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HYDROXYL ORIENTATIONS IN 2:1 PHYLLOSILICATES

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Abstract—The hydroxyl orientations in 31 dioctahedral and trioctahedral 2:1 phyllosilicate structures have been determined by electrostatic energy calculations. These structures included micas, brittle micas, and other related minerals exhibiting ordered as well as disordered cation distributions. The dioctahedral micas and brittle micas were examined with and without the interlayer cation. A range of orientations from 1.3° to 183.3° (the angle ρ between the O–H and (001) measured with respect to the M1 site) were found. The orientations for the dioctahedral structures represent a continuum of values whereas the trioctahedral species exhibit two possible orientations separated by an energy barrier. One orientation is near 90°; the other is near 180°. The latter orientation results from a concentration of charge on the interlayer (IC) and tetrahedral (T) sites at the expense of the octahedral (M) sites. A multiple regression analysis of all 31 structures, using as predictors the a and b cell parameters, d_{001}, and the charges for T, IC, M1, and M2 sites, was performed. This analysis indicated that the important factors are the charges for IC, T, and M2 sites. When treated as a separate group, one finds the same factors for the dioctahedral structures. The trioctahedral orientations are determined by the charge on the M2 site and the amount of tetrahedral rotation. Using these two predictor equations, the value of ρ can be estimated with a standard deviation of 4.7° and 2.9° for the dioctahedral and trioctahedral cases, respectively.

Key Words—Brittle Mica, Energy Calculations, Hydroxyl Orientation, Mica, Phyllosilicate.

INTRODUCTION

Comparatively little is known about the role of hydroxyl groups in mineral structures largely because the hydrogen atom is notoriously difficult to locate by standard X-ray diffraction techniques. In the absence of information about the location of the hydroxyl hydrogen (or the hydroxyl orientation), deductions about the existence and relative importance of hydrogen bonds are often made indirectly from steric considerations (Baur, 1972), by looking for anomalously short O–O distances (Hamilton and Ibers, 1968), or by some form of electrostatic bond sum (Donnay and Allmann, 1970). These are usually sufficient to rationalize most hydroxyl and water containing structures because these components play a relatively static role in the structure. The 2:1 phyllosilicates present a different problem since the OHs appear to interact actively with exchangeable cations, adsorbed water, and perhaps organic molecules. For example, the ease of exchange of the interlayer potassium has been shown to be directly influenced by the orientation of the structural OH groups (Bassett, 1960; Gilkes *et al.*, 1972; Giese, 1975a, 1977), while the existence of interactions between the OH of the silicate layer and interlayer water molecules has been demonstrated by Prost (1975).

The hydroxyls of the 2:1 phyllosilicates are part of the plane of oxygens which is shared by the tetrahedral and octahedral sheets. As a result, the hydroxyls lie between two sets of cations, the octahedral (M) sites on one side and the tetrahedral (T) and interlayer (IC) sites on the other. Since the M sites are closest to the hydroxyl, the electrostatic repulsion will favor an OH orientation which maximizes the M–H distances. In either a trioctahedral or dioctahedral structure, the maximum distances will result in an O–H directed away from the octahedral sheet toward the large ditrigonal cavity 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. Since, in general, the charges on the cations are linked so that the sum is 22 per formula unit, $O_{10}(OH)_2$, an increase or decrease in the cation charge of any site must be compensated by changes in the charges of the other sites. If this rearrangement alters the balance of forces at the hydroxyl hydrogen, the hydroxyl will reorient.

The general picture that has developed regarding the hydroxyl orientations in layer silicates is derived principally from the study of micas by infrared absorption spectroscopy (Vedder and McDonald, 1963; Serratosa and Bradley, 1958; Tsuboi, 1950; and others), neutron diffraction (Rothbauer, 1971; Joswig, 1972), and electrostatic energy calculations (Giese, 1971; Giese and Datta, 1973). These studies show that in trioctahedral micas the OH is approximately perpendicular to (001) while in the dioctahedral structures the OH tilts away from the normal in the direction of the vacant octahedral site (M1) making a small angle with (001). These orientations are readily explained in terms of repulsion between the hydrogen and the surrounding cations. However, the micas that have been studied in detail are phlogopite/biotite and muscovite, so that conclusions regarding OH orientations based on results from these two structures may not be applicable to phyllosilicates in general.

It is desirable at the very least to know the orienta-

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Table 1. Cation charge distributions, hydrogen positional parameters, and the value of ρ for all the structures used in the study.

MICA Dioctahedral	CATION CHARGES T	M2	M1	IC	HYDROGEN POSITIONS x	y	z	ρ		References[1]
margarite $2M_1$	3.500	3.000	0.000	2.	0.366	0.658	0.059	9.8	*	Takeuchi (1965)
	3.500	3.000	0.000	—	0.431	0.607	0.096	63.6	*	
margarite $2M_1$	3.500	3.000	0.000	2.	0.354	0.664	0.055	4.6		Guggenheim and Bailey (1977)
					0.627	0.346	0.936	14.2		
paragonite $2M_1$	3.750	3.000	0.000	1.	0.870	0.151	0.069	20.6	*	Burnham and Radoslovich (1963)
	3.750	3.000	0.000	—	0.910	0.118	0.092	54.3	*	
muscovite 1M	3.750	3.000	0.000	1.	0.255	0.000	0.129	15.0	*	Giese (1975b)
	3.750	3.000	0.000	—	0.340	0.000	0.180	51.6	*	
muscovite 3T	3.778	2.994	0.000	1.	0.096	−0.273	−0.042	14.3	*	Güven and Burnham (1967)
	3.778	2.994	0.000	—	0.113	−0.196	−0.060	53.2	*	
muscovite $2M_1$	3.750	3.000	0.000	1.	0.872	0.152	0.065	17.2	*	Güven (1971)
	3.750	3.000	0.000	—	0.913	0.120	0.089	52.0	*	
muscovite $2M_1$	3.750	3.000	0.000	1.	0.370	0.652	0.063	15.0	*	Rothbauer (1971)
	3.750	3.000	0.000	—	0.411	0.621	0.088	50.7	*	
muscovite $2M_2$	3.875	2.865	0.000	0.77	−0.142	0.157	0.060	9.5	*	Zhoukhlistov *et al.* (1973)
	3.875	2.865	0.000	—	−0.118	0.140	0.080	35.2	*	
phengite $2M_1$										
	3.848	2.804	0.000	1.	0.861	0.159	0.054	1.3	*	Güven (1971)
pyrophyllite 1Tc	3.848	2.804	0.000	—	0.874	0.152	0.071	21.6	*	
	4.000	3.000	0.000	0.	0.145	0.102	0.154	23.1	*	Wardle and Brindley (1972)
Trioctahedral										
xanthophyllite 1M	3.250	2.000	3.000	2.	0.573	0.500	0.300	97.9	*	Takeuchi (1965)
	3.250	2.333	2.334	2.	0.600	0.500	0.300	89.6		(disordered M sites)
phlogopite 1M	3.750	2.000	2.000	1.	0.116	0.000	0.301	85.9	*	Steinfink (1962)
phlogopite 1M	3.728	2.030	2.030	1.	0.094	0.000	0.304	92.0	*	Joswig (1972)
phlogopite 1M	3.750	2.000	2.000	1.	0.094	0.000	0.304	92.0	*	Hazen and Burnham (1973)
phlogopite 1M	3.750	2.000	2.000	1.	0.090	0.000	0.305	93.1	*	McCauley *et al.* (1973)
Mg-mica 1M	3.830	1.893	1.893	1.	0.600	0.000	0.300	91.5	*	Tateyama *et al.* (1974)
zinnwaldite 1M	3.789	1.423	3.000	1.	0.109	0.514	0.311	115.6	*	Guggenheim and Bailey (1977)
	3.789	1.949	1.949	1.	0.062	0.469	0.301	87.4		(complete disorder of M sites)
					0.054	0.544	0.301	124.5		(complete order of M sites)
annite 1M	3.703	2.063	2.063	1.	0.085	0.000	0.297	91.5	*	Hazen and Burnham (1973)
talc 1Tc	4.000	2.000	2.000	0.	0.229	0.167	0.217	91.0	*	Raynor and Brown (1973)
ferri-annite 1M	3.750	2.000	2.000	1.	0.611	0.000	0.306	87.4	*	Donnay *et al.* (1964)
	3.778	2.994	0.000	—	0.113	−0.196	−0.060	53.2	*	
muscovite $2M_1$	3.750	3.000	0.000	1.	0.872	0.152	0.065	17.2	*	Güven (1971)
	3.750	3.000	0.000	—	0.913	0.120	0.089	52.0	*	
muscovite $2M_1$	3.750	3.000	0.000	1.	0.370	0.652	0.063	15.0	*	Rothbauer (1971)
	3.750	3.000	0.000	—	0.411	0.621	0.088	50.7	*	
muscovite $2M_2$	3.875	2.865	0.000	0.77	−0.142	0.157	0.060	9.5	*	Zhoukhlistov *et al.* (1973)
	3.875	2.865	0.000	—	−0.118	0.140	0.080	35.2	*	
phengite $2M_1$	3.848	2.804	0.000	1.	0.861	0.159	0.054	1.3	*	Güven (1971)
	3.848	2.804	0.000	—	0.874	0.152	0.071	21.6	*	
pyrophyllite 1Tc	4.000	3.000	0.000	0.	0.145	0.102	0.154	23.1	*	Wardle and Brindley (1972)
Trioctahedral										
xanthophyllite 1M	3.250	2.000	3.000	2.	0.573	0.500	0.300	97.9	*	Takeuchi (1965)
	3.250	2.333	2.334	2.	0.600	0.500	0.300	89.6		(disordered M sites)
phlogopite 1M	3.750	2.000	2.000	1.	0.116	0.000	0.301	85.9	*	Steinfink (1962)
phlogopite 1M	3.728	2.030	2.030	1.	0.094	0.000	0.304	92.0	*	Joswig (1972)
phlogopite 1M	3.750	2.000	2.000	1.	0.094	0.000	0.304	92.0	*	Hazen and Burnham (1973)
phlogopite 1M	3.750	2.000	2.000	1.	0.090	0.000	0.305	93.1	*	McCauley *et al.* (1973)
Mg-mica 1M	3.830	1.893	1.893	1.	0.600	0.000	0.300	91.5	*	Tateyama *et al.* (1974)

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Table 1. Continued.

MICA Dioctahedral	CATION CHARGES T	M2	M1	IC	HYDROGEN POSITIONS x	y	z	ρ		References[1]
zinnwaldite 1M	3.789	1.423	3.000	1.	0.109	0.514	0.311	115.6	*	Guggenheim and Bailey (1977)
	3.789	1.949	1.949	1.	0.062	0.469	0.301	87.4		(complete disorder of M sites)
					0.054	0.544	0.301	124.5		(complete order of M sites)
annite 1M	3.703	2.063	2.063	1.	0.085	0.000	0.297	91.5	*	Hazen and Burnham (1973)
talc 1Tc	4.000	2.000	2.000	0.	0.229	0.167	0.217	91.0	*	Raynor and Brown (1973)
ferri-annite 1M	3.750	2.000	2.000	1.	0.611	0.000	0.306	87.4	*	Donnay *et al.* (1964)
lepidolite $2M_2$	3.840	2.260	1.100	1.	0.425	0.605	0.095	67.5		Sartori *et al.* (1973)
Li-mica 1M	3.813	1.917	1.917	1.	0.092	0.500	0.305	92.5	*	Takeda and Donnay (1966)
polylithionite 1M	4.000	1.900	1.200	1.	0.313	0.500	0.305	73.5	*	Takeda and Burnham (1969)
	4.000	1.000	3.000	1.	−0.074	0.500	0.404	183.3		(complete order of M sites)
biotite 1M	3.706	2.058	2.058	1.	0.103	0.500	0.302	88.6	*	Takeda and Ross (1975)
biotite $2M_1$	3.706	2.058	2.058	1.	0.949	0.085	0.099	84.3	*	Takeda and Ross (1975)
lepidolite $2M_2$	3.848	2.460	0.690	1.	0.390	0.361	0.081	39.9		Takeda *et al.* (1971)
Ba-mica 1M	3.750	1.667	1.666	2.	−0.055	0.000	0.377	166.7		McCauley and Newnham (1973)
	3.750	2.000	1.000	2.	0.291	0.000	0.363	20.9		(complete order of M sites)
	4.000	1.000	2.000	2.	−0.047	0.000	0.411	172.3		("super" Ba-mica; ordered M sites)

[1] An asterisk indicated that the particular structure was used in the linear regression analysis.

In general, there are two entries for the dioctahedral species; the first is for the normal structure while the second is for the same structure without an interlayer cation. Multiple entries for the trioctahedral species represent different arrangements of cations as indicated.

tions in as many phyllosilicate structures as possible. In addition, it would be very useful, especially in trying to understand the OH orientations in clays using micas as a model, if one could predict with reasonable accuracy what the orientation would be given a specific set of structural and chemical parameters. In order to do this, one must determine the orientations for a large number of layer silicates that exhibit as much chemical and structural variation as possible. An initial attempt at this was reported by Giese and Datta (1973) in a study of the muscovite polytypes 1M, 3T, and $2M_1$, and also by Giese (1973) who examined a small group of dioctahedral micas. Both studies indicated a significant variation in the angle between (001) and the hydroxyl and the variation appeared to be related to the amount of tetrahedral rotation. In these studies, as before, the minerals exhibited relatively little chemical and structural variation. The present study was undertaken to extend the investigation to a larger group of 2:1 phyllosilicates in order (1) to determine the OH orientations of these minerals, (2) to identify the factors in the structures which are most important in determining the OH orientation, and (3) to find, if possible, a simple means of predicting OH orientation without the necessity of a crystal structure refinement or lengthy calculations. The crystal structures used for the analysis represent a very wide range of variation both in chemistry and in structure.

CALCULATIONS

Determining the hydroxyl orientation by minimizing the calculated electrostatic potential energy has proven to be an accurate and straightforward procedure (Giese, 1971, 1976). The electrostatic potential energy is calculated as a function of the OH orientation, the minimum energy giving the equilibrium orientation. In contrast to the previous work, the minima in the present study have been found using a gradient search algorithm which is faster and more accurate than the interpolation method used earlier.

The assignment of cationic species to sites which are occupied by substituting ions is often complicated by inaccuracies in the chemical analysis and in the determination of the site occupancies during crystal structure refinement. In order to treat all of the structures in a uniform manner, it was assumed that the interlayer site, if occupied at all, was fully occupied by an ion with an integral charge of +1 or +2, depending on the nature of the mineral. This posed no problems except for the $2M_2$ muscovite (Zhoukhlistov *et al.*, 1973), where there was strong chemical and crystallographic evidence for partial occupancy. This was incorporated in the calculations as a charge less than 1.0 on the IC. Next, the charges on the tetrahedral sites were calculated from the chemical and crystallographic data given with the structure refinement. Finally, the octahedral charges were similarly calculated, but in many instances these values had to be adjusted slightly in order to give a zero electrostatic charge for the unit cell. Because these values may in some instances represent an arbitrary adjustment to the values as given in the original paper describing the crystal structure refinement, they are listed in Table 1.

One of the complicating factors in such a study is that

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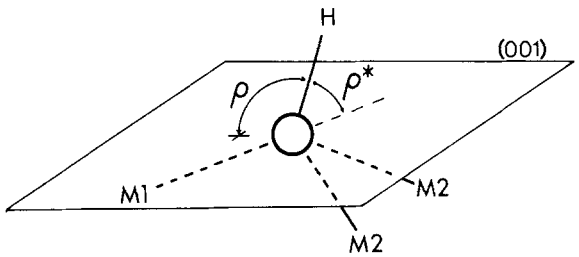


Figure 1. A schematic view of the OH, the (001) plane, and the M1 and M2 sites in a 2:1 phyllosilicate. The angle ρ is measured between (001) and OH with respect to the M1 site. The angle ρ^* is the angle between the M1–O direction and OH.

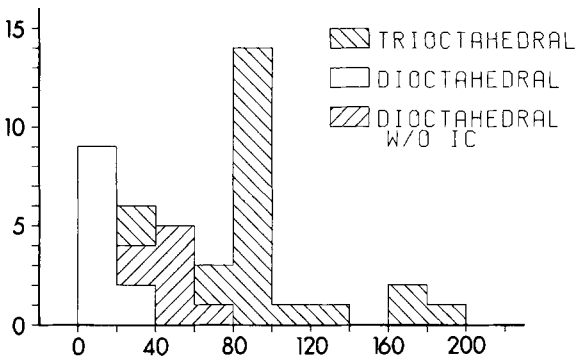


Figure 2. A histogram of the ρ values for all 31 structures included in this study. The major peaks centered at 0–20° and 80–100° represent dioctahedral and trioctahedral structures, respectively.

most of the structures exhibit cation disorder of the tetrahedral and, less commonly, of the octahedral sites. For disordered sites the charge assigned was commensurate with the proportion of the various cations substituting in the site. The resulting OH orientations therefore represent "average" positions that might be significantly different from the actual orientations in the structure. The magnitude of the differences between the hydroxyl orientations for a disordered and an equivalent ordered structure can be estimated by comparing the results for margarite with ordered Si and Al and muscovite with disordered tetrahedral sites. Similarly, the effect of order/disorder for the octahedral sites can be estimated by examining zinnwaldite with partial ordering and the synthetic Ba-mica with complete disorder. The electrostatic method of determining the hydroxyl orientation also permits one to investigate the effects of changes in the nature of the order/disorder by simply adjusting the cation charges to reflect the new distribution of charges and redetermining the orientation. In this manner, several structures that have disordered octahedral cations were artifically ordered, and their OH orientations were determined.

The structures used represent a sampling of structure refinements published through early 1978. All are not of the same accuracy, but previous work on the kaolin minerals indicated that the usual positional parameter errors encountered in a moderately accurate single crystal refinement are not a major source of error in the OH orientation (Giese and Datta, 1973). The one exception to this is the structure of the 1M muscovite (Soboleva and Zvyagin, 1969), which is clearly less accurate than all the others. The 1M polytype for muscovite is important and therefore an ideal 1M muscovite was constructed using the distance-least-squares approach of Meier and Villiger (1969) assuming the usual chemistry for a muscovite (Giese, 1975b). Several refinements have been published of fluoro- rather than hydroxy-micas, and these have been included in the present study by simply replacing the F^- in the structure with the hydroxyl oxygen.

It is common practice to describe the three octahedral sites in terms of M1 and M2. The distinction between the two types is that M1, a single site, has two hydroxyls arranged in the *trans* configuration while M2, two sites, have *cis* configurations. Moreover, in the 1M trioctahedral micas with space group C2/m, M1 lies on the mirror plane with the two equivalent M2 sites on opposite sides with their shared edges in the mirror plane. In dioctahedral micas, it is M1 that is vacant. For structures with extensive substitution of ions with greatly differing charges or vacancies, the refined structure shows only the average distribution of ions and vacancies and these sites are readily described in terms of M1 and M2. However, complete or partial ordering in such a situation easily presents arrangements where all three sites may be crystallographically different. Partial ordering in the octahedral sites is known for several 2:1 minerals (Bailey, 1975) but it is only in zinnwaldite where nomenclature problems arise. Here a single site is distinct in content and charge (+3) from the other two, nearly equal sites (+1.423 each). In this paper, the single high-charge site will be referred to as M1, and the other two sites will be called M2 even though these sites are named differently in the original paper. It should be noted also that the three sites are crystallographically distinct and that the single high-charge site has the OHs in the *cis* configuration.

RESULTS

In both the trioctahedral or dioctahedral structures, the layer has a pseudomirror plane of symmetry (or a real plane in the C2/m structures) perpendicular to the layer, passing through M1, bisecting the M2 sites, and containing the hydroxyl oxygen. The OH is restricted to orientations in or near this plane (depending on the symmetry), and therefore one may specify the orientation by a single angle, ρ, which is the angle between the OH and the (001) plane (see Figure 1). Since the OH may tilt away from or toward the M1 site, the absolute

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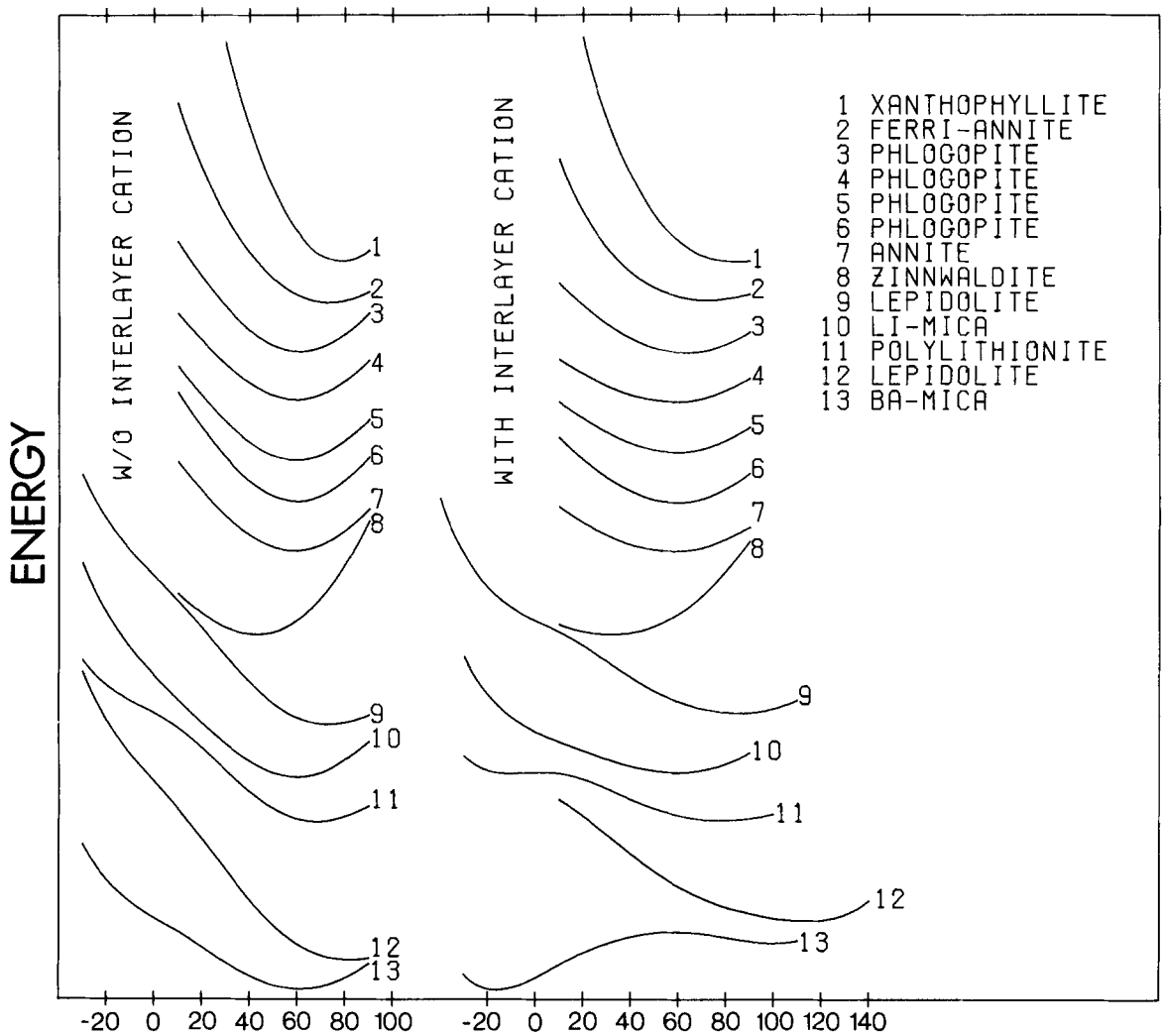


Figure 3. The variation of electrostatic energy as a function of OH orientation expressed as ρ^* for several trioctahedral structures. All curves are drawn to the same energy scale but they do not have a common origin. Their position in the figure is for convenience only and does not imply that one has a greater energy than another.

orientations reported here are the angles between the OH and (001) measured with respect to the M1 site (Figure 1). Values between 0° and 180° indicate that the OH is directed away from the octahedral sheet. Figure 2 is a histogram showing the distribution of the values of ρ calculated in this study. The trioctahedral and dioctahedral structures are represented by the largest and next largest peaks, respectively. The continuous distribution of orientations, however, is evident.

Dioctahedral orientations

Because M1 is vacant, the repulsion by the IC and T cations tilts the OH toward the vacant site. The M2–H distances are not very sensitive to changes in ρ, and therefore the OH easily reorients in response to the distribution of the different cations among the three kinds of site. The values for ρ vary between 1.3° and 23.1°, and, given appropriate cation distributions, larger variations seem possible. The largest value of ρ is for pyrophyllite. One might expect the smallest value to be for the brittle mica margarite, but this is not the case; phengite has a smaller angle than margarite in spite of the latter's divalent interlayer cation. In margarite the tetrahedral charge is reduced to compensate for the increased IC charge, thus maintaining approximately the same total T + IC repulsion. In principle, the smallest angle would be found for a structure with a +2 interlayer cation and the layer charge entirely on the M sites.

Trioctahedral orientations

Since all M sites are occupied, even small tilts away from the normal will increase substantially the M–H

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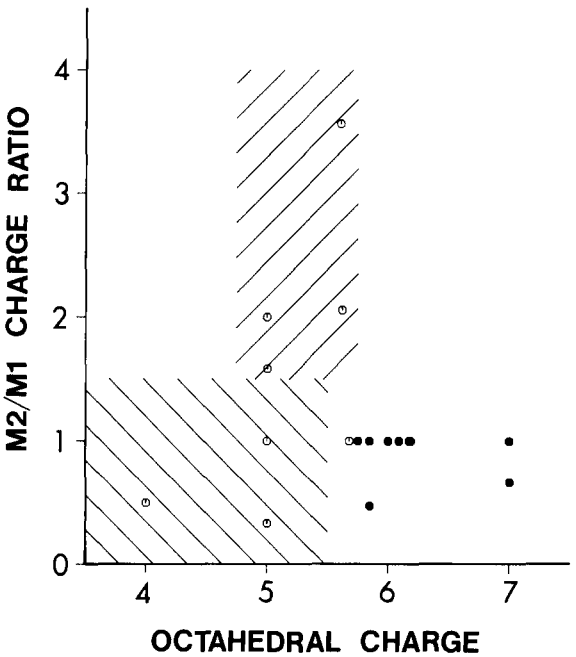


Figure 4. The trioctahedral structures are plotted in terms of total octahedral charge versus the ratio of the M2/M1 charge. Filled circles have simple, single minima energy curves, while open circles are complex. The hatched areas represent charge combinations leading to complex curves.

repulsion, and one would expect values of ρ to be near 90°. In general, the minerals follow this pattern with the exception of the synthetic Ba-mica which has the OH oriented nearly in the (001) plane, lying between the M2 sites. This is an unusual structure which has the bulk of the layer charge on the octahedral sites. The large charge on the T sites in combination with +2 for the IC and a small M charge results in a repulsion from the IC and T sites which is greater than the M–H repulsion.

Several other trioctahedral minerals have smaller than usual M charges due to substitution by Li and/or to vacant sites. To examine the situation for these as well as other more normal trioctahedral structures, electrostatic energies for a group of 13 have been calculated as a function of the OH orientation. The angle representing the orientation has been measured with reference to the M1–O line (extended beyond the oxygen) and is referred to as ρ^* (Figure 1). The calculated energies form simple, smooth curves for structures 1–8 (Figure 3, right side), but the other minerals, 9–13, exhibit a much more complex behavior. The latter have either a single minimum and an inflection or two minima. Because the inflections really represent second minima that have not fully developed, the complex curve structures exhibit two minima, one near $\rho^* = -10°$ and the other at angles greater than $\rho^* = 60°$. The lack of a smooth, single minimum in the potential energy curve suggests that the double minima represent distinct orientations separated by an energy barrier. This is very different from the dioctahedral structures. The importance of the interlayer cation in the formation of these anomalies has been verified by repeating the calculations as before but excluding the interlayer cation from the structure. The curves for structures 1–8 (Figure 3, left side) are unchanged except that they are a bit narrower, while the curves for structures 9–13 are greatly changed. The secondary minima or inflections at $\rho^* = -10°$ have either disappeared completely or are much less pronounced. The principal minima are now closer to the usual trioctahedral orientation of 90° ($\rho^* = 60°$). The curve for polylithionite retains a good bit of the secondary minimum. In this mineral the T sites are completely occupied by Si while the M sites have a correspondingly smaller charge.

The shapes of the curves in Figure 3 (right side) result from the charges on the three types of site, and, depending on the distribution of charge, one has either a simple curve as for structures 1–8 or a complex curve as for structures 9–13. The conditions under which one type or the other are to be found are not clear from the curves in Figure 3. There are various ways of representing the charge distribution among the cation sites but the one that shows a useful distinction between the two types of curve is a plot of total octahedral charge versus the ratio of the charges on the M1 and M2 sites. All orientations listed in Table 1 for the trioctahedral structures are plotted in this manner in Figure 4. The complex curve structures are shown as open circles while the normal curve structures are represented by filled circles. The field in the upper and lower left quadrants (shaded areas), including points on the M2/M1 = 1 line, have complex curves. The lower left shaded area contains complex curves for which the lower minimum is the one where $\rho^* = -10°$, while the other encompasses minima varying between $\rho^* = 60°$ and 120°.

EFFECT OF CATION ORDERING

Ordering of octahedral sites

The amount of octahedral substitution in dioctahedral structures is limited. In general, the M1 sites are vacant, and there is little deviation in the M2 sites from the normal charge of +3. Thus the problem of order/disorder in these sites appears at present to be minor and will not be discussed further.

Such is not the case for trioctahedral structures. All three octahedral sites are occupied to varying degrees by differently charged cations as well as by vacancies. Partial ordering is found in the structures zinnwaldite, xanthophyllite, and the lithium-containing micas lepidolite and polylithionite. Of these, only zinnwaldite, xanthophyllite, and polylithionite are uncomplicated by the presence of vacancies in the octahedral sites. Vacancies are a problem because they represent regions in the structure that are dioctahedral in nature.

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The electrostatic calculations based on the charge for a disordered site that contains vacancies as well as cations will yield an "average" hydroxyl orientation, but the two extremes that are being averaged are a nearly vertical OH orientation (trioctahedral) and an orientation in which the OH is closer to the (001) plane (dioctahedral). While the "average" may be arithmetically accurate, it is of limited use in understanding the hydroxyl orientations found in the real structure.

The extent of OH reorientation due to changes in the long range order of the M-site cations can be estimated by determining the OH orientations for a given structure as a function of the degree of ordering of the cations. This has been done for zinnwaldite, xanthophyllite, polylithionite, and the Ba-mica. The last structure shows no long range ordering but, as pointed out above, it is an example of a structure which has nearly the maximum possible charge on the T and IC sites. Polylithionite and the Ba-mica represent the structures most likely to have an anomalous OH orientation, and therefore their hydroxyls should be especially sensitive to M-site ordering.

As above (Figure 3), the electrostatic energy was calculated as a function of the orientation angle, ρ^*, for these four minerals. For each a curve was determined for the ordered structure and also a structure in which the cation charges were disordered. In addition, the ordering in zinnwaldite was of two types: one was a single site containing aluminum (+3) (designated here as M1) with the other two sites being disordered (+1.423 each); the second other was a single site of +3, another fully occupied by a divalent species (+2), and a third containing the remaining octahedral charge (+0.846). The latter type is referred to in Table 1 as "complete order of M sites." The Ba-mica has Al for Si substitution (Si/Al = 3). To investigate the effect of increasing the T and reducing the M charges, a third Ba-mica (called here "super" Ba-mica) was included in which all the T sites are occupied by Si and the M sites contained two Li (in M2) and one Mg (in M1). Polylithionite was examined in the partially ordered form and in a completely ordered state with Al in M1 and Li in the M2 sites.

The curves for xanthophyllite and zinnwaldite (Figure 5) are changed very little by ordering of the cations. The disordered structures have the OH more nearly vertical, while the OH tilts slightly away from the high charge site in the ordered arrangement. The Ba-mica is more complex as shown above (Figure 3), with two minima, one near $\rho^* = 100°$ and the other near $\rho^* = -10°$. For totally disordered M sites the lower energy is found for the latter, but upon ordering, the two minima reverse their relative energies. Therefore, in the real crystal where fractional atoms cannot exist, the hydroxyls will be oriented away from the normal, toward the low-charge M1 site. For this particular structure the hydroxyl orientation predicted by the electrostatic energy calculations using average cation charges does not yield an accurate OH orientation. The charge distribution in the artificial "super" Ba-mica with ordered M sites yields a ρ of 172.3°.

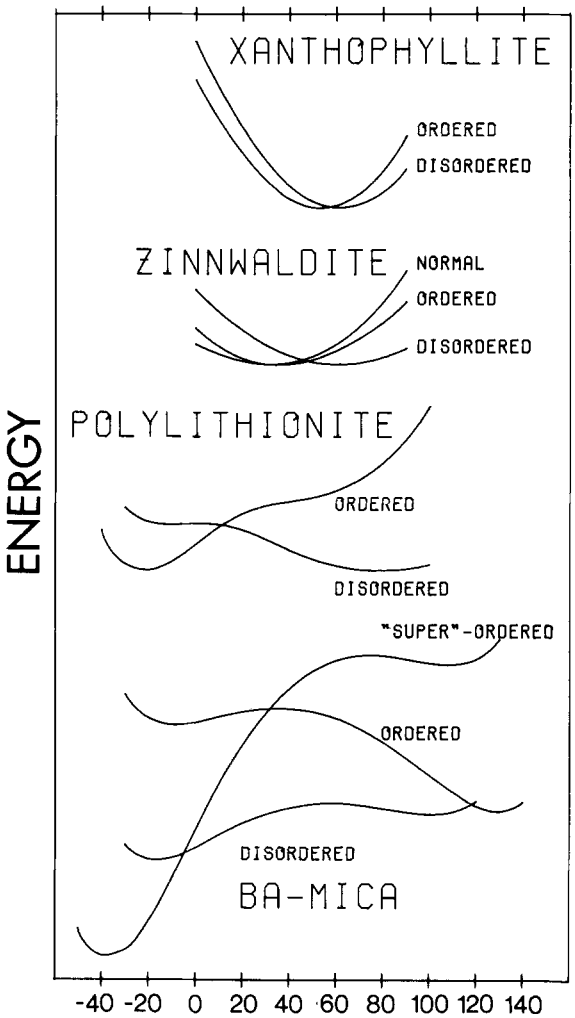


Figure 5. The effect of ordering of octahedral sites on several trioctahedral structures. Xanthophyllite and zinnwaldite have simple energy curves (Figure 3) and show little change in OH orientation upon ordering. Polylithionite and Ba-mica have complex curves, and the OH orientation is very sensitive to octahedral ordering.

The partially ordered polylithionite has the more stable of the two minima at 73.5°. The ordered arrangement makes this the less stable orientation, just the opposite of the Ba-mica. This undoubtedly is due to the extreme charge contrast between the one Al and the two Li ions.

These orientations as well as the data in Figure 4 suggest that all trioctahedral phyllosilicates will behave normally (simple, single minimum in the energy curve)

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for all values of the interlayer cation charge (0, +1, and +2), with the exception of those structures in the shaded regions of Figure 4. These structures contain charge combinations which give stable minima near $\rho^* = -10°$ or between 60° and 120°.

Ordering of tetrahedral sites

The first X-ray study of the margarite structure (Takeuchi, 1965) indicated that the silicon and aluminum ions were disordered. More recently it has been shown (Guggenheim and Bailey, 1977) that the tetrahedral sites are ordered with a regular alternation of the two ions. These two structures can be used to examine the influence of tetrahedral ordering on hydroxyl orientation. The value of ρ for the disordered structure is very nearly the arithmetic mean of the two independent hydroxyls in the ordered structure (Table 1). The difference in orientation between the latter two hydroxyls is about 10°. This should be a reasonable approximation of the possible variations (i.e., ±10°) that exist in real phyllosilicates as a result of the hydroxyls being near different arrangements of Si and Al ions in disordered T sites. Margarite contains as much or more aluminum (Si/Al = 1.0) than do most phyllosilicates, and hence the contrast between order and disorder in margarite should be comparable to the variation in other structures.

PREDICTING HYDROXYL ORIENTATIONS

If the hydroxyl orientations are largely determined by the cation charges, they can be used to predict the values of ρ by using multiple regression. For those structures having more than one unique T and/or M2 site (i.e., 3T muscovite and zinnwaldite) only the average T and M charges were used (Table 1). Only structures that have few or no vacancies in the M sites have been included, and, where available, ordered distributions of cations in the M1 and M2 sites were chosen rather than the disordered structure. All the structures listed in Table 1 that were used in the multiple regression analysis are marked by an asterisk in column 9. The amount of tetrahedral rotation was included in the analysis because it represents the single most important structural variable in the micas (unpublished results) and, by inference, in all 2:1 phyllosilicates. In addition, the *a* and *b* cell parameters as well as the thickness of the layer as represented by d_{001} were considered because these give some information about the dimensions of the sheets. There are many other possible predictors, such as the interatomic distances from the hydroxyl to the various anions and cations in the layer. However, it was felt that the most useful predictor equation should include only information readily available from X-ray data (cell dimensions and d_{001}) and chemical analysis (distribution of cations among the different sites), as well as tetrahedral rotation (McCauley and Newnham, 1971). It is true that the exact distribution of cations is not known except where a single crystal refinement is available, and even here, disorder prevents a unique assignment of charges. But given the cation composition of a 2:1 mineral, the range of possible cation distributions is limited, and each of the various possibilities can be examined separately.

The results of a multiple regression analysis are influenced by the data used for the analysis. The only problems encountered were for the trioctahedral structures. It is clear from the previous discussion that there are two possible orientations that are not part of a continuous series. Linear regression cannot encompass both possibilities. Therefore, all structures with the minimum near $\rho^* = -10°$ were arbitrarily excluded from the data set. Secondly, orientations with very small values (the other minimum of the complex curves, Figure 3) such as the Ba-mica are not included because these apparently are not compatible with the linear hypothesis. The resulting trioctahedral orientations cover values between approximately 115° to 75°. In general, the analysis is valid for those trioctahedral structures which lie outside the shaded areas in Figure 4.

Initially, the set of 31 structures in Table 1 was analyzed by stepwise, multiple linear regression using 8 predictors—the tetrahedral rotation, the *a* and *b* cell parameters, d_{001} (the latter for one layer), and the cation charges (IC, T, M1, and M2). The analysis indicated that only the IC, T, and M2 charges were significant in determining ρ. The equation

$$\rho^\circ = 653.516 - \underset{(3.409)}{31.043}(\mathrm{IC}) - \underset{(12.315)}{99.067}(\mathrm{T}) - \underset{(3.282)}{73.012}(\mathrm{M2})$$

accounts for 95.0% of the total variance, and it was significant at the 1% level. The errors in each of the coefficients are indicated below the equation in parentheses. The standard deviation for the difference between the observed and calculated ρs is 7.8° with extreme deviations of 9.3 and −26.1°. The analysis is successful in that ρ can be predicted with reasonable accuracy for all the trioctahedral and dioctahedral structures of the study. In terms of predicting as accurately as possible the value of ρ, it is better to treat the two types of structure separately.

The same procedure was followed for the separate treatment of dioctahedral and trioctahedral micas. For the former, the important predictors are the charges on the IC, T, and M2. The equation

$$\rho^\circ = 18.231 - \underset{(2.279)}{30.795}(\mathrm{IC}) - \underset{(12.990)}{82.021}(\mathrm{T}) + \underset{(21.374)}{57.958}(\mathrm{M2})$$

accounts for 94.4% of the variance. The standard deviation of the error is 4.7°, with maximum deviations of 9.2° and −10.0°. For the trioctahedral case the fac-

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tors are the charges on M1 and the tetrahedral rotation, α. The equation

$$\rho^\circ = 48.767 + 23.310(\text{M1}) - 0.851(\alpha)$$
$$\qquad\qquad\quad (2.477) \qquad (0.212)$$

explains 89.3% of the variance. The standard deviation for the errors is 2.9°, with maximum deviations of 4.6° and −6.0°. Since the estimation of α using chemical data only (McCauley and Newnham, 1971) is cumbersome, a second regression was computed excluding the α values from the data set. This new regression

$$\rho^\circ = -58.340 + 24.432(\text{M1}) + 26.273(\text{T})$$
$$\qquad\qquad\quad (2.995) \qquad (7.678)$$

explained 87.3% of the variance with a standard deviation of 3.2° and maximum deviations of 4.1° and −5.0°. This is almost as good a predictor as the first equation and is much more convenient to use, involving only the M1 and T charges.

It is curious that the charge on the M1 site does not play a very important role in predicting OH orientations for the combined group of di- and trioctahedral minerals because the presence or absence of an M1 cation determines whether the OH is near 90° (trioctahedral) or near 20° (dioctahedral). But as shown above (Figure 2), there is a continuum of orientations with two maxima representing these structure types. The dispersion about these two values is not strongly influenced by the M1 cation but is rather a result of the charge distribution between IC and M2.

These same three factors (IC, T, and M2) are the predictors for the dioctahedral phyllosilicates. The most important of these is the IC since the interlayer cation sits almost directly above the hydroxyl, and the H–IC distance is directly and strongly influenced by changes in ρ. The T charge is more diffuse, residing on six cation sites and therefore has a smaller effect on the hydrogen. Finally, the M2 sites are very close to the hydrogen, but the M2–H distance is relatively insensitive to ρ. M1, of course, can play no role here because the site is vacant.

The three filled M sites of the trioctahedral micas are such that a great deal of stability is imparted to the OH orientation. This stability precludes a major role for either IC or T. The major reorientations of the OH are the result of the charge distributions between M1 and M2, and it is the contrast between these two sites that determines the variation in ρ about 90°. Because M1 is a single site and M2 a two-fold site, as the terminology is used in this paper, the M1 charge will have the greater weight. The M1 charge itself accounts for 73.7% of the variance. The second factor shown to be important by the regression analysis is the tetrahedral rotation. This was implicated in an earlier study of dioctahedral micas (Giese, 1973). The argument that was developed at that time was that an increase in tetrahedral rotation brought some oxygens of the tetrahedral bases closer to the line connecting the IC and the hydroxyl oxygen. This results in an increased attraction between the hydrogen and one of these oxygens (the one in the mirror or pseudomirror plane) such that the OH is pulled away from the normal to (001), thereby decreasing the value of ρ.

CONCLUSIONS

A wide variation in OH orientations is observed in 2:1 phyllosilicates, both dioctahedral and trioctahedral. The angle ρ [between the OH and (001)] varies between 1.3° and 183.3° (measured with respect to the M1 site). The dioctahedral structures represent a single situation in which the OH can easily move closer to or farther away from the vacant M1 site as the distribution of charges varies among the IC, T, and M2 sites. In trioctahedral structures the three filled M sites create a stable OH orientation near the normal to (001). For some structures with relatively small M site charges or where the difference in the charges of M1 and M2 is large, two potential minima exist on either side of the perpendicular. The extent of the development of the secondary minimum and the reorientation away from 90° of each depends on the specific charge distribution.

For both the dioctahedral and single minima trioctahedral structures, multiple regression equations can closely predict the OH orientations. For the more complex trioctahedral structures, these equations give approximate directions, but are underestimates of the actual orientations.

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REFERENCES

Bailey, S. W. (1975) Cation ordering and pseudosymmetry in layer silicates: *Am. Mineral.* **60,** 175–187.

Bassett, W. A. (1960) Role of hydroxyl orientation in mica alteration: *Geol. Soc. Am. Bull.* **71,** 449–456.

Baur, W. H. (1972) Prediction of hydrogen bonds and hydrogen atom positions in crystalline solids: *Acta Crystallogr.* **B28,** 1456–1465.

Burnham, C. W. and Radoslovich, E. W. (1963) Crystal structures of coexisting muscovite and paragonite: *Carnegie Inst. of Wash. Yearbook,* 232–236.

Donnay, G. and Allmann, R. (1970) How to recognize O^{2-}, OH^- and H_2O in crystal structures determined by X-rays: *Am. Mineral.* **55,** 1003–1015.

Donnay, G., Morimoto, N., Takeda, H., and Donnay, J. D.

https://doi.org/10.1346/CCMN.1979.0270307 Published online by Cambridge University Press

H. (1964) Trioctahedral one-layer micas. I. Crystal structure of a synthetic iron mica: *Acta Crystallogr.* **17,** 1369–1373.

Giese, R. F. (1971) Hydroxyl orientation in muscovite as indicated by electrostatic energy calculations: *Science* **172,** 263–264.

Giese, R. F. (1973) Hydroxyl orientations—dioctahedral micas: 10th Clay Minerals Society Meeting, Banff, Abstracts, 36.

Giese, R. F. (1975a) The effect of F/OH substitution on some layer-silicate minerals: *Z. Kristallogr.* **141,** 138–144.

Giese, R. F. (1975b) Crystal structures of ideal, ordered one-layer micas: AFCRL-TR-75-0438, Environmental Research Papers, No. 526, 135 pp.

Giese, R. F. (1976) Hydroxyl orientations in gibbsite and bayerite: *Acta Crystallogr.* **B32,** 1719–1723.

Giese, R. F. (1977) The influence of hydroxyl orientation, stacking sequence, and ionic substitution on the interlayer bonding of micas: *Clays & Clay Minerals* **25,** 102–104.

Giese, R. F. and Datta, P. (1973) Hydroxyl orientations in the muscovite polymorphs $2M_1$, 3T and 1M: *Z. Kristallogr.* **137,** 436–438.

Gilkes, R. J., Young, R. C., and Quirk, J. P. (1972) The oxidation of octahedral iron in biotite: *Clays & Clay Minerals* **20,** 303–315.

Guggenheim, S. and Bailey, S. W. (1977) The refinement of zinnwaldite-1M in subgroup symmetry: *Am. Mineral.* **62,** 1158–1167.

Güven, N. (1971) The crystal structures of $2M_1$ phengite and $2M_1$ muscovite: *Z. Kristallogr.* **134,** 196–212.

Güven, N. and Burnham, C. W. (1967) The crystal structure of 3T muscovite: *Z. Kristallogr.* **125,** 163–183.

Hamilton, W. C. and Ibers, J. A. (1968) *Hydrogen bonding in solids,* W. A. Benjamin, Inc. New York, 284 pp.

Hazen, R. M. and Burnham, C. W. (1973) The crystal structure of one-layer phlogopite and annite: *Am. Mineral.* **58,** 889–900.

Joswig, W. (1972) Neutronenbeugungsmessungen an einem 1M-Phlogopit: *Neues Jahrb. Mineral. Monatsch.* **H1,** 1–11.

McCauley, J. W. and Newnham, R. E. (1971) Origin and prediction of ditrigonal distortions in micas: *Am. Mineral.* **56,** 1626–1638.

McCauley, J. W. and Newnham, R. E. (1973) Structure refinement of a barium mica: *Z. Kristallogr.* **137,** 360–367.

McCauley, J. W., Newnham, R. E., and Gibbs, G. V. (1973) Crystal structure of synthetic fluorophlogopite: *Am. Mineral.* **58,** 249–254.

Meier, W. M. and Villiger, H. (1969) Die Methode der Abstandsverfeinerung zur Bestimmung der Atomkoordinaten idealisierter Gerüststrukturen: *Z. Kristallogr.* **129,** 411–423.

Prost, R. (1975) Interactions between adsorbed water molecules and the structure of clay minerals: Hydration mechanism of smectites: *Proc. Int. Clay Conf.,* Mexico City, 351–359.

Raynor, J. and Brown, G. (1973) The crystal structure of talc: *Clays & Clay Minerals* **21,** 103–114.

Rothbauer, R. (1971) Untersuchung eines $2M_1$-Muskovits mit Neutronenstrahlen: *Neues Jahrb. Mineral. Monatsch.* **H4,** 143–154.

Sartori, F., Franzini, M., and Merlino, S. (1973) Crystal structure of a $2M_2$ lepidolite: *Acta Crystallogr.* **B29,** 573–578.

Serratosa, J. M. and Bradley, W. F. (1958) Determination of the orientation of OH bond axes in layer silicates by infrared absorption: *J. Phys. Chem.* **62,** 1164–1167.

Soboleva, S. V. and Zvyagin, B. B. (1969) Crystal structure of dioctahedral Al-mica 1M: *Sov. Phys. Crystallogr.* **13,** 516–519.

Steinfink, H. (1962) Crystal structure of a trioctahedral mica; phlogopite: *Am. Mineral.* **47,** 886–896.

Takeda, H. and Burnham, C. W. (1969) Fluor-polylithionite; a lithium mica with nearly hexagonal $(Si_2O_5)^{2-}$ ring: *Mineral. J. Jpn.* **6,** 102–109.

Takeda, H. and Donnay, J. D. H. (1966) Trioctahedral one-layer micas. III Crystal structure of a synthetic lithium fluormica: *Acta Crystallogr.* **20,** 638–646.

Takeda, H., Haga, N., and Sadanaga, R. (1971) Structural investigation of polymorphic transition between $2M_2$-, 1M-lepidolite and $2M_1$ muscovite: *Mineral. J. Jpn.* **6,** 203–215.

Takeda, H. and Ross, M. (1975) Mica polytypism: dissimilarities in the crystal structures of coexisting 1M and $2M_1$ biotite: *Am. Mineral.* **60,** 1030–1040.

Takeuchi, Y. (1965) Structure of brittle micas: *Clays & Clay Minerals* **13,** 1–25.

Tateyama, H., Shimoda, S., and Sudo, T. (1974) The crystal structure of synthetic Mg^{IV} mica: *Z. Kristallogr.* **139,** 196–206.

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. Jpn.* **23,** 83–88.

Vedder, W. and McDonald, R. S. (1963) Vibrations of the OH ions in muscovite: *J. Chem. Phys.* **38,** 1583–1590.

Wardle, R. and Brindley, G. W. (1972) The crystal structures of pyrophyllite, 1Tc, and of its dehydroxylate: *Am. Mineral.* **57,** 732–750.

Zhoukhlistov, A., Zvyagin, B. B., Soboleva, A. V., and Fedotov, A. F. (1973) The crystal structure of the dioctahedral mica $2M_2$ determined by high voltage electron diffraction: *Clays & Clay Minerals* **21,** 465–470.

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Резюме—Ориентации гидроксила в 31 диоктаэдрической и триоктаэдрической структуре 2:1 листового силиката определялись путем вычислений электростатической энергии. Эти структуры включали слюды, маргарит и другие родственные им минералы, характеризующиеся упорядоченным и не упорядоченным распределением катионов. Диоктаэдрические слюды и маргарит исследовались при наличии и отсутствии межслойного катиона. Был обнаружен диапазон ориентаций от 1,3° до 183,3° (угол между O-H и (001), измеренный по отношению к положению M1). Ориентации для диоктаэдрических структур неопределенны, в то время как триоктаэдрические образцы характеризуются двумя возможными ориентациями, разделенными энергетическим барьером. Одна ориентация близка к 90°; другая около 180°. Последняя ориентация является результатом концентрации зарядов в межслоях (IC) и тетраэдрах (CT) за счет октаэдров (M). Был выполнен многократный регрессионный анализ 31 структуры с использованием параметров a и b ячейки, d_{001}, и зарядов для T,IC,M1, и M2. Этот анализ показал, что важными факторами являются заряды для IC, T, и M2. Если диокта- эдрические структуры рассматривать как отдельную группу, они также обнаруживают те же факторы. Триоктаэдрические ориентации определяются зарядом на M2 и величиной вращения тетраэдров. С использованием этих двух предварительно полученных уравнений может быть определено значение ρ со стандартным отклонением 4,7° и 2,9° для случаев диоктаэдрических и триоктаэдрических структур соответственно.

Resümee—Die Hydroxylorientierungen in 31 dioktahedrischen 2/1 Phyllosilikatstrukturen sind durch elektrostatische Energiekalkulationen bestimmt worden. Diese Strukturen umfassen Glimmer, spröde Glimmer, und andere verwandte Mineralien, die sowohl geordnete wie nicht geordnete Kationenverteilungen aufweisen. Die dioktahedrischen Glimmer und brüchige Glimmer wurden mit und ohne Zwischenschichtkationen untersucht. Orientierungen von 1,3 bis 183,3° (der Winkel zwischen den OH und (001), gemessen mit Hinsicht auf den M1 Platz) wurden gefunden. Die Orientierungen für die dioktahedrischen Strukturen repräsentieren ein Kontinuum von Werten, wohingegen die trioktahedrischen Sorten zwei mögliche Orientierungen zeigen, die durch eine Energieschranke getrennt sind. Eine Orientierung ist fast bei 90°, die andere bei 180°. Die letztere Orientierung ist das Resultat einer Konzentration von Ladungen in den Zwischenschichtplätzen (IC) und den tetrahedrischen Plätzen (CT) auf Kosten der oktahedrischen Plätze. Eine multiple Regressionsanalyse aller 31 Strukturen wurde unternommen, indem die *a* und *b* Zellparameter, d_{001}, und die Ladungen für die T, IC, M1, und M2 Plätze für Vorraussagungen benutzt wurden. Diese Analyse weist darauf hin, daß die wichtigen Faktoren die Ladungen für die IC, T, und die M2 Plätze sind. Wenn die oktahedrischen Strukturen als seperate Gruppen behandelt werden, findet man dort dieselben Faktoren. Die trioktahedrischen Orientierungen werden durch die Ladungen der M2 Plätze und die Höhe der tetrahedrischen Rotation bestimmt. Wenn diese zwei Vorraussagungsgleichungen benutzt werden, kann der Wert von ρ mit mittlerer Abweichung von 4,7 und 2,9° für die dioktahedrischen beziehungsweise trioktahedrischen Fälle bestimmt werden.

Résumé—Les orientations hydroxyles dans 31 structures dioctaèdres et trioctaèdres phyllosilicates 2:1 ont été déterminées par calcul de l'énergie électrostatique. Parmi ces structures il y avaient des micas, des micas cassants, et d'autres minéraux apparentés exhibant des distributions de cations ordonnées et désordonnées. Les micas dioctaèdres et les micas cassants ont été examinés avec et sans le cation interfeuillet. Un étagement d'orientations de 1,3° à 183° (l'angle entre l'OH et (001) mesuré par rapport au site M1) a été trouvé. Les orientations pour les structures dioctaèdres représentent une série continue de valeurs, tandis que les espèces trioctaèdres exhibent 2 orientations possibles séparées par une barrière d'énergie. Une orientation est près de 90°, et l'autre est près de 180°. Cette dernière orientation résulte d'une concentration de charge sur l'interfeuillet (IC) et sur les sites tétraèdres (T) aux dèpens des sites octaèdres (M). Une analyse de régression multiple a été faite, utilisant comme pronostiquants les mailles paramètres *a* et *b*, d_{001} et les charges pour les sites T, IC, M1, M2, pour les 31 structures. Cette analyse a indiqué que les facteurs importants étaient les charges pour les sites T, IC, et M2. On trouve les mêmes facteurs pour les structures dioctaèdres si on les traite comme un groupe séparé. Les orientations trioctaèdres sont déterminées par la charge sur le site M2 et par la quantité de rotation tétraèdre. Une valeur pour ρ peut être estimée avec une déviation standard de 4,7° et 2,9° dans les cas dioctaèdres et trioctaèdres, respectivement, utilisant les équations pronostiquantes.

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