
Preparation and Properties of Hematite with Structural Phosphorus

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Abstract: Synthetic hematites prepared in the presence of phosphate can incorporate phosphorus (P) in forms other than phosphate adsorbed by ligand-exchange on the crystal surface. To investigate the nature of such occluded P, which is also found in some natural specimens, we prepared 13 hematites by aging ferrihydrite precipitated from $\text{Fe}(\text{NO}_3)_3\text{-KH}_2\text{PO}_4$ solutions. The P/Fe atomic ratio of the resulting hematites ranged from 0 to 3% and all incorporated significant amounts of OH. As P content is raised, particle morphology changes from rhombohedral to spindle or ellipsoid-shaped. Despite the grainy appearance in transmission electron microscope images, X-ray diffraction data indicate that the particles are single crystals. Specific surface area ranged from 66 to 91 $\text{m}^2 \text{g}^{-1}$, partly in micropores. The intensity of the absorption bands due to Fe^{3+} ligand field transition in the visible region, as measured by the second derivative of the Kubelka-Munk function, suggests that both OH and P contribute to an Fe deficiency in the structure. Such a deficiency is also apparent from the 104/113 peak intensity ratio in the X-ray diffraction patterns. The *c* unit-cell length increases with increasing P content. The infrared spectra exhibit four bands in the P-OH stretching region (*viz.*, at 936, 971, 1005, and 1037 cm^{-1}) which suggest that occluded PO_4 possesses a low symmetry. Congruent dissolution of P and Fe was observed on acid treatment of the hematites, the dissolution rate being negatively correlated with the P content. All observations are consistent with the occluded P in the hematites being structural. A model is proposed where P occupies tetrahedral sites in the hematite structure, thus resulting in an Fe deficiency and facilitating proton incorporation.

Key Words: $\alpha\text{-Fe}_2\text{O}_3$ • Hematite • Color • Crystal Chemistry • Dissolution • IR Spectra • Structural P • Structure

Clays and Clay Minerals; June 1999 v. 47; no. 3; p. 375-385; DOI: [10.1346/CCMN.1999.0470314](https://doi.org/10.1346/CCMN.1999.0470314)

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