Composition and temperature dependence of cation ordering in Ni-Mg olivine solid solutions: a time-of-flight neutron powder diffraction and EXAFS study

C. MICHAEL B. HENDERSON,[1,*] SIMON A.T. REDFERN,[2] RONALD I. SMITH,[3] KEVIN S. KNIGHT,[3] AND JOHN M. CHARNOCK[1]

[1]Department of Earth Sciences, University of Manchester, Manchester M13 9PL, U.K. and Daresbury Laboratory, CLRC, Warrington WA4 4AD, U.K.
[2]Department of Earth Sciences, Downing Street, University of Cambridge, Cambridge CB2 3EQ, U.K.
[3]ISIS, Rutherford Appleton Laboratory, CLRC, Chilton, Oxfordshire OX11 0QX, U.K.

ABSTRACT

The non-convergent ordering of Mg and Ni over the M1 and M2 sites of synthetic olivines has been studied using "time of flight" neutron powder diffraction and X-ray absorption spectroscopy (EXAFS). The compositional dependence of order/disorder at room temperature was established for solid solutions of general formula $(Mg_{1-x}Ni_x)_2SiO_4$, where $X = 0.15, 0.2, 0.25, 0.3, 0.5$, and 0.8 atoms Ni ($X_{Ni}$; i.e., mole fraction of Ni-olivine end-member). Ni orders into M1 with $K_D = (Ni/Mg \text{ in } M1)/(Ni/Mg \text{ in } M2)$ reaching a maximum of 9.5 at a composition of $Mg_{1.6}Ni_{0.4}SiO_4$. The temperature dependence of order/disorder at up to 1100 °C was determined for two samples ($X_{Ni} = 0.2$ and 0.5). Between about 600 and 750 °C the samples show an *increase* in order due to kinetic effects, while above 750 °C the samples show a progressive *decrease* in order and describe an equilibrium disordering path. Equilibrium data define a Ni-Mg, M1-M2 intersite exchange energy of 21.5 ± 1.9 kJ/mol. On cooling, the blocking temperature for cation exchange is about 800 °C.

The kinetics of disordering behavior were analyzed using a Ginzburg-Landau model giving activation energies for Mg-Ni exchange between M1 and M2 for samples of composition $Mg_{1.6}Ni_{0.4}SiO_4$ and $Mg_{1.0}Ni_{1.0}SiO_4$ of 145 ± 5 and 160 ± 5 kJ/mol, respectively. The model also shows that the characteristic time scale for re-equilibration of M1-M2 order decreases from around 2.5 s at 1000° to 0.03 s at 1300 °C. This points to the inapplicability of intracrystalline Ni-Mg partitioning for obtaining geothermometry and geospeedometry information for magmatic conditions. Ni K-edge EXAFS data show that samples with $X_{Ni} = 0.15, 0.2, 0.25$ and 0.3 all show Ni clustering on adjacent M1 sites, indicating the presence of domains of Ni-rich and Mg-rich regions on a nanolength scale of < 10 Å. These "precipitates" are at least an order of magnitude too small to be detectable by neutron powder diffraction. We suggest that the elastic strain at the interfaces between the Ni-rich precipitates and the Mg-rich matrix is responsible for the plateau or possible maximum in the *b* unit-cell parameter as a function of composition across the solid solution, which is observed at a composition of $Mg_{1.6}Ni_{0.4}SiO_4$ at room temperature. Comparison of our data with earlier studies at high *P* and *T* on $Mg_{1.0}Ni_{1.0}SiO_4$ olivine suggests that the effect of *P* is to increase the degree of order of Ni into M1 and to slow down the kinetics of intersite exchange with a $\Delta V_{disorder}$ of 0.039 J/bar.