X-RAY POWDER DIFFRACTION RIETVELD CHARACTERIZATION OF SYNTHETIC ALUMINUM-SUBSTITUTED GOETHITE

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Abstract—Rietveld X-ray powder diffraction (XRD) analysis has been evaluated as a procedure for characterizing Al-substituted goethite according to the Rietveld scale factor, unit-cell parameters, and atom positional parameters. The study was conducted with three synthetic goethite samples for which the degree of Al substitution for Fe determined by chemical analysis was 8.0 ± 0.4, 12.0 ± 0.4, and 20.1 ± 0.4 mole %. The weight fractions of crystalline material (WFCM) in the specimens, determined from the Rietveld scale factors after correcting for adsorbed water and impurities, were 0.878 (esd = 0.014), 0.919 (0.014), and 0.965 (0.015), respectively. The Al mole % substitutions, inferred from the Rietveld cell parameters according to the method of Schulze (1984), were 10.4 ± 2.5, 16.5 ± 2.6, and 17.1 ± 2.6, respectively. The cause of the significant difference between the second value and the chemical analysis result is not known. The atom positional parameters did not differ significantly within the sample suite and agreed satisfactorily with literature values. The results have demonstrated the value of using Rietveld XRD analysis to determine simultaneously the WFCM and Al mole % substitutions, as well as to confirm the non-hydrogen atom positions.

Key Words—Aluminum, Crystallinity, Goethite, Rietveld refinement, X-ray powder diffraction.

INTRODUCTION

Schulze (1984) refined methods proposed in the literature for relating % Al in goethite to changes in the dimensions of the unit cell according to systematic shifts in X-ray powder diffraction (XRD) line positions. After correction of peak positions for variations in structure factors and Lp factors across the size-broadened lines, he found that linear-regression least squares gave excellent fits between % substitution and the *b*- and *c*-parameters. The *c*-parameter was preferred to *b* for determining Al substitution due to its superior regression fit with mole % Al. Schulze proposed the following regression using data from a comprehensive suite of specimens covering the mole % substitution range 0–33%, obtained from a variety of preparative procedures:

$$\text{mole \% Al} = 1730 - 572.0\,c. \qquad (1)$$

The *c*-dimension was determined from the positions of the goethite 110 and 111 XRD lines, after correction for line shift, according to the relation:

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

The precision of the procedure was claimed to be ± 2.6 mole % Al.

The present study investigated the desirability of using the Rietveld (1969) method to obtain cell parameters for mole % Al determinations with Eq. (1), while simultaneously acquiring other descriptors that might be provided by the Rietveld method for goethite characterization. The Rietveld parameters considered, in addition to the cell parameters, were: scale factor, occupancy factor for the Fe and Al ions at the cation site, and the atom positional parameters.

The scale factors were used to estimate weight fractions of crystalline material (WFCM) by relating the intensity of the XRD pattern to that produced by a well-characterized reference material, as proposed by Jordan *et al.* (1990),

$$\text{WFCM} = \frac{\text{pattern integrated intensity for sample}}{\substack{\text{pattern intetrated intensity} \\ \text{for a 100\% ordered sample}}}. \qquad (3)$$

Jordan *et al.* (1990) proposed use of the term WFCM in preference to "amorphous content," which various diffraction workers have applied to describe collectively Bragg intensity deficits caused by short-range order and lattice irregularities, such as lattice strain, dislocations, and stacking faults. It was also of interest to consider whether cell parameters from Rietveld analysis agree with those determined by the Schulze method, which employs the Bragg angles of two lines. The Rietveld cation-site occupancy factor provides, at least in principle, a direct and alternative means to the Schulze method for determining the degree of Al substitution. The positional parameters were also of interest, following Cambier's (1986) suggestion that subtle structural changes may occur with substitution according to preparation procedure.

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248

Table 1. Estimation of mole % Al substitution in goethite specimens.

Value	Specimen 1	Specimen 2	Specimen 3
Chemical analysis			
Fe %—total	55.1 ± 0.3	52.5 ± 0.3	46.7 ± 0.3
—corrected[1]	54.5	51.4	45.6
Al %	3.4 ± 0.1	5.0 ± 0.1	8.2 ± 0.1
H_2O %—ignition loss	14.8	15.4	17.2
—adsorbed[2]	5.4	6.0	7.7
K %[3]	0.2	0.3	0.3
Impurities %[4]	0.3	1.1	1.5
Mole % Al[5]	8.0 ± 0.4	12.0 ± 0.4	20.1 ± 0.4
Lattice-parameter analysis (Schulze, 1984)			
Mole Al[6]	10.4 ± 2.6	16.5 ± 2.6	17.1 ± 2.6

[1] Fe content corrected for oxalate-soluble Fe.
[2] Assuming that ignition loss comprises H_2O from $(Fe,Al)O_2H$ plus adsorbed H_2O.
[3] Expressed as K_2O in the ignited samples.
[4] Assuming that the specimens comprise (1) goethite with Fe % and Al % as indicated in the table, (2) adsorbed water, and (3) impurities.
[5] Calculated with the "corrected" Fe % and the Al %, assuming that these amounts are associated as $(Fe,Al)O_2H$.
[6] Using the Rietveld c-lattice parameter (Table 2) and Eq. (1).

MATERIALS AND METHODS

Chemical analysis of materials

The three goethite samples analyzed in this study were aluminous goethite materials produced by the Aluminum Company of America (Alcoa), Pittsburgh, Pennsylvania. The method used was described by Golden (1978). A mixed aluminum hydroxide gel was prepared by coprecipitation of solutions of $Fe(NO_3)_3$ and $Al(NO_3)_3$ with a 3% v/v solution of NH_4OH. The pH of the suspension was adjusted to about 9 using the NH_4OH solution. The gel was stirred gently for 24 hr, after which it was washed several times with deionized water and then filtered. Subsequently, the gel was aged for 14 days at about 50°C in a 2 N solution of KOH containing various amounts of $Al(NO_3)_3$. The product was then washed thoroughly, filtered, and air dried.

The samples were chemically analyzed under the direction of the authors. Multi-element compositions were determined by the X-ray fluorescence (XRF) fusion procedure. The total-Fe results obtained by XRF were validated by a wet chemistry method in which 0.2 g material was dissolved in 50% v/v HCl acid; the Fe(III) was then reduced to Fe(II) with $SnCl_2$; and finally the Fe(II) was titrated with 0.1 N $K_2Cr_2O_7$ using a barium diphenyl ammine sulphonate indicator. The total Al results were verified by atomic absorption spectrometry (AAS) using 0.25-g samples dissolved in 50% v/v HCl acid, which was made up to 250 ml and then measured against standards matrix-matched for Fe (as $FeCl_3$) and HCl. The wet chemistry and AAS results gave excellent confirmation of the XRF analyses. The ammonium oxalate soluble Fe content (Schulze and Schwertmann, 1987) was also measured

as a check on the possible presence of ferrihydrite in the samples. The oxalate soluble Al content was not estimated. Finally, loss-on-ignition and thermogravimetric analyses were used to determine the amount of adsorbed H_2O in the samples. The results are summarized in Table 1. The Al contents according to chemical analysis were 8.0 ± 0.4, 12.0 ± 0.4, and 20.1 ± 0.4 mole %. The specimens are therefore designated the 8%, 12%, and 20% materials, respectively.

XRD data collection

Corundum (UCAR-C powder of nominal 1.0-μm particle size, marketed by Union Carbide) was employed as an external intensity standard material in determining the WFCM for the samples. Samples were not milled prior to mounting because transmission electron microscopy examination of the goethite specimens and the known particle size of the corundum material indicated that the particle sizes were sufficiently small to give reproducible XRD intensity data; the dimensions of the goethite specimens were found by scanning electron microscopy to be <0.1 μm. Samples were mounted for XRD using a front-pressing method, in which care was taken to reduce preferred orientation by lightly packing the sample. Step-scanned patterns were obtained with a Siemens D500 Bragg-Brentano diffractometer fitted with a Cu X-ray tube (35 kV, 30 mA) and a curved graphite diffracted-beam monochromator. The data were collected over the 2θ angular range 2°–155° to optimize definition of the angle-dependent Rietveld parameters and, therefore, definition of the scale factors. The collection data were: 1° divergence slit, 0.05° receiving slit, NaI detector; step size = 0.04°, counting time = 1 s per step, polarization correction factor = 0.80.
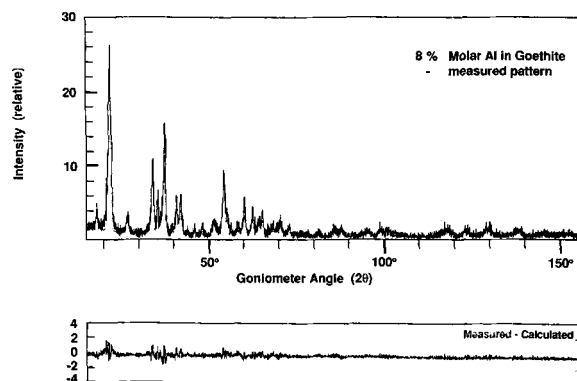
Figure 1. Comparison of measured and calculated X-ray powder diffraction patterns for the 8% Al-substituted goethite specimen.

Rietveld procedures

Calculations were made with a VAX-11/750 computer using software derived from the Rietveld DBW3.2 code of Wiles and Young (1981), as modified by Hill and Howard (1986). The refinement strategies for the goethite and corundum data sets were essentially those described by O'Connor and Raven (1988) with the additional feature that preferred orientation was included according to the March (1932) model proposed by Dollase (1986). The direction of preferred orientation nominated for the calculations was ⟨100⟩, based on the results of the electron diffraction study of Cornell *et al.* (1983). Use of a preferred orientation correction was necessary because the assumption of random orientation in initial calculations produced substantial disagreement between some of the corresponding x-positional parameters for the three specimens (see discussion below on heterotypism). Initial refinements with a pseudo-Voigt profile spread function showed that the experimental profiles were essentially Gaussian, i.e., $\gamma = 0.0$. The Gaussian full-width-half-maximum parameters, U and W, were used subsequently to assess the significance of broadening-induced peak shifts on cell-parameter estimates (see Results and Discussion).

The structural model used in the calculations was that described in detail by Megaw (1973) for the isomorphs diaspore and goethite. The structure consists of hexagonal close-packed oxygen atoms and hydroxyl groups, with cations occupying the octahedral positions. Ribbons of edge-sharing octahedra, extending along the *c*-axis direction, are cross-linked into a network structure by shared apical oxygens and hydrogen bonds. The similar ionic radii of Fe^{3+} (0.65 Å) and Al^{3+} (0.53 Å) (Shannon and Prewitt, 1969) facilitates the substitution of Al for Fe in the goethite structure. The crystal structure model placed all atoms in the Wyckoff 4c positions of orthorhombic space group

Pbnm having coordinates $\pm$(x, y, 0.25; 0.5 + x, 0.5 − y, 0.75). The x and y parameters for Fe/Al, O_1, and O_2 in the 8% material were refined commencing with the mean values for the parameters reported by Klug and Farkas (1981). The positional coordinates for the hydrogens were fixed at the means of the neutron diffraction values of Busing and Levy (1958), x = 0.412 and y = 0.088 and of Forsyth *et al.* (1968), x = 0.399 and y = 0.088. The Fe/Al site occupancy parameters were constrained such that the sum of the Fe and Al values was fixed at unity. The site occupancies for Fe and Al were set at the values indicated by chemical analysis (0.11, 0.17, and 0.27 for the 8%, 12%, and 20% samples, respectively) inasmuch as trial refinements involving relaxation of the Fe/Al occupancies failed to produce results of sufficient reliability for the determination of site occupancy. Refinements for the 12 and 20 mole % data sets used the 8% sample results as the initial values. The Rietveld results of principal interest are reported in Table 2. Figure 1 shows the excellent agreement between the measured and calculated patterns for the 8% sample.

The only corundum Rietveld parameter reported here is the scale factor, s = 9.18(7) × 10^{-4}, which is required for WFCM calculations.

Calculation of WFCM values

The scale factors were used to infer the WFCM for each goethite specimen based on the Rietveld quantitation methods proposed by Hill and Howard (1987), Bish and Howard (1988), and O'Connor and Raven (1988) for phase analysis of mixtures. For a single-phase specimen that is only partially crystalline, the WFCM relative to corundum as an external standard is given by:

$$WFCM = \frac{s(ZMV)\mu^*}{s_s(ZMV)_s\mu_s^*}. \quad (4)$$

Here, Z represents the number of formula units of mass M per unit cell, V is the unit-cell volume, and μ^* is the mass-attenuation coefficient of the sample. Subscript 's' designates quantities for the calibration standard.

The data used in the calculations are given in Table 3. The mass-attenuation coefficients were taken from the elemental tables of Hubbell *et al.* (1974), 11.0 cm, 50.2 cm, and 304 cm^2/g for O, Al and Fe, respectively. The cell volumes were calculated with the Rietveld parameters.

RESULTS AND DISCUSSION
WFCM estimates

The calculations for each specimen based on the Rietveld scale factors for the goethite specimens and the corundum standard are summarized in Table 3. The WFCM values for the 8%, 12%, and 20% speci-

Table 2.   Rietveld parameters of principal interest for Al-substituted goethite samples.

Rietveld parameter symbol	8% Substitution	12% Substitution	20% Substitution
Scale factor	$4.11 \times 10^{-4}(6)$	$4.44 \times 10^{-4}(6)$	$5.01 \times 10^{-4}(7)$
Atom parameters			
$x(Fe)$	$-0.0466(8)$	$-0.0484(8)$	$-0.0481(9)$
$y(Fe)$	$0.1480(4)$	$0.1462(4)$	$0.1462(4)$
$B(Fe)$	$0.62(7)Å^2$	$0.65(7)Å^2$	$0.72(8)Å^2$
$x(O_1)$	$0.2810(26)$	$0.2899(25)$	$0.2902(26)$
$y(O_1)$	$0.2010(13)$	$-0.2010(11)$	$-0.2011(11)$
$B(O_1)$	$-0.16(24)Å^2$	$-0.01(23)Å^2$	$0.21(23)Å^2$
$x(O_2)$	$-0.1901(31)$	$-0.1937(29)$	$-0.1920(29)$
$y(O_2)$	$-0.0513(16)$	$-0.0510(13)$	$-0.0509(13)$
$B(O_2)$	$1.31(35)Å^2$	$1.24(30)Å^2$	$1.47(30)Å^2$
Peak profile parameters			
U	$0.58(7)$	$0.41(5)$	$0.43(6)$
W	$0.80(2)$	$0.55(1)$	$0.58(2)$
Lattice parameters (Å)			
a	$4.5958(13)$	$4.5933(11)$	$4.5929(13)$
b	$9.889(3)$	$9.865(2)$	$9.848(2)$
c	$3.0063(9)$	$2.9956(7)$	$2.9897(7)$
Preferred orientation parameter—March (1932), Dollase (1986)			
r	$0.86(1)$	$1.02(1)$	$1.05(1)$
Crystallographic R-factors (%)			
R_p	24.4	23.6	23.9
R_{exp}	26.7	26.6	26.1
R_{wp}	33.0	31.8	31.6
R_B	9.6	8.5	8.6

Table 3.   Estimation of weight fraction of crystalline material[1] and mole % Al substitution in goethite specimens.

	α-alumina	8% Substituted goethite	12% Substituted goethite	20% Substituted goethite
Z	12	4	4	4
M (a.m.u.)	50.98	86.55	85.40	83.09
V (Å^3)	254.9	136.6	135.7	135.2
ZMV	155,938	47,291	46,355	44,935
μ^* (cm^2/g)	31.8	193.9	188.8	177.2
WFCM[2]	1.000	0.828	0.854	0.876
WFCM'[3]		0.878(14)	0.919(14)	0.965(15)

[1] Weight fraction of crystalline material (WFCM).
[2] WFCM calculated with Eq. (3).
[3] WFCM corrected for impurities and adsorbed H_2O according to WFCM' = WFCM/$(1 - \Delta)$, where Δ is the fractional content of impurities and adsorbed H_2O; see Table 1.

mens, after correction for adsorbed water and impurities, were 0.878 (14), 0.919 (14), and 0.965 (15), respectively. (The convention adopted in this paper for the esd value of a quoted result is enclosure in parentheses of the most significant figures for esd corresponding to the least significant figures of the quoted result.) Accordingly a small, significant increase in WFCM with Al substitution is apparent which we cannot explain.

Unit-cell parameters and Al-substitution estimates (modified Schulze method)

The values for *a, b,* and *c* in Table 2 are shown in Figure 2 superimposed on the data of Schulze (1984).

The plots indicate that the Rietveld determinations are qualitatively consistent with the Schulze plots in that the *b* and *c* values trend in the same way as the Schulze values in Figure 2. The Schulze regression on *c* for inferring mole % Al [Eq. (1) above] gives the results shown in Table 1. The agreement between the chemically derived and Rietveld values for the 8% and 20% samples is excellent given Schulze's assessment that Eq. (1) determines mole % Al to within $\pm 2.6\%$ at the 95% confidence level and given also the estimate of uncertainty in our cell parameters. The difference between the known value for the 12% sample and the Rietveld result of $16.5 \pm 2.6\%$ is significant, inasmuch as the maximum discrepancy between the two esti-
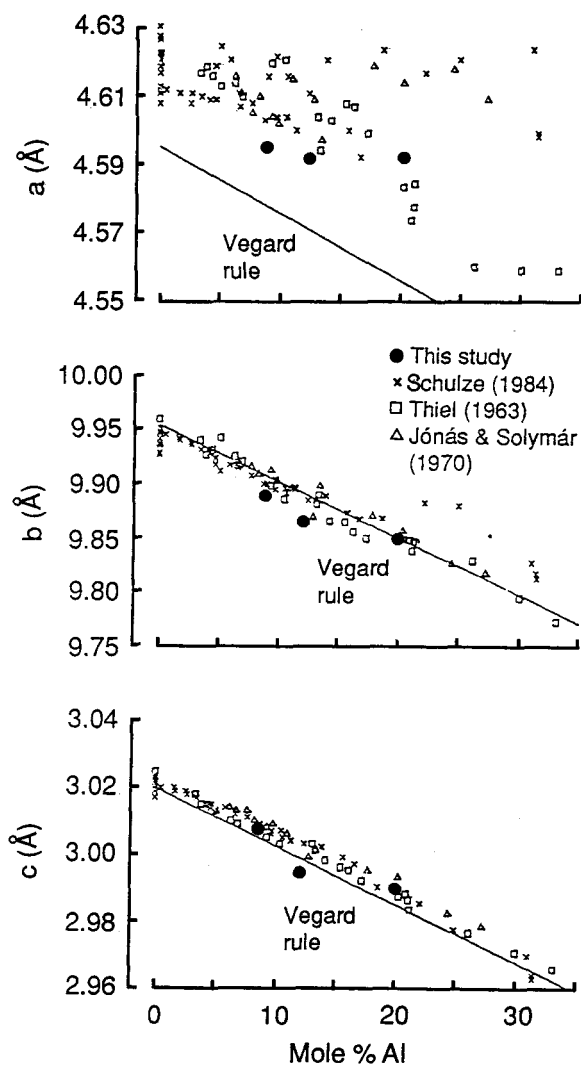
Figure 2. Plots of each cell parameter vs. mole % Al substitution shown superimposed on the plots of Schulze (1984). Large circles represent values from the present study.

mates should be 3%. The cause of the difference for the 12% sample is not obvious, given the attributes of the two methods. Shifts in peak positions due to line-broadening were considered as a possible source of bias in the Rietveld cell parameters [see, for example, Reynolds (1968) and Trunz (1976)] and, therefore, a possible cause of systematic error in estimates of mole % substitution by the Schulze method. Theoretical estimates of peak shift values were made using

$$y_{ci} \propto |F_i|^2 \cdot Lp_i \cdot \Phi_i,$$

where $|F_i|^2$ is the structure amplitude square calculated at profile point 'i,' Lp_i is the Lorentz-polarisation factor, and Φ_i is the profile spread function (O'Connor and Raven, 1988). The Rietveld parameters U and W in Table 2 were used to construct Φ_i in the calculation of y_{ci} across the peaks for the 111 and 110 lines [see Eq. (1)]. The results of the calculations showed that the shifts in peak positions for these lines were <0.01°. Therefore bias in the peak positions could not have caused discernible shifts in the estimates of mole % substitution calculated with the Rietveld *c* parameter.

Atom positional parameters

The positional parameters in Table 2 are compared in Table 4 with the values reported by Hill (1979) and Klug and Farkas (1981) for diaspore and by Forsyth *et al.* (1968) for goethite. The results do not indicate structural heterotypism within the set of three goethite specimens if esd's are considered. Moreover, no differences exist between the results obtained in this study and those reported in Table 4 for various goethites and diaspore samples. It is important to note that strong indications of structural heterotypism were obtained if preferred orientation effects were not included in the Rietveld refinement calculations.

SUMMARY AND CONCLUSION

The characterization of three Al-substituted goethite samples by the Rietveld method produced data not obtained previously by other methods.

Table 4. Comparison of x and y parameters for Fe/Al, O_1, and O_2 with values of Forsyth *et al.* (1968) for goethite, and of Hill (1979) and Klug and Farkas (1981) for diaspore.

	Fe/Al		O_1		O_2	
	x	y	x	y	x	y
8 mole % Al	−0.0466(8)	0.1480(4)	0.2810(26)	−0.2010(13)	−0.1901(31)	−0.0513(16)
12 mole % Al	−0.0484(8)	0.1462(4)	0.2899(25)	−0.2010(11)	−0.1937(29)	−0.0510(13)
20 mole % Al	−0.0481(9)	0.1462(4)	0.2902(26)	−0.2011(11)	−0.1920(29)	−0.0509(13)
Forsyth *et al.* (1968)	−0.0477	0.1461	0.2942	−0.1999	−0.1974	−0.0531
Hill (1979)	−0.04476(10)	0.14456(5)	0.28772(20)	−0.19882(1)	−0.19698(21)	−0.05350(1)
Klug and Farkas	−0.0463(6)	0.1438(3)	0.2874(10)	−0.1985(5)	−0.2066(9)	−0.0536(5)
(1981)	−0.0461(6)	0.1437(3)	0.2873(11)	−0.1977(6)	−0.2080(10)	−0.0538(5)
	−0.0481(7)	0.1446(4)	0.2814(14)	−0.1975(6)	−0.2060(12)	−0.0561(6)
	−0.0445(8)	0.1439(3)	0.2879(24)	−0.1966(7)	−0.2093(12)	−0.0538(6)

1. The Rietveld scale factors showed that the WFCMs for the three samples fell within the range 0.88–0.96.
2. The estimates of Al mole % substitution by the Schulze (1984) method using Rietveld c-parameters were in agreement with chemically derived values for the 8% and 20% samples, but not for the 12% sample.
3. Site occupancy factors for Fe/Al cations could not be determined with sufficient precision to measure directly the degree of substitution.
4. Corresponding atom positional parameters for the three samples did not differ significantly within the suite of samples examined; they also agreed with values reported in the literature for other goethite and diaspore studies. No indication of heterotypism in the results was found.

The results demonstrate the value of using Rietveld analysis to determine simultaneously the WFCM and Al mole % substitutions as well as to confirm the non-hydrogen atom positions.

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