RIETVELD REFINEMENT OF NON-HYDROGEN ATOMIC POSITIONS IN KAOLINITE

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Abstract—The structure of kaolinite (non-hydrogen atoms only) from Keokuk, Iowa, was refined in space group $C1$ using CuKα X-ray powder diffraction data and Rietveld refinement techniques ($R_{wp} = 12.3\%$). A distance least-squares (DLS) model for the initial atomic coordinates avoided a false minimum and unrealistic results characteristic of previous Rietveld refinements of kaolinite. All Keokuk samples examined contain small amounts of dickite. The profile of the mixture was calculated using a fixed set of dickite atomic parameters and by constraining the dickite profile parameters to those refined for kaolinite. Results indicate that the individual kaolinite layer is very similar to the dickite layer; bond distances, which are similar to dickite and nacrite, are: Si–O, 1.60–1.63 Å; Al–O, 1.87–1.97 Å. The tetrahedral rotation angle is 6.9°, compared with 7.3° for dickite and 7.4° for nacrite. Previous Rietveld refinements apparently suffered from poor preferred orientation models, failure to consider the presence of dickite as a second phase, and, most importantly, refinement to a false-minimum structure. The conclusions based on the earlier refinements must therefore be reevaluated, especially regarding the kaolinite space group and hydrogen positions. Existing X-ray and electron diffraction and spectroscopic data support the presence of C-centering in kaolinite.

Key Words—Crystal structure, Dickite, Kaolinite, Rietveld refinement, X-ray powder diffraction.

INTRODUCTION

Since the crystal structure of kaolinite, $Al_2Si_2O_5(OH)_4$, was outlined by Pauling in 1930, numerous structure studies have been made using X-ray and neutron powder diffraction, X-ray single crystal, and electron diffraction methods. Brindley and Robinson (1946) located the non-hydrogen atoms using X-ray powder-camera data consisting of about 60 reflections to $\sim100°2\theta$ (CuKα). They concluded that the symmetry of the kaolinite structure is triclinic with probable space group $C1$. Zvyagin (1960) used about 100 electron diffraction reflections, which resulted in a model having tetrahedral rotation of 11.4°. Drits and Kashaev (1960) performed a single crystal X-ray structure determination of kaolinite, but their study appears to have been hampered by the presence of twinning in their crystal (Bailey, 1980). Recently, Suitch and Young (1983) refined the structure of Keokuk kaolinite in space group $P1$ using both X-ray and neutron powder diffraction data and Rietveld methods (Rietveld, 1969). They used CuKα X-ray data to 81°2θ to refine all non-hydrogen atom positions and then used neutron data to refine the positions of the hydrogens and hydroxyl oxygens, keeping the positions of all other atoms fixed. They concluded that the non-hydrogen framework has $C1$ symmetry, but the hydrogens, particularly those of the inner-hydroxyl groups, violate C-centering. The hydrogens of the inner-hydroxyl groups are equivalent in space group $C1$. Simultaneously, Adams (1983) reported a refinement of St. Austell kaolinite in space group $C1$ using neutron powder diffraction data. His results for the non-hydrogen atom positions were equivalent to those of Zvyagin (1960), although the St. Austell kaolinite exhibits two-dimensional diffraction and consists of at least two kinds of kaolinite (Plançon and Giese, 1988). Adams located all hydrogen atoms and found no evidence for the absence of a C-centered lattice, contrary to the results of Suitch and Young (1983). The conclusion of Suitch and Young (1983) that kaolinite has a P rather than C lattice was met with skepticism (e.g., Thompson and Withers, 1987) and prompted a reexamination of Keokuk kaolinite by Young and Hewat (1988) using neutron powder diffraction data and Rietveld refinement methods, refining the positions of all atoms simultaneously. They again concluded that the hydrogens of the inner-hydroxyl ions significantly violate C-centering and that most non-hydrogen atoms are consistent with a C cell. There appears to be no obvious crystal chemical explanation, however, for the different inner-hydroxyl orientations if the remainder of the structure obeys C-centering.

The symmetry question notwithstanding, several significant problems exist with these refinements (Suitch and Young, 1983; Young and Hewat, 1988) and the resulting structural models of kaolinite. The Si–O bond distances in the Suitch and Young model range from 1.48 to 1.78 Å, far outside the range of normally accepted Si–O distances in silicates (e.g., Table 11.2 of Smyth and Bish, 1988). For example, the Si–O dis-
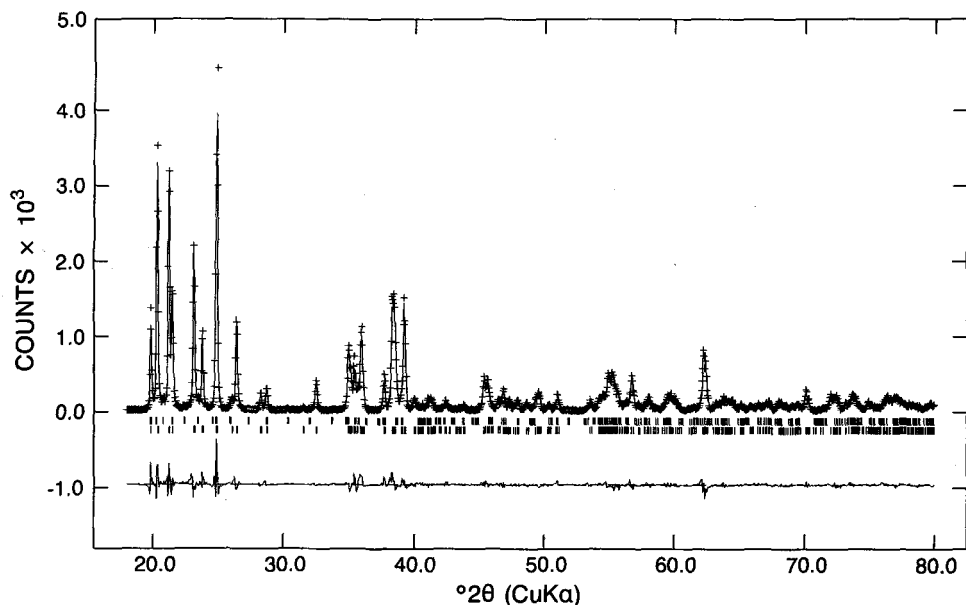
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Figure 1.   Observed (pluses) and calculated (solid line) X-ray powder diffraction pattern for Keokuk kaolinite from 18° to 80°2θ. Tic marks indicate positions for allowed reflections of dickite (upper) and kaolinite (lower). Both Kα₁ and Kα₂ reflections are shown. Lower curve is difference between observed and calculated profiles.

tances in nacrite range from 1.59 to 1.63 Å (Blount *et al.,* 1969), those in dickite range from 1.60 to 1.62 Å (Joswig and Drits, 1986), and those in pyrophyllite range from 1.60 to 1.63 Å (Lee and Guggenheim, 1981). The Si–O distances in the Young and Hewat model are unusual also, ranging from 1.43 to 1.79 Å, and the octahedral Al–O distances range from 1.66 to 2.06 Å. These Al–O distances also have a greater range than those found in nacrite (1.77 to 1.97 Å, Blount *et al.,* 1969), dickite (1.84 to 2.00 Å, Joswig and Drits, 1986), and pyrophyllite (1.89 to 1.93 Å, Lee and Guggenheim, 1981). Bond distances in both the Suitch and Young (1983) and the Young and Hewat (1988) kaolinite models suggest a need to re-evaluate the refinements.

Brindley *et al.* (1986) concluded that the Suitch and Young (1983) model of kaolinite is incompatible with the observed infrared spectrum, which shows a single sharp inner-hydroxyl vibration. Based on the Suitch and Young model, Brindley *et al.* suggested that kaolinite should exhibit two inner-hydroxyl vibration bands or a single broad band. In addition, Thompson and Withers (1987) showed that electron diffraction intensities calculated using the primitive Suitch and Young kaolinite structure do not agree with observed intensities, but Young and Hewat (1988) suggested that the departure from *C*-centered symmetry would be difficult to observe because most of the deviations from *C*-centering are in the *z* direction. Calculated X-ray powder diffraction patterns based on the Young and Hewat model, however, contain several weak, but probably measurable reflections violating *C*-centering [e.g., 010 at 9.96°2θ (CuKα), which has a calculated

relative intensity of 0.5], none of which have ever been documented in any kaolinite diffraction pattern. All of these observations demonstrated a need to refine the kaolinite structure further.

MATERIALS AND METHODS

All samples of kaolinite examined here were from geodes found near Keokuk, Iowa (Hayes, 1963) obtained from W. D. Keller and R. Gooley. All samples contained a minor amount of dickite, and the Keller samples contained minor quartz. No sample showed evidence of two-dimensional diffraction effects. The sample without quartz (Gooley) was used in the refinement.

The kaolinite was size fractionated by passing it through a 325-mesh sieve (45 μm) and back-mounting it in an aluminum holder, packing the sample against hard cardboard. No crushing or grinding was necessary. Data (Figures 1 and 2) were collected on an automated Siemens D-500 θ-θ diffractometer using CuKα radiation [λ = 1.5405981 (Deslattes and Henins, 1973) and 1.54439 Å for CuKα₁ and CuKα₂, respectively], incident- and diffracted-beam Soller slits, and a Kevex Psi solid-state Si(Li) detector. The detector is linear to about 4000 counts per second (cps) as determined by the single-absorber method; the highest intensity reflection used in the refinement was about 4800 cps. Using 1.0° divergence and receiving slits, the X-ray beam was completely within the sample area at angles >18°2θ. Data were collected in two parts to obtain comparable precision for the weaker high-angle reflections and the low-angle reflections. The first set of data was collected
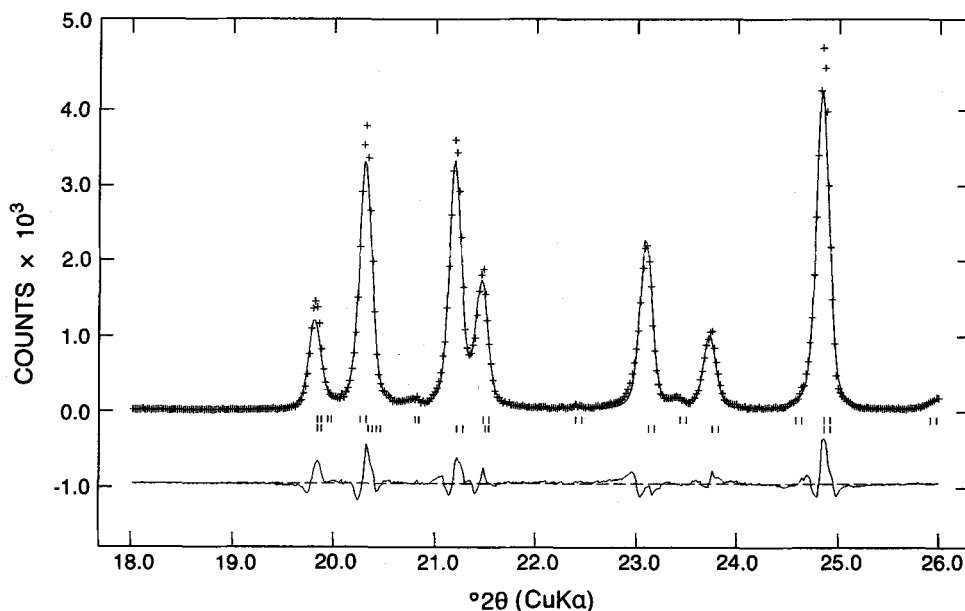
Figure 2. Expanded portion of Figure 1 showing data from 18° to 26°2θ. All data are as in Figure 1. Note absence of two-dimensional diffraction effects and presence of several obvious dickite reflections. Small offset between observed peak positions and calculated positions represented by vertical marks below reflections is due to a refined sample-displacement correction of ~90 μm, some of which is probably due to specimen transparency (linear absorption coefficient = 77.8 cm^{-1}).

over the angular range 10° to 90°2θ counting for 4.0 s every 0.02°2θ. Only the kaolinite 001 reflection occurs at <18°2θ, and this reflection was measured for completeness. The second data set was collected from 80° to 150°2θ counting for 12.0 s every 0.02°2θ.

The Rietveld refinement code GSAS (Larson and Von Dreele, 1988) used here incorporates features not available in most other Rietveld programs. The code accommodates multiple sets of data (e.g., the two series) and allows the constraint of numerous parameters in the refinement. For kaolinite, the initial structure model was obtained using the distance least-squares (DLS) method (Meier and Villiger, 1969; Villiger, 1969) and the Suitch and Young (1983) cell parameters after obtaining unsatisfactory Rietveld results using the Suitch and Young starting model. Distances for our

DLS model were averages from the dickite (Joswig and Drits, 1986), nacrite (Blount et al., 1969), and pyrophyllite (Lee and Guggenheim, 1981) structures and included all unique nearest-neighbor cation-anion and anion-anion distances in kaolinite. Inasmuch as all recent refinements have concluded that the non-hydrogen atoms obey C-centered symmetry (Adams, 1983; Suitch and Young, 1983; Thompson and Withers, 1987; Young and Hewat, 1988), space group $C1$ was used (Table 1) for both the DLS and Rietveld refinements. The origin in both refinements was fixed on O(3) at 0,1/2,0, conforming to the origin of Brindley and Robinson (1946).

The dickite structure (Joswig and Drits, 1986) was transformed to the setting suggested by Bailey (1963). Throughout Rietveld refinement, the dickite coordi-

Table 1. Unit-cell and refinement parameters for kaolinite and dickite.

Kaolinite	Space Group $C1$		
$a = 5.1554(1)$ Å	$b = 8.9448(2)$ Å	$c = 7.4048(2)$ Å	
$\alpha = 91.700(2)°$	$\beta = 104.862(1)°$	$\gamma = 89.822(1)°$	
Dickite[1]	Space Group Cc		
$a = 5.178(1)$ Å	$b = 8.937(2)$ Å	$c = 14.738(5)$ Å	$\beta = 103.82(2)°$

Range of data = 18°–150°2θ, 7151 observations, including 53 soft constraints.

$R_{wp}{}^2 = 12.28\%$ (12.14% without soft constraints).
$R_p{}^2 = 9.33\%$ (9.22% without soft constraints).

Preferred orientation coefficient = 0.990(2) (1.0 = no correction)

[1] Cell transformed according to Bailey (1963).
[2] R_{wp} = weighted profile residual, R_p = profile residual.

Table 2. Final atomic parameters for Keokuk kaolinite.

Atom	x	y	z	U_{iso} (Å)[1]
Si(1)	0.9942(15)[2]	0.3393(6)	0.0909(9)	0.0056(5)
Si(2)	0.5064(14)	0.1665(6)	0.0913(9)	0.0056(5)
Al(1)	0.2971(15)	0.4957(7)	0.4721(10)	0.0105(6)
Al(2)	0.7926(15)	0.3300(7)	0.4699(10)	0.0105(6)
O(1)	0.0501(17)	0.3539(9)	0.3170(10)	0.0090(8)
O(2)	0.1214(17)	0.6604(8)	0.3175(10)	0.0090(8)
O(3)	0.0	0.5	0.0	0.0090(8)
O(4)	0.2085(15)	0.2305(8)	0.0247(12)	0.0090(8)
O(5)	0.2012(15)	0.7657(8)	0.0032(12)	0.0090(8)
OH(1)	0.0510(17)	0.9698(8)	0.3220(12)	0.0114(8)
OH(2)	0.9649(18)	0.1665(8)	0.6051(11)	0.0114(8)
OH(3)	0.0348(17)	0.4769(9)	0.6080(11)	0.0114(8)
OH(4)	0.0334(18)	0.8570(9)	0.6094(12)	0.0114(8)

[1] $U_{iso} = B_{iso}/8\pi^2$.

[2] Values in parentheses are estimated standard deviations in the last place.

nates were fixed and only the cell parameters were varied. Most other parameters for dickite (e.g., profile, preferred orientation) were constrained to equal those refined for kaolinite. Both sets of data were used in the refinement, and data for $<18°2\theta$ (i.e., the 001 reflection) were excluded.

The pseudo-Voigt profile function described by Thompson *et al.* (1987) was employed with anisotropic peak broadening (Greaves, 1985; Larson and Von Dreele, 1988). A three-term cosine Fourier series modeled the background, and the March function preferred orientation correction (Dollase, 1986) with (001) as the preferred orientation plane was used. This correction remained at 0.99 ± 0.02 throughout the refinement. Manual adjustment of the correction to values as low as 0.2, in the direction expected for preferred orientation of platelets, always resulted in refinement of the value back to the correction reported here. Isotropic temperature factors were refined for groups of atoms in kaolinite (i.e., all Si, all Al, all hydroxyl oxygens, and all other oxygens grouped together). The ideal chemical composition for kaolinite was assumed and unit-site occupancies were assigned to all atoms.

In the early stages, in order to improve the stability of the Rietveld refinement, "soft" distance constraints were imposed, similar to the DLS method, on the kaolinite structure, although it is noteworthy that no difficulty was encountered without the distance constraints. A total of 53 constraints were used, eight tetrahedral distances of 1.61(2) Å, 12 octahedral distances of 1.91(2) Å, 12 O–O distances of 2.64(4) Å, 18 O–O distances of 2.81(4) Å, and three shared O–O distances of 2.42(2) Å. After converging with all parameters varied, distance constraints were removed, which resulted in shifts of $<2\sigma$ for all atom parameters except the x position of OH(2), which shifted $<3\sigma$. The final results (Table 2) are those obtained *with* the distance constraints making up 5.0% of the total minimization function $[M = \Sigma W_i(y_0 - y_i)^2]$ for all data.

RESULTS AND DISCUSSION

Rietveld refinement

When the Suitch and Young (1983) model of kaolinite was used as a starting model, Rietveld refinement converged to results similar to those of Suitch and Young or Young and Hewat, with unrealistic bond distances and a higher weighted-profile residual (18.0% vs. 12.3%). Refinement procedures used with the Suitch and Young model were identical to those used with the DLS starting model, *including* "soft" distance constraints. Attempts to obtain a more reasonable structure by dramatically raising the weight of the distance constraints on the Suitch and Young model did not significantly improve the results nor did eliminating the distance constraints. In addition, adjustment of the preferred orientation coefficient to values as low as 0.2 yielded no improvement in the atom positions, and the coefficient always refined toward 0.99, the value reported here. Thus, the use of the DLS-derived model was the most significant feature for a successful refinement. The Suitch and Young (1983) model likely represents a false-minimum structure for both X-ray and neutron data. The reason for the false minimum is not apparent, although it is not due to preferred orientation, the presence of dickite in the sample, or the choice of space group. The value of the preferred orientation coefficient, 0.99, indicating virtually no preferred orientation, is noteworthy and probably results from the back-packed mounting method and the low linear absorption coefficient of kaolinite (77.8 cm^{-1}), yielding a large sampling volume.

The resulting atom positions and temperature factors are given in Table 2, and the comparison between observed and calculated data is shown in Figure 1. Details of the profile in Figure 2 illustrate the absence of two-dimensional diffraction and the presence of dickite. The apparent underestimation of some calculated intensities between 20° and 40°2θ is due to peak shape effect, in which tails are overestimated and peaks are underestimated, but the integrated intensities are correct. Dickite reflections appear in Figure 2 of Suitch and Young and may exist in Figure 2 of Young and Hewat, although neither group acknowledged the presence of dickite or included it in their refinements. The magnitude of the estimated standard deviations (e.s.d.'s) on the atom positions is about 20% of those of Young and Hewat (1988), and the results of the present refinement represent the highest precision determination of kaolinite to date. Although the e.s.d.'s obtained in the present study can be directly compared with results of other Rietveld studies, Hill and Madsen (1984) suggested that the Rietveld method underestimates errors for data sets of more than a few thousand counts. Because $>15,000$ counts were accumulated here, the positional parameter e.s.d.'s may be optimistic. The temperature factors for kaolinite are similar to those
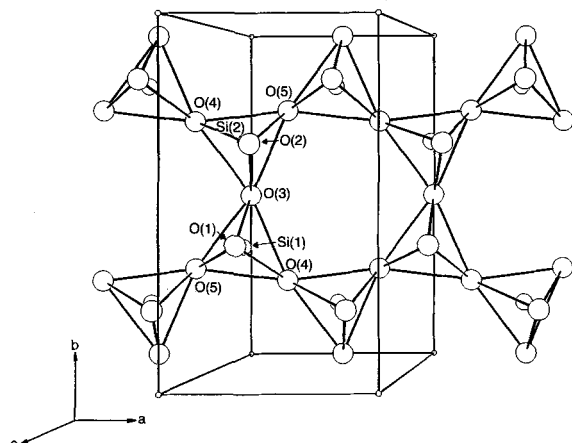
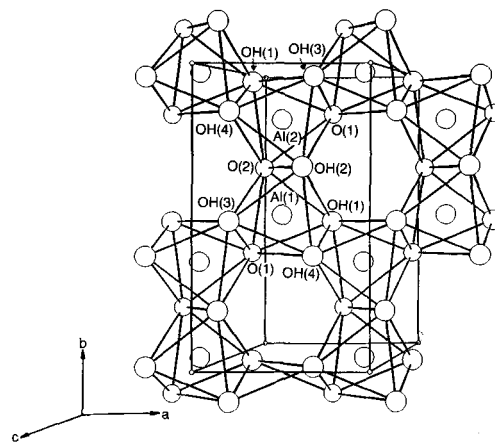Figure 3. Perspective drawing of tetrahedral sheet in ka-olinite structure.

Figure 4. Perspective drawing of octahedral sheet in kaolinite structure illustrating vacant octahedral site and significant shortening of octahedral shared edges.

obtained by Joswig and Drits (1986) for dickite, and no problems were encountered in their derivation. The large angular range of the present data probably contributed to the successful refinement of temperature factors.

The profile function used in the Rietveld refinement code GSAS accommodates anisotropic broadening of reflections, a major improvement to Rietveld codes. This analysis yields crystallite size and strain data significantly better than a simple Scherrer equation analysis, because it considers the profiles of *all* reflections. In kaolinite, anisotropic broadening is significant and relates to both sample and instrument effects. Instrumental effects were not included in the analysis, and, therefore, the reported magnitudes given below are minima for sizes and maxima for strain. Correction for instrumental broadening would decrease the sample-related broadening, thereby increasing the estimated domain sizes and reducing the amount of strain. The profile parameters indicated a coherent domain size of >960 Å in the *a-b* plane, a domain size of >5500 Å perpendicular to the *a-b* plane, <0.1% strain (<0.1% fluctuation in the *a* and *b* lattice parameters) in the *a-b* plane, and <0.4% strain along [001]. These parameters, thus, suggest that both strain and particle size contribute to the broadening in the sample. Contrary to expectations for a layer silicate occurring as platy crystallites (e.g., Keller, 1988, Figure 8), the particle-size data suggest that coherent domains in this kaolinite are rod shaped, elongated in the [001] direction, rather than platy. This configuration may result from nucleation of domains within a single crystallite in which the vacant octahedral site is in one of three possible structural positions 120° apart (e.g., see vacant occupancy A, B, C in Mansfield and Bailey, 1972).

Kaolinite structure

The kaolinite cell parameters (Table 1) are similar to those of Suitch and Young (1983), and the respective

interaxial angles are statistically identical. Minor differences between the respective *a, b,* and *c* dimensions are partly the result of using slightly different values for the wavelength of CuKα radiation. Likewise, the significant differences between our cell parameters and those determined by Young and Hewat (1988) are probably due to imprecision in their neutron wavelength.

The final scale factors for kaolinite and dickite, which are related directly to the volume fraction of each component, suggest that the sample contains about 4.6 wt. % dickite. For dickite, the *b* and *c* parameters and the β angle are comparable to those reported by Bailey (1963), but *a* is significantly larger than expected. This discrepancy may represent the true cell parameters of dickite in this sample, or it may relate to the difficulty in obtaining accurate cell parameters from such small quantities of dickite. Possibly, the dickite is intergrown with kaolinite on such a fine scale that the material differs from discrete dickite.

Selected bond distances and angles calculated using GSAS are given in Table 3, and Figures 3 and 4 illustrate the tetrahedral and octahedral sheets in kaolinite, respectively. Many aspects of the kaolinite structure are similar to the refined structures of other Al-Si layer silicates, e.g., dickite, nacrite, and pyrophyllite. For example, the Si-O (1.60-1.63 Å) and Al-O (1.87-1.97 Å) distances are close to those of dickite, nacrite, and pyrophyllite. The tetrahedral rotation angle, 6.9°, is close to the tetrahedral rotation angles for dickite (7.3°) and nacrite (7.4°). The rotation angle in our structure is significantly less than the 11.3° angle in the Zvyagin (1960) structure, the 11.1° rotation found by Drits and Kashaev (1960), or the angle of ~10° suggested by Brindley and Nakahira (1958). All Al-OH distances are shorter than the Al-O distances. In addition, both Al-OH(1) (inner-hydroxyl) distances in kaolinite are longer than all other Al-OH distances, resulting in a

Table 3. Selected interatomic distances and angles for Keokuk kaolinite.

Bond lengths (Å)				Bond angles (°)	
Tetrahedron Si(1)					
O(1)	1.626(5)	O(1)–O(3)	2.675(8)	O(1)–O(3)	111.6(4)
O(3)	1.609(5)	O(4)	2.707(7)	O(4)	112.6(3)
O(4)	1.628(5)	O(5)	2.648(8)	O(5)	109.5(4)
O(5)	1.617(5)	O(3)–O(4)	2.629(7)	O(3)–O(4)	108.6(4)
Mean	1.620	O(3)–O(5)	2.610(7)	O(5)	108.0(4)
		O(4)–O(5)	2.598(7)	O(4)–O(5)	106.4(4)
		Mean	2.645	Mean	109.9
Tetrahedron Si(2)					
O(2)	1.630(5)	O(2)–O(3)	2.651(7)	O(2)–O(3)	109.6(3)
O(3)	1.614(5)	O(4)	2.707(8)	O(4)	114.0(3)
O(4)	1.597(6)	O(5)	2.663(7)	O(5)	110.5(4)
O(5)	1.611(5)	O(3)–O(4)	2.577(7)	O(3)–O(4)	106.7(4)
Mean	1.613	O(3)–O(5)	2.593(7)	O(5)	107.0(4)
		O(4)–O(5)	2.606(7)	O(4)–O(5)	108.6(4)
		Mean	2.633	Mean	109.4
Octahedron Al(1)					
Unshared					
O(1)	1.930(6)	O(1)–O(2)	2.767(7)		
O(2)	1.965(5)	OH(1)	2.777(7)		
OH(1)	1.932(6)	OH(4)	2.851(8)		
OH(2)	1.880(6)	O(2)–OH(1)	2.784(7)		
OH(3)	1.892(6)	OH(3)	2.868(8)		
OH(4)	1.868(6)	OH(1)–OH(2)	2.818(8)		
Mean	1.911	OH(2)–OH(3)	2.800(8)		
		OH(4)	2.790(7)		
		OH(3)–OH(4)	2.780(7)		
		Mean	2.804		
		Shared	2.410(6)		
		O(1)–OH(3)	2.394(6)		
		O(2)–OH(2)	2.405(6)		
		OH(1)–OH(4)	2.403		
		Mean			
Octahedron Al(2)					
O(1)	1.969(5)	O(1)–O(2)	2.812(8)		
O(2)	1.936(5)	OH(1)	2.780(7)		
OH(1)	1.920(6)	OH(2)	2.872(7)		
OH(2)	1.884(6)	O(2)–OH(1)	2.791(6)		
OH(3)	1.900(6)	OH(4)	2.871(7)		
OH(4)	1.898(6)	OH(1)–OH(3)	2.828(9)		
Mean	1.918	OH(2)–OH(3)	2.800(7)		
		OH(4)	2.804(7)		
		OH(3)–OH(4)	2.805(7)		
		Mean	2.818		

Values in parentheses are estimated standard deviations in the last place.

closer approach of Al atoms to the inner-surface hydroxyl plane. The shared edges in the octahedra are short, ~2.4 Å, comparable with the shared edges in dickite, nacrite, and pyrophyllite. The Si–O(apical) [O(1) and O(2)] distances are among the longest Si–O distances in kaolinite, as they are in pyrophyllite, but opposite to what occurs in dickite. As Newnham (1961) noted for dickite, apical-to-basal oxygen distances are larger than basal-to-basal oxygen distances, reflecting elongation along c*. Also, the basal oxygen plane in kaolinite is corrugated like that of dickite. Atom O(4) [= O(3) in Newnham, 1961] is ~0.16 Å higher in the

cell than the other two basal oxygens (vs. ~0.17 Å in dickite). The major difference between kaolinite and dickite is the location of the vacant octahedral site in successive layers (Bailey, 1963). Otherwise, the individual layers are remarkably similar.

SUMMARY AND CONCLUSIONS

Our Rietveld refinement yielded the highest precision determination of the kaolinite structure to date and identified several complexities inherent in earlier studies. First, and most significantly, the Suitch and Young and Young and Hewat models apparently rep-

resent a false-minimum structure for both X-ray and neutron data. Our attempts to avoid this false minimum by dramatically varying the preferred orientation correction or raising the weights on distance constraints did not result in a more realistic structure. A DLS starting model solved this problem and yielded a successful refinement. Second, numerous weak reflections attributable to dickite exist in all of our X-ray patterns of Keokuk kaolinite (Figure 1). The same reflections are obvious in Figure 2 of Suitch and Young (1983) and may exist in Figure 2 of Young and Hewat (1988), although neither group acknowledged the presence of dickite or included it in their refinements. Inclusion of dickite in the refinement corrected for overlap of dickite reflections with those of kaolinite, resulting in a significant decrease in the weighted profile residual. Finally, calculated powder diffraction patterns based on the kaolinite structures determined by Suitch and Young (1983) and Young and Hewat (1988) contain several weak but probably measurable reflections that violate C-centering i.e., for which $h + k \neq 2n$ (e.g., 010 at $9.96°2\theta$, with a calculated intensity of 0.5). These reflections have not been observed in any kaolinite diffraction patterns.

Considering the problems inherent in the Suitch and Young and the Young and Hewat models for kaolinite and the diffraction and spectroscopic evidence opposing their conclusions, a neutron (or a combined neutron and X-ray refinement) of the kaolinite structure should be pursued starting with a better model. A refinement using neutron data should allow the question of symmetry to be answered definitely and should provide more accurate hydrogen positions than are presently available. Based on previous spectroscopic studies and the apparent problems of previous refinements, however, kaolinite probably has a C-centered Bravais lattice.

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