

Intersite partitioning of Mg and Fe in Ca-free high-pressure *C2/c* clinopyroxene

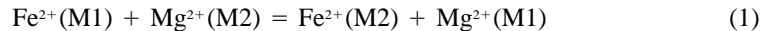
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ABSTRACT

The intracrystalline distribution of Mg and Fe²⁺ on the M1 and M2 octahedral sites in high-*P* *C2/c* (Mg,Fe)SiO₃ clinopyroxene has been determined on quenched samples using ⁵⁷Fe Mössbauer spectroscopy. Although the recovered samples that were measured had the low-*P* (*P2₁/c*) structure, the ordering state of the high-*P* polymorph is believed to have been preserved because the high-*P* *C2/c* → low-*P* *P2₁/c* transformation occurred at room temperature during the final stages of decompression of the experiments. Under such conditions significant cation diffusion is unlikely. Low temperature (81 K) Mössbauer spectra indicate that Fe²⁺ is strongly ordered onto the M2 sites, with an average $K_D \approx 4.0(8)$ for the intersite exchange reaction:



Because the samples were quenched from high temperature (1200–1275 °C) at 9.5 GPa, the temperature to which the measured ordering state corresponds remains problematic. However, a sample re-annealed at 1000 °C is more ordered than the original sample synthesized at 1275 °C, suggesting that high-temperature cation distributions in high-*P* clinopyroxene can be quenched in the multi-anvil experiments. Therefore, we conclude that the measured cation distributions correspond approximately to the conditions of the experiments. A small compositional dependence of cation ordering also exists, indicating subregular behavior across the binary join. A fit to the data yields $\Delta G_{\text{exch}}^{\circ} = -11.9$ (2.0) kJ/mol at 1275 °C for the exchange Reaction 1, which describes the ordering behavior on the octahedral sites in the clinopyroxenes.

Comparison with data for orthopyroxene, which were obtained mostly at 1 atm, indicates that the state of ordering in orthopyroxene and high-*P* clinopyroxene is similar, especially if cation ordering in the high-*P* clinopyroxene has a small pressure dependence. The similarities are consistent with the observed structural similarities between the two polymorphs.