

Diffusion and Activity of NiO in CaO-MgO-Al₂O₃-SiO₂ melts considering effects of a_{O_2} - and $\gamma_{Ni^{2+}}$

R. O. Colson, C. R. Keedy, and L. A. Haskin, Department of Earth and Planetary Sciences and McDonnell Center for the Space Sciences, Washington University, One Brookings Drive, St. Louis, MO 63130

Abstract:

Variations in activity coefficients for oxides in silicate melts are complex functions of silicate melt composition. For example, the activity coefficient (γ) for NiO shows a minimum when plotted against a parameter reflecting the degree of polymerization (or basicity or fraction of bridging oxygens) (e.g. Pretorius and Muan, 1992). In this paper, we propose that this complexity occurs in part because NiO is not an actual species in silicate melts. Variations in γ can be better understood and predicted if the activity of NiO is treated as the product of activities of Ni^{2+} and O^{2-} ions. Using voltammetric methods, we have measured independent activity coefficients for Ni^{2+} and O^{2-} for compositions between diopsidic and anorthitic melt and have found that variations in these values are more easily understood in terms of the melt composition and structure and permit qualitative variations in γ_{NiO}^o (activity coefficient of NiO relative to the free energy of formation reported in Robie and Waldbaum, 1968) to be predicted in compositions other than those studied. We suggest that a similar consideration of ionic behavior might improve our understanding of activity coefficients for other oxides in silicate melts as well. In addition, we report diffusion rates for Ni and free energies for the reaction $Ni^{2+} + O^{2-} \rightleftharpoons NiO + \frac{1}{2}O_2$ for melt compositions along the compositional joins CaMgSi₂O₆ - CaAl₂Si₂O₈ and CaMgSi₂O₆ - MgAl₂Si₂O₈.