Kinetics of iron redox reaction in silicate melts: A high temperature Xanes study on an alkali basalt

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Kinetics of iron redox reaction in silicate melts: A high temperature Xanes study on an alkali basalt

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Abstract. In Earth and Materials sciences, iron is the most important transition element. Glass and melt properties are strongly affected by iron content and redox state with the consequence that some properties (i.e. viscosity, heat capacity, crystallization...) depend not only on the amounts of Fe²⁺ and Fe³⁺, but also on the coordination state of these ions. In this work we investigate iron redox reactions through XANES experiments at the K-edge of iron. Using a high-temperature heating device, pre-edge of XANES spectra exhibits definite advantages to make in-situ measurements and to determine the evolution of redox state with time, temperature and composition of synthetic silicate melts. In this study, new kinetics measurements are presented for a basalt melt from the 31,000-BC eruption of the Puy de Lemptegy Volcano in France. These measurements have been made between 773 K and at superliquidus temperatures up to 1923 K.

1. Introduction

Introduction of transition metals in silicate glasses and melts generally induces complex changes in structure and physical properties. Not only two or more valence states coexist, each having its own structural role, but also their relative abundances depend on temperature, pressure, silicate composition and oxygen fugacity (e.g., [1]). Because iron is the most common transition metal in either natural or industrial silicate glasses, the difficulties originating in these possibly complex variations must be resolved to arrive at a better understanding of magmatic processes or to optimize vitrification and glass properties. Iron redox reactions in silicate melts have mainly been investigated from a thermodynamic standpoint. Thanks to an experimental redox database that is now extensive, reliable models of calculation of Fe³⁺/ΣFe as a function of temperature, melt composition and oxygen fugacity have been set up either empirically [2] or thermodynamically [3]. In contrast, the kinetics and mechanisms of these reactions still raise basic questions. In the first studies performed at superliquidus temperatures, the redox mechanisms were reported to be rate-limited by diffusion of oxygen either as
molecular O² or as O² ions [4,5]. Near the glass transition range, however, experiments on aluminosilicates have indicated that the limiting factor is diffusion of divalent cations (Ca²⁺, Mg²⁺, Fe²⁺) from the redox front to the surface, where a thin layer of crystalline material precipitates, accompanied by a counter flux of electron holes [6,7,8]. Understanding of redox processes in silicate melts has been hindered by a lack of in situ determinations of their kinetics as a function of temperature and melt composition. In previous papers, we have shown that the kinetics of iron redox reactions can be investigated by in situ X-ray absorption Near-Edge Structure (XANES) and Raman spectroscopies [9,10,11]: Determinations of the iron redox state for three synthetic pyroxen glass compositions have shown that the mechanisms of the redox reaction strongly depend on temperature. Under nonequilibrium conditions, diffusion of metal cations in supercooled liquids operates, as previously described in detail by Cooper and co-workers, and the presence of fast moving alkali cations enhances the kinetics of the redox reaction. Under equilibrium conditions, crystallization of metastable phases above the liquidus at the melt-atmosphere interface is no longer possible so that the kinetics is controlled by oxygen diffusion. In this new study, we have used the sensitivity of XANES to the Fe³⁺/ΣFe ratio to determine redox kinetics near the glass transition range as well as at superliquidus temperatures for a natural system, that is an alkaline basalt.

2. Experimental methods

2.1. Samples

Basalt samples from the 31,000-BC eruption of the Puy de Lemptegy Volcano in France, Chaîne des Puy, France, have first been melted at 1923K in atmospheric conditions. Their composition given by an average of 9-20 analyses made with a CAMECA SX50 electron microprobe is specified in Table 1.

<table>
<thead>
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<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Na₂O</th>
<th>CaO</th>
<th>MgO</th>
<th>K₂O</th>
<th>FeO</th>
<th>TiO₂</th>
<th>Others</th>
<th>Redox</th>
</tr>
</thead>
<tbody>
<tr>
<td>48.9</td>
<td>15.5</td>
<td>3.6</td>
<td>9.4</td>
<td>5.5</td>
<td>1.7</td>
<td>10.6</td>
<td>2.8</td>
<td>&lt; 2.0</td>
<td>0.27</td>
</tr>
</tbody>
</table>

Table 1: Chemical composition (wt %), redox (Fe³⁺/ΣFe) is analysed by wet chemical analyses using [9] adapted from Wilson methods [12]. The reproducibility of the redox ratios is ±0.05 %.

2.2. XANES spectroscopy experiments

For high-temperature XANES, the samples were loaded as 6 μm-powders in the 1-mm hole of the Pt-Ir10 % heating wire of the microfurnace developed by Richet et al. [13] and previously used for in situ XANES high temperature study [9,10,11,14]. The XANES spectra at the Fe K-edge were recorded at the ODE beamline of SOLEIL (Orsay, France). The ODE beamline is energy dispersive with a bent Si (311) polychromator crystal at the focal point of which the sample is placed. The beam size was 20 x 20 μm. Due to the fixed energy–position correlation in the diffracted energy band, a complete absorption spectrum was obtained from measurements of the intensity distribution on a position-sensitive detector. Because a spectrum is recorded in 1 to 7 s, this line is particularly well suited to investigate fast reduction kinetics at high temperatures. All XANES spectra were acquired in the energy range 7090 - 7250 eV with an accuracy of ± 0.02 eV. In all experiments, an metallic iron reference foil was used to provide an accurate internal energy calibration of the monochromator. The first inflection point of the Fe K-edge was set at 7111.08 eV. After normalization with the Xafs© software [15], we analyze XANES spectra with the following procedure. A parametric exponential function was used to interpolate the background over several eV intervals below and above the pre-edge. The function used is in the form

\[ y = a \times e^{b(x-x_0)} \]

where a and b are two adjusted variables and x₀ is the inflexion point of the mean resonance at the Fe-K edge of iron, determined by the Xafs© software. The intensity and centroid position of the pre-edge are calculated by fitting the data with two pseudo-Voigt functions (see Figure 1). The energy,
FWHM and intensity of the peak and the Gauss-Laurentz ratio are adjusted parameters. The Fe$^{3+}$/$\Sigma$Fe ratios are determined to within 0.05 from the calibration established for a variety of minerals [16] and are in good agreement with the value given in Table 1 for the glass at room temperature.

3. Temperature and time dependences of the XANES spectra

We determined the kinetics of the oxidation reaction between 873 and 1573 K for the initially reduced samples with Fe$^{3+}$/$\Sigma$Fe = 0.27. We focused our attention on the pre-edge feature of the XANES spectra, which is sensitive to the iron redox state and oxygen coordination [16,17]. Whereas the pre-edge of the reduced glass is made of two contributions at 7112.5 and 7114 eV, that of the oxidized glass shows an intense contribution at 7114 eV (see Figures 1 and 2a,b). In Figure 2b this contrast indicates that the initially re-melted basalt was essentially reduced and became largely oxidized at 1373 K as a function of time. All kinetic XANES experiments were made with the reduced starting glass (Table 1). Temperature-induced oxidation is clearly signaled by the shift to higher energies of both the pre-edge region and the main EXAFS resonance [9,10,11] due to the opposite variations of Fe$^{2+}$ and Fe$^{3+}$ concentrations.

4. Kinetics of iron redox reactions

Redox reactions are rate limited by diffusion because redox ratios vary linearly with the square root of time [6,7,8,11]. The XANES experiments made at 1373 and 1923 K (see insert of Figure 3) thus conform to this feature. But comparisons between the kinetics of redox reactions can be made only if the influence of the sample size is properly taken into account. This has been made by Magnien et al. [11] through the so-called redox diffusivity, \(D = \frac{r^2}{4t_{eq}}\), where \(t_{eq}\) is arbitrarily defined.
as the time needed to reach 99% of the equilibrium redox ratio and \( r \) is the sample thickness determined from XANES experiment as described by Munoz et al. [18]. Redox diffusivities thus characterize the kinetics of the redox reaction regardless of both the sample size and the kind of the diffusive mechanism implied. The values determined from our experiments are shown as black squares in Figure 3 for the re-melted basalt investigated.

![Log D (m² s⁻¹) vs. 10⁴/T (K⁻¹)](image)

**Figure 3.** High temperature redox diffusivity *versus* reciprocal temperature for the re-melted basalt samples investigated in black squares. The grey squares represent the redox diffusivities determined in the study of Magnien et al. [11]. In the insert kinetics of the XANES experiments made at 1373 and 1923 K.

The lack of redox diffusivities data at low temperature, typically below 1073 K, is due to the crystallization of the basalt that prevents us to obtain good kinetics experiments. At high temperatures, oxidation and reduction experiments were alternatively performed on the same samples. As suggested by Schreiber et al. [5] the oxidation and reduction kinetics could differ at high temperatures. Since we cannot distinguish the \( D \) values determined from both kinds of experiments, it follows that any difference between oxidation and reduction kinetics is within the experimental errors of the technique. Our high temperature redox diffusivities data agree with the data of Magnien et al. [11]: these results obtained on a basalt typical of Chaîne des Puy volcanism confirms that at high temperature, diffusion of oxygen is the rate-limiting factor for both oxidation and reduction, and accounts for similar kinetics of both kinds of reactions at high temperature.

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**References**


