

## **A Monte Carlo investigation of the thermodynamics of cation ordering in 2-3 spinels**

**ERIKA J. PALIN\* AND RICHARD J. HARRISON**

Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge CB2 3EQ, U.K.

### **ABSTRACT**

The Monte Carlo (MC) simulation technique is a powerful tool for the investigation of thermodynamic and kinetic phenomena in minerals, and is especially well suited to the study of cation ordering. We have performed MC simulations of eight end-member 2-3 spinels ( $X^{2+} = \text{Mg, Fe, Zn, Ni}$ ;  $X^{3+} = \text{Al, Fe}$ ) using pair interaction parameters,  $J_i$ , and chemical potentials,  $\mu$ , derived from atomistic simulations. The  $J_i$  values for all but one of these spinels are remarkably similar, despite their different character (normal vs. inverse). The sign of  $\mu$ , and hence the tendency to form a normal or inverse spinel, was correctly predicted in all cases. Agreement between the simulated and observed cation distributions as a function of temperature is good for the normal spinels and poor for the inverse spinels. Agreement could be greatly improved for the inverse spinels through relatively modest adjustments to the simulation parameters (usually increasing the strength of the tetrahedral-octahedral, T-O, interactions, and decreasing the magnitude of  $\mu$ ).

We have developed an atomistic random-mixing model for cation ordering in spinels and compared it with the macroscopic O'Neill-Navrotsky model. In so doing, we have determined the relative contributions of  $\mu$ , tetrahedral-tetrahedral (T-T), octahedral-octahedral (O-O), and T-O interactions to the O'Neill-Navrotsky coefficients  $\alpha$  and  $\beta$ . We found that the value of  $\beta$  depends on the relative enthalpy contributions of (T-T + O-O) vs. T-O interactions, a useful insight considering the large spread of values found experimentally to be taken by  $\beta$ .

We used the thermodynamic integration technique to quantify the entropy, and hence the amount of short-range order, present in the spinels studied. We found that there is virtually no short-range order in the normal spinels. There is significant short-range order in the inverse spinels, though in the experimentally accessible temperature range, the contribution of this short-range order to the entropy is comparatively small. At very low temperatures, we find that the octahedral cations in the inverse spinels become ordered, reducing the symmetry to  $P4_122$ , in agreement with other simulated findings for 2-3 spinels and experimental findings for 4-2 spinels.

**Keywords:** Spinel, thermodynamics, Monte Carlo simulation, O'Neill-Navrotsky model, short-range order