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Transformation of 2-line ferrihydrite to 6-line ferrihydrite under oxic and anoxic conditions

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ABSTRACT

Mineralogical transformations of 2-line ferrihydrite were studied under oxic and Fe^{3+}-reducing conditions to establish the role, if any, of 6-line ferrihydrite ("well" organized ferrihydrite) in the reaction pathway and as a final product. In oxic experiments, concentrated suspensions (0.42 mol/L Fe^{3+} in 0.1 mol/L $NaClO_4$) of freshly synthesized 2-line ferrihydrite, with and without 3% Ni^{2+}, were aged at an initial pH = 7.2 (unbuffered and unadjusted) and 25 °C for more than three years. X-ray diffraction, transmission electron microscopy, and Mössbauer spectroscopy measurements were performed on the solids after different aging periods. The primary mineralogical products observed were 6-line ferrihydrite and goethite, with minor hematite. Aggregation and crystallization of the 2-line ferrihydrite liberated protons and depressed suspension pH, but coprecipitated Ni^{2+} retarded this process. The joint, interrelated effects of Ni and pH influenced both the extent of conversion of 2-line ferrihydrite and the identity of the major transformation products. Six-line ferrihydrite dominated in the Ni ferrihydrite suspension, whereas goethite dominated in the absence of Ni. Aggregation-induced crystallization of 2-line ferrihydrite particles seemed responsible for 6-line ferrihydrite formation. Mineralogical changes to Ni ferrihydrite under anaerobic conditions were investigated at circumneutral pH using the Fe^{3+}-reducing bacterium *Shewanella putrefaciens*. Residual 6-line ferrihydrite dominated bioreduced samples that also contained goethite and magnetite. The conversion of 2-line ferrihydrite to 6-line ferrihydrite was considerably more rapid under anaerobic conditions. The sorption of biogenic Fe^{2+} apparently induced intra-aggregate transformation of 2-line ferrihydrite to 6-line ferrihydrite. Collectively, abiotic and biotic studies indicated that 6-line ferrihydrite can be a transformation product of 2-line ferrihydrite, especially when 2-line ferrihydrite is undergoing transformation to more stable hematite or magnetite.