

Iron concentration and the physical processes of dynamic oxidation in an alkaline earth aluminosilicate glass

GLEN B. COOK^{1,*} AND REID F. COOPER^{1,2,†}

¹Department of Materials Science and Engineering, University of Wisconsin–Madison, Madison, Wisconsin 53706, U.S.A.

²Department of Geology and Geophysics, University of Wisconsin–Madison, Madison, Wisconsin 53706, U.S.A.

ABSTRACT

Rutherford backscattering spectroscopy was used to investigate the persistence of cation-diffusion-limited oxidation in three, low-Fe²⁺-bearing MgO–Al₂O₃–SiO₂ glasses (base glass compositions along the enstatite–cordierite–liquid cotectic; total Fe levels of 0.04, 0.19, and 0.54 at%). The glasses were reacted in air at temperatures of 700–850 °C (~*T_g*), and changes in the composition of the near-surface region (≤2.5 μm) of the glass resulting from oxidation were characterized. The reaction morphology produced by oxidation at temperatures above 800 °C, for all of the glasses studied regardless of Fe concentration, was consistent uniquely with an oxidation process dominated by diffusion of Fe²⁺ cations to the free surface that was charge compensated by a (counter) flux of electron holes into the material. In the high-Fe material (0.54 at%), the activation energy for the cation-diffusion-limited reaction was estimated at ~475 kJ/mol. Below 800 °C, the two glasses with lowest Fe concentration displayed a reaction morphology consistent with oxidation occurring by the motion of an oxygen species. High levels of transition metal cations are not required to ensure the dominance of cation-diffusion-limited oxidation reaction in silicate glasses and melts; thus, monitoring internal Fe³⁺:Fe²⁺ equilibrium, even at trace amounts, seems untenable as an indicator of the diffusion behavior of molecular or ionic oxygen.

INTRODUCTION: PHENOMENOLOGY OF OXIDATION IN FE-BEARING ALUMINOSILICATE MELTS AND GLASSES

Chemical diffusion in silicate melts is of prime importance in several petrologic processes, including, for examples, the movement toward equilibration between a melt and the crystalline residuum with which it in contact and the dynamics of crystallization. Therefore, substantial energy has been expended in studies of chemical and tracer diffusion in both melts and their corresponding glasses. There are several significant review articles on the subject; of particular note are the recent ones by Hofmann (1980), Dunn (1986), and Chakraborty (1995).

Of course, as the primary constituent in these melts, there has been a particular interest in the diffusion of ionic and molecular/atomic oxygen. With regards to oxygen species diffusion, these review articles all note the same surprising result when comparing tracer experiments and chemical diffusion experiments: the tracer-diffusion data for oxygen in silicate melts and glasses predicts redox kinetics some 2–3 orders of magnitude slower than that seen experimentally. It is this fact that allowed Chakraborty (1995) to claim the behavior as “less

well understood” compared to the diffusion of cations; thus the question is raised as to whether redox chemical diffusion experiments are really indicating the behavior of oxygen diffusion, either molecular or ionic. There is, however, an additional fact: the apparent oxygen diffusion rate derived from redox studies is identical to that seen for tracer diffusion of divalent, network-modifier cations (Dunn 1982; Cook et al. 1990).

We have turned our attention to the dynamics of redox reactions in both glasses and melts; our efforts allow a resolution of the conundrum noted above. In redox reactions there exist several independent (i.e., parallel) kinetic mechanisms: it is the mechanism that dissipates the energy of the redox potential most rapidly that will dominate the behavior; furthermore, this dominant mechanism will often become clearly apparent in the morphology of the reaction, that is, in the reaction-induced spatial variation in composition.

For the oxidation reaction of a Fe²⁺-bearing amorphous silicate, three kinetic mechanisms (“modes”) can be argued as acting in parallel. As illustrated in Figure 1, these are (I) a flux of molecular oxygen; (II) a flux of oxygen ions (O²⁻) charge-compensated by a concurrent flux of electron holes (h[•]); and (III) a flux of network modifying cations to the free surface charge compensated by counterflux of electron holes (cf. Schmalzried 1983). In each case, the magnitude of the diffusive response to the gradient in oxygen chemical potential will be proportional to the product of the concentration (*c_i*) and the mobility (represented by the self-diffusion coefficient, *D_i*) of

*Present affiliation: Corning, Incorporated, Science and Technology Division, SP-PR-1-3, Corning, NY 14831.

†E-mail: cooper@engr.wisc.edu