



Thermoelastic and Structural Response of CoMgSiO_4 Olivine to High Temperature Treatment by *in situ* Neutron Powder Diffraction

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Natural olivine, dominantly $(\text{Mg,Fe})_2\text{SiO}_4$, is one of the most common constituent of the upper mantle and in the Earth's crust it is a fundamental component of igneous and metamorphic rocks of basaltic origin. The physical and structural response of olivine to changes of T , P and composition, yield essential information in order to determine thermodynamic, petrological and geophysical properties of this important mineral. Earlier neutron powder diffraction studies at high temperature *in situ* on natural and synthetic Mg-Fe olivines, had revealed a very interesting behaviour of reverse ordering of the octahedral cations with temperature whereby, an initial partial segregation of Fe^{2+} into site M1, is followed by a crossover with Fe^{2+} strongly segregating into site M2 (and Mg in site M1) up to the highest temperatures reached in the experiments.

In order to evaluate the contribution of isomorphic substitution to the activity-composition relations in this important rock-forming mineral, we undertook a study on a synthetic Co-Mg olivine therefore extending high temperature *in situ* investigations to a composition ruled by a transition metal indicated as having a strong site preference (for M1) in the same crystal structure. Our aim is that of evaluating the physical and crystal chemical parameters underpinning the non ideal behaviour of the olivine solid solution in response of temperature changes and isomorphic substitution.

Neutron powder diffraction data were collected on the POLARIS instrument at the ISIS Facility of the Rutherford Appleton Laboratory at five temperatures ranging from RT to 1000°C. The degree of cation ordering was determined from direct measure-

ments of site occupancies in the two octahedral M sites and described by the equilibrium constant of the exchange reaction K_D expressed as: $K_D = [\text{Co}(\text{M1}) * \text{Mg}(\text{M2})] / [\text{Co}(\text{M2}) * \text{Mg}(\text{M1})]$. The refinements were very stable with no evident correlations between populations and thermal parameters in the octahedral sites. No phase transition was observed within the temperature range investigated. Axial and volume thermal expansion coefficient ($\alpha_j = l_j^{-1} \cdot \partial l_j / \partial T$, $\alpha_V = V^{-1} \cdot \partial V / \partial T$) were calculated by weighted linear regression through the data points at different temperatures, yielding the following values: $\alpha_a = 9.5(1) \cdot 10^{-6}$, $\alpha_b = 12.5(1) \cdot 10^{-6}$, $\alpha_c = 12.7(2) \cdot 10^{-6}$, $\alpha_V = 3.51(4) \cdot 10^{-5} \text{ } ^\circ\text{C}^{-1}$. The thermal expansion of CoMgSiO_4 appears to be strongly anisotropic ($\alpha_a : \alpha_b : \alpha_c = 1.00 : 1.32 : 1.34$), similarly with what can be observed in the iso-structural Mg-Fe-olivines. The magnitudes of the principal unit-strain coefficients ($\varepsilon_1, \varepsilon_2, \varepsilon_3$), between room temperature and each measured T , of the strain-ellipsoid were calculated. The unit strain ellipsoid is oriented with $\varepsilon_1 \parallel c$, $\varepsilon_2 \parallel b$, $\varepsilon_3 \parallel a$ and $\varepsilon_1 > \varepsilon_2 > \varepsilon_3$. The magnitude of all the unit-strain coefficient slightly decreases with T up to $\sim 700\text{C}$ and then increases up to the maximum temperature reached. However, each trend appears to be continuous. The thermoelastic anisotropy, calculated on the basis of the unit-strain parameters between T_0 and each measured T , is almost maintained within the T -range investigated. The maximum anisotropy is observed between 20 and 300 $^\circ\text{C}$, with $\varepsilon_1 : \varepsilon_2 : \varepsilon_3 = 1.38 : 1.33 : 1.00$.

The HT structure refinements show that Co, despite its ionic size vs. Mg, has a marked preference for site M1 even at high temperatures. Such ‘‘anomalous’’ site preference of Co in Co-Mg olivine was already reported in previous studies and two competing forces have been invoked for this site partitioning: i) the preference of cations larger than Mg for site M2 and ii) a stronger covalent bonding of the d -orbitals in transition metal cations hosted in site M1. These two conflicting effects nearly neutralise each other in the case of Fe-Mg compositions thus explaining the essential lack of Fe-Mg ordering in natural olivines. Upon heating, the Co occupancy of site M1 shows an oscillatory behaviour whereby, after a noticeable decrease up to about 300 $^\circ\text{C}$, it climbs back up until approximately 800 $^\circ\text{C}$ to then decrease again by about 30% of its original value at the highest temperature reached in the experiment. This behaviour of the Co occupancy, evidenced by a K_D plot vs. T , is suggestive of a strong resistance offered by Co in site M1 to thermally induced disorder.