Temperature Dependent Cation Distribution in MgCo-Olivine

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Irrespective of their provenance, (Fe, Mg)-olivines invariably show (Fe, Mg)-distributions close to disorder, i.e. with little ordering tendencies, whereas (X, Mg)-olivines (X = Mn, Co, Ni) exhibit strong ordering. While Mn prefers the M2-site, Co and Ni fractionate into M1. The temperature dependencies of the equilibrium cation distribution coefficient

$$K_d = \frac{[X1][Mg2]}{[X2][Mg1]}$$

are known for the solid solutions MgXSiO\textsubscript{4} with X = Mn, Fe, and Ni [1, 2, 3, 4], but was missing for MgCo-olivine. Therefore, we have undertaken in-situ high temperature powder diffraction experiments with monochromatic synchrotron radiation (\(\lambda = 0.7099\) Å). These were carried out on the powder diffractometer installed at beam-line B2 using the OBI detector.

The starting material was prepared from a stoichiometric mixture of oxides and possessed an unknown Kd after quenching from 1200 °C. With a few holding points in between, the temperature was raised from ambient conditions to 600°C and kept constant for a time assumed to suffice for equilibration. Then, increasing temperatures were applied in steps of approx. 50 °C up to 1050 °C, each temperature being held for at least 90 min. Fig. 1 shows a diagram measured at 719 °C.

![Fig. 1: powder diagram of MgCoSiO\textsubscript{4}](image1)

Fig. 2: Refined [Co1] vs. time

![Fig. 2: Refined [Co1] vs. time](image2)

For obtaining additional information about the exchange kinetics the data collections at the various temperatures were carried out in 15-20 min runs expecting that, once the temperature is attained, Kd will asymptotically approach the new equilibrium. Fig. 2 shows however, that the situation is more complicated. Rietveld-refinements performed with the appropriate chemical and site constraints, indicate significant short-term fluctuations of the M1-occupation by Co and hence of Kd. Though counting statistics were less than satisfactory, there is a pattern implying that the driving force \(\Delta G\) oscillates about zero. This is also expressed by the cumulative analysis, where the [Co1] vs. time approach to the equilibrium exhibits a damped oscillation.
From all results of the cumulative data evaluations at the various temperature settings, the thermodynamic equilibrium cation distribution was obtained by least-squares linear regression analysis applied to data above \( T = 550 \, ^\circ\text{C} \). In Fig. 3, the equilibrium equations given by \( \ln KD = 1718(70)/T - 0.24(7) \) and the intersite exchange energies, enthalpy and entropy are calculated as \( -\Delta H_{\text{ex}} = 14.5(5) \, [\text{kJ/mol}] \) and \( \Delta S_{\text{ex}} = 1.7(5) \, [\text{J/mol}] \), respectively. The enthalpy is of the same order as 21.5 [kJ/mol] for MgNiSiO\(_4\) [3] with higher crystal field stabilization energy CSFE (see below) and 15.0 [kJ/mol] for MgFeSiO\(_4\). Fig.3 also indicates that the initial distribution in the quenched sample corresponds to a temperature of 600 °C.

The present results close the gap between MgFeSiO\(_4\) and MgNiSiO\(_4\). They can be related to literature data available for \( X = \text{Mn, Fe, Ni} \) olivines. A plot of \( \ln KD \) vs. the number of paired 3d-electrons calculated for temperatures of 273, 773 and 1173 K is given in the Fig. 4. With only one common fit parameter, \( \ln KD \) can also be linearized in terms of effective pair numbers. The plot shows that the number of 3d-electron pairs is an essential factor for the cation distribution. Starting from Mn with no paired electrons each pair reduces the ionic radius, which in turn causes increasing lattice energy and CSFE. Both effects favour the occupation of the smaller M1-site. Already for the case of (MgFe)SiO\(_4\), the volume effect of the larger M2-site is slightly overcompensated \( (-\Delta H_{\text{ex}} = 1.3 \, [\text{kJ/mol}] \) [4]), which explains the generally little cation order in rock forming olivines. These results were corroborated by corresponding powder diffraction experiments on the TOF-diffractometer ROTAX at the pulsed spallation source ISIS, UK [5].

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References