TRANSFORMATION OF AKAGANÉITE INTO GOETHITE AND HEMATITE IN ALKALINE MEDIA

R. M. Cornell[1] and R. Giovanoli[2]

[1] ETHZ Zürich, Laboratory of Inorganic Chemistry
CH-8092 Zürich, Switzerland

[2] University of Berne, Laboratory for Electron, Microscopy
Freiestrasse 3, CH-3000 Berne 9, Switzerland

Abstract—The conversion of akaganéite to goethite and/or hematite in alkaline media has been followed by X-ray powder diffraction and transmission electron microscopy (TEM). The rate of transformation fell and the amount of hematite in the product increased as the [OH⁻] decreased to <1 M. Kinetic studies and TEM indicated that the transformation involved dissolution of akaganéite followed by reprecipitation of goethite and/or hematite. The rate-determining step was the dissolution of akaganéite.

Silicate species retarded the formation of goethite + hematite principally by inhibiting dissolution of akaganéite; to a lesser extent, they interfered with the nucleation of goethite. Silicate modified the morphology of goethite, but not hematite.

Comparison of the transformation behavior of akaganéite with that previously observed for ferrihydrite indicated that the composition of the reaction product depended strongly on the transformation conditions, i.e., pH and the presence of foreign species. The nature of the solid precursor was important insofar as its degree of crystallinity governed the dissolution kinetics and its surface properties influenced interaction with any foreign species in the system.

Key Words—Akaganéite, Dissolution, Goethite, Hematite, Iron oxides, Transmission electron microscopy, X-ray powder diffraction.

INTRODUCTION

A characteristic feature of the iron oxide/hydroxide system is the variety of interconversions that take place between the different compounds. In general, these transformations involve either a topotactic reaction or a dissolution-reprecipitation mechanism. Interconversions between different iron oxides are important in soils and aquatic systems, in the formation of iron ore deposits, and in corrosion processes. They are also utilized industrially; e.g., magnetic iron oxide (γ-Fe_2O_3) is produced from goethite (α-FeOOH) in a series of steps involving dehydration to hematite (α-Fe_2O_3), reduction to magnetite (Fe_3O_4) and finally, re-oxidation to maghemite (γ-Fe_2O_3) (Winter, 1979).

One of the most intensively studied transformations is the conversion of ferrihydrite ($5Fe_2O_3 \cdot 9H_2O$) to goethite and/or hematite (Cornell *et al.*, 1989). The latter compounds appear to be the most stable of all the iron oxides and are the end members of many transformation pathways. This characteristic is probably responsible for the fact that these two compounds are widespread in natural systems. Preliminary experiments in this laboratory showed that in alkaline media at temperatures <100°C, the rate of conversion of iron oxides/hydroxides to goethite followed the order: ferrihydrite > γ-FeOOH > β-FeOOH > Fe_3O_4 ≫ γ-Fe_2O_3 > δ-FeOOH.

Comparison of the transformation behavior of these different compounds can provide information about the mechanisms of formation of goethite and hematite.

With the exceptions of lepidocrocite (Schwertmann and Taylor, 1972a) and ferrihydrite (Schwertmann and Murad, 1983; Cornell and Giovanoli, 1985) the transformations in alkaline media of the other compounds listed above have not been studied in any detail.

The present work considers the products and kinetics of the conversion of akaganéite (β-FeOOH) to goethite and hematite in alkaline media. A specific objective was to learn how the degree of ordering of a precursor influences the kinetics and products of the transformation. For this purpose, the behavior of akaganéite was compared with that of ferrihydrite (described in Cornell and Giovanoli, 1985) and lepidocrocite. Ferrihydrite is a poorly ordered material, and lepidocrocite is a crystalline material having a layer structure; differences in their transformation behavior from that of akaganéite (which has a tunnel structure) might, therefore, be expected.

A further aim of this investigation was to consider the effect of a foreign anion—monomeric silicate—on the kinetics of the transformation of akaganéite and on the morphology of the reaction products. Silicate was chosen because it is widespread in natural systems and is believed to retard goethite formation (Carlson and Schwertmann, 1981) and because laboratory experiments have shown it to retard markedly the transformation of lepidocrocite (Schwertmann and Taylor, 1972b) and ferrihydrite (Cornell *et al.*, 1987) to goethite.

The overall goal of the present investigation was to

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estimate the comparative importance of the nature of the precursor vs. the reaction conditions (e.g., pH, presence of foreign species) on the formation of goethite and hematite and ultimately to provide a better understanding of the formation of these oxides in natural systems.

EXPERIMENTAL

The transformation experiments were carried out by reacting 0.1 g of akaganéite (or, in some experiments, lepidocrocite) with 100 ml of KOH at 70°C for as long as 500 hr. Some long-term experiments were carried out at room temperature for 2 years. The solid was lightly ground in an agate mortar to break up aggregates; preliminary experiments indicated that the presence of aggregates led to erratic results. The concentration of KOH ranged from 0.005 M to 5 M; most experiments were carried out at between 0.01 and 1.0 M KOH. These levels of KOH were used to facilitate comparison with earlier studies of the transformation of ferrihydrite (Cornell and Giovanoli, 1985; Cornell *et al.,* 1987) and lepidocrocite (Schwertmann and Taylor, 1972a, 1972b), both of which involved KOH concentrations >0.1 M. The mechanisms by which these oxides transform into goethite/hematite are independent of pH, at least in the range 6 to 13 (Schwertmann and Taylor, 1972a; Schwertmann and Murad, 1983); hence, results obtained at high pH should be applicable to natural systems. Additional experiments involved alkaline transformations (0.1 to 1 M KOH) in the presence of either 5 M KNO_3 or silicate (10^{-5}–2×10^{-3} M, i.e., Si:Fe = 0.001–0.2). The reaction products were washed, dried at 50°C, and examined by X-ray powder diffraction (XRD), transmission electron microscopy (TEM), and scanning electron microscopy (SEM).

XRD patterns were obtained using a Guinier-Enraf camera (Mk IV) with $FeK\alpha_1$ radiation. The proportions of goethite and hematite in the product were estimated by comparison with a series of standards made by mixing known amounts of synthetic goethite and hematite. The 110 and 111 reflections of goethite and the 102 reflection of hematite were used.

The kinetics of the transformation were followed using a series of akaganéite-KOH suspensions. At predetermined intervals, samples were removed for XRD and TEM examination. The extent of transformation was expressed in terms of the disappearance of akaganéite; this facilitated measurements if the product was a mixture of goethite and hematite. The proportion of akaganéite remaining at any time was estimated with the aid of calibration curve made by mixing known amounts of synthetic akaganéite and goethite, or akaganéite, goethite, and hematite, depending on whether or not the product was a mixture of compounds. The 110 reflection of akaganéite was used for comparison. If a mixture of phases was produced, the goethite:hematite ratio in the calibration series was held constant.

Preliminary studies showed that this ratio varied only slightly during the reaction.

TEMs were obtained with a Hitachi H-600-2 (100 kV) electron microscope. The samples were dispersed ultrasonically in twice-distilled water, and a drop of suspension was dried on a carbon-coated bronze grid. Replicas were made by evaporating carbon and shadowing with chromium at 15°, followed by dissolving the oxide from the carbon coat with 1 M HF/HCl. SEMs were obtained on gold-sputtered samples in a JEOL JSM 840 scanning electron microscope.

Stock solutions containing 3×10^{-3} M H_4SiO_4 (pH 3) were prepared according to the method of Santschi and Schindler (1974). The adsorption of silicate on akaganéite or lepidocrocite was investigated by equilibrating 1 g of oxide in 100 ml of silicate solution ($[OH^-]$ = 0.5 M) for 24 hr. The solution was centrifuged, and the amount of silicate remaining in solution was measured by a molybdenum blue method (Vogel, 1961). The amount of silicate adsorbed by the oxide was found by difference.

Akaganéite was prepared by hydrolyzing 0.5 M $FeCl_3$ solution at 60°C for eight days. This material, which consisted of cigar-shaped crystals and had a BET surface area of 35 m^2/g, was used for most experiments. A second sample, consisting of rod-shaped crystals (BET surface area = 111 m^2/g) was prepared according to the method of Patterson and Tait (1977). Partly hydrolyzed $FeCl_3$ solution (OH:Fe = 0.5) was held at room temperature for 50 hr. The OH:Fe ratio was then increased to 2.75 with KOH, and the suspension was heated at 70°C for seven days. Lepidocrocite was prepared by the urotropin method of Brauer (1954). This material consisted of very thin, lath-like crystals and had a BET surface area of 77 m^2/g. Both oxyhydroxides were washed by dialysis and dried at 50°C.

RESULTS

Between pH 11 and 15, akaganéite transformed to goethite or a mixture of goethite + hematite. The kinetics of the reaction and, in turn, the proportion of hematite in the product depended principally on $[OH^-]$ and on the morphology (cigar-shaped or rod-shaped) of the crystals.

Reaction products (Table 1)

The cigar-shaped akaganéite crystals transformed to goethite in the range $[OH^-]$ = 0.5–2 M; outside this range, hematite + goethite were identified in the product. The proportion of hematite formed increased markedly as $[OH^-]$ decreased to <0.5 M. These results are qualitatively similar to those found by Cornell and Giovanoli (1985) for the effect of $[OH^-]$ on the transformation products of ferrihydrite. The XRD patterns of both goethite and hematite formed from akaganéite showed sharp lines ($2\theta < 0.2°$), indicating a well-crys-

Table 1. Proportion of hematite formed from akaganéite vs. [OH⁻].

[OH⁻] (M)	Hematite (%) from	
	Cigar-shaped crystals	Rod-shaped crystals
5	20	—
2	0	—
1	0	10
0.5	0	—
0.2	10	30
0.1	20	50
0.01	55	80
0.005	90	95

The other transformation product was goethite. The reaction was carried out at 70°C.

tallized product in all experiments. Lepidocrocite changed to goethite alone in the range [OH⁻] = 0.1–4 M.

Akaganéite (and lepidocrocite) could be induced to transform to a mixture of goethite + hematite, even in 1 M KOH, by increasing the ionic strength of the system to 6 M (by addition of KNO_3).

The addition of 10% seed crystals of either goethite or hematite to a suspension of akaganéite in 0.1 or 0.01 M KOH did not promote the formation of additional goethite or hematite.

The presence of silicate led to an increase in the amount of hematite in the product in 0.1 M KOH, but in the range 0.5–1.0 M KOH, only goethite formed, even in the presence of silicate concentrations as high as 2×10^{-3} M.

The proportion of hematite in the transformation product of the rod-shaped akaganéite was greater than for the cigar-shaped crystals at any particular [OH⁻] (Table 1). Even in 1 M KOH the rod-shaped sample was converted into a mixture of hematite (10%) + goethite.

Kinetics

Figure 1 shows that the plot of the extent of conversion of akaganéite to goethite or to goethite + hematite, vs. time was approximately sigmoidal. This shape was maintained over a range of OH⁻ concentrations and was independent of whether a single product or a mixture was obtained. The initial slow stage was considerably extended, and the rate of overall transformation fell as [OH⁻] decreased (Figure 1). Seeding the system with goethite did not reduce the slow stage nor accelerate the overall reaction.

Increasing the ionic strength to 6 M strongly retarded the reaction: in 1 M KOH with 5M KNO_3 added, only about 20% of the akaganéite had transformed after seven days, compared with 100% conversion within 24 hr in 1 M KOH alone.

Despite having a much higher surface area, the rod-shaped akaganéite changed to goethite + hematite far more slowly than did the cigar-shaped crystals (Figure
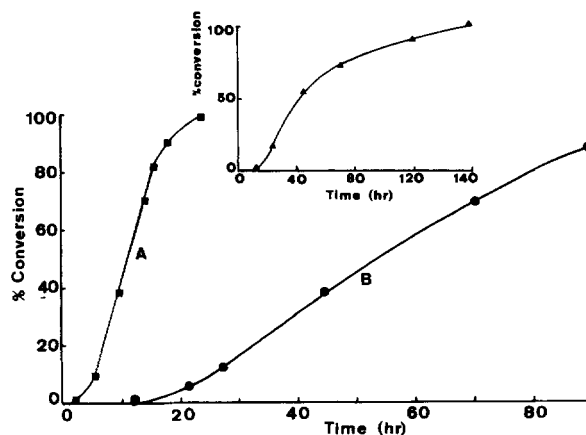

Figure 1. Extent of transformation of cigar-shaped akaganéite vs. time at 70°C: (A) 1 M KOH, (B) 0.1 M KOH. Inset: Extent of conversion of rod-shaped akaganéite vs. time in 1 M KOH, 70°C.

1, inset). At present, no explanation for this result can be offered.

The dissolution data could not be fitted to a first-order rate law (as can be the data for the transformation of ferrihydrite; see Schwertmann and Fischer, 1966), nor did they follow the cube root law (Hixon and Crowell, 1931). A good fit (0–90%), however, was obtained using the Avrami-Erof'ev law (Brown *et al.*, 1980):

$$(\ln(1 - \alpha))^{\frac{1}{2}} = kt,$$

where α is the extent of the transformation. The same law has been applied successfully to the acid dissolution of akaganéite (Cornell and Giovanoli, 1988). This finding, together with the observation that seeding did not influence the reaction, suggests that the rate-determining step in this transformation was the dissolution of akaganéite, not the nucleation or growth of the product. The Avrami-Erofe'ev law provided no information about the dissolution reaction apart from indicating that surface, not diffusion control operates.

Information about the formation of goethite + hematite from akaganéite was obtained from XRD patterns of samples taken at intervals during a transformation in 0.1 M KOH. The XRD pattern of the first sample (taken after 24 hr and corresponding to 5% transformation) showed reflections of both goethite and hematite indicating that both products nucleated during the initial stage of the reaction. Far more goethite than hematite nucleated in this system: after 24 hr, the ratio goethite/(goethite + hematite) = 4. This ratio remained about constant (±10%) during the entire transformation, suggesting that it was the extent of *nucleation* of each of the products that determined the final goethite/hematite ratio.
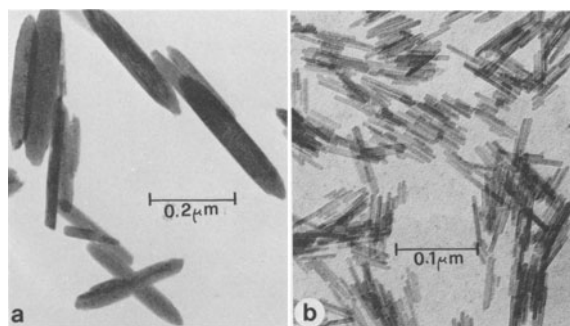
Figure 2. Transmission electron micrographs of akaganéite: (a) cigar-shaped crystals; (b) rod-shaped crystals.

Effect of silicate on the transformation

Even low levels of silicate (5×10^{-5} M) retarded the transformation in 1 M KOH to some extent; with 2×10^{-3} M silicate, only about 30% conversion had taken place after eight weeks (1 M KOH, 70°C). The retarding effect of silicate is, however, less than for ferrihydrite; according to Cornell *et al.* (1987), 10^{-3} M silicate inhibited the transformation in 1 M KOH for 3–4 months.

One effect of silicate was to extend the initial slow stage of the reaction from 3.5 hr (control, 1 M KOH) to 30 hr (10^{-4} M silicate). Seeding with goethite reduced the extent of the slow stage and thereby accelerated the overall reaction; it did not, however, overcome the effect of silicate completely. Schwertmann and Taylor (1972b) reported that although silicate strongly retarded the conversion of lepidocrocite to goethite in alkali media, the effect could be overcome entirely by addition of seed crystals of goethite. These authors, however, used comparatively low Si:Fe ratios (0.008) and very concentrated suspensions (12 g oxide/liter). In the present work, the Si:Fe ratio was as high as 0.2; under these conditions, the influence of silicate could not be eliminated by seeding.

Adsorption measurements showed that significant amounts of silicate adsorbed on both akaganéite and lepidocrocite in alkaline media. For example, in 0.5 M KOH, the maximum uptake of silicate corresponded to one adsorbed silicate ion/74 Å^2; for lepidocrocite, uptake was much less, with one silicate ion/212 Å^2 being adsorbed.

Electron microscopy

The akaganéite sample used for most experiments consisted of cigar-shaped crystals having an average
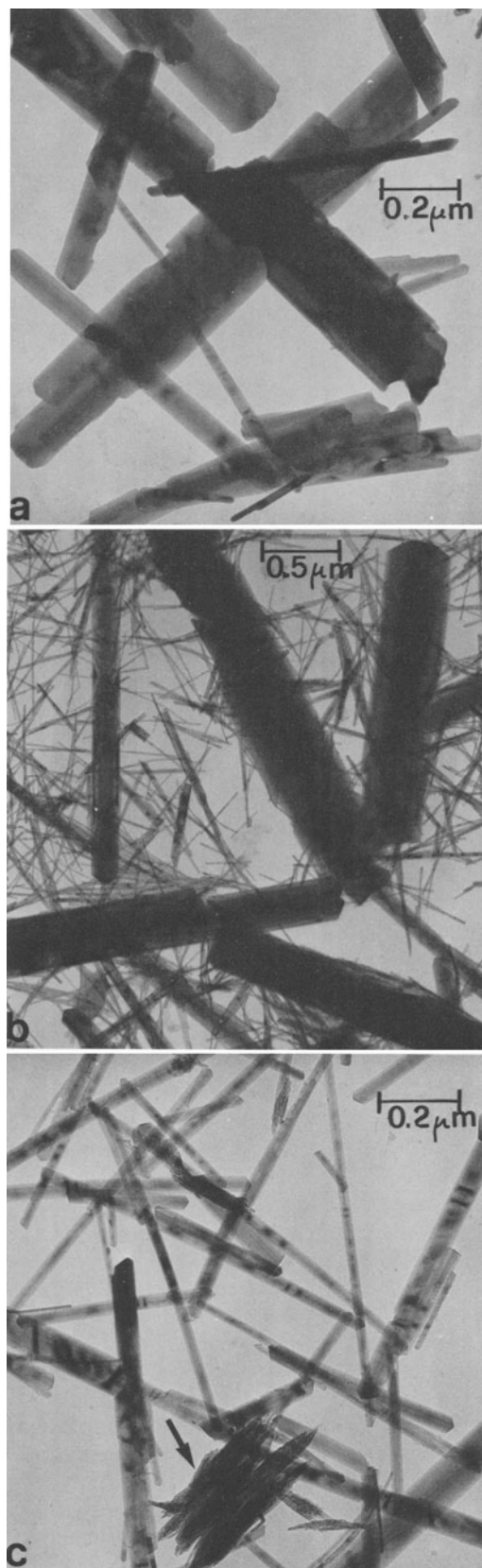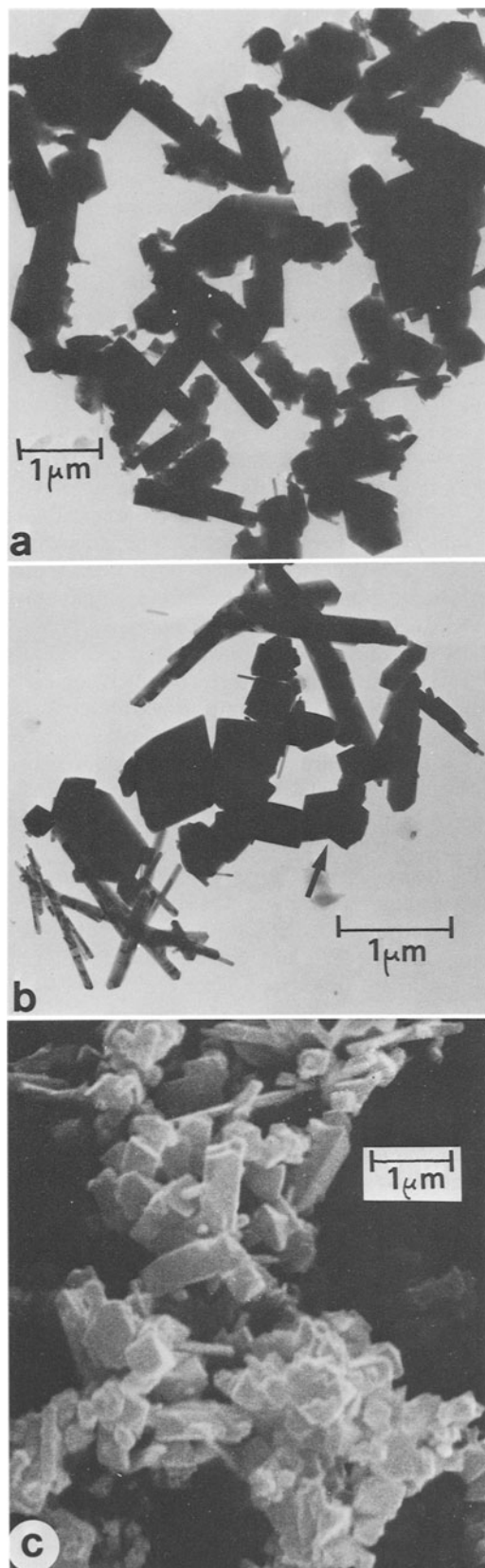
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Figure 3. Transmission electron micrographs of goethite formed from akaganéite in KOH: (a) acicular crystals formed from cigar-shaped akaganéite in 1 M KOH; (b) acicular crystals formed from rod-shaped crystals in 1 M KOH; (c) acicular crystals grown in 0.01 M KOH together with some partly dissolved crystals of cigar-shaped akaganéite (arrowed).

length of 3300 Å and an average width of 600 Å (Figure 2a). The second sample consisted of much smaller, rod-shaped crystals, as long as 600 Å and as wide as 60–150 Å (Figure 2b). Both types of crystals were elongated in the [001] direction.

Goethite obtained from akaganéite displayed a range of sizes and morphologies depending on the reaction conditions (Figure 3). The cigar-shaped akaganéite transformed in 0.5–1 M KOH to acicular crystals of goethite as long as 2.5 μm together with some smaller crystals, about 0.5 μm in length (Figure 3a). The large, acicular crystals were terminated by rectangular or very irregular faces. These crystals were defective, containing numerous shallow, irregular pits on the surfaces and at edges. The large size of the crystals suggests limited nucleation, whereas the surface imperfections indicate interference in growth, probably the result of temporary blocking by adsorbed OH^- of the mobility paths on the goethite nuclei. Similar large, defective crystals have been grown from ferrihydrite in 5 M KOH (Cornell and Giovanoli, 1985).

As the $[OH^-]$ level decreased, the goethite crystals became shorter and thinner. In 0.1 M KOH, the crystals were as long as 1.6 μm and 0.02–0.14 μm across, and in 0.01 M KOH, the crystals were somewhat shorter (0.3–1.2 μm) (Figure 3c). These crystals typically were terminated by well-formed 021 planes, a feature that is consistent with slower growth and a reduced level of interfering species than at higher $[OH^-]$.

Goethite grown from rod-shaped akaganéite consisted of acicular crystals as long as 2.3 μm, together with shorter acicular crystals and many thin, short crystals (Figure 3b).

The presence of silicate species ($1–2 \times 10^{-3}$ M) modified the morphology of goethite grown from akaganéite or lepidocrocite in 0.5 M KOH. The acicular crystals were shorter and thicker than those grown in the absence of silicate. In addition, some more or less hexagonal crystals and equant or bipyramidal crystals were observed (Figure 4a and 4b). A similar mixture of morphologies was noted for goethite grown from ferrihydrite in the presence of high levels of silicate, the shape modification being attributed to enhanced development of the 021 planes of goethite due to preferential adsorption of silicate species on these faces (Cornell et al., 1987; Cornell and Giovanoli, 1987).

In the presence of 2×10^{-3} M silicate in 0.5 M KOH, complete conversion of akaganéite to goethite at room temperature required two years. The crystals that grew

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Figure 4.   Electron micrographs of goethite grown from akaganéite in 0.5 M KOH in the presence of 2×10^{-3} M silicate: (a), (b) transmission electron micrographs of mixtures of acicular, hexagonal, and equant (arrow) crystals of goethite, 70°C; (c) scanning electron micrograph of a mixture of goethite crystals grown at room temperature over two years.
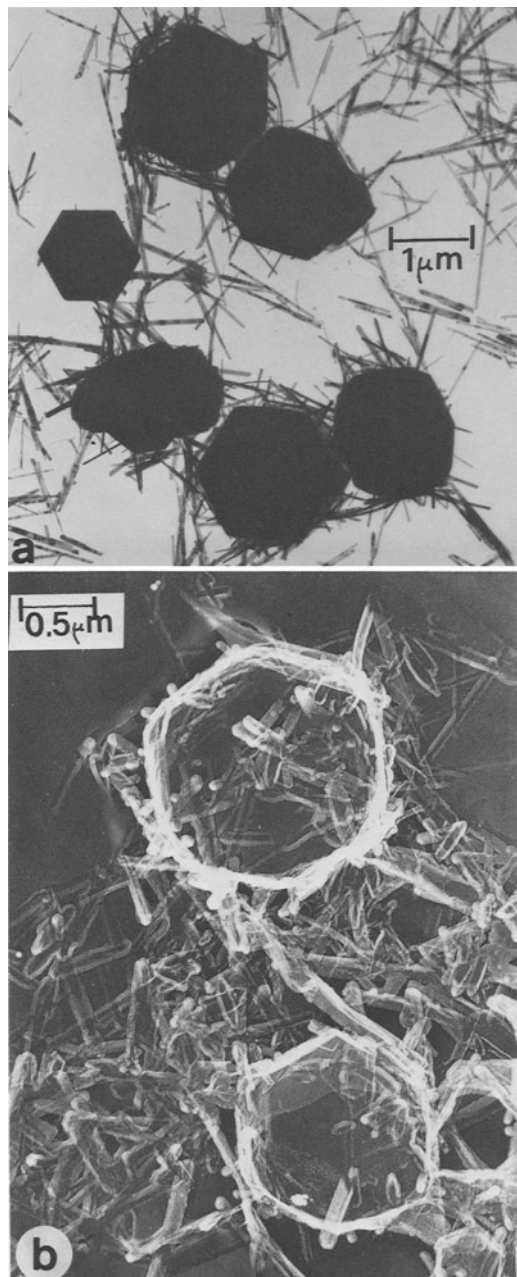
Figure 5. Transmission electron micrographs of hematite grown from akaganéite in 0.005 M KOH, 70°C: (a) hematite plates and hexagons together with acicular crystals of goethite; (b) replica of hematite plates (and goethite needles) grown in the presence of 5×10^{-4} M silicate.

to purple as the crystal increases in size from 0.1 to 1.0 μm and the adsorption spectrum changes are well documented (Winter, 1979). Such large plates of hematite have also been obtained from ferrihydrite, but only in 5–6 M KOH (Cornell and Giovanoli, 1985). In the presence of silicate (5×10^{-4} M), hematite also grew as large plates (Figure 5b). Ellipsoidal crystals similar to those of hematite grown from ferrihydrite in the presence of 10^{-4} M silicate (Cornell et al., 1987) were not observed.

Progress of the transformation of cigar-shaped akaganéite

In 1 M KOH, small crystals of goethite appeared during the earliest stage of the transformation and gradually increased in size. Some further nucleation continued to about 15% reaction.

TEM showed that the transformation involved the gradual dissolution of akaganéite and the simultaneous appearance of the reaction products. No ferrihydrite intermediate was detected at any stage of the transformation at any [OH⁻]. As the transformation proceeded, the akaganéite crystals became increasingly smaller. Initially, dissolution was concentrated at the ends of the crystals, which developed a pointed appearance (Figures 3c); with time, overall surface attack was also noted. Aggregation of the crystals as a preliminary stage before the appearance of hematite or goethite was not observed at any [OH⁻].

The morphological changes resulting from dissolution in KOH were quite different from those observed in HCl (Cornell and Giovanoli, 1988), although the same sample of akaganéite was used in each investigation. During acid dissolution the crystals first developed squared ends and then became steadily shorter; little surface attack took place.

Schwertmann and Taylor (1972a) reported that in the presence of sufficient silicate to inhibit goethite formation, the morphology of lepidocrocite changed from laths to cubes; this behavior was interpreted as dissolution of lepidocrocite followed by reprecipitation on the remaining crystals of lepidocrocite (goethite nuclei not being available as a sink for soluble ferric species). In the present work lepidocrocite recrystallized from laths to thin, diamond-shaped plates in the presence of 2×10^{-3} M silicate. Akaganéite, on the other hand, showed no evidence of recrystallization in the presence of silicate; if goethite formation was retarded or inhibited, the crystals of akaganéite remained unchanged. Uptake of silicate on lepidocrocite was less than on akaganéite; possibly because adsorption on lepidocrocite may have been localized. Adsorbed silicate may have been present only at the edges and not on the (010) surfaces of the crystals as is the case for phosphate (Lewis and Farmer, 1986). Thus, in the presence of sufficient silicate to block goethite nucleation, lepidocrocite was able to recrystallize onto lepido-

under these conditions were well-developed and as wide as 0.5 μm (Figure 4c).

Hematite grew from akaganéite in 0.01 M KOH as round or hexagonal plates between 1.3 and 2 μm in diameter (Figure 5a). This hematite was purple, undoubtedly due to the comparatively large size of the crystals. Variations in the color of hematite from red

crocite surfaces that were not blocked by adsorbed silicate. On the other hand, for akaganéite, the greater adsorption of silicate required a more uniform distribution of adsorbed species, in which case, recrystallization was more difficult to achieve.

DISCUSSION

Kinetic data and TEM evidence indicated that in alkaline media, akaganéite dissolved and reprecipitated as goethite or hematite. The rate-determining step was the dissolution of akaganéite, not nucleation or growth of the products. Goethite also forms from ferrihydrite (Schwertmann and Fischer, 1966) and lepidocrocite (Schwertmann and Taylor, 1972a) by a dissolution-reprecipitation mechanism. Hematite, on the other hand, forms from ferrihydrite by an internal dehydration-rearrangement mechanism (Feitknecht and Michaelis, 1962; Schwertmann and Fischer, 1966), and a similar mechanism might have been expected in the case of akaganéite. The hematite crystals were, however, 10- to 100-fold larger than those of the akaganéite precursor; for such large crystals to have formed by a solid-state transformation, preliminary aggregation of the akaganéite crystals must have taken place. No TEM evidence, however, was found for this aggregation step. An alternative possibility is that akaganéite dissolved and reprecipitated as ferrihydrite, which then transformed to hematite. No ferrihydrite intermediate was detected by TEM, however, at any stage of the transformation. Furthermore, hematite grows from a ferrihydrite-silicate system as ellipsoidal crystals (Cornell *et al.*, 1987), whereas the presence of silicate did not modify the morphology of hematite grown from akaganéite. Thus, in the akaganéite-KOH system, hematite, as well as goethite, formed from soluble ferric species released by dissolution of the solid precursor.

In solution, akaganéite undergoes a variety of transformations depending on the reaction conditions (Figure 6). In acid media it changes to hematite (Atkinson *et al.*, 1977; Hamada and Matijevic, 1982), and in reducing, alkaline conditions, it goes to magnetite (Blesa *et al.*, 1986); these transformations all involve dissolution of akaganéite as a preliminary step.

Although the different oxyhydroxides of iron dissolve according to different rate laws, the transformations in alkaline media of ferrihydrite (Cornell and Giovanoli, 1985), akaganéite, and lepidocrocite are similar in that all three compounds transformed to goethite in an intermediate pH range and to a mixture of goethite + hematite outside this region. For ferrihydrite, this variation in product composition has been attributed to variations in the rates of competitive formation of goethite and hematite with pH (Cornell *et al.*, 1989). The pH range in which goethite alone forms is much wider for ferrihydrite (pH 11.3–15, Cornell and Giovanoli, 1985) than that found in the present work for akaganéite or lepidocrocite. In all experi-
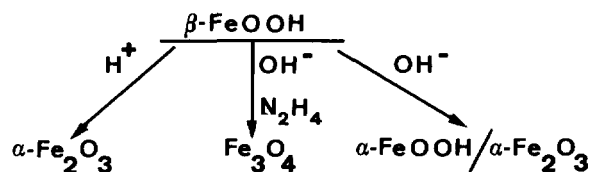

Figure 6. Schematic representation of conversions of akaganéite to other iron oxides.

ments, differences in the extent of the pH range over which hematite was excluded, and also the level of hematite in the product at any pH, appeared to be related to the kinetics of dissolution of the parent oxyhydroxide. Slow dissolution of the precursor, particularly in the initial stage of the transformation (during which a concentration of soluble ferric species sufficient to exceed the solubility product of goethite was built up), was associated with the presence of hematite in the product. Hence, any factor that retarded dissolution of the precursor should have hindered goethite formation and enabled the formation of hematite to become more competitive. Falling pH and increased ionic strength both have this effect, and so does increased crystallinity of the precursor. Of the three oxyhydroxides considered, ferrihydrite because of its poorly ordered structure dissolves most rapidly and akaganéite dissolves more slowly; in line with these rates of dissolution, the lowest pH above which only goethite formed increased in the order: ferrihydrite < lepidocrocite < akaganéite.

Hematite appears to have nucleated less readily than goethite. The fact that goethite nucleated quite readily in solution, provided that the critical supersaturation was exceeded, whereas hematite (which has a similar solubility product) did not, may be accounted for by assuming that the formation of hematite involved a higher activation energy barrier; this activation energy has been related to the need for dehydration, as well as to the desolvation of the soluble ferric species.

Silicate retarded the transformation of akaganéite as well as that of ferrihydrite (Cornell *et al.*, 1987) and lepidocrocite (Schwertmann and Taylor, 1972b). Whereas for ferrihydrite, stabilization against dissolution is the predominant mechanism involved (Cornell *et al.*, 1987), and for lepidocrocite, silicate simply interferes in nucleation of goethite (Schwertmann and Taylor, 1972b), for akaganéite, stabilization against dissolution and interference in goethite nucleation were both important.

Cornell *et al.* (1987) found that the maximum uptake of silicate on ferrihydrite in 0.5 M KOH corresponded to one silicate ion/33 Å² for a coprecipitated system and to one silicate ion/70 Å² if silicate were added to ferrihydrite; the transformation to goethite was far slower for the coprecipitated system. The extent of maximum adsorption of silicate (per unit area) for the

different iron oxyhydroxides (0.5 M KOH) increased in the order: lepidocrocite < akaganéite < ferrihydrite. Differences in the rates of conversion of these compounds to goethite were, presumably, related to differences in the level of silicate uptake. Hence, the effect of a foreign anion on goethite formation depends, at least in part, on the surface properties of the solid precursor.

CONCLUSIONS

In alkaline media, akaganéite transformed to goethite or hematite. Although hematite forms from ferrihydrite by a solid-state mechanism, its formation from akaganéite appears to have involved precipitation from soluble ferric species. Goethite formed from both oxyhydroxides by a dissolution-reprecipitation mechanism.

Silicate retarded the transformation of akaganéite principally by stabilization against dissolution, although it interfered somewhat with the nucleation of goethite. Silicate modified the morphology of goethite regardless of whether the goethite formed from akaganéite, lepidocrocite, or ferrihydrite. This result suggests that silicate acted by preferential adsorption on specific planes of the growing crystals of goethite. The morphology of hematite, on the other hand, was not modified by the presence of silicate, suggesting no preferential adsorption of silicate on hematite.

Goethite and hematite can be produced from different solid precursors, including ferrihydrite, akaganéite, and lepidocrocite. The reaction conditions, particularly pH and the presence of foreign species, have a decisive effect on the formation of goethite and hematite. The nature of the solid precursor is important insofar as its structure and degree of crystallinity influence the rate of dissolution. Surface properties of the precursor may also influence the extent of interaction between the solid and any foreign species and, hence, the kinetics of the transformation process.

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