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Fe site occupancy in magnetite-ulvöspinel solid solutions: A new approach using X-ray magnetic circular dichroism

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Abstract

Ordering of Fe^{3+} and Fe^{2+} cations between octahedral and tetrahedral sites in synthetic members of the magnetite-ulvöspinel (Fe_3O_4-Fe_2TiO_4) solid-solution series was determined using Fe $L_{2,3}$-edge X-ray magnetic circular dichroism (XMCD) coupled with electron microprobe and chemical analysis, Ti $L_{2,3}$-edge and Fe *K*-edge X-ray absorption spectroscopy (XAS), and unit-cell parameters. Microprobe analyses, cell edges, and chemical FeO determinations showed that bulk compositions were stoichiometric magnetite-ulvöspinel solid solutions. XMCD showed that the surface was sensitive to redox conditions, and samples required re-equilibration with solid-solid buffers. Detailed site-occupancy analysis gave Fe^{2+}/Fe^{3+} XMCD-intensity ratios close to stoichiometric values.

$L_{2,3}$-edge XAS confirmed that Ti^{4+} was restricted to octahedral sites. XMCD showed that significant Fe^{2+} only entered the tetrahedral sites when Ti content was >0.40 atoms per formula unit (apfu), whereas Fe^{2+} in octahedral sites increased from 1 apfu in magnetite to a maximum of ~1.4 apfu when Ti content was 0.45 apfu. As Ti content increased, a steady increase in Fe^{2+} in tetrahedral sites was observable in the XMCD spectra, concurrent with a slow decrease in Fe^{2+} in octahedral sites. Calculated magnetic moments decreased rapidly from magnetite (4.06 μ_B) to USP45 (1.5 μ_B), then more slowly toward ulvöspinel (0 μ_B). Two synthesized samples were maghemitized by re-equilibrating with an oxidizing buffer. XMCD showed that Fe^{2+} oxidation, with concomitant vacancy formation, was restricted to octahedral sites. Through the direct measurement of Fe oxidation states, XMCD results can be used to rationalize the magnetic properties of titanomagnetites, along with oxidized titanomaghemitized analogs, in Earth's crustal rocks.

Keywords: Titanomagnetite, titanomaghemite, cation site ordering, vacancy ordering, X-ray absorption spectroscopy, X-ray magnetic circular dichroism, magnetic moment