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 Fe3+-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 Fe3+ in 0.1 mol/L NaClO4) of freshly synthesized 2-line ferrihydrite, with and without 3% Ni2+, 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 Ni2+ 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 Fe3+-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 Fe2+ 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.

INTRODUCTION

Poorly crystalline Fe3+-oxides (ferrihydrites) that commonly exist in soils and sediments are thermodynamically unstable and, with time, transform to more crystalline Fe3+ oxides, e.g., goethite, hematite (Cornell and Schwertmann 1996). The transformation into crystalline Fe3+ oxides is widely believed to proceed via two competing mechanisms (Feitknecht and Michaelis 1962; Schwertmann and Murad 1983). Goethite formation involves the dissolution of ferrihydrite followed by nucleation and precipitation of the crystalline oxide in solution, whereas hematite forms through dehydration and internal atomic arrangement of the solid ferrihydrite, with less dependence on dissolution mechanism. The predominant mechanism depends primarily on suspension pH (Schwertmann and Murad 1983), with hematite formation achieving a maximum near pH 8 and goethite near pH 4 and 11.

Aggregation-based crystal growth and phase transformation has also been advanced as an alternative mechanism to explain the transformation of 2- to 3-nm ferrihydrite particles to poly-crystalline Fe3+ oxides at pH conditions where the Fe-oxide phase is relatively insoluble (Banfield et al. 2000). Moreover, Schwertmann et al. (1999) suggested that nano-particle aggregation was essential to induce crystallization of ferrihydrite to hematite. Ferrihydrite aggregation is maximal near the pH of zero net charge of the ferrihydrite “surface” (pH ~8), and crystallizing hematite nuclei are apparently supplied by a short-range dissolution process involving precursor aggregates.

Synthetic and natural ferrihydrites are poorly ordered, but both exhibit a continuum in structure from amorphous to partly crystalline (Carlson and Schwertmann 1981; Cornell and Schwertmann 1996). Ferrihydrite exhibits a range of XRD patterns; the least crystalline variety exhibits two broad peaks (2-line ferrihydrite), and the more crystalline variety exhibits six broad peaks (6-line ferrihydrite). Several structural models of 6-line ferrihydrite have been proposed, with the defective hematite structural model proposed by Chukrov et al. (1973) and Towe and Bradley (1967) being the most widely accepted. In contrast, Drits et al. (1993) proposed on the basis of XRD simulations that all natural and synthetic ferrihydrites are multi-component phases comprised of defect-free and defective ferrihydrite mixed with ultradisperse hematite. The main dif-

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1The terms two-line ferrihydrite and HFO (hydrous ferric oxide) are commonly used synonymously (Cornell and Schwertmann 1996). The term HFO (e.g., Dzombak and Morel 1990) is applied to a material synthesized in the laboratory by rapid hydrolysis of a Fe3+ salt solution, with approximately 4–8 h aging at pH 7.