Self diffusion of Si and O in dacitic liquid at high pressures

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ABSTRACT

Laboratory experiments have been conducted to determine simultaneously the self diffusivities of Si and O in synthetic dacite melt (NBO/T = 0.1) from 1 to 5.7 GPa and from 1355 to 1662 °C. Glasses enriched in 18O and 28Si were synthesized and mated to their isotopically normal counterparts to form diffusion couples used in the piston cylinder device (1 and 2 GPa) and multi-anvil apparatus (4 to 5.7 GPa). Profiles of isotope abundances were measured by secondary ion mass spectrometry. Self-diffusion coefficients for Si (D\text{Si}) are significantly lower than self-diffusion coefficients for O (D\text{O}) at all run conditions; for example, D\text{O} = 6.45 ± 0.65 × 10^{-14} m^2/s and D\text{Si} = 1.45 ± 0.45 × 10^{-14} m^2/s at 1 GPa and 1355 °C. The temperature dependence is similar, but not identical, for Si and O self diffusion at all pressures, yielding activation energies of 293–380 kJ/mol at 1 GPa, 264–305 kJ/mol at 2 GPa, and 155–163 kJ/mol at 4 GPa. The pressure dependence is similar for Si and O at all temperatures, giving activation volumes for Si and O that are –14.5 to –17.1 cm^3/mol at 1460 °C, –9.8 to –8.7 cm^3/mol at 1561 °C, and –8.8 to –9.3 cm^3/mol at 1662 °C. Self-diffusion coefficients for Si and O reach maximum values at roughly 5 GPa. The mode of Si and O self diffusion in dacitic liquids is constrained by the large activation volumes, D\text{O} ≈ 2 D\text{Si}, and predictions using the Eyring equation, which suggest that Si and O diffuse as molecular species at 1460 °C. At 1561 and 1662 °C, less negative activation volumes and predictions of the Eyring equation are consistent with diffusion of Si and O by a combination of mechanisms, including the formation of a high-coordinated intermediate species.

INTRODUCTION

Silicon (Si) and oxygen (O) are the major structural constituents of silicate melts. Bonding of the Si^{4+} and O^{2–} ions controls diffusion and viscous flow in silicate melts, so an understanding of the compositional and compressional effects on local melt environments is essential for modeling igneous processes, including the equilibration and extraction of silicate melts from a partially molten source region, the time scales for magma mixing, and rates of crystal growth and dissolution. The network former Si is variably coordinated by O in silicate melts, and Si-O molecular configurations influence the transport of Si and O. For this reason, measured diffusion coefficients for Si and O are powerful probes of dynamic melt structure that complement interpretations of nuclear magnetic resonance (NMR) studies (e.g., Liu et al. 1988; Stebbins and McMillan 1989; Xue et al. 1991) and molecular dynamics (MD) simulations (e.g., Rustad et al. 1990; Wasserman et al. 1991; Kubicki and Lasaga 1991; Bryce et al. 1999).

Local melt structure can be deduced from experimental diffusion studies by determining the nature of the species activated for diffusion. The size of the diffusing species has been estimated using the Eyring equation, which relates the self-diffusion coefficient to melt viscosity. For example, Oishi et al. (1975) in a study of calcium aluminosilicate, Yinnon and Cooper (1980) in a study of K-Sr silicate, Shimizu and Kushiro (1984) in a study of jadeite and diopside melts, and Rubie et al. (1993) in a study of Na_{2}Si_{5}O_{9} melt, accurately predicted melt viscosities using the Eyring equation with self-diffusion coefficients for O and jump distances for diffusion equal to the diameter of the O^{2–} anion (λ = 2.8 Å). The agreement between independently determined melt viscosities and those calculated using the Eyring equation with λ = 2.8 Å suggests that ionic diffusion of O is the rate-limiting step permitting viscous flow. Jump distances for diffusion that are greater than the diameter of the O^{2–} anion imply that O diffuses as part of a molecular complex. For example, Dunn (1982) suggested the diffusion of a large, molecular species [i.e., (SiO_4)^{4–}] based on good agreement between translation distances greater than the diameter of the O^{2–} anion in the Eyring equation and self-diffusion coefficients for O in diopside, Di_{58}An_{42}, and Di_{40}An_{60} melt compositions.

Stebbins and coworkers (e.g., Farnan and Stebbins 1994; Xue et al. 1991; and Liu et al. 1988) in interpretations of nuclear magnetic resonance (NMR) results, have proposed an alternative to ionic and molecular models for self diffusion of network formers involving a high-coordinated (five- or sixfold) Si transition state complex. The formation and subsequent disassociation of high-coordinated species passes network-forming Si and O ions through the silicate melt by incremental