Clays and Clay Minerals, Vol. 29, No. 4, 316–319, 1981.

NOTE

HYDROGEN ATOM POSITIONS IN DICKITE

Key Words—Atomic coordinates, Crystal structure, Dickite, Hydrogen, Hydroxyl, Neutron diffraction.

INTRODUCTION

The crystal structure of dickite has been known for some time (Newnham and Brindley, 1956; Newnham, 1961), but X-ray structure analyses have not located the hydrogen atoms of the hydroxyl groups. Some controversy exists concerning the orientation of these O–H groups[1]; several authors have suggested that long hydrogen bonds exist between each of the three inner-surface OH groups and the O atoms (Newnham and Brindley, 1956; Newnham, 1961; Farmer, 1964; Farmer and Russell, 1964), whereas others have indicated that only some of these OH groups are involved in hydrogen bonding (Serratosa *et al.*, 1962, 1963; Wolff, 1963; Ledoux and White, 1964; Wada, 1967). There is also some disagreement over the orientation of the remaining inner hydroxyl group in the kaolin-group minerals. For kaolinite itself, Serratosa *et al.* (1962, 1963) and Wolff (1963) considered that this O–H group is perpendicular to the 1:1 layer and directed towards the hexagonal hole in the tetrahedral sheet; however, Ledoux and White (1964) proposed an orientation towards the empty octahedral site.

Giese and Datta (1973) calculated the positions of the hydrogen atoms in each of the kaolin-group minerals using an electrostatic approach. For dickite they located the three inner-surface hydroxyls almost perpendicular to (001) in positions which are consistent with interlayer O–H . . . O hydrogen bonds. The remaining inner hydrogen atom was placed pointing towards the empty octahedral site. The orientation of this inner hydroxyl group almost parallel to (001) is consistent with the situation which exists in dioctahedral micas. Here, the analogous hydroxyl group makes an angle of ~15–20° with (001), and its projection onto (001) makes an angle of ~30° with b (see, e.g., Tsuboi, 1950; Vedder and McDonald, 1963; Rothbauer, 1971). However, one difference between the model of Giese and Datta and the situation found in the micas is that in the latter the hydroxyl is pointing outward, *away from* the octahedral sheet. Giese and Datta (1973) concluded that the O–H vector points *into* the octahedral sheet. It is also of interest to note that in a one-dimensional neutron diffraction study of a kaolinite:formamide intercalate, Adams *et al.* (1976) found that the inner hydroxyl made an angle of ~25° with (001) but pointed away from the octahedral sheet, i.e., it was oriented in a manner similar to that found in micas.

It was therefore considered fruitful to examine the structure of dickite using neutron diffraction to locate the hydrogen atoms and confirm the orientations of all O–H groups. Unfortunately, large crystals of dickite were not available, and only powder diffraction experiments could be performed. A one-dimensional scattering map, however, enabled the orientation of the hydroxyl groups to be deduced. In addition, a Rietveld profile refinement (Rietveld, 1969), which allows a full three-dimensional structural refinement using only powder data, was attempted. Although this technique has usually been applied to relatively simple structures, a few more complex oxide structures have been successfully refined (e.g., Von Dreele and Cheetham, 1974; Marinder *et al.*, 1980).

[1] The nomenclature used here follows that in Giese and Datta (1973).

EXPERIMENTAL

A sample of Australian dickite from Steetleys Ltd. was kindly supplied by Dr. D. A. Jefferson. It was ground for a minimum time in a ball mill, and a preliminary X-ray powder diffraction trace was indexed successfully using the information on JCPDS file card 10-430. The diffraction pattern showed only very small amounts of α-quartz impurity. For the neutron diffraction experiment the sample was packed into a 16-mm diameter vanadium sample tube 5 cm long. The data were collected for 72 hr using a high resolution powder diffractometer D1A (Hewat and Bailey, 1976) with a wavelength of 1.909 Å at 300°K. The scan was from 6° to 120°2θ in steps of 0.05°2θ (2279 points). The absorption of the sample was measured. Hewat (1979) showed that absorption can effectively be treated by adding an increment to the temperature factors of each of the atoms at the end of the structure refinement.

The data were treated using the powder-profile preparation and profile-refinement programs of Hewat (1973a, 1973b), and Fourier calculations were carried out using the *X-Ray System* of programs (Stewart *et al.*, 1972) with coherent scattering lengths taken from the *International Tables for X-Ray Crystallography*, Vol. IV, 1974, Kynoch Press, Birmingham (270–272).

RESULTS AND DISCUSSION

Hydrogen atom positions and structural refinement

The first model used to calculate a diffraction profile was that of Newnham (1961) which includes no hydrogen atom information. An overall scale factor, an overall isotropic temperature factor, and a parameter to allow for preferred orientation of the sample were refined, as were the unit-cell parameters with a data set restricted to 6°–85°2θ. A three-dimensional difference Fourier synthesis at this point located the three hydrogen atoms of the inner-surface hydroxyl groups. The positions of these atoms (Table 1, Figure 1) were consistent with the values given by Giese and Datta (1973) when transformed to the unit cell of Newnham (Bailey, 1963) and were close to a line between the hydroxyl oxygen and the corresponding oxygen atom of the neighboring clay layer. This arrangement appears to confirm the original supposition of Newnham and Brindley (1956) that all three of these hydrogen atoms in dickite are involved in hydrogen bonding. A similar situation does not hold for kaolinite or nacrite where the relationship between hydroxyl groups and oxygen atoms of the neighboring layer is not the same. Many infrared studies (e.g., Serratosa *et al.*, 1962, 1963; Wolff, 1963) and the computations of Giese and Datta (1973) and Giese (1973) have shown that only some of the inner-surface OH groups of these minerals are involved in hydrogen bonding.

These three hydrogen atoms were added to the model of the structure. To facilitate the location of the last hydrogen atom (of the inner hydroxyl group) a one-dimensional Fourier synthesis was computed (Figure 2). A negative peak can be seen at the position of the hydrogen atoms of the three inner-surface hydroxyls (the scattering length for hydrogen is negative). The only other negative peak occurs at $z \simeq 0.11$–0.12 and is considered to be due to this inner hydroxyl hydrogen atom. Thus, the O–H vector makes a small angle with (001) and points away

Copyright © 1981, The Clay Minerals Society

https://doi.org/10.1346/CCMN.1981.0290410 Published online by Cambridge University Press

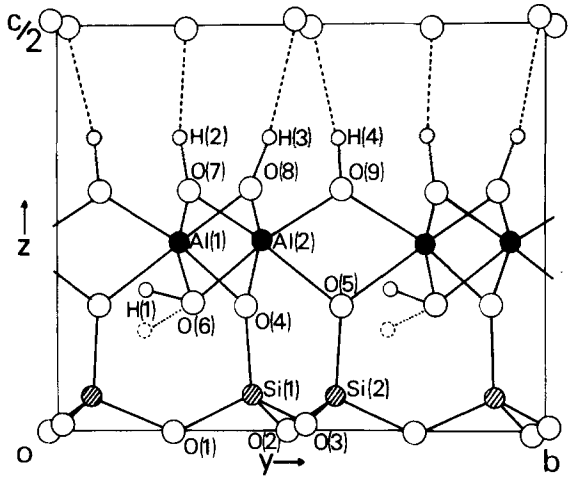


Figure 1. Projection of the structure of dickite down the a axis. The hydrogen atoms shown are in positions given by Giese and Datta (1973). The alternate hydrogen position for H(1) (· · · · ·) is that derived from the neutron diffraction data.

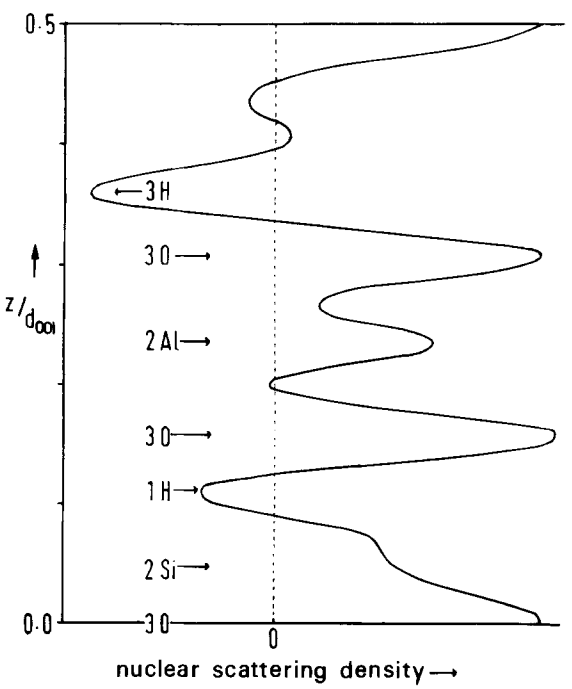


Figure 2. Projection of the nuclear scattering density for dickite onto a line normal to the clay basal planes.

from the octahedral sheet in a similar fashion to that found in the dioctahedral micas (e.g., Rothbauer, 1971) and probably in kaolinite (Adams *et al.*, 1976). A full three-dimensional difference Fourier synthesis was used to determine the position of this hydrogen atom (Table 1). The x and y parameters are very similar to those computed by Giese and Datta (1973), incidentally giving a projection of O–H onto (001) which makes an angle of ~30° with b, as is also the case in the dioctahedral micas. However, the z parameter is very different from that of Giese and Datta, i.e., 0.12 vs. 0.17.

The two models—one with z(H(1)) = 0.12 and one with z(H(1)) = 0.17—were refined using the neutron profile data initially from 6° to 85° and later extending from 6° to 120°2θ. All of the atom positions were then varied as were three thermal parameters (one for Si and Al, one for O, and one for H) and the parameters U, V, and W, which give the variation in width of the diffraction peak as a function of the Bragg angle (Hewat, 1973a). Final reliability indices, R_p,[2] were 0.173 for the model using the neutron-derived atom position and 0.196 for the model starting with the hydrogen atom position given by Giese and Datta (1973). The second of these two models did not refine to give the same final H position as the first. Although these two reliability indices are not very dissimilar, they show that the model with z ≈ 0.12 for H(1) fits the data better. Indeed, the refinement using the H atom position of Giese and Datta (1973) can be rejected at the 1% significance level (Hamilton, 1964), and all information given below is from the refinement using the neutron derived H-position (R_p = 0.173).

The non-hydrogen atoms were found not to have moved significantly from the positions given by Newnham (1961) and the esd's were greater than those of his X-ray study. The unit-cell parameters were: a = 5.168(2), b = 8.922(4), c = 14.447(7) Å, β = 107.8(2)°. Final atomic coordinates are given in Table 1 and hydrogen bonding information in Table 2. It appears that in dickite the inner O–H group makes an angle of ~20° with (001) and points away from the octahedral sheet. Not only has the position of H(1) been determined, but it can be seen that H(1) may be involved in a hydrogen bond O(6)–H(1) . . . O(3)

[2] $R_p = \Sigma|I_{nuc}(obs) - (1/c)\, I_{nuc}(calc)|/\Sigma I_{nuc}(obs)$, where c is the scale factor, and $I_{nuc}(obs)$ and $I_{nuc}(calc)$ are the intensities of the observed and calculated powder profile patterns at a particular 2θ value. R_p is often between 60 and 100% greater than the conventional crystallographic R at the same point in the refinement.

Table 1. Hydrogen atom positions in dickite.

		Coordinate given bu Giese and Datta (1973) transformed to cell of Newnham and Brindley (1956)			Coordinates deduced from Fourier map			Final neutron coordinates refined using Rietvald's technique[1]		
		x	y	z	x	y	z	x	y	z
Inner hydroxyl group	H(1)	0.496	0.185	0.174	0.460	0.200	0.120	0.468 (10)	0.173 (7)	0.132 (5)
Inner-surface hydroxyl group	H(2)	0.295	0.254	0.361	0.314	0.262	0.365	0.284 (11)	0.219 (6)	0.367 (5)
	H(3)	0.763	0.435	0.361	0.768	0.435	0.366	0.812 (11)	0.446 (8)	0.378 (4)
	H(4)	0.280	0.578	0.361	0.274	0.570	0.366	0.236 (10)	0.582 (6)	0.363 (5)

[1] Estimated standard deviations of last digit given in parentheses.

https://doi.org/10.1346/CCMN.1981.0290410 Published online by Cambridge University Press

Table 2. Hydrogen bonding geometry, using hydrogen atom position from the present study and non-hydrogen positions from Newnham (1961).

Bond a–b . . . c	a–b (Å)	b . . . c (Å)	∠ abc (°)
O(7)–H(2) . . . O(1 at 0.4554, 0.2627, 0.4939)	1.09 (6)	1.82 (6)	139 (4)
O(8)–H(3) . . . O(3 at 0.7646, 0.4895, 0.5058)	1.19 (6)	1.97 (6)	155 (5)
O(9)–H(4) . . . O(2 at 0.2587, 0.5276, 0.4942)	1.21 (5)	1.92 (5)	150 (4)
O(6)–H(1) . . . O(3 at 0.2646, 0.0105, 0.0058)	1.10 (6)	2.31 (6)	149 (6)

which had not been suspected previously (Table 2). This is the first time that a three-dimensional structural refinement has been obtained from a powdered clay sample.

Application of neutron diffraction to clay structures

To determine the hydrogen positions in clay minerals by neutron diffraction or, more generally, to refine the structures precisely by neutron diffraction requires either relatively large crystals (i.e., a minimum size of 0.5 mm^3) for single crystal experiments, or some development of the standard Rietveld profile refinement technique (specifically for two-dimensional solids) when such crystals are not available. Some success in this direction has recently been achieved by Riekel and Schöllhorn (1980) in their study of H_xTiS_2.

In both refinements of the present study, the final fit of observed and calculated profiles showed that the relatively high values of R_p were due to the peak shape and peak asymmetry. In the standard Rietveld profile refinement program (Hewat, 1973a), all peaks are considered to be of Gaussian form, and the half-width of the peak, H_k, is a function of the θ value at which the peak occurs, i.e., $H_k^2 = U\tan^2\theta_k + V\tan\theta_k + W$ (U, V, and W are refinable parameters). With clay minerals peaks due to basal reflections and those due to more general reflections commonly have different widths even at similar θ values. In addition, although it is possible, using the standard program, to ascribe a degree of asymmetry to the diffraction peaks, this is applied to every reflection. This procedure is obviously not appropriate because the 001 peaks were experimentally found to be symmetrical.

Any major advance in the use of the Rietveld profile technique for clay minerals must take account of the following two problems. It appears that basal reflections can be described by a Gaussian peak shape and one set of half-width parameters, whereas the remaining reflections need a new functional (asymmetric) description and a second set of half-width parameters. In addition, information about the type of disorder present might have to be built into the initial model. If these alterations can be made to the Rietveld profile method, there is great scope for structural studies of clay minerals and their intercalates.

Edward Davies Chemical Laboratory J. M. ADAMS
University College of Wales
Aberystwyth, Dyfed SY23 1NE
United Kingdom

Institut Laue-Langevin A. W. HEWAT
156X, 38042 Grenoble Cedex
France

REFERENCES

Adams, J. M., Reid, P. I., Thomas, J. M., and Walters, M. J. (1976) On the hydrogen atom positions in a kaolinite:formamide intercalate: *Clays & Clay Minerals* **24,** 267–269.

Bailey, S. W. (1963) Polymorphism of the kaolin minerals: *Amer. Mineral.* **48,** 1196–1209.

Farmer, V. C. (1964) Infrared absorption of hydroxyl groups in kaolinite: *Science* **145,** 1189–1190.

Farmer, V. C. and Russell, J. D. (1964) The infrared spectra of layer silicates: *Spectrochim. Acta* **20,** 1149–1173.

Giese, R. F., Jr. (1973) Interlayer bonding in kaolinite, dickite, and nacrite: *Clays & Clay Minerals* **21,** 145–149.

Giese, R. F., Jr. and Datta, P. (1973) Hydroxyl orientation in kaolinite, dickite and nacrite: *Amer. Mineral.* **58,** 471–479.

Hamilton, W. C. (1964) *Statistics in Physical Science:* Ronald Press, New York, 7–162.

Hewat, A. W. (1973a) The Rietveld computer program for the profile refinement of neutron diffraction powder patterns modified for anisotropic thermal vibration: Rutherford report RRL 73/239. Atomic Energy Research Establishment, Harwell, U.K.

Hewat, A. W. (1973b) Cubic-tetragonal-orthorhombic-rhombohedral ferroelectric transitions in perovskite potassium niobate. Neutron powder profile refinement of the structures: *J. Phys. C* **6,** 2559–2572.

Hewat, A. W. (1979) Absorption correction for neutron diffraction: *Acta Crystallog.* **A35,** 248–250.

Hewat, A. W. and Bailey, A. (1976) D1A. A high resolution neutron powder diffractometer with a bank of mylar collimators: *Nucl. Instrum. Methods* **137,** 463–471.

Ledoux, R. L. and White, J. L. (1964) Infrared study of the OH groups in expanded kaolinite: *Science* **143,** 244–246.

Marinder, B.-O., Werner, P.-E., Wahlström, E., and Malmros, G. (1980) Investigation on a new copper niobium oxide of $LiNb_3O_8$ type using chemical analysis and X-ray powder diffraction profile analysis: *Acta Chem. Scand.* **A34,** 51–56.

Newnham, R. E. (1961) A refinement of the dickite structure and some remarks on the polymorphism in kaolin minerals: *Mineral. Mag.* **32,** 683–704.

Newnham, R. E. and Brindley, G. W. (1956) The crystal structure of dickite: *Acta Crystallog.* **9,** 759–764.

Riekel, C. and Schöllhorn, R. (1980) Neutron diffraction study on structure and formation of H_xTiS_2 and D_xTiS_2: Annex to the Annual Report, 1979, Institut von Laue-Langevin, Grenoble, p. 197.

Rietveld, H. M. (1969) A profile refinement method for nuclear and magnetic structures: *J. Appl. Crystallog.* **2,** 65–71.

Rothbauer, R. (1971) Untersuchung eines $2M_1$-Muskovits mit Neutronenstrahlen: *Neues Jahrb. Mineral. Monatsh.* **4,** 143–154.

Serratosa, J. M., Hidalgo, A., and Vinas, J. M. (1962) Orientation of OH bonds in kaolinite: *Nature* **195,** 486–487.

Serratosa, J. M., Hidalgo, A., and Vinas, J. M. (1963) Infrared study of the OH groups in kaolin minerals: in *Proc. Int. Clay Conf., Stockholm, 1963,* **1,** I. Th. Rosenqvist and P. Graff-Petersen, eds., Pergamon Press, Oxford, 17–26.

Stewart, J. M., Kruger, G. J., Ammon, H. L., Dickinson, C. H., and Hall, S. R. (1972) The X-Ray System—version of June 1972. Update of April 1974: Techn. Rept. TR-194, Computer Science Center, Univ. Maryland, College Park, Maryland.

Tsuboi, M. (1950) On the positions of the hydrogen atoms in the crystal structure of muscovite as revealed by the infrared absorption study: *Bull. Chem. Soc. Japan* **23,** 83–88.

https://doi.org/10.1346/CCMN.1981.0290410 Published online by Cambridge University Press

Vedder, W. and McDonald, R. S. (1963) Vibrations of the OH ions in muscovite: *J. Chem. Phys.* **38,** 1583–1590.
Von Dreele, R. B. and Cheetham, A. K. (1974) The structures of some titanium and niobium oxides by powder neutron diffraction: *Proc. Roy. Soc. London* **A338,** 311–326.
Wada, K. (1967) A study of hydroxyl groups in kaolin minerals utilizing selective deuteration and infrared spectroscopy: *Clay Miner.* **7,** 51–61.
Wolff, R. G. (1963) Structural aspects of kaolinite using infrared absorption: *Amer. Mineral.* **48,** 390–399.

(Received 26 September 1980; accepted 14 February 1981)

Clays and Clay Minerals, Vol. 29, No. 4, 319, 1981.

BOOK REVIEW

Advanced Chemical Methods for Soil and Clay Minerals Research, edited by J. W. Stucki and Wayne L. Banwart. Volume C63 in the NATO Advanced Study Institutes Series, D. Reidel Publishing Company, Dordrecht (Holland), Boston, London, 1980, viii + 477 pp. $58.00, Dfl. 110.

This book is based on lectures given at a NATO Advanced Study Institute held at the University of Illinois in 1979. It comprises ten chapters by thirteen experts from European countries and the United States who were lecturers at the Institute. In the preface the editors state that relatively few soil and clay scientists are intimately acquainted with these more recently developed methods because of "insufficient opportunities to explore in depth the working principles of (these) developments," and because "the necessary equipment generally is unavailable unless collaborative projects are undertaken." To these reasons the reviewer will add that the basic theoretical backgrounds lie largely outside the area with which most mineralogists are conversant. The present volume is especially welcome because it presents both the theoretical backgrounds of these techniques and detailed accounts of their applications in soil and clay mineralogy. Readers who find the theoretical discussion hard to follow will still appreciate the importance of the applications and therefore will be encouraged to participate in collaborative research which may well be the first step towards "exploring in depth the working principles . . . ."

The various methods discussed can be mentioned only briefly here. Chapter 1 on Mössbauer spectroscopy by B. A. Goodman, 93 pp., presents a short account of the basic theory and experimental procedures and then discusses at length applications to chain and layer silicates and oxides. Most of the clay minerals are mentioned ("crostedite," p. 38, is a new spelling for cronstedtite!). Application of the technique to mineral alteration reactions (natural weathering, chemical processes, and thermal reactions) is very usefully discussed. Chapter 2, on neutron scattering methods, by D. K. Ross and P. L. Hall, 76 pp., gives an extensive theoretical treatment; about one-third of the chapter is allocated to applications, particularly to the clay-water system. Photoelectron spectroscopy is treated by C. Defosse and P. G. Rouxhet in Chapter 3, 35 pp., and by M. H. Koppelman in Chapter 4, 39 pp. The latter deals particularly with the chemistry of mineral surfaces. These two chapters are strongly application oriented. Nuclear magnetic resonance is dealt with in Chapter 5, 71 pp., by J. J. Fripiat, which is strongly oriented towards basic theory, and in Chapter 6, 13 pp., by W. E. E. Stone and J. Sanz which discusses applications of NMR to studies of micas. Electron spin resonance is treated in three chapters; Chapter 7, 59 pp., by J. C. Vedrine provides a detailed theoretical treatment, Chapter 8, 31 pp., by T. J. Pinnavaia discusses applications to inorganic-clay systems, particularly the behavior of interlayer cations in swelling clays, and Chapter 9, 28 pp., by M. B. McBride considers applications to clay-organic systems. Finally in Chapter 10, 15 pp., R. L. Schmidt introduces the reader to applications of photoacoustic spectroscopy.

In brief, this volume includes a wealth of information on the basic theory of these more recently developed methods and on their applications to soil and clay minerals which cannot be found elsewhere treated so fully and so conveniently. Each chapter has an extensive list of references. The paper, printing, and figures are all excellent. Doubtless an increased application of these methods in the study of clay minerals can be expected and sincere thanks must be expressed to NATO for sponsoring this Advanced Study Institute.

G. W. BRINDLEY

Copyright © 1981, The Clay Minerals Society

https://doi.org/10.1346/CCMN.1981.0290410 Published online by Cambridge University Press