NOTE

THE TRANSFORMATION OF FERRIHYDRITE INTO LEPIDOCROCITE

Ferrihydrite (5Fe₂O₃·9H₂O) is a poorly-ordered mineral that with time, transforms into goethite (α-FeOOH) and/or hematite (α-Fe₂O₃) (Feitknecht & Michaelis, 1962; Schwertmann & Fischer, 1966). Foreign ions frequently modify the kinetics of the competing processes involved in the transformation and thus alter the proportions of goethite and hematite in the product (Fischer & Schwertmann, 1975; Cornell & Schwertmann, 1979; Cornell, 1987). Divalent metal ions may also cause ferrihydrite to transform to a spinel phase (Cornell, 1988).

We report transformation of ferrihydrite to yet another mineral—lepidocrocite (γ-FeOOH). This interconversion was achieved in a slightly acidic environment under the influence of a reducing organic ligand, L-cysteine (HSCH₂CH(NH₂)COOH).

Lepidocrocite is usually synthesized by oxidation of a ferrous system. Although there have been reports of precipitation from acidic ferric perchlorate solution (Feitknecht & Michaelis, 1962; Murphy et al., 1976), formation from ferrihydrite has not been reported previously. As ferrihydrite and lepidocrocite are widespread and important minerals in soils and sediments, and as interactions between colloidal iron oxides and organic ligands are important in aquatic systems, the present investigation may serve to provide further details of interconversions between iron oxyhydroxides in natural systems.

Materials and methods

Ferrihydrite (1 g/l) was precipitated from ferric nitrate solution at pH 7 with 1 M KOH. The pH of the suspension was adjusted to 6-6.5 with imidazol buffer (0-08 M) after which a freshly prepared solution of cysteine was added to give a cysteine : Fe ratio between 0.1 and 0.4; in most experiments this ratio equalled 0.2. The suspensions were held in closed polypropylene flasks at 70 or 25°C for up to 7 days. To facilitate comparison with previous studies dealing with the effects of other foreign ions, no attempt was made to exclude oxygen.

The crystalline reaction products were washed, dried at 50°C and examined by powder X-ray diffraction (XRD) using a Guinier-Enraf camera with Fe-Kα₁ radiation. Transmission electron microscopy (TEM) and selected area diffraction were carried out with a Hitachi H-600-2 electron microscope operating at 100 kV. Some samples were shadowed with chromium at an angle of 15°.

The kinetics of the transformation to crystalline products were followed by taking subsamples during the reaction and dissolving the unconverted ferrihydrite by extraction with 0.1 M HCl for 30 min at 25°C (Cornell & Schneider, 1989). Preliminary tests showed that no dissolution of lepidocrocite occurred during this period. The extent of the transformation was expressed as Feₐ/Fe, where Feₐ is the acid-soluble material (i.e.
unconverted ferrihydrite) and \( \text{Fe}_t \) is the total Fe in the system. Fe was determined by atomic absorption spectroscopy.

The interaction between cysteine and ferrihydrite was followed using differential pulse polarography (Polaroid E 506 Metrohm polarograph).

**Results and discussion**

Cysteine accelerated the transformation of ferrihydrite to more crystalline products. In the absence of the additive, the transformation (to a mixture of goethite and hematite) was incomplete after 7 days (70°C), whereas with cysteine, complete conversion was achieved within 72 h even at 25°C. Kinetic measurements showed that ferrihydrite transformed into crystalline products increasingly rapidly as the cysteine : Fe ratio rose (Fig. 1).

With a cysteine : Fe ratio of 0.2, ferrihydrite transformed into lepidocrocite together with a trace of goethite. The sharp XRD lines of lepidocrocite indicated a well crystallized product. TEM showed that lepidocrocite grew as lath-like crystals with serrated ends terminating in well developed \((h0l)\) faces (Fig. 2). The crystals had lengths of up to 5000 Å and widths of up to 1500 Å. TEM examination of shadowed crystals showed the crystal thickness to range from 200 to 800 Å, and selected area diffraction indicated that the crystals lay with the basal \((010)\) plane parallel to the electron microscope grid.

![Figure 1](image-url)

**FIG. 1.** Plot of \( \frac{\text{Fe}_a}{\text{Fe}_t} \) as a measure of the degree of transformation of ferrihydrite into more crystalline products, vs. time: (A) cysteine : Fe = 0.1, reaction products = hematite and lepidocrocite; (B) cysteine : Fe = 0.2, products = lepidocrocite and a trace of goethite; (C) cysteine : Fe = 0.4, product = goethite. pH 6, 70°C. \( \text{Fe}_a \) = acid-extractable Fe; \( \text{Fe}_t \) = total Fe in the system.
Lepidocrocite was not the only product formed at pH 6 from a cysteine-ferrihydrite system. The composition of the reaction product depended on the cysteine : Fe ratio and changed from a mixture of hematite and lepidocrocite (cysteine : Fe = 0.1) to lepidocrocite with a trace of goethite (cysteine : Fe = 0.2) and finally to goethite only (cysteine : Fe = 0.4).

Polarography measurements showed that cysteine was oxidized to the disulphide (cystine) when brought into contact with ferrihydrite. Catalytic oxidation of cysteine by ferric ions and oxides with simultaneous reduction of the ferric ions is well documented (McAuliffe & Murray, 1972; Cornell & Schneider, 1989). In the present instance, interaction of cysteine with ferrihydrite led to partial reduction of the interfacial ferric sites together with oxidation of the organic ligand.

Bernal et al. (1959) indicated that lepidocrocite formed in ferrous systems via green rust and it was suggested that a topotactic transformation was involved although details of the
mechanism were not established. In the present investigation the solid precursor of lepidocrocite was the partly reduced ferrihydrite—not green rust. As the transformation proceeded, the colour of the suspension changed from the reddish brown of ferrihydrite to the orange yellow of lepidocrocite; colours suggesting the presence of green rust were not observed. Furthermore, no crystalline phase (indicative of green rust) intermediate between the original ferrihydrite and lepidocrocite was detected by either XRD or TEM.

Addition of seed crystals of lepidocrocite to a cysteine/ferrihydrite suspension (cysteine: Fe = 0.1) promoted enhanced formation of lepidocrocite suggesting that the transformation involves a dissolution/reprecipitation mechanism. The completely different morphologies of ferrihydrite (particles 30–50 Å in diameter) and the lepidocrocite product (Fig. 2) are also in accord with such a transformation mechanism.

Apparently, the partly reduced ferrihydrite dissolved more rapidly than the original material; the reaction product depended on the extent of partial reduction. With a cysteine: Fe ratio of 0.1, fewer than 10% of the interfacial ferric ions could have been reduced, so the dehydration/rearrangement processes within ferrihydrite that lead to hematite (Fischer & Schwertmann, 1975), were competitive with dissolution leading to lepidocrocite, and hence a mixture of products resulted.

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REFERENCES


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