A computational model of cation ordering in the magnesioferrite-qandilite (MgFe$_2$O$_4$-Mg$_3$TiO$_4$) solid solution and its potential application to titanomagnetite (Fe$_3$O$_4$-Fe$_2$TiO$_4$)

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Abstract

Cation ordering in the magnesioferrite-qandilite (MgFe$_2$O$_4$-Mg$_3$TiO$_4$) solid solution has been investigated using an interatomic potential model combined with Monte Carlo simulations. The dominant chemical interaction controlling the thermodynamic mixing behavior of the solid solution is a positive nearest-neighbor pairwise interaction between tetrahedrally coordinated Fe$^{2+}$ and octahedrally coordinated Ti$^{4+}$ ($J^\text{T} _\text{Fe-Ti}$). The predicted cation distribution evolves gradually from the Néel-Chevalier model to the Akimoto model as a function of increasing $J^\text{T} _\text{Fe-Ti}$ with $J^\text{T} _\text{Fe-Ti} = 1000 \pm 100$ K providing an adequate description of both the temperature and composition dependence of the cation distribution and the presence of a miscibility gap. Although Mg is a good analog of Fe$^{2+}$ in end-member spinels, a comparison of model predictions for MgFe$_2$O$_4$-Mg$_3$TiO$_4$ with observed cation ordering behavior in titanomagnetite (Fe$_3$O$_4$-Fe$_2$TiO$_4$) demonstrates that the analog breaks down for Fe$_2$O$_3$-rich compositions, where a value of $J^\text{T} _\text{Fe-Ti}$ closer to zero is needed to explain the observed cation distribution. It is proposed that screening of Ti$^{4+}$ by mobile charge carriers on the octahedral sublattice is responsible for the dramatic reduction in $J^\text{T} _\text{Fe-Ti}$. If confirmed, this conclusion will have significant implications for attempts to create a realistic thermodynamic model of titanomagnetite.

Keywords: Magnesioferrite, qandilite, titanomagnetite, cation distribution, computer simulations

Introduction

The titanomagnetite solid solution between magnetite (Fe$_3$O$_4$) and ulvöspinel (Fe$_2$TiO$_4$) is the dominant carrier of magnetic remanence in nature and is of central importance to paleomagnetic, rock magnetic, and mineral magnetic studies. Both end-members adopt the cubic inverse spinel structure at room temperature, with cations occupying two distinct types of crystallographic site (tetrahedral and octahedral). The distribution of Fe$^{3+}$, Fe$^{2+}$, and Ti$^{4+}$ cations between tetrahedral and octahedral sites has a profound impact on the intrinsic magnetic properties of titanomagnetite. The presence of tetrahedral Fe$^{2+}$ is of particular importance, as this has been linked to large increases in both magnetocrystalline anisotropy and magnetostriiction due to a dynamic Jahn-Teller distortion (Κακόλ et al. 1991a, 1991b; Church et al. 2011). However, despite numerous studies performed over many years with a range of increasingly sophisticated analysis techniques (see Pearce et al. 2010 for a review), there is still no consensus regarding the temperature and composition dependence of the cation distribution in titanomagnetite. For example, two of the most recent and detailed studies [Bosi et al. (2009) using X-ray single-crystal diffraction and Pearce et al. 2010 using X-ray magnetic circular dichroism] present results that are at opposite extremes of the range of previously reported cation distributions and that disagree dramatically in their assessment of when Fe$^{2+}$ first enters the tetrahedral site.

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