Structural Chemistry of Fe, Mn, and Ni in Synthetic Hematites as Determined by Extended X-Ray Absorption Fine Structure Spectroscopy

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Abstract: The incorporation of transition metals into hematite may limit the aqueous concentration and bioavailabity of several important nutrients and toxic heavy metals. Before predicting how hematite controls metal-cation solubility, we must understand the mechanisms by which metal cations are incorporated into hematite. Thus, we have studied the mechanism for Ni^{2+} and Mn^{3+} uptake into hematite using extended X-ray absorption fine structures (EXAFS) spectroscopy. EXAFS measurements show that the coordination environment of Ni^{2+} in hematite corresponds to that resulting from Ni^{2+} replacing Fe^{3+}. No evidence for NiO or $Ni(OH)_2$ was found. The infrared spectrum of Ni-substituted hematite shows an OH-stretch band at 3168 cm^{-1} and Fe-OH bending modes at 892 and 796 cm^{-1}. These vibrational bands are similar to those found in goethite. The results suggest that the substitution of Ni^{2+} for Fe^{3+} is coupled with the protonation of one of the hematite oxygen atoms to maintain charge balance.

The solubility of Mn^{3+} in hematite is much less extensive than that of Ni^{2+} because of the strong Jahn-Teller distortion of Mn^{3+} in six-fold coordination. Structural evidence of Mn^{3+} substituting for Fe^{3+} in hematite was found for a composition of 3.3 mole % Mn_2O_3. However a sample with nominally 6.6 mole % Mn_2O_3 was found to consist of two phases: hematite and ramsdellite (MnO_2). The results indicate that for cations, such as Mn^{3+} showing a strong Jahn-Teller effect, there is limited substitution in hematite.

Key Words: EXAFS • Fe Oxides • Hematite • Metal Substitution • Trace Elements • XAS • XRD

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