

THE INFLUENCE OF ALUMINUM ON IRON OXIDES. VIII. UNIT-CELL DIMENSIONS OF Al-SUBSTITUTED GOETHITES AND ESTIMATION OF Al FROM THEM

D. G. SCHULZE¹

Institut für Bodenkunde, Technische Universität München
8050 Freising-Weihenstephan, Federal Republic of Germany

Abstract—The unit-cell dimensions of synthetic, Al-substituted goethites showed that the *c* dimension is a linear function of Al substitution in the range 0–33 mole % Al, but that the *a* dimension is variable over this same range. The *b* dimension is also linearly related to Al substitution but is slightly more variable than the *c* dimension for Al substitutions of 20–33 mole %. The variability of the *a* dimension is postulated to be the result of structural defects. An improved procedure for estimating Al substitution from x-ray powder diffraction positions requires (1) calculation of the *c* dimension from the positions of the 110 and 111 diffraction lines using the formula: $c = (1/d(111)^2 - 1/d(110)^2)^{-1/2}$, and (2) estimation of Al substitution from the relationship: mole % Al = 1730 – 572.0*c*. The 95% confidence interval of the estimate is ±2.6 mole % Al when using this procedure, in contrast to ±4.0 mole % Al when the position of the 111 reflection alone is used.

Key Words—Aluminum, Goethite, Iron, Unit-cell dimensions, X-ray powder diffraction.

INTRODUCTION

The ionic substitution of aluminum for iron in goethite is well documented and has been shown to occur in goethites from soils (Norrish and Taylor, 1961; Janot *et al.*, 1971; Davey *et al.*, 1975; Nahon *et al.*, 1977; Bigham *et al.*, 1978; Fitzpatrick, 1978; Mendelovici *et al.*, 1979; Torrent *et al.*, 1980; Fitzpatrick and Schwertmann, 1981; Kämpf, 1981), oolitic iron ores (Scheiderhöhn, 1964; Schellmann, 1964), and bauxites (Jónás and Solymár, 1970). Al-substituted goethites can also be easily synthesized in the laboratory (Thiel, 1963; Jónás and Solymár, 1970; Golden, 1978; Lewis and Schwertmann, 1979a, 1979b; Fey and Dixon, 1981). Goethite is the most ubiquitous of the iron oxide minerals in soils and occurs in almost every type of soil environment (Schwertmann and Taylor, 1977). Al substitution ranges from zero to about 33 mole %. Fitzpatrick and Schwertmann (1981) showed that the amount of Al substitution in goethite varies among different soil environments and that Al substitution may be an indicator of past or present pedogenic conditions.

The Al³⁺ ion is slightly smaller than the Fe³⁺ ion, 0.53 Å vs. 0.65 Å (Shannon and Prewitt, 1969); thus, when Al substitutes for Fe in the goethite structure, the average size of the unit cell decreases. All other things being equal, the unit-cell size is related to the amount of Al substitution and is indicated by shifts of the goethite X-ray diffraction lines to smaller d-values.

Thiel (1963) studied Al-substituted goethites syn-

thesized under hydrothermal conditions at high pH and found that d(111) and the unit-cell dimensions decreased linearly with Al substitution. Jónás and Solymár (1970) attempted to duplicate the relationships found by Thiel, but on a plot of d(111) vs. mole % Al, their data deviated considerably from those of Thiel. They attributed the deviation to extra Al present as “amorphous free aluminum hydroxide” which they believed could not be completely washed out of their samples before analysis, but they gave no additional evidence for the existence of the extra Al. My measurements of d(111) and mole % Al for synthetic, Al-substituted goethites also deviated from those of Thiel (1963) and Jónás and Solymár (1971). For some synthesis series the data appeared to fall on a curve rather than the straight line predicted by Thiel, thereby casting doubt on the validity of the assumption that the unit-cell dimensions decrease linearly with Al substitution. Taylor and Schwertmann (1978) reported data which showed d(110) to be more variable than d(111) and d(130) for several Al-substituted goethites synthesized from the Fe²⁺ system. Their data suggested that the *a* dimension was the reason for the variability.

The shift of X-ray diffraction lines, particularly the 111 line (Norrish and Taylor, 1961), has commonly been used to estimate Al substitution in unknown goethites. Regression lines calculated from data for synthetic, Al-substituted goethites, particularly the data from Thiel (1963), are usually used as “standard” curves. This procedure could be in error if d(111) is influenced by factors other than Al substitution.

The purpose of this study was: (1) to determine why some goethite diffraction lines vary for samples with the same amount of Al substitution, and (2) to develop

¹ Present address: Department of Agronomy, Purdue University, West Lafayette, Indiana, 47907.

Table 1. Methods used to synthesize the goethites.

Sample	Procedure
<i>Synthesis from Fe³⁺ systems</i>	
31/0-31/7	Fe(NO ₃) ₃ and Al(NO ₃) ₃ solutions were precipitated using KOH and kept in 0.3 M KOH at 70°C for 14 days (Lewis and Schwertmann, 1979b; Schulze, 1982).
28/0-28/20	Fe(NO ₃) ₃ and Al(NO ₃) ₃ solutions were precipitated using KOH and kept in 0.35-0.4 M KOH at 70° for 14 days (Lewis and Schwertmann, 1979b; Schulze, 1982).
12/0-12/20	Fe(NO ₃) ₃ and Al(NO ₃) ₃ solutions were precipitated using NH ₃ , washed free of electrolytes, then kept in 2 M KOH at 70°C for 8 days (Lewis and Schwertmann, 1979b).
DL/9-DL/11	Fe(NO ₃) ₃ and Al(NO ₃) ₃ solutions were precipitated using KOH and kept in 0.1 M KOH at room temperature for 3 years (Lewis and Schwertmann, 1979b).
G-NK1	An Fe(NO ₃) ₃ solution was precipitated by adding NaOH pellets for a molar ratio of 1:3 (Fe:OH), then kept at 25°C for 14 days.
P24	Exact procedure was not known, but was similar to above in that Fe-hydroxide gel was kept in KOH.
<i>Synthesis from Fe²⁺ systems</i>	
3/0, 3/5, 4/10-4/33	FeCl ₂ -AlCl ₃ -NaHCO ₃ solutions were oxidized by bubbling air through them. pH rose from 7 to 8.2 during the reaction (Goodman and Lewis, 1981).
P146, P147, P150	FeCl ₂ solutions were oxidized by bubbling mixtures of O ₂ and CO ₂ through them. The pH was kept between 6 and 7 with NH ₄ OH (Schwertmann, 1959).
2(B)3	An FeCl ₂ -AlCl ₃ solution was adjusted to pH 11 with KOH, then slowly oxidized at room temperature over a period of 60 days by opening the bottle and swirling the contents once a day (Goodman and Lewis, 1981).

a better way of estimating Al substitution from X-ray powder diffraction line positions.

MATERIALS AND METHODS

Samples

Synthetic, Al-substituted goethites were used for this study because Al substitution in pure samples can be accurately determined after dissolution of the goethite. Brief descriptions of the synthesis procedures along with pertinent references are given in Table 1. The range in X-ray diffraction patterns from the different synthesis procedures is illustrated in Figure 1. In general, goethites from the Fe³⁺ system had sharper X-ray diffraction lines than goethites from the Fe²⁺ system.

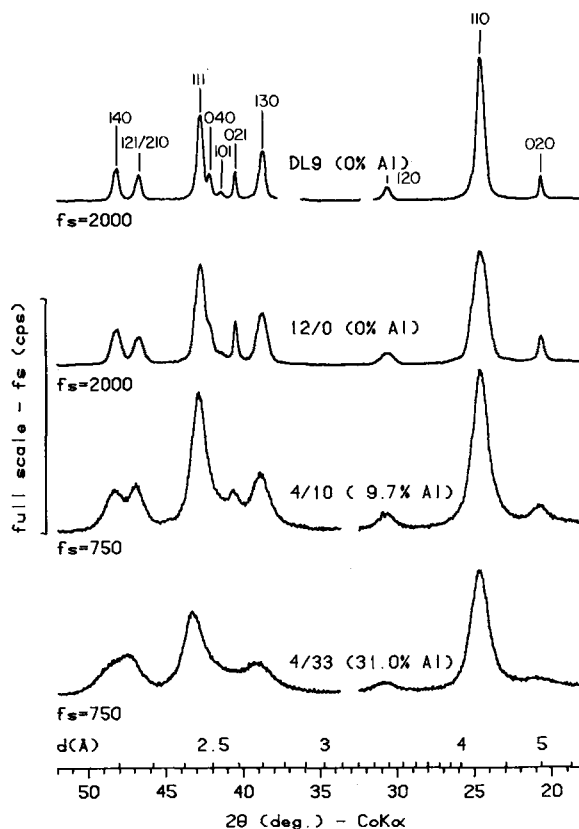


Figure 1. Representative X-ray powder diffraction diagrams covering the range of synthetic goethites studied. Peak designations give the Miller indices (*hkl*) of the lines.

X-ray powder diffraction

Instrumental. Self-supporting powder mounts were prepared by first gently grinding the sample in an agate mortar to break up large aggregates, then back-filling 150-200 mg of sample into an Al sample holder (11 × 20 mm sample area) and gently pressing the material against unglazed paper to minimize preferred orientation. Samples prepared in this way had a flat surface which appeared homogeneous and almost smooth to the naked eye. X-ray powder diffraction (XRD) data were obtained using CoK α radiation (35 kV, 25 ma) and a Philips PW 1050 vertical goniometer equipped with a 1° divergence slit, a 0.2 mm receiving slit, a 1° scatter slit, a diffracted-beam graphite monochromator, and a proportional detector. The XRD patterns were obtained by step-scanning from 18° to 52°2 θ at 0.02° or 0.01°2 θ increments using a counting time of 10 sec per increment. The maximum counting rate was <4000 counts/sec so that no dead-time correction was necessary. The digitized data were recorded on punched paper tape for input into a computer.

Measurement of XRD line positions. Special care was taken to measure the line positions because it was un-

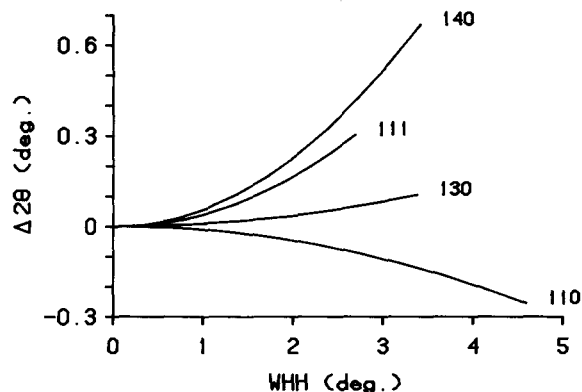


Figure 2. Curves relating line shift due to diffraction from small particles for selected goethite lines. These curves were calculated assuming crystallites with the same number of unit cells along the *a* and *b* axes but infinitely many along the *c* axis.

certain at the beginning of the study whether the observed variation in line positions was due to errors of measurement or to real differences in the samples. Gaussian-Cauchy curves were fitted to the data using a program developed by Janik and Raupach (1977) which was modified for X-ray data and for a Cyber 175 computer. Estimates of the height, width at half-height (WHH), and position of each peak were entered into the program, along with estimates for the baseline and relative amounts of Gaussian and Cauchy components (curve shape). The program then optimized these parameters using a least squares procedure. Plots of the observed and calculated patterns were made to assess visually the validity of the fitted parameters.

Goniometer calibration. The goniometer was carefully aligned according to the manufacturer's instructions. The 2θ scale was calibrated using powdered silicon metal (SRM640 from the National Bureau of Standards, Washington, D.C.) as an external standard. The maximum error of the 2θ scale was estimated to be $\pm 0.02^\circ 2\theta$.

Some samples were run using Si metal, reagent grade NaCl, or α - Al_2O_3 as an internal standard, but no significant differences were found between the same samples measured by both the external and internal standard methods.

Calculation of the unit-cell dimensions. XRD line positions can shift appreciably if diffraction occurs from very small particles (see Brindley, 1980, 128–132 for a review). These line shifts can occur if either the Lorentz-polarization factor, the structure factor, or both are not essentially constant over the angular range of a broad diffraction line. The influence of the Lorentz-polarization factor is greatest at small diffraction angles, and consequently its influence on the position of

Table 2. Corrections to observed 110, 111, and 130 line positions for line shifts caused by diffraction from small crystallites. The corrections are calculated for $\text{CoK}\alpha$ radiation.

WHH _{cor} ($^\circ 2\theta$) ¹	Correction ($^\circ 2\theta$)		
	110	111	130
0.1	0	0	0
0.2	0	0	0
0.3	0	0	0
0.4	0	0.01	0
0.5	0	0.01	0
0.6	0	0.02	0
0.7	-0.01	0.02	0
0.8	-0.01	0.03	0.01
0.9	-0.01	0.04	0.01
1.0	-0.01	0.05	0.01
1.1	-0.01	0.06	0.01
1.2	-0.02	0.07	0.01
1.3	-0.02	0.08	0.02
1.4	-0.02	0.09	0.02
1.5	-0.03	0.10	0.02

¹ WHH corrected for instrumental line broadening.

the goethite diffraction lines, which occur at $>20^\circ 2\theta$ for $\text{CoK}\alpha$ radiation, is minimal. The structure factor, however, can be important at any diffraction angle, and it accounts for shifts in broad diffraction lines at higher angles. Some of the goethites studied had very broad diffraction lines (Figure 1) and line shifts were expected.

Curves relating diffraction lines shifts to width at half-height (WHH) were calculated assuming goethite particles with the same finite number of unit cells along the *a*- and *b*-axes but infinitely many unit cells along the *c*-axis (Figure 2). Details of the calculation were given by Schulze (1982). These curves were used to correct the observed line positions and the corrected positions were used to calculate the *d*-values for each line. Values from Figure 2 for the 110, 130, and 111 lines are given in tabular form in Table 2 for the range in WHHs generally found for soil goethites.

The observed WHHs, *B*(obs), were corrected for instrumental line broadening, *b*, using the relationship: $B = B(\text{obs}) - b$, where *B* is the diffraction line broadening. The instrumental broadening was obtained from 20–5- μm quartz sand. This correction assumes that the line profiles have Cauchy shapes (Klug and Alexander, 1974, p. 635). This assumption is justified because the curve-fitting program showed that for most samples the diffraction lines were best fit by curves with Cauchy components >0.5 (1.0 being pure Cauchy).

The *d*-values for the 110, 130, and 111 lines were used to calculate the unit-cell dimensions (Table 3). The positions of these three lines could be determined accurately for all samples even when the lines were very broad. Other lines were either too weak or overlapped strong adjacent lines to the extent that their positions could not be determined as accurately for all

Table 3. Mole percent Al substitution and unit-cell dimensions of the samples studied.

Sample ¹	Mole % Al	Cell dimensions (Å)			Sample ¹	Mole % Al	Cell dimensions (Å)		
		<i>a</i>	<i>b</i>	<i>c</i>			<i>a</i>	<i>b</i>	<i>c</i>
31/0	0	4.613	9.950	3.022	P146	0	4.629	9.931	3.018
	0	4.612	9.953	3.022	P147	0	4.632	9.929	3.020
31/1	0.5	4.613	9.948	3.021	P150	0	4.629	9.938	3.018
31/2	1.7	4.612	9.943	3.020					
31/3	2.7	4.612	9.939	3.019	Thl	0	4.624	9.963	3.026
31/4	4.2	4.610	9.931	3.016	Thl	3.4	4.618	9.943	3.019
31/5	6.7	4.608	9.919	3.013	Thl	3.9	4.620	9.929	3.016
31/6	9.7	4.605	9.906	3.008	Thl	4.4	4.617	9.934	3.016
31/7A	11.3	4.601	9.897	3.005	Thl	5.1	4.614	9.945	3.014
31/7B	11.3	4.601	9.899	3.005	Thl	6.3	4.615	9.928	3.011
12/0	0	4.620	9.944	3.021	Thl	6.9	4.611	9.923	3.010
	0	4.618	9.944	3.021	Thl	9.3	4.621	9.900	3.006
12/5	4.7	4.620	9.920	3.015	Thl	10.4	4.622	9.888	3.004
12/10	9.0	4.617	9.902	3.009	Thl	13.1	4.605	9.883	3.004
12/15	12.4	4.612	9.887	3.004	Thl	13.3	4.595	9.892	3.002
12/20	15.7	4.601	9.875	3.000	Thl	14.2	4.604	9.867	2.999
28/0	0	4.614	9.954	3.023	Thl	15.5	4.609	9.866	2.997
	0	4.609	9.951	3.022	Thl	16.2	4.608	9.857	2.996
28/1	1.6	4.612	9.945	3.021	Thl	17.3	4.600	9.851	2.993
28/2	2.6	4.609	9.941	3.020	Thl	20.3	4.584	9.850	2.988
28/3	3.5	4.611	9.934	3.018	Thl	20.9	4.574	9.849	2.989
28/5	4.7	4.610	9.926	3.016	Thl	21.1	4.578	9.839	2.987
28/7	6.6	4.612	9.917	3.014	Thl	21.2	4.585	9.848	2.984
28/10	7.7	4.609	9.910	3.012	Thl	26.1	4.560	9.830	2.977
28/12	8.7	4.604	9.902	3.010	Thl	30.0	4.559	9.795	2.971
28/15	10.5	4.605	9.898	3.008	Thl	33.1	4.559	9.773	2.966
28/20	16.7	4.593	9.869	2.998					
DL/9	0	4.628	9.951	3.023	JS	0	4.621	9.939	3.024
DL/10	5.9	4.622	9.920	3.015	JS	6.3	4.617	9.919	3.015
DL/11	10.6	4.617	9.894	3.006	JS	6.8	4.612	9.920	3.014
P24	0	4.623	9.949	3.022	JS	7.7	4.606	9.918	3.014
G-NK1	0	4.624	9.951	3.023	JS	8.3	4.611	9.911	3.011
3/0	0	4.632	9.940	3.024	JS	9.3	4.605	9.915	3.009
3/5	5.1	4.626	9.914	3.014	JS	9.8	4.603	9.905	3.010
4/10	9.7	4.623	9.897	3.007	JS	11.0	4.616	9.898	3.007
4/15	13.9	4.622	9.891	3.003	JS	12.8	4.610	9.871	3.000
4/20	18.6	4.625	9.870	2.991	JS	13.4	4.598	9.900	3.002
4/25	22.1	4.618	9.885	2.986	JS	17.8	4.620	9.872	2.996
4/30	24.9	4.622	9.882	2.978	JS	20.3	4.615	9.858	2.994
4/33	31.0	4.625	9.828	2.970	JS	24.4	4.619	9.827	2.983
2(B)3	31.4	4.600	9.818	2.964	JS	27.2	4.610	9.818	2.979
	31.4	4.599	9.813	2.963					

¹ Thl = values calculated from data given by Thiel (1963). JS = values calculated from data given by Jónás and Solymár (1971). Samples 31/7A and 13/7B contained a trace of hematite, sample 2(B)3 a trace of lepidocrocite but the quantities are so small that the error induced in the chemically determined Al substitution was judged to be negligible. Lines without sample designations indicate duplicate determinations of the cell dimensions of the previous sample.

samples, even when using the computer curve-fitting program.

The cell dimensions of the synthetic, Al-substituted goethites studied by Thiel (1963) and Jónás and Solymár (1970) were calculated from the published 130, 021, 111, and 140 line positions (Table 3). These line positions could not be corrected for shifts caused by small particle size because WHHs were not given.

Chemical analysis

The Al content of the synthetic samples was determined by dissolving 10 mg of sample in 2 ml of conc.

HCl in a 25-ml volumetric flask. The flask was heated to about 150°C on a sand bath until the sample dissolved, and allowed to cool before being filled to 25 ml with distilled water. Fe and Al were determined in the solution using a Perkin-Elmer Model 420 atomic absorption spectrometer.

Samples 3/5 and 4/10 through 4/33 were dissolved using the dithionite-citrate-bicarbonate (DCB) procedure (Mehra and Jackson, 1960), but they were first treated with the citrate-bicarbonate buffer at 70°C for 30 min to remove any possible adsorbed Al prior to dissolution.

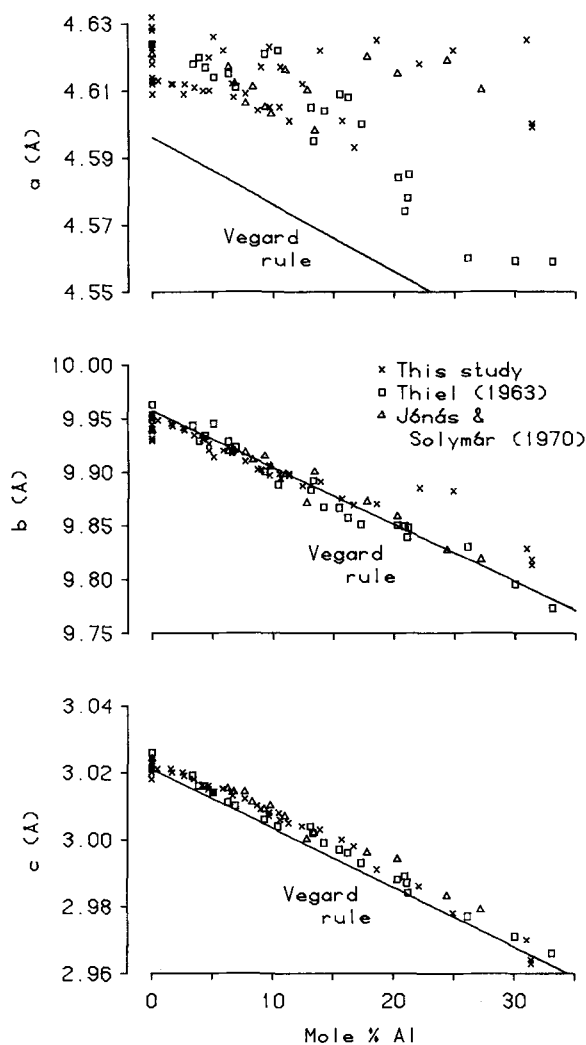


Figure 3. Unit-cell dimensions of synthetic goethites as a function of Al substitution. Cell dimensions for drawing the Vegard lines were taken from JCPDS (1974) card 17-536 (starred) for goethite and card 5-355 (starred) for diaspore.

RESULTS AND DISCUSSION

Unit-cell dimensions

The three unit-cell dimensions are plotted as a function of Al substitution in Figure 3. The *a* dimension shows only a general trend to smaller values with increasing Al substitution and varies considerably for samples with almost the same amount of Al substitution (Table 3). The *b* dimension shows a much greater linear relationship with Al substitution, but deviates somewhat more for substitutions > 20 mole % Al than for substitutions between 0 and 20 mole % Al. The *c* dimension shows the greatest linear dependency on Al substitution and the least deviation from a straight line.

When the correction for line shifts due to the small particle size effect (Figure 2, Table 2) were not made, the *maximum* change in the calculated cell dimensions of the samples with the largest WHHs (Series 3 and 4) was -0.006 , $+0.020$, and $+0.007$ Å for the *a*, *b*, and *c* dimensions, respectively. For the *a* dimension, this change is much smaller than the observed variation (Figure 3), and the correction did not significantly reduce the differences among samples. For the *c* dimension, which is a linear function of Al substitution, the correction led to significantly better agreement in *c* for samples with similar amounts of Al substitution but with large differences in WHH.

Goethite has an orthorhombic unit cell, and the *d*-value for a given line with Miller indices *hkl* is related to the cell dimensions, *a*, *b*, *c*, as follows: $d(hkl) = [(h/a)^2 + (k/b)^2 + (l/c)^2]^{-1/2}$. Thus, the large amount of scatter in the *a* dimension is reflected in the *d*-values of diffraction lines with $h \neq 0$, and because the scatter in *a* is not a function of Al substitution, the larger the contribution of *a* to the *d*-value of a given diffraction line, the poorer the dependency of that line on Al substitution. The positions of the 110, 111, and 021 lines are therefore successively better functions of Al substitution. The differences in *d*(111) vs. mole % Al substitution noted by Jónás and Solymár (1970) are accounted for by the variability of the *a* dimension (Figure 3) as is the much larger scatter in *d*(110) vs. Al substitution than for *d*(111) or *d*(130) in the data shown by Taylor and Schwertmann (1978; their Figure 9).

The *b* and *c* dimensions are closely approximated by the Vegard rule, the linear interpolation between the two end members of a solid solution, but the *a* dimension is not (Figure 3). The positive deviation of *a* from the Vegard line explains why Fey and Dixon (1981) found *d*(111) for goethites synthesized from the Fe^{2+} system to fall above the Vegard line.

The large amount of scatter in the *a* dimension is probably caused by structural defects. Structural considerations give some clues as to why the *a* dimension is more sensitive to these defects than the *b* or *c* dimension. The structure of goethite (α -FeOOH) and isostructural diaspore (α -AlOOH) is based on the hexagonal close packing of oxygen atoms with 6-fold coordinated metal atoms (M) occupying octahedral positions (Ewing, 1935; Hoppe, 1941). The metal atoms are arranged in double rows to form what can be described as double chains of octahedra which run the length of the *c* axis (Ewing, 1935). Because the *c* dimension and, for the most part, the *b* dimension decrease linearly with Al substitution, the integrity of the double chains is apparently preserved in the direction of the *b* and *c* axes, i.e., in the *b-c* plane. This would be expected because within the double chains all bonds are covalent and each octahedron shares four of its edges with neighboring octahedra (Ewing, 1935; his

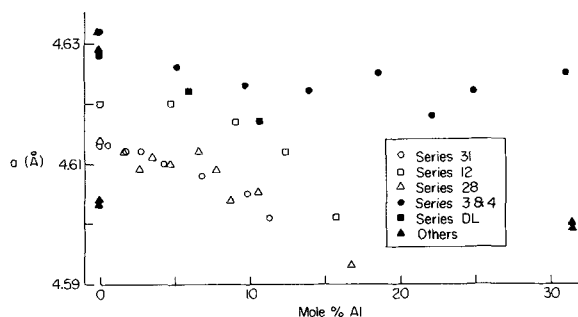


Figure 4. a dimensions vs. Al substitution for goethites synthesized under different conditions.

Figure 1), a configuration which is relatively stable. The linkage of these double chains to each other, however, is only by shared apical oxygens and hydrogen bonds (Ewing, 1935; his Figure 2), a less stable bonding situation than shared octahedral edges. Because of the relatively weak bonding between chains, the stacking of the double chains along the a -axis could be easily disrupted during crystal growth. Additional work is necessary, however, before a most probable model for the defects can be proposed.

If the defects are introduced during crystal growth, a correlation should exist between the a dimension and the synthesis procedure, as is, indeed, the case (Figure 4). The samples synthesized at room temperature (Series 3 and 4 and Series DL) have larger a dimensions than those synthesized at 70°C (Series 31, 28, and 12). Higher temperatures apparently result in the formation of goethites with fewer structural defects. Of the three groups synthesized at 70°C, the group synthesized in the presence of 2 M KOH had larger a dimensions than the two groups synthesized in the presence of 0.3–0.4 M KOH. The higher OH concentration favors a larger goethite crystallization rate, and this faster crystallization rate apparently leads to larger numbers of structural defects. The larger amount of scatter in the data for Series 28 compared to Series 31 was caused by differences in the timing and order of which the solutions were mixed together during the synthesis procedure.

Estimating Al substitution from cell dimensions

Estimating Al substitution in goethite using XRD diffraction lines with $h \neq 0$ such as $d(111)$ will have an inherent uncertainty because of the variability of the a dimension. The remainder of this paper will show how the c -dimension can be used to provide a better estimate of Al substitution.

The linear regression of mole % Al onto $d(111)$,

$$\text{mole \% Al} = 2086 - 850.7 d(111), \quad (1)$$

is highly significant ($r^2 = 0.96$, $n = 81$). The 95% con-

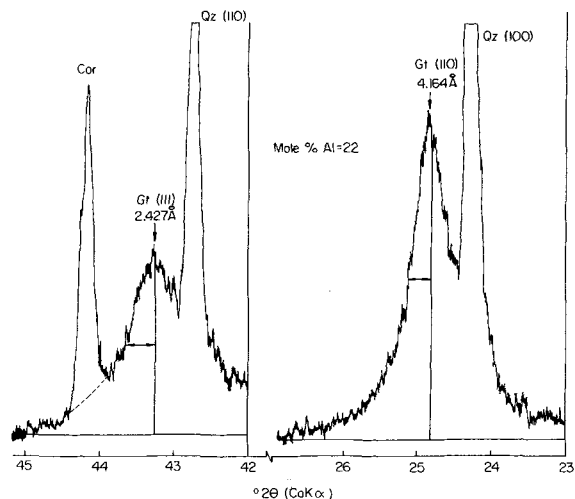


Figure 5. Measurement of X-ray powder diffraction line positions for a soil goethite with 22 mole % Al. Gt = goethite, Qz = quartz, Cor = corundum (CoK α , $\frac{1}{4}^\circ/\text{min}$, time constant = 4 sec, 200 cps full scale).

fidence interval is bounded by almost straight lines, so that the same confidence interval of ± 4.0 mole % Al can be used for the whole range of the regression (2.40 to 2.46 Å). The regression line for the c dimension is:

$$\text{mole \% Al} = 1730 - 572.0 c, \quad (2)$$

with $r^2 = 0.98$ and $n = 81$. The 95% confidence interval of the estimate is ± 2.6 mole % Al and again is, for practical purposes, the same over the range of the regression (2.95 to 3.03 Å). For $d(111)$, two samples must differ by > 8.0 mole % Al to be significantly different at the 95% level, whereas when the c dimension is used, two samples must differ by only 5.2 mole % Al to be significantly different. Clearly, the c dimension is a more precise estimator of Al substitution.

No strong $00l$ lines exist that could be used for estimating Al substitution from the c dimension directly. Fortunately, the c dimension can be calculated from the positions of the 110 and 111 diffraction lines using the formula:

$$c = [(1/d(111))^2 - (1/d(110))^2]^{-1/2}. \quad (3)$$

The 110 and 111 lines are the two strongest goethite lines and can be measured even when relatively small amounts of goethite are present, and in the presence of hematite or lepidocrocite. The accuracy of ± 2.6 mole % Al corresponds to a maximum possible error of $\pm 0.02^\circ 2\theta$ for the 110 line position and $\pm 0.035^\circ 2\theta$ for the 111 line position when using CoK α radiation. Slightly more error can be tolerated in the 111 line position because it occurs at larger angles than the 110 line. Measurements to an accuracy of $\pm 0.02^\circ$ are possible using an internal standard and careful graphical

measurements of line positions so that the accuracy of ± 2.6 mole % is realistic for careful measurements.

Figure 5 illustrates the estimation of Al substitution for a soil goethite. The sample (sample SA69) is from the saprolitic sandstone C horizon (120–140 cm) of the Inanda Soil Series, Port Edward, South Africa (Fitzpatrick, 1978). The sample was ground to approximately silt size, then admixed with 25% corundum (Fisherbrand polishing alumina, 1 micron, No. 12 265 1K, Fisher Scientific Co., Pittsburgh, Pennsylvania) as an internal standard. The “true” positions of the corundum lines were taken from Brown (1980).

Several important points are illustrated by Figure 5. First, an internal standard should be used to correct for errors caused by possible misalignment of the goniometer. Second, the corundum 110 line position was determined at $\frac{1}{2}$ peak height because the $K\alpha_1$ and $K\alpha_2$ components of the line are partially resolved, and the *peak* position may not accurately represent the true line position when using the weighted average $K\alpha$ X-ray wavelength for the calculations. Third, quartz is a common interfering mineral in most samples. For the sample in Figure 5, the goethite has a significant amount of Al substitution, and the goethite peaks can be measured despite a rather large amount of quartz. For goethites with low amounts of Al substitution, the goethite 111 line and the quartz 110 line are closer together, and the exact position of the goethite line may be difficult to determine, in which case a maximum Al substitution can be estimated from the estimated 111 position. The 110 goethite and 100 quartz lines are slightly farther apart and fewer problems should occur. In many samples, quartz interference can be reduced or eliminated by particle size fractionation, concentration of iron oxides by boiling in NaOH (Kämpf and Schwertmann, 1982), high gradient magnetic separation (Schulze and Dixon, 1979), or by using differential X-ray diffraction (Schulze, 1981). Fourth, the positions of the goethite lines should be determined from the position of a line which divides the upper $\frac{1}{3}$ to $\frac{1}{2}$ of the diffraction peak into two “mirror image” halves. Only the upper $\frac{1}{3}$ to $\frac{1}{2}$ of the 111 goethite line is symmetrical, the lower part is skewed to lower 2θ angles when the lines are broad because of the presence of the goethite 040 line (Figure 1). For this reason and because of interference from quartz, the WHH should be estimated from the high-angle side of the peaks (Figure 5). When reporting data on soil goethites, it is recommended that $d(110)$ and $d(111)$ and their WHHs and heights be reported along with their estimated Al substitution.

A step-by-step procedure for estimating % Al substitution in an unknown goethite is as follows. Carefully measure the position and WHH for the goethite 110 and 111 lines using an internal standard. Correct the observed WHHs for instrumental broadening caused by the goniometer by subtracting the instrumental

WHH from the observed WHH. If the corrected WHH is $>0.6^\circ 2\theta$, correct the line positions for shifts caused by the small particle size effect by adding the values from Table 2 to the observed line positions. This correction need not be made if the corrected WHH $<0.6^\circ$ because the correction does not have a significant effect on estimated Al substitution in this range. Note that the corrections are in units of $^\circ 2\theta$, not Å; although they were calculated for $\text{CoK}\alpha$ radiation, their use for $\text{CuK}\alpha$ radiation should introduce no appreciable error in the estimated Al content. Calculate $d(110)$ and $d(111)$ for each line using the corrected positions. Calculate the c dimension using Eq. (3), then use Eq. (2) to estimate mole % Al substitution.

ACKNOWLEDGMENTS

This project was supported in part by a grant from the Deutsche Forschungsgemeinschaft, Project Schw 90/33-1. I thank Prof. U. Schwertmann for supplying samples and for the many stimulating discussions throughout the course of this research. Thanks also to R. M. Taylor for many discussions and suggestions at the beginning of this project, to David Lewis and Nestor Kämpf who synthesized some of the goethite samples and to Birgit Gallitscher and Christine Wagner for doing the chemical analyses. Joe White and Don Franzmeier kindly read the manuscript and offered helpful suggestions.

LITERATURE CITED

- Bigham, J. M., Golden, D. C., Bowen, L. H., Buol, S. W., and Weed, S. B. (1978) Iron oxide mineralogy of well-drained Ultisols and Oxisols: I. Characterization of iron oxides in soil clays by Mössbauer spectroscopy, X-ray diffractometry, and selected chemical techniques. *Soil Sci. Soc. Amer. J.* **42**, 816–825.
- Brindley, G. W. (1980) Order-disorder in clay mineral structures: in *Crystal Structures of Clay Minerals and Their X-ray Identification*, G. W. Brindley and G. Brown, eds., Mineralogical Society, London, 125–195.
- Brown, G. (1980). Associated minerals: in *Crystal Structures of Clay Minerals and Their X-ray Identification*, G. W. Brindley and G. Brown, eds., Mineralogical Society, London, 361–410.
- Davey, B. G., Russell, J. D., and Wilson, M. J. (1975). Iron oxide and clay minerals and their relation to colours of red and yellow Podzolic soils near Sydney, Australia: *Geoderma* **14**, 125–138.
- Ewing, F. J. (1935). The crystal structure of diasporite: *J. Chem. Phys.* **3**, 203–207.
- Fey, M. V. and Dixon, J. B. (1981) Synthesis and properties of poorly crystalline hydrated aluminous goethites. *Clays & Clay Minerals* **29**, 91–100.
- Fitzpatrick, R. W. (1978) Occurrence and properties of iron and titanium oxides in soils along the eastern seaboard of South Africa: Ph.D. Thesis, Univ. of Natal, Pietermaritzburg, South Africa, 203 pp.
- Fitzpatrick, R. W. and Schwertmann, U. (1981) Al-substituted goethite—an indicator of pedogenic and other weathering environments in South Africa: *Geoderma* **27**, 335–347.
- Golden, D. C. (1978) Physical and chemical properties of

- aluminum-substituted goethite: Ph.D. Thesis, North Carolina State Univ., Raleigh, North Carolina, 174 pp.
- Goodman, B. A. and Lewis, D. G. (1981) Mössbauer spectra of aluminous goethites (α -FeOOH): *J. Soil Sci.* **32**, 351–363.
- Hoppe, W. (1941) Über die Kristallstruktur von α -AlOOH (Diaspor) und α -FeOOH (Nadeleisenerz): *Z. Kristallogr.* **103**, 73–89.
- Janik, J. L. and Raupach, M. (1977) An iterative least-squares program to separate infrared absorption spectra into their component bands. *CSIRO, Div. of Soils Tech. Paper* **35**, 37 pp.
- Janot, C., Gibert, H., de Gramont, X., and Biais, R. (1971) Étude des substitutions Al-Fe dans des roches latéritiques: *Bull. Soc. Fr. Minéral. Cristallogr.* **94**, 367–380.
- JCPDS (1974) *Selected powder diffraction data for minerals—Data Book*; Joint Committee on Powder Diffraction Standards, Swarthmore, Pennsylvania.
- Jónás, K. and Solymár, K. (1970) Preparation, X-ray, derivatographic and infrared study of aluminum-substituted goethites: *Acta Chim. Acad. Sci. Hung.* **66**, 383–394.
- Kämpf, N. (1981) Die Eisenoxidmineralogie einer Klimasequenz von Böden aus Eruptiva in Rio Grande do Sul, Brasilien: Ph.D. Thesis, Technische Universität München, Freising-Weihenstephan, German Federal Republic, 271 pp.
- Kämpf, N. and Schwertmann, U. (1982) The 5-M-NaOH concentration treatment for iron oxides in soils: *Clays & Clay Minerals* **30**, 401–408.
- Klug, H. P. and Alexander, L. E. (1974) *X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials*: Wiley, New York, 966 pp.
- Lewis, D. G. and Schwertmann, U. (1979a) The influence of Al on iron oxides. Part III. Preparation of Al goethites in M KOH. *Clay Min.* **14**, 115–126.
- Lewis, D. G. and Schwertmann, U. (1979b) The influence of aluminum on the formation of iron oxides. IV. The influence of [Al], [OH], and temperature: *Clays & Clay Minerals* **27**, 195–200.
- Mendelovici, E., Yariv, Sh., and Villalba, R. (1979) Aluminum-bearing goethite in Venezuelan laterites. *Clays & Clay Minerals* **27**, 368–372.
- Mehra, O. P. and Jackson, M. L. (1960) Iron oxide removal from soils and clays by a dithionite-citrate-bicarbonate system buffered with sodium bicarbonate: in *Clays and Clay Minerals, Proc. 7th Natl. Conf., Washington, D.C., 1958*, Ada Swineford, ed., Pergamon Press, New York, 317–327.
- Nahon, D., Janot, C., Karpoff, A. M., Paquet, H., and Tardy, Y. (1977) Mineralogy, petrography and structures of iron crusts (ferricretes) developed on sandstones in the western part of Senegal: *Geoderma* **19**, 263–277.
- Norrish, K. and Taylor, R. M. (1961) The isomorphous replacement of iron by aluminium in soil goethites: *J. Soil Sci.* **12**, 294–306.
- Schellmann, W. (1964) Zur Rolle des Aluminiums in Nadeleisenerz-Ooiden: *N. Jb. Miner. Mh.* **2**, 49–56.
- Scheiderhöhn, P. (1964) Über das Vorkommen des Aluminiums in einer ooidische Eisenerze enthaltenden marinen Schichtfolge: *Beitr. Miner. Petrogr.* **10**, 141–151.
- Schwertmann, U. (1959) Über die Synthese definierter Eisenoxide unter verschiedenen Bedingungen. *Z. Anorg. Allg. Chemie* **298**, 337–348.
- Schwertmann, U. and Taylor, R. M. (1977) Iron oxides: in *Minerals in Soil Environments*, J. B. Dixon and S. B. Weed, eds., Soil Sci. Soc. Amer., Madison, Wisconsin, 145–180.
- Schulze, D. G. (1981) Identification of soil iron oxide minerals by differential X-ray diffraction: *Soil Sci. Soc. Amer. J.* **45**, 437–440.
- Schulze, D. G. (1982) The identification of iron oxides by differential X-ray diffraction and the influence of aluminum substitution on the structure of goethite: Ph.D. Thesis, Technische Universität München, Freising-Weihenstephan, German Federal Republic. University Microfilms International, Ann Arbor, Michigan. 167 pp.
- Schulze, D. G. and Dixon, J. B. (1979) High gradient magnetic separation of iron oxide and other magnetic minerals from soil clays. *Soil Sci. Soc. Amer. J.* **43**, 793–799.
- Shannon, R. D. and Prewitt, C. T. (1969) Effective ionic radii in oxides and fluorides: *Acta Cryst.* **B25**, 925–946.
- Taylor, R. M. and Schwertmann, U. (1978) The influence of aluminum on iron oxides. Part I. The influence of Al on Fe oxide formation from the Fe(II) system: *Clays & Clay Minerals* **26**, 373–383.
- Thiel, R. (1963) Zum System α -FeOOH- α -AlOOH: *Z. Anorg. Allg. Chem.* **326**, 70–78.
- Torrent, J., Schwertmann, U., and Schulze, D. G. (1980) Iron oxide mineralogy of some soils of two river terrace sequences in Spain: *Geoderma* **23**, 191–208.

(Received 12 January 1983; accepted 7 May, 1983)

Резюме—Размеры элементарной ячейки синтетических, Al-замещенных гетитов указывали на то, что размерность c является линейной функцией замещения Al в диапазоне от 0 до 33 молярных % Al, тогда как размерность a является переменной на том же самом диапазоне. Размерность b также являлась линейно зависимой от замещения Al, но проявляла слегка большую изменчивость чем c для замещения Al в диапазоне 20 до 33 молярных %. Предлагается, что изменчивость размерности является результатом структурных дефектов. Улучшенная процедура для оценки замещения Al на основе положений линий рентгеновской порошковой дифракции требует: (1) вычисления размерности c на основе положений 100 и 111 дифракционных линий используя формулу: $c = (1/d(111)^2 - 1/d(110)^2)^{-1/2}$ и (2) оценки замещения Al из соотношения: молярные % Al = $1730 - 572,0 c$. 95% уровень статистической достоверности этой оценки равен $\pm 2,6$ молярных % Al при использовании этой процедуры, в противоположность 4,0 молярных % Al когда только используется положение отражения 111. [E.G.]

Resümee—Die Größen der Einheitszellen von synthetischen, Al-substituierten Goethiten zeigten, daß die c -Dimension eine lineare Funktion der Al-Substitution im Bereich von 0–33 Mol.-% Al ist, daß aber die a -Dimension in diesem Bereich variiert. Die b -Dimension zeigt ebenfalls eine lineare Abhängigkeit von der Al-Substitution, variiert aber etwas mehr als c bei Al-Substitution zwischen 20–33 Mol.-%. Es wird vorgeschlagen, daß die Variation der a -Dimension das Ergebnis von Gitterfehlern ist. Eine verbesserte Vorgangsweise zur Abschätzung der Al-Substitution aus der Lage der XRD-Linien erfordert (1) die Berechnung der c -Dimension aus der Lage der 110 und 111 Linien, wozu die Formel $c = (1/d(111)^2 - 1/d(110)^2)^{-1/2}$ zu verwenden ist und (2) die Abschätzung der Al-Substitution aus der Beziehung: Mol.-% Al = $1730 - 572,0 c$. Das Konfidenzintervall der Abschätzung beträgt $\pm 2,6$ Mol.-% Al, wenn man diese

Vorgangsweise angewendet, im Gegensatz zu $\pm 4,0$ Mol.-% Al, wenn die Lage des 111 Reflexes allein berücksichtigt wird. [U.W.]

Résumé—Les dimensions de la maille-mère de goethites synthétiques substituées par Al ont montré que la dimension c est une fonction linéaire de la substitution par Al sur l'étendue 0–33 mole % d'Al, mais que la dimension a est variable sur cette même étendue. La dimension b était aussi apparentée linéairement à la substitution par Al, mais s'est montrée quelque peu plus variable que c , pour la substitution par Al de 20–33 mole %. On a proposé que la variabilité de la dimension a est un résultat de défauts structuraux. Un procédé amélioré pour estimer la substitution par Al à partir de positions de droite XRD exige (1) le calcul de la dimension c à partir des positions des droites de diffraction 110 et 111 en employant la formule : $c = (1/d(111)^2 - 1/d(110)^2)^{-1/2}$, et (2) l'estimation de la substitution par Al à partir de la relation: mole % d'Al = $1730 - 572,0 c$. L'intervalle de confiance 95% de cette estimation est $\pm 2,6$ mole % d'Al en employant ce procédé, en contraste avec $\pm 4,0$ mole % d'Al lorsque seule la position de la réflexion 111 est utilisée. [D.J.]