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Kinetics and mechanisms of iron redox reactions in silicate melts: The effects of temperature and alkali cations

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Abstract

The kinetics and the mechanisms of iron redox reactions in molten Fe-bearing pyroxene compositions have been investigated by Raman spectroscopy and X-ray absorption Near Edge Structure (XANES) experiments at the iron K-edge. The former experiments have been made only near the glass transition whereas the latter have also been performed from about 1300 to 2100 K. The same kinetics are observed with both techniques. They are described by characteristic times that depend primarily on temperature and not on the initial redox state. At high temperatures, where both kinds of reactions could be investigated, these times are similar for oxidation and reduction. From these characteristic times we have calculated as a function of temperature and composition a parameter termed effective redox diffusivity. For a given melt, the diffusivities follow two distinct Arrhenius laws, which indicate that the mechanisms of the redox reaction are not the same near the glass transition and at high temperatures. As is now well established, diffusion of divalent cations is the dominant mechanism at low temperatures but the enhanced kinetics observed for alkali-bearing melts indicate that Li^+ and Na^+ also participate in ionic transport. At superliquidus temperatures, in contrast, diffusion of oxygen represents the dominant mechanism.

1. INTRODUCTION

Transition metals exert a complex influence on the structural and physical properties of silicate glasses and melts because their redox state strongly depends on temperature, pressure, chemical composition and oxygen fugacity (e.g., Mysen and Richet, 2005). In this respect, iron, the most abundant transition element, is of particular importance since its redox state not only affects all steps of magma formation and crystallization, but also glassmaking because of its frequent occurrence in melts of industrial interest.

Hitherto 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 $Fe^{3+}/\Sigma Fe$ as a function of temperature, melt composition and oxygen fugacity have been set up either empirically (e.g., Kress and Carmichael, 1991; Nikolaev et al., 1996) or thermodynamically (Ottonello et al., 2001). 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 O_2 or as O^{2-} ions

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(Goldman and Gupta, 1983; Schreiber et al., 1986; Wendlandt, 1991). Near the glass transition range, however, experiments on aluminosilicates have indicated that the limiting factor is diffusion of divalent cations (Ca^{2+}, Mg^{2+}, Fe^{2+}) from the redox front to the surface, where a thin layer of crystalline material precipitates, accompanied by a counter flux of electron holes (Cook et al., 1990; Cooper et al., 1996a).

It is a fact now well established that the mechanism controlling the kinetics of redox reactions is that which lowers the free energy of the system most quickly (Cooper et al., 1996a). By doing so, such a mechanism dissipates the gradient of oxygen chemical potential between the melt and the atmosphere fastest even though it does not ensure a minimum Gibbs free energy for the system. The factors to be considered in this respect are the products of the ion concentrations and mobilities of the diffusing species that can participate in the redox reaction. Because the temperature dependence of mobility differs markedly between network-former and network modifier ions (Gruener et al., 2001), it follows that different mechanisms may predominate in different temperature intervals. An important task thus is to determine which ions diffuse in redox reactions and how their relative contributions might vary with temperature.

As a matter of fact, understanding of redox processes in silicate melts has been hampered by a lack of *in situ* determinations of their kinetics as a function of temperature and melt composition. In particular, the role of alkali elements has to be investigated specifically because the contribution of these cations to the transport of electrical charge should depend on whether they are network modifiers or charge compensators for trivalent cations in tetrahedral coordination. In two previous papers, we have shown that the kinetics of iron redox reactions can be investigated *in situ* in a consistent way with X-ray absorption Near-Edge Structure (XANES) experiments and with Raman spectroscopy observations (Magnien et al., 2004, 2006).

In this new study, our aim has been to make use of the sensitivity of both methods to the $Fe^{3+}/\Sigma Fe$ ratio to determine the influence of the nature of alkali cations on redox kinetics near the glass transition range as well as at superliquidus temperatures. For this purpose, we have investigated oxidized and reduced samples of three different melts. The starting material was dubbed Pyrox because its composition is that of the diopside pyroxene ($CaMgSi_2O_6$) to which 10 wt% “FeO” has been added. We then prepared the two other PyrLi and PyrNa samples by substituting partially either Li_2O or Na_2O for CaO and MgO (at constant Ca/Mg) ratio) in the Pyrox composition. To complement these results, we have also made Rutherford back-scattering (RBS) experiments because this technique yields valuable information about the morphology of oxidation reactions and, thus, on the mechanisms of redox reactions at lower temperatures (Cook et al., 1990; Cook and Cooper, 2000; Smith and Cooper, 2000).

2. EXPERIMENTAL METHODS

2.1. Sample preparation

The ~60-g samples were synthesized from SiO_2, MgO, $CaCO_3$, $NaCO_3$, $LiCO_3$ and Fe_3O_4 (Rectapur from VWR). The mixes were ground for 1 h under alcohol in an agate mortar. The products were heated slowly up to 1300 K in air in covered Pt crucibles to decompose the carbonate and then melted up to 1900 K. We finally quenched the samples in a few seconds by dipping the bottom of the platinum crucible into distilled water. This procedure was repeated three times to ensure glass homogeneity. Examination of glass fragments by optical microcopy did not show crystalline phases. Likewise, no crystallization was generally observed during the experiments. The only exceptions are the PyrLi and Pyrox samples for which slight narrow peaks appeared during the Raman experiments performed after annealing at 1070 K.

The chemical compositions of the samples are listed in Table 1 as determined by electron microprobe analyses performed on several glass chunks for each sample. To obtain highly reduced samples, the materials were remelted in a graphite crucible for 17 min at 1900 K. Under these conditions a mean Fe^{3+}/Fe^{tot} ratio of 0.100 ± 0.003 was obtained as determined from Mössbauer spectroscopy, wet chemical and electron microprobe analyses (see Magnien et al., 2004). The room-temperature glass densities were determined from Archimedean measurements made with toluene as an immersion liquid (Table 1).

In Table 1 we also list the standard glass transition temperatures that were first measured to determine the temperature range of the kinetic redox experiments. For oxidized samples, they were derived from viscometry performed on the samples with the creep apparatus described by Neuville and Richet (1991). For the reduced samples, they were obtained from differential scanning calorimetry experiments made with a Sétaram-121 calorimeter (Linard et al., 2001).

2.2. X-ray absorption measurements

Two series of XAS experiments were made at ESRF (Grenoble, France) on the ID24 and BM30B (FAME) beamlines. The storage ring was operated at 6.0 GeV with injection currents of 200 mA in a 2/3 filling mode. Although experiments were faster on ID24 than on FAME, similar absorption spectra could be recorded in transmission mode with both beamlines because of the small effective thickness of the sample .

On the FAME line, the energy was monochromatized with a conventional double crystal Si (220) monochromator. The photon energy was scanned stepwise through changes of the Bragg angle of both crystals. For our Fe-rich samples, the data were collected in transmission with a beam size of 50 × 80 μm. During scans, we kept the beam position constant, with a size of about 150–200 μm^2. The monochromator was composed of two Si (220) crystals with an angular resolution of 1/40,000°, the second crystal being dynamically bent during the energy scan (Proux et al., 2006, 2005). As spectra were recorded in 90 s, the FAME line is particularly adapted for investigation of oxidation near the glass transition where the kinetics are slow.

The ID24 beamline is energy dispersive with a bent Si (311) polychromator crystal at the focal point of which the sample is placed (Pascarelli et al., 2006). The beam size was 20 × 20 μm. Due to the fixed energy-position correla-