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# DISSOLUTION OF IRON OXIDES AND OXYHYDROXIDES IN HYDROCHLORIC AND PERCHLORIC ACIDS

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**Abstract**—The dissolution of synthetic magnetite, maghemite, hematite, goethite, lepidocrocite, and akaganeite was faster in HCl than in $HClO_4$. In the presence of $H^+$, the $Cl^-$ ion increased the dissolution rate, but the $ClO_4^-$ ion had no effect, suggesting that the formation of Fe-Cl surface complexes assists dissolution. The effect of temperature on the initial dissolution rate can be described by the Arrhenius equation, with dissolution rates in the order: lepidocrocite > magnetite > akaganeite > maghemite > hematite > goethite. Activation energies and frequency factors for these minerals are 20.0, 19.0, 16.0, 20.3, 20.9, 22.5 kcal/mole and $5.8 \times 10^{11}$, $1.8 \times 10^{10}$, $7.4 \times 10^{7}$, $5.1 \times 10^{10}$, $2.1 \times 10^{10}$, $3.0 \times 10^{11}$ g Fe dissolved/m²/hr, respectively. The complete dissolution of magnetite, maghemite, hematite, and goethite is well described by the cube-root law, whereas that of lepidocrocite is not.

**Key Words**—Acid, Akaganeite, Dissolution, Goethite, Hematite, Iron oxide, Lepidocrocite, Maghemite, Magnetite.

## INTRODUCTION

Iron oxides and oxyhydroxides are of widespread occurrence in soils and rocks. Their dissolution in soil solutions releases ions which may be essential for plant growth or which may interact with other nutrients modifying their availability to plants. The dissolution of such material is also of considerable relevance to trace element geochemistry, magnetic susceptibility of soils, and geochemical prospecting.

Most dissolution studies of iron oxides have been confined to their preferential dissolution from soils so that other minerals could be concentrated and studied (Mitchell *et al.*, 1964). In pedological studies soils or clays have been extracted with sodium pyrophosphate, acid ammonium oxalate, and sodium dithionite, and the extracted iron has been labelled as organically bound, amorphous, and crystalline iron oxides, respectively (McKeague *et al.*, 1971). Little is known, however, about the dissolution of iron oxides and oxyhydroxides in strong acids.

Earlier studies on the subject dealt with the mechanism of dissolution (Cornell *et al.*, 1976) and the effect of crystal morphology on dissolution of goethite (Cornell *et al.*, 1974). The present report is concerned with the acid dissolution of three iron oxides (magnetite, maghemite, and hematite) and three iron oxyhydroxides (goethite, lepidocrocite, and akaganeite), collectively referred to as oxides throughout this paper, and the relationship between the differences in dissolution rates of these minerals and their crystal structures.

## EXPERIMENTAL

### *Preparation and characterization of samples*

Magnetite samples consisting of ~0.1 μm equant crystals (Figure 1) were prepared by a precipitation technique (Sidhu *et al.*, 1978). Magnetite was heated at 220°C for 3 hr to obtain maghemite of identical morphology. Hematite was obtained by heating maghemite at 650°C for 3 hr to form sintered aggregates of ~0.1-μm size particles. Microcrystalline goethite, akaganeite, and lepidocrocite was prepared from ferric nitrate (Atkinson *et al.*, 1968), ferric chloride (Atkinson *et al.*, 1977), and ferric perchlorate (Murphy *et al.*, 1976) solutions, respectively. All three oxyhydroxides consisted of anhedral, 1-μm size, acicular crystals. The preparations were characterized by X-ray powder diffraction, electron microscopic, thermal, and chemical analyses to ensure that they were monomineralic. Surface areas were measured by the BET $N_2$-sorption technique so that dissolution rates for unit surface area of the oxide could be calculated.

### *Dissolution*

In the dissolution experiments either 50 mg of oxide was used per 40 ml of acid or 400 mg of oxide per 100 ml of acid. The dissolution rate had been found previously to be independent of solid:solution ratio within this range. Kinetic runs were carried out either in 50-ml polypropylene centrifuge tubes using a controlled-environment incubator shaker or polythene bottles in a water bath. Dissolution rates at various shaking speeds were found to be similar so that the results obtained by the two techniques may be compared.

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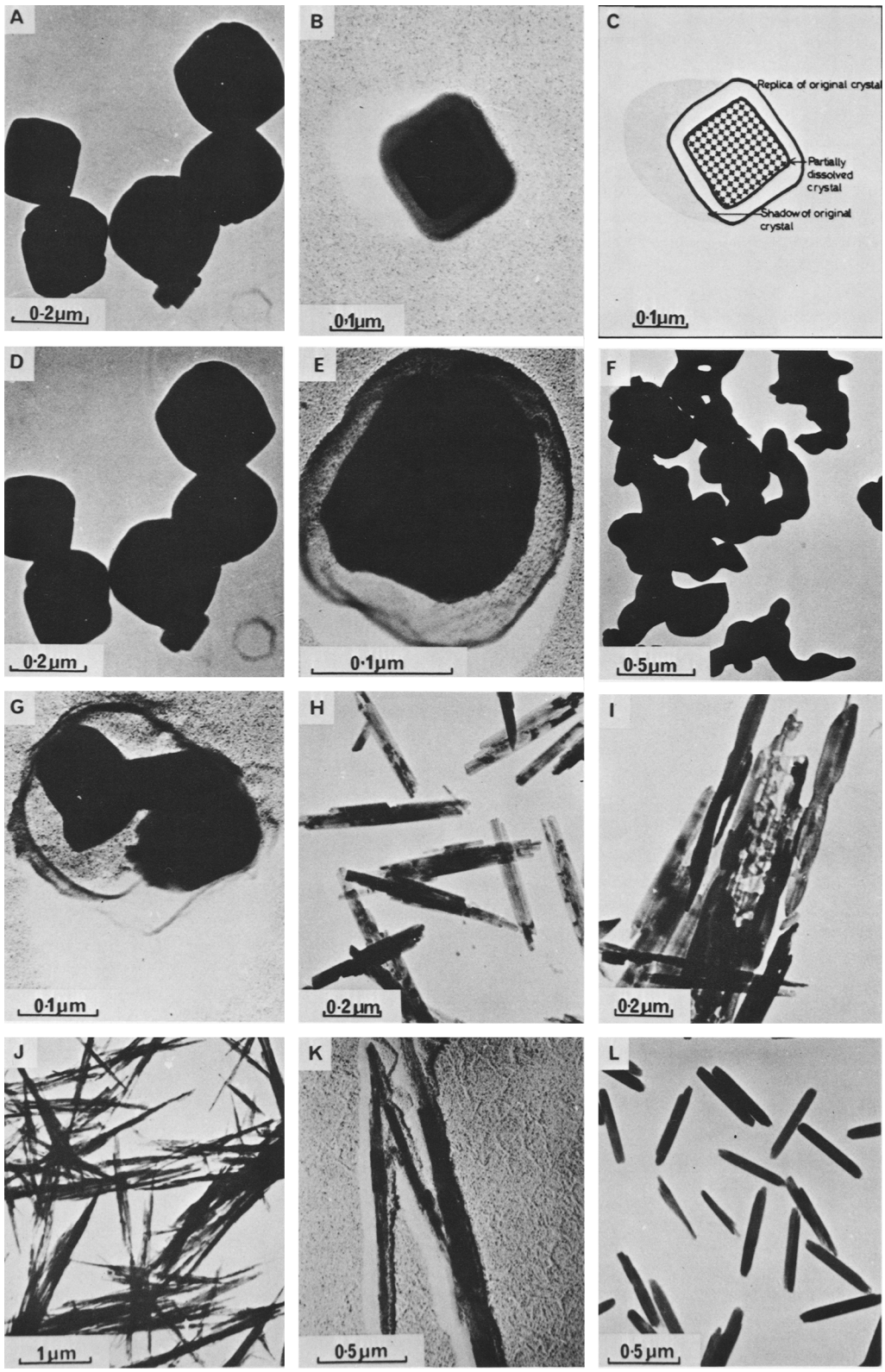
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The experiments were carried out with either HCl or $HClO_4$. In most experiments 0.5 M acid was used, but in some the acid concentration ranged from 0.1 to 2.0 M. The effect of ionic strength on dissolution rate was studied by varying the ionic strength by adding known amounts of NaCl or $NaClO_4$ to 0.5 M HCl. Dissolution was carried out at 10°, 20°, 25°, 35°, 45°, and 60°C.

The rate of reaction was determined by measuring the amount of Fe dissolved after various time intervals. Samples were withdrawn from the suspension with a plastic syringe and filtered through a 0.22-$\mu$m Millipore filter. Iron was analyzed by atomic absorption spectrometry. $Fe^{2+}$ was determined by dichromate titration (Vogel, 1961). Analyses of standard specimens and recovery of added $Fe^{2+}$ indicated that oxidation did not occur during analysis.

*Transmission electron microscopy (TEM)*

A TEM-replica technique was used to determine the effect of acid dissolution on the shape of oxide particles. Dilute suspensions of oxides were sprayed with an atomizer onto a freshly cleaved mica surface. This surface was next shadowed with Pt at an angle of 45° and then coated with carbon at 90°. The resultant carbon film containing the oxide particles was floated onto a water bath and transferred to an acid bath. After suitable intervals (i.e., dissolution times) the film was transferred through a series of three water baths and picked up on a microscope grid for TEM examination. At this stage the film contained the partly dissolved oxide particles surrounded by shadowed replicas showing their original shape (Figures 1b, 1c).

Normal TEM micrographs were also taken of oxide particles and of particles recovered from acid solutions after various periods of dissolution.

## RESULTS AND DISCUSSION

*Early stages of dissolution*

Plots of Fe released vs. time for the dissolution of all iron oxides were approximately linear during the early stages of dissolution (Figure 2). A very small amount of Fe dissolved rapidly from hematite, goethite, and akaganeite; this Fe may have been from an amorphous impurity. The $Fe^{2+}/Fe^{3+}$ ratio for magnetite dissolution remained constant indicating congruent dissolution. The dissolution rates which are referred to in the following section were obtained from the slope of the linear portion of these plots. The effects of different variables on the dissolution rate of the various iron oxides were similar and are described below using magnetite dissolved at 25°C as an example.

Increasing the ionic strength using $NaClO_4$ at a constant HCl concentration produced only a slight increase in the dissolution rate of all oxides. When NaCl was used to increase the ionic strength of an HCl solution, an almost exponential increase in rate was observed. Representative data for magnetite are shown in Figure 3. Dissolution rates of all iron oxides increased exponentially with increasing concentration of HCl and linearly with increasing concentration of $HClO_4$. Representative data for magnetite are shown in Figure 4. Krestov *et al.* (1973) observed a linear increase in dissolution rate of hematite in 0.5–9 M HCl and considered the dissolution to be a first order reaction.

Dissolution of all iron oxides in 0.5 M NaCl at pH 6 was very slow; no iron could be detected in solution after 24 hr. Increasing the chloride concentration at a constant proton concentration produced an approximately exponential increase in dissolution rate for all iron oxides. Representative data for magnetite dissolution at two proton concentrations are shown in Figure 5. These results show that protons are required for the dissolution of iron oxides and that the chloride ion is not essential, although this ion may greatly accelerate dissolution in the presence of protons. The perchlorate ion behaves as an indifferent ion in that it is not involved in iron oxide dissolution.

To explain the role of chloride in accelerating dissolution, a Fe-Cl complex has been suggested that forms on the oxide surface with a consequent reduction in the surface positive charge (Cornell *et al.*, 1976). Such a complex reduces the repulsion between the oxide surface and protons in solution and thereby increases the dissolution rate. Complex formation may also weaken the attractive force between the surface $Fe^{3+}$ or $Fe^{2+}$ and neighboring $O^{2-}$ ions and, hence, facilitate the breakdown of Fe–O bonds. Dissolution rates for hematite in $HNO_3$ and $H_2SO_4$ have been reported to decrease for acid strengths above 7 M, whereas a similar effect was not observed for HCl (Krestov *et al.*, 1973). This decrease may be due to the formation

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Figure 1. Transmission electron micrograph of iron oxides used in dissolution studies. (A) equant magnetite crystals; (B) shadowed replica of original magnetite crystal containing the partly dissolved crystal which demonstrates isotropic dissolution; (C) diagram in explanation of (B), (see also Sidhu *et al.*, 1977); (D) equant maghemite crystals formed by oxidation of the magnetite crystals shown in (A), note the unchanged morphology; (E) shadowed replica of maghemite crystals showing isotropic dissolution, explanation as for (C); (F) sintered aggregates of hematite crystals formed by oxdidation of magnetite; (G) shadowed replica of hematite aggregate showing embayment and anisotropic dissolution, explanation as for (C); (H) acicular goethite crystals with characteristic 'splintered' ends (Atkinson *et al.*, 1968); (I) partly dissolved goethite showing highly anisotropic dissolution (Cornell *et al.*, 1976); (J) aggregates of acicular lepidocrocite crystals; (K) shadowed replica of lepidocrocite crystals showing anisotropic dissolution, explanation as for (C); (L) acicular crystals of akaganeite.

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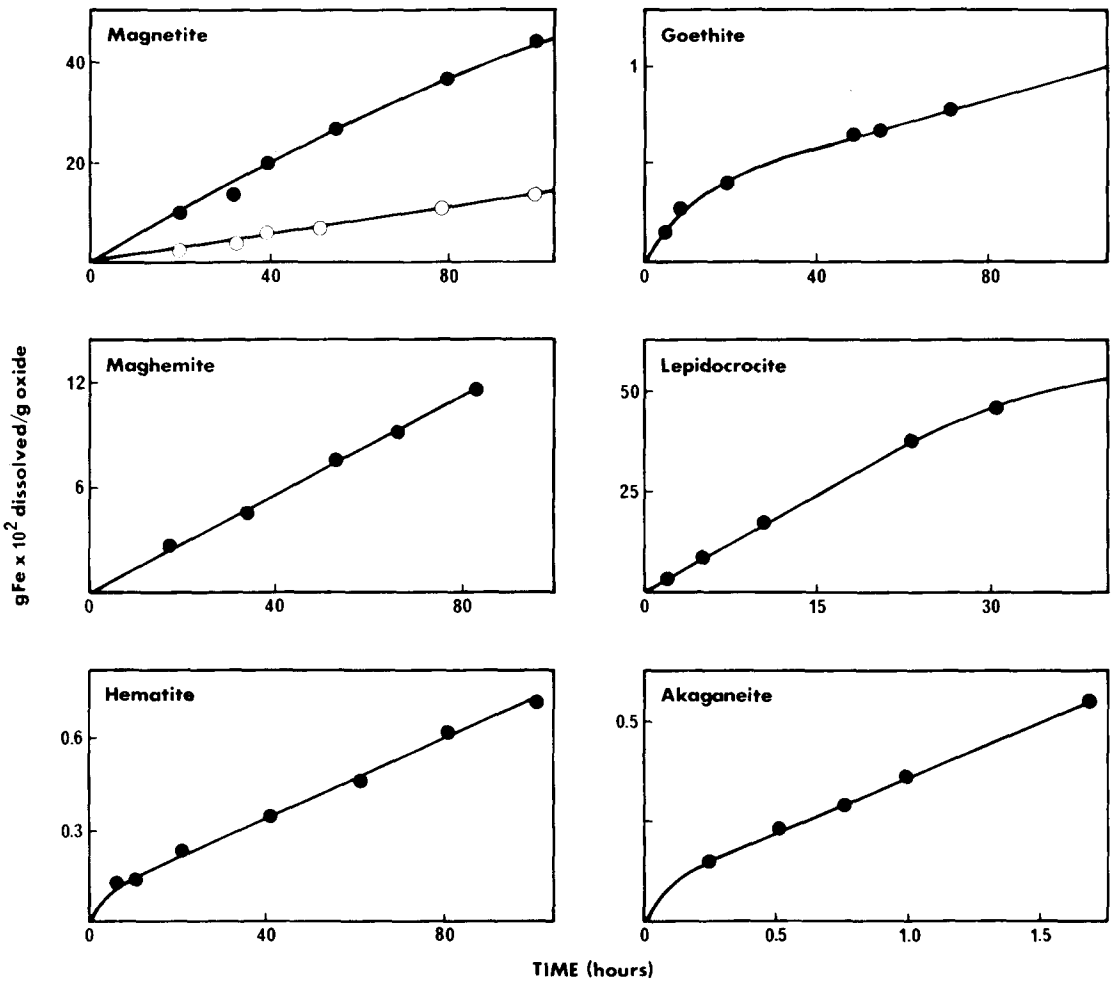



Figure 2. Dissolution of iron oxides in 0.5 M HCl. The upper and lower lines for magnetite represent total Fe and $Fe^{2+}$, respectively.

of passive oxide and salt films in strong O-containing acids.

*Comparison of dissolution rates*

The dissolution rates per unit surface area of various iron oxides in 0.5 M HCl at 25°C were estimated from the linear regions of the dissolution curves and are given in Table 1. The dissolution rates are in the order: lepidocrocite > magnetite > akaganeite > maghemite > hematite > goethite, a sequence that must be the result of differences in the chemical composition and crystal structure of these minerals. In the crystal structure of magnetite and maghemite, oxygen ions are cubic close packed with iron occupying both octahedral and tetrahedral sites, whereas in hematite oxygen ions are hexagonally close packed, and iron is present only in octahedral sites. The principal differences between

Table 1. Dissolution rates per unit surface area of replicate samples of magnetite, maghemite, hematite, goethite, lepidocrite, and akaganeite in 0.5 N HCl at 25°C.

| Dissolution rate per unit surface area (g Fe dissolved × $10^4$/m²/hr) | | | | | |
|---|---|---|---|---|---|
| Magnetite | Maghemite | Hematite | Goethite | Lepido-crocite | Akaganeite |
| 3.46 | 0.98 | 0.13 | 0.03 | 6.24 | 1.25 |
| 3.48 | 0.99 | 0.13 | 0.06 | 6.61 | 1.43 |
| 3.48 | 0.99 | 0.14 | 0.07 | | 1.50 |

Table 2. Average activation energies and frequency factors for the dissolution of various iron oxides and oxyhydroxides in 0.5 N HCl.

| Mineral | Activation energy (kcal/mole) | Frequency factor (g Fe dissolved/m²/hr) |
|---|---|---|
| Magnetite | 19.0 | $1.8 \times 10^{10}$ |
| Maghemite | 20.3 | $5.1 \times 10^{10}$ |
| Hematite | 20.9 | $2.1 \times 10^{10}$ |
| Goethite | 22.5 | $3.0 \times 10^{11}$ |
| Lepidocrocite | 20.0 | $5.8 \times 10^{11}$ |
| Akaganeite | 16.0 | $7.4 \times 10^{7}$ |

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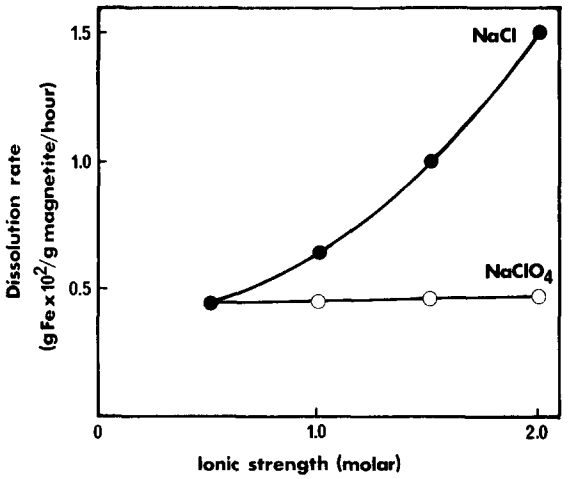



Figure 3. Effect of ionic strength on the dissolution of magnetite. Ionic strength was raised by dissolving NaCl or $NaClO_4$ in 0.5 M HCl.

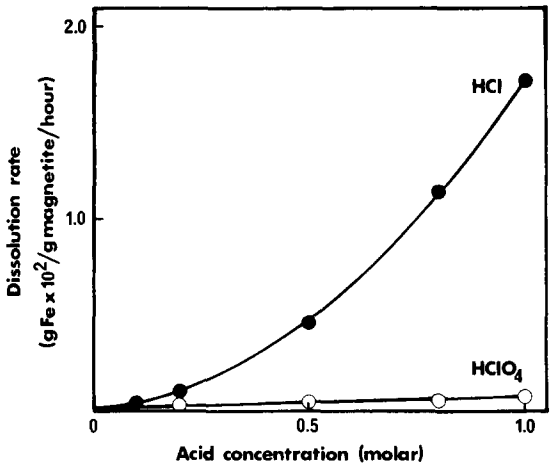



Figure 4. The effect of concentration and nature of acid on the dissolution of magnetite.

magnetite and maghemite are the presence of $Fe^{2+}$ in magnetite and the existence of cation vacancies in maghemite. The ionic radius of $Fe^{2+}$ (0.74 Å) is larger than that of $Fe^{3+}$ (0.64 Å), so that the $Fe^{2+}$–O bond will be longer and weaker than the $Fe^{3+}$–O bond. Because the acid dissolution of iron oxides involved the breakdown of Fe–O bonds (Cornell *et al.*, 1976), the dissolution of magnetite might be expected to be faster than that of maghemite. In maghemite one ninth of the cation sites that are normally occupied in magnetite are vacant. The presence of cation vacancies is energetically unfavorable (Kullerud *et al.*, 1969) and should make maghemite particularly susceptible to acid attack and dissolve faster than magnetite. However, the experimental evidence is to the contrary and suggests that the effect of cation vacancies in maghemite is outweighed by the presence of $Fe^{2+}$ in magnetite.

Another factor that may also be responsible for the more rapid dissolution of magnetite is that dissolution of $Fe^{3+}$ compounds can be accelerated by the presence of $Fe^{2+}$ in solution which reduces $Fe^{3+}$ ions exposed at crystal surfaces (Fischer, 1973).

To identify the reasons for different dissolution rates, the effect of temperature on dissolution rate was investigated. The relationship between dissolution rate and temperature for the iron oxides was described by the Arrhenius equation:

$$K = Ae^{-E/RT},$$

where K = dissolution rate, A = frequency factor, E = activation energy, T = absolute temperature, and R = gas constant. The values of E and A were calculated from the slope and intercept of ln K vs. 1/T plots for each specimen; average values for each mineral are given in Table 2.

Despite the close similarity of their structures, the activation energies for the dissolution of magnetite and maghemite in 0.5 M HCl are different, i.e., 19.0 and 20.3 kcal/mole, respectively. Differences in activation energy are generally related to bond strengths (Glasstone *et al.*, 1941) and may in this case be due to the relative weakness of the $Fe^{2+}$–O bond in magnetite. Differences in dissolution rates apart from those due to activation energies are incorporated in the frequency factor A. If the dissolution rate per unit surface area is used to calculate the frequency factor, A includes the effects of acid concentration, the number of reactive sites per unit surface area, and a chloride adsorption factor in the case of dissolution in HCl (Cornell *et al.*, 1974). The values of the frequency factors for magnetite and maghemite were found to be $1.8 \times 10^{10}$ and $5.1 \times 10^{10}$ g Fe dissolved/m²/hr, respectively. The higher frequency

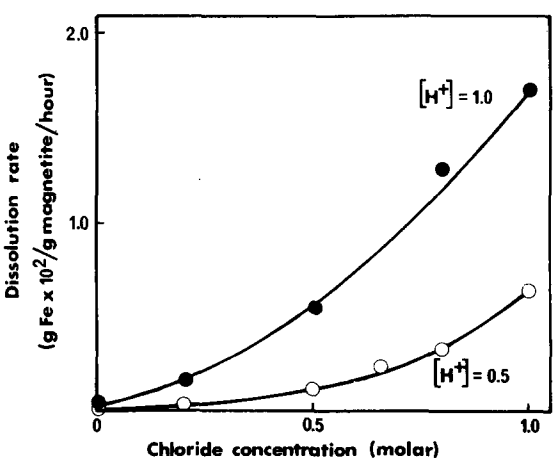



Figure 5. The effect of chloride concentration on the dissolution of magnetite. Chloride concentration at $[H^+] = 1.0$ was varied using combination of HCl and $HClO_4$ and at $[H^+] = 0.5$ by combination of HCl, $HClO_4$, NaCl, $NaClO_4$.

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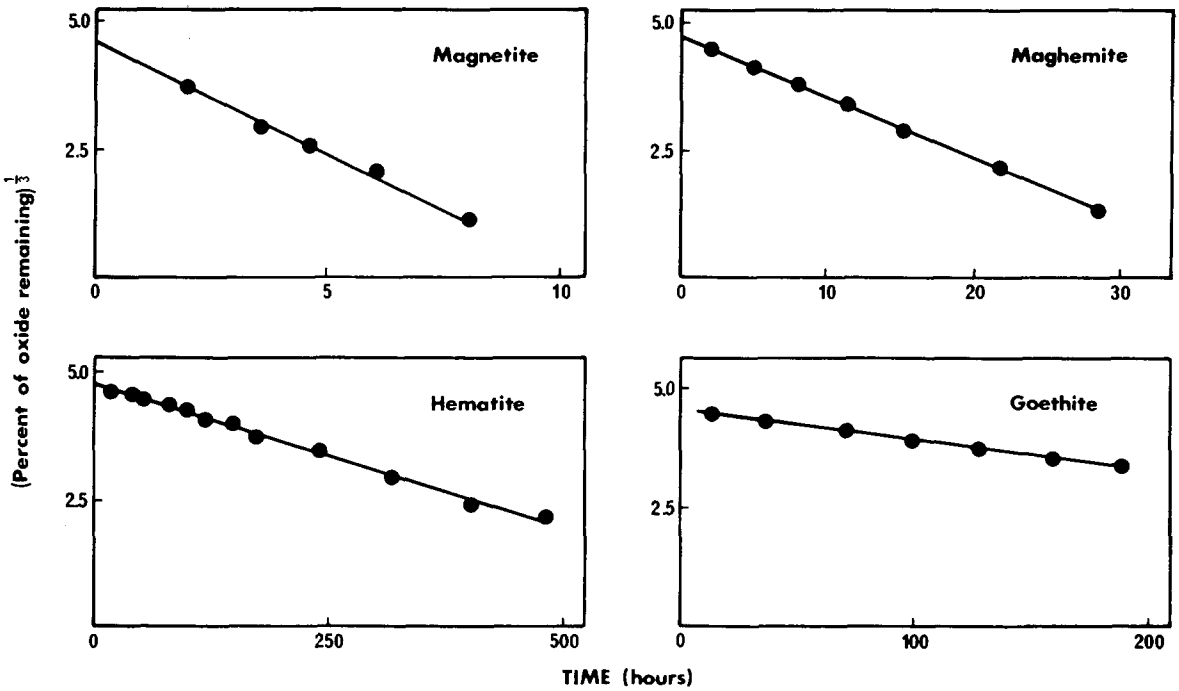



Figure 6. Cube root plots of dissolution data for magnetite, maghemite, hematite, and goethite.

factor for maghemite is consistent with the hypothesis that the presence of vacant cation sites at the surface of maghemite should increase the dissolution rate of maghemite in comparison with that of magnetite. Thus, the frequency factor for maghemite acts in the opposite sense to the effect of higher activation energy, but it is not sufficient to outweigh the unfavorable effect of the larger activation energy.

Hematite has the same chemical composition as maghemite, but it is denser (5.26 g/cm$^3$ vs. 4.88 g/cm$^3$) and does not contain comparable cation vacancies. These differences and the occurrence of Fe solely in octahedral sites may be responsible for the much slower dissolution of hematite relative to maghemite despite the similar activation energies and identical composition of these minerals. The activation energy (20.9 kcal/mole) for hematite dissolution is twice that reported by Krestov *et al.* (1973) for dissolution in 0.5–9 M HCl.

Lepidocrocite has a more open structure than goethite and dissolves more rapidly. In lepidocrocite double sheets of octahedra are hydrogen-bonded together by zig-zag chains of –O–H–O–H–O in planes parallel to the octahedral sheets (Deer *et al.*, 1962). Between each double sheet of octahedra there are channels oriented parallel to the x-axis. During HCl dissolution proton attack may occur along these channels as well as on the surface. There are no similar channels in goethite. The more rapid dissolution of lepidocrocite relative to goethite is due to both a much larger frequency factor and a lower activation energy.

The crystal structure of akaganeite has not been accurately determined, but the crystal morphology is very different from that of goethite and lepidocrocite. Ultrathin sections of akaganeite particles have shown that they are either square or circular in cross section (Mackay, 1962; Watson *et al.*, 1962). The particles are not true single crystals, but consist of assemblages of parallel rods each with a diameter of about 30 Å. Acid attack could occur along the entire length of these rods as well as at the outer surface of the particles thereby influencing both activation energy and the frequency factor.

The activation energies (Table 2) of these iron oxides vary in the following order: goethite > hematite > maghemite > lepidocrocite > magnetite > akaganeite. On the basis of activation energies alone, dissolution rates should vary in the reverse order. The actual dissolution rates, however, were in the order: lepidocrocite > magnetite > akaganeite > maghemite > hematite > goethite. The favorable activation energies for akaganeite and magnetite were outweighed by the unfavorable frequency factors as compared to lepidocrocite. Despite its peculiar morphology, akaganeite has a particularly small frequency factor so that notwithstanding its low activation energy it dissolved slowly.

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*Complete dissolution*

Complete dissolution of all oxides was carried out in 0.5 N HCl at 60°C. The shapes of dissolution curves for magnetite, maghemite, hematite, and goethite were similar and showed a decrease in dissolution rate with progressive dissolution. The dissolution data were fitted to the cube root law (Hixon and Crowell, 1931).

$$W^{1/3} = W_0^{1/3} - kt$$

Where $W_0$ is the initial weight of the sample, W is the weight of the sample after time t, k is a constant, and t is the dissolution time. This relationship describes the data quite well (Figure 6) for magnetite, maghemite, hematite, and goethite, demonstrating that dissolution rate is proportional to the surface area. Isotropic dissolution of magnetite and maghemite was indicated by electron microscopy of replicas (Figure 1) which showed that dissolution occurred uniformly in all directions on the crystal surface.

The kinetic curves for the dissolution of hematite at 60°C were slightly sigmoidal in shape suggesting a relatively slow dissolution of some less soluble, minor (~5%) component followed by a more rapid dissolution of the remainder. This effect and sigmoidal character is not evident in the cube root plot. Hematite was obtained by heating magnetite, a process which involved some sintering of former magnetite particles (Figure 1). The average crystal sizes for the hematites were calculated from X-ray powder diffraction line breadths (Klug and Alexander, 1954). These sizes were smaller than those determined by electron microscopy and indicate that individual hematite particles (~1300 Å) consisted of several coherently diffracting single crystals (~450 Å) rather than of one single crystal. It is possible that the acid preferentially dissolved material at the interfaces between individual crystals in hematite and split them into smaller particles with a resultant increase in surface area. Such a reaction is likely to increase the surface area and hence the dissolution rate.

Although the complete dissolution of goethite followed the cube root law, electron microscope observations (Figure 1) showed that dissolution was not uniform on all surfaces (Cornell *et al.*, 1975, 1976). Lepidocrocite did not dissolve uniformly which may be responsible for dissolution following a zero order rate law. The complete dissolution of akaganeite was not investigated.

All six iron oxides discussed in this paper have been reported in soils, and it is significant that in ancient mature soils only the three least soluble minerals (i.e., hematite, goethite, maghemite) are common (Schwertmann and Taylor, 1977). However, the synthetic iron oxides used in the study may not closely resemble those occurring naturally. Furthermore, the weathering environment is not well simulated by acid solutions so that studies of iron oxide dissolution under more realistic conditions are required before differences in the abundance of iron oxides in natural systems can be related to their chemical properties.

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**Резюме**—Растворение синтетического магнетита, маггемита, гематита, гетита, лепидокрокита и акаганеита происходило быстрее в HCl, чем в $HClO_4$. В присутствии $H^+$, ион $Cl^-$ увеличивал скорость реакции, а ион $ClO_4^-$ не имел никакого эффекта. Это указывает на то, что формирование поверхностных комплексов Fe-Cl содействует растворению. Эффект температуры на начальную скорость реакции может быть описан формулой Аррениуса, при порядке скоростей растворения: лепидокрокит > магнетит > акаганеит > маггемит > гетит. Энергии активации и факторы частот для этих минералов были соответственно: 20,0, 19,0, 16,0, 20,3, 20,9, 22,5 ккал/моль и $5{,}8 \times 10^{11}$, $1{,}8 \times 10^{10}$, $7{,}4 \times 10^{7}$, $5{,}1 \times 10^{10}$, $2{,}1 \times 10^{10}$, $3{,}0 \times 10^{11}$ грамма Fe растворенного/м²/час. Полное растворение магнетита, маггемита, гематита и гетита хорошо описывается законом кубического корня, однако растворение лепидокрокита не совпадает с этим законом. [E.C.]

**Resümee**—Synthetischer Magnetit, Maghemit, Haematit, Goethit, Lepidokrokit, und Akaganeit löste sich in HCl schneller als in $HClO_4$. In Gegenwart von $H^+$ vergrößerte $Cl^-$ die Lösungsgeschwindigkeit, während $ClO_4^-$ ohne Einfluß war. Dies deutet darauf hin, daß die Bildung von Fe-Cl-Oberflächenkomplexen die Auflösung fördert. Der Temperatureffekt auf die anfängliche Lösungsgeschwindigkeiten kann durch die Arrhenius-Gleichung beschrieben werden, wobei sich für die Lösungsgeschwindigkeiten folgende Reihenfolge ergibt: Lepidokrokit > Magnetit > Akaganeit > Maghemit > Haematit > Goethit. Die Aktivierungsenergien bzw. Häufigkeitsfaktoren dieser Minerale sind 20,0, 19,0, 16,0, 20,3, 20,9, 22,5 kcal/Mol bzw $5.8 \times 10^{11}$, $1{,}8 \times 10^{10}$, $7{,}4 \times 10^{7}$, $5{,}1 \times 10^{10}$, $2{,}1 \times 10^{10}$, $3{,}0 \times 10^{11}$ g Fe gelöst/m²/hr. Die vollständige Auflösung von Magnetit, Maghemit, Haematit, und Goethit wird durch das Kubikwurzelgesetz beschrieben, während es für die von Lepidokrokit nicht gilt. [U.W.]

**Résumé**—La dissolution de magnétite, maghémite, hématite, goethite, lépidocrocite, et d'akaganéite synthétiques était plus rapide dans HCl que dans $HClO_4$. En présence d'$H^+$, l'ion $Cl^-$ a augmenté l'allure de dissolution, mais l'ion $ClO_4^-$ n'avait aucun effet, suggérant que la formation de complexes Fe-Cl de surface aide la dissolution. L'effet de la température sur l'allure de dissolution peut être décrite par l'équation d'Arrhenius avec les allures de dissolution dans l'ordre suivant: lépidocrocite > magnétite > akaganéite > maghémite > hématite > goethite. Les énergies d'activation et les facteurs de fréquence pour ces minéraux sont 20,0, 19,0, 16,0, 20,3, 20,9, 22,5, kcal/mole et $5{,}8 \times 10^{11}$, $1{,}8 \times 10^{10}$, $7{,}4 \times 10^{7}$, $5{,}1 \times 10^{10}$, $2{,}1 \times 10^{10}$, $3{,}0 \times 10^{11}$ g Fe dissolu/m²/hr, respectivement. La dissolution complète de magnétite, maghémite, hématite, et de goethite est bien décrite par la loi de racine cubique, tandis que celle de la lépidocrocite ne l'est pas. [D.J.]

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