

Fe-Mg interdiffusion experiments in olivine

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We are conducting a series of experiments on Fe-Mg interdiffusion in olivine from 600-800°C using Rutherford backscattering (RBS) to measure concentration profiles produced by diffusion. Two mm thick slices of pure synthetic forsterite are cut parallel to (001) from a Union-Carbide boule and polished on one side. After annealing at 800°C to remove possible damage from the polishing, samples are packed in powder of an Fe-bearing olivine (San Carlos, NM olivine or synthetic fayalite) and sealed in an evacuated silica tube along with a solid buffer assemblage (NNO or QFM). The samples are held at temperature, quenched, and the forsterite crystal is separated from the powder and cleaned, revealing a still-polished surface. Compositional depth profiles are obtained by Rutherford backscattering from the polished surface with a 2 or 3 MeV 4He⁺ beam. The profiles are consistent with a strong compositional dependence of the Fe-Mg interdiffusion coefficient. As observed by others at higher temperatures, Fe-rich compositions have diffusivities that are approximately 2 orders of magnitude higher than Mg-rich compositions. Variability of duplicate experiments led us to investigate the rate equilibration of the NNO assemblage at these modest temperatures because of the dependence of Fe-Mg interdiffusion on oxygen fugacity. NNO reaction rates are rapid on the diffusion time scale. Unlike many previous diffusion experiments of the same design with other systems, our data do not appear to be consistent with rapid diffusion in the powder relative to diffusion in the single crystal, changing the boundary conditions from "surface composition constant" to those of a semi-infinite system (with a highly composition-dependent diffusivity). This is perhaps a consequence of the relatively rapid rate of Fe-Mg interdiffusion in olivine single crystals compared with diffusivities in previous systems investigated. Additional experimental designs are being explored to obviate these difficulties and make use of the sensitivity of RBS to measure short (< 200 nm) compositional profiles to complete the olivine Fe-Mg interdiffusion data set for lower temperatures.

Fluids in the system CaO-Al₂O₃-SiO₂- H₂O (CASH) – Thermodynamic modeling of experimental results

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Solubilities of corundum (Al₂O₃), wollastonite (CaSiO₃), grossular (Ca₃Al₂Si₃O₁₂) and zoisite (Ca₂Al₃Si₃O₁₂(OH)) in pure water have been experimentally determined in piston-cylinder apparatus at P up to 5 GPa and T of 400 - 800°C. Except for Al₂O₃, solubility increases with both P and T. Zoisite shows clearly incongruent dissolution behavior. Grossular and wollastonite dissolve congruently.

Gerya & Perchuk (1997) and Gerya et al. (2004) have shown that pure H₂O can be treated as a solution of molecules in (1) "liquid-like" (clustered) state, and (2) "gas-like" (free) state. X_{liq} = mole fraction "liquid-like" water. With this, Gerya et al. (2005) reproduced well the extensive solubility data on SiO₂. Simplified, the description is

$$\Delta G_r = \Delta H_r^\circ - T\Delta S_r^\circ + \int_{T_0}^T \Delta C_{p,r} dT - T \int_{T_0}^T \frac{\Delta C_{p,r}}{T} dT + \dots$$

$$+ \int_{P_0}^P \Delta V_r dP + RT \ln \left(\frac{\prod_i X_{\text{species},i}^{n_i}}{(X_{\text{Liq}} X_{\text{H}_2\text{O}})^m} \right)$$

where ΔG_r , ΔH_r° , ΔS_r° , $\Delta C_{p,r}$, ΔV_r are the usual standard state molar thermodynamic parameters of the dissolution reaction; X_i = mole fraction of dissolved oxide i , n_i = moles of dissolved oxide i , m = moles of H₂O consumed. This model has been successfully applied to the available experimental data.

The above formalism requires explicit data on speciation. However, barring this, a simple "component" approach for oxides can be used to approximately model aqueous CASH fluids from less than 0.2 (e.g., Xie and Walther, 1994) to 3 GPa. "Mixing terms" are needed for oxide pairs like SiO₂/Al₂O₃, which appear to interact strongly in the solution.

References

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