
Effect of Phosphate on the Crystallization of Hematite, Goethite, and Lepidocrocite from Ferrihydrite

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Abstract: We investigated the crystallization of ferrihydrite prepared by hydrolysis of $\text{Fe}(\text{NO}_3)_3$ solutions containing phosphate. Crystallization was studied at different pH (3– 9), temperatures (298, 323, and 373 K), and initial P/Fe atomic ratios for periods to 730 d. Generally, crystallization was inhibited or only poorly crystallized lepidocrocite was formed at $\text{P/Fe} > 2.5\%$. Phosphate favored the formation of hematite over goethite at all temperatures for most of the pH and P/Fe ranges investigated. This result is consistent with a model in which phosphate acts as a template for hematite formation, in analogy with other anions, such as oxalate. However, goethite was preferentially formed at alkaline pH and $\text{P/Fe} > 1\%$, probably because high phosphate concentration resulted in a large increase in the negative charge of the ferrihydrite particles. This resulted in turn in less aggregation, a process that is known to precede dehydration to hematite. Phosphate greatly influenced the morphology of hematite and goethite. Hematite was often ellipsoidal or spindle-shaped. Twinned goethite crystals with a hematite core were formed at alkaline pH at $\text{P/Fe} > 1\%$. Both hematite and goethite particles incorporated phosphate in an occluded form not desorbable by repeated alkali treatments.

Key Words: Crystallization • Ferrihydrite • Goethite • Hematite • Lepidocrocite • Phosphate

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