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HYDROGEN POSITIONS IN DICKITE

Key Words—Atomic coordinates, Crystal structure, Dickite, Hydrogen, Hydroxyl, X-ray diffraction.

INTRODUCTION

The crystal structure of dickite was initially determined by Newnham and Brindley (1956) and refined from single crystal, film X-ray data by Newnham in 1961. Newnham was unable to locate the hydroxyl hydrogen atoms from his data which gave an R-factor of 7.5%. The unit cell of dickite contains two kaolinite layers, related by a glide plane. In each layer there are four hydroxyl groups; one is situated in the plane of atoms shared by tetrahedra and octahedra (inner hydroxyls), whereas the remaining three form the outer surface of the octahedral sheet (inner-surface hydroxyls) as distinct from hydroxyls on the surface of clay crystals.

Controversy has existed regarding the orientation of these hydroxyl groups. Farmer (1964), Newnham and Brindley (1956), Newnham (1961), and Farmer (1974) suggested that weak hydrogen bonds exist between each of the inner surface hydroxyls and the corresponding basal oxygen in the next layer. Based on infrared studies, Wada (1967), Ledoux and White (1964), Serratosa *et al.* (1962), and Wolf (1963), however, stated that only some of these hydroxyls are involved in hydrogen bonding and that the location of the inner hydrogen was uncertain. Serratosa *et al.* (1962), however, in their study of kaolinite, considered the inner hydroxyl to be essentially perpendicular to the 1:1 layer and oriented toward the hexagonal hole in the tetrahedral sheet. Wolf (1963) shared this view, but Ledoux and White (1964) favored a model where that hydroxyl was directed towards the empty octahedral site.

By a technique minimizing electrostatic energy, Giese and Datta (1973) calculated the positions of the hydrogen atoms. They concluded that the inner-surface hydroxyl hydrogens are almost normal to (001), whereas the inner hydrogen points toward the empty octahedral hole nearly parallel to (001). In micas, the inner O–H bond points away from the octahedral sheet (Giese, 1979). From neutron powder diffraction, Adams and Hewat (1981) refined Newnham's (1961) structure and located and refined hydrogen positions from a difference Fourier map. Significant discrepancies exist, however, between their refined hydrogen positions and those obtained from the calculations of Giese and Datta (1973). In addition, Rozdestvenskaya *et al.* (1982) refined the structure of dickite from X-ray diffraction data and found the hydrogen coordinates to be at variance with the theoretical calculations of both Giese and Datta (1973) and Bookin *et al.* (1982) and with the neutron values of Adams and Hewat (1981).

We therefore undertook this study to obtain more accurate X-ray diffraction determined hydrogen positions in hopes of confirming one or more of the earlier work.

EXPERIMENTAL

The crystal used in this study came from the Smithsonian Institution #115645 (origin = St. Clair, Pennsylvania). A plate-like single crystal (~0.02 × 0.15 × 0.15 mm) was used on an Enraf-Nonius CAD4 diffractometer for the data collection (MoKα radiation). The previously reported space group *Cc* was confirmed. The cell parameters were refined from 18 reflections distributed through reciprocal space. Crystal data are: F.W.($Al_2Si_2O_5(OH)_4$) = 258.2, Z = 4, a = 5.149(2), b = 8.922(3), c = 14.395(3) Å, β = 96.76(2)°,

Table 1. Positional parameters of non-hydrogen atoms and equivalent isotropic thermal parameters.[1]

Atom	x	y	z	B(A²)
Si (1)	0.0121 (2)	0.4013 (1)	0.04073 (9)	0.45 (1)
Si (2)	−0.0010 (1)	0.07259 (9)	0.0403 (1)	0.46 (1)
Al (1)	−0.0861 (3)	0.2523 (1)	0.23166 (9)	0.56 (1)
Al (2)	0.4194 (3)	0.4174 (1)	0.2308 (1)	0.56 (1)
O (1)	−0.0419 (6)	0.2382 (3)	−0.0061 (2)	0.72 (4)
O (2)	0.2550 (6)	0.4714 (3)	−0.0065 (2)	0.72 (4)
O (3)	−0.2354 (6)	0.5067 (3)	0.0073 (2)	0.83 (4)
O (4)	0.0782 (6)	0.3910 (3)	0.1518 (2)	0.65 (4)
O (5)	0.0056 (6)	0.0815 (3)	0.1514 (2)	0.61 (4)
OH (1)	0.5832 (5)	0.2749 (3)	0.1567 (2)	0.70 (4)
OH (2)	0.2454 (6)	0.2769 (3)	0.2957 (2)	0.80 (4)
OH (3)	0.2485 (6)	0.8948 (3)	0.2984 (2)	0.64 (4)
OH (4)	0.3234 (6)	0.5839 (3)	0.2956 (2)	0.71 (4)

[1] Standard deviations from the least squares refinement are in parentheses.

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Table 2. Positional and isotropical thermal parameters for hydrogen atoms.

	x	y	z	B(Å²)
HOH (1)	0.492 (18)	0.196 (9)	0.133 (7)	4.6 (2.1)
HOH (2)	0.295 (15)	0.270 (7)	0.344 (7)	2.3 (1.6)
HOH (3)	0.300 (13)	0.940 (6)	0.344 (5)	1.2 (1.2)
HOH (4)	0.279 (11)	0.564 (5)	0.354 (4)	0.2 (1.0)

[1] Standard deviations from the least squares refinement are in parentheses.

$V = 656.7(6)$ Å^3, $D_x = 2.614$ g/cm^3, $\mu(MoK\alpha) = 8.16$ cm^{-1}, $\lambda(MoK\alpha) = 0.71069$ Å. The intensities of 4045 reflections (2615 independent) were measured by the θ-2θ scan technique to $2\theta \leq 90°$ using graphite monochromatized MoKα radiation (⅔ time on peak and ⅙ on each background to a maximum of 120 sec). Three intensity standards monitored after every 7200 sec of X-ray exposure varied less than 2% throughout data collection. Orientation was maintained by checking three reflections after every 150 reflections and recentering all 18 reflections when necessary. The data were reduced in the normal fashion and corrected for absorption by the empirical psi scan method. A total of 1527 reflections ($I \geq 3\sigma$) were considered observed and used in the refinement (29 with $\sin\theta/\lambda < 0.18$ and the 00*l* reflections were omitted due to probable anisotropic extinction effects).

Hydrogen atoms were located from a difference Fourier map based on refined non-hydrogen atom positions, starting from those of Newnham (1961). Refinement by full-matrix least squares ($\Sigma w(|kFo| - Fc|)^2$ minimized and $w^{-1} = \sigma^2_{counting} + (0.05F_0^2)^2$), including these hydrogen atoms with variable coordinates and isotropic thermal parameters, converged (max shift/error < 0.33) with final R values of 0.046 and 0.053

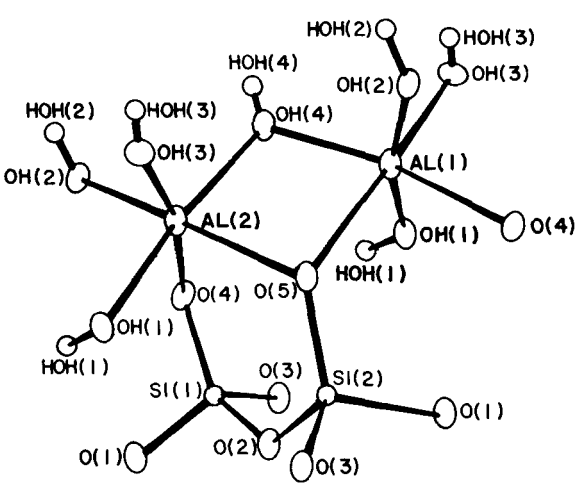


Figure 1. Perspective view of the structure of dickite.

Table 3. Hydrogen coordinates in dickite.

		Rozdestvenskaya *et al.* (1982)			Giese and Datta (1973) coordinates transformed to cell of Newnham and Brindley (1956)			Adams and Hewat (1981) neutron coordinates			Present work		
		x	y	z	x	y	z	x	y	z	x	y	z
Inner hydroxyl	H (1)	0.441	0.256	0.145	0.496	0.185	0.174	0.468 (10)	0.173 (7)	0.132 (5)	0.492 (18)	0.196 (9)	0.133 (7)
Inner-surface hydroxyl	H (2)	0.285	0.268	0.362	0.295	0.254	0.361	0.284 (11)	0.219 (6)	0.367 (5)	0.295 (15)	0.270 (7)	0.344 (7)
	H (3)	0.294	0.918	0.352	0.263	0.935	0.361	0.312 (11)	0.946 (8)	0.378 (4)	0.300 (13)	0.940 (6)	0.344 (5)
	H (4)	0.288	0.583	0.356	0.280	0.578	0.359	0.236 (10)	0.582 (6)	0.363 (5)	0.279 (11)	0.564 (5)	0.354 (4)

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Table 4. Bond distances and angles involving hydrogens.

Hydrogen bond distances (Å) and angles (°)	
OH (1)–H (1)	0.874 (85)
OH (2)–H (2)	0.728 (99)
OH (3)–H (3)	0.801 (71)
OH (4)–H (4)	0.895 (63)
Hydroxyl-hydrogen-oxygen angles (°)	
OH (2)–H (2)–O (1)	175.7 (7.5)
OH (3)–H (3)–O (3)	145.1 (6.4)
OH (4)–H (4)–O (2)	172.1 (5.0)
Bond angles involving hydrogen (°)	
Al (2)–OH (1)–H (1)	121 (7)
Al (2)–OH (2)–H (2)	112 (6)
Al (2)–OH (3)–H (3)	128 (5)
Al (2)–OH (4)–H (4)	114 (3)
Al (1)–OH (1)–H (1)	120 (6)
Al (1)–OH (2)–H (2)	136 (6)
Al (1)–OH (3)–H (3)	128 (5)
Al (1)–OH (4)–H (4)	136 (3)

(weighted) for the 1527 reflections. All calculations were done with CAD4-SDP programs on a PDP 11/34 computer. Atomic scattering factors were taken from the International Tables for X-ray Crystallography (1974).

DISCUSSION

The final positional parameters of the non-hydrogen and hydrogen atoms are shown in Tables 1 and 2, respectively. Figure 1 shows a perspective view of the structure of dickite. The positional parameters of the non-hydrogen atoms are in good agreement with those of Newnham (1961). Table 3 shows a comparison of hydrogen positions with those of previous workers. The hydrogen bond parameters are in Table 4. Compared with the neutron diffraction results, significant discrepancies exist in the inner-surface hydrogen positions, e.g., y coordinate of H(2) and x coordinate of H(3), part of which is undoubtedly due to the artificial shortening of covalent bonds involving hydrogens observed in X-ray diffraction studies. In general, and especially for the inner-hydroxyl hydrogen, the agreement with the neutron diffraction values is good. The present results are also in good agreement with the calculated values of Giese and Datta (1971) except for the z coordinate of the inner hydrogen. The X-ray diffraction results (only 494 independent reflections) of Rozdestvenskaya *et al.* (1982) for the inner hydrogen, however, are clearly in serious disagreement with either our results or the neutron diffraction results of Adams and Hewat (1981).

In conclusion, the general agreement of this work with the neutron diffraction work of Adams and Hewat (1981) should settle any doubts concerning the hydrogen positions resulting from studies such as the X-ray diffraction work of Rozdestvenskaya *et al.* (1982).

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