INFLUENCE OF ORGANIC ANIONS ON THE CRYSTALLIZATION OF FERRIHYDRITE

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Abstract—Hydroxy-carboxylic acids inhibit the crystallization of ferrihydrite in the pH range 9–11 in the order

citric > meso tartaric > L–tartaric ≫ lactic

and favor hematite formation relative to goethite in the order

L–tartaric > citric > meso tartaric > lactic.

The crystal shape of hematite can change from hexagonal plates to acicular in the presence of these acids. The influence of the acids on the crystallization rises with increasing concentration and with falling pH.

The effectiveness in suppressing crystallization depends on whether and how strongly the acid adsorbs on ferrihydrite and how strongly it complexes with Fe^{3+} in solution. Inhibition of crystallization of hematite is believed to be due to the di- and tricarboxylic acid linking ferrihydrite particles in an immobile network. Goethite formation is suppressed by the acid complexing with Fe in solution and hindering nucleation; strongly adsorbing acids also adsorb on the nuclei and hinder further growth. Certain acids can induce hematite formation because they contain a group which acts as a template for nucleation of hematite.

Key Words—Crystallization, Ferrihydrite, Goethite, Hematite, Hydroxy-carboxylic acid.

INTRODUCTION

It has been demonstrated that organic compounds retard or inhibit the crystallization of Fe oxides from ferrihydrite in soils (Schwertmann, 1966). Laboratory studies have shown that anions of simple organic acids (Schwertmann *et al.*, 1968; Schwertmann, 1969) and fulvic acids from a soil (Kodama and Schnitzer, 1977) have a great effect on both the rate of crystallization and the nature of the crystalline product. Oxalate favors hematite over goethite (Fischer and Schwertmann, 1975). Organic anions such as citrate may act through adsorption on ferrihydrite or hematite (Schwertmann *et al.*, 1968). The same mechanism seems to operate with fulvic acid at a low fulvic acid:Fe ratio, whereas at a higher ratio, complexation of Fe in solution completely inhibits any oxide precipitation (Kodama and Schnitzer, 1977).

The aim of the present study was to investigate more specifically the effect of organic anions on the transformation of ferrihydrite to crystalline products and to determine the mechanism by which the anions operate. The experiments were carried out at pH 9–11 and at 70°C because under these conditions, in the absence of organic acids, crystalline products could be obtained in a reasonable length of time, and both hematite and goethite are usually formed. At lower pH and room temperature crystallization is too slow. Long term experiments carried out at 20°C and at pH 6 (conditions resembling those in soils) in the presence of organic acids (10^{-3} M) gave no crystalline product even after 12 months. In contrast, at higher pH (~11), crystallization is rarely influenced if at all by organic acids, and fur-thermore, goethite is very strongly favored over hematite.

Earlier work (Schwertmann, 1969), involving higher concentrations of acid (10^{-2} M), showed that the acids fall into two groups: (1) those that completely inhibit crystallization at pH 9–10 (the hydroxy-carboxylic acids), and (2) those that only retard crystallization and also alter the ratio of goethite to hematite formed (the carboxylic acids). In the present investigation most experiments involved the hydroxy-carboxylic acids, because by varying their concentration, these acids could be used to cover the whole range from complete inhibition to complete crystallization and from pure goethite to pure hematite. Furthermore, because these acids differ in the size, shape, and structure of the molecule and in the number of carboxyl and hydroxyl groups available for bonding, information about how they interfere with Fe-oxide formation could be expected.

EXPERIMENTAL METHODS

Ferrihydrite (9.5 mmoles Fe in a final volume of 200 ml) was precipitated from 5×10^{-2} M Fe(III) nitrate solution with 2.5 M KOH and the pH raised to a value between 9 and 11. This process took approximately 5 minutes. A solution of Merck reagent grade organic acid [lactic, meso tartaric, L–tartaric, citric, oxalic, succinic, malonic, maleic, or malic (=cis butenedioic) acid] was added to a final concentration in suspension of 10^{-2}–10^{-5} M, the pH readjusted if necessary, and the suspension placed in a 70°C oven. Most of the results refer to a standard reaction time of 24 hr. During and

Table 1. Effect of different concentrations of citric acid on crystallization of ferrihydrite.[1]

Citric acid conc.	Composition of product		
	Goethite %	Hematite %	Ferrihydrite %
0	100	0	0
10^{-5} M	85	15	0
10^{-4} M	0	10	90
10^{-3} M	0	0	100
10^{-2} M	0	0	100

[1] pH = 10, 70°C, 24 hr.

after the heating period, the suspension was sampled and washed, and the total Fe (Fe_t) and oxalate-soluble Fe (Fe_o) (Schwertmann, 1964) were determined. The ratio Fe_o/Fe_t was taken as a measure of the proportion of ferrihydrite left unchanged. Fe was determined by atomic absorption spectroscopy (Perkin Elmer 420 Atomic Absorption Spectrophotometer). The composition of the crystalline fraction was determined after oven drying at 50°C from an X-ray powder diffractogram (dried powder pressed gently against filter paper to avoid orientation; Philips PW 1300 diffractometer with CoKα radiation and a diffracted beam graphite monochromator) by comparing the area of the (110) peak of goethite and the (120) peak of hematite with the same peaks in mixtures of synthetic standards of comparable peak widths. Electron micrographs (Zeiss EM 10 electron microscope at 80 kV) were obtained after dispersing the solid sample in alcohol and evaporating a drop of the suspension to dryness on a carbon-coated copper grid.

The extent of adsorption of organic anions on ferrihydrite at various pH values was found by agitating a suspension of ferrihydrite and organic acid for 24 hr at 20°C and filtering it through a 0.22-μm Millipore filter. The organic acid remaining in the filtrate was determined by digestion with a mixture of chromic (5×10^{-3} M) and sulphuric acid (96%) at ~80°C followed by back

Figure 2. Fe_o/Fe_t as a measure of the degree of transformation of ferrihydrite to goethite vs. time in the presence of various acids (10^{-3} M) and 6% goethite seeds (pH 9.8, 70°C).

titration with Fe(II) sulphate solution (10^{-2} M), using diphenylamine as the indicator. The amount of acid adsorbed was found by difference.

RESULTS

The factors which influence the effect of organic acids in the crystallization of ferrihydrite are acid concentration, pH, and the nature of the acid.

Acid concentration and pH

The ability of a hydroxy-carboxylic acid to retard crystallization rises as the concentration of acid in solution increases (Table 1) and as the pH decreases (Figure 1). Above pH 11 even 10^{-2} M acid did not influence crystallization. Below pH 11 crystallization was retarded to a varying degree (Figure 1) depending on the nature of the acid (see below).

Nature of the acid

The nature of the acid affects the rate of crystallization and the composition of the end product, i.e., the goethite:hematite ratio.

Rate of crystallization. All of the hydroxy-carboxylic acids studied reduced the rate of crystallization below a certain pH and above a certain concentration, but to a varying degree. For *citric acid* the ferrihydrite was unchanged after 24 hr over the pH range 9–10.5 in the presence of 10^{-2} M and 10^{-3} M acid. At 10^{-4} M acid
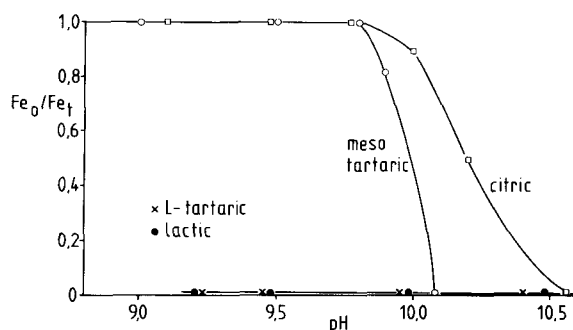

Figure 1. Fe_o/Fe_t as a measure of the degree of transformation of ferrihydrite to goethite and/or hematite vs. pH in the presence of various organic acids at 10^{-4} M concentration (24 hr, 70°C).
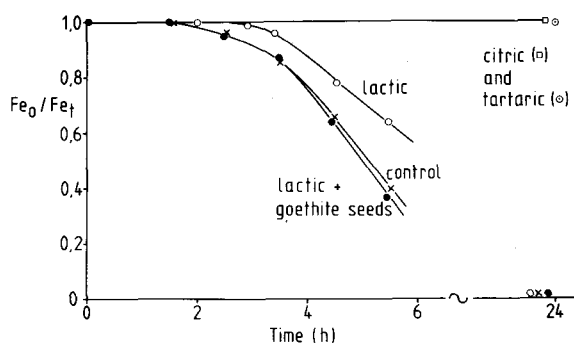
Table 2. Adsorption of organic acids on ferrihydrite at pH 9 and 20°C.[1]

Initial acid in solution	Adsorption from solution			
	Meso tartaric %	L-tartaric %	Citric %	Lactic %
10^{-2} M	31	35	n.d.	0
10^{-3} M	50	45	50	0

[1] 100 ml of acid + 9.5 mmole of Fe.
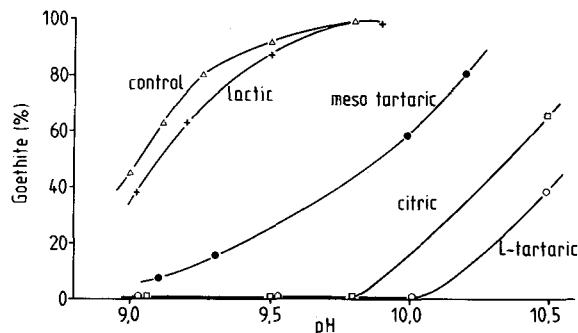
Figure 3. Relation between goethite formed and pH in the presence of various organic acids at 10^{-5} M concentration (70°C, 24 hr; 100 − goethite = hematite).
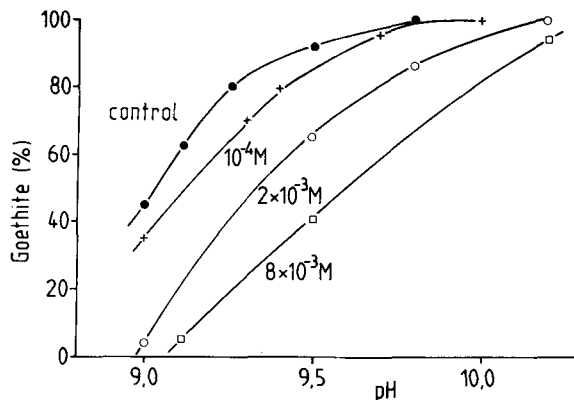

Figure 4. Proportion of goethite formed between pH 9.0 and 10.2 at various concentrations of lactic acid (70°C, 24 hr; 100 − goethite = hematite).

(Figure 1) partial inhibition below pH 10.5 and complete inhibition below pH 9.8 was noted, whereas no effect was measured at 10^{-5} M acid. At pH 10 and 10^{-3} M acid, complete crystallization (to hematite) was possible only after 16 days. The crystallization time was even longer (weeks) at lower pH (8.5) or at higher acid concentrations (10^{-2} M); at very high acid levels ($>10^{-1}$ M), crystallization may be inhibited indefinitely.

For the two *tartaric acids* no conversion took place at 10^{-2} and 10^{-3} M over the pH range of 9.0–10.5. At 10^{-4} M the two forms behaved differently. L–tartaric acid did not inhibit crystallization within 24 hr, whereas with meso tartaric acid no crystallization took place below pH 9.8 (Figure 1). With *lactic acid* complete conversion to goethite and/or hematite took place within 24 hr even at a concentration of 8×10^{-3} M, but the rate was reduced. This is shown for 10^{-3} M concentration at pH 9.8 in Figure 2.

From these results the order of inhibition of crystallization is citric > meso tartaric > L–tartaric ≥ lactic. Of the two other hydroxy-carboxylic acids not studied in detail, malic acid came after L–tartaric and 5,sulphosalicylic acid just before lactic acid in the above sequence. The *dicarboxylic acids* (oxalic, succinic, malonic, and maleic) were much less efficient. At 10^{-2} M concentration these acids only partially inhibited crystallization. Preliminary results with the latter acids suggested that as the concentration decreased the order of their effectiveness as inhibitors changed.

Table 2 shows the extent of adsorption of the hydroxy-carboxylic acids on ferrihydrite. Those acids (citric, tartaric) which inhibit crystallization at 10^{-2} and 10^{-3} M concentration were adsorbed to a significant degree, whereas lactic acid, having only a very weak effect, was not adsorbed. At 10^{-4} M, L–tartaric acid, although adsorbed to a large extent, did not inhibit crystallization possibly because the degree of coverage is too low for this acid to have an effect. The area per tartaric acid molecule is approximately 110 Å², 600 Å², and 7000 Å² (meso tartaric) and 4000 Å² (L–tartaric) for

acid concentrations of 10^{-2} M, 10^{-3} M, and 10^{-4} M, respectively, assuming an average surface area of 200 m²/g (Schwertmann and Fischer, 1973).

Hematite:goethite ratio. At organic acid concentration of 10^{-5} M complete crystallization takes place above pH 9; therefore, the effect of the acids on the hematite:goethite ratio can be evaluated. As compared to the control, all four hydroxy-carboxylic acids led to more hematite relative to goethite (Figure 3).

The hematite:goethite ratio decreases in the order: L–tartaric > citric > meso tartaric ≥ lactic. This order is different from that for inhibition of crystallization which suggests that inhibition of crystallization and suppression of goethite may involve different mechanisms. It is particularly noteworthy, that far more hematite forms in the presence of L–tartaric than with meso tartaric acid. The hematite-favoring effect increases with increasing concentration of the acid and with decreasing pH as shown for lactic acid in Figure 4.

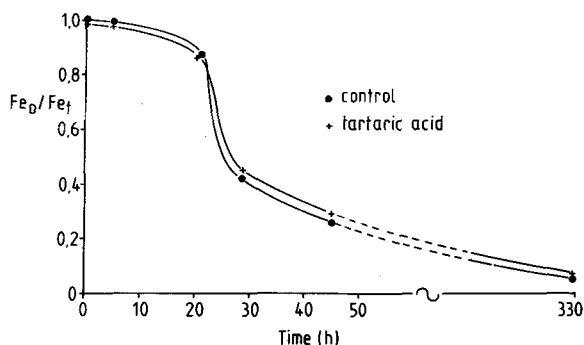Whether these acids actually encourage hematite to

Figure 5. Change of Fe_o/Fe_t with time during the transformation of ferrihydrite to goethite and hematite at pH 8.3 and 70°C in the presence of 5×10^{-4} M L–tartaric acid.
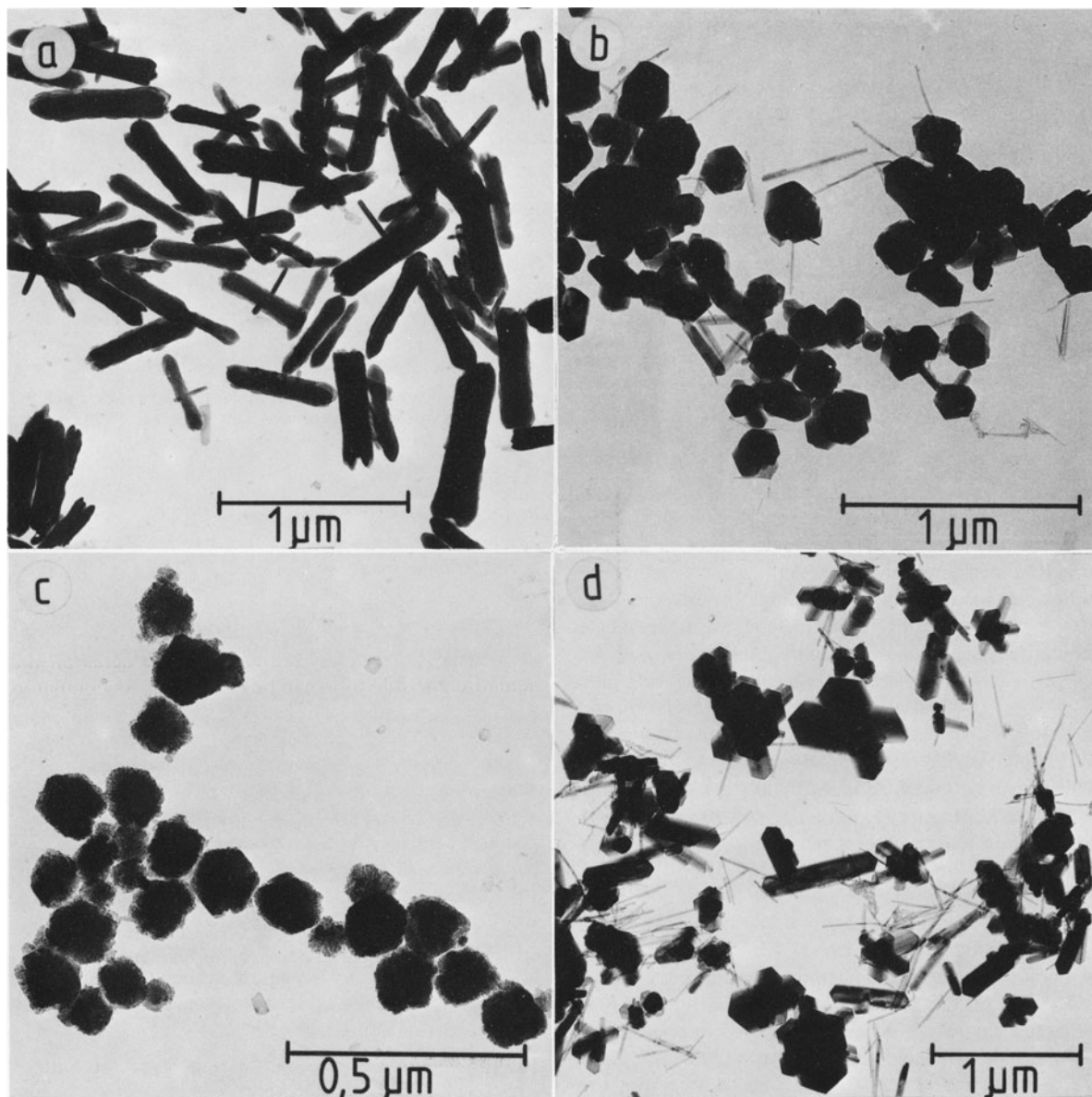
Figure 6.   Electron micrographs of iron oxide products: (6a) 10^{-4} M citric acid, pH 10, acicular hematite; (6b) 10^{-5} M oxalic acid, pH 9, platy hematite; (6c) 5×10^{-4} M L–tartaric acid, pH 9, serrated platy hematite; (6d) 10^{-5} M citric acid, pH 10.5, acicular and partly twinned goethite (65%) and platy hematite (35%) which has partly induced epitaxial growth of goethite.

form was investigated by comparing the kinetics of crystallization of a control system and one containing 5×10^{-4} M L–tartaric acid at pH 8.3 (Figure 5). The overall rate of crystallization appeared to be the same in both systems, but in the control, 45% of the crystalline fraction (>90%) was goethite and 55% was hematite, while in the presence of the L–tartaric acid, hematite was the sole product. Thus, in this system the formation of hematite was accelerated by the presence of L–tartaric acid. Succinic, malonic, maleic, oxalic, and malic acids were intermediate between lactic and

the other hydroxy-carboxylic acids in their effect on hematite formation. At pH 9.6 at 10^{-5} M concentration the amount of hematite formed ranged from 50% with succinic to 70% with malic acid.

Electron micrographs

Hematite produced in the presence of 6×10^{-3} M citric acid was acicular instead of platy because of preferential growth in the z-direction (Schwertmann *et al.*, 1968). Similar acicular hematite was produced in this study at 10^{-4} M citric acid (Figure 6a). Thin outgrowths
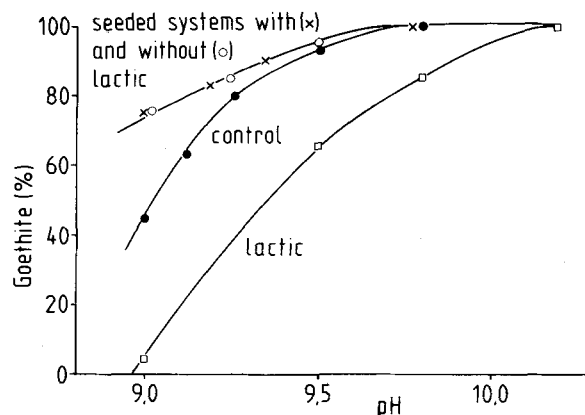
Figure 7. Effect of seeding with 6% goethite on the formation of goethite from ferrihydrite in the presence of 2×10^{-3} M lactic acid as a function of pH (70°C, 24 hr; 100 − goethite = hematite).

perpendicular to the main crystal are common. The usual hexagonal plates of hematite were formed (together with goethite needles) at 10^{-5} M citric acid and also in the presence of oxalic, succinic, malonic, and maleic acid, even at 10^{-2} M concentration (Figure 6b). The hexagonal shape of hematite is poorly developed (Figure 6c) in smaller crystals, and a granular internal structure is visible indicating its genetic relationship with ferrihydrite (Fischer and Schwertmann, 1975). The goethite crystals vary widely in shape between thin needles and thick twins (Figure 6d) but appear not to be modified by the organic acid.

Seeding with goethite

It seemed possible that there might be a time after the transformation started beyond which addition of organic acid to ferrihydrite would have no effect on the reaction. This was verified for lactic acid. At pH 9.8 and with 10^{-3} M acid, 23% hematite (77% goethite) was formed when the acid was added at the start of the reaction, only 5% hematite when it was added after 1 hr, and no hematite when it was added after 3.5 and 6 hr (i.e., the same result as with no addition). In each case the system was analyzed 24 hr after the start of the reaction. These data suggest that the acid hindered the nucleation of the goethite and that once sufficient nuclei had formed, the inhibiting effect of the acid was overcome. An analogous case for the effect of Al on the nucleation of goethite was described by Lewis and Schwertmann (1979).

This idea was confirmed by further experiments in which goethite was added to the system at the start of the reaction. Adding 6% seeds of goethite to a system containing ferrihydrite and lactic acid, i.e., an acid that only *weakly* retards crystallization, increased the rate at which goethite formed, raising it to the level found for the control system (Figure 2). The amount of goe-
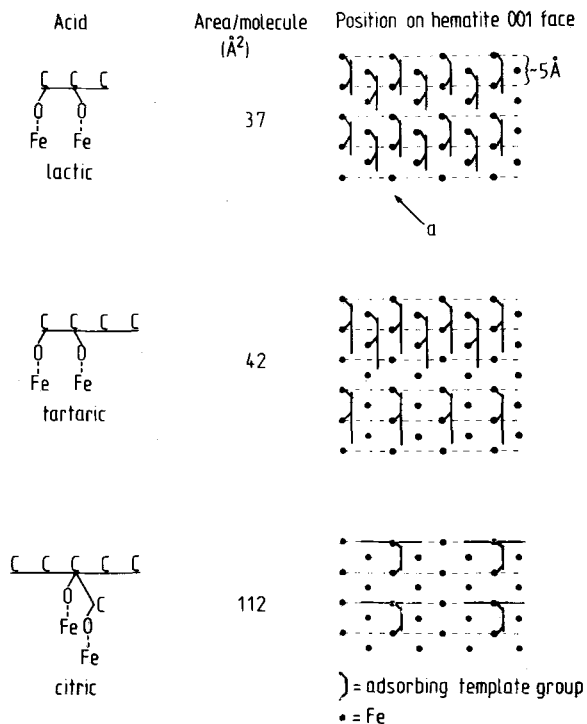

Figure 8. Schematic arrangement of organic acids on the (001) face of hematite.

thite in the final product in the pH range of 9.0–9.8 was also increased and was the same as that in a seeded system in which lactic acid was absent (Figure 7). In contrast, in the presence of an acid that *strongly* inhibits crystallization, e.g., 10^{-3} M meso tartaric acid, and at pH 10, addition of 80% goethite seeds did not encourage further goethite to form from ferrihydrite. Adding 10% seeds of hematite to a system of ferrihydrite without acid at a series of pH values from 9 to 11 did not increase the proportion of hematite formed.

DISCUSSION

Depending on the nature of the acid and the conditions of synthesis, organic acids had two effects on the formation of goethite and/or hematite from ferrihydrite. At lower concentrations they increased the proportion of hematite at the expense of goethite, whereas at higher concentrations they retarded or inhibited crystallization. In order to explain these effects, the mechanism for the formation of goethite and hematite from ferrihydrite must be known. It was proposed earlier (Schwertmann and Fischer, 1966), that hematite formation involves aggregation of ferrihydrite followed by nucleation and crystal growth within the aggregate. In contrast, for goethite formation, the ferrihydrite dissolves into small, probably monomeric units which nucleate and feed the goethite crystal in bulk solution. Both mechanisms operate competitively.
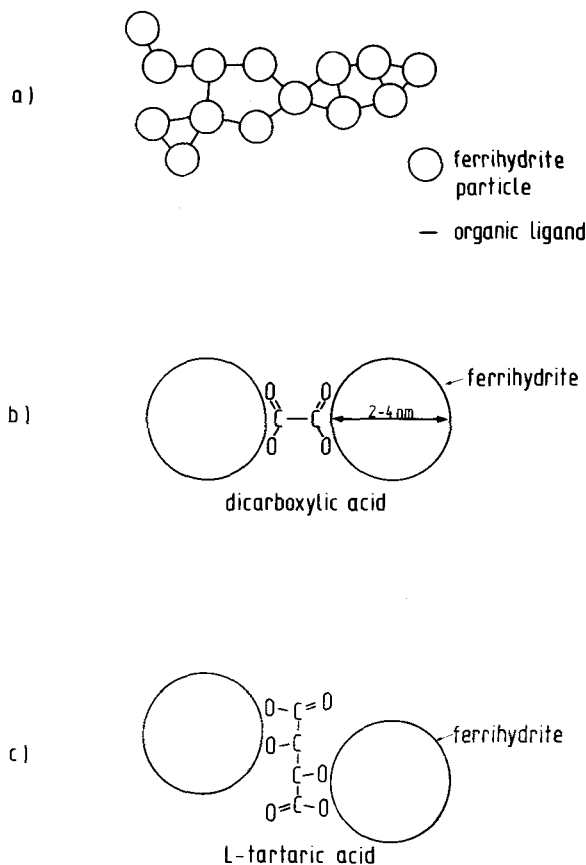
Figure 9.   Possible ways of linking ferrihydrite particles with organic molecules.

There are, therefore, three ways in which organic molecules might interfere in the crystallization process: (1) by adsorption on ferrihydrite, thereby preventing its dissolution (to form goethite) or the nucleation of hematite within the ferrihydrite aggregate; (2) by association of the organic ligand with Fe in solution (complexation) and/or at the surface of goethite nuclei and crystals, thus inhibiting nucleation and/or crystal growth; and (3) by acting as a template for and thereby favoring the formation of hematite (Fischer and Schwertmann, 1975).

Adsorption on ferrihydrite

Whether or not adsorption of organic molecules prevents the dissolution of ferrihydrite should partly depend on the degree of surface coverage. Adsorption of organic anions at the goethite surface can involve one or two Fe atoms as shown for oxalate (Parfitt et al., 1977). There is no detailed information about the surface structure of ferrihydrite, but as ferrihydrite and hematite have related structures (Towe and Bradley, 1967) results obtained using hematite would at least give an estimate of trends to be expected although the ferrihydrite is less ordered. Possible arrangements of

the organic anions at the (001) plane of hematite are shown in Figure 8 together with their size. With 10^{-2} M tartaric acid enough anion is adsorbed from solution to give a uniform surface coverage of 1 molecule/110 Å² (see p. 404) (saturation coverage = 1 molecule/42 Å², Figure 8). With 10^{-3} M acid the molecules are even more widely distributed (1 molecule/600 Å² and 1 molecule/300 Å² for tartaric and citric acid, respectively) and could hardly block all the dissolution sites to produce monomers for goethite nucleation. In fact, the organic acids encourage the ferrihydrite to dissolve to some extent ($\sim$1%) leading to a measurable amount of Fe in solution (3 ppm).

Hematite formation, however, might be prevented even at low coverage. The citrate and tartrate molecules, 6–10 Å long, could link the ferrihydrite particles (diameter 2–4 nm) to form a relatively immobile network (Figure 9a) in which the area of direct contact between the particles is reduced and their internal "coalescence" to hematite becomes impossible. This is partly supported by an unexpectedly low surface area found for natural and synthetic ferrihydrites containing organic compounds (Schwertmann and Fischer, 1973), possibly because their internal surface is not easily accessible to the adsorbing gas.

An acid's ability to stabilize ferrihydrite in this way will depend on whether it can adsorb in the pH range considered and on the groups involved. It seems probable that the acids could bridge between two particles through two (or more) COOH groups (Figure 9b). The bridging effect seems to be strengthened by COOH/OH pairs (Figure 9c) because of stronger adsorption. Therefore, the hydroxy-di(tri)carboxylic acids such as citric and tartaric acid are particularly strong inhibitors, whereas the dicarboxylic acids are only effective at higher concentration (e.g., malic acid is far more effective than succinic acid). Lactic acid, although having a COOH/OH pair, is a weak inhibitor because it lacks a second group for bridging.

If it is assumed that only 10% of the acid in solution adsorbs on the ferrihydrite (1 g present, density = 3.96 g/cm³), 6 ligands per 1 particle at 10^{-2} M and 6 per 1000 particles at 10^{-5} M concentration can be calculated. Although the amount of adsorption varies with solution concentrations, this example shows that even when adsorption is low, there are enough ligands adsorbing to stabilize the ferrihydrite through the network mechanism at concentrations $\geq 10^{-3}$ M and to stabilize it partially at 10^{-4} M concentration, thereby retarding hematite crystallization.

Association of organic ligands with Fe in solution (complexation) and/or at the surface of goethite nuclei and crystals

Lower levels of hydroxy-carboxylic acids can suppress goethite formation even when there is complete

crystallization to hematite. Because goethite forms via solution, it is possible that the organic ligands associate with the iron in solution (complexation) and/or at the surface of nuclei or crystals. This disturbs the octahedral shell of $Fe(OH)_4^-$ monomers or the surface Fe consisting of OH and OH_2 groups, thereby retarding or even inhibiting their condensation to form nuclei or to let the crystal grow. Long induction periods are the result.

This effect should depend on the extent to which the organic ligands complex with Fe in solution and/or the affinity of the anion or complex for the goethite surface. Both are reflected by the stability constant K; the stability constant for citric acid is higher (log K = 12.5) than that for lactic acid (log K = 6.4, Sillen and Martell, 1964), and consequently citric acid could form more Fe complexes and so interfere more strongly in nucleation and crystal growth. This difference is probably due to the fact that lactic acid only forms monodentate complexes, whereas with citric acid tridentate complexes are possible.

The low complexing ability of lactic acid compared to citric and tartaric acid has been noted in other studies; lactic acid does not complex strongly with Al^{3+}, and so unlike citric and tartaric acid, it cannot cause the breakdown of micas (Robert and Karimi, 1975). Also, it does not form a strong complex with Ca^{2+} and so does not slow down the rate of formation of calcium carbonate as strongly as the other hydroxy-carboxylic acids (Kitano and Hood, 1965).

The concept described is supported by the observation that the interference with crystallization can be overcome by seeding the system with goethite as long as the affinity of the ligand for Fe is not too strong. Therefore, 6% seeds added to a system with lactic acid (2×10^{-3} M) completely cancelled the interference whereas with meso tartaric acid (10^{-3} M), even 80% seeds had no effect.

Induction of hematite formation

Besides favoring formation indirectly by suppressing goethite, organic acids can also encourage hematite by inducing its nucleation. This was demonstrated for oxalate by Fischer and Schwertmann (1975). In iron oxalate the spacing of 5.58 Å between the iron atoms to which the carboxyl groups are bonded is similar to the lattice parameter $a_0 = 5.041$ Å in hematite and to the distance between iron atoms in the partly ordered ferrihydrite. Fischer and Schwertmann (1975), therefore, suggested that a pair of carboxyl groups separated by one carbon–carbon bond could act as a template for the nucleation of hematite within the ferrihydrite aggregate and thus, encourage its formation.

This concept can be extended to the acids studied in the present work. The hydroxy-(di)-carboxylic acids all contain a template group (i.e., a pair of bonding groups

consisting of two carboxyls or a carboxyl/OH pair separated by one carbon–carbon bond), but hematite induction varies. With 10^{-5} M acid at pH 9.6 it ranges from 10% with lactic acid to 100% with L-tartaric and citric acid (without acid: 5%). These variations can be explained if not only the presence of a template group, but also adsorption onto ferrihydrite *through this group* is assumed to be necessary.

Adsorption of *lactic* acid onto ferrihydrite is extremely low in the pH range studied, and consequently it is unable to induce hematite nucleation. At a lower pH the acid may adsorb more strongly, and so hematite nucleation could be encouraged. Although *oxalic* acid leads to 100% hematite formation at pH 6 and concentrations $>5 \times 10^{-3}$ M (Fischer and Schwertmann, 1975), it does so much less strongly above pH 9 and at lower concentrations most probably because there is hardly any adsorption. Parfitt *et al.* (1977) found that adsorption of oxalic acid on goethite is negligible above pH 8; this is probably the case for ferrihydrite as well.

Meso tartaric acid has two OH/COOH pairs available for bonding to ferrihydrite:

meso tartaric acid   L–tartaric acid
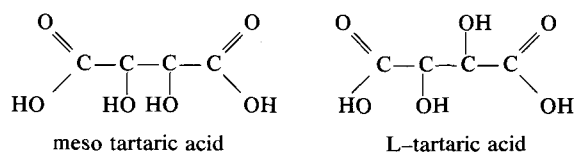
Theoretically it could have a double template effect, but it does not favor hematite as strongly as its isomer *L–tartaric* acid which adsorbs to a similar extent (Table 2). One explanation could be that the meso form does not preferentially adsorb through the template group, because the OH groups are adjacent, but through the COOH groups.

Although at 10^{-5} M acid and pH 9.6 both *citric* and L–tartaric acid gave 100% hematite; L–tartaric generally favors hematite more than citric acid. At pH 10.5 ~20% more hematite formed in the presence of L–tartaric than with citric acid (10^{-5} M) (Figure 3). Furthermore, at 10^{-4} M 100% hematite was formed with L–tartaric acid between pH 9 and 10, but no crystallization took place with citric acid, and at pH 10.5, 55% hematite was formed with L–tartaric and only 10% with citric acid. This stronger effect of L–tartaric acid could be due to the fact that this acid is the only one studied having two template groups arranged symmetrically in the molecule. This property of the molecule could mean that a double template effect can operate with every molecule that adsorbs, and hematite is more strongly favored than with, for example, citric acid, which has one template group at right angles to a COOH pair and for which a proportion of the molecules probably adsorbs through the carboxyl groups.

The above concept seems to contradict the earlier suggestion that organic acids inhibit the crystallization

of hematite by using the COOH groups (or COOH/OH pairs) to link particles of ferrihydrite together and so prevent or retard the aggregation which precedes hematite formation. However, whether the organic acid favors or inhibits hematite must depend strongly on the concentration of acid in this system. With L–tartaric at high concentrations ($>10^{-3}$ M) enough ligands are present (6 ligands/10 particles) to hold the ferrihydrite in a comparatively immobile network, while with 10^{-4} M acid (6 ligands/100 particles) nucleation could be induced in regions in which adsorption has occurred followed by crystal growth at these sites from particles on which the acid had not adsorbed. The area of ferrihydrite (total surface 200 m²/g) covered by the adsorbed template groups at 10^{-4} M acid is very low ($<0.018\%$), but when it is considered that only a minute proportion of nuclei is necessary to form crystals, it is possible to visualize how a small number of templates can induce crystallization in the whole system.

CONCLUSIONS

It has been shown that organic acids, in particular the hydroxy-carboxylic acids, can (1) retard crystallization of ferrihydrite to hematite, (2) suppress goethite formation, and (3) in some cases, encourage hematite formation. A mechanism for each effect has been proposed that considers adsorption on ferrihydrite, complexation of Fe in solution, adsorption on goethite crystals, and nucleation of hematite through a template group. The effect of the various organic acids depends on their nature and concentration as well as on the pH of the system. At present an infrared investigation is underway to test the proposed mechanisms.

ACKNOWLEDGMENTS

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Резюме—Гидрокси-карбоксильные кислоты препятствуют кристаллизации ферригидрита в диапазоне pH 9–11 в порядке

лимонная > мезо винная > L–винная ≫ молочная

и способствуют образованию гематита относительно гетита в порядке

L–винная > лимонная > мезо винная > молочная.

Кристаллическая форма гематита может быть изменена вследствие присутствия этих кислот. Влияние этих кислот на кристаллизацию увеличивается с увеличением концентрации кислоты и с уменьшающейся pH.

Эффективность в подавлении кристаллизации зависит от того, в какой степени кислота адсорбируется ферригидритом и насколько прочные комплексы с Fe^{3+} она образует в растворе. Предполагается, что кристаллизация гематита затрудняется благодаря связыванию двух- и трех-карбоксильной кислотой ферригидритных частиц в неподвижное соединение. Образование гетита подавляется кислотой, соединяющейся с Fe в растворе и препятствующей образованию ядер кристаллизации; сильно адсорбирующие кислоты также адсорбируются ядрами и препятствуют их дальнейшему росту. Некоторые кислоты могут вызвать образование гематитов потому что они содержат группу, которая способствует образованию центров кристаллизации гематита.

Resümee—Verschiedene Hydroxycarbonsäuren verhindern die Kristallisation des Ferrihydrits zu Goethit und Hämatit im pH-Bereich 9–11 in der Reihenfolge

Citronensäure > Meso-Weinsäure > L–Weinsäure ≫ Milchsäure

und begünstigen Hämatit auf Kosten von Goethit in der Reihenfolge

L–Weinsäure > Citronensäure > Meso-Weinsäure > Milchsäure.

Der Säureeinfluß steigt mit steigender Konzentration und fallendem pH. In Gegenwart der Säuren sind die Hämatitkristalle nicht sechseckig sondern leistenförmig.

Die Unterdrückung der Kristallisation hängt davon ab, wie stark die Säure vom Ferrihydrit adsorbiert wird und wie stark sie das Fe^{3+} in der Lösung komplexiert. Es wird angenommen, daß die Kristallisation des Hämatits dadurch verhindert wird, daß die organischen Anionen die Ferrihydritteilchen zu einem starren Netzwerk verknüpfen. Die Goethitbildung wird dagegen durch Komplexierung des Fe und Verhinderung der Keimung bzw. des Kristallwachstums gestört. Einige Säuren wirken als ''Schablone'' fördernd auf die Kristallisation des Hämatits.

Résumé—Les acides hydroxy-carboxyliques inhibent la cristallisation de ferrihydrite sur une étendue de pH de 9 à 11 dans l'ordre

citrique > meso-tartarique > L–tartarique ≫ lactique

et favorisent la formation d'hématite pas rapport à la goethite dans l'ordre

L–tartarique > citrique > meso-tartarique > lactique.

La forme en crystal de l'hématite peut être modifiée par la présence de ces acides. L'influence de ces acides sur la cristallisation croît proportionnellement à l'accroissement de la concentration d'acide et au décroissement du pH.

L'efficacité de suppression de la cristallisation dépend de ce que, et comment l'acide adsorbe sur la ferrihydrite et de quel degré il se complexe avec Fe^{3+} en solution. On croit que l'inhibition de la cristallisation de l'hematite est due à l'acide di- et tricarboxylique liant des particules de ferrihydrite dans un entremeshement immobile. La formation de goethite est réprimée par l'acide se complexant avec Fe en solution et empêchant la nucléation; ces acides fortement adsorbants adsorbent aussi sur les noyaux et empêchent tout accroissement ultérieur. Certains acides peuvent induire la formation d'hématite parce-qu'ils contiennent un groupe qui agit comme moule pour la nucléation de l'hématite.