

EFFECT OF SIMPLE SUGARS ON THE ALKALINE TRANSFORMATION OF FERRIHYDRITE INTO GOETHITE AND HEMATITE

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Abstract—The transformation of ferrihydrite to goethite and hematite in the pH range 9–13 is retarded by the presence of simple sugars ($\geq 10^{-4}$ M concentration). The retarding effect is related to the extent of adsorption of the sugar on ferrihydrite. Maltose and glucose adsorb strongly and inhibit the transformation by preventing both aggregation and dissolution of the ferrihydrite. Sucrose adsorbs to a much lesser extent than the other sugars and appears to hinder the nucleation and growth of goethite in solution.

Hematite formation relative to that of goethite is favored by the sugars in the order: maltose > glucose > sucrose. Maltose and glucose cause hematite to grow as prismatic crystals rather than as hexagonal plates and also lead to a new type of twinned goethite; one with epitaxial outgrowths of goethite on a prismatic crystal of hematite. In alkaline media glucose and maltose are partly transformed into a mixture of different sugars and hydroxycarboxylic acids, and it is probable that modification of the hematite crystal shape is due to the presence of the degradation products rather than to the nature of the original sugar.

The results of this work suggest that cyclic molecules influence the transformation of ferrihydrite to a lesser extent than do acyclic molecules.

Key Words—Ferrihydrite, Goethite, Hematite, Morphology, Sugar, Synthesis.

INTRODUCTION

The main outlines and many of the details of the mechanisms by which goethite and hematite form from ferrihydrite have been well established (Fischer and Schwertmann, 1975; Schwertmann and Murad, 1983). Less is known, however, about the effect of foreign anions, both organic and inorganic, on the pathways of crystallization. As such species are commonly associated with ferrihydrite in soil and in living organisms, their influence on the transformation process should be taken into account.

In an earlier investigation, the effect of hydroxycarboxylic acids was considered (Cornell and Schwertmann, 1979). This work has now been extended to another class of organic molecules, that of the simple sugars: glucose, sucrose, and maltose. The α -D forms of such sugars occur in nature.

These compounds were chosen to test the effect of single and double ring systems where steric effects might be expected to be important. Furthermore, these sugars represent elementary units in the amino-polysaccharide chitin. This material forms the organic matrix in the teeth of limpets—*Patella vulgata*. Lowenstamm (1962) found crystals of goethite in these teeth, but how these crystals formed is not clear. Growth may be affected by the presence of the chitin. Studies with simple sugars might indicate how more complicated molecules influence the growth of bio-inorganic minerals.

Other investigators have been concerned with the

conditions for production of soluble iron-sugar complexes in alkaline media and in avoiding precipitation of iron hydroxide (Charley *et al.*, 1963; Müller, 1967; Barker *et al.*, 1974). As stable iron-sugar complexes result only when the ligand is in considerable excess, these authors used ligand:iron ratios $\geq 5:1$ which are sufficient to prevent precipitation. In the present study the aim was to determine the influence of the sugars on the transformation of ferrihydrite. Consequently, the concentration of the sugar in the system was low enough (ligand:Fe ≤ 0.1) to permit partial or complete transformation.

MATERIALS AND METHODS

Transformation studies were carried out using suspensions of ferrihydrite (0.1 g/ml) which had been precipitated from ferric nitrate solution (0.1 M) at pH 7 with 1.0 M KOH. After precipitation, the pH was raised to between 9 and 13 and a solution of sugar added to give a final sugar concentration of 10^{-3} – 10^{-5} M. The sugars (α -D-glucose, α -D-sucrose, α -D-maltose monohydrate) were AR quality and supplied by Fluka AG. The suspensions were held at 70°C, usually for a standard time of 24 hr. Other studies over a range of temperatures (25°–70°C) suggest that although the *rate* of transformation depends on the temperature, the *mechanisms* of the conversion of ferrihydrite to goethite and hematite do not (Fischer and Schwertmann, 1975; Cornell and Schwertmann, 1979; Schwertmann and Murad, 1983). Hence, results obtained here at 70°C might

be expected to apply at the lower temperatures of natural systems.

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., ferrihydrite) remaining and Fe_T is the total Fe content (Schwertmann, 1964). Fe was determined by atomic absorption spectroscopy.

The crystalline fraction 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 found with the aid of calibration patterns. Transmission electron micrographs were obtained using standard techniques with a Hitachi HU-12 electron microscope.

The extent of adsorption of the sugars on goethite, hematite, and ferrihydrite was found by equilibrating 0.5–1 g of oxide with 100 ml of sugar solution (pH 11) for 90 min at 25°C, centrifuging, and measuring the optical activity of the supernatant with a Perkin Elmer 241 polarimeter. The amount of sugar adsorbed was found by difference.

In alkaline media sugars are gradually transformed into other products. Preliminary experiments showed, however, that the sugars studied here could be held in aqueous solution (pH 11) at room temperature for 2 hr without any change in the optical rotation of the solution: this finding suggests that the sugars were still unchanged. It was also found that adsorption was complete within 60 min. All adsorption measurements were made, therefore, after a 90-min equilibration period.

RESULTS

The extent and rate of conversion and the ratio of hematite to goethite in the product depended on the pH of the system, the type of sugar present, and the sugar concentration. The effectiveness of a sugar in retarding conversion increased with rising sugar concentration and fell as the pH rose. For maltose and glucose, a ligand:iron ratio of 0.1 was sufficient to cause partial inhibition of the transformation of ferrihydrite up to pH 13; sucrose required a ligand:iron ratio of 0.5 to achieve the same effect. The inhibiting ability of these sugars was inferior to that of a hydroxy-carboxylic acid, such as citric acid (Table 1). At ligand:iron ratios ≤ 0.001 (10^{-5} M), the rate and products of the transformation appeared to be independent of the presence of sugar.

Extent of conversion

Figure 1 compares the effectiveness of sugars (10^{-4} M) in inhibiting conversion up to pH 12 over a 24-hr period. Complete conversion occurred for all suspensions, except that containing citrate, within a few days. Sucrose inhibited conversion to a far lesser extent than

Table 1. Effect of simple sugars and citric acid (10^{-4} M) on the transformation of ferrihydrite.

Organic species	Ferrihydrite (%)	Goethite (%)	Hematite (%)
Control	0	97	3
Sucrose	0	85	15
Glucose	20	60	20
Maltose	25	0	75
Citric acid	100	0	0

pH = 11, 70°C, 24 hr.

maltose or glucose and also required a higher threshold (5×10^{-3} M) for complete inhibition.

Kinetics

At ligand:iron ratios ≥ 0.01 all three sugars reduced the rate of transformation. The sigmoid kinetic curves shown in Figure 2 (10^{-3} M) are typical of the conversion of ferrihydrite into goethite and/or hematite (Fischer and Schwertmann, 1975). The initial induction period corresponded to the formation of nuclei: once this stage was passed, the reaction became first order with respect to the amount of ferrihydrite remaining. The presence of sugar in the system increased the induction period and also the time for conversion of half the ferrihydrite ($t_{1/2}$). For 10^{-3} M sucrose, the induction time increased from 3.5 hr (control) to 7 hr and $t_{1/2}$ from 7 hr to 27 hr. Maltose and glucose extended the induction period much further—possibly indefinitely.

In a series of experiments over the pH range 10 to 11.6, the addition of 6% seed crystals of goethite to a suspension containing sucrose (either 10^{-3} or 10^{-4} M) reduced the induction time to the same value as for the control but did not influence $t_{1/2}$. In the pH range over which hematite usually predominated, seeding with goethite caused an increase in the amount of goe-

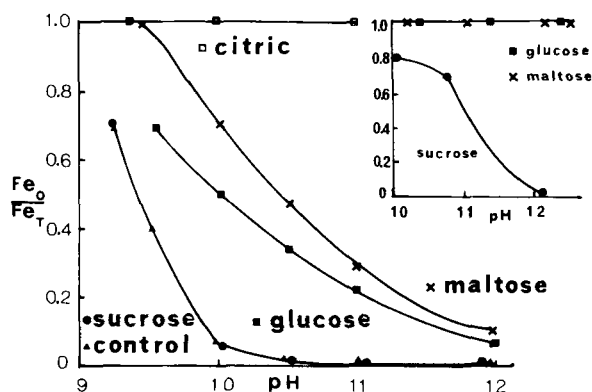


Figure 1. Fe_o/Fe_T as a measure of the degree of transformation of ferrihydrite to goethite and/or hematite vs. pH in the presence of various sugars at 10^{-4} M concentration (24 hr, 70°C). Inset: for sugars at 10^{-3} M concentration. (Fe_o = oxalate-soluble Fe; Fe_T = total Fe).

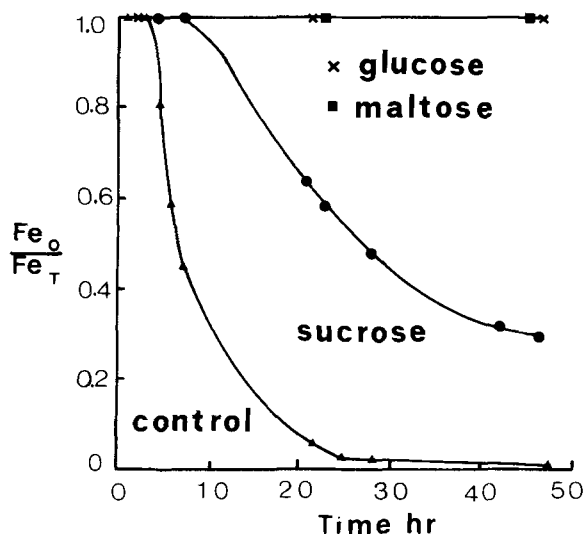


Figure 2. Fe_o/Fe_T as a measure of the degree of transformation of ferrihydrite into goethite vs. time in the presence of various sugars at 10^{-3} M concentration (pH 11.6, 70°C) (Fe_o = oxalate soluble Fe; Fe_T = total Fe).

thite in the final product (over and above the contribution from the seeds). Seeding of suspensions containing maltose or glucose had no effect on either the products or the kinetics of the reaction.

Further experiments showed that the addition of maltose or glucose to a suspension of ferrihydrite (pH 11.6, 10^{-3} M sugar) 4 hr after the start of the reaction (i.e., after the induction period had been passed) halted further transformation; 3–5% goethite had already formed, but this amount of goethite did not have a seeding effect. In a similar experiment with sucrose, the transformation of ferrihydrite was retarded, but did go to completion.

These observations suggest that maltose and glucose ($\geq 10^{-3}$ M) immobilized ferrihydrite and prevented both dissolution (which leads to goethite) and aggregation (which leads to hematite). Sucrose on the other hand, appeared to interfere with the nucleation and growth of goethite in solution.

Adsorption of sugars on iron oxides

It is reasonable to assume that inhibition of the transformation was the result of the adsorption of sugar on

Table 2. Adsorption of sugars (10^{-3} M) on iron oxides.

Oxide	Maltose (%)	Sucrose (%)	Glucose (%)
Ferrihydrite	25	3	22
Hematite	30	8	34
Goethite	60	17	42

pH = 11, 20°C .

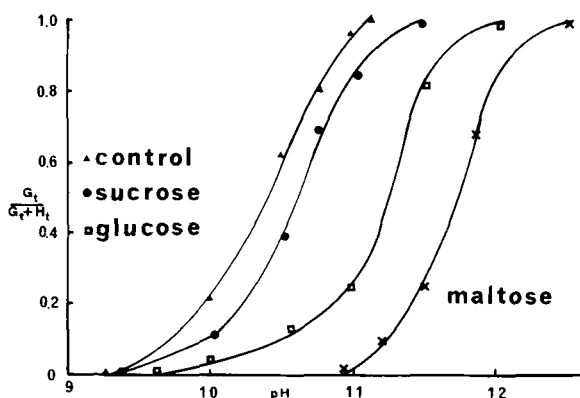


Figure 3. Proportions of goethite and hematite formed between pH 9.5 and 12.5 in the presence of various sugars at 10^{-4} M concentration (24 hr, 70°C).

the ferrihydrite. Variations in the degree of adsorption were probably responsible for differences between the sugars in their effect on the transformation. Table 2 shows that sucrose adsorbed on all iron oxides to a much lesser extent than maltose or glucose.

Stability constants for ferric complexes of the sugars studied here do not seem to have been determined; however, Charley *et al.* (1963) and Müller (1967) estimated the binding abilities of various sugars with iron in solution using potentiometric titrimetry and polarography, respectively, and found that the binding ability decreased in the order glucose = maltose \gg sucrose. This sequence is in line with the inhibition of transformation found in the present work.

Products of transformation

If the level of sugar in the system was not high enough to inhibit the transformation altogether, the presence of sugar encouraged the formation of hematite relative to goethite (Figure 3). Maltose and glucose (10^{-4} M) favored hematite up to pH 12.5 and pH 12, respectively (control to pH 11). Although sucrose also enhanced the formation of hematite, its effect was far less pronounced.

With 10^{-4} M sugar, hematite was favored over goethite in the order: maltose > glucose \gg sucrose. This order changes at pH 13; with glucose (10^{-3} M) the crystalline portion (66%) consisted entirely of hematite, and for maltose, the crystalline fraction (22%) was about 50% goethite (reaction time of six weeks).

Order of addition of sugar to the system

The sugar was normally added after precipitation of the ferrihydrite, but in one series of experiments the sugar was present before precipitation (10^{-4} M sugar, pH 11) (Table 3). The degree of transformation was reduced for all sugars by about 10% suggesting that coprecipitation increased adsorption. Presumably the

Table 3. Transformation products when sugar is added before precipitation of ferrihydrite.

Sugar	Ferrihydrite (%)	Goethite (%)	Hematite (%)
Sucrose	8	17	75
Glucose	40	25	35
Maltose	50	0	50

pH = 11, 70°C, 24 hr, 10⁻⁴ M sugar.

original solutions contained iron-sugar complexes which precipitated as iron-sugar-hydroxides. Except for maltose, which always induced the formation of 100% hematite at pH 11, the addition of sugar before precipitation favored the formation of hematite.

Electron microscope observations

Transmission electron microscopy showed that maltose and glucose (10⁻⁴ M) modified the shape of the hematite crystals, whereas sucrose, even at a concentration of 10⁻³ M, did not.

Maltose. At pH 10 and with a sugar level of 10⁻⁵ M, regular platelets of hematite with an average diameter of 0.016 μm formed. At the same pH, but with 10⁻⁴ M sugar, the hematite formed entirely as prismatic crystals similar to those reported for citric acid (Schwertmann *et al.*, 1968; Cornell and Schwertmann, 1979). These prismatic crystals are probably due to preferential growth of the basal faces, probably as the result of adsorption of some species from solution on the prismatic faces (Schwertmann *et al.*, 1968).

The surfaces and ends of the prismatic crystals were commonly irregular or fibrous (Figure 4a); such distortions may be a further indication of the adsorption of some organic species during growth. Usually two or three thin outgrowths projected from the parent crystal more or less perpendicular to the (110) faces. No goethite was detectable by XRD and these dendrites seemed, in any case, distinct from the usual goethite outgrowths. They were probably outgrowths of hematite.

At higher pH (>11) the hematite formed as plates (usually with outgrowths of goethite) as well as prismatic crystals. The proportion of prismatic hematite relative to platy hematite fell with increasing pH. Above pH 11 goethite and hematite formed in the presence of 10⁻⁴ M maltose. The goethite was present as acicular crystals and as epitaxial twins with centers of hematite; i.e., it was similar to that formed at pH 11-12 in the absence of sugar. Some very pointed acicular particles were noted, but, in general, shape modification was rare.

Two kinds of epitaxial twins of goethite were noted: (1) those with a center of plate-like hematite; and (2) those with outgrowths of goethite around a center of prismatic hematite (Figure 4b, 4c, arrowed). The sec-

ond kind of epitaxial twin does not seem to have been reported before. It differed from the first type in that only two or three outgrowths of goethite were present (in contrast to possibly six around platy hematite) and that these outgrowths appear to have nucleated on opposite faces of the hematite. In some crystals, the goethite outgrowths were joined across the hematite. In general, the goethite was thicker and narrower than the acicular crystals, possibly because the twinned crystal fell on the grid with the (010) face of the goethite outgrowth perpendicular to the electron beam.

The first stage in the formation of these twins must have been the growth of a crystal of hematite upon which the goethite nucleated. Thereafter, both goethite and hematite probably grew simultaneously, each most rapidly along the c axis. The hematite centers showed a variety of shapes (from hourglass to prismatic). This variety, together with a proportion of platy hematites in the product, suggests that the degree of adsorption of maltose on the growing hematite varied from one crystal to another.

Further information was obtained from twinned crystals that had been partly dissolved in HCl (Figure 4d). Signs of preferential attack were detected locally near the junction of the goethite and the hematite indicating the existence of strains in this part of the crystal. The mismatch at the contact plane between the goethite and the hematite was 20%. The goethite crystals in these samples developed a frayed appearance which indicates the presence either of intergrowths or strains. Goethite grown at pH 11-12 in the absence of maltose showed more uniform dissolution behavior.

It is concluded, therefore, that although the presence of maltose had no obvious influence on the shapes of the goethite crystals, it led to some interference with crystal growth and hence to internal strains.

Glucose. Concentrations of 10⁻⁴ M glucose induced the formation of prismatic hematite but to a much lesser extent than did maltose (Figure 5).

Sucrose. Even 10⁻³ M sucrose did not modify the shape of the hematite crystals; however, at this concentration, sucrose influenced the shape of goethite to some extent leading to rather distorted acicular particles at pH 12 (Figure 6a) and to wedge-like outgrowths on hematite at lower pH (Figure 6b).

DISCUSSION

Cornell and Schwertmann (1979) suggested a model for the retardation of the transformation of ferrihydrite by hydroxy-carboxylic acids and proposed that even when much less than a monolayer of anion is adsorbed, it nevertheless stabilizes the ferrihydrite by linking two or more spheres of ferrihydrite per molecule through the COOH and/or OH groups. A network of particles is so formed that is resistant to both aggregation and

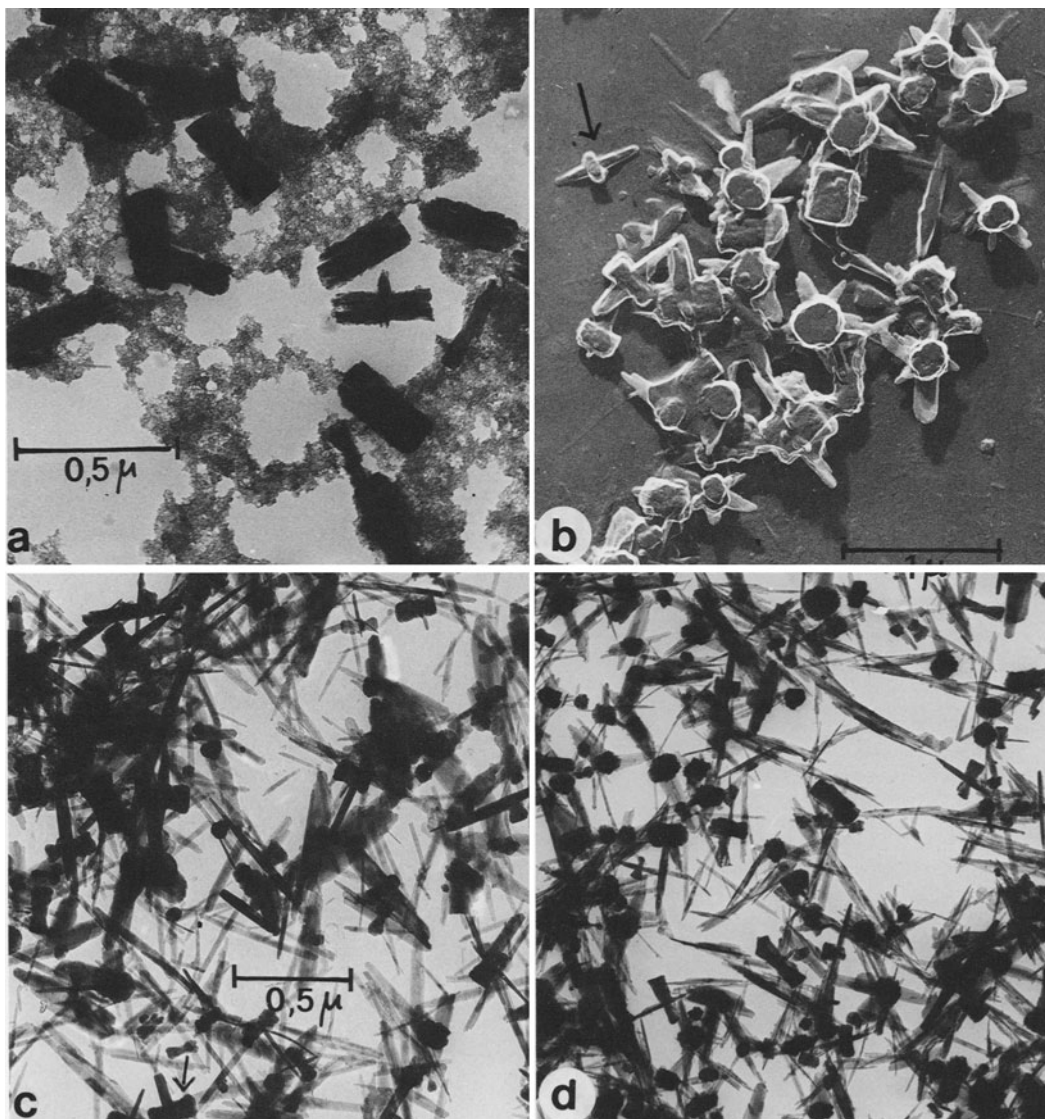


Figure 4. Transmission electron micrographs of iron oxides formed in the presence of maltose (10^{-4} M). (a) Prismatic crystals of hematite together with ferrihydrite (70%), pH 10.1; (b) replica of the two types of epitaxially twinned crystals of goethite (pH 11.7); (c) mixture of hematite (50%) and twinned and acicular goethites (pH 11.7); (d) as in (c) after 50% dissolution.

dissolution. A similar model can account for the ability of sugars to retard the transformation. At a concentration of 10^{-3} M sugar, adsorption of $\sim 5\%$ of the sugar would be sufficient to inhibit conversion through the particle linking mechanism, whereas monolayer coverage would require 33% adsorption (surface area of ferrihydrite ~ 200 m²/g). At high levels of adsorption both mechanisms may operate. The dramatic change from no inhibition to total inhibition when the concentration of sucrose in the system was raised from 2×10^{-3} to 5×10^{-3} M (total adsorption is only $\sim 3\%$),

however, suggests that here inhibition involved the particle-linking mechanism.

Adsorption is expected to involve the OH groups of the sugars. Kröplein (1974) found that the strong interactions of monosaccharides with aluminum oxide depended upon the sugars possessing three adjacent OH groups with an axial, equatorial, axial orientation. α -D-glucose lacks this arrangement and did not interact with aluminum oxide at any pH, but adsorbed on ferrihydrite. This performance suggests that for the latter material, a less specific arrangement of adsorbing



Figure 5. Transmission electron micrograph of hematite (70%) and goethite (30%) formed in the presence of 10^{-4} M glucose (pH 11.1, 70°C).

groups was required and further suggests that particle linking, rather than surface adsorption was involved.

Influence of cyclic and acyclic molecules on conversion

Under alkaline conditions sugars are degraded to a greater or lesser degree. The extent of this degradation appears to be time dependent. Alkali destroys the fructose portion of sucrose, for example, but in the present

work, sucrose remained intact over the 24 hr needed for a standard experiment. In glucose solutions at any pH, an equilibrium situation exists between the α and β forms (Rees, 1977). In addition, in the presence of alkali, glucose transforms into a mixture of fructose, mannose, glucose, and, possibly, a small percentage of acyclic glucose (Hough and Richardson, 1979). Polarimetry measurements on solutions of glucose indicate that at 70°C and pH 11, some transformation takes

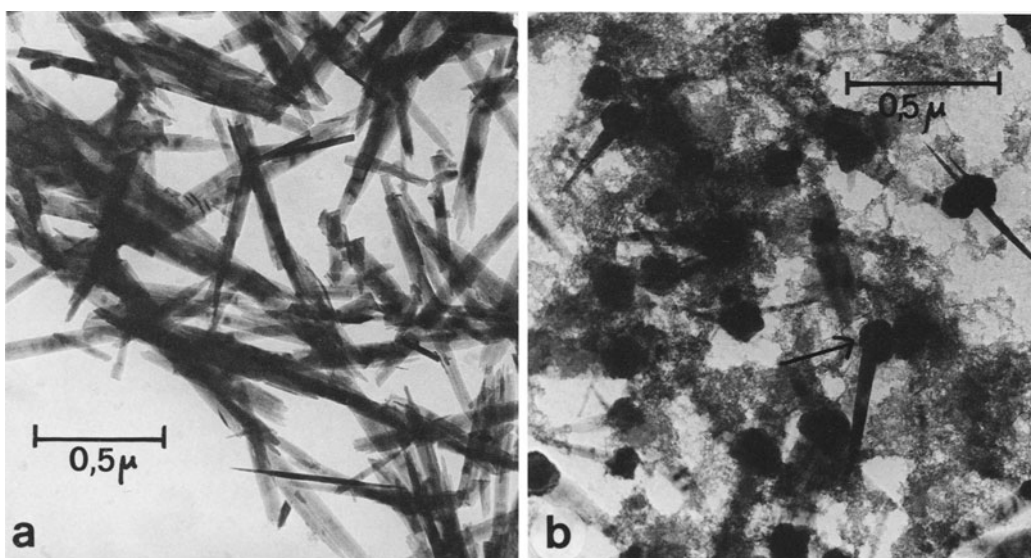


Figure 6. Transmission electron micrographs of iron oxides formed in the presence of 10^{-3} M sucrose (70°C). (a) Goethite (pH 12); (b) ferrihydrite (80%) and platy hematite (15%) with epitaxial wedge shaped outgrowths of goethite (arrowed) (pH 9.6).

place after 24 hr. Under these conditions, maltose also appears to degrade to some extent; Machell and Richards (1960) showed the reaction products to be a complex mixture of hydroxy-carboxylic acids, such as glycolic acid and saccharinic acid.

One of the questions considered in the present study was the effectiveness of cyclic molecules in influencing the transformation of ferrihydrite. The glucose solutions consisted predominantly of cyclic molecules, but the possibility of an acyclic fraction cannot be discounted. As only low levels of adsorption were needed to inhibit the transformation, the effect of glucose could have been due to the acyclic rather than the cyclic molecules. This hypothesis is reinforced by experiments involving α -D-sorbitol and methyl glucose. Sorbitol is a linear molecule and is formed from glucose by conversion of the aldehyde group of the latter into an alcohol group. Sorbitol (10^{-3} M) strongly inhibited the transformation of ferrihydrite and at lower concentrations (10^{-4} M) favored hematite. Methyl glucose has a methyl group at the C1 position which stabilizes the molecule against transformation: in the present experiments it was, therefore, present as a cyclic molecule. Neither methyl glucose (a single-ring system) nor sucrose (a double-ring system) strongly inhibited the transformation of ferrihydrite, enhanced the formation of hematite, or influenced the morphology of hematite. Thus, small cyclic molecules appear to have far less influence on the transformation of ferrihydrite in alkaline media than do linear molecules of similar size and composition. The reason for this difference could involve both steric factors and charge considerations.

Cornell and Schwertmann (1979) showed that hydroxy-carboxylic acids have a marked influence on the conversion of ferrihydrite; thus, it seems probable that at least part of the effect of maltose must have been due to partial degradation of the sugar to these acids.

Preferential formation of hematite

All three sugars favored hematite relative to goethite, although the influence of the sucrose was not very marked. The effect of the sugars was probably due to their adsorption on ferrihydrite which (when adsorption was not great enough to inhibit transformation altogether) created conditions favorable for the nucleation of hematite; i.e., aggregation of ferrihydrite was encouraged at pHs where, in the absence of sugar, dissolution started to predominate. At pH 10 to 12 the presence of sugar did not encourage the dissolution of ferrihydrite. The fact that sucrose favored ferrihydrite to only a limited extent can be accounted for by its low adsorption on ferrihydrite.

Enhancement of aggregation was probably the reason for the increased formation of hematite in the presence of glucose and maltose. For certain carboxylic and hydroxy-carboxylic acids, a template effect which further favors hematite probably operates (Fischer and

Schwertmann, 1975; Cornell and Schwertmann, 1979). The essential feature of this mechanism is that the molecule adsorbs through two groups separated by one carbon-carbon bond. All three sugars possess a hydroxyl pair at C3/C4; however, no evidence exists that adsorption actually involved this pair. Although maltose and glucose adsorbed on ferrihydrite to a similar extent, maltose favored hematite more strongly. The difference in behavior is probably related to the presence of hydroxy-carboxylic acids among the degradation products of maltose.

Modification of hematite crystal shape

Matijevic and Scheiner (1978) and Sapieszko and Matijevic (1980) produced hematites with a variety of crystal shapes, either by hydrothermal decomposition of ferric-organic chelates in alkaline media, or by forced hydrolysis of acidified ferric solutions in the presence of various inorganic anions. In the present work, a further modification was produced via conversion of ferrihydrite; here, adsorption of an organic species on the hematite during growth was probably responsible for the crystal shape.

It is noteworthy that the organic acids (oxalic and l-tartaric) that strongly enhance hematite formation by adsorption on ferrihydrite through a template group did not cause the formation of prismatic crystals; more or less distorted platelets resulted. Two different forms of adsorption were probably concerned: one required a preferred orientation on ferrihydrite, the other, a specific arrangement of adsorbing groups on the prismatic faces of hematite. Different adsorbing groups may have been involved, and for the adsorption on hematite, a wider separation between these groups may have been required. In solutions of maltose, one of the acidic degradation products was probably responsible for the shape modification. A linear molecule that covered a comparatively large area of hematite may have been an essential requirement. This condition could have been met by iso-saccharinic acid which has a structural resemblance to citric acid.

Morphology of goethite

Glucose and maltose also adsorbed on goethite but did not alter crystal shape. The acicular form predominated for goethite because the structure is dominated by a framework of double chains of iron-anion octahedra along the c direction. As additional molecules add most readily at the ends of these chains, growth in the c direction was favored and the acicular crystal resulted. Changes in crystal shape were difficult to effect. Partial blocking of adsorption sites on the (001) faces led to shorter, wider needles, and adsorption on other faces altered widths or thicknesses to some extent and also introduced local surface distortions. In fact, rather distorted acicular crystals formed in the presence of 10^{-3} M sucrose. A second modification of goethite

that also formed in the presence of sucrose was a wedge-like outgrowth of goethite on a center of hematite. The triangular shape was probably the result of adsorption of sugar at the ends of the chains of octahedra.

The organic molecules investigated to date (carboxylic and hydroxy-carboxylic acids and simple sugars) favored hematite over goethite when they did not inhibit crystallization altogether. At present, hematite has not been detected in living organisms, whereas goethite has. The reason for this may be that no ferrihydrite, the necessary precursor of hematite, is present and that goethite is formed in living organisms from Fe(II) rather than from Fe(III).

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Резюме—Преобразование ферригидрита в гетит и гематит в диапазоне pH 9–13 замедляется при присутствии простых сахаров ($\geq 10^{-4}$ м концентрации). Замедляющий эффект связан со степенью адсорбции сахара на ферригидрите. Мальтоза и глюкоза адсорбируются сильно и задерживают преобразование, препятствуя агрегации и растворению ферригидрита. Сахароза адсорбируется в значительно меньшей степени, чем другие сахара и, вероятно, препятствует образованию зародышей и росту гетита в растворе.

Сахара благоприятствуют формированию гематита по отношению к формированию гетита в следующем порядке: мальтоза > глюкоза >> сахароза. Мальтоза и глюкоза способствуют росту гематита скорее в форме призматических кристаллов, чем гексагональных пластинок, и приводят также к новому типу двойникового гетита, типа с эпитаксиальными отростками гетита на призматическом кристалле гематита. В щелочной среде глюкоза и мальтоза частично преобразуются в смесь различных сахаров и обискарбонновых кислот. Это возможно, что на модификацию вида кристалла гематита влияет скорее присутствие продуктов расщепления, чем природа первоначального сахара.

Результаты этой работы указывают на то, что циклические молекулы влияют на превращение ферригидрита в меньшей степени, чем ациклические молекулы. [E.G.]

Resümee—Die Umwandlung von Ferrihydrit in Goethit und Haematit im pH-Bereich von 9–13 wird durch die Anwesenheit von einfachen Zuckern ($\geq 10^{-4}$ m Konzentration) verzögert. Der Verzögerungseffekt hängt vom Ausmaß der Zuckeradsorption an Ferrihydrit ab. Maltose und Glucose werden gut adsorbiert und verhindern die Umwandlung, indem sie sowohl die Aggregatbildung als auch die Auflösung von Ferrihydrit verhindern. Sucrose wird zu einem viel geringeren Ausmaß als die anderen Zucker adsorbiert und scheint die Keimbildung und das Wachstum von Goethit in der Lösung zu beeinträchtigen.

Die Bildung von Haematit im Vergleich zu der von Goethit wird von den Zuckern in folgender Reihenfolge begünstigt: Maltose > Glucose \gg Sucrose. Maltose und Glucose bewirken, daß Haematit eher in Form von prismatischen Kristallen als in Form von hexagonalen Plättchen wächst und führen darüberhinaus zu einer neuen Art von verzwilligtem Goethit; eine mit einem epitaktischen Wachstum von Goethit auf einem prismatischen Haematitkristall. In alkalischen Medien werden Glucose und Maltose zum Teil in eine Mischung aus verschiedenen Zuckern und Hydroxycarboxyl-Säuren umgewandelt und es ist wahrscheinlich, daß verschiedene Ausbildungen der Haematitkristallform auf die Anwesenheit der Abbauprodukte zurückzuführen sind und weniger auf die Art des ursprünglichen Zuckers.

Die Ergebnisse dieser Arbeit deuten darauf hin, daß zyklische Moleküle die Umwandlung von Ferrihydrit in einem geringeren Ausmaß beeinflussen als azyklische. [U. W.]

Résumé—La transformation de ferrihydrite en goethite et en hématite sur l'étendue de pH 9–13 est retardée par la présence de sucres simples (concentration $\geq 10^{-4}$ M). L'effet de retardation est apparente à l'étendue de l'adsorption du sucre sur la ferrihydrite. La maltose et la glucose adsorbent fortement et inhibent la transformation en empêchant à la fois l'aggrégation et la dissolution de la ferrihydrite. La sucrose adsorbe beaucoup moins que les autres sucres et semble s'interposer à la nucléation et à la croissance de la goethite en solution.

La formation de l'hématite relative à celle de la goethite est favorisée par les sucres dans l'ordre: maltose > glucose \gg sucrose. A cause de la maltose et de la glucose l'hématite croit en cristaux prismatiques plutôt qu'en plaques hexagonales et un nouveau type de goethite jumellé est formé, avec des croissances epitaxiales de goethite sur un cristal prismatique d'hématite. Dans un milieu alcalin, la glucose et la maltose sont partiellement transformées en un mélange de sucres différents et d'acides hydroxycarboxyliques, et il est probable que la modification de la forme du cristal d'hématite est due à la présence des produits de dégradation plutôt qu'à la nature du sucre original.

Les résultats de ce travail suggèrent que les molécules cycliques influencent la transformation de la ferrihydrite moins que les molécules acycliques. [D. J.]