AMORPHOUS MATERIALS: PROPERTIES, STRUCTURE, AND DURABILITY†

Quantification of the kinetics of iron oxidation in silicate melts using Raman spectroscopy and assessment of the role of oxygen diffusion

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ABSTRACT

A diopside composition silicate glass containing 8 wt% Fe2O3 was prepared from melt equilibrated at 1500 °C and different redox conditions in the range log fO2 = −0.7 (air) to log fO2 = −6. The Fe2+/Fe3+ was measured using Mössbauer spectroscopy. The Mössbauer data were used to calibrate Raman-scattering intensity variations of the same samples as a function of oxidation state, providing a simple empirical method to determine the redox ratio of this glass. This new Micro-Raman-based method has been used to quantify redox profiles across partially oxidized samples. No significant Fe2+/Fe3+ gradients were found (values were constant from the surface to the center), although the average oxidation state was observed to increase as a function of time. The former result contrasts with O self-diffusion profiles measured with the ion microprobe on diopside glasses prepared at similar experimental conditions, for which strong isotopic gradients were found at the sample scale (corresponding to a self-diffusion coefficient for O at 1450 °C of 1 × 10−15 m2/s). Local oxidation of Fe in the melt therefore appears to occur independently of long-range diffusion of O from the sample surface. A mechanism capable of explaining this observation is proposed based upon the fact that redox gradients result in the generation of electromotive forces. This results in a powerful driving force to wipe out redox gradients through fast electron transfer. However, migration of electrons alone would result in unfavorable charge gradients, in particular at the surface of the sample. At the temperature of our experiments, the local mobility of O is apparently sufficient to compensate the migration of electrons. Despite rapid charge transfer, the bulk oxidation state of our sample is nevertheless limited by the addition of external O. The time dependence of the bulk oxidation state of our samples can be modeled by a constant rate of O diffusion across the interface of 2.1 × 10−7 m/s. However, the bulk oxidation state of the liquid is also found to be concordant with variations calculated assuming that diffusion of O is the rate-limiting mechanism. This apparent paradox may be explained if the characteristic time-scales of O self-diffusion in the sample volume and of O incorporation at the sample surface are similar. We suggest that this is indeed the case, given that both of these processes are likely to be limited by the frequency of bond-breaking and bond-forming events in the liquid.

Keywords: Diffusion, kinetics, melt properties, Raman spectroscopy, oxygen, oxidation

INTRODUCTION

Iron is by far the most abundant heterovalent component of geological silicate liquids, and such samples may show significant variation in their Fe2+/Fe3+ ratio (i.e., Carmichael 1991). These variations are potentially important given that a wide range of physical, chemical, and structural properties of silicate melts (e.g., density, viscosity, phase equilibria, and electrical conductivity) are sensitive to the relative proportions of Fe2O3 and FeO (e.g., Dingwell 1991; Toplis et al. 1994; Toplis and Carroll 1995; Mysen and Richet 2005). At thermodynamic equilibrium, it is known that the Fe2+/Fe3+ ratio of molten silicates is controlled by the combined effects of O fugacity (fO2), temperature, pressure, and liquid composition (e.g., Kress and Carmichael 1988) and several models have been developed over the years to quantify these relationships (e.g., Sack et al. 1980; Kilinc et al. 1983; Kress and Carmichael 1988; Ottonello et al. 2001; Moretti 2005). However, in rapidly evolving geological systems, for example during volcanic eruptions, thermodynamic equilibrium cannot necessarily be assumed, and some consideration of the kinetics of the oxidation-reduction process is required. In this respect, the elementary rate-limiting step...