Clays and Clay Minerals, Vol. 31, No. 5, 352–356, 1983.

HYDROGEN ATOM POSITIONS IN KAOLINITE BY NEUTRON PROFILE REFINEMENT

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Abstract—A structure refinement of kaolinite made using the Rietveld neutron profile refinement technique has given non-hydrogen atom positions which were not significantly different from those given by B. B. Zvyagin in 1960. All of the hydrogen atoms have been located; the three inner-surface hydrogen atoms are involved in interlayer hydrogen bonds with lengths of 2.95(4), 2.95(4), and 3.06(4) Å with O–H . . . O angles of 168(4)°, 144(4)°, and 146(4)° respectively. The inner hydrogen atom is located in a position consistent with that found earlier in dickite and muscovite which are the only dioctahedral layer silicates studied by neutron diffraction to date. The O–H vector makes an angle of 34° with the (001) plane, away from the octahedral sheet, and the projection of the vector on to (001) is at ~30° to the b axis.

Key Words—Crystal structure, Hydrogen, Kaolinite, Neutron profile refinement, O–H vector, Rietveld method.

INTRODUCTION

The general structure of kaolinite is well known and has been derived in some detail over many years (see e.g., Brindley and Robinson, 1945, 1946; Brindley and Nakahira, 1958; Drits and Kashaev, 1960; Zvyagin, 1960; Mansfield and Bailey, 1972). The positions of the hydrogen atoms in all of the kaolin minerals, however, are controversial. Some authors have suggested that all of the inner surface hydroxyl groups take part in hydrogen bonds to the neighboring clay layers (e.g., Newnham and Brindley, 1956; Newnham, 1961; Farmer, 1964; Farmer and Russell, 1964; Wieckowski and Wiewiora, 1976), whereas others have stated that only *some* of the OH groups are involved in hydrogen bonding (e.g., Serratosa *et al.*, 1962, 1963; Wolff, 1963; Ledoux and White, 1964; Wada, 1967; Giese and Datta, 1973).

For dickite, recent neutron diffraction studies (Adams and Hewat, 1981) have located the hydrogen atoms and shown that all of the inner surface hydroxyl groups are involved in interlayer hydrogen bonds. The orientation of the inner hydroxyl group has also been derived: the projection of this O–H onto (001) makes an angle of ~30° with b, and the group makes an angle of 20° with (001) and points *away from* the octahedral sheet, as has also been found for dioctahedral micas (Rothbauer, 1971). Giese and Datta (1973) and Giese (1973) proposed hydrogen atom positions in kaolinite based on electrostatic energy calculations which are themselves dependent upon the non-hydrogen atomic positions of Zvyagin (1960). The position derived for the inner hydrogen atom, however, gave an inner hydroxyl group that pointed *towards* the empty octahedral site, opposite to the orientation found by neutron diffraction for dioctahedral micas (Rothbauer, 1971), dickite (Adams and Hewat, 1981), and kaolin in the kaolin : formamide intercalate (Adams *et al.*, 1976).

To determine the hydrogen atom positions in kaolinite directly, a neutron diffraction study was undertaken. A full three-dimensional structure refinement was performed using the Rietveld profile refinement technique (Rietveld, 1969; Hewat, 1980) which has already been used successfully to locate the hydrogen atoms in dickite (Adams and Hewat, 1981) and other layered materials, e.g., $HTiNbO_5$ (Rebbah *et al.*, 1982).

EXPERIMENTAL

A kaolinite sample from Greensplat pit, St. Austell, was packed into a 16-mm vanadium sample-tube 5 cm long. Neutron powder diffraction data were collected for 22 hr using a D1A high resolution diffractometer (Hewat and Bailey, 1976) with a wavelength of 1.909 Å at 300°K. The diffraction pattern showed the presence of a small amount of α-quartz; the 2θ regions where diffraction maxima from α-quartz occurred were deleted from the data. The scan was from ~6° to 145°2θ in steps of 0.05°2θ, i.e., 2779 points were monitored.

The data were treated using the powder-profile preparation and profile refinement programs of Hewat (1973), and Fourier and geometric 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, 1973, Kynoch Press, Birmingham (270–272). The space group used for all calculations was $C1$. Because of the relatively low quality of the data, due to the high percentage of hydrogen atoms in kaolinite with their attendant high diffraction background levels and also due to some asymmetry of the non-basal re-

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Table 1. Hydrogen atom positions in kaolinite.[1]

		x	y	z
Inner hydroxyl group	H(6)	−0.827(4)	0.128(2)	0.226(2)
Inner-surface hydroxyl groups	H(1)	−0.205(3)	0.163(2)	−0.249(2)
	H(2)	−0.813(3)	0.024(2)	−0.278(3)
	H(3)	−0.696(4)	0.356(2)	−0.254(3)

[1] Estimated standard deviations at the last digit are given in parentheses.

flexions, it was not considered fruitful to extend the refinement to use the lower symmetry space group $P1$.

RESULTS AND DISCUSSION

Structure refinement

The basic model used for the kaolinite structure was that of Zvyagin (1960) which contained no information about the positions of the hydrogen atoms. Initially the data were restricted to a maximum 2θ of 120° and the only parameters allowed to refine were the scale factor, an overall temperature factor, the cell parameters, and the counterbank zero point (Z). Several cycles of profile refinement gave R_{pw}[1] = 35%. A difference (F(obs) − F(calc)) Fourier map clearly showed the two hydrogen atoms bonded to O(1) and O(2); these were in positions which agreed with the predictions of Giese and Datta (1973). Inclusion of these atoms reduced R_{pw} to 28%. A further difference synthesis then showed two further regions of negative neutron scattering density at ~1 Å from O(3) and O(6), but these were not at the appropriate positions predicted by Giese and Datta (1973). When these two additional hydrogen atoms were added to the model, R_{pw} decreased to 23%. At this point the full 145° data set was employed: the positional parameters of all atoms were allowed to vary as were a peak asymmetry factor, the three parameters describing the width of the diffraction peaks (U, V, and W), a preferred orientation parameter (Hewat, 1973) and four isotropic temperature factors for the Al, Si, O, and H atoms. When refinement was complete R_{pw} was 20%, equivalent to a conventional crystallographic R of 11%.

As in the dickite refinement (Adams and Hewat, 1981), the non-hydrogen atoms were found not to have moved significantly (3 σ combined) from the starting positions (Zvyagin, 1960). The esd's for the positions of the Si and Al atoms were relatively high (0.02 Å in x, y, and z) because of the relatively low scattering lengths of these atoms for neutrons. The unit-cell parameters were found to be: a = 5.136(2), b = 8.946(4), c = 7.392(4)Å, α = 91.7(2), β = 104.5(2), γ = 89.8(2)°. As in the neutron profile refinement of dickite (Adams and Hewat, 1981), some asymmetry of non-basal reflections was observed and was one of the reasons for the relatively high e.s.d.'s observed.

Hydrogen atom positions

The positions of the three inner-surface hydrogen atoms derived here (Table 1) show that all three H atoms are involved in interlayer hydrogen bonds (Table 2). All of the O–H and H . . . O distances appear reasonable, and although some of the O–H . . . O angles deviate from linearity, they are within the range regularly found for inorganic structures (Hamilton and Ibers, 1968). Indeed, it has been pointed out by several authors (Hamilton, 1962; Chidambaram, 1962; Fuller, 1959) that linearity in hydrogen bond formation appears to be the exception rather than the rule. The geometry of the hydrogen bonds, however, shows that they are rather weak, with the O(3)–H(3) . . . O(7) bond being the weakest. These observations agree with those made by Wieckowski and Wiewiora (1976) on the basis of infrared spectroscopic data.

Information on the position of the inner hydrogen atom is given in Figures 1 and 2 and Table 3. The position is consistent with that found in dickite (Adams and Hewat, 1981) and muscovite (Rothbauer, 1971), which are the only dioctahedral layer silicates studied by neutron diffraction to date. In all of these minerals

[1] R_{pw} (the weighted profile reliability index) = $100\sqrt{\Sigma\, w(y(obs) - 1/c(calc))^2}/\sqrt{\Sigma\, w(y(obs))^2}$, where w is the weight of each data point and y(obs) and y(calc) are the observed and calculated profile intensities for that point; c is the scale factor.

Table 2. Hydrogen bonding geometry.[1]

Bond a–b . . . c	a–b (Å)	b–c (Å)	a–c (Å)[2]	abc (°)
O(1)–H(1) . . . O(8 at −.223, .175, −.128)	0.93 (4)	2.04 (4)	2.95 (4)	168 (4)
O(2)–H(2) . . . O(9 at −.696, −.003, −.136)	1.10 (4)	1.99 (4)	2.95 (4)	144 (4)
O(3)–H(3) . . . O(7 at −.723, .321, −.128)	1.03 (4)	2.17 (4)	3.06 (4)	146 (4)

[1] The hydrogen atom positions are from the present study and the non-hydrogen atom positions are from Zvyagin (1960).
[2] The O . . . O distances differ slightly from those of Zvyagin because of the different unit-cell parameters. Zvyagin gives 2.89, 2.90 and 3.02 Å, whereas Wieckowski and Wiewiora (1976) give 3.00, 3.04 and 3.10 Å from infrared data.

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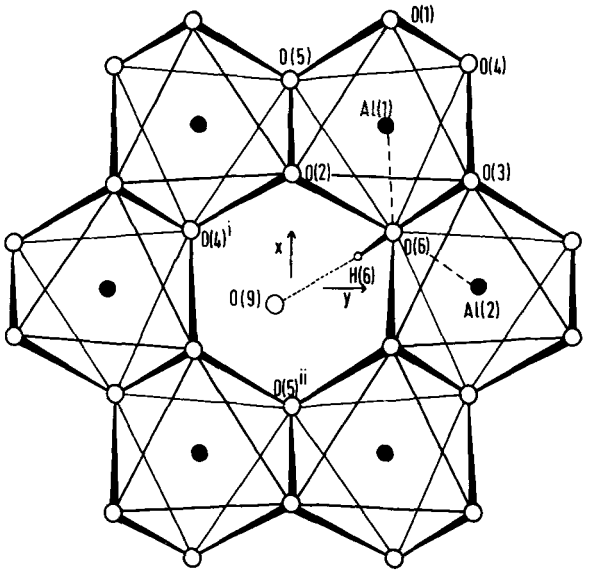


Figure 1. The hydroxyl vector is almost symmetrical with respect to two Al–O bridging (O(6)) vectors in kaolinite (as is also the case in dickite and muscovite). Part of the octahedral sheet is shown, projected on to the basal plane. The close contact between H(6) and the basal oxygen, O(9), is shown.

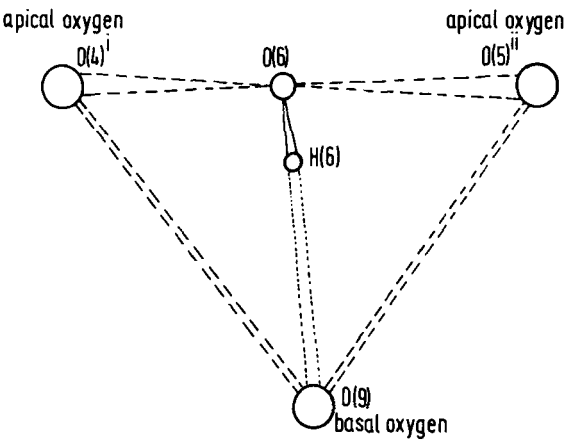


Figure 2. Close approaches of the inner hydroxyl to oxygen atoms. Distances are given in Table 3. The projection is on to a plane perpendicular to the basal plane and passing through O(4)^{i} and O(5)^{ii}. N.B. O(4) is at $-\frac{1}{2} + x$, $-\frac{1}{2} + y$, z relative to O(4); O(5)^{ii} is at $-1 + x$, y, z relative to O(5).

the projection of the O–H vector is at ~30° to the b axis. Thus, the O–H vector bisects the two Al–$O_{bridging}$ vectors in projection (Figure 1). The H atom is close to three oxygen atoms of silicate tetrahedra; in all three structures the atom is closest to the basal oxygen and a little further from two apical oxygens (Figure 2). The sum of van der Waals radii for H and O is ~2.60 Å. In the muscovite structure all three H . . . O distances are of this value or greater, and it would appear that no hydrogen bonds are formed. With the two 1:1 layer silicates the H . . . O_{basal} distances are <2.6 Å, and the possibility exists of very weak hydrogen bond formation.

In kaolinite and dickite, Giese and Datta (1973) calculated, using an electrostatic model, that the inner hydroxyl group should have the orientation found here relative to the b axis, but they suggested that in both minerals the O–H vector pointed *into* the octahedral sheet rather than *away from* it. It is not readily apparent why this orientation should exist. Giese (1979) said that for micas the electrostatic repulsion will favor "an O–H orientation which maximizes the M(octahedral)-H distances . . . the maximum distances will result in an O–H directed away from the octahedral sheet towards the large ditrigonal vacity of the tetrahedral sheet. Opposing this orientation is the repulsion from the interlayer and tetrahedral cations which are further away but which are more numerous and commonly have larger charges. Thus the OH orientation represents a balance between the repulsions from these two sets of sites." At face value these arguments suggest that in the kaolin minerals the hydroxyl group should make a larger angle with (001)—away from the octahedral sheet—than in micas, because the forces tending to push the hydrogen atom towards the octahedral sheet are less than in micas because of the lack of interlayer cations, i.e., the repulsion from the tetrahedral sheet

Table 3. Geometry around the inner hydroxyl atom in kaolinite and related dioctahedral layer silicates.[1]

	Kaolinite	Dickite (Adams and Hewat, 1981)	Muscovite (Rothbauer, 1971)
O–H (Å)	0.87 (4)	1.10 (6)	0.929 (4)
H . . . O_{basal} (Å)	2.38 (4)	2.31 (6)	2.570 (4)
O . . . O_{basal} (Å)	3.23 (4)	3.31 (6)	3.356 (2)
H ↔ O_{apical} (Å)	2.62 (4), 2.78 (4)	2.60 (6), 2.61 (6)	2.679 (4), 2.689 (4)
∠O–H . . . O_{basal} (°)	166 (4)	149 (6)	142.6 (3)
∠ between projection of O–H vector on (001) and the b axis (°)	32	30	30
∠ between O–H vector and (001) cleavage (°)	34	20	12

[1] See also Figure 1.

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in kaolin is less than that from the tetrahedral sheet *and* interlayer cations in micas. It may be that the differences in hydroxyl orientation given by electrostatic calculations for kaolin minerals and micas are a result of different stacking modes and of differences in the 1:1 and 2:1 layers themselves. However, the angles observed between the O–H vector and (001) in the neutron diffraction studies undertaken to date (Table 3) are compatible with the simple view given above: 12° in muscovite, 20° in dickite, 34° in kaolinite, and ~25° in the kaolinite : formamide intercalate (Adams *et al.*, 1976). The fact that the hydrogen atom is offset at all from the center of the ditrigonal vacity is a result of the dioctahedral character if the kaolin layer with consequent asymmetric repulsion of two Al^{3+} cations with no counterbalancing cations in the third octahedral site.

It should be noted that all refinements in this study were made using space group *C*1, i.e., the two parts of the unit cell related by the C-face centering were treated as equivalent. If the true space group were *P*1, these two parts of the structure would be independent with unrelated hydrogen atom positions, and there should have been evidence of half occupancy of pairs of hydrogen atom sites on the difference Fourier map. No such evidence was found.

CONCLUSIONS

The recent application of Rietveld profile refinement methods to kaolinite and dickite (Adams and Hewat, 1981) has shown that in both cases all of the inner surface hydrogen atoms are involved in interlayer hydrogen bonding. In addition, it is apparent that the inner hydrogen atoms point away from the octahedral sheet in both minerals. That these results are reasonably reliable is confirmed by a recent accurate single crystal X-ray study of dickite (Rozdestvenskaya *et al.*, 1982)

ACKNOWLEDGMENTS

The authors thank Mr. S. Heathman and Dr. A. W. Hewat for assistance in collecting the neutron diffraction data.

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(Received 30 April 1982; accepted 6 April 1983)

Резюме—Усовершенствование структуры каолинита при помощи техники Ретвельда по нейтроновому профилю определило расположение неводородных атомов, которое незначительно отдичалось от расположения, определенного Б. Б. Звягиным в 1960 году. Все атомы водорода были определены; три внутренно-поверхностные атомы водорода были включены в межслойные водородные связи с расстояниями 2,94(4), 2,95(4), и 3,06(4) Å и углами O–H . . . O, равными 168(4)°, 144(4)°, и 146(4)°, соответственно. Внутренный атом водорода находится в положении, согласуюшемся с положением, найденном ранее в диките и мусковите, которые до сих пор явдяются единственными двухвосьмигранными слоистыми силикатами, исследованными путем нейтронной дифракции. Вектор O–H наклонен к плоскости (001) под углом 34°, по направлению от восьмигранного слоя, а проекция вектора на плоскость (001) составляет угол 30° с осью b. [E.G.]

Resümee—Es wurde eine Strukturverfeinerung von Kaolinit durchgeführt, wobei die Rietveld'sche Neutronenprofilverfeinerungstechnik verwendet wurde. Diese Untersuchung ergab für die Nichtwasserstoffatome Positionen, die sich von denen, die z.B. B. B. Zvyagin (1960) angegeben hat, nicht wesentlich unterscheiden. Alle Wasserstoffpositionen wurden bestimmt; die drei Wasserstoffatome auf der inneren Oberfläche sind an der Zwischenschichtwasserstoffbindung beteiligt, die Abstände von 2,95(4), 2,95(4), und 3,06(4) Å mit einem O–H . . . O Winkeln von 168(4)°, 144(4)°, und 146(4)° aufweisen. Das innere Wasserstoffatom ist in einer Position, die mit der bereits früher in Dickit und Muskovit bestimmten Position übereinstimmt. Dickit und Muskovit sind die einzigen dioktaedrischen Schichtsilikate, die bisher mit Neutronendiffraktion untersucht wurden. Der O–H Vektor bildet einen Winkel von 34° mit der (001) Ebene von der Oktaederschicht weg. Die Projektion des Vektors auf (001) bildet einen Winkel von etwa 30° zur *b*-Achse. [U.W.]

Résumé—Un raffinement de la structure de la kaolinite en utilisant la technique de raffinement de profil de neutrons de Rietveld a donné des positions d'atomes non-hydrogène qui ne différaient pas de manière significative de celles données par B. B. Zvyagin en 1960. On connait les positions de tous les atomes hydrogène; les trois atomes d'hydrogène de la surface intérieure sont impliqués dans des liens hydrogène intercouche, avec des longueurs de 2,95(4), 2,95(4), et 3,06(4) Å avec des angles OH . . . O de 168(4)°, 144(4)°, et 146(4)°, respectivement. L'atome d'hydrogène intérieur se trouve dans une position pareille à celle trouvée précédemment dans la dickite et dans la muscovite, qui sont jusqu'à présent les seuls silicates à couches dioctaèdrales etudiées par diffraction de neutrons. Le vecteur O–H fait un angle de 34° avec le plan (001), dans un sens opposé à la feuille octaèdrale, et la projection du vecteur sur (001) est à ~30° de l'axe *b*. [D.J.]

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