

THE INFLUENCE OF ALUMINUM ON IRON OXIDES. PART II. PREPARATION AND PROPERTIES OF Al-SUBSTITUTED HEMATITES

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Abstract—Aluminum-substituted hematites ($\text{Fe}_{2-x}\text{Al}_x\text{O}_3$) were synthesized from Fe-Al coprecipitates at pH 5.5, 7.0, and in 10^{-1} , 10^{-2} , and 10^{-3} M KOH at 70°C. As little as 1 mole % Al suppressed goethite completely at pH 7 whereas in KOH higher Al concentrations were necessary. Al substitution as determined chemically and by XRD line shift was related to Al addition up to a maximum of 16–17 mole %. The relationship between the crystallographic a_c parameter and Al substitution deviated from the Vegard rule. At low substitution crystallinity of the hematites was improved whereas higher substitution impeded crystal growth in the crystallographic z -direction as indicated by differential XRD line broadening. At still higher Al addition crystal growth was strongly retarded. The initial Al-Fe coprecipitate behaved differently from a mechanical mixture of the respective “hydroxides” and was, therefore, considered an aluminous ferrihydrite.

Key Words—Aluminum, Ferrihydrite, Goethite, Hematite, Iron.

INTRODUCTION

Most pedogenic minerals form from solution. Parent minerals continuously supply the necessary constituents to the soil solution from which the new minerals are synthesized by precipitation. Because the soil solution usually contains foreign ions and molecules, the final nature of the pedogenic neoformation is often markedly different from what would be expected from a pure system with no extraneous components. For example the mineral type and composition may be altered or crystal development may be impeded in one or more directions. In some cases complete inhibition of crystallization may occur.

The effect of Al on the pedogenic formation of Fe-oxides (=all compounds in the system Fe–O–H) gives a good example of this influence of foreign ions in the soil solution. Irrespective of whether the Si level is above or below the limit (~ 1 ppm SiO_2) for clay silicate formation, any Al present in the system still exerts some influence on the iron oxides being produced concurrently.

Al substitution in sedimentary (Correns and Engelhardt, 1941) and soil goethites (Norrish and Taylor, 1961) is the best known example of this interaction of Al on Fe-oxide formation. Aluminum-substituted hematites have been found in bauxites (Beneslavsky, 1957; Janot and Gibert, 1970; Perinet and Lafont, 1972, 1972a) and in soils (Nahon, 1976; Schwertmann et al., 1977). Aluminum-substituted hematites have also been synthesized by several workers, generally by heating mixtures of freshly precipitated oxides at high temper-

atures ($\sim 1000^\circ\text{C}$) (see v. Steinwehr, 1967) but only occasionally at temperatures at or below 100°C by aging coprecipitates under conditions more relevant to pedogenesis (Callière et al., 1960; Gastuche et al., 1964, Wolska, 1976).

This paper presents results of similar low temperature syntheses of aluminiferous hematites and discusses the effect of Al on the formation and on the nature and properties of synthetic Fe(III)oxides.

MATERIALS AND METHODS

Three aging series were prepared:

(1) Series 1: 5 mmoles of Fe + Al (from nitrates) were coprecipitated with 0, 5, 15, and 30 mole % Al at pH 7, washed salt free and kept for 34 days in 100 ml water at 70°C at pH 5.5 and 7.0.

(2) Series 2: As before, but with 15 mmoles of Al + Fe in 250 ml and 16 steps of Al addition between 0 and 35 mole % kept for 77 days at pH 7.

(3) Series 3: 5 moles of Fe as $\text{Fe}(\text{NO}_3)_3$ was added to a standard solution of potassium aluminate in 10^{-3} , and 10^{-2} , and 10^{-1} M KOH. In all cases the amount of Al was at least half that of Fe so that changes in the Al concentration during crystal growth would be slight. At lower Al concentration the volume was, therefore, increased. The samples were kept for 14 days at 70°C.

Samples were washed and dried at 60°C. Prior to further analysis residual ferrihydrite was removed with pH 3.0 NH_4 oxalate and solid $\text{Al}(\text{OH})_3$ phases by a 1-hr treatment of 300 mg of sample with 5 N NaOH at 70°C. Milder NaOH treatments were not successful as indicated by XRD after treatment. The cell parameters of hematites were calculated from d -spacings of the (300) and the (214) X-ray powder diffraction peaks after correction by reference to the 2θ value of the (511) peak of admixed 20% $\text{Pb}(\text{NO}_3)_2$. The peaks were recorded at a goniometer speed of $\frac{1}{4}^\circ 2\theta/\text{min}$. Due to strong line

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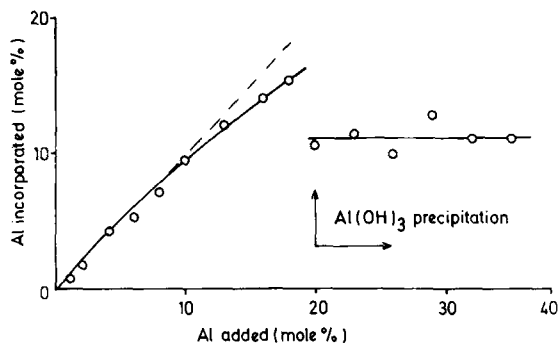


Figure 1. Al addition and Al substitution in synthetic hematites.

broadening in many samples accuracy of line position measurements is limited.

The widths at half height (WHH) were determined for as many peaks as possible and these values were empirically corrected for instrumental and α_1 - α_2 dispersion broadening by reference to the 2θ -WHH function of the well crystalline $\text{Pb}(\text{NO}_3)_2$ which exhibits no line broadening due to particle size or disorder.

Differential thermograms of freshly precipitated ferrihydrites were run with a Linseis instrument using approximately 60-mg samples and a heating rate of $10^\circ\text{C}/\text{min}$. The temperature was calibrated with KNO_3 and quartz.

Fe and Al were determined by atomic absorption both after dissolution in HCl for total compositions or in pH 3.0 NH_4 oxalate for the selective dissolution of ferrihydrite (Schwertmann, 1964).

RESULTS AND DISCUSSION

Mineralogy of the end product

As indicated by Fe_0/Fe_t values which were <0.01 , crystallization of the Fe-oxides was essentially complete in series 1 at 5 mole % Al addition after 34 days and in series 2 at ≤ 10 mole % addition after 77 days (Table 1). Only hematite was formed except at zero Al addition where 10–20% goethite was formed as well. An addition of only 1 mole % Al completely suppressed the goethite. A suppressing effect of small amounts of Al on goethite was also described by Gastuche et al. (1964) and Wolska (1976).

At Al additions between 20 and 35 mole % Al, transformation of ferrihydrite to hematite was increasingly incomplete (see Fe_0/Fe_t in Table 1) (Wolska, 1976). Also, increasing amounts of bayerite and gibbsite were formed. In series 1 crystallization is slower at pH 5.5 than at pH 7.

Because high alkalinity strongly favors goethite formation from ferrihydrite, much higher Al concentrations are necessary in KOH than in water to suppress the goethite completely (series 3, Table 2). In 10^{-3} M KOH pure hematite was only formed at $>2 \cdot 10^{-3}$ M Al whereas in 10^{-2} M KOH goethite could always be de-

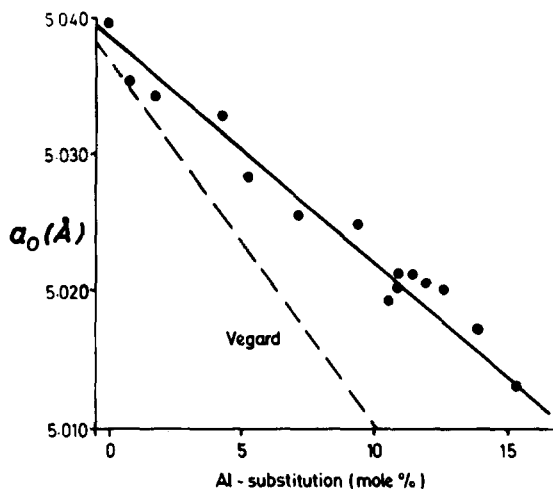


Figure 2. Al substitution and a_0 parameter of synthetic hematites.

tected up to an Al concentration of 10^{-2} M (Lewis and Schwertmann, in prep.). As seen from the Fe_0/Fe_t data crystallization was much more complete than at pH 7 (series 1 and 2) in spite of higher Al concentrations but a weak trend for a retarding influence of Al was also noticeable from slightly increasing Fe_0/Fe_t values with increasing Al concentration.

Aluminum substitution

The Al added and Al incorporated into the hematite as determined chemically after removal of external Al are closely related (Figure 1). The relationship is slightly curved. At 18 mole % Al addition a maximum sub-

Table 1. Properties of aging products from Al ferrihydrite after 77 days of aging at pH 7 and 70°C .

Al added mole %	Mineralogy ¹	Properties of Al-hematite				
		Fe_0/Fe_t	$\text{Al}_0/\text{Al}_0 + \text{Fe}_0$	Al substitution mole %	a_0 (Å)	MCD ± 0.01 (Å)
0	H,g	0.005	—	0	5.0395	402
1	H	0.010	—	0.8	5.0353	534
2	H	0.006	—	1.8	5.0342	769
4	H	0.006	—	4.3	5.0328	549
6	H	0.007	—	5.3	5.0283	671
8	H	0.014	—	7.2	5.0255	509
10	H	0.008	—	9.5	5.0249	272
13	H,f	0.14	0.10	12.0	5.0210	n.d.
16	H,f	0.31	0.13	14.0	5.0171	73
18	H,F	0.48	0.15	15.4	5.0129	57
20	H,F,b,gi	0.56	0.15	10.6	5.0191	94
23	H,f,b,gi	0.36	0.15	11.5	5.0210	n.d.
26	H,F,b,gi	0.55	0.14	10.0	5.0182	n.d.
29	H,f,b,gi	0.20	0.15	12.7	5.0198	95
32	H,F,b,gi	0.41	0.17	11.0	5.0188	79
35	H,f,B,gi	0.23	0.17	11.0	5.0213	144

¹ H = hematite; g = goethite; F,f = ferrihydrite; gi = gibbsite; B,b = bayerite. Capital letter indicates dominant, small letters indicate subdominant.

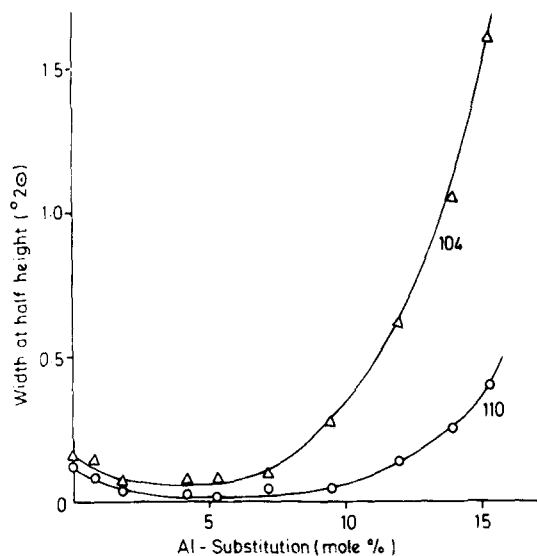


Figure 3. Al substitution and width at half height of the (104) and (110) line of synthetic hematites.

stitution of about 16 mole % is reached (series 2). Above 18 mole % addition, crystalline $\text{Al}(\text{OH})_3$ is formed as a separate phase and the Al substitution falls off to a somewhat lower but nearly constant value at about 11–12%. A constant Al mole % of approximately 15% was also found in the remaining ferrihydrite. The $\text{Al}(\text{OH})_3$ phase obviously acts as a competitor for Al.

The same upper limit of about 15% substitution was also found in the 10^{-3} M KOH run of series 3 (Table 2). This is not surprising because the Al added was always greater than 18 mole %.

A similar upper limit of substitution (between 15 and 18%) was obtained by Muan and Gee (1956) and by v. Steinwehr (1967) in hematites prepared at 1000°C . Wefers (1967) found minimum a_0 (from 300) values of 5.012

Table 2. Properties of aging products from ferrihydrite in 10^{-1} – 10^{-3} M KOH aluminate solutions at 70°C after 14 days.

Experimental conditions			Properties of end product				
Al conc. M	KOH conc. M	Al/Al + Fe mole % added	Fe_0/Fe_t	Mineralogy ¹	Al/Al + Fe mole % incorporated	a_0 of hem. (Å)	WHH ² (214)/(300)
$2 \cdot 10^{-3}$	10^{-3}	44.4	n.d.	H,gi	14.9	5.020	1.30
$3 \cdot 10^{-3}$	10^{-3}	37.5	0.09	H,(gi)	14.0	5.020	1.28
$4 \cdot 10^{-3}$	10^{-3}	44.4	0.11	H,gi	15.4	5.018	1.38
$5 \cdot 10^{-3}$	10^{-3}	50.0	0.06	H,gi,b	14.7	5.017	1.49
$2 \cdot 10^{-3}$	10^{-2}	44.4	n.d.	G,H	12.4	5.036	1.09
$4 \cdot 10^{-3}$	10^{-2}	44.4	0.004	H,g	11.6	5.034	1.03
$6 \cdot 10^{-3}$	10^{-2}	54.5	0.02	H,g	12.7	5.030	1.13
$8 \cdot 10^{-3}$	10^{-2}	66.5	0.06	H,g	13.2	5.028	1.09
	10^{-2}	66.7	0.08	H,(g)	13.9	5.019	1.17
$3 \cdot 10^{-2}$	10^{-1}	75.0	n.d.	H,g	13.4	5.031	1.13

¹ See Table 1.

² Width at half height.

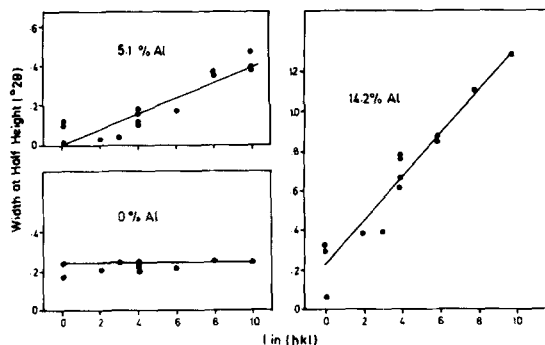


Figure 4. Relationship between width at half height and l in (hkl) of synthetic hematites with varying Al substitution.

Å at 250°C from which he probably underestimated Al substitution to $\approx 10\%$ because of using the Vegard rule (see below). The lowest a_0 found by Wolska (1976) was also 5.012 Å. It seems, therefore, that the hematite structure tolerates only half as much Al substitution as the goethite structure where 33% seems to be an upper limit (Thiel, 1963). This is confirmed by the 10^{-2} M KOH series in which, however, the Al content as determined chemically cannot be used to measure substitution in hematite because Al substituted goethites occur as an impurity. From the position of their (111) line these goethites are more highly substituted ($\approx 30\%$) than the hematites.

Unit-cell parameters of hematites

All the XRD lines measured show a consistent and regular decrease of their corresponding d-spacings. The same applies to the a_0 values as calculated from the (300) line (Figure 2). The trend in the c_0 values is not as clear and the scattering is much higher than with a_0 . This is due mainly to the broadening of the (214) peak used for calculation of c_0 .

In spite of the scattering, it appears that the decrease in a_0 with increasing Al substitution is less than expected from a linear relationship between hematite and corundum (Vegard rule). A consistent although smaller deviation from the Vegard rule was also measured for Al hematites produced at 1000°C (v. Steinwehr, 1967) whereas for low temperature Al hematites Callière et al. (1960) and Wolska (1976) found an even higher and nonlinear deviation. If real, this higher deviation must, therefore, be due to the mode of formation at low temperature. The geometrical and chemical reasons for a deviation from the Vegard rule are extensively discussed by v. Steinwehr (1967).

Al substitution as taken from the unit cell parameter only slightly increases with Al concentration in the 10^{-3} M KOH series but is more pronounced in the 10^{-2} M KOH series. Although the absorption bands are broadened, preliminary IR measurements clearly indicate a trend for a decrease in wave numbers of all three Fe–O vi-

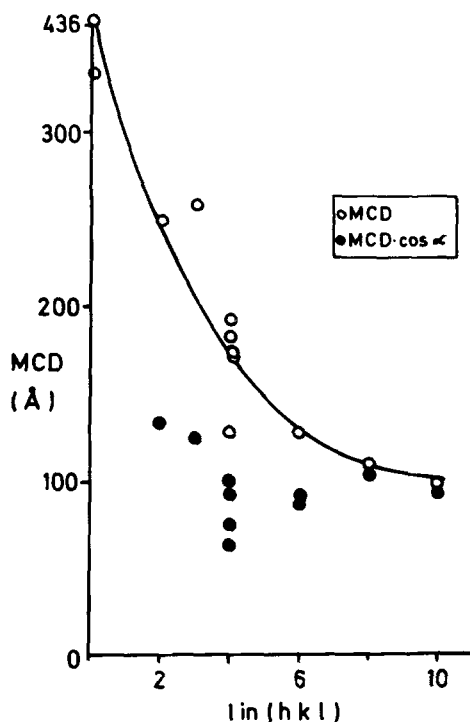


Figure 5. Relationship between mean crystallite dimension (MCD) and l in (hkl) before and after angular correction of synthetic hematites.

bration modes due to Al substitution. This means that the absorption bands do not move towards corundum (442, 569, 635 cm^{-1}) as does the unit cell size. An explanation for this (M. Sayin, pers. comm.) might be that the smaller Al cation attracts O from the neighboring Fe-O_6 -octahedron thereby lengthening the Fe-O bond.

Crystallinity

The influence of Al on the crystallinity (morphology and disorder) of hematites can be seen from a more detailed consideration of the corrected XRD line width at half height (WHH). The WHH of a particular line shows an interesting dependence on Al substitution (Figure 3). The WHH of all lines, irrespective of whether they correspond to near-basal (104) or nonbasal (110) planes show a minimum between 3 and 5% substitution. This indicates that a certain, although low, substitution improves crystallization. It suggests a lattice strain relief through small amounts of the smaller Al cation in the octahedral position. A similar observation was made for synthetic goethites (to be published elsewhere). At higher substitution, the lines become increasingly broader.

From Figure 3 it also becomes obvious, that not all the lines are equally broad. Such a *differential line broadening* of hematites was noticed by Perinet and Lafont (1972). A measurement of up to 16 lines shows that line width of Al-substituted hematites but not of

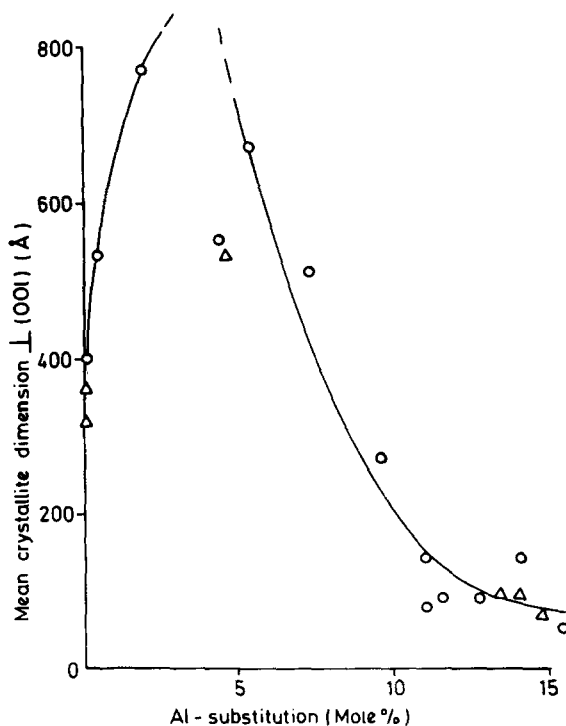


Figure 6. Al substitution and mean crystallite dimension perpendicular to (001) of synthetic hematites.

unsubstituted ones increases significantly with increasing l in (hkl) (Figure 4). This relationship can be interpreted simply as a *reduced* growth of the hematite crystal in the z -direction in the presence of Al. The result would be that a particular diffraction line is broader the more it approaches (001), i.e., with increasing l in (hkl). An analogous case was demonstrated by Klug and Alexander (1974) for platy $\text{Ni}(\text{OH})_2$.

Although aging time was shorter, differential line broadening was less expressed (10^{-3} M KOH) or even absent (10^{-2} M KOH) in series 3 indicating the better conditions for crystallization at higher alkalinity (Table 2). In order to estimate the so-called mean crystallite dimension (MCD) in the z -direction, i.e., the thickness of the plates, the Scherrer formula was used for 11 measurable lines with $l \neq 0$ and the resulting MCD values were corrected for their angular position with regard to (001). This was simply done by multiplying MCD with $\cos \alpha$ where α is the angle between the plane chosen and the 001 plane.²

As seen from Figure 5 the angular correction evens out most of the dependence of MCD on l and yields

$$^2 \text{MCD}_{\perp(001)} = \frac{0.9 \cdot \lambda \cdot 54.7}{b \cdot \cos \theta} \cdot \cos \alpha$$

where MCD is the mean crystallite dimension (Å), λ the wavelength of X-radiation, b the corrected half width, θ the Bragg angle of the line used, and α the angle between the plane chosen and the 001 plane.

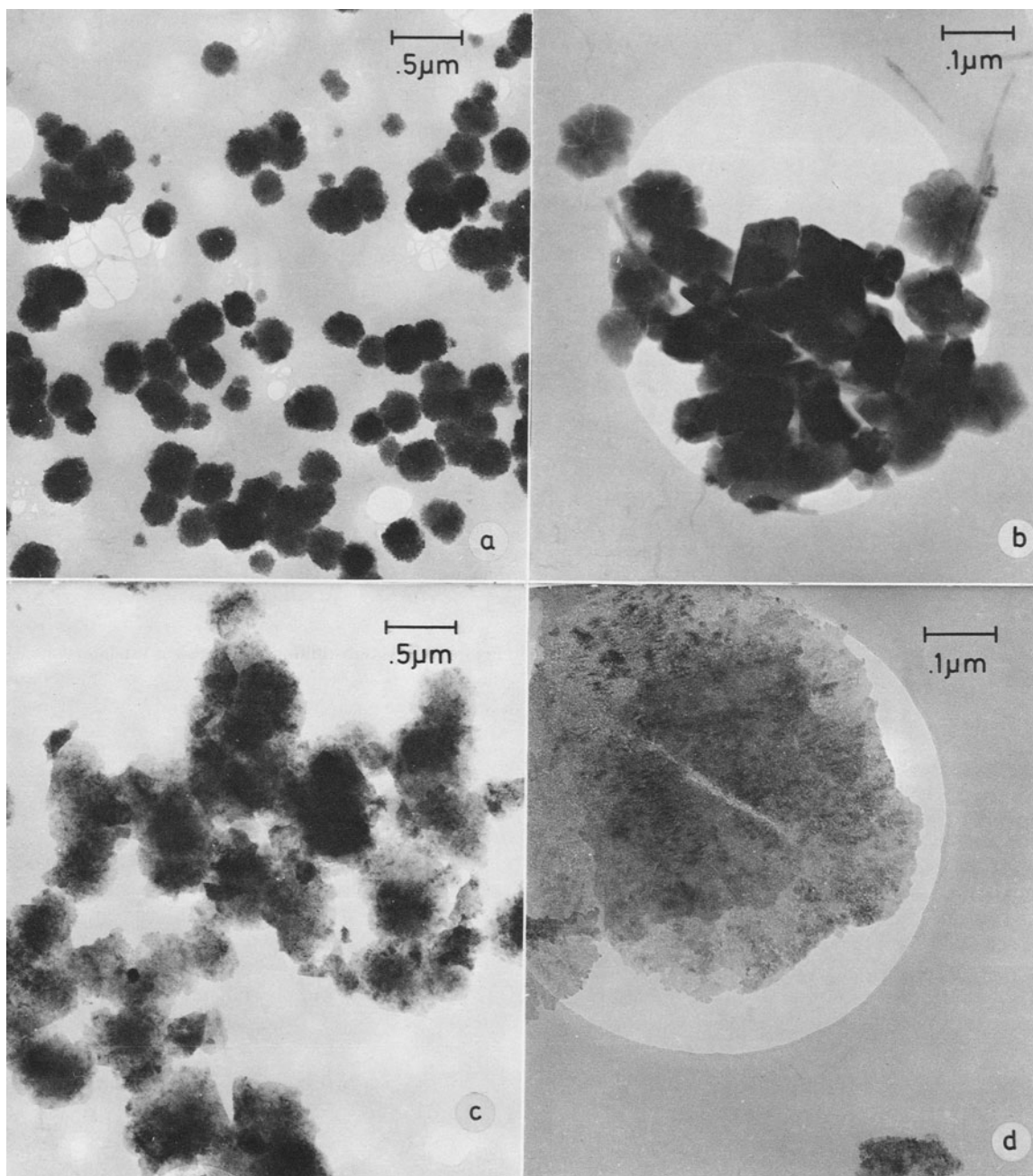


Figure 7. Electron micrographs of synthetic hematites of different Al substitution (mole %). 7a: 1.8; 7b: 0.8; 7c: 15.4; 7d: 13.4%.

similar MCD values for all lines. These MCD values depended clearly on Al substitution (Figure 6) indicating that crystal growth is particularly influenced by Al in the z-direction (the thickness of the plate), whereas the growth in the x- and y-direction, i.e., the size of the plate, is much less influenced. Again, a maximum occurs between 3 and 5% substitution.

By contrast, an *enhanced* rather than a reduced

growth of hematite in the z-direction which led to needlelike crystals was found earlier and was probably caused by blocking the prismatic faces through preferential adsorption of citrate anions (Schwertmann et al., 1968). A preferential adsorption of fulvic and humic acid on prismatic faces of gibbsite was recently observed by Parfitt et al. (1977).

The influence of Al on crystal growth is well reflected

Table 3. Total and oxalate-soluble Fe and exothermic peak temperature (DTA) of freshly precipitated aluminous ferrihydrite.¹

Al _i (mole %)	Fe _t (%)	Fe _o (%)		Fe _o /Fe _t		Exothermic peak tem- perature °C
		2 hr	5 min	2 hr	5 min	
0	57.8	58.9	52.1	1.02	0.90	316
5.5	50.3	50.8	42.2	1.01	0.84	384
10.6	52.5	52.4	39.6	1.00	0.76	438
15.2	45.9	45.8	39.8	1.00	0.87	474
17.5	43.6	42.9	32.8	0.98	0.75	514
20.8	44.5	43.8	30.5	0.98	0.69	564

¹ Fe_t = total Fe; Fe_o = oxalate-soluble Fe.

in electron micrographs. Platy crystals, 150–300 nm in diameter with lobed but sharp edges prevail throughout. They appear thicker at lower Al substitution (Figure 7a) but become increasingly thinner and larger as substitution increases (Figures 7c, d), illustrating the preferential growth \perp to (001). At low substitution, thicker and much smaller (50–100 nm) hexagonal or rhombohedral plates with smooth edges occur in addition and also transitional forms with hexagonal outline but lobed edges (Figure 7b). A few lenticular crystals uncommon for hematite were also formed (not shown) in agreement with the results of Biaïs et al. (1973).

Properties of the precursor: Al-ferrihydrite

The precursor of Al hematite appears to be an aluminous ferrihydrite although the existence of such a phase has not yet been established. Indication from XRD is difficult to obtain because of extremely low crystallinity. However, as shown from Figure 8, fresh coprecipitates of Al and Fe "hydroxide" show a strong increase of the exothermic peak temperature with increasing Al content from 316°C at zero Al to 564°C at 25 mole % added Al, whereas the endothermic peak temperature is fairly constant (141–154°C). Also, the exothermic peak becomes progressively weaker and broader. This does not apply to mechanical mixtures of these phases. A further shift of these peaks to even higher temperatures (up to 650°C) occurred after 92 days of aging under water at pH 7, indicating further stabilization of the aluminous ferrihydrites. During this time a separate Al phase (mainly gibbsite) forms only when ≥ 25 mole % Al is added.

The stabilizing effect of Al on ferrihydrite is also seen from its oxalate solubility. Although still completely soluble after 2 hr of extraction a much shorter extraction (5 min) shows a definite trend for lower solubility of the freshly precipitated products with increasing Al content (Table 3).

CONCLUSIONS

Generally, with increasing amounts of added Al, increasing proportions are incorporated into the hematite

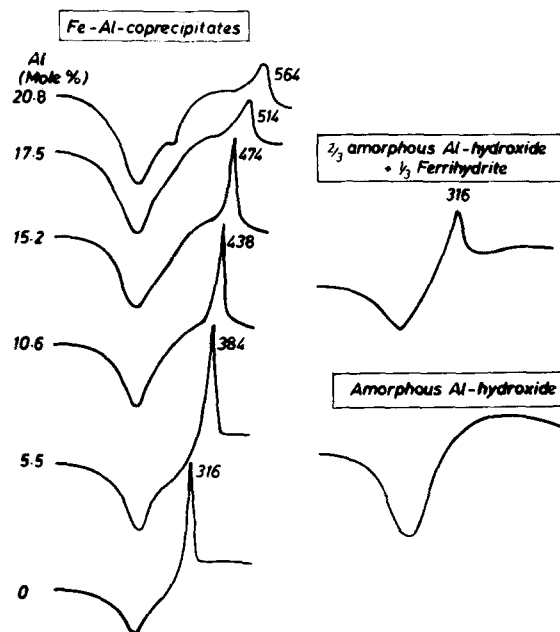


Figure 8. DTA thermograms for Al ferrihydrites with increasing Al content.

structure. However, for the same amount of added Al, the extent of incorporation and the effect on crystallization varies with the form of Al and the pH of the system. An effective way to incorporate Al is obviously to start with a coprecipitate, i.e., with an aluminous ferrihydrite, and maintain a pH during aging close to minimum solubility, i.e., around pH 7–8. Aging at pH 4 or in highly alkaline medium is less effective. Also, a separate solid Al phase, e.g., amorphous Al hydroxide, gibbsite, or clay silicates, is less efficient in supplying Al (to be published elsewhere). This indicates, in connection with d.t.a. and solubility data (Table 1), that the coprecipitate is not purely a mechanical mixture of the respective oxides but possibly an Al-substituted ferrihydrite.

Goethite and hematite do not appear to form from ferrihydrite by the same mechanism. Goethite is apparently formed from Al-ferrihydrite through a solution phase and can, therefore, incorporate Al from a surrounding Al-containing solution (to be published elsewhere). In contrast, it was shown earlier, that hematite is nucleated and formed within ferrihydrite aggregates (Fischer and Schwertmann, 1975). The presence of ferrihydrite around the growing hematite crystal apparently isolates the crystal from the surrounding solution so that Al from solution is less likely to be incorporated into the growing crystal than Al coprecipitated with the ferrihydrite.

At low substitution, Al seems to have a favorable effect on crystallization, whereas increasing substitution leads to retarded growth in the z-direction and/or structural disorder and finally inhibition or severe re-

tardation of hematite crystallization. As found earlier with citrate (Schwertmann et al., 1968) crystal morphology is strongly influenced by Al through an alteration of the relative growth rate along the various crystallographic directions.

Experiments are under way to find out if surface properties of Al substituted hematites such as zero point of charge and specific adsorption are also influenced by Al substitution.

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Резюме—Гематиты (Fe_{2-x}Al_xO₃) с замещающим алюминием были синтезированы путем соосаждения Fe-Al при pH равном 5,5 и 7,0 и в 10⁻¹, 10⁻², и 10⁻³ М КОН при 70°C. Всего лишь 1 моль-% Al полностью подавлял гетит при pH = 7, в то время как в КОН необходимы более высокие концентрации Al. Замещение Al, как определяется химически и по линейному смещению в методе дифракции рентгеновских лучей (ДРЛ), зависит от добавления Al до максимум 16–17 моле-%. Соотношение между кристаллографическим параметром a₀ и замещением Al отклоняется от правила Vegarda. При низком замещении кристалличность гематитов улучшалась в то время как при более значительном замещении рост кристалла происходил в кристаллографическом z-направлений, как следовало из дифференциального линейного расширения в методе ДРЛ. При еще более значительном добавлении Al рост кристаллов резко замедлялся. Изначально совместно осажденный Al-Fe вел себя не так как механическая смесь соответствующих "гидроокисей" и, таким образом, рассматривается как алюминиевый железогидрит.

Résumé—Aus Fe–Al-Koppräzipitaten wurden Al-substituierte Hämatite ($\text{Fe}_{2-x}\text{Al}_x\text{O}_3$) bei pH 5,5 und 7,0 und in 0,1, 0,01, und 0,001 M KOH bei 70°C synthetisiert. Nur 1 Mol-% Al genügte, um bei pH 7 Goethit vollständig zu unterdrücken, während dazu in KOH sehr viel höhere Al-Konzentrationen nötig waren. Die Al-Substitution—chemisch und röntgenographisch bestimmt—war bis 16–17 Mol-% mit der Al-Zugabe korreliert. Die Beziehung zwischen dem a_0 der Hämatitzelle und der Al-Substitution wich von der Vegard-Regel ab. Bei tiefer Substitution wurde die Kristallinität der Hämatite verbessert, bei höherer das Wachstum in der kristallographischen Z-Richtung behindert, angezeigt durch differentielle Röntgenliniengreiterung. Bei noch höherem Al-Zusatz wird die Kristallisation bei pH 7 sehr stark verzögert. Der Ausgangs-Koppräzipitat verhielt sich anders als ein mechanisches Gemisch der beiden Hydroxide und ist daher offenbar ein Al-substituierter Ferrihydrit.

Résumé—Des hématites substituées d'aluminium ($\text{Fe}_{2-x}\text{Al}_x\text{O}_3$) ont été synthétisées de coprécipités de Fe–Al à des pH de 5,5, 7,0, et à 10^{-1} , 10^{-2} , et 10^{-3} M KOH à 70°C. Une môle-% d'Al a suffi à complètement supprimer la goéthite à un pH de 7, tandis que des concentrations plus élevées de Al étaient nécessaires pour KOH. La substitution d'Al déterminée chimiquement et par décalage de droite de diffraction aux rayons-X est apparentée à l'addition d'Al jusqu'à un maximum de 16–17%. La parenté entre le paramètre cristallographique a_0 et la substitution d'Al a dévié de la règle de Vegard. A substitution basse, la cristallinité des hématites était améliorée, tandis qu'à des niveaux de substitution plus élevés, la croissance de cristaux était réprimée dans la direction cristallographique z, comme l'indique l'élargissement différentiel des droites de diffraction aux rayons-X.