High temperature behaviour of Mg-Fe olivine by *in situ* neutron diffraction.

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Olivine single crystals of mantle composition and origin (Fa10-Fa12) investigated by *in situ* neutron diffraction at high temperature, show that Fe^{2+} and Mg undergo two stages of cation *ordering* with *increasing* temperature. A slight preference of Fe^{2+} for site M1, culminating at about 850°C, is followed by a reverse ordering scheme. A cross-over between the two ordering regimes occurs at about 900°C (complete disorder). With further heating Fe^{2+} progressively and strongly segregates into site M2 up to 1300°C, the limit of our experiments. Mössbauer spectroscopy showed no Fe oxidation. Similarly, in a synthetic sample of Fa50Fo50, upon heating to 900°C at the Fe-FeO oxygen buffer, Fe slightly prefers site M1 below ≈600°C, progressively disordering on heating to this temperature. Above 630°C (site preference cross over - T_c) Fe progressively segregates into M2, as observed by powder neutron diffraction.

The cation ordering behaviour correlates with temperature dependent M1-M2 site geometry and it appears that vibrational entropy, crystal field effects, and changes in bond characteristics could play a part in the dynamics of cation partitioning. The temperature dependence of site ordering is modelled using a Landau expansion of the free energy of ordering of the type $\Delta G = -hQ + gTQ + {}^{a}/_{2}(T-T_c)Q^2 + {}^{b}/_{4}Q^4$, with a/h = 0.00406 K^{-1}, b/h = 2.3, T_c = 572 K and g/h = 0.00106 K^{-1}. The high-temperature ordering behaviour across the forsterite-fayalite join will have a bearing on the activity-composition relations of this important rock-forming mineral, and indicate that Fe-Mg olivine solid solutions become less ideal as temperature increases.