American Mineralogist, Volume 91, pages 880–893, 2006

Direct determination of cation site occupancies in natural ferrite spinels by $L_{2,3}$ X-ray absorption spectroscopy and X-ray magnetic circular dichroism

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Abstract

Cation distributions in natural ferrite spinels, some containing large amounts of Mg, Ti, Mn, and Zn, have been investigated using the element-, site-, and symmetry-selective spectroscopic techniques of $L_{2,3}$ X-ray absorption spectroscopy (XAS) and X-ray magnetic circular dichroism (XMCD). By comparing XMCD data with calculated spectra, the site occupancies of the Fe cations have been determined. From the analysis of natural ferrite spinels with formulae very close to that of pure magnetite (Fe_3O_4), a standard XMCD spectrum for natural magnetite is proposed. Magnetites with small numbers of cation vacancies due to oxidation (solid solutions with maghemite, γ-Fe_2O_3) show that all the vacancies occur in octahedral sites. Ti $L_{2,3}$ XAS of oxidized Ti-bearing magnetites (hereafter referred to titanomagnetites) shows that Ti is tetravalent occurring on the octahedral site with $10Dq$ ~2eV; Fe $L_{2,3}$ XMCD spectra indicate that the vacancies occur in both tetrahedral and octahedral sites. Mn $L_{2,3}$ XAS of the Mn-rich ferrite spinels shows that Mn is predominantly ordered onto the tetrahedral site with an Mn^{2+}:Mn^{3+} ratio of 0.85:0.15. Mn- and Zn-rich ferrite spinels have an excess of cations over 3.0 per 4-oxygen formula unit. The sign of the XMCD for Mn corresponds to a parallel alignment of the Mn moments with the Fe^{3+} moments in the tetrahedral sublattice.

This work demonstrates clearly that combined XAS and XMCD provides direct information on the distribution of multivalent cations in chemically complex magnetic spinels.

Keywords: Analysis, chemical (mineral), natural ferrite spinel, magnetite, major and minor elements, magnetic properties, order-disorder, site vacancies in natural ferrite spinel, XAS (XMCD), XRD data, microprobe analysis, Fe^{2+}/Fe^{3+} ratio, cation distribution