
Effect of pH on the Formation of Goethite and Hematite from Ferrihydrite

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Abstract: Storage of ferrihydrite in aqueous suspensions at 24° C and pHs between 2.5 and 12 for as long as three years resulted in the formation of goethite and hematite. The proportions and crystallinity of these products varied widely with the pH. Maximum hematite was formed between pH 7 and 8, and maximum goethite at pH 4 and at pH 12. The crystallinity of both products, as indicated by X-ray powder diffraction line broadening and magnetic hyperfine field values and distribution widths, was poorer, the lower the proportion of the corresponding product in the mixture. The existence of two competitive formation processes is suggested: goethite is formed via solution, preferably from monovalent Fe(III) ions $[\text{Fe}(\text{OH})_2^+$ and $\text{Fe}(\text{OH})_4^-]$, and hematite by internal rearrangement and dehydration within the ferrihydrite aggregates. This concept relates the proportions of goethite and hematite to the activity of the Fe(III) ion species in solution, and implies that conditions favorable for the formation of goethite are unfavorable for that of hematite and vice versa.

Key Words: Ferrihydrite • Goethite • Hematite • Mössbauer spectroscopy • pH • X-ray powder diffraction

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