

# Redox Reaction In Silicate Melts Monitored By “Static” *In-Situ* Fe K-edge XANES Up To 1180°C

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**Abstract.** A new experimental setup to measure *in-situ* kinetics of redox reactions in silicate melts is presented. To study the progress of the Fe-redox reaction, the variation of the signal is recorded at an energy, where the difference between the spectra of the oxidized and reduced Fe in the melt is largest (“static XANES”). To control the redox conditions, the gas atmosphere could be changed between to types of gases using computer-controlled valves (N<sub>2</sub>:H<sub>2</sub> and air, respectively). In this way, a number of reduction/oxidation cycles can be monitored *in-situ* and continuously. Applied at the Fe K-edge in molten silicates, we obtained a set of high quality data, which includes the very first steps of the redox reaction. An Avrami-type equation is used to investigate rate-controlling parameters for the iron oxidation/reduction kinetics for two melts (basaltic and Na trisilicate) for temperatures up to 1180°C.

**Keywords:** redox, iron, melt, equilibria, kinetics

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## INTRODUCTION

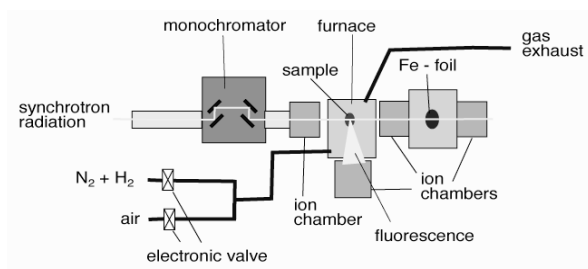
The kinetics and mechanism of redox reactions of iron in silicate melts are still under debate, e.g. [1], [2]. As XANES is sensitive to the oxidation state of a given element it is possible to unravel the rate-controlling parameters and mechanism of redox reactions, using *in-situ* high temperature XANES. We developed a new method to monitor the oxidation and reduction process in silicate melts that we may call here “static XANES”, since the monochromator is not moved during these measurements but tuned to a specific energy where the difference of the XANES for the reduced and oxidized Fe in the melt is largest.

## EXPERIMENTAL

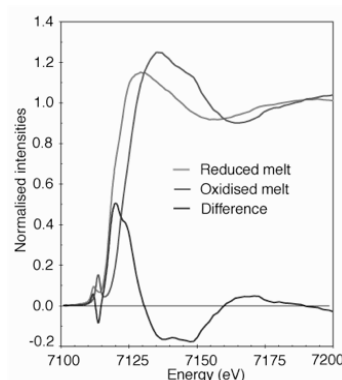
A furnace designed for high temperature *in-situ* XANES [3] was used. The furnace consists of an electrically heated PtRh-wire placed in a gas-tight

aluminum housing. Samples are placed directly on the PtRh-wire. For temperature control, a thermocouple is in contact with the molten sample. The incoming beam and the fluorescence radiation pass through windows made of Mylar foil. Oxidizing and reducing conditions are imposed by flushing the furnace with air or with mixtures of H<sub>2</sub> and N<sub>2</sub>, respectively (Fig. 1).

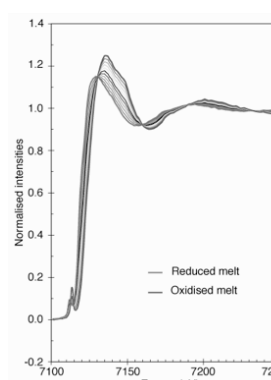
Reactions that take place within a couple of minutes, and that are reversible, may be studied using a technique, that we may call here “static” XANES. Instead of scanning quickly the monochromator energy while the reaction is proceeding (Quick-XANES), the change in the signal during a reaction and its back-reaction is recorded at a fixed energy. After completion of one cycle (reaction and back reaction) a further energy position may be set and the reaction cycle repeated. This can be repeated for several energy positions. For determining the reaction rate with high sensitivity, the energy position should be in the range where the difference in the spectra of the two end-



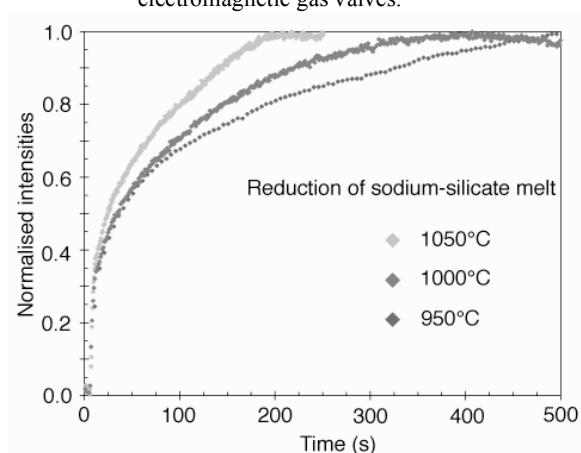
**FIGURE 1** The XAFS spectrometer setup used for the *in-situ* measurements. The signal was collected in fluorescence mode using a Lytle-detector. The reaction can be started in a controlled way by switching the electromagnetic gas valves.



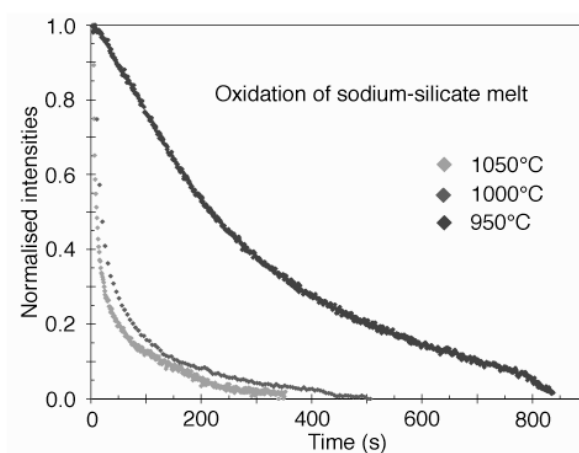
**FIGURE 2** Normalised Fe K-edge XANES of Fe in Na-silicate melt under oxidizing and reducing conditions. The difference is largest at 7122 eV.



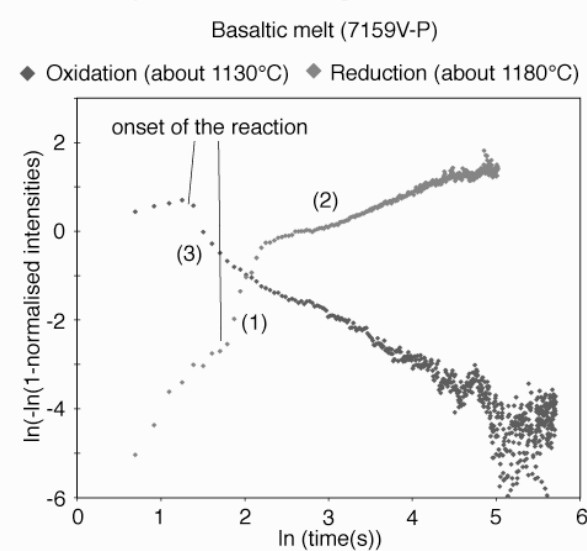
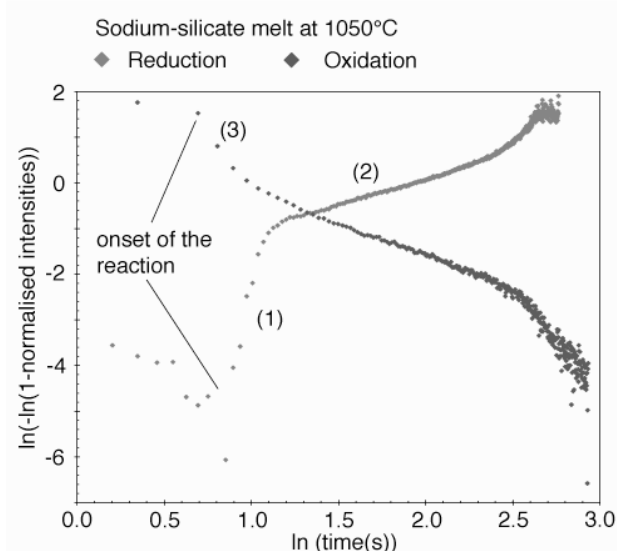
**FIGURE 3** XANES of melts with mixed ferric-ferrous ratios calculated from Fig. 2



**FIGURE 4** Changes in the intensity at 7122 eV as a function of time during reduction of iron-doped sodium-silicate melt.



**FIGURE 5** Changes in the intensity at 7122 eV as a function of time during oxidation of iron-doped sodium-silicate melt



**FIGURE 6** Avrami-type plots of the time-dependant variations obtained for the iron-doped sodium-silicate melt at 1050°C (left) and basaltic melt at 1180°C (right).

member oxidation states is largest (Fig. 2). The data were collected at the Hamburger Synchrotronstrahlungslabor (HASYLAB). A Si (111) four-crystal monochromator was used, providing a very high-energy resolution ( $E/\Delta E = 12200$  or  $0.5$  eV at  $6$  keV). We used this technique to study the oxidation and reduction of a sodium-silicate melt ( $\text{Na}_2\text{Si}_3\text{O}_7$  doped with  $5$  wt.%  $\text{Fe}_2\text{O}_3$ ) and a basaltic melt (ca.  $13$  wt%  $\text{Fe}_2\text{O}_3$ ).

## RESULTS

Using the normalised Fe K-edge XANES of the reduced and oxidized melt, the variation of the XANES for melts with varying ferric-ferrous ratios can be calculated (Fig. 3). The change of intensity at the “most sensitive” energy position for the reaction is a linear a function of the calculated mixture.

The redox reactions in sodium-silicate and basaltic melts proved to be reversible. So, several cycles of oxidation and reduction of a single sample could be performed at different temperatures for both types of melts (Fig. 4). The reaction progress was successfully monitored in both directions yielding an exponential increase and decrease of the signal during reaction. The observed variations of the signal as a function of time are complex and no simple (e.g) exponential function could be fitted to the observed curves. This indicates that rather complex reaction processes occur that lead to the observed variation trend. Both oxidation and reduction of silicate melts are fast and are completed within  $10$ - $15$  minutes at the temperatures investigated. Reduction and oxidation seem to follow different reaction mechanisms, as the variation trends of the two processes are different.

## DISCUSSION

In order to determine rate-controlling parameters, the kinetics may be investigated using the Avrami law in its linearized form [4]:

$$\ln(-\ln(1-X)) = n \ln(t) + \ln(Z) \quad (1)$$

in which  $X$  is the reaction progress,  $Z$ , the rate constant,  $n$  is a mechanistic constant and  $t$ , the time.

In Avrami diagrams (see Fig. 6), different reaction mechanisms are discernable by different straight segments of the plotted function. Reduction of iron in both compositions is characterised by at least two

different mechanisms a very fast one (1) followed by a second mechanism (2). The Avrami plots of the oxidation cycles are different to the reduction cycles, especially at the beginning of the reaction: the first part after the onset of the reaction shows significant curvature (3).

## POSSIBLE SOURCES OF ERROR

Changes of the intensity may not only display changes in the oxidation state, but also changes in the sample geometry. It is therefore very important that the melt remains stable on the loop, without any motion (including thermally induced movements of the heating loop). However, since physical properties of silicate melts (such as viscosity and interface (wetting) behavior) change strongly with the iron oxidation state, it is quite possible that sample movements occur. We could observe, for example, that the reduced basaltic melt creeps up the thermocouple. For the time-resolved measurements with the basaltic composition we had to remove the thermocouple from the melt. For in-situ measurements on silicate melts, an optimum control of the heating sample holder is crucial.

## CONCLUSIONS

Fast reactions can be followed *in-situ* at high temperatures using “static” XANES, only limited by the sampling rate of the electronics. Redox reactions in silicate melts using hydrogen as reducing agent are reversible within tens of minutes. Oxidation and reduction reactions in this particular experimental setup seem to follow different structural mechanisms but remains reversible and cyclic.

## ACKNOWLEDGMENTS

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