

ACID DISSOLUTION OF AKAGANÉITE AND LEPIDOCROCITE: THE EFFECT ON CRYSTAL MORPHOLOGY

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Abstract—The rate of dissolution of akaganéite in HCl increased with time over the bulk of the reaction leading to a sigmoid dissolution vs. time curve. The bulk of the dissolution of lepidocrocite could be described by the cube root law. Transmission electron microscopy examination of partly dissolved crystals of akaganéite showed that acid attack proceeded mainly along the [001] direction. Initially, the tapered ends of the crystals became squared, and as dissolution continued the lengths of the crystals decreased steadily. At the same time, the crystals were gradually hollowed out. Acid attack was most pronounced at the edges of the crystals of lepidocrocite and appeared to involve a disruption of the hydrogen bonds that link the sheets of octahedra making up the structure. Defects also acted as sites for preferential acid attack. Dissolution of multi-domainic crystals involved preferential attack along the domain boundaries, as well as at the edges of the crystals. Single-domain crystals were well developed, but appeared to contain internal imperfections, which promoted the formation of holes on the otherwise unreactive (010) faces.

Key Words—Akaganéite, Dissolution, Iron, Lepidocrocite, Morphology, Transmission electron microscopy.

INTRODUCTION

Iron oxides and oxyhydroxides are widespread in soils and sediments. Their dissolution can release ions which may be essential to plant growth or which may interact with other nutrients, thus limiting their availability to plants. Studies of their dissolution may be of value in clarifying mechanisms of chemical weathering and, hence, soil formation; for example, the transformation of lepidocrocite to goethite proceeds through dissolution of the thermodynamically less stable phase (Schwertmann and Taylor, 1972).

Dissolution of goethite (α -FeOOH) by proton attack has been studied intensively, and particular attention has been given to changes in the morphology of the crystals during the reaction (Cornell *et al.*, 1974, 1975; Schwertmann, 1984; Lim-Nunez and Gilkes, 1987). The rate law and mechanism of dissolution in HCl have also been established; the rate-determining step involves protonation of the surface together with formation of a chloride-Fe surface complex (Cornell *et al.*, 1976).

Two other polymorphs of FeOOH, akaganéite (β -FeOOH) and lepidocrocite (γ -FeOOH), dissolve in HCl by a mechanism similar to that reported for goethite (Sidhu *et al.*, 1981). Dissolution of these oxyhydroxides has, however, been studied in much less detail than that of goethite. The morphological aspects of the dissolution process have been neglected, and only the first few percentages of dissolution of akaganéite have been considered; the later stages of dissolution have not been investigated.

The present investigation extends earlier studies of the acid dissolution of akaganéite and lepidocrocite. The main aim of this work was to follow changes in crystal morphology as dissolution proceeded and to identify the sites of attack. Although a brief examination of partly dissolved lepidocrocite was made by Sidhu *et al.* (1981), the crystals used were highly aggregated, and little information about the sites of attack was obtained. In the present work, dissolution experiments were performed on well-dispersed, well-developed crystals on which morphological changes were easily observed. Morphological studies of partly dissolved crystals of akaganéite have not been made before. A second aim of this study was to obtain complete dissolution curves for both oxyhydroxides.

EXPERIMENTAL METHODS

For each kinetic experiment, a suspension was prepared by adding 0.1 g of oxyhydroxide to 100 ml of preheated 0.5 M HCl. The suspension was maintained at 76°C in a stoppered, insulated glass vessel containing a side arm, and stirred vigorously with a magnetic stirrer. Heating was by means of a hot plate. At intervals, samples were withdrawn through the side arm and filtered through a 0.22- μ m Millipore filter. Fe was analyzed by atomic absorption spectroscopy. The partly dissolved residues were examined by transmission electron microscopy (TEM).

Transmission electron micrographs were obtained using a Hitachi H-600-2 (100 kV) electron microscope. For TEM examination the samples were dispersed in

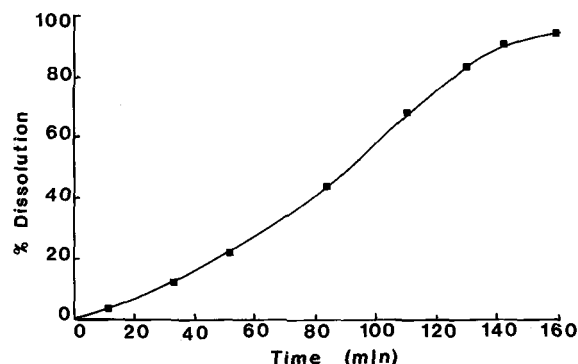


Figure 1. Extent of dissolution of β -FeOOH vs. time; 0.5 M HCl, 76°C.

twice-distilled water using an ultrasonic treatment, and a drop of suspension was dried on a carbon-coated bronze grid. Some samples were shadowed with chromium at an angle of 19°.

Synthetic akaganéite (BET surface area = 27 m²/g) was prepared by heating a solution of 0.5 M FeCl₃·6H₂O at 60°C for 8 days. Samples of lepidocrocite were prepared by passing air through FeCl₂ solutions held either at pH 6 (sample 1) or at pH 7 (sample 2), according to the method of Giovanoli and Brüttsch (1974). Sample 1 (BET surface area = 18 m²/g) contained a large proportion of multi-domainic crystals, whereas sample 2 (BET surface area = 14 m²/g) consisted mainly of single-domain crystals. Both oxyhydroxide samples were well washed and dried at 50°C.

RESULTS

Dissolution kinetics

The plot of percentage dissolution vs. time for akaganéite was sigmoid (Figure 1). The dissolution data were fitted to a number of different rate equations, but only the Avrami-Erofe'ev law (cf. Bamford and Tipper, 1980),

$$(-\ln(1 - \alpha)^{1/3}) = kt,$$

where α = extent of dissolution, gave a linear plot to 95% reaction. Application of this rate law indicates that the reaction was surface, rather than diffusion, controlled.

Figure 2 shows that although dissolution of lepidocrocite was initially very rapid, the final 20–30% proceeded slowly. The first 70% reaction followed the cube root law (Hixon and Crowell, 1931);

$$1 - \left(\frac{w}{w_0}\right)^{1/3} = kt,$$

where w_0 is the initial weight of the sample and w is the weight of the sample after time t . This equation implies that dissolution was surface controlled, three dimensional, and that the crystal shape was maintained

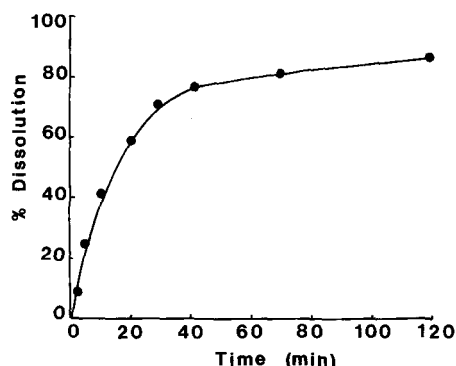


Figure 2. Extent of dissolution of γ -FeOOH (sample 1) vs. time; 0.5 M HCl, 76°C.

during the reaction. This is a reasonable description of the reaction because TEM showed that the lath-like shape of the particles was maintained over most of the reaction. The marked decrease in rate during the final stage of the reaction probably reflects a considerable drop in sample surface area as a result of the disappearance of the smaller crystals. The crystals of lepidocrocite had a wide size distribution. Segal and Sellars (1982) showed that oxides having a very narrow size distribution obey the cube root law for at least 90% dissolution, whereas for a sample having a non-uniform size distribution, this law is followed for only 60–70% of the reaction.

TEM observations

Akaganéite. The crystals of akaganéite were elongated along the [001] direction and lay on (100) and (010) faces on the electron microscope grid. The crystals were spindle shaped and had an average length of 3300 Å and an average width of 600 Å (Figure 3a). Some twinned crystals were also present.

Partial dissolution produced a striking change in the morphology of the crystals from spindles to rectangular rods. During dissolution the ends of the crystals became squared (Figures 3b and 3d). This dissolution behavior contrasts with that observed for acicular crystals of goethite in which the ends of the crystals become increasingly tapered during dissolution (Cornell *et al.*, 1974). The change from spindle-shaped to rod-shaped took place during the first 10% dissolution, and the rectangular shape thereafter persisted, with the crystals becoming increasingly shorter. Although rare corrugations at the sides of the crystals were present, dissolution appeared to proceed mainly along the [001] direction. The average width of ~600 Å was maintained to at least 80% dissolution (Figures 3e and 3f).

During the early stages of the reaction a few small, square crystals were noted (Figure 3d arrowed; Figure 3f); the amount of these crystals increased as the reaction proceeded. These square particles appeared to be crystals whose lengths had decreased to such an extent (<600 Å) that they lay end on, on the electron

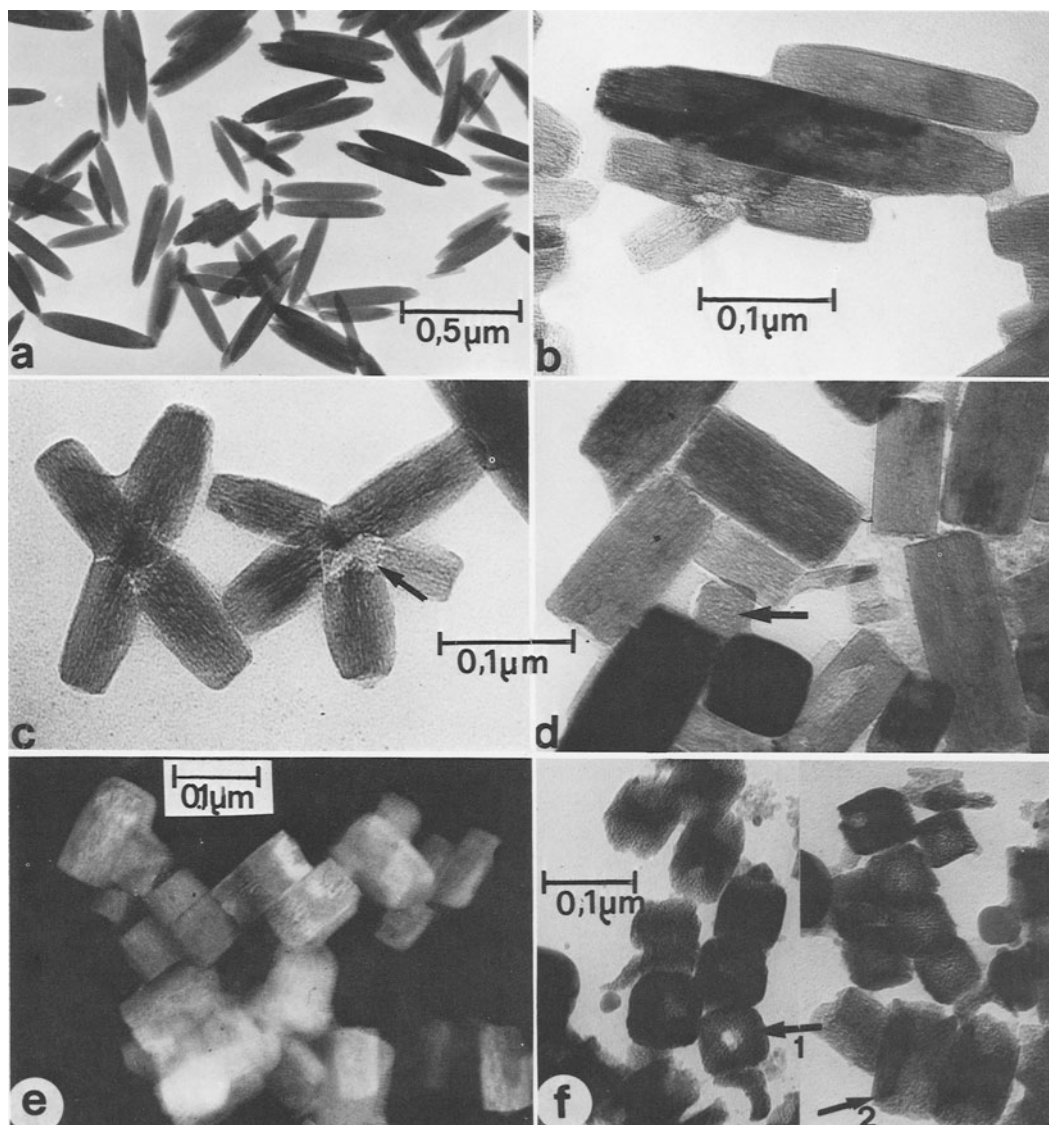


Figure 3. Transmission electron micrographs of β -FeOOH: (a) original crystals; (b) after 10% dissolution in 0.5 M HCl, 76°C; (c) twinned crystals after 10% dissolution; the ends of the arms of the twins are squared and some attack at the twin plane can be seen (arrow); (d) after 25% dissolution; arrow indicates a crystal lying on end; (e) Cr-shadowed (19°), partly dissolved (50%) crystals; (f) after 80% dissolution; arrow 1 indicates central hole in a crystal lying on end (i.e., (001) face), arrow 2 shows hollowing of a crystal lying on (100).

microscope grid. The dimensions of the square crystals were practically invariant ($500 \times 600 \text{ \AA}$) during most of the reaction, providing further evidence that dissolution along the [100] and [010] axes of the crystals was minimal. In the later stages of the reaction a central hole was often observed in the square crystals (Figure 3f). Apparently, the acid attack led to a gradual hollowing out of the crystals leaving the shell of the original crystal more or less intact. Some evidence of hollowing was also noted for shortened crystals lying on the (100) or (010) faces, and whose ends had developed a somewhat concave appearance (Figure 3f, arrow).

Twinned crystals were attacked more readily at the twin boundary; the ends of the crystals also became squared (Figure 3c). Inasmuch as the twin plane is a region of strain, preferential dissolution in this region would be expected (cf. goethite, Cornell *et al.*, 1974). During the later stages of dissolution no twinned crystals were observed, suggesting that rapid dissolution at the twin plane may have caused these crystals to disintegrate earlier in the reaction.

Lepidocrocite. Crystals of lepidocrocite were elongated in the [001] direction and lay on the (010) face on the

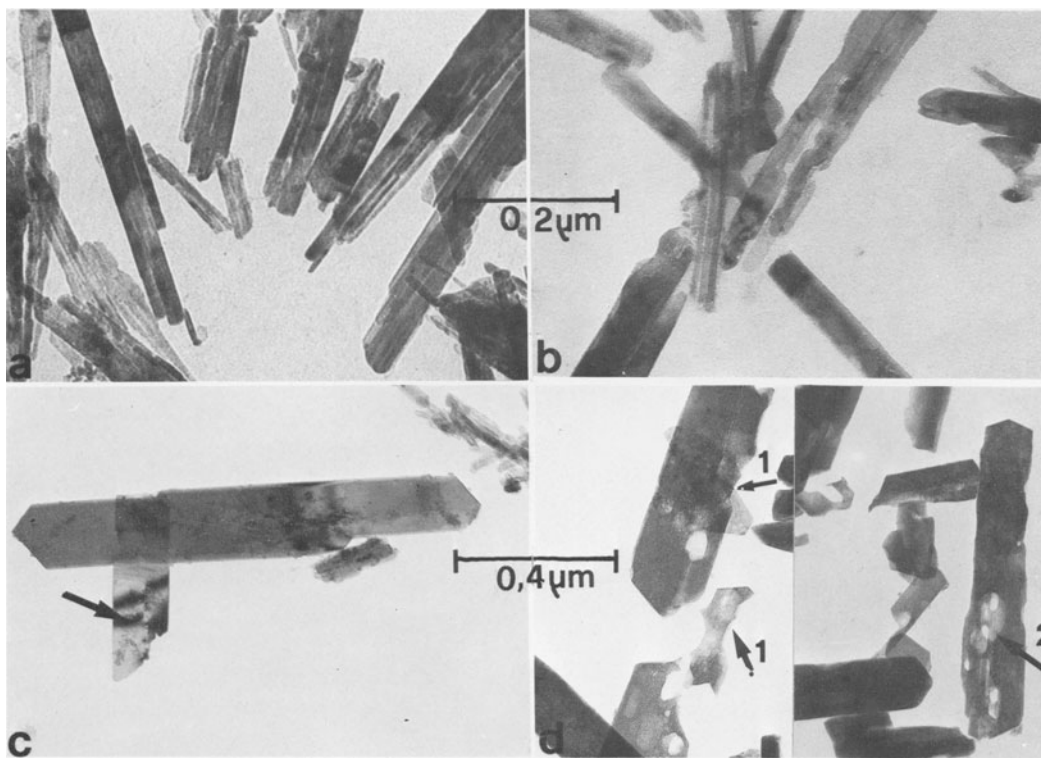


Figure 4. Transmission electron micrographs of γ -FeOOH: (a) multi-domainic crystals, sample 1; (b) sample 1 after 40% dissolution; (c) large, single-domain crystals and smaller crystals, sample 2; (d) sample 2 after 40% dissolution; arrow 1 indicates attack at the side; arrow 2 indicates hole formation at the surface of crystals.

electron microscope grid. TEMs of partly dissolved, single-domain and also multi-domainic crystals were obtained. Sample 1 consisted of crystals with lengths ranging from 1400 to 5000 Å and widths ranging from 200 to 1400 Å. These crystals were commonly multi-domainic and consisted of several domains 100–200 Å across (Figure 4a).

Acid attack was mainly at the sides of the crystals and at the boundaries between the domains (Figure 4b). As the reaction proceeded the crystals became shorter and extremely corrugated. Although fissures developed along the domain boundaries, other attack on the (010) faces was minimal. The crystals remaining after about 70% dissolution were ~3000 Å in length and presumably contained fewer defects than those that dissolved more rapidly. These crystals disappeared by becoming shorter and thinner; no corrugations or fissures developed. Multi-domainic crystals were almost entirely absent, suggesting that they had disintegrated at an earlier stage, or, alternatively, that the intergrowths observed at the ends of some of the crystals had dissolved preferentially.

Sample 2 consisted of large (10,000 Å in length) single-domain crystals together with some smaller (<1000 Å in length) crystals (Figure 4c). Morphological investigations were concerned only with the large crystals which were as much as 15,000 Å in length and

1600 Å in width. They were commonly terminated by well-developed (101) faces. Some irregularities along the sides of the crystals were noted, and numerous and irregularly distributed extinction contours on the (010) faces suggested the presence of some internal disorder.

Dissolution was rapid both at the sides of the crystals and at localized imperfections on the basal surfaces. Holes and fissures developed along the sides of the crystals from the start of the reaction; the most concentrated attack was located at the sides. Some holes were also noted on the (010) faces in the early stages of dissolution, but attack appeared most pronounced after about 40% dissolution (Figure 4d).

DISCUSSION

Akaganéite has the hollandite structure and contains tunnels running parallel to the [001] direction (i.e., the *c* axis). These tunnels are bounded by double chains of $\text{Fe}(\text{O},\text{OH})_6$ octahedra linked by corner sharing and by very weak hydrogen bonds. The tunnels open at the ends of the crystals and are filled with and stabilized by Cl^- ions (Figure 5; see also, Ellis *et al.*, 1976).

TEM showed that acid attack was almost exclusively at the ends of the crystals. Rapid dissolution in this region appeared to be the combined result of proton penetration of the tunnels together with destabilization of the structure by removal of the Cl^- ions. Initially,

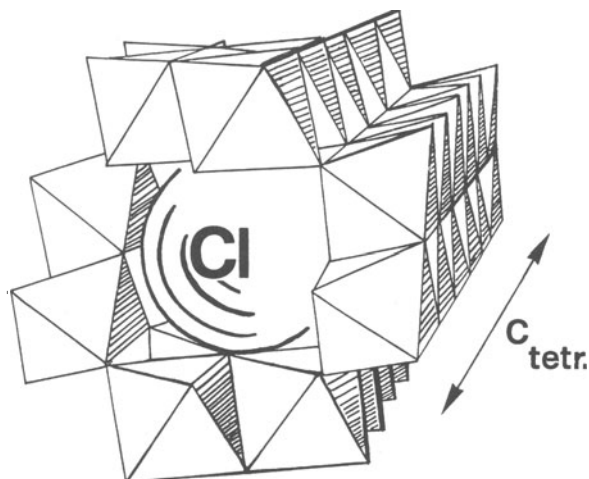


Figure 5. β -FeOOH (akaganéite) structure with the Cl^- ion wedged in the tunnel. The c -axis is along the double chains of $\text{Fe}(\text{O},\text{OH})_6$ octahedra.

proton attack could have disrupted part of an $\text{Fe}(\text{O},\text{OH})_6$ octahedron, thereby facilitating removal of the Cl^- ion which occupies the whole tunnel space. Once this ion had been removed, further disruption of the unwieldy 2×2 arrangement of octahedra would have been more likely, and dissolution could have proceeded increasingly readily. Probably disruption of the octahedral chains and removal of the Cl^- ions reinforced each other and accelerated the disintegration of the crystal.

During dissolution the crystals became hollowed out in the [001] direction. Although this feature was observed only in the later stages of the reaction, it probably developed during the early stages of the reaction. Breakdown of the crystal could have taken place in a cycle of steps, with a certain amount of hollowing being followed by rapid collapse of the surrounding shell, the whole process then being repeated.

Watson *et al.* (1962) considered that the somatoidal crystals of akaganéite had a so-called substructure and consisted of bundles of hollow rods, each rod having a cross section of 30 Å. For such a substructure, fissuring of the surfaces of the crystals as a result of preferential dissolution at the boundaries between the rods might be expected. In the present work, no surface fissuring during dissolution was observed; this result is in line with the high-resolution transmission electron microscopy study of Galbraith *et al.* (1979), which indicated that crystals of akaganéite were crystallographically homogeneous.

TEM showed that the lepidocrocite crystals dissolved preferentially at their edges. Acid attack was apparently concentrated here because the mineral consists of corrugated sheets of $\text{Fe}(\text{O},\text{OH})_6$ octahedra held together only by hydrogen bonds (Figure 6). These bonds were probably readily disrupted by proton attack, leading to the formation of holes at the edges of the crystals.

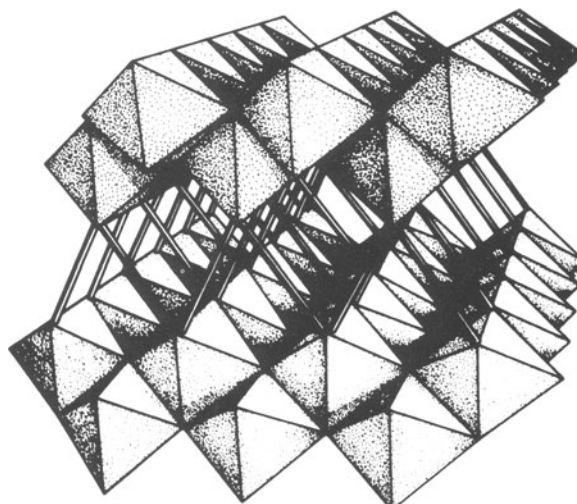


Figure 6. γ -FeOOH (lepidocrocite) structure. Sheets of $\text{Fe}(\text{O},\text{OH})_6$ octahedra are linked only by hydrogen bonds. The c -axis is along the sheets; the b -axis is perpendicular to the sheets.

The formation of such holes can be compared to the behavior observed during thermal decomposition of lepidocrocite. Here, because of the weak links between the sheets, pores formed at the edges of the crystals (Giovanoli and Brüttsch, 1974).

Except at domain boundaries or at surface imperfections, attack at the (010) face was slight. The surfaces of the sheets of octahedra in lepidocrocite are unreactive to phosphate adsorption as well as to acid attack (Lewis and Farmer, 1986). For phosphate adsorption, lack of reactivity has been attributed to the absence of singly coordinated hydroxyl groups (through which phosphate coordinates) on the (010) faces; only doubly coordinated hydroxyl groups are present on these faces (Lewis and Farmer, 1986). The absence of singly coordinated OH groups may also account for the resistance of the surfaces of the crystals to acid attack.

Lepidocrocite crystals having different morphologies have been noted by other authors (Schwertmann and Thalmann, 1976). Like goethite, lepidocrocite can display a multi-domainic character. The intergrowths are parallel to the long axis of the crystal and, as for goethite, assist in the acid dissolution of the crystals. These intergrowths develop in rapidly grown crystals (Schwertmann and Thalmann, 1976). The large well-developed crystals (sample 2) were the result of slower growth. Although these crystals appeared to be well formed, partial dissolution revealed that they contained many random, internal irregularities. These imperfections may have been the result of mistakes in stacking the layers of octahedra perhaps as a result of fluctuations in growth rate or due to interference from anions in the system; to date, their cause has not been investigated.

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