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COMPARISON OF ORIENTATIONS OF OH-BONDS IN LAYER SILICATES BY DIFFRACTION METHODS AND ELECTROSTATIC CALCULATIONS

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Abstract—Orientations of OH-vectors in structural hydroxyl groups of layer silicates were defined both from diffraction data and calculations of electrostatic energy. The comparison of the results showed that for the hydroxyls of the 2:1 layers of chlorites and micas the positions of the hydroxyl protons are mainly determined by electrostatics. For the hydroxyls of dickite, amesite, and the brucitic sheets of chlorite, the results derived by the two methods differed systematically from each other, pointing to a change in the nature of the bond in these OH-groups.

Key Words—Chlorite, Dickite, Electrostatic calculations, Hydroxyl vectors, Mica, X-ray diffraction.

INTRODUCTION

Hydroxyl-group protons play an important role in the formation of layer silicates (Kukovsky, 1973; Norrish, 1973). For example, the location of protons in muscovite and biotite is an important factor in determining the strength of the bonds between K cations and the 2:1 layers. These bonds affect the stability of these micas as well as the mechanisms of their structural transformation. Proton positions in the structures of layer silicates are also important in the interpretation of spectral data, e.g., infrared spectroscopy (IR) (Farmer, 1974), nuclear magnetic resonance (NMR) (Kalinchenko *et al.*, 1973), and γ-resonance (Bookin *et al.*, 1978).

On the other hand, because of the difficulties in determining the coordinates of light atoms by X-ray diffraction structural analysis, crystal structure refinements of layer silicates have not generally included proton positions, and only a few papers containing proton coordinates (Liebich *et al.*, 1979; Phillips *et al.*, 1980; Anderson and Bailey, 1981; Swanson and Bailey, 1981) are available. In this respect, neutron diffraction methods have considerable advantages; however, more rigid requirements regarding crystal size and complex equipment have restricted applications of this method only to muscovite-2M_1 (Rothbauer, 1971), phlogopite (Joswig, 1972), and triclinic chlorite (Joswig *et al.*, 1980). Direct measurement of electron diffraction intensities with accuracies of 10–15% by the oblique-texture electron diffraction method has opened new opportunities for refinement of crystal structures of finely dispersed layer silicates, including the determination of proton coordinates. Such opportunities were successfully demonstrated for muscovite-2M_1 (Tsipursky and Drits, 1977).

Despite the success of diffraction methods in structural analysis, the localization of protons by diffraction remains a more complex problem than the refinement of heavy atom positions. The success of other methods in determining OH-bond orientations in layer silicate structures, e.g., spectroscopic techniques (Farmer, 1974; Kalinichenko *et al.*, 1973) is limited and not sufficiently accurate. On the other hand, Giese proposed a method involving calculations of electrostatic energy with fixed OH-bond lengths (Giese, 1971; Giese and Datta, 1973; Datta and Giese, 1971). Such an approach is attractive in that it permits the use of the available structural refinements of layer silicates and supplements these data with estimates of OH-vector orientations. Giese applied the model of point ions with formal charges equal to the weighted valencies of the ions occupying a given crystallographic position. This approach takes into account neither the repulsion of electrons nor the charge transfer due to the covalency of the bond. Therefore, before applying this method, it is necessary to make sure of the reliability of the results obtained. Giese and coworkers showed that results obtained by this method are in agreement with the diffraction data for compounds of the XOOH type (X = Al, Fe, Mn, and Y) and for some hydroxides (Giese *et al.*, 1971; Giese, 1976). Because of the absence of the experimental proton positions for all refined layer silicates they were only able to check their calculations in the case of muscovite-2M_1 (Datta and Giese, 1973) and in the less important case of phlogopite (Giese, 1979). Hence, it is not absolutely certain that such calculations can be applied to the other layer silicates.

The main objective of the present work was to compare the orientations of OH-bonds in layer silicates as

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determined by diffraction methods and from electrostatic calculations.

METHODS AND RESULTS

This study is based on crystal structure refinement of four micas with different polytypic modifications and different compositions, together with dickite, amesite, and two chlorites. These minerals have two types of hydroxyl groups. In micas, the hydroxyl groups are inside the 2:1 layers at the boundary between the octahedral and tetrahedral sheets. Dickite, amesite, and chlorite, in addition to "inner" hydroxyls, contain "inner-surface" hydroxyls.

Crystal structures of muscovite-$2M_1$, phengite-$1M$ and celadonite-$1M$ were refined by the electron diffraction method with direct measurement of intensities of diffracted electrons, as described by Tsipursky and Drits (1977), while those of dickite and protolithionite-$3T$ were refined by an X-ray diffraction method using an automated Syntex $P2_1$ diffractometer. Chemical compositions of these samples, unit-cell parameters, and atomic coordinates, except of the protons, are given in the works cited in Table 1. For these structures we obtained Fourier difference maps, constructed after introduction of anisotropic thermal parameters. These maps revealed several diffuse maxima in close proximity to the oxygen atom of the hydroxyl. The coordinates of the most intense peak was used to determine the location of the hydroxyl hydrogen. These coordinates depend markedly on the number of reflections used in the Fourier analysis and lead to considerable fluctuations in the length of the OH-bond; however, the orientation of the OH-bond was altered only slightly. For example, using all observed intensities of reflections to construct the difference synthesis for celadonite gave a maximum that corresponded to an OH-bond length of 0.76 Å, while using just the most intense reflections gave a maximum with an OH-bond length of 0.64 Å. Orientation of the OH-vector in these cases differed only by 1–2°.

Using the least-squares method for refinement of the proton position led to a considerable change in the bond lengths. Similar results were obtained for chantalite (Liebich *et al.*, 1979), amesite (Anderson and Bailey, 1981), and two chromian chlorites (Phillips *et al.*, 1980). Therefore, the coordinates of hydrogen in Table 1 are specified by the length of the bond R_{OH} determined from the Fourier difference map, the polar angle between the OH-vector and the (001) layer plane, and the azimuthal angle between the OH-vector projected on the (001) plane and the a axis. A positive polar angle shows that the orientation of the OH-vector is outside the octahedral sheet, and that the azimuthal angle is measured relative to the positive direction of the b axis.

In addition to the original data, we used published coordinates for the hydroxyl hydrogen in chlorites (Phillips *et al.*, 1980; Joswig *et al.*, 1980). Of the two refined chromian chlorites, we selected that from Siskiyou County, California, because the coordinates of hydrogens for its structure were also obtained by the difference-synthesis method. These data were also compared with those for amesite, obtained by Anderson and Bailey (1981) and Giese (1980).

The accuracy in determining the proton coordinates in all of the structures, except that of triclinic chlorite (Joswig *et al.*, 1980) is approximately the same and amounts to about 0.1 Å along each axis, about an order of magnitude larger than the standard deviations of the oxygen atoms. The estimation of the accuracy of angle values, which determine the orientation of the OH-bonds, met with difficulties. The standard deviations of several degrees given by Phillips *et al.* (1980), for the O–H. . .O angles for the Day Book Body chlorite are distinctly underestimated because the authors apparently took into account only the uncertainties in oxygen atom coordinates as determined from the accuracy of the OH-bond length. If the estimation of accuracy for the angles is calculated from the coordinates by the rule of propagation of errors for independent variables, a considerable overestimation of errors will result due to their correlated motion. With regard to the angles derived from the refinement of the structures using photographic registration of intensities (Lipson and Cochran, 1953), the accuracy in the estimation of the polar angle ρ can be assumed to be about 2–3°, while that of the azimuthal angle ψ, increasing with increase of ρ, is about 5° for OH-bonds with ρ angles of less than 80°. The position of protons in triclinic chlorite (Joswig *et al.*, 1980) were determined with excellent precision, characteristic of neutron diffraction techniques.

The calculations of electrostatic energy were made with an EC-1022 computer by the Ewald method which sums over both the direct and reciprocal lattices. The COULOMB program permits rapid calculation of both the full electrostatic energy of the crystal and the partial energy that depends on the coordinates of the proton. In addition, the variation in atomic coordinates and unit-cell parameters within the range of experimental standard deviations was investigated. The latter procedure showed that if an OH-bond length of 0.97 Å is used in the calculations, the fluctuations in the angle of the OH-vectors did not exceed 1–2°. The polar coordinates of the hydroxyls, obtained on the basis of diffraction and calculated data, are given in Table 1.

If the orientation of OH-bonds in hydroxyls of 2:1 layers of micas and chlorites is considered, the divergence of the polar angle does not exceed 3°, which corresponds to the errors in both methods. Taking into account the range of the ρ values between $-14°$ and 89°, such accuracy is quite satisfactory.

The azimuthal angle ψ coincides nearly with the experimental data for the micas with disordered cation distribution (muscovite, phengite). For celadonite and protolithionite, micas with ordered cation distribu-

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Table 1. OH-bond orientation in the structures of analyzed minerals by diffraction and calculation methods.

Mineral		Polytype	Space group	Final R-factor	R_{OH} (Å)	Experiment ρ	Experiment ψ	Calculation ρ	Calculation ψ	Literature
Muscovite[1]		$2M_1$	$C2/c$	0.03	0.93	12	60	15	60	Rothbauer, 1971
Muscovite		$2M_1$	$C2/c$	0.05	1.06	12	60	15	60	Tsipursky and Drits, 1977
Phengite		$1M$	$C2/m$	0.07	1.20	17	0	17	0	Tsipursky and Drits, 1977
Celadonite		$1M$	$C2$	0.06	0.77	−14	1	−14	8	Tsipursky, 1979
Protolithionite		$3T$	$P3_112$	0.04	0.59	73	193	70	180	Pavlishin *et al.*, 1981
Dickite	H1				0.96	14	193	−16	238	
	H2				0.96	83	−53	70	−48	Rozdestvenskaya
	H3	$2M_1$	Cc	0.04	0.80	72	59	63	70	*et al.*, 1982
	H4				0.90	72	183	66	195	
Chromian	H1				0.92	87	201	90	—	
chlorite	H2	IIb-4	$C\bar{1}$	0.06	0.97	84	20	79	−38	
	H3				0.96	83	19	75	107	Phillips *et al.*,
	H4				0.98	88	292	87	194	1980
Triclinic	H1				0.96	89	—	90	—	
chlorite	H2	IIb-4	$C\bar{1}$	0.03	0.96	86	116	80	121	
	H3				0.96	86	12	80	4	Joswig *et al.*,
	H4				0.96	86	245	80	238	1980
Amesite[2]	H1				0.87	90	—	82	—	
	H11				0.68	60	—	82	—	
	H2				0.92	64	—	82	—	Anderson and Bailey, 1981
	H22	$2H_2$	$C1$	0.05	0.91	75	—	82	—	Giese, 1980
	H3				0.83	80	—	89	—	
	H33				0.90	61	—	89	—	
	H4				0.90	73	—	82	—	
	H44				0.93	72	—	83	—	

[1] These results duplicate those of Datta and Giese (1973).

[2] The calculated results are from Giese (1980) for the amesite refined by Hall and Bailey (1979). The latter paper does not contain experimental proton positions. The most recent study of the same polytype modification of amesite (Anderson and Bailey, 1981) gave the proton positions, but the distribution of cations has another character. Both of these amesites have very close compositions. In such conditions the calculated ρ angle depends very little on the pattern of cation distribution (Bookin and Drits, 1982).

tions, the calculated values of ψ deviate from the diffraction results by slightly more than the expected accuracy.

Quite a different situation was observed for the "inner surface" hydroxyls of dickite and the hydroxyls of the brucitic sheet of chlorites (H2, H4) (see Table 1). Of the nine hydroxyls, the calculated polar angle coincides with the experimental value within the range of error for only proton H4 in chromian chlorite. In all other samples the calculated angle was less than the experimental one by 5–13°. For dickite, the azimuthal direction of the OH-vector derived from diffraction data differed from the calculated angles by 5°, 11°, and 12° in the same direction. In chlorites, the difference between experimental and calculated ψ angles was not as systematic in direction.

The greatest discrepancy was detected for proton H1 in the "inner" hydroxyl of dickite. According to the electrostatic calculations this proton must be inside the vacant octahedron as in celadonite; however, it actually has a positive ρ angle, as in muscovite, and is rotated by 47° around the c* axis from a pseudo-mirror plane, as in protolithionite. It should be noted that for proton H1 in the "inner" hydroxyl of dickite another position is possible because an additional maximum exists in the Fourier difference map at a distance of 0.8 Å from the hydroxyl oxygen atom. This maximum is located near the pseudo-mirror plane and here also has a positive ρ angle of 16°.

DISCUSSION

The orientations of the OH-bond for the hydroxyl in the 2:1 layer silicates, obtained by diffraction methods agree well with those calculated on the basis of the point-charge model. The largest deviations were found for samples with alternative cation distribution over different crystallographic positions. For example, in the studied phengite, the number of di- and trivalent cations

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Table 2. Hydrogen bridge lengths O–O, and difference between calculated and experimental ρ angles for surface hydroxyls.

	Dickite		Chromium chlorite		Triclinic chlorite		Amesite[1]			
	O–O (Å)	$\Delta\rho$	O–O (Å)	$\Delta\rho$	O–O (Å)	$\Delta\rho$	O–O (Å)	$\Delta\rho$	O–O (Å)	$\Delta\rho$
OH2	2.950	13°	2.914	5°	2.915	6°	2.81 (2.75)	−18°	2.76 (2.78)	−7°
OH3	3.118	9°	2.913	8°	2.916	6°	2.73 (2.81)	−9°	2.80 (2.78)	−28°
OH4	2.952	6°	2.852	1°	2.906	6°	2.83 (2.79)	−9°	2.83 (2.81)	−11°

[1] The first values are the O–O distances for amesite, refined by Hall and Bailey (1979) and studied by Giese (1980). The values in parentheses are those of amesite, refined by Anderson and Bailey (1981).

occupying octahedral positions, exceed by 0.04 the amount required for an ideal dioctahedral structure. These "extra" cations may occupy the empty octahedra M(1) or the interlayer positions. Whereas the second possibility leads to a lower calculated value of the total electrostatic energy, the first assumption leads to better agreement of the polar angles obtained by the two independent methods. A difference synthesis confirmed the presence of a small number of cations in the "empty" octahedra.

If ionic substitutions are numerous, the distribution of cations over different crystallographic positions can be inferred from their scattering power and from the dimensions of the polyhedra. Quantitative distribution of different cations is difficult to determine if the number of components exceeds two. Thus, for protolithionite, the presence of Li^+, Al^{3+}, Fe^{3+}, and Fe^{2+} cations, as well as vacancies in the octahedral sheets, makes the ordered model proposed by Pavlishin *et al.* (1981) somewhat uncertain. To improve the correlation between calculated and experimental azimuthal angles of the OH-vector, the average charge of cations in the trans-position must slightly exceed that of cations in the cis-octahedron, whose dimensions are almost equal to that of the trans-octahedron.

Regarding the accuracy of the initial physical bonding proposals, a model with formal charged ions implies that the hydrogen of the hydroxyl groups should be completely ionized, i.e., be present in the structure in the form of a proton with the charge of +1, whereas the determination of its position by X-ray diffraction established the presence of electron density on the proton. This discrepancy can be eliminated by assuming that all bonds in the layer silicates are not purely ionic, but are partially covalent, leading to the appearance of effective charges. The magnitude of such effective charges may be derived from formal charges by a simple proportionality factor. In this case the results of the electrostatic calculation do not change, and the electron charge is responsible for the X-ray scattering. Therefore, the direction of the electron density maximum on the bond coincides with the oxygen–proton direction, but the distance from this maximum to the oxygen can differ considerably from that between the nuclei.

From the point of view of the nature of the interlayer bonds involving the hydroxyl group hydrogens, the "inner surface" hydroxyls of 1:1 minerals and the brucitic sheets of chlorites are also of particular interest. Basal oxygens in the adjacent layer can become acceptors of the bond. Interlayer O–O distances of 2.72–3.12 Å suggest the presence of hydrogen bonds in the minerals mentioned above. The nature of the O–H. . .O in kaolinite minerals has been investigated mostly by infrared spectroscopy, but because of the absence of distinct features revealing hydrogen bonds, there is no single opinion on this problem (Cruz *et al.*, 1973; Wieckowski and Wiewiova, 1976; Datta and Giese, 1973). The correlation between the orientations of OH-bonds obtained by diffraction methods and by electrostatic calculations helps in the solution of this problem. Systematic deviations between experimental and calculated orientations of the OH-vector show that the bond of the "inner surface" hydroxyls of dickite and the brucitic sheets in chlorite differs considerably from the bond in the hydroxyls of the 2:1 layers, pointing to the importance of charge transfer in hydrogen bonds.

Thus, from the present work, the absence of agreement between calculated (Giese, 1980) and experimentally determined (Anderson and Bailey, 1981) orientations of OH-bonds for the two "inner" and six "inner surface" hydroxyl groups in amesites may have resulted not only from experimental errors and a different pattern of cationic replacements, but from the more complex nature of the chemical bond.

The data in Table 1 show that in the dickite and chlorite samples all of the experimentally determined polar angles for surface hydroxyls are larger than the calculated angles, whereas for amesite the reverse is true. Such dependence correlates well with the hydrogen bridge length. In the first three structures, the shortest O–O distance is 2.85 Å (OH4 hydroxyl of chromian chlorite), the others being 2.91–2.95 Å and 3.12 Å (see Table 2), whereas, in the amesite structures all O–O distances are less than 2.85 Å. From the data in Table 2 the difference in ρ angles, obtained by the two methods, is positive where the hydrogen bridge length is larger than 2.85 Å, negative for shorter lengths, and negligible for the OH4 hydroxyl in chromian chlorite.

CONCLUSIONS

The studies by Giese and co-workers (Giese, 1971; Giese and Datta, 1973; Datta and Giese, 1971; Giese, 1976), and the results of the present paper establish thus

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two classes of minerals for which the electrostatic calculations predict hydroxyl orientations if detailed information on the geometry of the structure is available. In some minerals, such as protolithionite, the comparison of the calculated and experimental positions of the protons assists in understanding the distribution of cations throughout nonequivalent positions. On the other hand, minerals exist for which such calculations give only very rough estimations. Here, it is necessary to consider not only the hydroxyls that play roles in hydrogen bonding, but other hydroxyls as well, such as the inner OH-groups of dickite and amesite.

The validity of the electrostatic calculations in some particular cases cannot be generalized for all minerals of the same class; because the influence of the hydrogen bridge length is complex, the coincidence may be fortuitous.

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Резюме—Ориентация OH-векторов структурных гидроксильных групп слоистых силикатов была определена как из дифракционных данных, так и из расчетов электростатической энергии. Сравнение результатов показало, что для гидроксилов 2:1 слоев слюд и хлоритов положение гидроксильных протонов в значительной степени определяется электростатикой. Для гидроксилов диккита, амезита, и бруситовой сетки хлоритов результаты, даваемые этими двумя методами, систематически отличаются друг от друга, что указывает на изменения в природе химических связей для этих OH-групп.

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Resümee—Die Orientierungen von OH-Vektoren in strukturellen Hydroxylgruppen von Schichtsilikaten wurden sowohl durch Diffraktionsergebnisse als auch durch Berechnungen der elektrostatischen Energie bestimmt. Der Vergleich der Ergebnisse zeigt, daß für die OH-Gruppen der 2:1 Lagen von Chlorit und Glimmer die Lagen des Hydroxylprotons vor allem durch die elektrostatischen Verhältnisse bestimmt werden. Für die Hydroxylgruppen von Dickit, Amesit, und den Brucitlagen von Chlorit weichen die Resultate, die bei beiden Methoden erhalten wurde, systematisch voneinander ab, was auf eine Änderung des Bindungscharakters in diesen OH-Gruppen hindeutet. [U.W.]

Résumé—Les orientations de vecteurs-OH dans des groupes hydroxyles structuraux de silicates à couches ont été définies à partir de données de diffraction et de calculs d'énergie électrostatique. La comparaison des résultats a montré que pour les hydroxyles des couches 2:1 de chlorites et de micas, les positions des protons hydroxyles étaient principalement determinées par l'électrostatique. Pour les hydroxyles de dickite, d'amésite, et les feuillets brucitiques de chlorite, les résultats dérivés par les deux méthodes différaient systématiquement l'un de l'autre, indiquant un changement de la nature de la liaison dans les groupes-OH. [D.J.]

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