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SPECIAL COLLECTION: MECHANISMS, RATES, AND TIMESCALES OF GEOCHEMICAL TRANSPORT PROCESSES IN THE CRUST AND MANTLE

Fe-Mg diffusion in spinel: New experimental data and a point defect model†

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Abstract

We have measured Fe-Mg interdiffusion rates ($D_{Fe\text{-}Mg}$) in synthetic Mg-Al spinel and a natural (Mg,Fe) aluminous spinel from Sri Lanka ($X_{Fe} \sim 0.07$) at atmospheric pressure over a range of different oxygen fugacities {$\log_{10}(f_{O_2}[Pa]) = -14$ to -10} and temperatures (750–900 °C). Diffusion couples made of single-crystal spinel and thin films of hercynitic composition ($X_{Fe} \sim 0.5$) were used for the diffusion anneals. The experimentally induced diffusion profiles were analyzed by Rutherford backscattering Spectroscopy to retrieve true depth concentration profiles for Fe. These were fitted numerically by an explicit finite difference scheme that allows compositionally dependent interdiffusion processes to be modeled by relating self- and interdiffusion coefficients. Synthesis of data from the two diffusion couples indicate that: (1) $D_{Fe\text{-}Mg}$ depends on X_{Mg} of spinel, with increasing diffusion rates with increasing X_{Mg}. This behavior is opposite of that found in silicates. (2) Self-diffusion coefficients could not be determined from these experiments, but the results indicate that $D_{Fe}/D_{Mg} > 100$. (3) $D_{Fe\text{-}Mg}$ in Mg-spinel is independent of oxygen fugacity, whereas it depends strongly and nonlinearly on oxygen fugacity for the natural spinel. This observation indicates that the mechanisms of diffusion are different in the two kinds of spinel (Fe-bearing vs. Fe-free), which is also seen in the difference in activation energy obtained for these. Moreover, the nonlinear dependence on oxygen fugacity indicates that diffusion occurs by an interstitial mechanism at low-oxygen fugacities and by a vacancy mechanism at high-oxygen fugacities in natural, Fe-bearing spinel. (4) Simple Arrhenius relations that describe the data within the range of experimental conditions are: Synthetic magnesium spinel: $Q_{Fe\text{-}Mg} = 219 \pm 19$ kJ/mol, $\log_{10}D_{Fe\text{-}Mg} = -7.76 \pm 0.90$ [m²/s]. Natural Fe-bearing spinel for $\log_{10}(f_{O_2}$ [Pa]$) = -12$}: $Q_{Fe\text{-}Mg} = 139 \pm 18$ kJ/mol, $\log_{10}D_{Fe\text{-}Mg} = -12.33 \pm 0.85$ [m²/s]. A model based on point defect considerations that describes the temperature as well as oxygen fugacity dependence of $D_{Fe\text{-}Mg}$ in Fe-bearing spinel is: D [m²/s] = D_v [m²/s]f_{O_2} [Pa]$^m\exp\{-Q_v$ [J/mol]/RT [K]} + D_i [m²/s]f_{O_2} [Pa]$^{-m}\exp(-Q_i$ [J/mol]/RT [K]), with $D_v = 1.07 \times 10^{-9} \pm 1.55 \times 10^{-9}$ m²/s, $Q_v = 131 \pm 66$ kJ/mol, $D_i = 1.03 \times 10^{-17} \pm 7.32 \times 10^{-17}$ m²/s, $Q_v = 130 \pm 80$ kJ/mol and $m = 0.34 \pm 0.18$. Poor coverage of T-f_{O_2} space by available experimental data results in large uncertainties in the fit parameters. As a result, these expressions are useful for understanding the diffusion behavior in spinels, but not for extrapolation and calculation of diffusion coefficients for cooling rate or other related calculations. Until the parameters can be better constrained through the availability of more data, we recommend that for such calculations, the parameters noted above for Fe-bearing spinels be used for compositions and f_{O_2} conditions that are close to those of the experiments. (5) $D_{Fe\text{-}Mg}$ in spinel is faster than $D_{Fe\text{-}Mg}$ in olivines, pyroxenes, and garnets at most conditions.

Keywords: Spinel, diffusion coefficient, diffusion mechanism, point defect, thin films, pulsed laser deposition, Rutherford backscattering spectroscopy