

SYNTHESIS AND PROPERTIES OF POORLY CRYSTALLINE HYDRATED ALUMINOUS GOETHITES

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Abstract—Al-substituted goethites were prepared by rapid oxidation of mixed $\text{FeCl}_2\text{-AlCl}_3$ solutions at pH 6.8 in the presence of CO_2 at 25°C. A combination of Al substitution and adsorption of CO_2 reduced crystal size (except for an increase at small additions of Al) and produced unusual thin, porous particles. Product goethites had surface areas up to 283 m^2/g and unit-cell expansions induced by hydration. Substitution of Al for Fe reduced the 111 spacing and increased infrared OH-bending vibrational frequencies. Al substitution split the goethite dehydroxylation endotherm during differential thermal analysis into a doublet and increased the temperature of all reactions. Both cold and hot alkali solutions dissolved Al from the goethite structure.

After drying the product in vacuo at 110°C, X-ray powder diffraction data indicated minimal deviation from Vegard's law for the goethite-diaspore solid solution up to about 30 mole % Al substitution. Goethite prepared in the presence of 40 mole % Al had a 111 spacing of 2.403 Å corresponding to 36 mole % structural Al if Vegard's law was obeyed. Rapid oxidation of mixed $\text{FeCl}_2\text{-AlCl}_3$ solutions appears to be conducive to a higher degree of Al substitution in goethite than alkaline aging of hydroxy-Fe(III)-Al coprecipitates.

Key Words—Aluminum, Diaspore, Goethite, Infrared, Synthesis, Vegard's law, X-ray powder diffraction.

INTRODUCTION

Substitution of Fe by Al in the crystal structure of goethite ($\alpha\text{-FeOOH}$) and hematite ($\alpha\text{-Fe}_2\text{O}_3$) is important because: (1) It influences the alkaline extraction of Al from bauxites that contain these minerals (Benešlavsky, 1957; Solymár and Jónás, 1971; Janot and Gilbert, 1970); (2) The degree of substitution can be used to investigate laterite development (Nahon *et al.*, 1977); (3) It correlates with soil color and organic matter accumulation in Oxisols (Fey and le Roux, 1977); and (4) It modifies the surface properties of goethite (Norrish and Taylor, 1961; Golden *et al.*, 1977).

For goethite, Norrish and Taylor (1961) found up to 25 mole % Al substitution by chemical analysis of concentrates obtained from soils after alkaline digestion. By alkaline autoclaving Thiel (1963) synthesized goethite containing up to 33 mole % Al, a level recognized by Schwertmann and Taylor (1977) as the probable upper limit of Al tolerated by the goethite structure. However, as much as 47 mole % Al has been reported for goethites synthesized from sulfate solutions (Bronevoi and Furmakova, 1975). In certain Oxisols, up to 46 mole % Al was measured in dithionite extracts even after correcting for Al removed by a separate treatment with acidified ammonium oxalate (Fey and le Roux, 1977). Thus, the miscibility gap observed by Thiel (1963) for the $\alpha\text{-FeOOH}\text{-}\alpha\text{-AlOOH}$ solid solution may

merely represent the solubility limit of Al-goethite in alkaline media.

Vegard's law states that the lattice parameters of a solid solution series change linearly with composition between those of the pure end members of the series (Klug and Alexander, 1974, p. 562). In practice this law is not always obeyed, and the main problem in the X-ray diffractometric estimation of Al substitution in goethite is that the deviation from Vegard's law measured for soil goethites (Norrish and Taylor, 1961) is greater than that in synthetic goethites (Thiel, 1963). It was therefore considered necessary to test the use of X-ray powder diffraction (XRD) for estimating Al in goethites prepared under controlled condition at a pH prevalent in soils rather than by the usual alkaline aging. The objectives of the present study were to determine (1) the effect of degree of hydration on the unit-cell dimensions of Al-goethite, (2) the effect of pretreatments normally used for removing amorphous material and crystalline hydroxy-Al on the dissolution of Al from goethite, and (3) the relationship between the composition of Al-goethite and unit-cell dimensions and how close this relationship approaches Vegard's law.

MATERIALS AND METHODS

Goethites were prepared by the method of Schwertmann (1959) which employs aqueous oxidation of FeCl_2 in the presence of CO_2 . Weighed quantities of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ were mixed to give Al/(Al + Fe) molar ratios of 0, 5, 10, 20, 30, and 40% and diluted in Pyrex glass beakers to 1200 ml with deionized water such that the final concentration was fixed at

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0.021 M. Each solution was rapidly brought to, and then maintained at pH 6.8 with vigorous stirring using a Metrohm E512/E473/E415 automatic titration system and 5 M KOH as titrant, until the suspension was fully oxidized by an O₂:CO₂ gas mixture of 1:10 to inhibit lepidocrocite formation (Schwertmann and Fitzpatrick, 1977). The gas mixture was introduced through a fritted glass bubbling tube at a rate of approximately 60 ml CO₂/min for pure Fe solution and reduced proportionately for the aluminous solutions so that the period required for complete oxidation was approximately the same (8–10 hr) in each case. After adjusting to pH 6 with HCl, the suspensions were washed by centrifugation until they dispersed in deionized water, equilibrated daily in dialysis tubing with water for 3 days or until the bath was free of excess salt, and then dried by evacuation after freezing in liquid nitrogen.

To determine H₂O content, subsamples were heated at various temperatures in tared, covered, Pt crucibles and weighed after cooling in a desiccator. X-ray powder diffraction (XRD) analysis was made on self-supporting powder mounts, prepared by back-filling and then gently pressing approximately 100 mg of material in aluminum frames against filter paper. A Philips Norelco instrument was used with CuK α radiation and a diffracted beam graphite monochromator.

Changes in size of the goethite unit cell were determined from measured spacings of the 111 reflection (Norrish and Taylor, 1961) using an average of three or four repeated scans made at rates of 0.25 or 0.125°/min. The standard deviation at each measurement was not more than 0.0013 Å. Powdered Pb(NO₃)₂ was periodically employed as an internal standard. The width of the 111 line at half maximum intensity was used to calculate a relative value for mean crystallite dimension (MCD) using the Scherrer formula (Klug and Alexander, 1974, p. 689). Correction for instrumental line broadening was made on the basis of the nearest quartz line obtained from a 1:3 mixture of >1.5- μ m size quartz powder and freeze-dried ferrihydrite.

Diluted aliquots of the original dialysed suspensions were dried on carbon/Formvar-coated grids for examination with a Hitachi HU-11E electron microscope with an accelerating voltage of 75 kV. Surface area was determined by the B.E.T. method after evacuating to 1–2 \times 10⁻⁵ torr at room temperature, then measuring N₂ adsorption gravimetrically. Suspensions containing 5–10 mg of material, dispersed by sonification for \leq 30 sec in 1–2 ml water, were dried on 25-mm AgCl discs and examined with a Perkin-Elmer Model 283 infrared spectrophotometer. Pressed pellets were also prepared for infrared spectroscopy (IR) using a 0.5-mg freeze-dried subsample and 300 mg of KBr.

Selective dissolution analyses were made with acidified ammonium oxalate (Schwertmann, 1964) for 1–2 hr in the dark (5 mg/ml), with 5 N KOH for 1 hr at

70°C (3 mg/ml), and the 5 N NaOH for 2 min at room temperature (3 mg/ml). Residues were centrifuge washed with 1 N KCl and water, dried from acetone at 110°C in vacuo, and analyzed by XRD and IR and for total Fe and Al by atomic absorption analysis (AA) of 6 N HCl solutions obtained by digestion on a steam-plate. Mixed standards were employed (Searle and Daly, 1977), and 1000 ppm K was used to suppress Al ionization.

For differential thermal analysis (DTA), 10-mg subsamples were diluted and mixed with 40 mg of calcined Al₂O₃, equilibrated in vacuo over saturated Mg(NO₃)₂ for 4 days, sandwiched around the thermocouple between layers of alumina, and heated at 10°C/min using a Stone Model KA-2H apparatus with Model J2 furnace assembly. Sample temperature was measured as block temperature.

RESULTS AND DISCUSSION

Examination of the XRD patterns of synthetic preparations (Figure 1) indicates that goethite formed over the whole composition range (0–40 mole % Al/(Al + Fe)); the strength of the 110 line indicates a relatively uniform abundance. No other crystalline material was detected. The XRD reflections at angles greater than 45°2 θ are extremely broad and weak, and, particularly for high Al contents, some of the peaks are barely discernable.

Effect of Al and H₂O on unit-cell parameters

Increasing amounts of Al in the preparations resulted in a shift of the 111 line to higher angles (Figure 1a), indicating the incorporation of Al into the goethite structure (Correns and Engelhardt, 1941; Norrish and Taylor, 1961; Correns and Thiel, 1963; Thiel, 1963; Jónás and Solymár, 1970). Deviation from Vegard's law was substantial (solid circles, Figure 2), particularly for Al contents in excess of 10 mole %. After heating the samples at 110°C for 60 hr a pronounced shift of the 111 goethite line to lower spacings was evident (Figure 1b and open circles, Figure 2), and a sharpening of the peaks occurred suggesting a greater mean crystallite dimension (MCD) (Figure 3). To test whether any of the residual deviation from Vegard's law following this treatment could be attributed to remaining adsorbed water, samples were heated at 110°C for 24 hr in a vacuum oven connected to a conventional mechanical pump; the samples containing 30 and 40 mole % Al shifted further (Figure 2). Following this treatment, the deviation from Vegard's law was small and of similar magnitude to that reported by Thiel (1963). The highly hydrated condition of these goethites appears to have expanded the unit cell in contrast to the reduction caused by Al for Fe substitution. A similar effect with Al-ferrihydrites caused a shift to the broad 2.5-Å maximum to higher values with increasing Al for Fe sub-

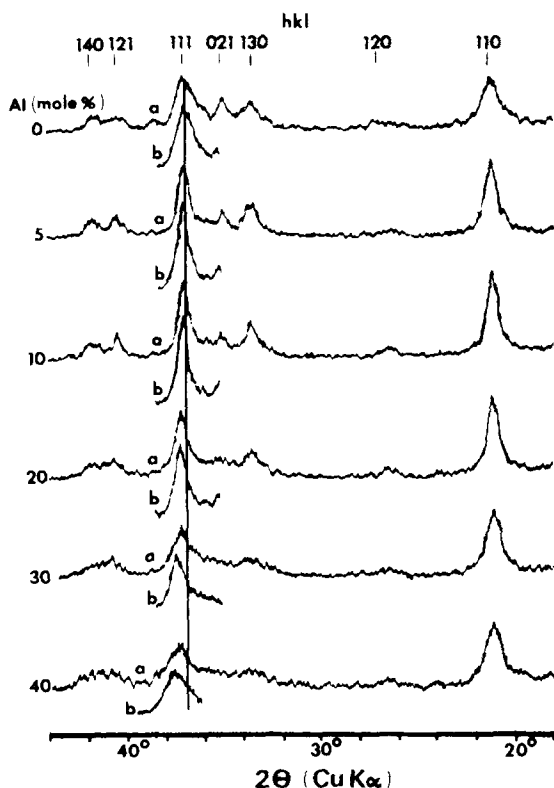


Figure 1. X-ray powder diffraction patterns of synthetic Al-goethites; (a) freeze-dried; (b) after heating at 110°C for 60 hr.

stitution (to be reported elsewhere). Hydration is believed to account for the displacement of the 020 line of boehmite to higher values in pseudoboehmite (Papée *et al.*, 1958) and produced a similar shift of the 020 line in poorly crystalline synthetic lepidocrocite (Cy-Chain Chen and J. B. Dixon, in preparation), and in lepidocrocite embedded in keratose sponges (Towe and Rützel, 1968).

If Vegard's law was obeyed in this system, Figure 2 indicates that the material to which 40 mole % Al was added initially, contained goethite with at least 36 mole % Al, and possibly more if some residual water was still present. Thus, most, if not all of the Al was probably incorporated into the α -FeOOH structure. This conclusion is supported by thermogravimetric data (Table 1) which indicate that the product contained a single hydroxyl for each Fe atom. The difference between theoretical and measured weight loss (about 2% H₂O, column 5) is ascribed to the presence of some residual adsorbed water. The composition of three products was determined by AA analysis of Al and Fe in HCl digests. The lower totals obtained for sample G30Al (Table 2) are possibly due to surface adsorbed carbonate (see below). The calculated molar Al/(Al + Fe) ratios of these products correspond well with those of the initial

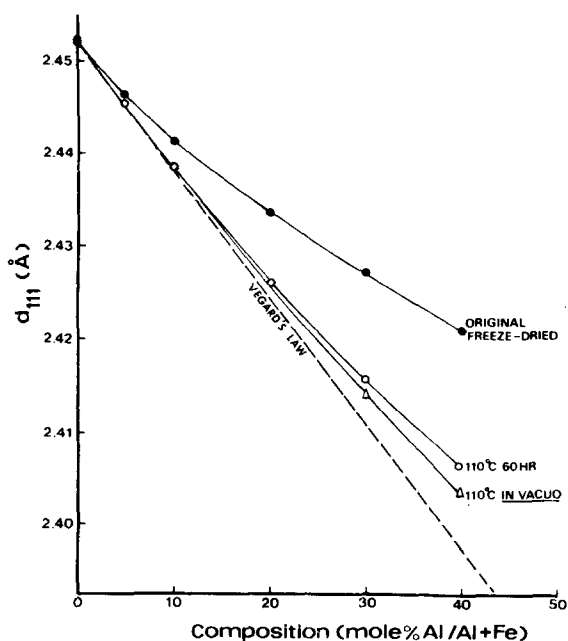


Figure 2. Variation in $d_{(111)}$ for synthetic goethites as a function of Al added to preparation.

solutions from which they were prepared (Table 2, column 1).

The initial purpose of oxalate- and alkali-dissolution treatments was to remove extraneous material (particularly amorphous hydroxy-Al) which was not incorporated into the goethite structure during synthesis, thus permitting a closer estimate of the actual Al content of goethite in the products. From the lower Al contents of the residues (Table 3) it is evident that Al was removed preferentially by all three treatments. Also, both XRD and IR estimates indicated a lower Al/(Al + Fe) in the residual goethite, suggesting that at least some of the dissolved Al originated in the goethite structure. After hot KOH treatment of sample G40Al, a pronounced decrease in XRD line broadening and a sharpening of IR absorption bands occurred, implying that some further crystal growth or the dissolution of finer particles accompanied the removal of Al. In the case of oxalate treatment, on the other hand, the relatively poor agreement between chemical and physical estimates of Al substitution is consistent with possible intercalation of oxalate anions in the goethite, similar to that already noted for adsorbed water, which would have resulted in an underestimation of the degree of Al substitution by XRD and IR (see below). There is, therefore, less certainty as to whether Al was preferentially removed from the goethite structure during oxalate extraction than was removed during alkaline treatments, for which agreement between the three methods is much closer (Table 3). Results to be presented elsewhere indicate that even relatively well-

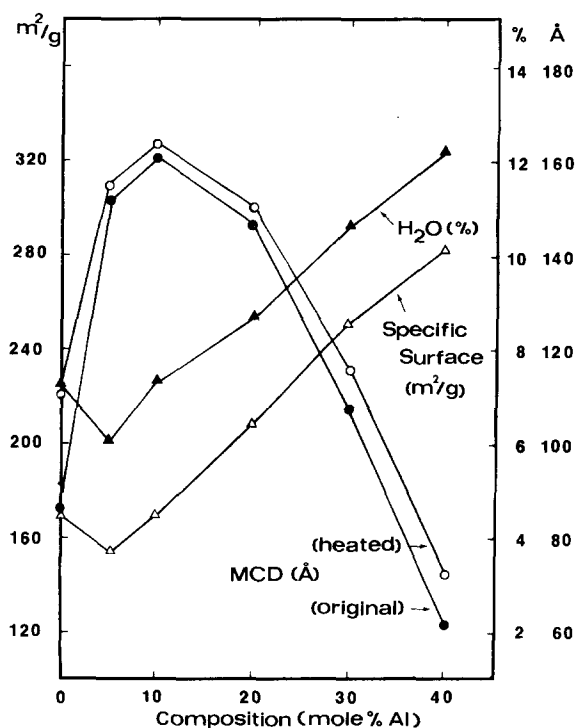


Figure 3. Relationship of mean crystallite dimension (MCD) before and after heating at 110°C for 60 hr, specific surface area, and adsorbed water to composition of synthetic products.

crystallized, naturally occurring Al-goethite will lose some of its Al in strongly alkaline media provided the aluminate concentration in solution is low.

Physical properties of the products

An initially sharp increase in the MCD due to Al addition to the goethites is in agreement with the results

Table 1. Weight loss (%) of synthetic products containing Al-goethite.

Initial composition Al/ (Al + Fe) (mole %)	Weight loss (%)				Theoretical ⁵
	110°C ¹	Evacuation ^{1,2}	110°-200°C ³	110°-300°C ⁴	
0	6.3	7.3	10.6 ⁶	11.7	10.1
5	5.7	6.1	9.5 ⁶	12.5	10.3
10	6.6	7.4	5.7	12.4	10.5
20	7.4	8.7	8.0	12.6	10.8
30	8.4	10.6	7.3	12.8	11.2
40	10.6	12.2	6.6	14.1	11.7

¹ Freeze-dried weight basis.

² Evacuation at room temperature prior to surface area measurements.

³ Based on oven-dry weight at 110°C.

⁴ Calculated on the basis of 110°C evacuated weight.

⁵ H₂O in (Fe_{1-x}Al_x)OOH where x = moles Al.

⁶ Conversion of goethite to hematite took place at 200°C in these samples and at 300°C in the others.

Table 2. Chemical analysis of synthetic Al-goethites.¹

Sample	Fe ₂ O ₃	Al ₂ O ₃	H ₂ O 110°-950°C	H ₂ O 110°C	Total	Molar Al/ (Al + Fe)
G5Al	80.2	2.8	12.2	5.7	100.9	5.4
G30Al	60.5	16.4	14.0	8.4	99.3	29.8
G40Al	51.9	21.9	14.4	10.6	98.8	39.1

¹ Weight percent based on freeze-dried weight.

of Fitzpatrick *et al.* (1978) and Taylor and Schwertmann (1978) for both Ti- and Al-substituted goethites (Figure 3). Between compositions of 20 and 40 mole % Al, a large decrease in MCD took place. The difference in measured MCD values before and after heating presumably resulted from a heterogeneous distribution of adsorbed water within the material. The difference in MCD at low Al contents, for which the goethite spacing had not shifted significantly after heating, implies a condensation of structural units independent of structural dimensions.

The trends in adsorbed water and surface area values closely follow that expected from MCD values. The surface areas of these materials were considerably higher than those commonly measured for synthetic goethites by similar methods (Greenland and Oades, 1968; Atkinson *et al.*, 1977). These high values are attributed in part to the thin, irregular, porous particles that are evident in the electron micrographs.

The effect of Al substitution on morphology was pronounced (Figure 4). Al-free goethite consisted of lenticular particles, each composed of rod-like subunits oriented parallel to its long axis. This striped appearance was also evident in some of the large laths of lepidocrocite (inset) which formed when CO₂ was withheld from the system, as found also by Schwertmann and Fitzpatrick (1977), and is reminiscent of a similar substructure observed by Cornell *et al.* (1974) after the partial dissolution of well-crystallized goethite in HCl and by Watson *et al.* (1962) in crystals of synthetic β-FeOOH. Even if this striated appearance was due to radiation damage in the electron beam, as suggested by Galbraith *et al.* (1979), it was not commonly observed and must therefore be indicative of a distinct substructure because of its regularity.

Products laths of the 5- and 10-mole % Al preparations were more irregular than those prepared in the Al-free system. Furthermore, the linear substructure appeared to be considerably disrupted, with electron-dense domains and adjacent transparent areas forming an overall reticular, spotted pattern. This pattern contrasted with the regularity and compactness of acicular goethite particles formed with 10 mole % Al in the absence of CO₂² and suggests that the unusual morphol-

² Taylor and Schwertmann (1978) also reported the inhibition of lepidocrocite formation by Al in the Fe(II) system.

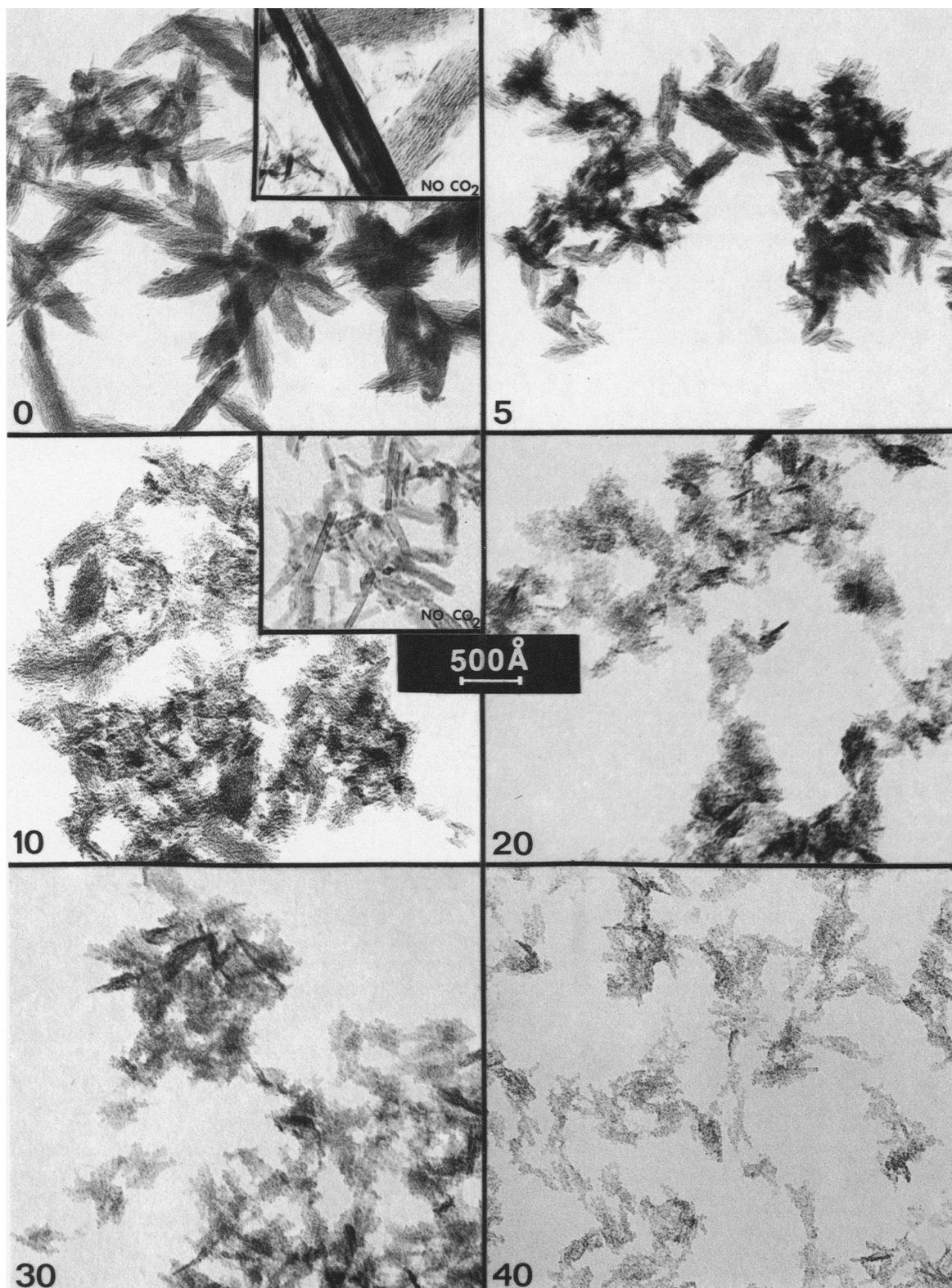


Figure 4. Morphology of synthetic Al-goethites. Numbers indicate preparative Al/(Al + Fe) (mole %). Insets compare products (lepidocrocite and Al-goethite) obtained in the absence of CO₂.

Table 3. Estimates of Al substitution (mole %) in goethite residues from different treatments.

Sample	Original ¹ Al/(Al + Fe)	Treatment	Al/(Al + Fe)		
			Chemical (HCl)	XRD ²	IR ³
G5Al	5.4	Oxalate	5	5	4
G30Al	29.8	Oxalate ⁴	27	23	22
G40Al	39.1	Oxalate	34	26	23
G30Al	29.8	Cold NaOH	20	17	19
G40Al	39.1	Hot KOH	7	10	6

¹ From Table 2.

² Estimated from 111 spacing using curve for 110°C in vacuum treatment in Figure 2.

³ Estimated from 500 cm⁻¹ band position on IR spectra (Figure 6).

⁴ One-hour treatment only.

ogy of these goethites was due to inhibition of crystallization by carbonate, similar to that occurring in hydroxyl-Al systems (Serna *et al.*, 1977). Russell *et al.* (1975) showed that carbonate is adsorbed by goethite from CO₂. IR absorbance peaks of CO₂ were also found in the present study.

Increasing disorder continued as the Al content increased to 40 mole % and was characterized by an almost complete disruption of the chain-like subunits into irregular clusters of nearly spherical particles about 30 Å wide. The small particle size may be due in part to the particle size of the substrate, but the increase in size with Al content is evident in spite of any contribution made by the substrate.

Irrespective of degree of particle regularity, a common and distinct feature of the particles shown in Figure 4 is the presence of electron transparent interstices separating the darker regions. The location of adsorbed water in these interstices could explain the excess water held by the more aluminous goethites (Table 1). Kohyama *et al.* (1978) suggested that the appearance of such interstices in halloysites could be due to dehydration in the electron microscope.

More greatly disordered particles which developed in the presence of 10 mole % Al compared with the pure system did not reflect the increase in MCD (Figure 3). XRD effects presumably arose from the overall structure of the particles whose lath-shaped morphology was increasingly disrupted with greater Al substitution. The increase in less electron-dense Al substituted for Fe contributed to less absorbance contrast in the electron beam.

The breakdown of the linear substructure into very small, equidimensional particles with increasing Al for Fe substitution supports the suggestion of Murphy (1973) that goethite crystals are composed of coalesced linear arrays of tiny (15–30 Å) spherical polycations. It is also in agreement with the findings of Thiel (1963) and Weed *et al.* (1976) that the primary morphological change resulting from Al substitution in acicular goe-

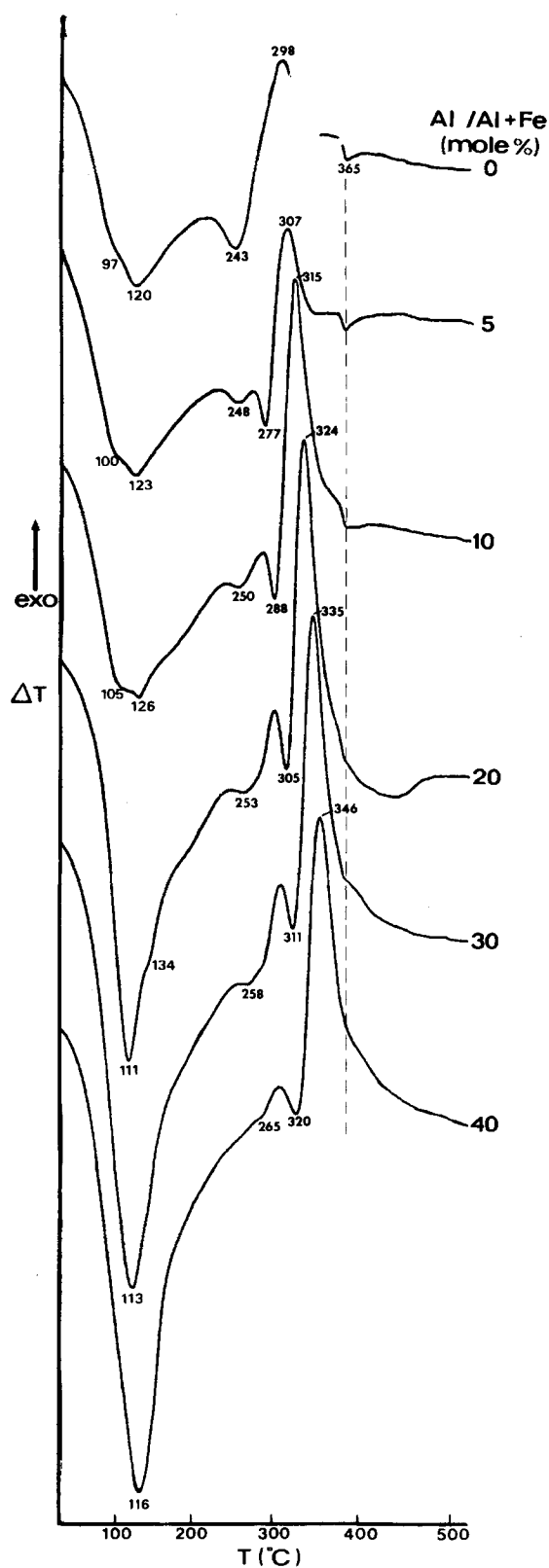


Figure 5. Differential thermal analysis curves for synthetic Al-goethites.

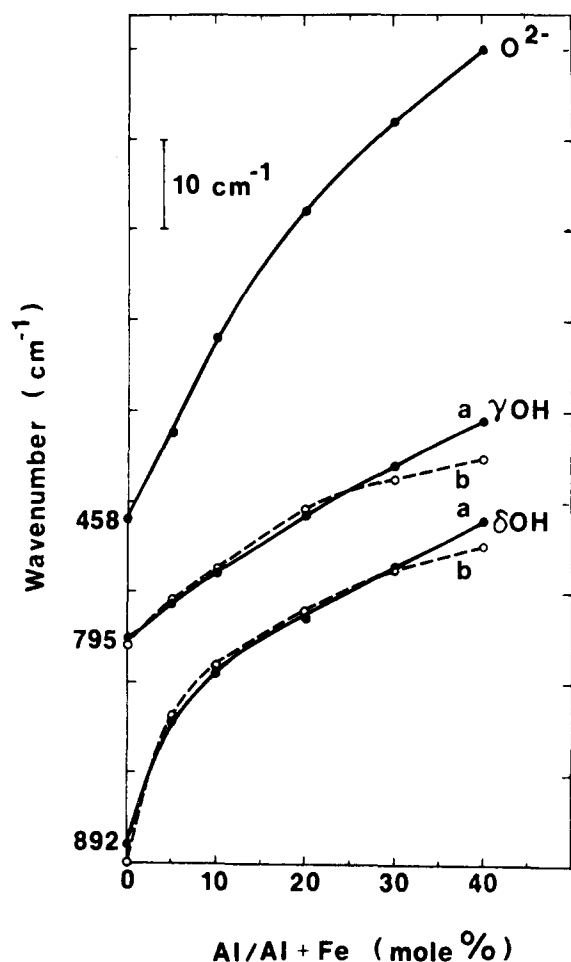


Figure 6. Frequency of goethite infrared absorption bands in the 900, 800, and 500 cm^{-1} regions as a function of Al content during synthesis. (a) KBr pellets; (b) air-dry films on AgCl.

thite is a preferential shortening in the *c* or needle-axis direction (van Oosterhout, 1960).

Differential thermal analysis

The most important features on DTA curves of the products (Figure 5) are: (1) a shoulder on the low temperature side of the first endotherm which became larger and eventually obscured the original peak as the Al content increased; (2) the splitting of the dehydroxylation endotherm at 250°–300°C into a doublet as a result of Al substitution; (3) an exotherm immediately following the latter, which became larger with increasing Al content; and (4) a shift of all peaks to progressively higher temperatures as Al increased. (The small apparent endothermic effect at 365°C is of instrumental origin unrelated to the sample).

Feature (1) suggests that two types of adsorbed water were present with different affinities for the surface, such that the more weakly adsorbed water (97°–116°C endotherm) increased in both quantity and strength of

Table 4. IR vibration frequencies of oxalate adsorbed on goethite as a function of Al substitution.

Sample	Al/(Al + Fe) ¹ (mole %)	Vibration frequency (cm^{-1})		
		I	II	III
G5Al	5	1710	1682	1402
G30Al	27	1723	1698	1415
G40Al	34	1725	1700	1418

¹ By HCl dissolution and atomic absorption.

adsorption as the Al content increased, and that the more strongly adsorbed component (120°–134°C endotherm) became less significant and difficult to resolve in the products with high Al content. This behavior may possibly be related to an additional, distinct type of adsorbed water associated with interstices in the granular particles discussed above. The shape of the curves between the low-temperature dehydration endotherm and the dehydroxylation reaction indicates that some residual adsorbed water was probably still being expelled from the structure up to the onset of dehydroxylation.

Feature (2) probably reflects the substitution of Al for Fe, as only a single dehydroxylation peak can be observed in the DTA pattern of Al-free goethite at 243°C. The temperature of the first peak of the doublet increased from 248° to 265°C with increasing Al substitution, and the second peak had a corresponding temperature range of 277°–320°C. The first peak probably had the same origin as the 243°C peak of pure goethite, whereas the second peak was possibly due to expulsion of hydroxyl associated with structural Al. This doublet could only be resolved by packing the sample close to the thermocouple; however, it was not merely a geometric effect because only one peak is present on the thermogram of the Al-free goethite. Norrish and Taylor (1961) mentioned a similar doublet for natural specimens of Al-goethite, and Kelly (1956) found that artificial mixtures of two goethites of different crystallinity also gave doublets in this region. The usual decrease in the temperature of goethite decomposition with particle size reduction (MacKenzie, 1957, p. 301) seems to be counteracted by the increased thermal stability imparted by Al incorporation into the structure, as noted by de Villiers and van Rooyen (1967) for lepidocrocite.

The exothermic peak between 298° and 346°C showed the same temperature variation with Al content as did the second peak of the lower temperature (endothermic) doublet (in contrast to the first peak of the doublet which exhibited only about half the increase in temperature over the 0–40 mole % Al range). Because no lepidocrocite was present, the exotherm may be due to the transformation of ferrihydrite to hematite (MacKenzie, 1957). However, Weiser and Milligan (1940; cited in MacKenzie, 1957) showed by electron diffraction that some ferrihydrite-like gels consist of microcrystalline hematite. Thus, the exotherm may be

due as much to crystal growth and structural perfection as it is to crystallization per se. Hematite formed by thermal decomposition of goethite (Rooksby, 1961) has a very small ultimate crystal size (i.e., the goethite particles transform pseudomorphically to multi-domain polycrystallites of hematite), and only with further heating is the hematite structure perfected to give a regular periodicity. Therefore, if the initial goethite particles were sufficiently finely divided, the resultant fine hematite particles might have undergone a further, spontaneous crystallization to a stage dictated by the prevailing temperature. Conceivably such a reaction would be exothermic. This hypothesis is in agreement with the increasing size of the exotherm as Al content increased to 20 mole %. The decrease in size of the exotherm for the 40 mole % Al sample may be due to a cancellation by the adjacent endotherm. Also, further crystal growth of hematite as postulated above may have been inhibited by the additional Al present in the goethite. Aluminum hydroxide gels do not exhibit a similar exotherm on their heating curves and are thus excluded (MacKenzie, 1957, p. 319).

Infrared spectroscopy

The OH-stretching band of goethite at 3180 cm^{-1} became broader but did not change frequency with increasing Al substitution (data not shown). On the other hand, the OH-bending vibration bands at ~ 900 and 800 cm^{-1} and the stronger band at 450 cm^{-1} shifted to higher frequencies as a result of Al substitution (Figure 6). Residues from oxalate treatment produced three bands in the $1700\text{--}1400\text{ cm}^{-1}$ region, and the absorption frequency of each band increased with Al substitution (Table 4) which corresponds with the higher frequencies for oxalate adsorption on gibbsite than on goethite surfaces (Parfitt *et al.*, 1977a, 1977b).

Aluminum substitution increased the frequency of the three major goethite absorption bands in the longer wavelength region (Figure 6). At lower Al contents, the data for samples dispersed in KBr pellets (a) are essentially the same as those for air-dried films on AgCl discs (b). However, with 30 and 40 mole % Al in the product, the vibrational frequencies for air-dried samples appeared to be less affected by Al substitution than those for the pelletized samples. This situation is analogous to the difference in XRD data before and after heating at 110°C in vacuo (Figure 2), and suggests that adsorbed water may have been responsible for the difference in the IR data (evacuation during pellet pressing would have removed much of the water otherwise present in air-dried films). This suggestion was confirmed by sedimenting the sample containing 40 mole % Al onto an AgCl disc, which was then placed in an evacuable glass cell fitted with Irtran windows. Using the same pump employed during pellet pressing, evacuation of the cell for 10 min produced an upward shift in δOH of about

4 cm^{-1} , which corresponds closely with the difference observed in Figure 6 (curves a and b).

With increasing Al substitution the goethite absorption maxima moved towards those of diasporite (1073 and 969 cm^{-1} for the OH-bending vibrations; Ryskin, 1974), though at different rates (Figure 6). Since the separation of these two peaks is of the same magnitude in both diasporite and goethite, Al substitution affected in-plane (δOH) vibrations more than out-of-plane (γOH) vibrations. The increased frequency in going from goethite to diasporite can be ascribed to a shortening (and thus strengthening) of the hydrogen bonds (Schwartzmann and Sparr, 1969). The difference in the shift of these two vibration modes may be due to the decrease in particle size with ionic substitution (Figure 4), because the data of Caillère and Pobeguín (1966) indicate that in diasporite there is a similarly large displacement of δOH relative to γOH when Fe substitutes for Al. It is assumed that the band at $450\text{--}550\text{ cm}^{-1}$ is due to oxygen-displacement (Farmer, 1974). It is both stronger and more sensitive to the degree of Al substitution (Figure 6) than either of the OH-bending vibrations. Its relationship to Al content was therefore used to estimate the degree of Al substitution in residues from various selective dissolution treatments (Table 3). The effect of decreasing cell size with Al substitution was presumably counteracted by water adsorbed in interstitial positions, and thus produced the differences in curves a and b of Figure 6 at high Al contents. The apparent underestimation (Table 3) of Al substitution in residues from oxalate treatments by both XRD and IR (see above), may be explained, therefore, by an intercalation reaction with the relatively large amount of adsorbed oxalate substituting for ligand adsorbed water, and thus having an effect similar to that of water on both XRD spacings and IR vibration frequencies.

Over a narrower range of Al substitution (4–22 mole %), Jónás and Solymár (1970) observed an approximately linear relationship between the δOH band frequency and Al substitution which was, however, moderately sensitive to morphological changes. The present results confirm the conclusion of Farmer (1974) that although IR spectroscopy is useful in detecting the formation of a solid solution, it is usually a poor indicator of its limits.

Hydration properties in natural goethites similar to those reported here have not been detected. The distinctive morphology of these synthetic Al-goethites may be partly responsible for their hydration characteristics. The high surface area of these goethites appears to be due in part to the influence of carbonate adsorbed on the goethite surface during crystal growth. This might represent a realistic simulation of other foreign ion effects (i.e., silicate, phosphate) during goethite formation in soils. In terms of current theories concerning the variation of specific anion adsorption

with pH (Hingston *et al.*, 1968), the common acicular morphology of goethite prepared by Greenland and Oades (1968) from Fe(III) precipitated in sodium carbonate solution could be explained by minimal adsorption of carbonate under the more alkaline pH conditions of their experiments.

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Резюме—Al-замещенные гетиты были приготовлены путем быстрого окисления смешанных растворов FeCl₂-AlCl₃ при pH = 6,8 в присутствии CO₂ при температуре 25°C. Сочетание замещения Al и адсорбции CO₂ уменьшало размер кристаллов (исключая их увеличение при малых добавках Al) и производило необычно тонкие, пористые частицы. Полученные гетиты имели площади поверхности до 283 м²/г и расширение элементарных ячеек, вызванное гидратацией. Замещение алюминия ферритом уменьшило 111 параметр решетки и увеличило инфракрасные OH-изгибающие колебательные частоты. Замещение Al расщепило эндотермальные кривые дегидроксиляции гетита во время дифференциального термического анализа в дуплет и увеличило температуру всех реакций. Оба, холодный и горячий щелочные растворы вытесняли Al из структуры гетита. После высушивания продукта в вакууме при 110°C, данные по рентгеновской порошковой дифракции показали минимальное отклонение от закона Вегарда для твердых растворов гетита-диаспора до около 30 молярных % замещения Al. Гетит, приготовленный в присутствии 40 молярных % Al, имел 111 расстояние, равное 2,403 Å, что соответствует 36 молярных % структурного Al, если применить закон Вегарда. Быстрое окисление смешанных растворов FeCl₂-AlCl₃ может скорее привести к замещению Al в гетите, чем щелочное старение совместных осадков гидрокси-Fe(III)-Al. [E.C.]

Resümee—Al-substituierte Goethite wurden durch schnelle Oxidation von FeCl₂-AlCl₃-Lösungsgemischen bei pH 6,8 und bei der Anwesenheit von CO₂ bei 25°C hergestellt. Eine Kombination von Al-Substitution und CO₂-Adsorption reduzierte die Kristallgröße (ausgenommen einer Vergrößerung der Kristalle bei geringer Al-Zugabe) und erzeugte ungewöhnlich dünne, poröse Partikel. Die erzeugten Goethite hatten eine Oberfläche bis zu 283 m²/g und zeigten Vergrößerungen der Einheitszelle aufgrund von Hydratation. Die Substitution von Al für Fe reduzierte den 111-Abstand und vergrößerte die OH-Deformations-schwingungsfrequenzen im Infrarot. Bei der Differentialthermoanalyse wurde die Dehydroxylierungs-Endotherme des Goethit durch Al-Substitution in ein Dublett aufgespalten und erhöhte die Temperatur aller Reaktionen. Sowohl kalte als auch heiße Alkali-Lösungen lösten Aluminium aus der Goethitstruktur.

Röntgenpulverdiffraktometer-Daten zeigten nach dem Trocknen des Produktes im Vakuum bei 110°C eine minimale Abweichung von Vegard'schen Gesetz für Goethit-Diaspor-Mischkristalle bis zu 30 Mol-% Al-Substitution. Goethit, der in der Anwesenheit von 40 Mol-% Al hergestellt wurde, hatte einen 111-Abstand von 2,403 Å, was bei Gültigkeit des Vegard'schen Gesetzes 36 Mol-% Al in der Struktur entspräche. Die schnelle Oxidation von FeCl₂-AlCl₃-Lösungsgemischen scheint für eine höhergradige Al-Substitution im Goethit förderlicher zu sein als die Alterung durch alkalische Lösungen von Hydroxy-Fe(III)-Al-Mischfällungen. [U.W.]

Résumé—Des goethites substituées à l'Al ont été préparées par oxidation rapide de solutions mélangées FeCl₂-AlCl₃ à un pH de 6,8 en présence de CO₂ à 25°C. Une combinaison de substitution à Al et d'adsorption de CO₂ a réduit la taille du cristal (sauf pour un agrandissement lors de l'addition de petites quantités d'Al) et a produit des particules rares, minces, et poreuses. Les goethites produites avaient des aires de surface jusqu'à 283 m²/g et des expansions de maille induites par hydratation. La substitution d'Al à Fe a réduit l'espacement (111) et a accru les fréquences vibrationnelles pliant OH de l'infrarouge. La substitution d'Al a divisé l'endotherme de déshydroxylation de la goethite pendant l'analyse thermique différentielle en un doublet et a accru la température de toutes les réactions. Des solutions chaudes et froides alcalines ont dissolu l'Al de la structure de la goethite.

Après avoir séché le produit in vacuo à 110°C, des données de diffraction poudrée aux rayons-X ont indiqué une déviation minimale de la loi de Vegard pour la solution solide goethite-diaspore jusqu'à près de 30 mole % de substitution d'Al. La goethite préparée en présence de 40 mole % d'Al avait un espacement (111) de 2,403 Å correspondant à 36 mole % d'Al structural si la loi Vegard était suivie. L'oxidation rapide de solutions mélangées FeCl₂-AlCl₃ semble être plus favorable à un plus haut degré de substitution d'Al dans la goethite que le vieillissement alcalin de coprécipités hydroxy-Fe(III)-Al. [D.J.]