al., 2004, 2008). At 5000 ppm redox increased by 2% after 2 hours of exposure of the sample to the X-ray beam. For the 5000 ppm sample the redox variation is almost negligible. At 1000 ppm the redox variation is of the order of 40%, with an increase from a redox value of 0.23 to 0.34 in only 50 minutes. Finally, for the 500 ppm sample the redox varies from 0.35 to 0.5, corresponding to an increase of 40% after only 34 minutes of acquisition time.

For this last sample we have displaced the beam spot on the sample by 3 mm and we have observed the same photoreduction effect in the first two spectra measured with 16 minutes of interval. This indicates that the measurement is reproducible and that the result depends on the time of exposition of the sample to the X-ray beam.

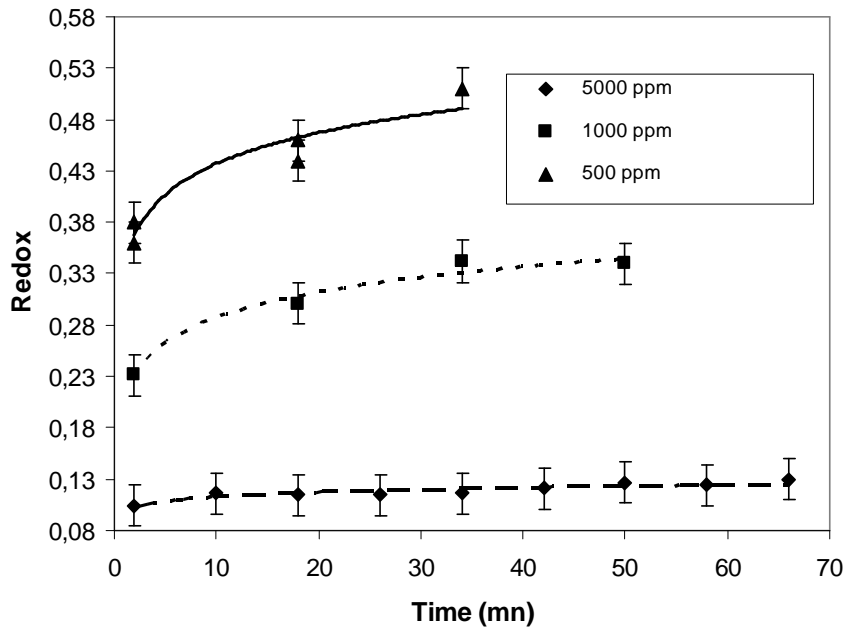


Figure 2 –Kinetics of photoreduction by the X-ray beam for samples with 500 ppm (solid line), 1000 ppm (dotted line) and 5000 ppm (long dashed line) of Fe_2O_3 %. The phenomenon increases when the amount of iron diminishes (Gonçalves Ferreira et al., 2012).

Our results show that photoreduction is amplified when iron is present as a trace element. For the silicate melts of geochemical interest that have been studied so far in previous works by different authors the total amount of iron is such that $Fe_2O_3 \geq 5000$ ppm (0,5% wt) and this effect doesn't need to be taken into account. However for the glasses we are interest in this study, photoreduction by the X-ray beam has a crucial impact on the redox measurements at room temperature.

Using the Cyberstar gas blower the samples were heated and new spectra were measured by analysing the sample with 540 ppm iron, collecting one spectrum every 8min while increasing the temperature at a rate of 10°C/min from room temperature up to 500°C. The pre-edge of the normalised spectra after 2, 34 and 90 minutes have been analysed to compute the redox value. Those spectra correspond respectively to temperatures of 25°C, 50°C and 500°C. The redox values obtained at different times and temperatures have been computed and these are plotted in Figure 3.

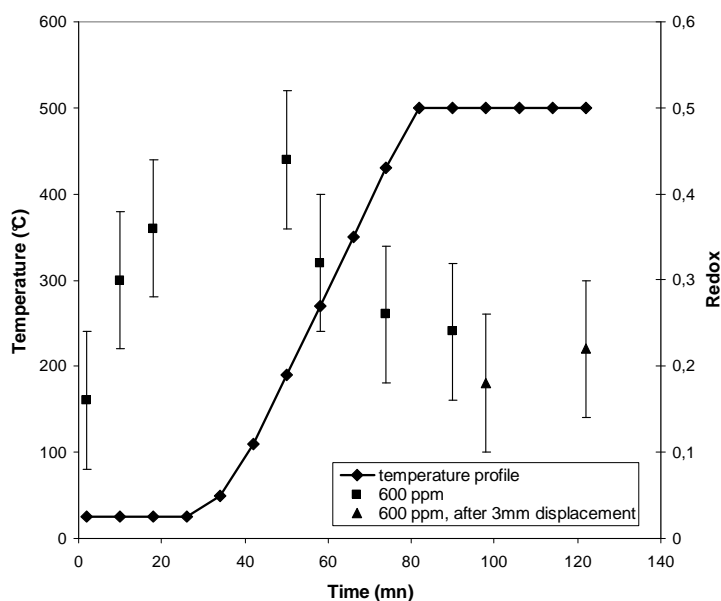


Figure 3 – Evolution of the redox with time and temperature for the sample with 500 ppm iron. The photoreduction effect disappears when the measurements are made at a temperature of 500°C.

We first observe an increase in redox due to the photoreduction effect of the X-ray beam. Then, as the temperature exceeds 200°C, the redox decreases and stabilises around its initial value. After 98 minutes, the beam spot has been moved by 3mm to hit another part of the sample and the measurements at 500°C have been repeated: the initial redox state was again measured. From this experiment, we can conclude that the photoreduction effect is reversible and can be prevented by making the measurements at temperatures between 450 and 500°C, instead of room temperature.

The photoreduction effect is reversible and can be avoided when the measurements are made at a temperature of 450°C-500°C instead of room temperature. A possible mechanism of this phenomenon would be the production of localised defects in the glass matrix by the X-ray photons. Those defects would provide the charges needed for electron exchanges with neighbouring Fe atoms responsible by the redox changes. Relaxation of these defects would be enabled by a temperature increase that would stop this phenomenon. The nature of the defects D/D+ created by the X photon interaction with the matrix and responsible for the redox changes could be O²⁻/O⁻ or Na⁺/Ca²⁺.

This effect was even more important in a previous series of experiments at FAME in July 2010 (experiment 30-02 966) where the flux of photons was of 10⁷ per second and per μm² a value high enough such that within the acquisition time of a single spectrum complete reduction of the sample was already attained. At BM26 the flux of photons of 8,3x10⁴ per second and per μm² is low enough to enable the phenomenon to be observed between a series of successive spectra within the counting times needed. Within our error bars the same amount of iron is reduced by the beam regardless of the iron content of the sample.

The analysis and interpretation of our data took us some time, which contributed to the delay in this report.

However, this work was accepted for publication in *Chemical Geology* (*Gonçalves Ferreira et al., 2012*) and is in this moment under press.

Our work was also appreciated during several scientific meetings and will be continued by a PhD thesis (French ANRT funds) to start beginning 2013.

References :

Magnien V., Neuville D.R., Cormier L., Mysen B.O. 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., Hazemann J-L., de Ligny D., Pascarelli S., Vickridge I., Pinet O. and Richet P. (2008) Kinetics and mechanisms of iron redox reactions in silicate melts: The effects of temperature and alkali cations. *Geochim. Cosmochim. Acta.*, 72, 2157-2168

Gonçalves Ferreira P., de Ligny D., Lazzari O., Jean A., Cintora Gonzalez O. and Neuville D. R. (2012) X-ray effect on the equilibrium redox state of iron-bearing earth alkali silicate glasses. *Chemical Geology* (in press)