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

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We have measured Fe-Mg interdiffusion in a synthetic Mg-spinel ($MgAl_2O_4$) and a natural (Fe,Mg)-spinel (X_{Mg} ~ 0.93) by depositing thin films (~ 100 nm) of an iron-rich (X_{Fe} ~ 0.5) spinel composition on polished surfaces of single crystals. Experiments were carried out at controlled oxygen fugacity (buffered by a continuously flowing gas mix of CO and CO_2) at atmospheric pressure and at temperatures between 700 and 900 °C. Concentration gradients and film thicknesses were measured by Rutherford Backscattering Spectroscopy (RBS); surfaces of samples were also inspected using optical microscopy, SEM, EBSD and white light interference microscopy. The diffusion profiles were fitted using a finite difference numerical method that accounted for mass balance between thin film and substrate, and compositional dependence of diffusion coefficients. It was found that diffusion behavior in Mg-spinel (activation energy, fO_2-dependence) is different from that in (Fe,Mg)-spinel. Diffusion rates are found to depend on (Fe/Mg) of spinel crystals and in contrast to the behavior in silicates, diffusion rates are found to increase with Mg-content of spinel. fO_2-dependence of the diffusion coefficient in (Fe,Mg)-spinel is non-linear and shows a minimum at an oxygen fugacity of ~ 3 x 10^{-17} bars in the temperature range of the study. A similar behavior is known for diffusion in magnetite in the literature [1], and has been shown to result from diffusion occuring by an interstitial mechanism at reducing conditions and by a vacancy mechanism at more oxidizing conditions. We have been able to find an expression based on such a point defect model that describes all available data in the literature on Fe-Mg diffusion in spinel (this study, [2],[3]) well. Without consideration of the point defect mechanism, the data appear to be widely discrepant with one another. This underscores the necessity of understanding point defect mechanisms of diffusion for describing diffusion behavior and calculation of diffusion coefficients for modeling different natural situations.

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