

Model independent phase equilibrium constraints on the ferrosilite activity in the binary Fe-Mg orthopyroxene solid solution

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ABSTRACT

Compositional reversals of orthopyroxene solid solution (Opx) on the enstatite (En, MgSiO_3)-ferrosilite (Fs, FeSiO_3) join equilibrated with hematite (Hm, Fe_2O_3), magnetite (Mt, Fe_3O_4), and quartz (Qz) were obtained in piston-cylinder apparatus in the pressure range 10–25 kbar at temperatures of 800 and 950 °C. A double-capsule technique with the Hm-Mt external buffer was employed to ensure the presence of both Fe oxides in the run products. Starting materials were crystalline mixtures of synthetic Opx with $X_{\text{Fs}} [= \text{Fe}/(\text{Fe}+\text{Mg})] = 0.05$ and 0.45, reagent Mt, Hm, and natural Qz. Run products were carefully examined using optical microscopy, back-scattered (BSE) imaging, and wavelength dispersive electron microprobe analysis. Despite the differences in the rates of forward and backward reactions $\text{Fs (in Opx)} + \text{Hm} = \text{Mt} + \text{Qz}$ (1), very tight compositional brackets (less than 0.01 X_{Fs}) were obtained at each P - T . At 800 °C, midpoints of the compositional brackets are: 0.195/10 kbar, 0.24/15, 0.29/20, and 0.34/25; at 950 °C: 0.21/15 kbar, 0.25/20, and 0.295/25 kbar. Activities of Fs, recalculated from these compositions using either Berman and Aranovich (1996) or Holland and Powell (1998) data sets for the pure end-member reaction (1), show negative deviation from ideal mixing. Strongly temperature dependent enthalpy of mixing is required to make these activity values consistent with the configurational entropy of the solid solution deduced from the site occupancy measurements. A simple mixing model with a linearly varying temperature-dependent W term, similar to that of Berman and Aranovich (1996), adequately reproduces the experimental data.