

FACTORS THAT GOVERN THE FORMATION OF MULTI-DOMAINIC GOETHITES

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Abstract—Transmission electron microscopic (TEM) examination has shown that multi-domainic crystals of synthetic goethite consist of almost parallel intergrowths, each of which is slightly misoriented with respect to its neighbors. These intergrowths emanate from a central nucleus within the crystal. They can nucleate along both the x and y crystal axes, but subsequent growth is mainly in the z direction.

The formation of multi-domainic goethites from ferrihydrite was favored by high pH (≥ 13) and, at lower pHs, by the addition of NaNO_3 to the system. Decreasing the temperature of synthesis from 70° to 20°C also enhanced domain formation. The nucleation of domains was confined to the initial stage of goethite formation. Domains probably formed when crystal growth was very rapid or when adsorbed species blocked the appropriate sites on the nucleus material.

Key Words—Domains, Goethite, Intergrowths, Iron, Synthesis, Transmission electron microscopy.

INTRODUCTION

Acicular and twinned crystals of goethite commonly show intergrowths or domains which parallel the long (i.e., z) axis of the crystal (Cornell *et al.*, 1974). These intergrowths are usually of unequal lengths. They are most easily seen where they project at the ends of the crystal; the boundaries between domains on the crystal surface are rarely visible. Intergrowths can apparently accelerate the dissolution and, hence, the weathering of goethite (Cornell *et al.*, 1974). Goethite has an extremely stable structure and dissolves more slowly in acid than the other iron oxides and oxyhydroxides (Siddhu *et al.*, 1981). Domain boundaries, however, are particularly susceptible to acid attack, and during dissolution they develop holes and fissures which assist in the disintegration of the crystal (Cornell *et al.*, 1974).

Multi-domainic crystals are common in synthetic goethites and have been observed in the natural mineral (Smith and Eggleton, 1983). Information about the factors that control intergrowth formation is limited. In the present work, the effect of pH, foreign anions, and temperature on intergrowth formation was investigated. These variables were chosen because an earlier study had shown them to influence the size and habit of goethite crystals (Cornell and Giovanoli, 1985). Also of interest were (1) the growth stage during which domains nucleate, and (2) the arrangement of the domains within the crystal. The degree of multi-domainic character of goethites synthesized under different conditions as shown by transmission electron microscopy (TEM) was correlated with the synthesis conditions.

EXPERIMENTAL METHODS

Goethite was grown from ferrihydrite that had been precipitated at pH 8–9 from 0.01 M ferric nitrate solution with 1 M KOH. The KNO_3 produced when the ferrihydrite was precipitated was washed out of the sample by centrifugation. The washed ferrihydrite was resuspended in water and the pH adjusted to between 11 and 13.5 with 1 M KOH. Typically, a suspension of ferrihydrite (0.1 g/100 ml) was held at 70°C for 24 hr. Schwertmann and Murad (1983) showed that the mechanism by which goethite forms is independent of pH. The results obtained in the present experiments should, therefore, apply equally to goethites grown at lower pH.

The effect of pH on the formation of multi-domainic goethites was tested with a series of ferrihydrite suspensions the pHs of which varied by 0.1 pH unit for each successive suspension, from 11.0 to 13.5. A second series of experiments involved the addition of different levels of NaNO_3 (0.01–5 M) to suspensions of ferrihydrite in which the pHs also ranged from 11 to 13.5. These experiments were aimed at testing the effect of foreign, monovalent ions on intergrowth formation. Additional experiments were carried out at 20° , 50° , 70° , and 90°C . Only two pHs, 12.3 (at which single-domain goethites predominated) and 13.1 (at which most crystals were multi-domainic), were used. After the ferrihydrite had converted to goethite, the samples were washed and dried at 50°C .

The methods used to follow the kinetics of the transformation have been described elsewhere (Cornell and

Table 1. Effect of pH, foreign anions, and synthesis temperature on the percentage of multi-domainic goethite crystals.

pH	T (°C)	NaNO ₃ [M]	t _{1/2} ¹ (hr)	Multi-domainic crystals (%) ²
11.0	70	—	7.5	5
12.0	70	—	6.5	5–10
12.3	70	—	6.0	10
12.4	70	—	6.0	10
12.5	70	—	3.0	10–15
12.6	70	—	3.0	25–35
12.7	70	—	3.0	40–50
12.8	70	—	2.5	60–80
12.9	70	—	2.5	80–90
13.0	70	—	2.0	90–95
13.5	70	—	2.0	95–100
12.3	70	5	10.0	100
12.3	70	2	8.8	100
12.3	70	1	6.0	100
12.3	70	0.1	6.0	40–50
12.3	70	0.01	6.0	25–30
12.3	90	—	1.4	5
12.3	70	—	6.0	10
12.3	50	—	10.5	20
12.3	20	—	24.0	20
13.1	90	—	nd	90–95
13.1	70	—	nd	90–95
13.1	50	—	nd	100
13.1	20	—	nd	100

¹ t_{1/2} is the time required for conversion of half the ferrihydrite to goethite. nd = not determined.

² The percentage of multi-domainic crystals was estimated by counting the number of crystals with intergrowths and expressing this fraction as a percentage of the total.

Giovanoli, 1985). Several goethite samples were dissolved by shaking them in 6 M HCl (0.1 g oxide/100 ml) for different lengths of time. The suspensions were filtered and the extent of dissolution estimated by measuring the iron released by atomic absorption spectroscopy (AAS). The partly dissolved crystals were examined by TEM.

Transmission electron micrographs (Hitachi HU-12A and H-600-2 electron microscopes, 125 kV) were obtained after the solid sample was dispersed in twice-distilled water and a drop of suspension was evaporated to dryness on a carbon-coated copper grid. Additional information about the morphology of the crystals came from TEM examination of thin sections cut approximately at right angles to the *x*, *y*, and *z* axes of the crystals (i.e., the [100], [010], and [001] directions, respectively). Thin sections were prepared by embedding the crystals in methacrylate and sectioning them with a Reichert Om U2 ultramicrotome, equipped with a diamond knife. The thickness of the sections was estimated from their interference colors and ranged from 200 to 400 Å.

A multi-domainic crystal consisted of almost parallel intergrowths that emanated from a central nucleus and grew along the *z* axis. The percentage of multi-do-

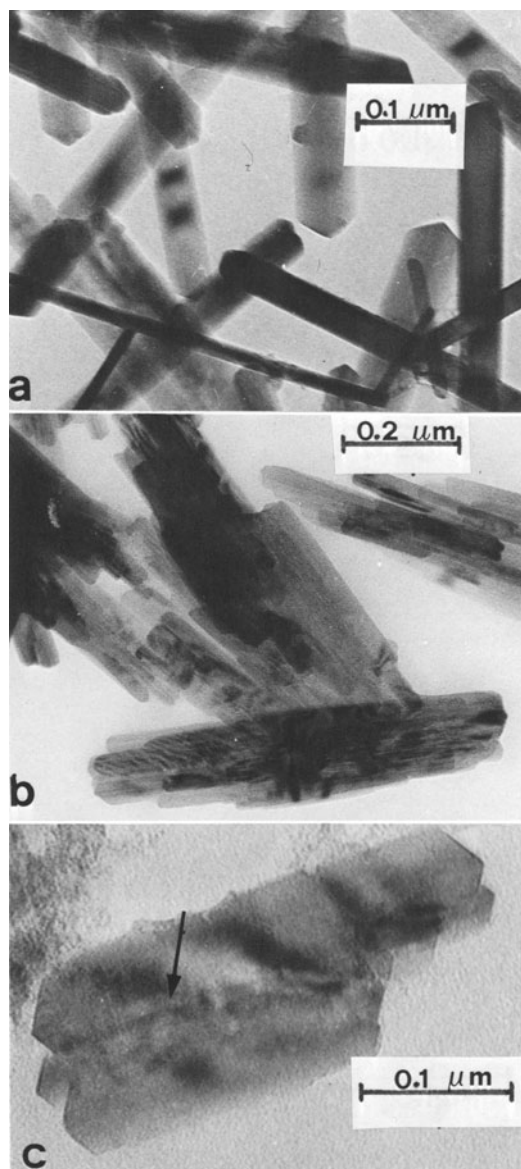


Figure 1. Transmission electron micrographs of (a) a predominantly single-domain goethite grown at pH 12, 70°C; (b) multi-domainic goethite grown at pH 13, 70°C; (c) a multi-domainic crystal of goethite showing the divergence of domains (arrow); the formless background material is ferrihydrite.

mainic crystals in a sample was found by counting the number of crystals that contained domains and expressing this fraction as a percentage of the total. Several hundred crystals were examined for each sample.

RESULTS

Intergrowth formation

The effect of synthesis conditions on the domainic character of a particular goethite are herein expressed

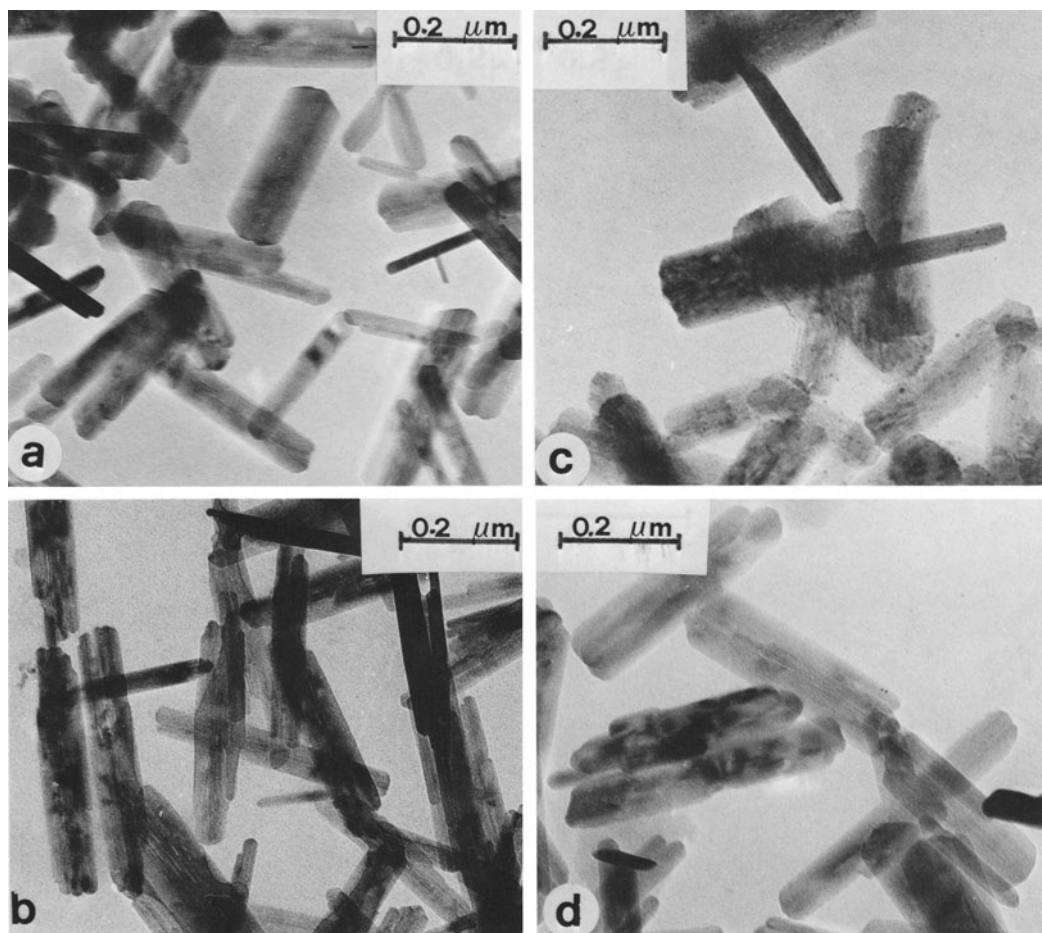


Figure 2. Transmission electron micrographs of goethites grown (a) at pH 12.3, 70°C with 0.01 M NaNO_3 added; (b) at pH 12.3, 70°C with 1 M NaNO_3 added; (c) at pH 12.3, 20°C; (d) at pH 13.1, 90°C.

as the percentage of multi-domainic crystals in the sample. Growth conditions, such as pH, presence of foreign ions, and temperature, also influenced the average number of domains per crystal and the degree of uniformity of these domains.

Effect of pH

Whether goethites were multi-domainic or not was governed, above all, by the pH of the system (Table 1). Acicular goethites grown at pHs between 11 and 12.5 were predominantly single domain. Only 5–10% of the crystals contained intergrowths, and usually two or three intergrowths were present in each multi-domainic crystal (Figure 1a). At pH > 12.5 the percentage of multi-domainic crystals in a sample increased sharply, reaching 90–100% at pH \geq 13 (Figure 1b). Multi-domainic goethites grown at high pH contained several domains. Inequalities in the lengths of individual domains within a crystal increased with rising pH.

Twinned goethite crystals followed a similar pattern to the acicular crystals. At pH 11–12, epitaxial twins

(i.e., goethite outgrowths on hematite centers—see Cornell and Giovanoli, 1985) coexisted with acicular crystals. The arms of some of these twins contained a few fairly uniform intergrowths. At higher pH, star-shaped twins (without hematite) were produced (Cornell and Giovanoli, 1985). The star-shaped twins contained numerous intergrowths, the number and irregularity in length of which increased with increasing pH.

Earlier studies showed that as the pH of the system was increased to \geq 12, the rate of transformation of ferrihydrite into goethite increased markedly (Cornell and Giovanoli, 1985). Thus, the increase in multi-domainic character of goethite with increasing pH appears to have been related to the increased rate of crystal growth.

Effects of foreign anions

Cornell and Giovanoli (1985) established that goethites grown at pH 12.3 in the presence of 5 M NaNO_3 are predominantly multi-domainic. This effect was

considered in more detail in the present investigation using a range of salt concentrations (0.01 to 5 M, Table 1). A control goethite grown at pH 12.3 contained about 10% multi-domainic goethite crystals. In the presence of 0.01 M NaNO_3 , this proportion increased to 25–30%. The domains in these crystals were wide and comparatively uniform in length (Figure 2a). This level of salt corresponded to an anion:Fe ratio of one and was sufficient to give more than a monolayer of adsorbed anion on the goethite surface, even assuming only 10% adsorption. As the concentration of NaNO_3 in the system was increased, the percentage of multi-domainic crystals rose, until at 1 M NaNO_3 , every crystal in the sample contained several intergrowths (Figure 2b). At even higher levels of NaNO_3 , the situation was complicated by the high ionic strength of the system; a high ionic strength favors the formation of twins (Cornell and Giovanoli, 1985). The crystals grown at the highest ionic strengths contained numerous intergrowths and, in addition, showed etch pits and extinction contours that indicate that there had been interference in crystal growth. Even 0.01 M salt enhanced domain formation at all pHs.

Although salt concentrations between 0.01 and 1.0 M favored intergrowth formation, they did not affect the rate of goethite crystallization. Higher levels of NaNO_3 (2–5 M) retarded the rate of transformation of ferrihydrite; the reaction half time, i.e., the time for the conversion of half the ferrihydrite, increased from 6 hr for the control system (pH 12.3) to 10 hr for a suspension containing 5 M NaNO_3 (Table 1). Apparently this increase was due to the increased viscosity of the system.

Temperature effects

Goethite grown at pH 12.3 and 70°C was predominantly single domain. Syntheses at 50° or 20°C produced slightly more domainic crystals in the goethite; about 20% of the crystals contained two or three very uniform domains (Figure 2c and Table 1).

Highly multi-domainic goethites were produced at pH 13.1 at all temperatures of synthesis (20°–90°C). At 50°C (and even more so at 20°C) inequalities in domain length increased. At a synthesis temperature of 90°C, fewer intergrowths per crystal were produced and the uniformity of domains improved within a given crystal (Figure 2d). The increase in temperature did not, however, reduce the percentage of multi-domainic crystals within a sample.

Stage at which domains form

A series of goethites was synthesized at pH 12.3 by adding enough NaNO_3 at different stages of the reaction to give a final concentration of 5 M. The control sample contained about 10% multi-domainic crystals, whereas the presence of salt at the beginning of the reaction

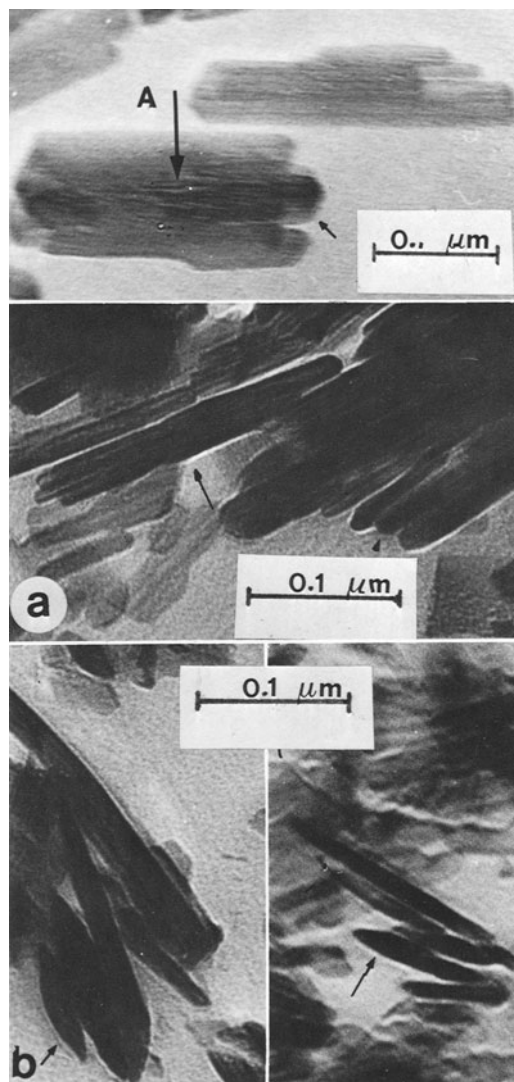


Figure 3. Transmission electron micrographs of thin sections of multi-domainic goethites: (a) sections of crystals with several intergrowths arising from a central region (arrowed). Arrow A indicates dehydration channels; (b) Typical cross sections taken almost at right angles to the z axis (arrowed).

produced intergrowths in all crystals. The influence of the salt was reduced if it was added after 10% reaction (i.e., 30% of the product crystals were multi-domainic) and was negligible if it was added after 50% reaction.

Goethite was also grown by a two-stage method (cf. Cornell and Giovanoli, 1985). A solution of ferric nitrate having an OH:Fe ratio of 0.5 was aged at room temperature for 48 hr to produce seed nuclei. The pH was then raised to 12.5 and crystal growth allowed to proceed at 70°C. This method produced goethite in which all crystals were single domain.

These experiments suggest that domains nucleated during the initial stages of goethite formation.

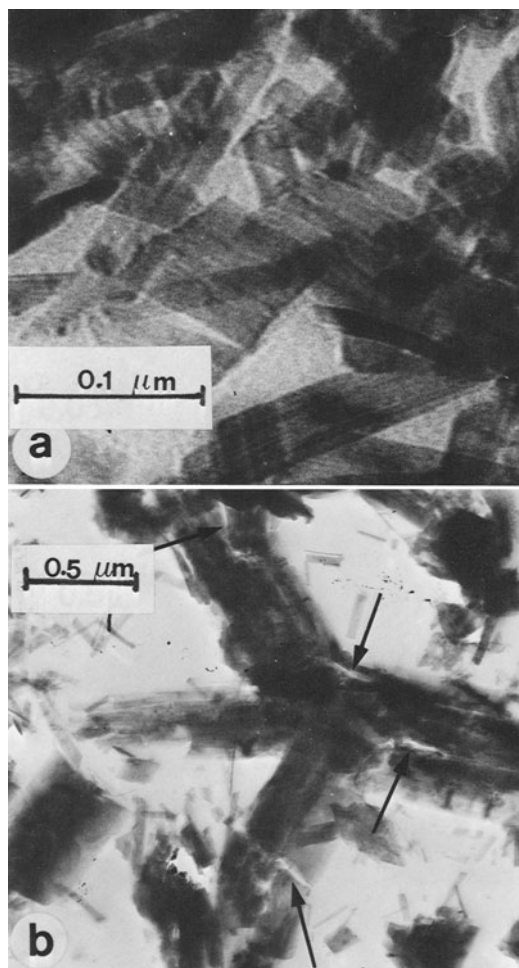


Figure 4. Transmission electron micrographs of thin sections of goethite crystals: (a) section with partly separated domains (arrow); (b) fractures in the arms of star-shaped twins (arrowed).

Electron microscopy results

Crystal morphology. The average lengths and widths of the acicular crystals examined ranged from 2000 to 6000 Å and from 200 to 600 Å, respectively. The widths of the intergrowths ranged between 80 and 300 Å; hence, intergrowths could not be observed in crystals having widths ≤ 100 Å. Individual domains in a crystal were commonly of unequal lengths indicating that they had grown at different rates (Figure 1b). Differences in rates of growth appeared to be most pronounced at high pH. Goethites grown at lower pH (12) usually contained two or three intergrowths arranged along the y axis (Figures 1a and 2a). Goethites grown at higher pHs or in the presence of high concentrations of NaNO_3 consisted of several intergrowths stacked side by side and one above the other (Figures 1b and 2b).

Cornell *et al.* (1983) suggested that domains might

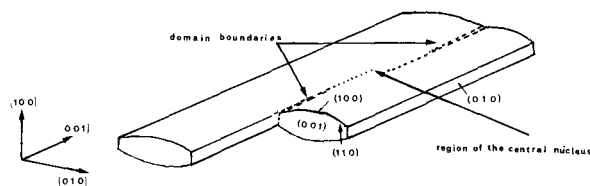


Figure 5. Schematic representation of a multi-domainic crystal. Divergence at domain boundaries has been exaggerated.

nucleate on the (010) faces of the parent crystal. Thin sections taken almost at right angles to the x (i.e., [100]) and y (i.e., [010]) axes showed, however, that domains appeared to arise from a central point within the parent crystal. Figure 3a shows examples of sectioned crystals containing several intergrowths; these intergrowths do not extend the entire lengths of the crystals, but appear to have nucleated somewhere in the center and then grown in one direction only, along the z (i.e., [001]) axis.

Typical cross sections of both single-domain and multi-domainic goethites taken almost at right angles to the z axis are shown by the arrows in Figure 3b. These sections are more or less spindle shaped and appear to be bounded by (110) or perhaps (021) faces. These faces predominated in all cross sections, although limited development of the (100) and (010) faces was common. Similar sections of goethite were observed by Schwertmann (1984).

In some samples, the pressure of the sectioning knife caused the crystals to part along the domain boundaries. Figure 4a shows a section cut almost at 90° to the x axis consisting of three domains that have spread apart like the sections of a fan. Crystals grown in the presence of salt tended to part more readily than others during sectioning, perhaps because the divergence between domains in such crystals was greater than in crystals grown under other conditions. Fracturing during sectioning was common for large crystals. Figure 4b shows a large twinned crystal containing a fracture from the twin boundary down the center of one arm. Adjacent arms contain cross-wise cracks. Thus, the channels and spaces reported by other workers may possibly have been the result of stresses experienced during sectioning (Smith and Eggleton, 1983). Although these channels appear to be artefacts produced by the sectioning technique, they may, nevertheless, reflect the presence of areas of strain in the crystal.

Some sections in Figures 3 and 4 show channels having a spacing of 30–40 Å (arrow A, Figure 3a). These are dehydration channels. They indicate the onset of dehydration to hematite and are the result of heating by the electron beam (cf. Watari *et al.*, 1979). These channels should not be confused with domain boundaries.

TEM examination of both intact and sectioned crystals showed that multi-domainic crystals typically consist of almost parallel intergrowths that have developed from a central nucleus and grown along the z axis. Each intergrowth is slightly misoriented with respect to its neighbors (Figure 1c). The divergence between domains is probably not more than a few hundredths of a degree. A schematic drawing of a multi-domainic crystal is shown in Figure 5.

Synthetic, acicular goethite usually gives rise to a $[100]$ zone electron diffraction pattern. In earlier publications the crystal was assumed, therefore, to be lying on the (100) face and also, the (100) face was assumed to be the predominant crystal face in synthetic goethite (Atkinson *et al.*, 1968; Cornell *et al.*, 1974). Sections taken parallel to different crystal axes showed, however, that the most extensively developed faces were the (110) faces. Although a single-domain crystal should lie on a (110) face, multi-domainic crystals in which the depressions separating the domains are shallow, could lie in the $[100]$ zone and, hence, give rise to the $[100]$ zone electron diffraction pattern.

Partly dissolved acicular crystals. Acid attack proceeded most rapidly at structural imperfections and served to identify such regions. Partly dissolved crystals were examined to see whether regions which showed an enhanced susceptibility to acid attack were always associated with domain boundaries.

During the initial stages of dissolution, single-domain crystals became pointed. The individual domains in multi-domainic crystals also developed pointed ends (Figure 6a, arrowed), which suggests that acid attack at the boundaries may have proceeded inwards from the ends of the crystals. TEMs of sectioned, partly dissolved crystals showed that holes developed in the end faces of the crystals (Figure 6b, arrowed). As dissolution continued, holes and fissures appeared along the domain boundaries on the surface of the crystal.

Crystals grown by the two-stage seeding process were single domain and appeared to be completely without defects; they dissolved uniformly. Other goethites, both single-domain and multi-domainic crystals showed irregularly distributed regions of preferential attack over the whole surface, in addition to that which took place at the domain boundaries (Figure 6c). Crystals grown in the presence of 5 M NaNO_3 showed more signs of this type of attack than did other goethites, suggesting that a high level of foreign anions enhanced the formation of local imperfections.

DISCUSSION

Multi-domainic goethites did not appear to be simply aggregates of parallel crystals or fibers, similar to those found, for example, in asbestos. TEMs of sectioned crystals showed that intergrowths arose from a central nucleus within the crystal. These intergrowths

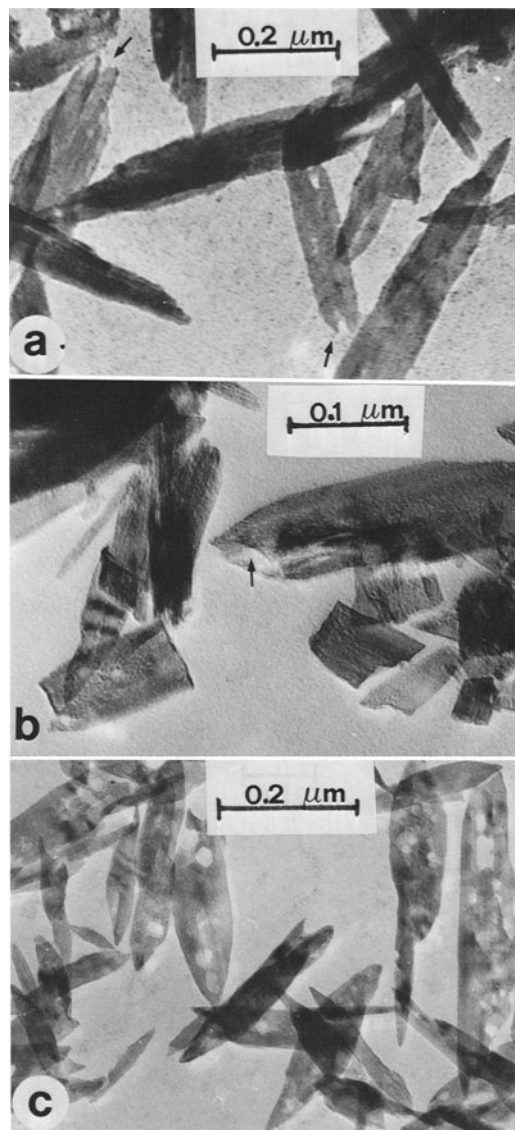


Figure 6. Transmission electron micrographs of partly dissolved goethites: (a) after 30% dissolution—individual domains have developed pointed ends (arrowed); (b) thin sections of the sample in (a); note hole in end face of central crystal (arrow); (c) salt-grown goethite (5 M NaNO_3) after 50% dissolution.

may have nucleated along both the x and y axes, but subsequent growth was mainly in the z direction. Each intergrowth was slightly misoriented with respect to its neighbors. These multi-domainic goethites resembled the lineage-type crystals described by Buerger (1934). Such crystals consisted of a number of lineages or sub-units growing from a central seed crystal. The lineages had the same structure as the seed but were slightly misoriented with respect to each other. As a result of this misorientation, the lineages were visible at the surface of the crystal.

A previous high-resolution TEM (HRTEM) study of the boundaries between domains showed them to be extremely coherent (Cornell *et al.*, 1983), with no evidence of spaces or highly disordered regions. HRTEM also showed, however, that dislocations were locally present along the boundaries. Thus, the slight mismatch between domains was presumably taken up by a series of widely spaced dislocations in accord with the model of Read and Shockley (1952). These dislocations could have served as sites of enhanced acid attack. Furthermore, because they extended through the crystal, their presence could have been responsible for the formation of fissures along the domain boundaries.

Multi-domainic goethites appear to have formed either as a result of very rapid growth or the presence of adsorbed foreign impurities. For domains to have formed, the growth of the nucleus must have been interrupted. Two essential steps in the growth of the nucleus are adsorption of a growth unit onto the nucleus and the later migration of the adsorbed species over the surface to a suitable site where it joins the structure.

In a highly supersaturated system (i.e., at high pH), the rate of adsorption was so rapid that growth units did not have time to order completely, and mis-stackings were introduced into the structure. Any factor that reduced the rate of adsorption could have reduced the formation of intergrowths. This situation was most readily achieved during syntheses at lower pH; however, even at high pH, intergrowths were reduced by the incorporation of Al into the goethite structure. As the level of Al in the system increases, both the rate of growth and the average number of domains per crystal fall (Schwertmann, 1984; Schulze and Schwertmann, 1984). Al is thought to reduce the rate of growth because it is present as a complex divalent ion ($\text{Al}(\text{OH})_2^{2-}$) at $\text{pH} > 11$, and adsorption of the complex monovalent iron species ($\text{Fe}(\text{OH})_4^-$) is favored (Mann *et al.*, 1985).

High levels of NaNO_3 in the system also retarded crystal growth, but at the same time encouraged intergrowth formation. In alkaline media, Na^+ may take part in ion-pair formation on the surface of goethite (cf. Davis and Leckie, 1978). Such ion pairs could be represented as: $>\text{FeOH} + \text{Na}^+ \rightleftharpoons >\text{FeO}^- - \text{Na}^+ + \text{H}^+$. These ion pairs may have interfered with the surface mobility of the adsorbed growth units. If appropriate migration pathways were blocked, even very slow adsorption was unable to prevent the formation of intergrowths and other types of defects. Adsorption of foreign species is probably responsible for the presence of intergrowths in natural goethites. The surface mobility of adsorbed growth units might also have been expected to depend on temperature. The increase in

the multi-domainic character of the goethite at lower synthesis temperatures is in line with this expectation.

Intergrowths arose from a central nucleus. The present work has shown that their formation was limited to the early stages of growth, probably due to the fact that nucleation of intergrowths only took place along the x and y axes of the nucleus. Lewis and Schwertmann (1980) showed that goethite crystals reach their maximum dimensions along the x , and to a lesser extent, along the y axes, during the earliest stage of growth; hence, intergrowth nucleation should be confined to this growth period. Subsequent growth was along the z axis, and structural mis-stackings introduced during the later stages of growth gave rise to structural defects, but not to intergrowths.

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