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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% Fe_2O_3 was prepared from melt equilibrated at 1500 °C and different redox conditions in the range $\log f_{O_2} = -0.7$ (air) to $\log f_{O_2} = -6$. The Fe^{2+}/Fe_T 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 Fe^{2+}/Fe_T 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^{-11} m^2/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