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FAST AND SLOW PHOSPHATE SORPTION BY GOETHITE-RICH NATURAL MATERIALS

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Abstract—Although phosphate sorption by goethite and other less-abundant Fe oxides strongly influences the concentration of this anion in the soil solution and aquatic environments, relatively little is known on the P-sorption characteristics of natural goethites. For this reason, we examined the P-sorption capacity and time course of P sorption of 10 goethite-rich soil, ferricrete and lake ore samples, in which the content and nature of mineral impurities were unlikely to affect P sorption significantly. Phosphate sorption could be adequately described by a modified Freundlich equation including a time term. The amount of P sorbed after 1 day of equilibration at a concentration of 1 mg P/liter ranged widely (0.36–2.04 μmol P/m^2). The total P sorbed after 75 days of equilibration varied less, in relative terms (1.62–3.18 μmol P/m^2), i.e., a higher slow sorption tended to compensate for a lower initial (fast) sorption. Total sorbed P ($\bar{X}$ = 2.62, SD = 0.52 μmol P/m^2) was similar to the sorption capacity of synthetic goethites, suggesting a common sorption mechanism and the predominance of one type of crystal face, which, according to previous transmission electron microscope observations, might be the (110).

The extent of the slow reaction correlated to the ratio between micropore surface area and total surface area, as well as to oxalate-extractable Fe, which is an estimation of the ferrihydrite content. Ferrihydrite impurities might affect the slow reaction by contributing to the microporosity of some samples. Silicate adsorbed on the surface of the goethites was readily desorbed during phosphate sorption and did not significantly affect the extent of the slow sorption process.

Key Words—Adsorption, Ferrihydrite, Goethite, Iron oxides, Phosphate, Porosity, Silicate, Sorption.

INTRODUCTION

Phosphate concentration in the soil solution and aquatic environments is markedly influenced by Fe oxides, of which goethite is usually the most abundant. Fe oxides seem to sorb phosphate by ligand exchange with surface OH groups monocoordinated with Fe atoms (Parfitt, 1978). However, other mechanisms, such as precipitation, cannot be excluded (Jonasson *et al.*, 1988; Martin *et al.*, 1988). Synthetic goethites frequently have a phosphate sorption capacity of about 2.5 μmol P/m^2 at moderately acid to neutral pH values (Hingston, 1981; Cabrera *et al.*, 1981; Borggaard, 1983a; Ainsworth *et al.*, 1985; Anderson *et al.*, 1985; Torrent *et al.*, 1990). This value is compatible with the formation of a binuclear surface complex on the (110) faces, which are the ones observed under the transmission electron microscope (TEM) (Schwertmann, 1984; Mann *et al.*, 1985), rather than the generally assumed (100) faces.

Few, mostly indirect, data are available on the P-sorption capacity of natural goethites. Phosphate sorption has been estimated from the difference in P sorption between untreated and deferrated soil samples (e.g., Borggaard, 1983b), from the slope of regression equations of P sorbed against the calculated surface area of goethite in soil samples (Peña and Torrent, 1984), or by measuring P sorption and surface area in goethite-rich samples and disregarding, for the calculations, the contribution of other minerals to P sorption and surface area (Schwertmann and Schieck, 1980). Under these different assumptions, natural goethites appear to have P-sorption values similar to those of their synthetic counterparts. Natural and synthetic goethites differ, however, in the relative contribution of the slow sorption process to the total P sorption. Most synthetic goethites sorb little phosphate after a few hours or days of equilibration with phosphate. For 31 synthetic samples widely differing in their crystal habit and size, Torrent *et al.* (1990) found that, on average, 90% of the total sorbed P after 75 days had already been sorbed by the first day. Similar results were reported by Cabrera *et al.* (1981) and Parfitt (1989). Natural goethites (and other Fe oxides) show a more marked slow reaction (Schwertmann and Schieck, 1980; Parfitt, 1989). Several hypotheses have been put forward to explain slow sorption: 1) replacement of silicate bonding goethite crystals by phosphate (Barrow, 1987); 2) slow diffusion through a coating of metal phosphate (van der Zee and van Riemsdijk, 1991); and 3) slow diffusion due to surface aberrations caused by Al substitution (Ainsworth and Sumner, 1985). Micro- and mesoporosity was found to enhance slow P sorption by lepidocrocite (Cabrera *et al.*, 1981; Madrid and Ar-

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Table 1. Mineralogical and chemical properties of the goethite-rich materials.

Sample	Origin	Other minerals[4]	Fe_d[5] (g/kg)	Al_d[5] (g/kg)	Fe_o[5] (g/kg)	Fe_{HCl}[5] (g/kg)	Al substitution (mole %) XRD	Al substitution (mole %) Chemical	MCD_{110}[6] (nm)	Specific surface area EGME (m^2/g)	Specific surface area BET-N_2 (m^2/g)	Micropores[7] (%)
Bou 1	friable soil[1]	Qu, Ta	325	9	5.7	370	1	5.5	14	129	110	0
Bou 2	hollow root concretion[1]	Qu, Ta	390	17	5.9	410	6	8.5	17	213	107	0
Bou 5a	ferricrete[1]	Qu, Chr, Ta	455	17	5.9	520	7	7.0	23	82	62	34
Tib 3	ferricrete[1]	Gb, Chr	280	57	0.6	295	20	29.5	25	96	78	0
Moi 1	ferricrete[1]	Qu, Chr, Ta	360	9	3.8	385	2	5.0	23	73	55	47
38B	lake ore (crust)[2]	Fh, Qu	465	<1	144.5	485	0	<0.5	10	214	182	52
47A	lake ore (pisolitic)[2]	Qu, Fh	435	22	14.4	480	7.5	9.5	11	143	123	37
K1	soil concretions[3]	Qu, Fh	490	<1	34.4	515	0	<0.5	12	86	37	0
Fe29	friable soil	Qu	440	12	1.0	485	5.5	5.5	12	54	53	0
Fe8b	ferricrete	Qu	485	2	3.3	545	4	1.0	36	36	25	8

[1] Schwertmann and Latham (1986).
[2] Schwertmann *et al.* (1987).
[3] Schwertmann (1988).
[4] Qu = quartz; Ta = talc; Chr = chromite; Gb = gibbsite; Fh = ferrihydrite.
[5] d = CBD-extractable; o = oxalate-extractable; HCl = HCl-extractable.
[6] Mean crystallite dimension perpendicular to (110).
[7] N_2-SA of micropores as percentage of total SA.

ambarri, 1985) and is likely to have the same effect on natural goethites (Parfitt, 1989).

This work was undertaken to characterize the P-sorption properties of natural goethites. We examined the P-sorption capacity and time course of the phosphate sorption processes of natural goethite-rich materials and their relation to the properties of goethite. In the samples studied, the presence of minerals other than goethite was considered to have little effect on P sorption.

MATERIALS AND METHODS

Samples

Ten goethite-rich materials (Table 1) were used. The first 4 samples came from Oxisols formed on peridotite in New Caledonia, where the low Al content of the parent material and the high degree of weathering have led to an extreme concentration of Fe oxides in the soil. Two transmission electron micrographs (Figure 1) exemplify the variability of the samples taken for study: acicular multidomainic crystals with domains parallel to the crystallographic *c*-direction (Bou 1), and irregularly-shaped, near-equidimensional crystals without discernible domains (Bou 5a). Sample Moi 1 is a goethitic ferricrete from a river terrace in the same area. It has been described, together with the first 4 samples, by Schwertmann and Latham (1986). Samples 38B and 47A are goethite accumulations in Finnish lakes (Schwertmann *et al.*, 1987), which appear as pieces of crust (38B) or pisolites (47A). Sample K1 comes from concretions in a gley soil from the Neth-

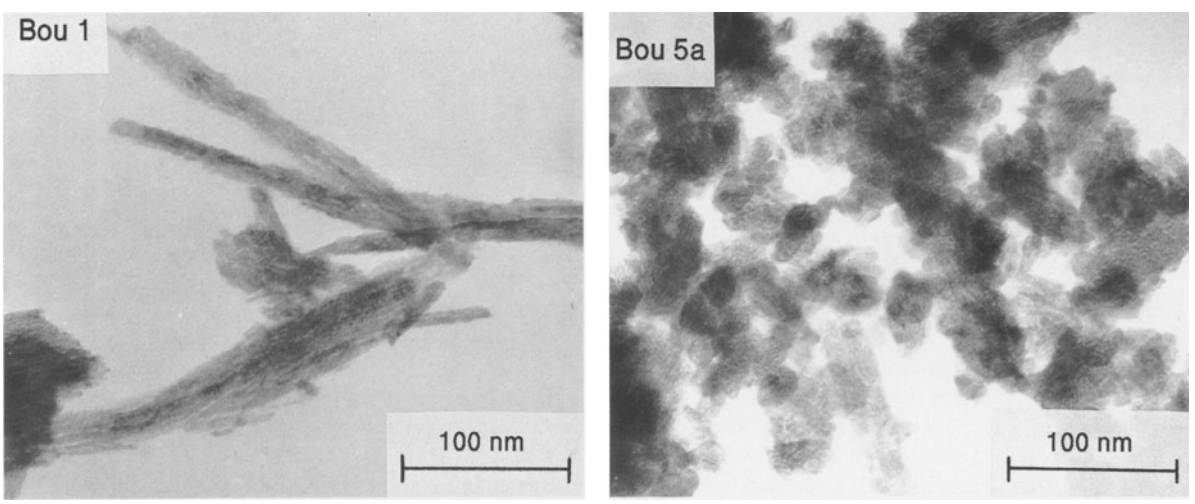


Figure 1. Transmission electron micrographs of samples Bou 1 (acicular, multidomain crystals) and Bou 5a (irregularly-shaped, near-equidimensional crystals without discernible domains).

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erlands. Sample Fe29 is a friable material from an Oxisol formed on serpentinite near Orissa, India. Sample Fe8b is from a Jurassic limestone plateau near Kehlheim/Donau, Germany, where deep *terra fusca* soils contain goethite concretions and pieces of ferricrete resulting, most likely, from the paleoweathering of limestone.

Chemical and mineralogical characterization of the samples

If cemented, the samples were ground in an agate mortar until there was an absence of grittiness. Citrate-bicarbonate-dithionite (CBD)-extractable Fe and Al (Fe_d, Al_d) were determined by the method of Mehra and Jackson (1960), although extraction (10 mg of sample in 5 ml of CB) was carried out at 50°C for 24 hr with dithionite added at 8 hr intervals. The CBD extracts were oxidized by bubbling with air for 4 hr, before determining CBD-extractable Si and P (Si_d, P_d) by the methods of Hallmark *et al.* (1982) and Murphy and Riley (1962), respectively. To prevent citrate interference in the determination of P_d, 0.8 ml of ammonium heptamolybdate (54 g/liter) at pH 7 were added to 0.8 ml of the oxidized extract before addition of the mixed reducing reagent. Acid ammonium oxalate-extractable Fe (Fe_o) was determined according to Schwertmann (1964). Hydrochloric acid-extractable Fe and P (Fe_{HCl}, P_{HCl}) were determined by treating 5-mg samples with 8 ml of 9 M HCl at 44°C for 48 hr. Before P determination by the method of Murphy and Riley (1962), the HCl extract was taken to pH 2 with NaOH. The determination of Fe and Al in all extracts was carried out by atomic absorption spectrophotometry.

The mineralogical composition of the samples, the mean crystallite dimension (MCD), and Al substitution of the goethites were studied by X-ray powder diffraction (XRD), as described by Schwertmann and Latham (1986). Specific surface area was determined by adsorption of ethylene glycol-monoethyl ether (EGME) (Carter *et al.*, 1965), and by the BET method, using N_2 as adsorbate in a Quantasorb Jr. surface area analyzer. The presence of micropores (<2 nm) in the samples was evaluated with the t-plot method, from which the surface area of the micropores was calculated (Gregg and Sing, 1982).

P sorption-related experiments

The phosphate sorption curve of each sample was constructed by preparing 4 suspensions in 0.002 M $CaCl_2$ at pH 5 (with this electrolyte, P sorption depends little on pH in the neutral to moderately acid range (Barrow, 1987), making it relatively unimportant not to adjust the pH to a specified value for the different suspensions). The amounts of sample were chosen to give, 1 day after P addition, P concentrations in solution of about 0.2, 1, 3, and 10 mg/liter by addition, in 20–80 ml, of 48, 70, 100, and 270 μg of P (as KH_2PO_4), respectively. These amounts had been estimated from a previous, similar sorption experiment (10-mg samples in 5 ml of 0.002 M $CaCl_2$ with 100 μg of P). The suspensions were reciprocately shaken (2.5 strokes/s) at 25°C for 1 day, and then for 1 min daily until day 124 after P addition. The suspensions (which had a pH = 4.8 ± 1) were centrifuged at selected times and portions of the supernatant were analyzed for P and Si by the methods cited before. For P, analysis was done at days 1, 3, 8, 19, 43, 84, and 124 and, for Si, at days 1, 3, 8, 19, 43, 61, and 124 after P addition. To describe P sorption, the following modified Freundlich equation (Barrow and Shaw, 1975) was used:

$$X = Ac^b t^d \quad (1)$$

where X is the amount of P sorbed, c is the solution concentration, t is time, and A, b and d are constants typical of each sample.

The KOH-extractable P and Si (P_{KOH}, Si_{KOH}) were determined by shaking (2.5 strokes/s) 25-mg samples with 40 ml of 0.1 M KOH at 25°C for 66 hr, and analyzing these two elements in the supernatant by the methods cited earlier. The Si soluble in $CaCl_2$ (Si_{CaCl_2}) was determined by extracting 25-mg samples with 40 ml of 0.002 M $CaCl_2$ at 25°C for 24 hr. Finally, isotopically-exchangeable P was determined at day 180 after P addition for the suspension of the sorption experiment that had a P concentration within the 0.2–0.8 mg/liter range. After adding 0.25 to 1.25 μCi of carrier-free ^{32}P (as Na_2HPO_4), the suspensions were shaken for 24 hr and their supernatants analyzed for ^{31}P (Murphy and Riley, 1962) and for ^{32}P by Cerenkov counting (Beckman 6000 TA Liquid Scintillator).

RESULTS AND DISCUSSION

Mineralogical and chemical properties of the samples

Mineralogical and chemical properties of the samples are given in Table 1. Goethite was the only Fe oxide detected by XRD, except for samples 38B and K1, in which ferrihydrite was present. If taken as a measure of ferrihydrite, the Fe_o/Fe_d ratios of these two samples (0.31 and 0.07) indicate that about one third and less than one tenth of the Fe oxides are ferrihydrite. Owing to the presence of minerals other than goethite, many samples had Fe_d values lower than those expected for this mineral (500–600 g/kg, depending on water and Al contents). After the CBD or HCl treatments, significant amounts of undissolved material remained for samples Bou 1, 2 and 5a, Tib 3 and Moi 1. After the HCl treatment, which yielded higher amounts of Fe than the CBD treatment, the residues were whitish for samples Bou 1 and 2, in agreement with the presence of XRD-detectable quartz and talc. In samples Bou 5a, Tib 3 and Moi 1, the residue was brown, suggesting that some goethite-rich material could not be dissolved by the acid (probably due to insuffi-

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Table 2. Phosphate forms and sorption properties.

Sample	Phosphate forms[1]				Constants of Eq. (1)			P sorbed at day 75 at 6 mg P/liter (μmol/m^2)[2]	Total P sorbed[3] (μmol/m^2)[2]	Isotopically-exchangeable P (% of sorbed P)
	P_d (mg/kg)	P_{HCl} (mg/kg)	P_{KOH} (mg/kg)	P_{KOH} (μmol/m^2)[2]	A (μmol/m^2)[2]	b	d			
Bou 1	155	150	66	0.02	0.84	0.123	0.097	1.60	1.62	44
Bou 2	45	45	38	0.01	2.03	0.092	0.065	3.17	3.18	43
Bou 5a	115	70	17	0.01	0.76	0.173	0.160	2.07	2.08	31
Tib 3	1250	1530	520	0.22	1.26	0.133	0.093	2.39	2.61	32
Moi 1	400	410	73	0.04	1.02	0.124	0.140	2.50	2.54	42
38B	195	150	27	0.00	0.36	0.289	0.379	3.13	3.13	31
47A	3500	4450	1170	0.31	0.59	0.200	0.227	2.27	2.58	41
K1	2400	2290	370	0.32	0.81	0.168	0.210	2.72	3.04	31
Fe29	650	640	59	0.04	1.43	0.087	0.068	2.23	2.27	53
Fe8b	910	920	385	0.49	1.11	0.126	0.149	2.64	3.13	48

[1] d and HCl as in Table 1; KOH = 0.1 M KOH-extractable.
[2] Per m^2 of N_2 surface area.
[3] P sorbed at 6 mg P/liter + P_{KOH}.

cient grinding). Samples 38B, 47A, K1, Fe29 and Fe8b yielded only very small amounts of brownish residue.

Minerals accompanying goethite undoubtedly affect both the surface area (SA) and the P-sorption properties of the samples. Some minerals (quartz, chromite) have low specific surface areas (SSA) and P-sorption capacities. Thus, the P-sorption properties of the goethite in the samples in which these minerals are the main impurities can be reasonably estimated from the P-sorption properties of the whole sample. Talc (present in Bou 1, 2 and 5a, and Moi 1), by contributing significantly to SA, but little to P sorption, can lead to an underestimation of the P actually sorbed by goethite. In those samples containing gibbsite or ferrihydrite, the ratio (experimentally determined) between P sorbed and SA will be a good estimation of the true amount of P sorbed per unit SA of goethite. The reason is that gibbsite has a sorption capacity per unit SA similar to that of goethite (White, 1980). This is also true for ferrihydrite (Borggaard, 1983a).

The goethites differed widely in mean crystallite dimension perpendicular to the (110) plane (MCD_{110}), and EGME- or N_2-SSA. The N_2-SSA ranged between 25 and 182 m^2/g and was 10 to 30% lower than the EGME-SSA, as often observed for Fe oxides. For samples Bou 2 and K1, the EGME-SSA more than doubled the N_2-SSA. No ready explanation can be offered for these discrepancies. In the following sections, P sorption will be reported with reference to the N_2-SSA; this has been the most commonly used method by researchers dealing with P sorption. Five samples (Bou 5a, Moi 1, 38B, 47A, and Fe8b) had micropores, contributing to 8–52% of the total SSA.

The Al/(Fe + Al) mole-fraction values calculated from the XRD data ranged from 0 to 0.20, being generally lower than those calculated from Al_d and Fe_d. This can be due to the ability of CBD to extract Al from sources other than goethite, such as gibbsite in sample Tib 3, or talc in samples Bou 1 and Bou 2. No clear relationship was found between Al mole fraction and other goethite properties.

Phosphate forms and sorption capacity

Data on P forms and sorption properties are shown in Table 2. Significant amounts of phosphate were released by CBD or HCl. The two methods yielded similar results, the average extracted P ranging between 45 and 4000 mg/kg. Of this P, usually less than one-third could be extracted by 0.1 M KOH, which is the extractant frequently used to estimate the phosphate adsorbed on the surface of Fe oxides (Cabrera *et al.*, 1981; Willett *et al.*, 1988; Torrent *et al.*, 1990). The CBD- or the HCl-extractable P not removed by KOH could be P occluded in the goethite or P in phosphate minerals. Relatively large amounts of occluded P are usually found in soil Fe oxides (Taylor and Schwertmann, 1974; Schwertmann and Fanning, 1976; Norrish and Rosser, 1983). Since penetration of the phosphate ion into the goethite structure seems to be impeded by sterical hindrance, it is likely that, if phosphate occurs in an occluded form, it occupies gaps between individual crystals in goethite aggregates.

Eq. (1) adequately described P sorption (R^2 = 0.891–0.995 for its logarithmic form). Constant A, i.e., the P sorbed (per unit N_2-SSA) after 1 day at an equilibrium concentration of 1 mg P/liter, ranged widely (0.36–2.03 μmol P/m^2). In contrast, the range in sorbed P after 75 days at 6 mg P/liter was, in relative terms, narrower (1.62–3.13 μmol P/m^2). The sum of this amount and the P_{KOH} ('total sorbed P' of Table 2) has a mean value of 2.62 (SD = 0.52) μmol P/m^2. A mean value of 2.73 (SD = 0.41) μmol P/m^2 is obtained when sample Bou 1 is excluded. This sample has a low (1.62 μmol P/m^2) sorption value (probably due to the "diluting" effect of relatively large amounts of quartz and talc impurities). The latter mean value coincides with the mean 2.74 (SD = 0.20) μmol P/m^2 value of 31 synthetic goethites (Torrent *et al.*, 1990). The similarity is re-

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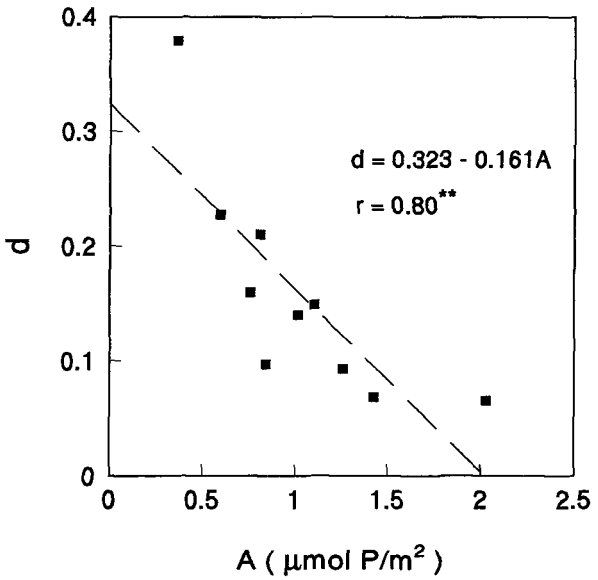


Figure 2. The relationship between constants d and A of Eq. (1).

markable, inasmuch as natural samples have impurities, and the conditions were not identical in the two sets of sorption experiments.

If, as suggested by Parfitt (1978), phosphate is adsorbed as a binuclear surface complex on contiguous A-type hydroxyls of the goethite crystal faces, a simple crystallographical calculation (Torrent *et al.*, 1990) gives phosphate sorption capacities of 2.77, 5.96, 0, and 2.51 µmol P/m² for faces (100), (010), (001), and (110), respectively. Given such contrasting values, a simple explanation for the relatively similar P-sorption capacity of goethites is that only one type of crystal face dominates in most synthetic and naturally occurring crystals. The fact that, as for synthetic samples, TEM observations show that natural goethites are also bound by (110) faces (Smith and Eggleton, 1983; Amouric *et al.*, 1986) supports this unifying principle. An alternative hypothesis to explain the constancy of P-sorption capacity in natural crystals (Ainsworth *et al.*, 1989) is that, when the SA is above a threshold value, the goethite crystals can be described as spheres or cubes rather than needles of various morphologies. Then, all the major crystal faces contribute to adsorption, resulting in an average site density that does not change with further decrease in crystal size. However, for synthetic goethites of widely different morphologies, it is difficult to accept that different combinations of faces of widely contrasting site densities such as (100) and (010) can yield an essentially constant sorption capacity per unit SA.

Slow phosphate sorption

The constants of Eq. (1) indicate that a higher slow sorption tended to compensate for a lower initial sorption. In other words, the exponent d, which is a measure of the extent of the time-dependent sorption, was negatively correlated to A (Figure 2). Similarly, the exponent affecting concentration, b, was correlated to A ($b = 0.257 - 0.104$ A; $r = .82^{**}$), i.e., a lower P sorption at low equilibrium concentration was compensated by a higher increase in sorption with increasing equilibrium concentration.

Slow sorption accounted for a substantial part of the total sorption in most samples, in contrast with its low importance in synthetic goethites, as mentioned before. The magnitude of the slow sorption (estimated by d) was related to the ratio between the SA of micropores and the total SA ($d = 0.105 + 0.30$ (SA of micropores/total SA); $r = .69^{*}$). Exponent b also correlated to this ratio ($b = 0.118 + 0.19$ (SA of micropores/total SA); $r = .69^{*}$). Diffusion of phosphate to adsorption sites in micropores (on crystals surfaces, between domains of contiguous crystals) is a hypothesis compatible with the positive effects of time and concentration in promoting more phosphate sorption.

A significant correlation was found between d and Fe_o ($d = 0.117 + 0.0019\ Fe_o$; $r = .88^{**}$), suggesting that the presence of ferrihydrite impurities also enhances slow sorption. This effect might be partly due to the porous nature of this mineral, as it has been observed for synthetic ferrihydrites (Willett *et al.*, 1988). However, except for samples 38B and 47A, the Fe_o values were low. Thus, the contribution of intrinsic ferrihydrite porosity to total porosity must also be low (even when ferrihydrite has a higher specific SA than goethite). For this reason, microporosity of samples Bou 5a, Moi 1 and Fe8b, in which $Fe_o/Fe_d < 0.02$, can be almost exclusively ascribed to goethite.

The significance of the regressions of d against either porosity or Fe_o-content drops markedly when sample 38B, which is high in microporosity and ferrihydrite content, is excluded. However, in a multiple regression equation of d against porosity and Fe_o, 80% of the variance is still explained (86% for the 10 samples). Figure 3 illustrates this relationship.

Silicate release versus phosphate sorption

Of those anions competing with phosphate for the adsorption sites on the hydroxylated goethite surfaces, silicate is, by far, the most abundant in soils and aquatic environments. For this reason, we studied the Si forms and the release of silicate during the P-sorption experiments (Table 3). Relatively large amounts of silicate were removed by the CBD treatment, the highest value corresponding to sample 38B (51.1 g/kg). This sample has Si-rich ferrihydrite as its major impurity (Schwertmann *et al.*, 1987). For the other samples, Si_d ranged between 1.4 and 12.3 g/kg. Much smaller amounts of Si (8–30% of Si_d) were removed by the KOH treatment, which provides a pH at which adsorbed P is released from an Fe oxide surface (Barrow,

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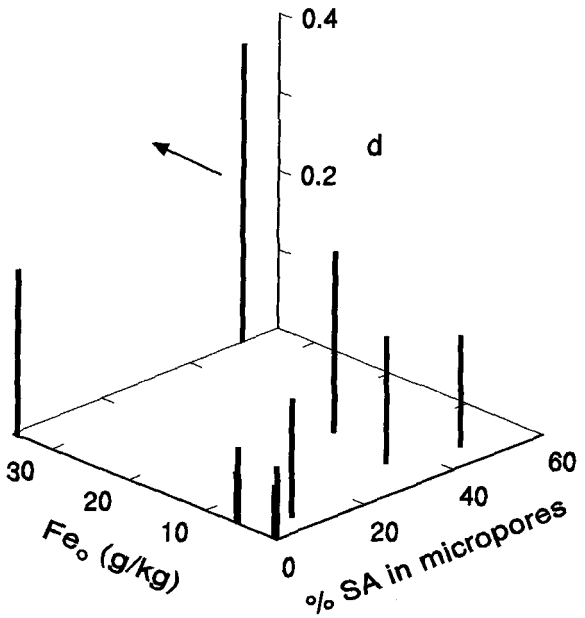


Figure 3. Constant d as a function of Fe_o-content and the percentage of SA in micropores.

1987). Consequently, the relatively significant amounts of $Si_d - Si_{KOH}$ can be allocated to silicate intimately associated to goethite (and, to a lesser extent, to the small amounts of accompanying ferrihydrite). This silicate probably fills the narrow spaces between crystals, and also bonds the individual crystals in goethite aggregates, as observed in other natural goethites (Smith and Eggleton, 1983). Alternatively, Si^{4+} may replace Fe^{3+} in the goethite structure but, so far, little quantitative importance has been ascribed to this type of substitution (Schwertmann and Taylor, 1972).

Phosphate sorption resulted in silicate release. In all samples, the amount of silicate released at a certain time did not depend significantly on the initial level of P added. For this reason, only the average amounts of Si released at selected times are shown in Table 3. During the first day, from 0.07 to 0.67 μmol Si/m^2 were released. These amounts were from 1.5 to 3.5 times higher than those released by $CaCl_2$ alone, indicating the positive effect of phosphate sorption on silicate desorption. The silicate released after 124 days ranged from 0.11 to 1.77 μmol Si/m^2 and was correlated, in a near 1:1 relationship, to Si_{KOH} (Si released = 0.21 + 0.76 Si_{KOH}; r = .96***). In short, phosphate seemed to extract that silicate removable by the relatively harsh KOH treatment, while leaving silicate intimately associated to goethite essentially untouched. Therefore, the contention of Barrow (1987) and Parfitt (1989) that phosphate can replace silicate bonding goethite microcrystals can be applied to only a relatively small proportion of the goethite-associated silica.

The molar ratio of Si-released/P-sorbed for the 1–124 day period ($\Delta Si/\Delta P$ of Table 3) ranged between 0.06 and 1.14 and was positively correlated to Si_{KOH} ($\Delta Si/\Delta P$ = 0.20 + 0.40 Si_{KOH}; r = .80**). In other words, the greater the proportion of the surface covered by silicate, the more silicate was released per mol of phosphate. On the other hand, the constant, d, was not significantly correlated with Si_{KOH} (nor with Si_d). All this suggests that "surface" silicate is easily replaced by phosphate, and therefore, does not contribute to slow P sorption.

Isotopic exchange

From 31 to 53% of the sorbed P was isotopically exchangeable 180 days after P addition. For the 15 synthetic goethites studied by Torrent (1991), that percentage ranged between 37 and 62% (unpublished results). The reasons for this relatively small difference might be the same as those that make slow sorption more marked in natural goethites (e.g., microporosity and ferrihydrite impurities). However, for the group of natural materials studied here, no relationship was found between isotopically-exchangeable P and any of

Table 3. Si forms and Si release after phosphate addition.

Sample	Si forms[1]				Si released after P addition		
	Si_d (g/kg)	Si_{KOH} (g/kg)	Si_{KOH} (μmol/m^2)	Si_{CaCl_2} (μmol/m^2)	1 day (μmol/m^2)	124 days (μmol/m^2)	$\Delta Si/\Delta P^2$ (mol/mol)
Bou 1	12.1	1.97	0.64	0.15	0.33	0.67	0.68
Bou 2	9.3	0.96	0.32	0.10	0.32	0.57	0.33
Bou 5a	4.9	0.64	0.37	0.06	0.13	0.22	0.10
Tib 3	1.4	0.22	0.10	0.02	0.07	0.11	0.06
Moi 1	12.3	3.00	1.95	0.35	0.59	1.71	1.14
38B	51.1	11.40	2.24	0.25	0.41	1.77	0.72
47A	10.4	3.05	0.89	0.19	0.33	1.09	0.64
K1	4.7	0.53	0.51	0.10	0.22	0.75	0.37
Fe29	14.2	1.50	1.01	0.27	0.67	1.11	0.80
Fe8b	11.9	0.90	1.28	0.40	0.61	1.64	0.89

[1] d and HCl as in Table 2; $CaCl_2$ = soluble in 0.002 M $CaCl_2$.
[2] Si-released/P-sorbed for the 1–124 days period after P addition.

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the properties listed in Tables 1 and 2, suggesting that other factors must influence isotopic exchange.

SUMMARY AND CONCLUSIONS

The phosphate sorption capacity at specified experimental conditions did not differ much between the goethite-rich samples studied, being similar to that of many synthetic goethites. Consequently, P sorption by goethite might be controlled by one type of crystal face that is dominant in both natural and synthetic crystals. TEM observations by several authors point at the (110) face. The relatively constant P-sorption capacity of goethite supports the concept of estimating the surface area of this mineral in mixtures with less active P sorbents, as discussed by Schwertmann (1988).

The contribution of slow sorption to the total P sorption increased with increasing microporosity and ferrihydrite content. This fact is compatible with the idea that the slow sorption is due to the diffusion of phosphate to adsorption sites in micropores. These pores might be pores on the surface, between domains or between goethite crystals, or might pertain to the accompanying ferrihydrite.

Silicate sorbed on the surface of goethite was easily replaced by phosphate and did not seem to affect the extent of the slow sorption.

The percentage of sorbed P that was isotopically exchangeable was slightly lower than for synthetic goethites and was not related to any of the properties of the materials studied.

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