VERIFICATION OF THE TRICLINIC CRYSTAL STRUCTURE OF KAOLINITE

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Abstract—On the basis of neutron diffraction studies, the two inner-hydroxyl ions in highly ordered kaolinite were recently shown to be differently oriented. One of the inner-hydroxyl ions points generally toward a hole in the octahedral sheet and the other toward a hole in the tetrahedral sheet. These orientations and the locations of the other atoms in the primitive triclinic unit cell have now been determined for a sample of Keokuk kaolinite with improved precision compared with that reported earlier. Rietveld structure refinement was carried out for the entire crystal structure simultaneously (99 atom positional and 17 other parameters) with each of two newly collected sets of high-resolution neutron powder diffraction data. The different orientations of the inner-hydroxyl ions are the most marked evidence that the unit cell is not C centered. The positions of the inner-surface hydrogen atoms provide further evidence in that all differ from a C-centered relationship by six to eight estimated standard deviations in their y coordinates. The cell is, therefore, not centered. The space group is $P1$.

Key Words—Inner hydroxyl, Kaolinite, Neutron powder diffraction, Rietveld structure refinement, Triclinicity.

INTRODUCTION

Two recent papers (Adams, 1983; Suitch and Young, 1983) reported conflicting results for the orientations of the two inner-hydroxyl ions in the unit cell of kaolinite and, thereby, conflicting conclusions about the similarity and differences between the "kaolinite" layer in dickite and that in kaolinite. Adams (1983) reported that both were oriented the same way, with the O–H vector pointing away from the octahedral sheet. Suitch and Young (1983) reported that the two inner-hydroxyl ions were differently oriented, one pointing toward and one away from the octahedral sheet. They stated that this orientational difference constituted the principal difference between the "kaolinite" layers in kaolinite and dickite. Both groups of authors used Rietveld structure refinements with powder diffraction data. Adams used neutron diffraction data only, which were collected on the high-resolution D1A instrument at the Institut Laue-Langevin. Suitch and Young used X-ray diffraction data for refinement of the non-hydrogen atom positions and then neutron data, collected at the High-Flux Beam Reactor at Brookhaven National Laboratory, for refinement of the hydrogen and hydroxyl-oxygen positions.

Because Adams used a C-face-centered space group, his Rietveld refinements were constrained to report identical orientations for the two inner-hydroxyl ions. He also made a scattering-density difference map ("Fourier"), however, on which he looked for but did

not find evidence of a second position for the inner-hydroxyl hydrogen atoms.

The Suitch and Young (1983) result for the inner-hydroxyl orientations has been questioned by later workers as not being "unambiguous" (Thompson, 1984), as being open to "serious doubt" (Thompson and Withers, 1987), and that it was not consistent with current interpretations of infrared spectroscopic data (D. K. Smith, Pennsylvania State University, University Park, Pennsylvania, private communication, 1984). In view of the growing controversy, and because the Suitch and Young conclusion about the inner-hydroxyl ion orientations was in fact based on a single neutron diffraction pattern from a single sample, we considered it worthwhile to carry out another set of Rietveld refinements with new neutron data collected from a new sample on a different instrument (the one used by Adams). The new data supported refinement of the positional parameters of all atoms simultaneously, a desirable procedure that was not possible with the data available in the earlier Suitch and Young work.

MATERIALS AND METHODS

The kaolinite sample was a mixture of the "best" material handpicked from several geodes found near Keokuk, Iowa (Hayes, 1963; Keller *et al.,* 1966). The "best" material displayed no "sharp-rise-slow-fall" characteristics in the X-ray powder diffraction pattern, which are usually seen in the 19–25°2θ range (CuKα

Table 1. Starting coordinates for the inner-hydroxyl hydrogen half-atoms in the centering-imposed model.

Atom	x	y	z
H1A	0.253	0.038	0.362
H1B	0.223	0.063	0.269
H5A	0.723	0.563	0.269
H5B	0.753	0.538	0.362

radiation) and which are generally ascribed to layer stacking faults or to layer-to-layer shifting of the Ael vacancies (see, e.g., Plançon and Tchoubar, 1975, 1977; Reynolds, 1983; Tchoubar, 1984). The near absence of such characterizations can be noted in the diffraction pattern shown in Figure 2a of the present paper. This selection of specimen is critical to the credibility of the detailed results because the layer-to-layer faults were not modeled in the Rietveld refinement program used nor, in fact, have they been modeled in any such program known to the authors. Because such kaolinite material is in short supply, the authors are grateful to W. D. Keller for sharing his and to S. W. Bailey for turning over to them his remaining supply so that the total sample could be of convenient size for neutron powder diffraction.

Neutron powder diffraction data were collected with the D1A high-resolution multi-counter diffractometer system at the Institut Laue-Langevin, Grenoble (Hewat and Bailey, 1976), operating with a wavelength close to 1.95 Å. Two fully independent sets of data were collected over the range 6–155°2θ. The second (PNKAO86), obtained about 6 months after the first (PKAOLIN), was collected to have about three times the total counts of the PKAOLIN set. Set PNKAO86 was, therefore, the preferred set when only one set was used.

Rietveld whole-pattern-fitting crystal-structure refinement (Rietveld, 1969; Young and Wiles, 1981) was carried out initially at the Institut Laue-Langevin with a VAX 8600 version of the program described in earlier form by Hewat (1973) and now incorporating Howard's (1981) reflection profile model. More exhaustive refinements were then carried out at the Georgia Institute of Technology with the current version of the computer program described by Wiles and Young (1981), modified to make proper use of the multiple-counter data.

Considerable asymmetry in the lower angle reflection profiles was noted. The computer program used at the Georgia Institute of Technology (DBW3.2S, version 8705) was not equipped to model it well. Therefore, after refinement procedures had been carried through with PKAOLIN and PNKAO86 data, the key procedures were repeated with a truncated set of data, PKAO86A, which was set PNKAO86 with the data <42.75°2θ removed. Because this truncation omitted the strong peaks most affected by asymmetry, it had

Table 2. Kaolinite atom coordinates and inner-hydroxyl hydrogen atom site occupancies obtained with the split-atom model.[1]

Atom	Coordinates		
	x	y	z
Al1	0.346 (3)	0.493 (2)	0.472 (2)
Al2	0.352 (4)	0.823 (2)	0.463 (2)
Al3	0.846 (3)	0.993 (2)	0.472 (2)
Al4	0.852 (4)	0.323 (2)	0.463 (2)
Si1	0.042 (3)	0.339 (2)	0.074 (2)
Si2	0.062 (3)	0.660 (2)	0.083 (2)
Si3	0.542 (3)	0.839 (2)	0.074 (2)
Si4	0.562 (3)	0.160 (2)	0.083 (2)
O1	0.110	0.342	0.307
O2	0.158 (3)	0.655 (2)	0.305 (2)
O3	0.057 (2)	0.494 (1)	−0.016 (2)
O4	0.254 (2)	0.223 (1)	0.017 (2)
O5	0.248 (3)	0.759 (1)	−0.013 (2)
O6	0.610	0.842	0.307
O7	0.658 (3)	0.155 (2)	0.305 (2)
O8	0.557 (2)	−0.010 (1)	−0.016 (2)
O9	0.754 (2)	0.723 (1)	0.017 (2)
O10	0.748 (3)	0.259 (1)	−0.013 (2)
OH1	0.103 (3)	−0.037 (1)	0.316 (2)
OH2	0.017 (3)	0.163 (2)	0.579 (2)
OH3	0.097 (2)	0.466 (2)	0.593 (2)
OH4	0.086 (3)	0.850 (2)	0.603 (2)
OH5	0.603 (3)	0.463 (1)	0.316 (2)
OH6	0.517 (3)	0.663 (2)	0.597 (2)
OH7	0.600 (3)	0.966 (1)	0.593 (2)
OH8	0.586 (3)	0.350 (2)	0.603 (2)
H1A	0.211 (6)	0.059 (3)	0.347 (8)
H1B	0.177 (7)	0.058 (4)	0.269 (9)
H2	0.143 (3)	0.167 (2)	0.722 (2)
H3	0.071 (3)	0.499 (2)	0.717 (2)
H4	0.079 (3)	0.811 (2)	0.715 (2)
H5A	0.677 (7)	0.558 (4)	0.269 (9)
H5B	0.711 (6)	0.559 (3)	0.347 (8)
H6	0.643 (3)	0.667 (2)	0.722 (2)
H7	0.570 (3)	−0.001 (2)	0.717 (2)
H8	0.579 (3)	0.311 (2)	0.715 (2)

Site Occupancies			
H1A	H1B	H5A	H5B
1.18 (13)	−0.18 (13)	1.09 (12)	−0.09 (12)

[1] Results from Reitveld refinement CN with C centering imposed and each inner-hydroxyl hydrogen atom initially assigned to two sites, as shown in Table 1, with half-occupancy in each.

the effect of reducing the R-values slightly and, thereby, of making the distinction between results for different refinement models more evident. The principal final results presented here are, therefore, based on the Rietveld refinements made using the PKAO86A data.

Two kinds of starting models were used. In the C models a C-face-centered relationship was imposed on all atoms except the two inner-hydroxyl hydrogen atoms, H(1) and H(5). In the second kind of model, the C-centering constraint was removed and the positional parameters of all atoms (except one required to fix the cell origin) were refined as independent variables in space group $P1$. Starting coordinates were based on

Table 3.   Tests of possible inner-hydroxyl mutual orientations.

	Site occupancy					R values (%)		
RR	H1A	H1B	H5A	H5B	Symbol	R_{wp}	R_i	R_B
CR	1	0	0	1	U U	2.34	2.34	
CQ	0	1	1	0	D D	2.35	2.36	
CP	0	1	0	1	D U	2.25	2.26	6.58
CM	1	0	1	0	U D	2.26	2.26	6.52
CS	0.03 (13)	0.97 (13)	−0.06 (15)	1.06 (15)		2.25	2.26	6.48
CN	1.18 (13)	−0.18 (13)	1.09 (12)	−0.09 (12)		2.25	2.26	6.53
CL	0.5	0.5	0.5	0.5		2.28	2.29	6.52
5I	1	0	1	0	U D	2.03	2.03	4.90

RR = Rietveld refinement; U = up, D = down, for z component of O–H vector; R_{wp} = weighted R for whole pattern; R_i = ratio of R_{wp} to $R_{expected}$ (i.e., to be expected if the only errors were the counting statistical fluctuations); R_B = "R-Bragg," i.e., an R based on Bragg intensities (see, e.g., Wiles and Young, 1981).

Suitch and Young (1983). The Brindley and Robinson (1946) cell setting was used throughout.

The C models permitted a stringent test of whether the two inner-hydroxyl ions were oriented similarly or differently. In the first refinements, each of the two inner-hydroxyl H atoms was represented by two half-atoms, A and B, placed initially in the positions derived from the Suitch and Young results such that the O–H(1A) and O–H(5B) vectors pointed toward the octahedral sheet and the O–H(1B) and O–H(5A) vectors pointed away from it (Table 1). The H(1A) and H(5B) positions, but not their site occupancies, were then constrained to maintain a C-face-centering relationship as they were varied in the refinement process. The H(1B) and H(5A) positions were similarly constrained to each other. The positions of all atoms were allowed to vary under the imposed C-face-centering constraint in the refinement. The site occupancies of the four H(1) and H(5) positions were assigned initial values of 0.5 and then allowed to vary independently under the constraint that the sum of the occupancies for the A and B sites for a given H atom must be equal to one. The rational for this strategem was to give the two inner-hydroxyl O–H vectors the maximum opportunity to become similarly oriented in the refined model if those orientations were consistent with the data. This stratagem also avoided any possibility that the two inner-hydroxyl O–H vectors the maximum opportunity to different orientations only because of some bias produced by nonequivalence of the other atoms between the two half cells; any bias introduced by this stratagem was toward equivalence of the two orientations.

RESULTS

Table 2 shows the positional parameters obtained for all atoms and the site occupancies obtained for the inner-hydroxyl hydrogen atoms if C centering was imposed and each inner-hydroxyl hydrogen atom was initially placed, half in each, in two sites (Rietveld refinement CN). Similar results were obtained with both PKAOLIN and PNKAO86 sets of data. The site occupancies for H(1B) and H(5B), which were not con-

strained to each other, were refined away. Therefore, the only inner-hydroxyl H atoms left in the structure were H(1A) and H(5A), the two H atoms which cause the O(H1)–H(1) vector to point toward the octahedral sheet and the O(H5)–H(5) vector to point away from it, toward the tetrahedral sheet.

Because of the C centering imposed on all other atoms, the two halves of the unit cell provided identical surroundings for H(1A) and H(5B) (also for H(1B) and H(5B)) at the outset of the Rietveld refinements with the C models. Thus, the only differences that could develop between the two halves was the difference in the inner-hydroxyl "half-atom" site occupancies. Crystallographically, then, the converse result, i.e., that of the A set refining away and the B set remaining as fully occupied, should be indistinguishable (as long as the C centering is imposed as stated). The survival of the A set rather than the B set, or vice versa, is simply equivalent to a shift of the cell origin. Such a shift is without crystallographic consequence in this model in which no symmetry elements exist that limit the choice of origin. Which set, A or B, actually refined away would be expected to be a matter of starting chance.

This ambivalence was tested with a series of Rietveld refinements of C models in which the H(1A), H(1B), H(5A), and H(5B) site occupancies were fixed at various values (Table 3). Rietveld refinements CP and CM show (Table 3) that the two possibilities for differing orientations for the two inner-hydroxyl ions, up-down and down-up, are equally good. In Rietveld refinements CN and CS the site occupancies were allowed to refine. There, also, the two modes of differing orientations were equally good.

The orientation models in which the two inner-hydroxyl ions were similarly oriented, either both "down" or both "up" (Rietveld refinements CR and CQ) gave distinctly higher R values than did the models with one up and one down, enough higher so that they could be rejected.

The penultimate model represented in Table 3, that of statistical disorder causing A and B sites to be equally occupied, cannot be so readily rejected solely on the

Table 4.   Rietveld structure-refinement results for kaolinite obtained with the two full 6–155°2θ sets of data.[1]

Atom	RR	Refined atomic parameters ($\times 10^3$) in kaolinite x	y	z
Al1	5G	354 (10)	505 (5)	470 (6)
	5H	363 (12)	498 (6)	453 (7)
Al2	5G	373 (8)	829 (5)	451 (6)
	5H	375 (9)	823 (6)	435 (6)
Al3	5G	876 (10)	997 (5)	470 (6)
	5H	869 (11)	997 (6)	454 (7)
Al4	5G	848 (9)	331 (5)	460 (6)
	5H	848 (10)	324 (5)	453 (6)
Si1	5G	067 (8)	349 (4)	056 (4)
	5H	055 (9)	335 (5)	041 (5)
Si2	5G	083 (7)	650 (4)	086 (5)
	5H	072 (10)	668 (6)	073 (6)
Si3	5G	543 (7)	841 (4)	076 (5)
	5H	555 (10)	836 (5)	071 (6)
Si4	5G	561 (8)	181 (3)	067 (5)
	5H	547 (10)	173 (5)	046 (5)
O1	5G	110	342	307
	5H	110	342	307
O2	5G	148 (7)	661 (4)	290 (5)
	5H	140 (8)	652 (4)	270 (5)
O3	5G	082 (7)	488 (4)	973 (4)
	5H	090 (7)	482 (4)	966 (4)
O4	5G	259 (6)	220 (3)	980 (4)
	5H	258 (7)	215 (4)	970 (4)
O5	5G	234 (7)	768 (3)	965 (4)
	5H	225 (7)	765 (4)	951 (4)
O6	5G	626 (9)	843 (5)	294 (5)
	5H	617 (10)	845 (6)	275 (5)
O7	5G	685 (7)	157 (4)	307 (5)
	5H	665 (8)	152 (4)	301 (5)
O8	5G	548 (7)	003 (3)	976 (4)
	5H	541 (7)	002 (4)	963 (5)
O9	5G	771 (6)	725 (3)	030 (4)
	5H	775 (8)	719 (4)	017 (4)
O10	5G	766 (7)	262 (4)	982 (4)
	5H	764 (7)	262 (4)	974 (5)
OH1	5G	117 (7)	967 (4)	312 (5)
	5H	118 (8)	955 (4)	288 (6)
OH2	5G	024 (7)	172 (4)	584 (5)
	5H	014 (9)	157 (4)	571 (5)
OH3	5G	128 (7)	465 (4)	585 (4)
	5H	122 (8)	463 (4)	571 (4)
OH4	5G	106 (6)	843 (4)	599 (4)
	5H	099 (7)	829 (4)	588 (4)
OH5	5G	607 (7)	468 (3)	304 (4)
	5H	605 (8)	471 (4)	291 (5)
OH6	5G	524 (7)	660 (4)	591 (5)
	5H	519 (9)	658 (4)	585 (5)
OH7	5G	593 (6)	974 (4)	577 (4)
	5H	598 (7)	973 (4)	571 (5)
OH8	5G	582 (7)	369 (3)	585 (5)
	5H	585 (7)	361 (4)	562 (5)
H1	5G	244 (8)	072 (4)	344 (5)
	5H	241 (9)	060 (5)	323 (5)
H2	5G	173 (8)	187 (4)	713 (6)
	5H	168 (8)	167 (5)	704 (6)
H3	5G	073 (8)	526 (4)	705 (5)
	5H	075 (11)	508 (5)	693 (7)
H4	5G	083 (8)	838 (4)	715 (5)
	5H	063 (9)	833 (5)	688 (7)
H5	5G	691 (8)	552 (4)	252 (5)
	5H	694 (9)	553 (5)	229 (6)
H6	5G	623 (8)	647 (4)	720 (6)
	5H	605 (9)	633 (5)	699 (6)

Table 4. Continued.

| Atom | RR | Refined atomic parameters ($\times 10^3$) in kaolinite | | |
		x	y	z
H7	5G	593 (8)	982 (4)	722 (6)
	5H	586 (10)	997 (5)	700 (7)
H8	5G	606 (7)	295 (4)	704 (5)
	5H	608 (9)	290 (4)	696 (6)

Lattice parameters (Å and degrees)

RR	a	b	c	α	β	γ
5G	5.1490 (0) [2]	8.9335 (1) [2]	7.3844 (1) [2]	91.930 (1)	105.042 (1)	89.791 (1)
5H				91.943 (1)	105.053 (1)	89.803 (1)

Other data

RR	Nominal wavelength (Å)	R_{wp} (%)	R_i	R_{exp} (%)	R_B	η	Data set
5G	1.9102	2.35	2.22	1.06	5.26	0.49 (8)	PNKAO86
5H	1.9500	2.72	1.31	2.03	6.29	0.43 (5)	PKAOLIN

[1] RR = Rietveld refinement. See footnote to Table 3 for the various Rs. η is the mixing parameter in the pseudo-Voigt profile function used.

[2] Not comparable because a different wavelength was used.

basis of the R values in the table. The refinement process itself, however, consistently rejected that model. That equal-occupancy model was the actual starting model for the Rietveld refinements in which the inner-hydroxyl site occupancies were allowed to vary. Those site occupancies did refine consistently, with both the PKAOLIN and the PNKAO86 data, so that either only the A set or only the B set survived, never both. Furthermore, the standard deviations were small enough (see Rietveld refinements CN and CS in Table 3) to assure that the occupancies for the A and B sites for a given inner-hydroxyl hydrogen atom are decidedly different, essentially 1 and 0 or 0 and 1. (Further detailed crystallographic analysis in explanation of this point is presented in Young, 1988.) These orientational differences are readily seen in the computer-drawn 100 projection presented in Figure 1. The two halves of the kaolinite unit cell are definitely not equivalent. The cell is primitive, not face centered.

The C-centering constraint imposed on the other ions was therefore released, and full refinements were carried out in which the positional parameters of all atoms (except the one chosen to fix the origin of the unit cell) were allowed to vary independently (space group $P1$). These Rietveld refinements were carried out separately with both new sets of data (final Rietveld refinements 5G with PKAOLIN data and 5H with PNKAO86 data) and with the truncated set, PKAO86A. The numerical results obtained with the two full-range sets of data are given in Table 4. The Rietveld refinement results obtained from these two different data sets agree generally within one or two estimated standard deviations. Even though 116 parameters (99 positional and 17 others) were varied simultaneously, the

standard deviations are smaller than those reported by Suitch and Young (1983). The values of the positional parameters themselves generally agree with the Suitch and Young values within 3 standard deviations (combined). (See Eq. (3) of Suitch and Young for the transformation between the cell setting used there for the neutron diffraction results and the cell setting used both there for the X-ray diffraction results and here for all results.) The best results, however, were obtained with the truncated set of data, PKAO86A, because most of the debilitating effects of uncorrected profile asymmetry were therein avoided, and substantially smaller R values were obtained. These results are presented in Table 5 (Rietveld refinement 5I) and should be taken
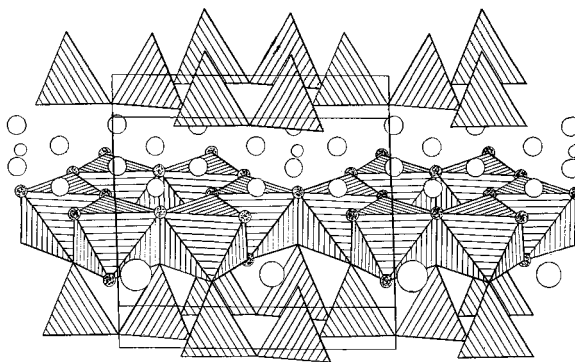

Figure 1. Computer-drawn 100 projection of the structure found. Open circles = hydrogen atoms. Stippled circles = OH⁻ and O²⁻ ions coordinating Al atoms. SiO₄ tetrahedra and Al(O,OH) octahedra are shown simply as geometric objects. Inner-hydroxyl hydrogen atoms are shown lowest in the figure. Note differing orientations of the two inner-hydroxyl ions.

Table 5. Best values of the atom positional parameters in Keokuk kaolinite.[1]

| Atom | Coordinates | | |
	x	y	z
Al1	0.352 (9)	0.501 (5)	0.471 (6)
Al2	0.370 (9)	0.830 (4)	0.447 (5)
Al3	0.862 (11)	−0.001 (5)	0.465 (6)
Al4	0.852 (8)	0.329 (4)	0.464 (5)
Si1	0.058 (8)	0.347 (4)	0.058 (4)
Si2	0.076 (8)	0.654 (5)	0.088 (5)
Si3	0.551 (7)	0.842 (4)	0.080 (5)
Si4	0.571 (8)	0.171 (4)	0.069 (5)
O1	0.110	0.342	0.307
O2	0.156 (7)	0.659 (4)	0.289 (5)
O3	0.089 (6)	0.487 (3)	−0.022 (4)
O4	0.261 (6)	0.227 (3)	−0.018 (4)
O5	0.242 (7)	0.765 (3)	−0.029 (4)
O6	0.626 (9)	0.845 (5)	0.296 (5)
O7	0.685 (6)	0.154 (3)	0.311 (4)
O8	0.549 (6)	−0.001 (3)	−0.019 (4)
O9	0.772 (6)	0.720 (3)	0.038 (4)
O10	0.772 (6)	0.260 (4)	−0.014 (4)
OH1	0.116 (7)	−0.033 (4)	0.312 (5)
OH2	0.018 (7)	0.170 (4)	0.583 (4)
OH3	0.126 (6)	0.469 (3)	0.589 (4)
OH4	0.106 (6)	0.837 (4)	0.597 (4)
OH5	0.609 (7)	0.465 (4)	0.308 (4)
OH6	0.525 (7)	0.657 (3)	0.597 (4)
OH7	0.593 (6)	−0.028 (4)	0.581 (4)
OH8	0.590 (6)	0.367 (3)	0.591 (4)
H1	0.237 (7)	0.068 (4)	0.343 (5)
H2	0.159 (8)	0.185 (4)	0.712 (6)
H3	0.063 (7)	0.527 (4)	0.704 (5)
H4	0.078 (8)	0.832 (4)	0.713 (5)
H5	0.682 (8)	0.552 (4)	0.256 (5)
H6	0.620 (7)	0.650 (4)	0.726 (5)
H7	0.593 (7)	−0.021 (4)	0.722 (5)
H8	0.611 (7)	0.292 (4)	0.700 (5)

Lattice parameters (Note: The indicated precision is much higher than the probable accuracy.)

a = 5.14971 (4) Å	b = 8.93507 (7) Å	c = 7.38549 (5) Å
α = 91.9283 (4)°	β = 105.0439 (4)°	γ = 89.7921 (5)°

R-values

R_{wp} = 2.03%	R_1 = 2.03%	R_B = 4.90%

[1] Results obtained from Rietveld refinement 5I made with the truncated set of data, PKAO86A. The various Rs are explained in the footnote to Table 3.

as the best values found to date for the atom positions in highly ordered kaolinite. Figure 2b shows the quality of the neutron powder diffraction data used (PKAO86A) and the quality of the fit of the calculated to the observed diffraction pattern.

Comparing the positional parameter values listed in Table 5 for the two half cells with those in Table 2, one sees that for the non-hydrogen atoms the departure from a C-face-centering relationship (i.e., the two half cells related by the translation (½)a + (½)b) exceeds 3 estimated standard deviations (combined) in only 3 of the 39 cases (x of O3–O8, x of OH3–OH7, and y of OH4–OH8 by 5, 4, and 6 estimated standard deviations, respectively). All inner-surface hydrogen atoms obey C centering within 3 estimated standard devia-

tions in their x and z coordinates, but depart from it by 6–8 estimated standard deviations in their y coordinates. The x coordinates of the inner-hydroxyl hydrogen atoms depart from the C-centering relationship by about 5 estimated standard deviations. Thus, some minor but real departures from C centering exist in several of the x,y positions.

The most marked departure from C-face centering exists in the z coordinates of the two inner-hydroxyl H ions. The difference between them is 0.092(7) for Rietveld refinement 5G, 0.094(8) for Rietveld refinement 5H, and 0.086(7) for Rietveld refinement 5I. Each of these values exceeds by more than 10 standard deviations the zero value required for C-face centering, i.e., for the two inner hydroxyls to be oriented the same

Kaolinite, PKAOLIN, 310787, RKAON5H
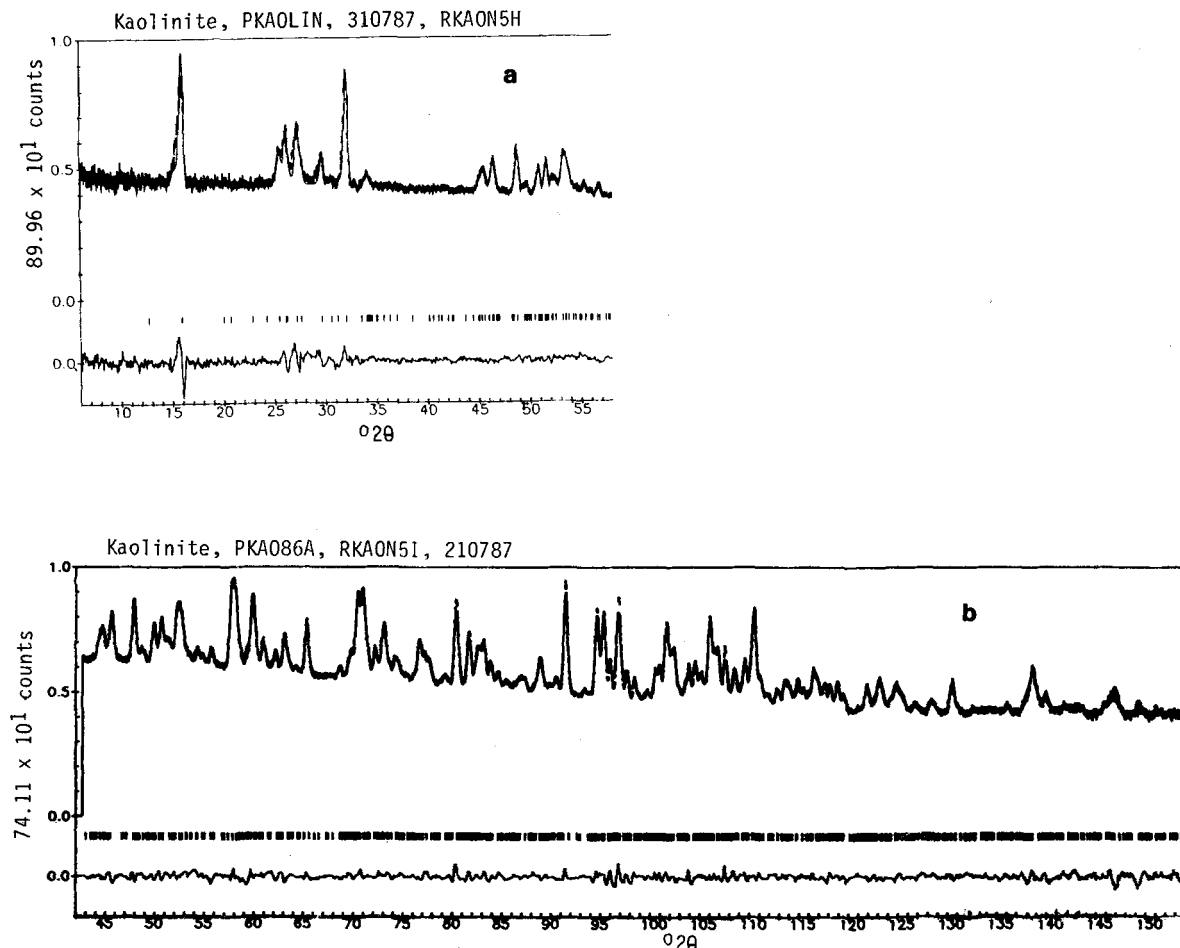

Kaolinite, PKAO86A, RKAON5I, 210787

Figure 2. Rietveld refinement plots for Keokuk kaolinite structure refined from high-resolution neutron powder diffraction data. (a) Lower angle portion for Rietveld refinement 5G, data PNKAO86. Note absence of "fast-rise, slow-fall" character normally seen in the 25–35°2θ range in patterns of kaolinites and attributed to layering faults. Data below 42.75°2θ were not used for final refinements because of the uncorrected asymmetry in that region. Background is high because of the strong incoherent scattering of thermal neutrons by the eight hydrogen (of 34) atoms in the unit cell. (b) Rietveld refinement 5I, data PKAO86A, showing data range used for the final refinements. Observed pattern shown in upper field by dots (vertical bars show statistical counting errors). Pattern calculated from best-fit model is shown by solid-line curve. Difference, observed minus calculated, is shown in the lower field. Short vertical bars in the intermediate field show positions of possible Bragg reflections.

way. They are decidedly not oriented in the same way. It is principally in this way that the "kaolinite" layer in kaolinite differs distinctively from that in dickite. In dickite, the two inner-hydroxyl ions are similarly oriented and obey a C-centering relationship (Adams and Hewat, 1981).

The effect of this or any difference in z parameters could not, of course, be sensed with only hkO data. The fact that the differences in the two inner-hydroxyl orientations is due preponderantly to the difference in their z parameters, whereas the x parameters differ by only half as much and only 5 estimated standard deviations, 0.055(11), from a C-centered relationship, may explain why Thompson and Withers (1987) were not able to detect the departure from C centering.

Selected interatomic distances and angles, based on the improved positional parameter values and their estimated standard deviations in Table 5, are given in Table 6. Computer program ORFFE4 (1985) was used. Not unexpectedly, all eight of the O–H distances in the hydroxyl ions are within about 2 standard deviations of 1.00 Å. All inner-surface hydroxyl ions are involved in hydrogen bonding, as they are in dickite (Adams and Hewat, 1981). The angles that the inner-surface O–H vectors make with the a,b plane (which is, effectively, the mixed O,OH atom plane) range from 50(3)° to 87(27)°. The differing orientations of the two inner-hydroxyl ions constitute the principal difference between the "kaolinite" layer in kaolinite and that in dickite.

Table 6. Orientation angles and internal distances for the hydroxyl ions in kaolinite.[1]

Inner-hydroxyl ion orientations		
	Angle (degrees) with	
Vector	a,b plane	a,c plane
O(H1)–H(1)	+12 (2)	56 (3)
O(H5)–H(5)	−22 (2)	51 (3)

Internal O–H distances (A)		Inner-surface hydroxyl ion angles with a,b plane (deg)	
O–H	Distance	Vector	Angle
O(H1)–H(1)	1.01 (5)		
O(H2)–H(2)	1.02 (5)	O(H2)–H(2)	63 (3)
O(H3)–H(3)	1.09 (5)	O(H3)–H(3)	50 (3)
O(H4)–H(4)	0.91 (5)	O(H4)–H(4)	66 (12)
O(H5)–H(5)	1.01 (5)	O(H6)–H(6)	75 (4)
O(H6)–H(6)	0.96 (5)	O(H7)–H(7)	87 (27)
O(H7)–H(7)	1.05 (5)	O(H8)–H(8)	50 (3)
O(H8)–H(8)	1.05 (5)		

[1] Based on results listed in Table 5 from Rietveld refinement 5I.

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