RETENTION OF COBALT BY PURE AND FOREIGN-ELEMENT ASSOCIATED GOETHITES

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Abstract—Retention studies of the cobalt-goethite system were carried out using synthetic, star-shaped and lath-shaped pure, Al-, Cd-, Cu- and Si-associated goethites. Aluminium and Si are commonly occurring foreign elements in natural goethites. The goethites were prepared by coprecipitating Fe and the foreign element under controlled conditions and characterized by X-ray diffraction, transmission electron microscopy, specific surface area determination and 2 M HCl extraction. The foreign-element associated goethites contained ~3, ~5 and ~9 mole % Al, ~4 mole % Cd and ~3 mole % Cu incorporated by isomorphous substitution but only ~0.4 mole % of probably occluded Si. Crystal size and shape but also number of defects and domains, and hence specific surface area, unit-cell dimensions and reactivity towards 2 M HCl, exhibited great variability among the goethites. Accordingly the amounts of Co sorbed from initially 10^{-7} M Co in 0.1 M $Ca(NO_3)_2$ in relation to pH (3–8) and reaction time (2–504 h) were very different for the eight goethites. The affinity of Co is highest for Cd- and lowest for Cu-goethite. These samples also form the extremes regarding time-dependent sorption with Cu-goethite showing the smallest and Cd-goethite the largest increase in sorption with increasing reaction time. The Co uptake was not caused by precipitation Co(III) oxides due to Co(II) oxidation, since oxygen exclusion during sorption had no effect on the amount of Co sorbed. The amounts of sorbed Co extracted by 2 M HCl decreased with increasing sorption time but 40–87% of sorbed Co remained unextracted after 48 h, most in Cu-goethite and least in lath-shaped pure goethite. The strong retention suggests Co uptake by diffusion into micropores and fissures resulting from structural defects and intergrowths. The diffusion coefficients range from $3 \cdot 10^{-19}$ to $6 \cdot 10^{-17}$ cm²/s with the highest values for Al- and Si-associated goethites emphasizing the importance for Co immobilization, and hence availability, of foreign-element associations in goethite.

Key Words—Al-goethite, Cd-goethite, Co-extraction, Co-sorption, Cu-goethite, Micropore diffusion, Si-goethite.

INTRODUCTION

Numerous studies exist on trace metal binding by pure goethites. In nature goethite is, however, not pure. It is associated with foreign elements which can either be incorporated by isomorphous substitution of the central Fe^{3+} ion in the octahedra or by an occlusion in defects of the crystal structure. Isomorphous substitution with Al^{3+} has been found to occur frequently in proportions of up to 30 mole % (Norrish and Taylor 1961, Schulze and Schwertmann 1984, Kosmas *et al* 1986). Many trace elements have also been found in close association with goethite because of sorption, substitution and occlusion (Bruemmer *et al* 1988, Borggaard 1990, Gerth 1990, Kumar *et al* 1990). Among those are elements like Co, Cu and Cd, which can be incorporated by isomorphous substitution (Gerth 1990, Kumar *et al* 1990). On the other hand, Si seriously retards goethite crystallization and seems to be incorporated in goethite because of occlusion (Cornell *et al* 1987, Quin *et al* 1988, Gerth *et al* 1993). Natural goethites were found to contain up to 7% SiO_2 (Fordham and Norrish 1983). Although these foreign-element associations are known to change goethite struc-

ture and morphology, their effects on the retention of trace metals by goethite seem unresolved.

The purpose of this investigation was to show the effects of foreign-element incorporation in goethite on the Co retention behaviour of the substituted goethites. Cobalt was chosen because of its significance to plant and animal nutrition (Alloway 1990). Pure and foreign-element (Al, Cd, Cu and Si) associated goethites were synthesized to study the effect of crystal morphology and structural changes on Co sorption and extractability.

MATERIALS AND METHODS

Preparation and characterization of the goethites

Various pure and foreign-element associated goethites were prepared as described by Gerth (1990).

Pure goethite. Method 1, lath-shaped crystals, GL: Within a period of 30 min 50 ml of 1 M $Fe(NO_3)_3$ solution were titrated to pH 4.5 with ~150 ml 1 M NaOH under vigorous stirring. After stirring the suspension for additional 30 min. 500 ml of 1 M NaOH were added. The final suspension was aged for 24 h at

room temperature ($\sim$21°C) followed by seven days at 70°C in a waterbath.

Method 2, star-shaped crystals, GS: 50 ml of 1 M $Fe(NO_3)_3$ solution was rapidly mixed with 650 ml of 0.7 M NaOH previously heated to 70°C and aged at this temperature for seven days.

Foreign-element associated goethite. The foreign-element associated goethites (GM, where M is Al, Cd, Cu or Si) were prepared by method 1 by mixing the $Fe(NO_3)_3$ solution with Al and Cu nitrate or Na silicate before NaOH addition. Goethites were prepared at initial molar $M/(M + Fe)$ ratios of 0.01 (Si), 0.05 (Cu and Al), 0.1 (Al) and 0.2 (Al). The suspensions were aged for seven days at 70°C at pH 13.5.

After aging the materials were washed until salt free, dried at 60°C and gently crushed. Because of the aging procedure the samples are considered to be stable suggesting no recrystallization during the Co retention studies described below.

A Cd-substituted goethite (GCd), which was prepared as part of another investigation, is included in this study (sample L2Cdc in Gerth 1990).

Characterization

Physical analyses. The surface area was measured by N_2-adsorption (single-point determination at P/P_0 0.3) by means of a Micromeritics Flowsorb II 2300. X-ray powder diffractograms (XRD) were obtained from a Siemens D 500/501 diffractometer instrument using Cu-Kα radiation and a diffracted-beam monochromator by step scanning (step size 0.02° 2θ, 1 s count time). The samples were mixed with 10% $Pb(NO_3)_2$ as an internal standard. The unit-cell dimensions (a, b, and c) were determined as described by Gerth (1990).

Specimens for transmission electron microscopy (TEM) were prepared by placing a drop of a diluted aqueous goethite suspension onto a formvar coated Cu-grid. Samples were investigated at magnifications of 28,000 and 100,000 times using a Philips 400 electron microscope operated at 100 keV.

Chemical analyses. In order to remove any non-incorporated foreign element or ferrihydrite from the surface, 40 mg of the products was shaken for 2 h with 20 ml 0.2 M ammonium oxalate, pH 3 in the dark (Schwertmann 1964). The total contents of foreign element and Fe were determined after complete dissolution in concentrated HCl. The difference between the total content and the oxalate-extractable fraction was used to calculate the mole percentage of incorporated foreign element $(M/(M + Fe) \times 100)$. The zero point of charge (ZPC) was determined by the salt titration technique (Gillman 1984).

To determine the fraction of exchangeable foreign element in the goethites 20 mg of the products was shaken with 10 ml of 0.1 M $Ca(NO_3)_2$ for various time intervals between 4 h and 504 h. The kinetics of dissolution was studied at 21°C by shaking 20 mg goethite with 10 ml 2 M HCl for various time intervals between 2 h and 400 h.

Cadmium, Cu and Fe in the extracts were determined by flame atomic absorption spectroscopy (AAS), and Al and Si were determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES).

Sorption and extraction

Sorption. The sorption experiments were carried out according to the method of Gerth *et al* (1993) with slight modifications. Aliquots of aqueous goethite suspension corresponding to 20 mg goethite were pipetted into each of ten 20 ml-polyethylene bottles, which formed an experimental unit for the determination of one pH-sorption relationship. After adding 1 ml 1 M $Ca(NO_3)_2$ and small volumes of HNO_3 or $Ca(OH)_2$ solution to get final pH values in the range 3–8, the volume was adjusted to 9 ml with deionized water and the bottles were shaken on an end-over-end shaker for 14 days. Then 1 ml 10^{-6} M Co(II) nitrate tagged with the ^{57}Co (Amersham, CTS1) was added and the bottles shaken end-over-end at room temperature ($\sim$20°C) for various time intervals between 2 h and 504 h. Thus Co sorption was studied at an initial Co concentration of 10^{-7} M in 0.1 M $Ca(NO_3)_2$ as supporting electrolyte and a Co to goethite ratio of 0.05 μmol Co per g goethite. At the end of the shaking period, the bottles were centrifuged and 1 ml of the clear supernatant was mixed with 4 ml of a scintillation cocktail (Packard Pico-Fluor 40) and counted in a liquid scintillation counter (Packard Tri-Carb 1900 CA). The amount of sorbed Co was taken as the difference between the initial and final solution concentrations.

Similar experiments were carried out under anaerobic conditions using an argon chamber. Goethite suspensions and the solutions were placed in the chamber, which was purged overnight with argon (10 ml/min). Before and after mixing as described above, argon was bubbled through the suspensions and solutions for five min. After shaking for 168 h or 504 h, the capped bottles were centrifuged and aliquots taken for Co determination. Except for the centrifugation and counting, all steps were performed in the argon chamber.

Exchangeable Co. The clear supernatant of samples that had reacted for 72 h was siphoned off to 1 ml and 9 ml of fresh 0.1 M $Ca(NO_3)_2$ was added. The solid was redispersed and the bottles were shaken for an additional 72 h. After centrifugation solution Co was determined radiochemically as described above and exchangeable Co was calculated after correction for entrained Co.

Extraction of sorbed Co. Extractions with 2 M HCl were used to assess the release kinetics of sorbed Co. Samples, which had sorbed Co for 24, 168 and 504 h

Table 1. Selected characteristics of the synthetic goethites including the mole% of Al, Cd, Cu or Si before (initial) and after (final) 2 h extraction with oxalate, crystal length and width, determined by transmission electron microscopy (TEM), unit-cell dimensions determined by XRD, specific surface area (SSA), zero point of charge (ZPC) and initial dissolution rate in 2 M HCl.

Sample	Fe_o/Fe_t[1]	M_o/M_t[1]	Mole% Initial	Mole% Final	TEM Length (nm)	TEM Width (nm)	Unit cell dimensions (nm) a	Unit cell dimensions (nm) b	Unit cell dimensions (nm) c	SSA[3] (m^2/g)	ZPC	Initial diss. rate[3] (mol m^{-2} $s^{-1} \times 10^{-8}$)
GS	0.005				1800	200	0.4614	0.9964	0.3025	35	6.9	3.39
GL	0.007				200	70	0.4620	0.9960	0.3025	69	6.8	1.72
GAla	0.008	0.155	3.33	2.81	250	90	0.4627	0.9940	0.3020	26	7.2	2.88
GAlb	0.009	0.148	5.64	4.89	230	80	0.4627	0.9932	0.3019	25	7.3	2.23
GAlc	0.009	0.125	9.61	8.63	180	80	0.4627	0.9919	0.3014	25	7.3	1.10
GCd[2]	0.016	0.222	4.76	3.79	200	25	0.4639	1.0016	0.3036	68	7.3	1.65
GCu	0.010	0.277	4.52	3.34	400	10	0.4619	0.9982	0.3021	99	7.1	1.41
GSi	0.008	0.815	1.90	0.36	600	200	0.4619	0.9959	0.3025	40	7.0	2.53

[1] Ratio of oxalate-extractable Fe and elements (Fe_o and M_o) to total Fe and elements (Fe_t and M_t).
[2] Unit-cell dimensions from Gerth (1990).
[3] Surface area and initial dissolution rate were measured before oxalate extraction.

were tested. After measuring pH, the 10 ml suspensions were centrifuged and 6 ml of the supernatant was replaced by 1 ml 10 M HCl to give a final volume of 5 ml with an HCl concentration of 2 M. After shaking for 4 h, the samples were centrifuged and 1 ml supernatant was replaced by 1 ml 2 M HCl. The shaking continued for further 48 h. After centrifugation 1 ml of the supernatant was replaced by 0.5 ml conc. HF caused complete dissolution of the solid. The Co concentrations in the supernatants and HF solution were determined radiochemically as described above and extracted Co calculated from these concentrations after correction for entrained Co. Dissolved Cd, Cu and Fe were determined by AAS and dissolved Al and Si by ICP-AES.

Calculation of diffusion coefficients. Sorption data at constant pH were interpolated from the pH-sorption relationships at different reaction time intervals and plotted against the square root of reaction time. In case of linearity this plot suggests that the uptake of Co is controlled by diffusion into the goethite crystals and can be described by the equation

$$M_T = M_0 + kt^{1/2} \tag{1}$$

where M_T is the total sorption of metals (in moles$\cdot$ cm^{-2}) at reaction time t in seconds, M_0 the amount of metals on the surface at zero time (in moles$\cdot cm^{-2}$) and k the parabolic rate constant (in moles$\cdot cm^{-2}\cdot s^{-0.5}$). Diffusion coefficients (D in $cm^2\cdot s^{-1}$) were calculated using a diffusion model for one-dimensional transport in a semi-infinite medium (Crank 1975) which was also applied by White and Yee (1986) in a similar context:

$$M_t = 2C_0(Dt/\pi)^{1/2} \tag{2}$$

where C_0 (in moles$\cdot cm^{-3}$) is the surface concentration which is constant throughout the diffusion process and M_t (in moles$\cdot cm^{-2}$) the total amount of metals trans-

ferred into the mineral at time t. Because C_0 could not be measured directly it was assumed that this fraction is represented by M_0 (intercept of equation 1) which can be converted into C_0 using the specific surface area of the goethite sample and the density of goethite being 4.37 g$\cdot cm^{-3}$.

RESULTS AND DISCUSSION

Characteristics of the goethites

X-ray diffraction confirmed goethite as the only crystalline phase in all samples. Selected properties of the goethites are shown in Table 1. The mole percentages of incorporated foreign elements ($100\cdot M/(M + Fe)$) before and after oxalate extraction to remove poorly ordered material (<2% of Fe removed by oxalate) show foreign element enrichment of this phase, particularly in the GSi sample. In contrast, the major part of Al, Cd and Cu is evenly distributed within the goethites as shown by the straight line in Figure 1, where the percentages of the three metals extracted by 2 M HCl are plotted against %Fe. This pattern is obviously not followed by GSi showing preferential Si release during the HCl extraction (Figure 1) in agreement with the high amount of Si extractable by oxalate (Table 1).

The exchangeability of Al, Cd, Cu and Si in the foreign-element associated goethites was determined by shaking the samples with 0.1 M $Ca(NO_3)_2$ for various time periods up to 3 weeks. Again the GSi sample behaved differently, inasmuch as up to 30% of the Si was released, whereas <4% of the metals in GAl, GCd and GCu could be exchanged (data not shown). The very high Si release may be important for the interpretation of the Co retention results discussed later.

The particle size and morphology of the products are highly variable as shown by TEM (Figure 2). Sample GCd (not shown) is similar to GL. Intergrowths or domains (Cornell and Giovanoli 1986, Mann *et al* 1985)
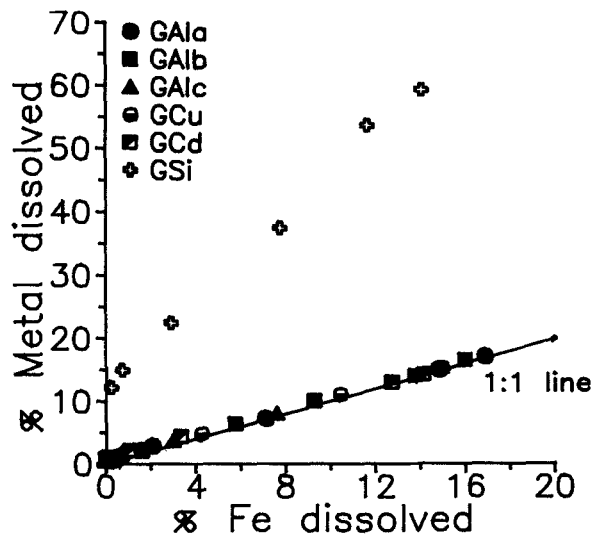
Figure 1. Percentages of Fe and foreign-elements (Al, Cd, Cu and Si) dissolved in 2 M HCl.

Figure 2. Transmission electron micrographs of the synthetic goethites; bar equals 1 μm.

are seen, although to different extent, in all samples (Figure 2). Multi-domainic crystals as in sample GS were found to contain micropores between the domains (Schwertmann 1984). Average lengths and widths of single crystals are highly variable (Table 1). The effect of the preparation mode is clearly demonstrated by the star-shaped crystals resulting from method 2 (GS) compared to the lath-shaped particles in other samples synthesized by method 1. The morphology of the Al-goethites varied slightly with increasing Al substitution up to ~9 mole% which is in agreement with the small effects commonly observed with goethites containing < ~10 mole% Al (Mann *et al* 1985). In contrast, a substitution of Fe by only 3–4 mole% Cd and Cu results in major but different changes of crystal morphology. Copper causes an elongation (length ~400 nm) and narrowing (width ~10 nm) of the crystals which appear needle-like (Figure 2) as was also observed by Kumar *et al* (1990). The crystals of sample GCd appear also elongated (not shown in Figure 2) with the same length as the particles of sample GL (~200 nm) but are markedly reduced in width (~25 nm vs. ~70 nm of GL). In the presence of Si relatively large crystals are formed (sample GSi: length ~600 nm, width ~200 nm) which are multi-domainic (Figure 2). This effect could be due to the presence of strongly sorbing silicate anions linking together goethite particles (Cornell *et al* 1987, Quin *et al* 1988). Furthermore, this sample exhibited the smallest XRD line-broadening of all samples.

Changes in the unit-cell parameters relative to pure goethite give evidence of an isomorphous substitution of the central Fe^{3+} ion in the octahedra of the goethite structure. The three Al-goethites exhibit the same a
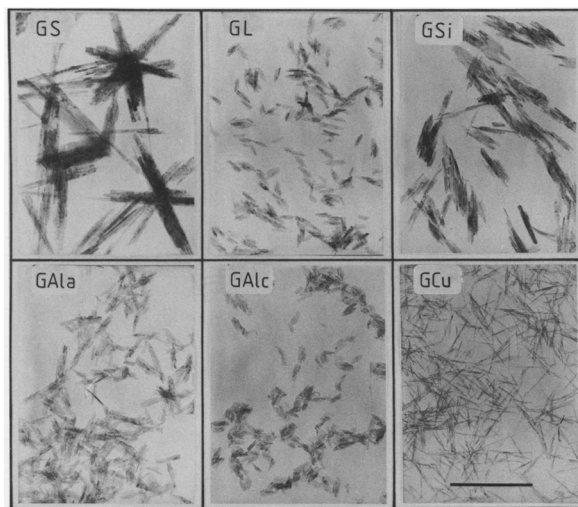
parameter which is slightly higher as compared to sample GL (Table 1). The b and the c dimension, however, decrease linearly with increasing Al substitution as found by Schulze (1984). Ideally, the substitution of Fe by the smaller Al ion should lead to a reduction of all unit-cell parameters but due to structural defects the a dimension is variable (Schulze 1984, Schulze and Schwertmann 1984, Kosmas *et al* 1986). These defects are believed to be micropores (Schulze and Schwertmann 1984).

In general, the changes in the unit-cell dimensions can be related to the amount and the ionic radius of the particular metal incorporated in octahedral coordination (Gerth 1990). Accordingly, the large Cd^{2+} ion causes a strong and almost congruent increase of all unit-cell parameters of sample GCd. A slight deviation is observed in the a dimension which at greater than ~2 mole% expands at a reduced rate according to the ionic radius of Cd^{2+} in tetrahedral coordination (Gerth 1990). The strong expansion of the unit-cell can be expected to also affect the structure of the surface and surface reactivity. The effects of Cu^{2+} incorporation on the unit-cell dimensions of sample GCu are in close agreement with the observations of Gerth (1990) and Kumar *et al* (1990). In this sample, only the b parameter is increased whereas the a and the c dimensions remain almost unchanged. This phenomenon was explained by the Jahn-Teller-effect which causes a strong distortion of the octahedra along the crystallographic a-axis (Gerth 1990). As a consequence, crystal growth is inhibited in the a–b plane leading to the needle-like morphology of crystals (Figure 2). Also, the relative position of hydroxyl groups on the surface is presumably altered, possibly leading to different sorption properties as compared to pure goethite.
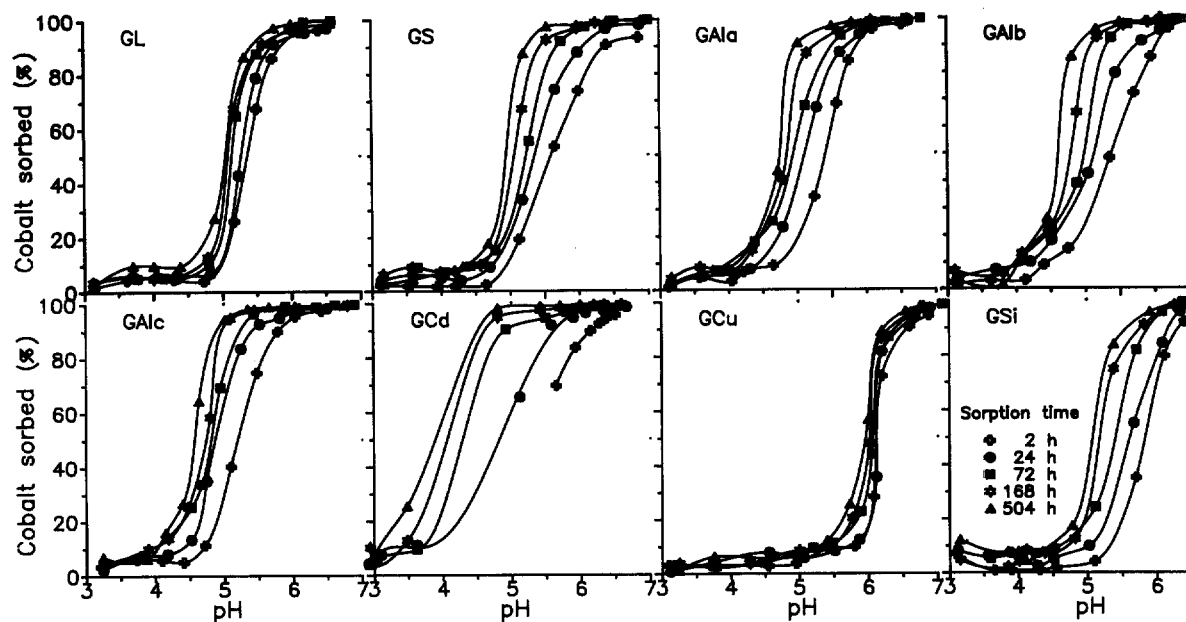
Figure 3. Sorbed Co versus pH for the various goethites in relation to sorption time. Initial Co concentration 10^{-7} M, solid : solution ratios 1:500, background electrolyte 0.1 M $Ca(NO_3)_2$.

The incorporation of Si did not cause any change of the unit-cell dimensions as also shown by Cornell *et al* (1987) and Quin *et al* (1988). This indicates that the close association of this element with goethite occurs by occlusion and not by isomorphous substitution. Thin sections of Si associated goethites show a mottled contrast (Smith and Eggleton 1983) which is indicative of discontinuities in the structure. The difficulty of incorporating Si into octahedral coordination in the goethite structure is a consequence of its strong preference for tetrahedral coordination (Cornell *et al* 1987).

The specific surface area of the goethites, which is a measure of the outer surface area, exhibits great variability (Table 1). Depending on the element, incorporation of foreign elements can obviously lead either to an increase or a decrease, as seen by comparing GL (69 m²/g) with GCu (99 m²/g) and GAl (25 m²/g). The increase following Cu substitution is in accordance with the decrease of crystal width observed by TEM (Figure 2) but the general relation between the specific surface and foreign-element incorporation in goethite is not simple, because the incorporation may change the number of defects and domains in addition to crystallite size and shape (Cornell and Giovanoli 1986). Hence, Al substitution can lead to higher or lower specific surface areas depending on preparation procedure and substitution rate (Schulze and Schwertmann 1984, 1987). Since the samples contained variable amounts of poorly crystalline (oxalate-extractable) Fe oxides (Table 1) and since such oxides have higher specific surfaces than crystalline Fe oxides (Borggaard 1990)

their contribution to the measured surface area should also be recognized.

In contrast to most other characteristics, the zero point of charge (ZPC) is about seven for all goethites (Table 1). This may indicate rather uniform surface charge properties of the samples, although titrations were not performed.

The structural stability of the goethites is shown by the initial dissolution rate within the first 168 h of extraction with 2 M HCl (Table 1). Within this time period 3–10% of total Fe were dissolved. A substitution by Cd and Cu seems to increase the stability of goethite whereas highly domainic materials like GS and GSi (Figure 2) clearly dissolve faster. The decrease of the dissolution rate with increasing Al substitution is in agreement with the results of Schwertmann (1984).

Cobalt retention

The effect of reaction time on the pH dependent sorption of cobalt (the so-called sorption edge) is shown in Figure 3 for the different goethites. At the low Co concentration level in the system (0.05 μmol/g) the sorption edge can be regarded as the so-called limiting curve, the position of which does not change at a further decrease of the Co concentration (Benjamin and Leckie 1981). Furthermore, the low Co concentration ensures sorption far below saturation, since the number of binding sites on Fe oxides corresponds to ~ 5 μmol/ m² (Borggaard 1990), which is orders of magnitude larger than maximum sorption (0.05 μmol/g) in this

study. Although considerably higher degrees of substitution have been reported for Al in goethites (Norrish and Taylor 1961, Schulze and Schwertmann 1984, Kosmas *et al* 1986), incorporation of relatively small amounts was preferred in view of the low contents of Cd and Cu, which can be expected in natural goethites. Thus the relations between structural changes and specific sorption effects caused by different foreign elements were studied at comparable and sufficiently high foreign-element content.

The sorption process appears to be composed of two steps including an initial fast adsorption onto binding sorption sites on the surface followed by a translocation to sites of higher binding energy, e.g., in the interior of the solid phase. With increasing sorption time the curves are displaced to lower pH values, corresponding to more Co being taken up at longer reaction times (Figure 3). The displacement taken as the difference between the pH values at 50% sorption (pH_{50}) after 2 h and 504 h of reaction ranged from 0.2 (GCu) to 1.5 (GCd) pH units. Commonly observed data on the time dependent sorption of Co, other heavy metals and oxyanions by goethite and other Fe oxides lie between these extremes (Bruemmer *et al* 1988, Borggaard 1990, Gerth *et al* 1993). The relative affinity of Co to the different synthetic goethites as expressed by the pH_{50} after 504 h of reaction time decreased in the order GCd(3.9) > GAlc(4.6) = GAlb(4.6) > GAla(4.7) > GS(4.8) > GL(5.0) > GSi(5.1) > GCu(5.9). This means that at constant pH Co sorption decreased in this sequence (Figure 3). From the extreme positions of GCd and GCu it is concluded that incorporated Cd and Cu each had dramatic and completely different effects on the sorption properties of the particular substituted goethite. The extreme octahedral distortion in sample GCu possibly changed the relative positions of the surface hydroxyl groups with negative consequences for the surface complexation of Co. In contrast, Cd substitution strongly increased the reactivity of the surface for Co. By analogy to the almost congruent increase of the unit-cell parameters, it is assumed that the average distances between the surface hydroxyl groups changed accordingly. This possibly created new types of binding sites with a special affinity for certain Co species.

In accordance with slow sorption, the desorption of bound Co is also slow indicating that part of the Co is firmly held, probably at interior rather than outer surface sites. Hence, after 72 h of sorption <10% of the Co could be mobilized by a 72 h desorption with 0.1 M Ca(NO$_3$)$_2$ at pH 5–6.5 (outside this pH range the release percentage was <2). Similar hysteresis was found by Padmanabham (1983).

Obviously, more efficient extractants are needed than Ca(NO$_3$)$_2$ to extract the sorbed Co. This is elucidated by the results in Table 2, where samples, which had been reacted with Co for 24 h, 168 h (data not shown) and 504 h, were extracted by 2 M HCl. Except for the

Cu substituted goethite, approximately ⅓ of the sorbed Co was extracted after 4 h and further 4–25% during a following 48 h treatment. The extractability depended on the sorption time decreasing in the order 24 h > 168 h > 504 h. The extractability of Co in GCu is remarkably low leaving 72–87% unextracted by 2 M HCl (as detected by complete dissolution using HF) compared to 40–46% for GL and ~60% for the other foreign-element substituted goethites.

The Co percentage extracted by 2 M HCl depends on the pH of sorption, or probably more correctly, on the Co loading (Figure 4b). At increasing pH Co loading increases (Figures 3 and 4a) but possibly onto sites of decreasing binding strength as suggested by Benjamin and Leckie (1981) resulting in the observed increased extractability at higher pH (Figure 4b).

The ratios between extracted Co and Fe and between Co and Al, Cd, Cu or Si are considerably higher for the first than for the second period (Table 2) indicating uneven distribution of Co in the goethites. Sorbed Co appears to be somewhat concentrated at more accessible sites. However, 40–87% seems to be randomly distributed within the crystals, inasmuch as this percentage is not released before complete solid dissolution. Undoubtedly most of the more accessible Co has been sorbed by poorly crystalline Fe oxides, since the pools of Fe (and foreign elements) extracted by oxalate and 2 M HCl are in fair agreement and since both extracts exhibit similar enrichment with Al, Cd, Cu and, in particular, Si (Tables 1, 2). A Co enrichment of the poorly crystalline fraction with relatively high surface area seems logical, because the sorption capacity of Fe oxides is roughly determined by their specific surface area (Borggaard 1990).

Exclusion of oxygen during Co sorption had no effect on the amount of Co sorbed by the GL and GCd samples (Figure 4a) indicating that the Co removal from solution during the sorption experiments carried out under atmospheric air as discussed above is a result of sorption and not of oxidation of Co followed by precipitation of Co(III) oxide. However, less sorbed Co was extracted by 2 M HCl from samples, where sorption occurred under aerobic conditions, than from samples run in the argon chamber (Figure 4b). Apparently, the binding strength, and hence inaccessibility, of a minor part of the sorbed Co has increased in the presence of oxygen. The discrepancy between the sorption being unaffected and the extraction behaviour being affected by oxygen is hard to explain. Oxidation of Co(II) to Co(III) to form CoOOH as suggested by Schenck *et al* (1983) could explain the lower extractability from samples exposed to oxygen but this would certainly be reflected in differences between the sorption curves. Thus the different extraction behaviour depending on the presence and absence of oxygen may simply be due to experimental error. However, the possibility of Co oxidation upon sorption cannot be

Table 2. The amounts of Co sorbed from an initial 10^{-7} M solution by the goethites at pH 5 and 6 after 24 h and 504 h reaction time and the percentages of Co, Fe and foreign elements extracted by 2 M HCl after 4 h and 48 h extraction, together with the residual Co released by complete dissolution of the goethites in HF.

Sample	Sorption time (h)	Sorption pH	Total[1] sorption (nmol/g)	2 M HCl extraction time (h)						HF extracted cobalt (%)
				4			48			
				Elements dissolved, in % of total						
				Co	Fe	Foreign[2]	Co	Fe	Foreign[2]	
GS	24	5.5	37.0	35.3	0.24		10.1	0.78		63.0
		6.0	44.0	36.1			10.7			56.0
	504	5.5	48.7	33.9			9.1			55.6
		6.0	49.1	32.6			8.8			57.0
GL	24	5.5	39.4	37.3	0.23		25.9	1.36		42.0
		6.0	45.7	41.1			23.0			40.0
	504	5.5	48.6	35.8			17.6			43.0
		6.0	49.3	37.5			15.3			46.0
GAla	24	5.5	43.2	34.4	0.30	0.78	9.8	0.88	0.93	61.0
		6.0	47.1	32.1			9.6			65.0
	504	5.5	48.6	33.1			8.8			58.0
		6.0	49.6	32.1			7.4			61.0
GAlb	24	5.5	44.6	34.1	0.02	0.52	9.2	0.72	0.70	62.1
		6.0	49.0	31.6			7.8			59.8
	504	5.5	49.0	31.7			8.8			57.6
		6.0	49.2	30.5			6.7			63.9
GAlc	24	5.5	47.0	34.6	0.01	0.51	8.8	0.43	0.47	60.3
		6.0	48.9	31.1			7.7			64.9
	504	5.5	49.2	32.6			6.5			61.8
		6.0	49.6	31.0			6.1			61.1
GCd	24	5.5	45.9	37.9	0.13	0.92	8.1	0.93	1.93	53.1
		6.0	48.2	36.7			7.5			57.3
	504	5.5	46.0	35.4			6.6			63.7
		6.0	49.0	33.3			5.8			63.0
GCu	24	5.5	4.2	11.9	0.49	1.08	2.7	2.05	2.13	86.3
		6.0	17.6	25.6			3.1			73.0
	504	5.5	6.1	11.5			1.9			87.2
		6.0	18.0	25.0			2.2			71.8
GSi	24	5.5	27.5	28.8	0.24	12.2	4.1	1.21	5.3	74.0
		6.0	42.1	31.6			4.0			63.0
	504	5.5	41.7	28.1			3.9			69.0
		6.0	47.9	31.2			3.7			67.0

[1] Interpolated from plots of cobalt sorption versus pH (Figure 3).
[2] Al, Cd, Cu and Si.

excluded. During coprecipitation with Fe, Co added as Co(II) is incorporated as Co(III) into the goethite structure by isomorphous substitution (Gerth 1990).

Micropore diffusion

The slow sorption and strong retention of Co suggest Co uptake by diffusion in micropores and fissures reflecting the presence of structural defects, intergrowths or domains, although to different extent in all the goethites. The possibility of diffusion was evaluated by interpolating sorption data at a certain level of initial sorption (e.g., at the pH of 15% sorption after 2 h) from the curves in Figure 3 and plotting them versus the square root of reaction time as shown in Figure 5. For all goethites except sample GCd linear relationships were obtained which could be described by Equation

1 although linearity, as shown by the dashed lines, did not always apply to the whole reaction time period of 504 h. Thus, the time-dependent increase of Co sorption was apparently controlled by diffusion with the exception of sample GCd (Figure 5). The parameters of the regression equations based on sorption data at the pH of 15% of initial sorption are summarized in Table 3 together with diffusion coefficients D calculated from them using Equation 2. Only the solid-line section of the curves in Figure 5 was used in these calculations. For sample GL sorption data were interpolated at different levels of initial sorption from 5 to 20% to show that the diffusion coefficients are variable to some extent but not as a function of pH. The values are slightly higher than those calculated by Bruemmer et al (1988) for the diffusion of Ni, Zn and Cd into Si-associated
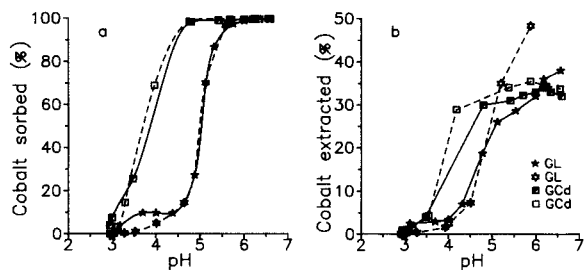
Figure 4. Sorption of Co onto lath-shaped (GL) and Cd-substituted (GCd) goethites after 504 h (a) and Co extracted by 2 M HCl (b), under aerobic (——) and anaerobic (– – –) conditions. Initial Co concentration 10^{-7} M, solid : solution ratios 1:500, background electrolyte 0.1 M Ca(NO$_3$)$_2$.

Table 3. Parameters for equation 1 (M$_0$: in moles·cm^{-2} and k: in moles·m^{-2}·s$^{-1/2}$) and equation 2 (C$_0$: in moles·cm^{-3}, and D: in cm^2·s^{-1}) as calculated from interpolated sorption data at the pH of different % sorption after 2 h (see explanation in text).

Sample	% Sorption (2 h)	pH	M$_0 \times 10^{-14}$	k $\times 10^{-17}$	C$_0 \times 10^{-8}$	D $\times 10^{-18}$
GS	15	5.25	1.44	6.98	2.20	7.91
GL	5	4.81	0.24	1.05	0.71	1.69
	10	4.96	0.45	1.97	1.36	1.44
	15	5.05	0.76	3.05	2.29	1.39
	20	5.11	0.98	3.90	2.95	1.37
GAla	15	4.91	1.68	15.0	1.91	48.3
GAlb	15	4.75	1.85	9.76	2.03	18.2
GAlc	15	4.78	2.15	16.1	2.35	36.8
GCu	15	5.96	0.56	1.58	2.41	0.34
GSi	15	5.34	0.98	12.9	1.50	58.7

goethite ($3 \cdot 10^{-20}$ to $2 \cdot 10^{-19}$ cm^2·s^{-1}) using a different procedure. Between samples the D values vary significantly ranging from $3 \cdot 10^{-19}$ to $6 \cdot 10^{-17}$ cm^2·s^{-1} and can be classified as low (GCu and GL), intermediate (GS) and high (GSi and Al-goethites). These differences probably reflect the amount of structural defects serving as pathways for diffusing metals.

It can be assumed that the needle-like crystals of GCu exhibit the highest degree of structural order due to reduction of crystal growth in the a–b plane and hence fewer defects. The thicker lath-shaped crystallites of sample GL are composed of several needle-like units with partly domainic character which suggests the presence of more defects. Cobalt diffusion into the star-shaped multi-domainic crystals of sample GS is faster because of the numerous micropores between the domains. For sample GSi and the Al substituted

goethites the very high D values can probably be related to numerous defects arising from the occlusion of Si and the incorporation of Al, respectively.

From a practical point of view, Si and Al are the most interesting foreign elements because their association with goethite is common in nature and probably contributes significantly to the time-dependent fixation of trace metals by goethite in soils. The character of the defects in these materials is not well understood but they are likely to be of a similar size as the diffusing ionic species. This is indicated by the difficulty with which bound metals are extracted even after prolonged acid attack using 2 M HCl. Micropore diffusion and immobilization suggest the possibility of solid solution formation by three-dimensional coordination of Co ions in small defects.
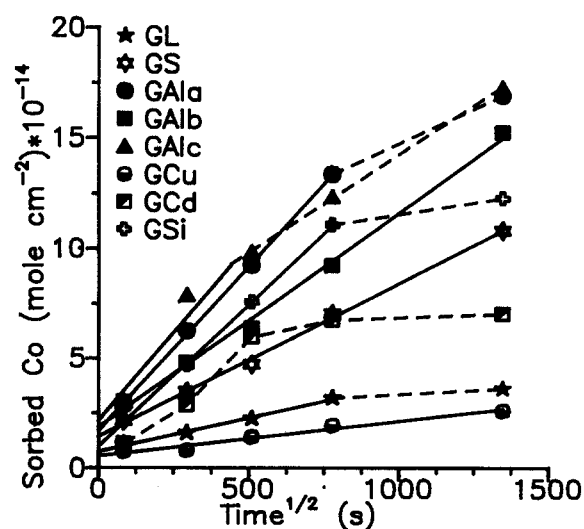

Figure 5. Sorbed Co versus the square root of sorption time; data interpolated at the pH of 15% sorption after 2 h (only the solid parts of lines have been used in the calculations of the diffusion coefficients, see explanation in text).

SUMMARY AND CONCLUSIONS

The binding of trace amounts of Co by goethite is highly affected by the type of foreign-element associated with the goethite crystals. In goethite, Al, Cu and Cd become incorporated by isomorphous substitution while Si is associated by occlusion. Aluminium, Cu and Cd in the structure cause significant structural changes like defects, octahedral distortion and change in the unit-cell parameters. A method designed to synthesize pure lath-shaped goethite yields large multi-domainic laths when Si is added and thin needles on the addition of Cu. The crystals of Cd and Al substituted goethite are lath-shaped but different from pure crystals in length and thickness.

As a result of structural changes and surface modifications, the affinity of Co is highest for Cd- and lowest for Cu-goethite. The time-dependent increase of sorbed Co is also minimal for Cu-goethite and highest for Cd-goethite with intermediate effects for pure, Si associated, and Al substituted materials.

Bound Co is extracted to negligible extent by re-

suspending reacted goethite in freshly added supporting electrolyte for the time period of the sorption step. Cobalt is significantly mobilized only by dissolution of the solid. Using 2 M HCl as an extractant not more than about $\frac{1}{3}$ of the sorbed Co is mobilized after 4 h. Sorbed Co is most difficult to extract from Cu-goethite and most easily extracted from pure lath-shaped material. Proportions of Co not extracted after 48 h range from 40 to more than 80% depending on the type of goethite. Immobilization increases with sorption time.

The time-dependency of sorption can be related to a diffusion of Co into the goethite crystals. Diffusion coefficients (D) range from $0.3 \cdot 10^{-18}$ to $6 \cdot 10^{-17}$ cm$^2 \cdot$ s^{-1} depending on micropores and structural defects in the goethite. Highest D values are found for goethite containing Si and Al, respectively, both of which are commonly associated with goethite in soils. The kind of structural defects created by these two elements is not fully understood and deserves further investigation. The results indicate that incorporated Si or Al can strongly promote the migration and immobilization of trace elements in soil goethite. The difficulty with which Co is re-mobilized after diffusion into the crystal suggests solid-solution formation in the goethite crystal.

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