

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

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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.