

EFFECT OF SILICATE SPECIES ON THE TRANSFORMATION OF FERRIHYDRITE INTO GOETHITE AND HEMATITE IN ALKALINE MEDIA

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Abstract—The transformation of ferrihydrite to goethite and/or hematite in alkaline media is strongly retarded by the presence of silicate species. These species probably stabilize ferrihydrite by adsorbing on the particles of ferrihydrite and linking them into an immobile network.

At concentrations low enough for the transformation to proceed, silicate species promote the formation of hematite and hinder the nucleation of goethite. The presence of silicate species modifies the morphology of both reaction products. Hematite forms ellipsoidal single crystals, commonly displaying outgrowths of goethite. Silicate species in solution appear to enhance the development of the (021) faces of goethite, probably by preferential adsorption on these faces; at high levels of silicate species, goethite crystals adopt a pseudo-hexagonal habit. This morphology has not been observed previously for goethite.

Key Words—Ferrihydrite, Goethite, Hematite, Morphology, Silicate, Transmission electron microscopy.

INTRODUCTION

Ferrihydrite ($\sim\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$) is a poorly ordered compound which, with time, transforms into goethite and/or hematite. The transformation into more crystalline products proceeds via two competing pathways: (1) dissolution-reprecipitation leading to goethite and (2) internal aggregation and rearrangement leading to hematite (Feitknecht and Michaelis, 1962; Schwertmann and Fischer, 1966). Which end product predominates depends on the pH and the temperature of the system. Foreign ions and compounds also influence the nature of the reaction product and modify its crystal habit. Previous investigations on the influence of species such as oxalate, aluminum, hydroxy-carboxylic acids, and simple sugars have helped clarify the details of the transformation mechanism (Fischer and Schwertmann, 1975; Lewis and Schwertmann, 1979; Cornell and Schwertmann, 1979; Cornell, 1985).

In view of their prevalence in natural systems, the effect of silicate ions on the properties of ferrihydrite has been studied intensively (Schwertmann and Thalmann, 1976; Pyman *et al.*, 1979; Carlson and Schwertmann, 1981; Schwertmann and Fechter, 1982; Karim, 1984; Anderson and Benjamin, 1985). Silicate ions modify the solubility, surface area, and dehydroxylation behavior of ferrihydrite. Furthermore, silicate species strongly retard the transformation of ferrihydrite into goethite and hematite. Little attention, however, has been paid to the actual transformation of ferrihydrite into more crystalline products.

In the present report, we describe the effect of different levels of monomeric silicate species (hereafter

referred to as “silicate”) on the kinetics and products of the transformation of ferrihydrite to goethite and/or hematite. These silicate species probably consisted of a mixture of H_4SiO_4 , H_3SiO_4^- , and $\text{H}_2\text{SiO}_4^{2-}$, with the doubly charged species predominating at high pH. In addition, changes in the morphology of the reaction products induced by the presence of silicate are reported. A range of silicate concentrations (10^{-5} – 10^{-3} M), comparable to those found in soils, was used. At pH 4–7 and at 20°C these levels of silicate in solution prevent the transformation from taking place in a reasonable length of time; hence the present experiments were carried out at pHs ≥ 9 and at 70°C. Fischer and Schwertmann (1975), Cornell and Schwertmann (1979), and Schwertmann and Murad (1983) showed that the mechanism by which ferrihydrite transforms into goethite or hematite is independent of pH and temperature. Hence, the results obtained under the conditions used in the present investigation will also apply to natural systems.

EXPERIMENTAL METHODS

Transformation studies were carried out using suspensions of ferrihydrite (0.1 g/100 ml) precipitated from ferric nitrate solution (0.1 M) at pH ≥ 9 using 1 M KOH. In most experiments, the silicate was coprecipitated with Fe^{3+} , but in several experiments it was added to already formed ferrihydrite. In both sets of experiments, the initial concentration of silicate ranged from 10^{-5} to 10^{-3} M (i.e., Si:Fe = 0.001 to 0.1). Subsequent results refer to initial silicate ion concentrations unless otherwise stated. The suspensions were held at 70°C

Table 1. Effect of different levels of silicate in the system on the transformation of ferrihydrite.

Silicate (M)	Composition of product (%)		
	Ferrihydrite	Goethite	Hematite
0	1	96	3
1×10^{-5}	4	90	6
5×10^{-5}	30	50	20
1×10^{-4}	36	30	34
5×10^{-4}	100	0	0
1×10^{-3}	100	0	0
1×10^{-3}	100	0	0

Silicate species coprecipitated with ferrihydrite. pH 11, 70°C, 48 hr.

¹ pH 13.

for periods of 24 to several hundred hours depending on the level of silicate in the system and the time required to complete an experiment. The final concentration of silicate in solution was lower than the initial concentration. In a number of experiments, silicate was replaced by citrate, phosphate, aluminum or maltose, in order to compare the inhibiting action of silicate with that of other inhibiting agents.

During and after the heating period, the suspension was sampled and washed. The extent of transformation was expressed as the ratio Fe_o/Fe_t , where Fe_o is the oxalate-soluble material (i.e., unconverted ferrihydrite) and Fe_t is the total Fe content (found by complete dissolution of the sample in 4 M HCl) (Schwertmann, 1964). Fe was measured by atomic absorption spectroscopy.

The crystalline residue was dried at 50°C, and X-ray powder diffraction (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 peaks of goethite and the 102 peak of hematite were used for the comparison.

Transmission electron micrographs were obtained with Hitachi HU-12 A (125 kV) and Hitachi H-600-2 (100 kV) electron microscopes equipped with a Tracor TN 2000 or TN 5400 (respectively) energy-dispersive X-ray spectrometer. For TEM examination, the samples were dispersed in twice-distilled water using an ultrasonic treatment, and a drop of suspension was dried on a carbon-coated, bronze grid. In some experiments, the crystals of goethite were coated with a film which X-ray fluorescence spectra showed to contain Si. This precipitate was probably an artifact which arose during preparation of the sample for electron microscopy. Scanning electron micrographs (SEMs) were taken of crystals of natural goethite that were found inside a quartz geode. The geode, which probably came from Brazil, was purchased locally in Berne. XRD showed

Table 2. Comparison of the inhibitor power of silicate in the system with that of other inhibitors.

Species ¹	Ferrihydrite untransformed after 24 hr (%)	
	pH 11	pH 13
Silicate	100	100
Al^{3+}	5	0
Citrate	100	10
Phosphate	100	25
Maltose	100	100

¹ Concentration = 10^{-3} M, 70°C.

the crystals growing inside the geode to consist of goethite. These crystals were extracted, suspended in twice-distilled water, and cleaned ultrasonically. They were then sputtered with gold for SEM examination.

Infrared (IR) spectra were recorded using KBr pellets on a Perkin Elmer IR 580 spectrophotometer.

Stock solutions containing 2×10^{-3} M H_4SiO_4 (pH 3) were prepared according to the method of Santschi and Schindler (1974). The adsorption of silicate species on goethite or ferrihydrite was investigated by equilibrating 0.1 or 1.0 g of oxide in 100 ml of silicate solution (pH 9–12.5) for 24 hr. The solution was filtered and the amount of silicate ion remaining in solution was measured by a molybdenum blue method (Vogel, 1961). The amount of silicate ions adsorbed by the oxide was estimated by difference.

RESULTS

The presence of silicate in solution influenced the rate and extent of the conversion of ferrihydrite and the ratio of hematite to goethite in the final product. The effectiveness of the silicate in retarding conversion increased with rising concentration of silicate and fell as the pH rose. A third factor influencing these parameters was the point at which the silicate was added. Silicate retarded the transformation of ferrihydrite more strongly if it was coprecipitated with Fe^{3+} .

The increasing degree of retardation with rising concentration of silicate, expressed as the percentage of unconverted ferrihydrite left after 48 hr (pH 11), is shown in Table 1. At pH 11 complete conversion took place in the presence of 10^{-5} M silicate ion (Si:Fe = 0.001) in ~100 hr (control ~48 hr), but in the presence of 10^{-3} M silicate ion (Si:Fe = 0.1), ferrihydrite remained unchanged for over eight months. Even at pH 13, 10^{-3} M silicate inhibited the transformation of ferrihydrite to goethite for 3–4 months.

In Table 2 the inhibiting action of silicate (10^{-3} M) is compared with that of several foreign species. At pH 11, all the species listed, with the exception of Al^{3+} , prevented the transformation of ferrihydrite (24 hr). At pH 13, however, the inhibiting action of all species, except maltose, was considerably less than that of the silicate.

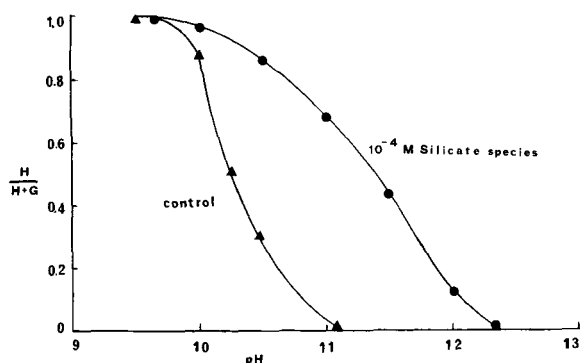


Figure 1. Hematite/(hematite + goethite) ratio vs. pH. 70°C; silicate and Fe³⁺ coprecipitated.

Reaction products

The presence of silicate favored the formation of hematite relative to goethite (Table 1). In the control system, no hematite formed at pH > 11. In contrast, some hematite formed in the presence of 10⁻⁴ M silicate (Si:Fe = 0.01) at pH 12 (Figure 1). Anderson and Benjamin (1985) reported similar results. These observations refer to a system in which silicate was coprecipitated with Fe³⁺. If silicate was added to already-formed ferrihydrite, the conversion to hematite was still favored over goethite, but to a lesser extent. For example, coprecipitation of silicate with Fe³⁺ at pH 11 led to 70% hematite in the final product, whereas silicate added after precipitation gave rise to a product containing <30% hematite.

Salt in a silicate-ferrihydrite system strongly enhanced the formation of hematite. In a system containing 10⁻⁴ M silicate (Si:Fe = 0.01) and 2 M NaNO₃ (pH 12.5), hematite made up 50% of the product. The salt appeared to have a synergistic effect with the silicate because at pH 12.5, neither silicate nor salt alone led to the formation of hematite. Torrent and Guzman (1982) showed that hematite is favored over goethite in soils with low water activity; for example, dry or saline soils. In such soils where silicate is also present, an enhancement of the hematite-promoting effect might be expected.

Adsorption of silicate on iron oxides

Ferrihydrite has a great capacity to take up silicate; Anderson and Benjamin (1985) reported as much as 35 mole % silicate retained by ferrihydrite. Silicate also absorbs strongly on goethite; adsorption reaches a maximum at about pH 9 (close to the pK_a of silicic acid) and is significant at pH 11 (Hingston *et al.*, 1967; Sigg and Stumm, 1981). Inasmuch as most of the present experiments were carried out at pH > 11, some information about the degree of adsorption of silicate on ferrihydrite and goethite at higher pHs was required. Table 3 shows the effect of pH on the uptake of silicate

Table 3. Uptake of silicate by ferrihydrite.¹

pH	Percentage silicate taken up	
	Silicate and Fe ³⁺ coprecipitated	Silicate added to ferrihydrite
9	99	99
10	99	99
11	99	99
12	99	80
12.5	90	45

¹ 0.1 g ferrihydrite. Silicate in solution = 10⁻⁴ M.

(10⁻⁴ M, i.e., Si:Fe = 0.01) by ferrihydrite. If silicate was added prior to precipitation, 99% of the silicate was removed from the supernatant solution even at pH 12: at higher pHs the bulk of the silicate was taken up by ferrihydrite. Similar results were observed both for higher (10⁻³ M) and lower levels of silicate. The maximum amount of silicate taken up by the ferrihydrite in these experiments was 9.6 mole %. Much less H₂SiO₄²⁻ was removed from solution if the silicate was added after the precipitation of ferrihydrite (Table 3). At pH 12.5, only half the silicate added was adsorbed, corresponding to one silicate ion/600 Å² (10⁻⁴ M silicate added and a B.E.T. surface area of 200 m²/g for ferrihydrite). Differences in uptake if silicate was added before or after precipitation decreased with decreasing pH.

IR spectra of both siliceous ferrihydrite and ferrihydrite containing adsorbed silicate showed a broad band at ~930 cm⁻¹, which was missing from the spectrum of pure ferrihydrite. The band at ~930 cm⁻¹ was also observed by Carlson and Schwertmann (1981) who considered it to be due to the Si-O stretch, which in fully polymerized SiO₂ is at ~1100 cm⁻¹. They attributed the downward shift to the presence of Si-O-Fe bonds. Such linkages could exist both at the surface and within particles of ferrihydrite.

The adsorption of silicate on goethite (B.E.T. surface area 70 m²/g) was measured at pH 11 and 12.5. The level of adsorption decreased with rising pH from ~40% to 10%. Additional measurements were made over a range of silicate ion concentrations at pH 12.5. This pH was chosen because the habit of the crystals formed at high pH was gradually modified by increasing amounts of silicate in the system. Even using 10⁻³ M silicate, a monolayer of adsorbed silicate ions (corresponding to one silicate ion/60 Å²) was not reached (Table 4). If goethite formed in the presence of 10⁻⁴ M silicate at pH 12.5, 90% of the silicate remained in the supernatant liquid at the completion of crystal growth. The remainder is presumed to have been adsorbed on the goethite.

Kinetics

Conversion vs. time curves for systems with and without silicate consisted of an initial induction period

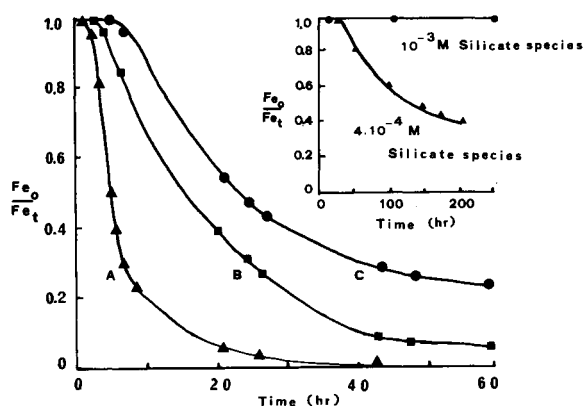


Figure 2. Fe_o/Fe_t as a measure of the degree of transformation of ferrihydrite into goethite vs. time. (A) control; (B) silicate added after precipitation of ferrihydrite; (C) silicate coprecipitated with Fe^{3+} . pH 12, 70°C, initial Si:Fe = 0.005 (i.e., 5×10^{-5} M). Inset = higher levels of silicate coprecipitated with Fe^{3+} .

(during which goethite nucleated, cf. Cornell and Giovanoli, 1985) followed by a faster transformation stage (Figure 2). A plot of $\ln Fe_o/Fe_t$ against time was linear over the main part of the transformation indicating a first-order reaction. Even low levels of silicate retarded the transformation significantly. The half-conversion time, at which $Fe_o/Fe_t = 0.5$, increased linearly with the initial concentration of silicate in the system.

The addition of silicate to the ferrihydrite did not retard the transformation as strongly as did coprecipitation of the silicate with Fe^{3+} (Figure 2). This observation suggests that the order in which the silicate and Fe^{3+} were precipitated influenced the reactivity of the ferrihydrite.

A different situation exists for the Al-ferrihydrite system. Lewis and Schwertmann (1979) found that an aluminous ferrihydrite transformed to goethite more rapidly than did ferrihydrite that had been precipitated before the addition of Al (0.05–0.2 M Al). They suggested that aluminous ferrihydrite dissolves more rapidly than ferrihydrite, leaving an open structure, which in turn breaks down readily.

To determine whether or not silicate hindered the nucleation of goethite as well as the dissolution of ferrihydrite, suspensions of ferrihydrite that had been coprecipitated with 5×10^{-5} – 5×10^{-4} M silicate (pH 12) were seeded with 10% (by weight) goethite. A slight increase in the rate of conversion was noted for the system having the lowest concentration of silicate. At higher concentrations, seeding with goethite did not enhance the rate of transformation, suggesting that the silicate acted mainly by stabilizing the ferrihydrite. Such a result appears to conflict with Schwertmann and Taylors' (1972) finding that seeding with goethite can overcome the retarding effect of silicate. These authors, however, studied the influence of silicate on the for-

Table 4. Extent of surface coverage of different levels of silicate on goethite.¹

Silicate (M)	Area of adsorbed silicate (\AA^2)
1×10^{-3}	160
5×10^{-4}	300
1×10^{-4}	1600
5×10^{-5}	3000
1×10^{-5}	16,000

¹ pH = 12.5.

mation of goethite from lepidocrocite (γ - $FeOOH$), not ferrihydrite; dissolution of lepidocrocite did not appear to be suppressed to any degree by the presence of silicate. Other experiments in the present investigation showed that seeding increases the rate of goethite formation (and the amount of goethite relative to hematite in the end product at lower pH) in systems in which small amounts ($\sim 5 \times 10^{-5}$ M, i.e., Si:Fe = 0.005) of silicate were added *after* precipitation of ferrihydrite. Thus, silicate appears to hinder the nucleation of goethite, an effect, however, that is outweighed by its strong stabilizing action on ferrihydrite.

Electron microscopy

Goethite. At pH 12.5, where the sole reaction product is goethite, low levels (10^{-5} – 5×10^{-5} M) of silicate promote the formation of well-developed acicular crystals having rounded ends (Figure 3a; cf. Figure 6, Cornell and Giovanoli, 1985, for electron micrographs of goethite grown in the absence of silicate species). The average length of the crystals is 4000 \AA ; their average width is 800 \AA . As the level of silicate was increased to 10^{-4} M, shorter, wider crystals displaying well-developed terminal (021) faces were produced (Figure 3b). The highest concentration of silicate (10^{-3} M) led to an apparent alteration of goethite morphology, and pseudo-hexagonal crystals of goethite formed (Figure 4). Such crystals had a superficial resemblance to the hexagonal platelets of hematite which formed at lower pH in the absence of silicate and were initially thought to be crystals of hematite. XRD, however, showed only goethite to be present. These crystals of goethite were, in fact, very short, thick laths, and their pseudo-hexagonal shape appeared to be due to enhanced development of the terminal (021) planes. These planes probably predominated because silicate adsorbed on them preferentially and thereby retarded their growth to some extent. In the presence of 10^{-3} M silicate, about one adsorbed silicate ion exists per 160 \AA^2 (Table 4), far from a monolayer coverage, but if adsorption is confined mainly to one plane, a high density of adsorbed silicate could exist in a limited region of the surface.

The pseudo-hexagonal crystals were usually single domain. They were commonly darker along the *c* axis, which suggests that they were bounded by a few, well-developed (110) faces (i.e., the predominant crystal

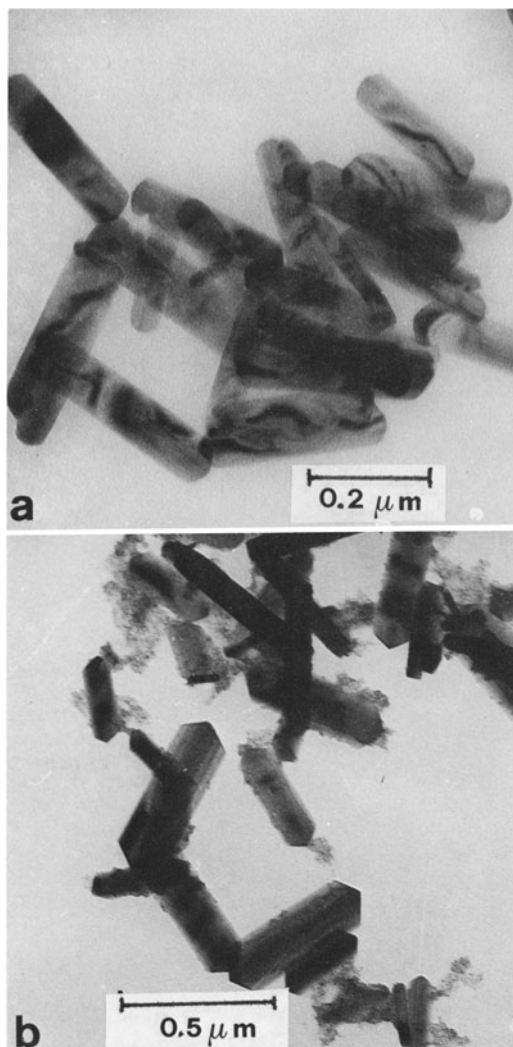


Figure 3. Transmission electron micrographs of goethite: (a) acicular crystals grown in the presence of 10^{-5} M silicate (Si:Fe = 0.001); (b) goethite and some ferrihydrite grown in 10^{-4} M silicate (Si:Fe = 0.01). pH = 12.5.

faces in goethite, Schwertmann, 1984). Probably the rod-like and rhombohedral crystals also visible in Figure 4 are pseudohexagonal crystals lying on one of the (110) faces or on end.

Such a pseudohexagonal morphology has not been observed before for goethite. The structure of goethite is dominated by chains of double octahedra which are parallel to the c axis and which induce the acicular habit of the crystals. Goethite usually retains its acicular shape despite the presence of foreign species in solution. Interference with growth by species such as OH^- leads to long, thin crystals whose growth in the a and b directions has been retarded (Cornell and Giovanoli, 1985). Alternatively, if ≥ 15 mole % Al is incorporated in the crystal structure, growth in the c

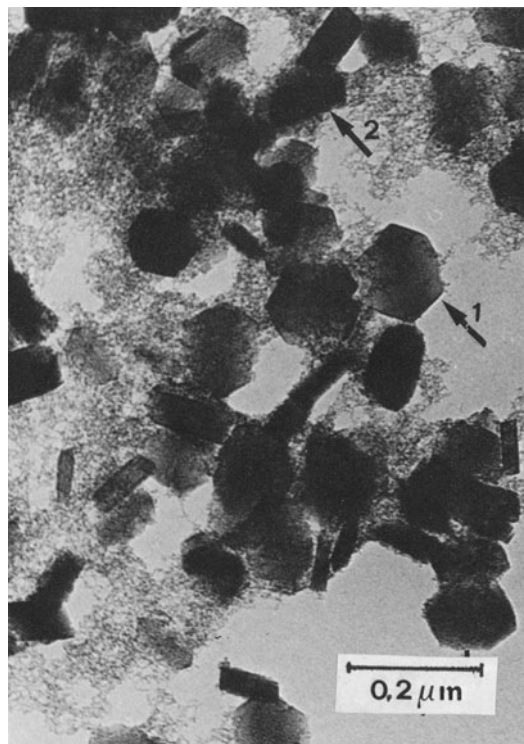


Figure 4. Transmission electron micrograph of goethite and some ferrihydrite formed in the presence of 10^{-3} M silicate (Si:Fe = 0.1). pH = 12.5, 70°C. Arrow 1 = crystal having typical pseudo-hexagonal morphology; arrow 2 = rod-shaped goethite.

direction is retarded, leading to platy crystals (Mann *et al.*, 1985).

Hematite. Silicate promotes the formation of ellipsoidal crystals of hematite (6000–9000 Å in diameter) instead of the typical hexagonal plates (Figure 5a). The grainy appearance of these crystals is probably inherited from the primary structure of the ferrihydrite aggregate from which the hematite formed. Hematite grown in the presence of silicate gave a sharp XRD pattern suggesting that the ellipsoids in Figure 5 are single crystals. Ellipsoidal hematite has also been grown in the presence of oxalate, and its shape was associated with the interaction between adsorbed oxalate and ferrihydrite (Fischer and Schwertmann, 1975). Analogy with these oxalate-grown crystals suggests that the shape of the silicate-grown hematite may be due to the adsorption of silicate on ferrihydrite rather than on hematite. Ellipsoidal hematite also forms in the presence of phosphate (Ozaki *et al.*, 1984).

If hematite and goethite coexisted in the product, goethite was mainly present as outgrowths on the hematite. At a pH of ≥ 11 , only two outgrowths of goethite formed on opposite sides of the hematite nucleus. At pH 9, however, several thin needles of goethite were

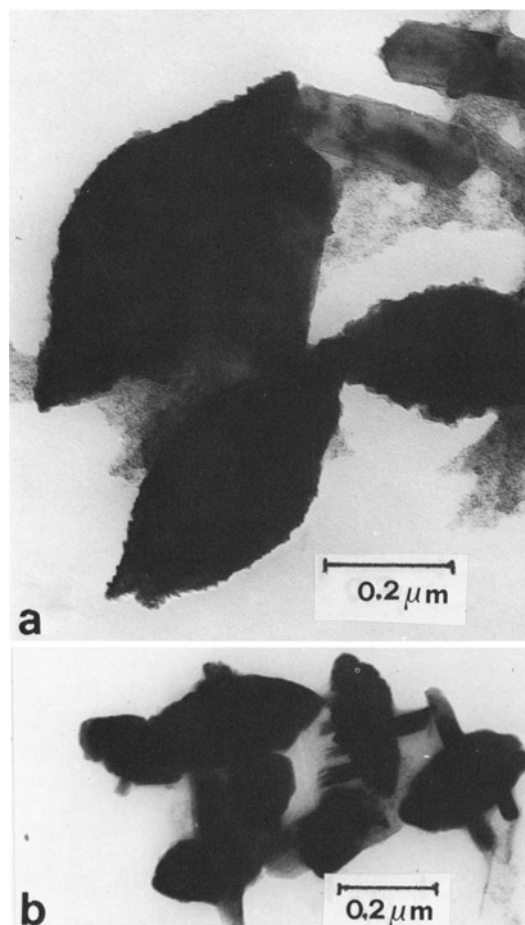


Figure 5. Transmission electron micrographs of hematite formed in the presence of 10^{-4} M silicate: (a) ellipsoidal hematite and some goethite and ferrihydrite, pH = 11.5; (b) ellipsoidal hematite containing numerous outgrowths of goethite, pH = 9.

noted projecting from the hematite surface (Figure 5b). Giovanoli (1980) noted for buserite grown in the presence of SiO_2 , outgrowths that had nucleated only on certain areas of the parent crystal, presumably because the other sites were blocked by adsorbed silicate. The same mechanism may apply to the goethite-hematite system.

Crystallinity of goethite

The presence of silicate in the system tended to improve the crystallinity of goethite. As shown by XRD, the uncorrected width at half height of the 110 peak decreased from $0.8^\circ 2\theta$ for the control to $0.35^\circ 2\theta$ for the silicate-grown goethite. TEMs showed the silicate-grown goethites to be well formed and thicker than the control. In addition, the domainic character of the goethite was reduced by the presence of the silicate. Goethite

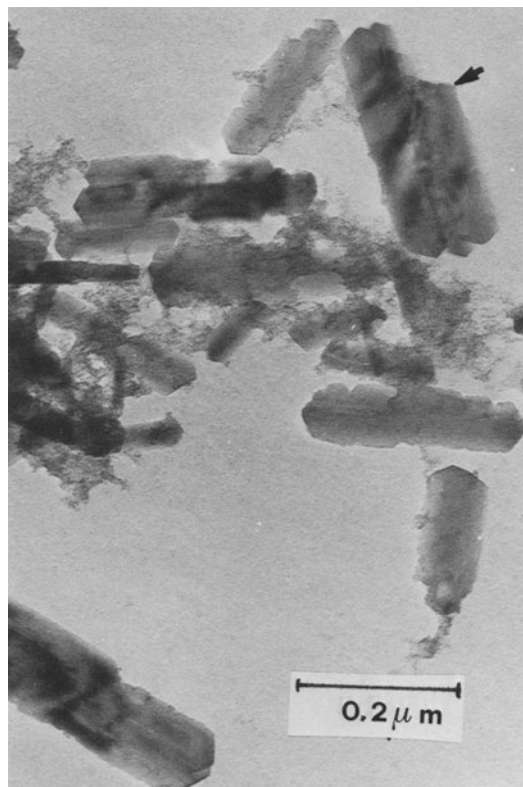


Figure 6. Transmission electron micrograph of multidomainic goethite (and some ferrihydrite) grown in the presence of 10^{-3} M silicate, pH = 13. Arrow indicates crystal with several intergrowths arising from a central point within the crystal.

grown at pH 13 is usually highly domainic (Cornell *et al.*, 1974; Cornell *et al.*, 1983; Cornell and Giovanoli, 1986), but the silicate reduced the number of domains per crystal to two or three well-formed intergrowths (Figure 6). Goethite grown at pH 13 in the presence of 10^{-3} M silicate retained the acicular shape. At this pH, the silicate apparently was still able to retard the transformation of ferrihydrite, but its adsorption on goethite appeared to be less than that needed to modify the shape. These observations suggest that the silicate contamination that arises when goethite is grown in glass vessels under alkaline conditions, may improve the crystallinity of the product. The improvement in the crystallinity of synthetic goethite in the presence of silicate appears to be the result of the inhibition of nucleation by the silicate. The few nuclei that form grow slowly to large crystals. Large, perfect crystals of natural goethite appear to have been produced under similar conditions. An example of such a natural goethite is shown in Figure 7, an SEM of a large, perfect goethite crystal, about 1 mm in length, which was found inside a quartz geode. This needle apparently started growing under hydrothermal conditions in a silicate-

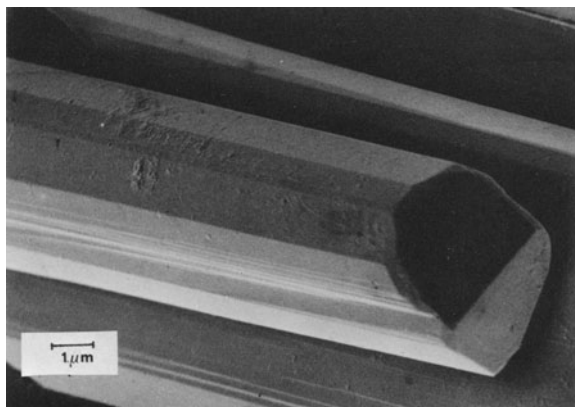


Figure 7. Scanning electron micrograph of a twinned goethite needle which was found inside a quartz geode.

rich solution. Part of the crystal is now an inclusion in the quartz of the geode.

DISCUSSION

The strong stabilizing effect of silicate on ferrihydrite is similar to that of certain organic anions. Levels of silicate too small to give a monolayer coverage, nevertheless hinder the transformation of ferrihydrite for many weeks at high pH. Therefore, the silicate acts mainly by the particle-linking mechanism proposed earlier for the hydroxy-carboxylic acids (Cornell and Schwertmann, 1979). The silicate ion has as many as four coordinating groups through which it can link different particles of ferrihydrite (diameter 20–40 Å), thus forming an immobile network. Much less silicate is required to immobilize ferrihydrite by this mechanism than by surface adsorption. For example, 10^{-4} M silicate corresponds to one ion/600 Å², which is much less than monolayer coverage. On the other hand, this concentration provides about six silicate ions/particle of ferrihydrite, i.e., more than enough to suppress the transformation of ferrihydrite by linking the ferrihydrite particles into a less reactive network.

The IR spectra suggest that silicate coordinates to ferrihydrite through a ligand-exchange mechanism (cf. Huang and Stumm, 1973; Schindler *et al.*, 1976; Cornell and Schindler, 1980). At present, the question of how the silicate ions are taken up by the ferrihydrite remains unanswered. The kinetic studies showed that the ferrihydrite coprecipitated with the silicate was less reactive than that to which the same amount of silicate had been added. For steric reasons, Si⁴⁺ should not replace structural Fe in ferrihydrite: the difference between the two ferrihydrites may be due to the extent to which the silicate species was associated with the ferrihydrite. In a coprecipitated system at pH 12, for example, about 20% more silicate was taken up by

ferrihydrite than in the system in which the silicate was added to the ferrihydrite.

Both the silicate and the Al hinder the formation of goethite and, thus, indirectly favor hematite. The hematite-promoting effect of the silicate is greater than that of Al, probably because Al only interferes with goethite formation in solution. On the other hand, Si is incorporated into the goethite lattice with difficulty, whereas Al can replace as much as one third of the Fe in the structure. Schwertmann and Taylor (1972) reported that only 0.2 mole % Si⁴⁺ can be accommodated, presumably because Si⁴⁺ strongly favors tetrahedral coordination, whereas the cation sites in goethite require octahedral coordination. These considerations are in accord with Goldschmidt's (1937) observation that the ease with which an element can be incorporated in a host structure depends on its ionic radius and charge.

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REFERENCES

- Anderson, P. R. and Benjamin, M. M. (1985) Effect of silicon on the crystallization and adsorption properties of ferric oxides: *Environ. Sci. Technol.* **19**, 1048–1053.
- Carlson, L. and Schwertmann, U. (1981) Natural ferrihydrites in surface deposits from Finland and their association with silica: *Geochim. Cosmochim. Acta* **45**, 421–429.
- Cornell, R. M. (1985) Effect of simple sugars on the alkaline transformation of ferrihydrite into goethite and hematite: *Clays & Clay Minerals* **33**, 219–227.
- Cornell, R. M. and Giovanoli, R. (1985) Effect of solution conditions on the proportion and morphology of goethite formed from ferrihydrite: *Clays & Clay Minerals* **33**, 424–432.
- Cornell, R. M. and Giovanoli, R. (1986) Factors that govern the formation of multi-domainic goethites: *Clays & Clay Minerals* **34**, 557–564.
- Cornell, R. M., Mann, S., and Skarnulis, A. J. (1983) A high-resolution electron microscopy examination of domain boundaries in crystals of synthetic goethite: *J. Chem. Soc. Faraday Trans. 1* **79**, 2679–2684.
- Cornell, R. M., Posner, A. M., and Quirk, J. P. (1974) Crystal morphology and the dissolution of goethite: *J. Inorg. Nucl. Chem.* **36**, 1937–1946.
- Cornell, R. M. and Schindler, P. W. (1980) Infrared study of the adsorption of hydroxy-carboxylic acids on α -FeOOH and amorphous Fe(III) hydroxide: *Colloid Polymer Sci.* **258**, 1171–1175.
- Cornell, R. M. and Schwertmann, U. (1979) Influence of organic anions on the crystallization of ferrihydrite: *Clays & Clay Minerals* **27**, 402–410.
- Feitknecht, W. and Michaelis, W. (1962) Über die Hydrolyse von Eisen(III)-perchlorat-Lösungen: *Helv. Chim. Acta* **26**, 212–224.

- Fischer, W. R. and Schwertmann, U. (1975) The formation of hematite from amorphous iron(III) hydroxide: *Clays & Clay Minerals* **23**, 33–37.
- Giovanoli, R. (1980) Layer structured manganese oxide hydroxides. VI. Recrystallization of synthetic buserite and the influence of amorphous silica and ferric hydroxide on its nucleation: *Chimia* **34**, 308–310.
- Goldschmidt, V. M. (1937) The principles of distribution of chemical elements in minerals and rocks: *J. Chem. Soc.*, 655–673.
- Hingston, F. J., Atkinson, R. J., Posner, A. M., and Quirk, J. P. (1967) Specific adsorption of anions: *Nature* **215**, 1459–1461.
- Huang, C. P. and Stumm, W. (1973) Specific adsorption of cations on hydrous γ - Al_2O_3 : *J. Coll. Interface Sci.* **43**, 409–420.
- Karim, Z. (1984) Characteristics of ferrihydrites formed by oxidation of FeCl_2 solutions containing different amounts of silica: *Clays & Clay Minerals* **32**, 181–184.
- Lewis, D. G. and Schwertmann, U. (1979) The influence of aluminium on the formation of iron oxides. IV. The influence of $[\text{Al}]$, $[\text{OH}]$, and temperature: *Clays & Clay Minerals* **27**, 195–200.
- Mann, S., Cornell, R. M., and Schwertmann, U. (1985) The influence of aluminium on iron oxides: XII. High resolution transmission electron microscopic (HRTEM) study of aluminous goethites: *Clay Miner.* **20**, 255–262.
- Ozaki, M., Kratochvil, S., and Matijevic, E. (1984) Formation of monodispersed spindle-type hematite particles: *J. Colloid Interface Sci.* **102**, 146–151.
- Pyman, M. A. F., Bowden, J. W., and Posner, A. M. (1979) The point of zero charge of amorphous coprecipitates of silica with hydrous aluminium or ferric hydroxide: *Clay Miner.* **14**, 87–92.
- Santschi, P. H. and Schindler, P. W. (1974) Complex formation in the ternary systems Ca^{2+} - H_4SiO_4 - H_2O and Mg^{2+} - H_4SiO_4 - H_2O : *J. Chem. Soc. Dalton*, 181–184.
- Schindler, P. W., Fürst, B., Dick, R., and Wolf, P. (1976) Ligand properties of surface silanol groups. 1. Surface complex formation with Fe^{3+} , Cu^{2+} , Cd^{2+} and Pb^{2+} : *J. Colloid Interface Sci.* **55**, 469–471.
- Schwertmann, U. (1964) Differenzierung der Eisenoxide des Bodens durch Extraktion mit Ammoniumoxalat-Lösung: *Z. Pflanzenernähr. Düng Bodenkd.* **105**, 194–202.
- Schwertmann, U. (1984) The influence of aluminium on iron oxides: IX. Dissolution of Al-goethite in 6 M HCl: *Clay Miner.* **19**, 9–19.
- Schwertmann, U. and Fechter, H. (1982) The point of zero charge of natural and synthetic ferrihydrite and its relation to adsorbed silicate: *Clay Miner.* **17**, 471–476.
- Schwertmann, U. and Fischer, W. R. (1966) Zur Bildung von α - FeOOH und α - Fe_2O_3 aus amorphem Eisen(III) hydroxide: *Z. Anorg. Allg. Chem.* **346**, 137–142.
- Schwertmann, U. and Murad, E. (1983) The effect of pH on the formation of goethite and hematite from ferrihydrite: *Clays & Clay Minerals* **31**, 277–284.
- Schwertmann, U. and Taylor, R. M. (1972) The influence of silicate on the transformation of lepidocrocite to goethite: *Clays & Clay Minerals* **20**, 159–164.
- Schwertmann, U. and Thalman, H. (1976) The influence of Fe(II) , $[\text{Si}]$, and pH on the formation of lepidocrocite during oxidation of aqueous FeCl_2 solutions: *Clay Miner.* **11**, 189–200.
- Sigg, L. and Stumm, W. (1980) The interaction of anions and weak acids with the hydrous goethite (α - FeOOH) surface: *Colloids and Surfaces* **2**, 101–117.
- Torrent, J. and Guzman, R. (1982) Crystallization of Fe(III) -oxides from ferrihydrite in salt solution: Osmotic and specific ion effects: *Clay Miner.* **17**, 463–469.
- Vogel, A. I. (1961) *A Text-book of Quantitative Inorganic Analysis*: 3rd ed., Longmans, London, p. 809.

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