NOTES

EFFECTS OF PHOSPHATE ON IRON OXIDE DISSOLUTION IN ETHYLENEDIAMINE-N,N,N′,N′-TETRAACETIC ACID AND OXALATE

The content of poorly crystalline iron oxides, mainly ferrihydrite, in soils is commonly determined by the oxalate method and less commonly by the ethylenediamine-N,N,N′,N′-tetraacetic acid (EDTA) method (Schwertmann, 1964; Schwertmann *et al.,* 1982; Borggaard, 1981, 1988). Comparable amounts of iron are dissolved by the two methods from many soils (Borggaard, 1988), and both ligands presumably act via surface complexation (Chang and Matijevic, 1983; Zinder *et al.,* 1986). Recently, however, various differences in the dissolution mechanisms have been suggested (Borggaard, 1990). In contrast to EDTA, oxalate is rather unstable and decomposes, for example, in the presence of light (Schwertmann, 1964). Decomposition of oxalate leads to the formation of iron(II), which may accelerate the dissolution of iron oxide (Cornell and Schindler, 1987).

Furthermore, EDTA, having four carboxyl groups, has been postulated to be adsorbed onto iron oxide surfaces by the formation of tetranuclear surface complexes at room temperature (Borggaard, 1990). Such surface complexes may retard or inhibit iron oxide dissolution because several bonds must be broken before the iron-EDTA complex can be released (Chang and Matijevic, 1983). Oxalate is bidentate and forms binuclear (and monodentate) surface complexes (Parfitt *et al.,* 1977; Cornell and Schindler, 1987), which obviously cannot prevent the dissolution of crystalline iron oxide (Borggaard, 1982, 1988). If the surface complexes are different, however, the EDTA and oxalate methods should respond differently if competing anions, such as phosphate, are present simultaneously. Phosphate should increase the dissolution rate in EDTA because it eliminates or suppresses the formation of tetranuclear surface complexes, whereas the competition for adsorption sites should slow down the dissolution in oxalate.

The purpose of this paper is to test the hypothesis of different mechanisms for the dissolution of iron oxides in EDTA and oxlate due to different surface complexes. Therefore, adsorption and dissolution properties of the system iron oxide-EDTA/oxalate with and without phosphate were investigated for various synthetic iron oxides.

EXPERIMENTAL

Iron oxides. Except for the ferrihydrite, the iron oxides were the same as prepared and described previously (Borggaard, 1983). So-called goethite 1 was prepared by 2 days' aging of a mixture of iron(III) nitrate and sodium hydroxide solutions (OH/Fe = 3.5) at 60°C, and goethite B was prepared by 3 days' aging at room temperature of a mixture of iron(III) nitrate and sodium hydroxide solutions (OH/Fe = 1.0) followed by 2 days' aging at pH 12.3 and 55°C. Hematite 4 was prepared by heating feroxyhite at 560°C for 20 hr. Maghemite 2 was prepared by bubbling air for ~6 hr through an iron(II) chloride solution at 45°C maintained at pH ~7 by ammonia addition. Lepidocrocite 1 was prepared by 1 day's shaking of a mixture of iron(III) sulfate, sodium thiosulfate, and potassium iodate.

Ferrihydrite, prepared by slow hydrolysis of iron(III) at pH ~7, contained 51.8% Fe and exhibited two broad X-ray powder diffraction (XRD) humps at ~2.4 and ~1.5 Å.

Adsorption. Two, 1-g portions of goethite 1 or hematite 4 or 0.2-g portions of lepidocrocite 1 were weighed into centrifuge tubes and suspended in 8 cm³ of water and 7 cm³ of water plus 1 cm³ of 1 M KH_2PO_4 (pH 5.0), respectively. After overnight shaking, 2 cm³ of 0.1 M oxalate (pH 5.0) plus 0.1 cm³ of ^{14}C-labeled oxalic acid (0.1 μCi, from Du Pont NEN) were added to both tubes. The tubes were shaken for 2 hr and centrifuged. The oxalate concentration was determined by mixing 0.5 cm³ of the clear supernatant with 5 cm³ of a scintillation cocktail and analyzing the mixture with a liquid scintillation counter. The difference between oxalate concentrations before and after shaking with the iron oxide was considered to be the amount of oxalate adsorbed.

Similarly, EDTA adsorption was determined by replacing oxalate with 0.1 M EDTA (pH 5.0) and using ^{14}C-labeled EDTA (0.1 μCi, from Amersham). In the
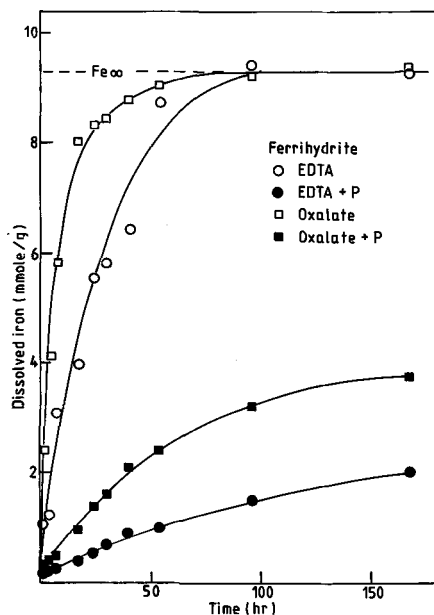
324

Figure 1.   Dissolution profiles for ferrihydrite in 0.02 M ethylenediamine-N,N,N′,N′-tetraacetic acid (EDTA) and oxalate with or without 0.2 M phosphate. pH, 5.0; temp., ~20°C.

Figure 2.   Dissolution profiles for goethite 1 in 0.02 M ethylenediamine-N,N,N′,N′-tetraacetic acid (EDTA) and oxalate with or without 0.2 M phosphate. pH, 5.0; temp., ~20°C.

samples containing both EDTA and phosphate, adsorbed phosphate was calculated from the difference between phosphate concentrations, determined by the molybdenum blue method, before and after shaking with the iron oxide.

For adsorbed oxalate and EDTA the coefficient of variation was ~10%, whereas for phosphate adsorption the coefficient of variation was as much as ~25%.

Dissolution. Four dissolution series were carried out for each iron oxide at pH 5 and room temperature (~20°C). Each series consisted of 10 portions of 50 mg of iron oxide in polyethylene bottles. Twenty-five cubic centimeters of 2 M ammonium acetate (pH 5.0) was added to all bottles. Fifteen cubic centimeters of water was added to the bottles in two of the series, whereas 5 cm³ of water plus 10 cm³ of 1 M KH_2PO_4 (pH 5.0) was added to bottles in the other two series. After all bottles had been shaken for 3 days in a reciprocal shaker, 10 cm³ of 0.1 M EDTA (pH 5.0) was added to the bottles in two series (with and without phosphate) and 10 cm³ of 0.1 M ammonium oxalate (pH 5.0) to the bottles in the other two series. Bottles containing oxalate were wrapped in tinfoil to exclude light. The bottles were shaken from 2 to 168 hr (ferrihydrite) or from 8 hr to 20 days (the other iron oxides). After shaking, the solid was separated from solution by centrifugation.

The iron concentration was determined in the clear supernatants by flame atomic absorption spectroscopy using standards containing the same salts and in the same concentrations as in the samples. Standards and
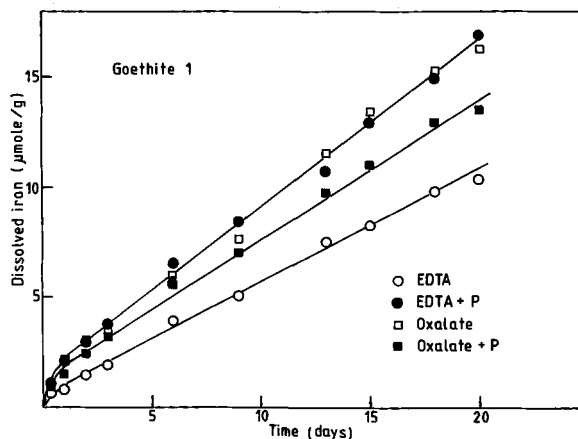
samples were introduced via a laboratory-built flow injection system to avoid blocking of the burner system. All determinations were carried out in duplicate or triplicate; the coefficient of variation was <6%.

RESULTS AND DISCUSSION

The dissolution profiles for ferrihydrite and goethite 1 at room temperature are shown in Figures 1 and 2. Ferrihydrite dissolved much faster than goethite. In the absence of phosphate all ferrihydrite dissolved during 4 days, whereas <0.2% goethite dissolved during 20 days. For the most reactive crystalline iron oxide sample, lepidocrocite 1, the extent of dissolution was <2% and <5% in EDTA and oxalate, respectively.

The addition of phosphate changed the dissolution profiles, but in different ways depending on the iron oxide. In the dissolution of ferrihydrite, phosphate drastically reduced the dissolution rate for both ligands (Figure 1); however, goethite dissolved faster in EDTA but more slowly in oxalate, if phosphate was present (Figure 2). The other crystalline iron oxides (goethite B, hematite 4, maghemite 2, and lepidocrocite 1) behaved like goethite 1, shown in Table 1, which gives the slopes of the various dissolution profiles. These slopes corresponded to the linear or almost linear part of the dissolution profiles, which, as shown for goethite 1 in Figure 2, also exhibited initial curved parts corresponding to fast dissolution. Such fast initial dissolution was observed by Schwertmann (1984) and may have been due to dissolution of surface iron at corners and edges.

Excluding ferrihydrite, the rate of dissolution increased almost linearly with increasing specific surface area of the iron oxides (Table 1). Thus, expressed in terms of square meters, the rate of dissolution of the crystalline iron oxides in EDTA was 0.039 ± 0.009

Table 1. Rate of dissolution (taken as the slope of the dissolution profile) of various synthetic iron oxides in 0.02 M solutions of ethylenediamine-N, N, N', N'-tetraacetic acid (EDTA) and oxalate with or without 0.2 M phosphate.[1]

Mineral	EDTA (μmole/day)	Phosphate + EDTA (μmole/day)	Oxalate (μmole/day)	Phosphate + oxalate (μmole/day)	Spec. surface area (m^2/g)
Goethite 1	0.51	0.79	0.78	0.65	16
Goethite B	2.6	4.5	4.1	2.9	82
Hematite 4	2.4	3.4	3.3	1.9	64
Maghemite 2	1.6	8.3	6.7	5.0	30
Lepidocrocite 1	9.1	29	23	12	221
Ferrihydrite[2]	4.2×10^3	460	16×10^3	1.2×10^3	328

[1] At pH 5 and room temperature ($\sim$20°C).
[2] Calculations correspond to <65% ferrihydrite dissolved and time <50 hr.

μmole Fe/(day m^2). Similarly, the rate of dissolution of goethite and hematite in dithionite was found to depend on the specific surface area but not on the mineral form (Torrent *et al.,* 1987). Furthermore, the amounts of fluoride and phosphate adsorbed by various iron oxides were independent of the mineral form, but increased linearly with increasing specific surface area (Borggaard, 1983; Goldberg and Sposito, 1984). The amounts of EDTA and oxalate adsorbed by goethite 1, hematite 4, and lepidocrocite 1 were also found to be independent of the mineralogy (Table 2); however, the reactivity of iron oxides did not always appear to be independent of mineralogy. In oxalate, the calculated dissolution rates per square meter for lepidocrocite 1 and maghemite 2 were higher than those for the goethites and hematite 4 (Table 1). Zinder *et al.* (1986) found different dissolution rates for goethite and hematite in oxalate. Although the amount of phosphate adsorbed per square meter depended on crystal morphology for hematite species it bore no relation to morphology for goethite species (Barron *et al.,* 1988; Torrent *et al.,* 1990).

Ferrihydrite dissolved much faster than can be accounted for by its higher specific surface area (Table 1). Together with the different behavior in the presence of phosphate, this rapid dissolution emphasizes the difference between ferrihydrite and other crystalline iron oxides.

The retarding effect of phosphate on the dissolution of ferrihydrite in both ligand solutions and on the dissolution of the other iron oxides in oxalate (Figure 1; Table 1) is similar to the reported suppressing effect of silicate on ferrihydrite dissolution in oxalate (Saleh and Jones, 1984; Parfitt and Childs, 1988). In oxalate, this effect may be explained by competition for adsorption sites between oxalate and phosphate, both forming binuclear surface complexes on iron oxides (Parfitt *et al.,* 1977; Cornell and Schindler, 1987). In agreement, a blocking of "specific dissolution sites" by species, such as phosphate and silicate, was considered by Cornell *et al.* (1989) to retard ferrihydrite dissolution and therefore its transformation into crystalline iron oxides.

In contrast with dissolution in oxalate, phosphate accelerated the dissolution of crystalline iron oxide in EDTA (Figure 2; Table 1). Furthermore, without phosphate, all iron oxides dissolved faster in oxalate than in EDTA (Table 1). The dissolution pathways in EDTA and oxalate must therefore be different. Both ligands are anions of carboxylic acids and are considered to act via surface complexation mechanisms (Chang and Matijevic, 1983; Zinder *et al.,* 1986; Borggaard, 1990). Oxalate is, however, bidentate, whereas EDTA has four carboxylate groups and may therefore form tetranuclear surface complexes. As pointed out by Borggaard (1990), the size and flexibility of the EDTA molecule and the distances between singly coordinated hydroxyl groups on iron oxides should enable formation of such complexes. To accomplish dissolution, one of the four iron ions complexed to EDTA must be released together with the EDTA molecule. This process requires considerable energy to break several bonds (Chang and Matijevic, 1983). Release of surface iron complexed to oxalate (binuclear surface complex) requires fewer bonds to be broken (less energy). Therefore, the formation of binuclear and tetranuclear surface complexes with oxalate and EDTA, respectively, may explain the higher dissolution rates found for all iron oxides in oxalate than in EDTA without phosphate (Table 1).

Table 2. Oxalate and ethylenediamine-N,N,N',N'-tetraacetic acid (EDTA) adsorbed by synthetic iron oxides in the absence and presence of 0.1 M phosphate.[1]

Mineral	Oxalate (μmole/ m^2)	Phosphate + oxalate (μmole/ m^2)	EDTA (μmole/ m^2)	Phosphate + EDTA[2] (μmole/m^2)	Surface sites[3] (μmole/ m^2)
Goethite 1	2.4	1.8	1.6	1.2 (1.8)	7.3
Hematite 4	2.4	1.4	1.2	1.2 (1.3)	5.1
Lepidocrocite 1	2.5	1.6	1.3	1.0 (1.4)	5.9

[1] At pH 5 and room temperature ($\sim$20°C).
[2] Values in brackets are amounts of phosphate adsorbed.
[3] Values correspond to fluoride adsorption taken from Borggaard (1983).

Furthermore, the increased dissolution rate of the crystalline iron oxides in EDTA following the addition of phosphate could have been due to a reduction in number of ligator groups per EDTA molecule because of competition for adsorption sites between phosphate and EDTA.

This hypothesis is strongly supported by the results in Table 2. The iron oxides adsorbed 2.5 μmole/m^2 of oxalate at pH 5, which is similar to values found by Parfitt et al. (1977) and Cornell and Schindler (1987) and to the amounts of phosphate adsorbed by various iron oxides (Borggaard, 1983; Goldberg and Sposito, 1984; Torrent et al., 1990). This value is about half the number of adsorption sites (Table 2), in agreement with binuclear surface complexation of oxalate. After addition of phosphate, adsorbed oxalate was reduced and the dissolution rate decreased (Table 1), in support of the surface complexation mechanism (Zinder et al., 1986).

In contrast, the iron oxides only adsorbed 1.3 μmole/m^2 of EDTA (Table 2). Comparable amounts were found by Chang et al. (1983) and Rueda et al. (1985) to be adsorbed at pH 5 by hematite and goethite, respectively. Considering the number of adsorption sites, this value indicates that one EDTA molecule occupies four adsorption sites, i.e., forms a tetranuclear surface complex. The area of a fully "extended" EDTA molecule is 100 Å^2 (Chang et al., 1983), and at pH 5 EDTA has four negative carboxylate groups and two positive amino groups. Furthermore, free rotation about the single bonds in EDTA allows adaptation of correct configurations. Therefore, there seems to have been no hindrance for the four carboxylate groups in EDTA to have reacted with four contiguous hydroxyl groups at the iron oxide surface occupying ~100 Å^2 (Borggaard, 1983).

Interestingly, almost the same amounts of EDTA were adsorbed with and without addition of phosphate (Table 2). These results indicate a change in the number of carboxyl groups in EDTA to surface iron ions from four in the absence of phosphate to two in the presence of phosphate. The resulting binuclear iron oxide-EDTA surface complex probably resembled the oxalate surface complex in reactivity, although the reactivity of the two complexes was not necessarily identical, because the nature of the two ligands is different.

In conclusion, phosphate affected iron oxide dissolution in EDTA and in oxalate differently; in oxalate, the rate of dissolution decreased, but in EDTA it increased for crystalline iron oxides after phosphate addition. The difference may be explained by formation of tetranuclear and binuclear (as in oxalate) surface complexes in EDTA without and with phosphate, respectively, the former retarding the dissolution of crystalline iron oxide. In contrast, ferrihydrite (and other poorly crystalline iron oxides) readily dissolved in EDTA, although it probably also forms tetranuclear

surface complexes (Borggaard, 1990). Increased bond energies due to increased crystallinity may account for the difference in reactivity towards EDTA of poorly crystalline and well-crystallized iron oxides.

Chemistry Department   OLE K. BORGGAARD
Royal Veterinary and
     Agricultural University
40. Thorvaldsensvej
DK-1871 Frederiksberg C
Denmark

REFERENCES

Barron, V., Herruzo, M., and Torrent, J. (1988) Phosphate adsorption by aluminous hematites of different shapes: Soil Sci. Soc. Amer. J. 52, 647–651.

Borggaard, O. K. (1981) Selective extraction of amorphous iron oxides by EDTA from soils from Denmark and Tanzania: J. Soil Sci. 32, 427–432.

Borggaard, O. K. (1982) Selective extraction of amorphous iron oxides by EDTA from selected silicates and mixtures of amorphous and crystalline iron oxides: Clay Miner. 17, 365–368.

Borggaard, O. K. (1983) Effect of surface area and mineralogy of iron oxides on their surface charge and anion adsorption properties: Clays & Clay Minerals 31, 230–232.

Borggaard, O. K. (1988) Phase identification by selective dissolution techniques: in Iron in Soils and Clay Minerals, J. W. Stucki, B. A. Goodman, and U. Schwertmann, eds., Reidel, Dordrecht, The Netherlands, 83–98.

Borggaard, O. K. (1990) Dissolution and adsorption properties of soil iron oxides: Dissertation, DSR-Forlag, Copenhagen, 122 pp.

Chang, H.-C. and Matijevic, E. (1983) Interactions of metal hydrous oxides with chelating agents. IV. Dissolution of hematite: J. Colloid Interface Sci. 92, 479–488.

Chang, H.-C., Healy, T. W., and Matijevic, E. (1983) Interactions of metal hydrous oxides with chelating agents. III. Adsorption on spherical colloidal hematite particles: J. Colloid Interface Sci. 92, 469–478.

Cornell, R. M. and Schindler, P. W. (1987) Photochemical dissolution of goethite in acid/oxalate solution: Clays & Clay Minerals 35, 347–352.

Cornell, R. M., Giovanoli, R., and Schneider, W. (1989) Review of the hydrolysis of iron(III) and the crystallization of amorphous iron(III) hydroxide hydrate: J. Chem. Technol. Biotechnol. 46, 115–134.

Goldberg, S. and Sposito, G. (1984) A chemical model of phosphate adsorption by soils. II. Non-calcareous soils: Soil Sci. Soc. Amer. J. 48, 779–783.

Parfitt, R. L. and Childs, C. W. (1988) Estimation of forms of Fe and Al: A review and analysis of contrasting soils by dissolution and Mössbauer methods: Aust. J. Soil Res. 26, 121–144.

Parfitt, R. L., Farmer, V. C., and Russell, J. D. (1977) Adsorption on hydrous oxides. I. Oxalate and benzoate on goethite: J. Soil Sci. 28, 29–33.

Rueda, E. H., Grassi, R. L., and Blesa, M. A. (1985) Adsorption and dissolution in the system goethite/aqueous EDTA: J. Colloid Interface Sci. 106, 243–246.

Saleh, A. M. and Jones, A. A. (1984) The crystallinity and surface characteristics of synthetic ferrihydrite and its relationship to kaolinite surfaces: Clay Miner. 19, 745–755.

Schwertmann, U. (1964) Differenzierung der Eisenoxide des Bodens durch Extraktion mit Ammoniumoxalat-Lösung: Z. Pflanzenernähr. Düng. Bodenk. 105, 194–202.

Schwertmann, U. (1984) The influence of aluminum on iron oxides: IX. Dissolution of Al-goethites in 6 M HCl: *Clay Miner.* **19,** 9–19.

Schwertmann, U., Schulze, D. G., and Murad, E. (1982) Indentification of ferrihydrite in soils by dissolution kinetics, differential X-ray diffraction and Mössbauer spectroscopy: *Soil Sci. Soc. Amer. J.* **46,** 869–875.

Torrent, J., Schwertmann, U., and Barron, V. (1987) The reductive dissolution of synthetic goethite and hematite in dithionite: *Clay Miner.* **22,** 329–337.

Torrent, J., Barron, V., and Schwertmann, U. (1990) Phosphate adsorption and desorption by goethites differing in crystal morphology: *Soil Sci. Soc. Amer. J.* **54,** 1007–1012.

Zinder, B., Furrer, G., and Stumm, W. (1986) The coordination chemistry of weathering: II. Dissolution of Fe(III) oxides: *Geochim. Cosmochim. Acta* **50,** 1861–1869.