

Structural environment and oxidation state of Mn in goethite-groutite solid-solutions

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ABSTRACT

Both X-ray absorption and diffraction techniques were used to study the structural environment and oxidation state of Mn in goethite-groutite solid solutions, $\alpha\text{-Mn}_x\text{Fe}_{1-x}\text{OOH}$, with $x_{\text{Mn}} \leq 0.47$. Rietveld refinement of X-ray diffraction (XRD) data was employed to investigate the statistical long-range structure. The results suggest that increasing x_{Mn} leads to a gradual elongation of Fe and Mn occupied octahedra which, in turn, causes a gradual increase of the lattice parameter a and a gradual decrease of b and c in line with Vegard's law. X-ray absorption fine structure (XAFS) spectra at the $\text{MnK}\alpha$ and $\text{FeK}\alpha$ edges revealed, however, that the local structure around Fe remains goethite-like for $x_{\text{Mn}} \leq 0.47$, while the local structure around Mn is goethite-like for $x_{\text{Mn}} \leq 0.13$, but groutite-like for higher x_{Mn} . The spectral observations were confirmed by XAFS-derived metal distances showing smaller changes around Fe and larger changes around Mn as compared with those determined by XRD. Therefore, the XAFS results indicate formation of groutite-like clusters in the goethite host structure for $x_{\text{Mn}} > 0.13$, which remain undetected by XRD. The first prominent resonance peak in the X-ray absorption near-edge spectra (XANES) of the Mn goethites was 17.2 to 17.8 eV above the Fermi level of Mn (6539 eV), in line with that of Mn^{3+} reference compounds, and well separated from that of Mn^{2+} and Mn^{4+} compounds. Therefore, Mn in goethite is dominantly trivalent regardless of whether the samples were derived from Mn^{2+} or Mn^{3+} solutions. This may indicate a catalytic oxidation of Mn^{2+} during goethite crystal growth similar to that found at the surface of Mn oxides.