

FACTORS AFFECTING ORIENTATION OF OH-VECTORS IN MICAS

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Abstract—The orientation of the OH-vectors in hydroxyl groups of micas of different compositions, polytype modifications, and symmetry were calculated by the method of minimization of electrostatic energy. The orientations are strongly affected by the peculiarities of structures, and even slight deviations from the ideal dioctahedral periodicity can introduce a correction of as much as 10° to the value of the polar angle. Ordering of cations in octahedra lead to twisting of the OH-bond towards the octahedron with lower charge and larger dimension. The latter is less true for cation ordering in tetrahedra. Because of these factors and the dependence of the hydrogen position on the coordinates of heavy atoms, such calculations can give reliable results only if the structure has been refined with high precision. Different polytypes of micas displayed the same orientation of the OH-vectors with respect to the axes of a separate layer, if the stacking sequence did not introduce specific distortions of the 2:1 layer.

Key Words—Celadonite, Electrostatic calculations, Glauconite, Hydroxyl vectors, Mica, Muscovite, Phengite.

INTRODUCTION

In a previous work we showed that the orientation of the OH-vectors in hydroxyl groups of micas, obtained by calculations of electrostatic energy, agree well with those established experimentally for the limited number of the structures where the positions of the hydroxyl hydrogen were localized by diffraction (Bookin *et al.*, 1982). The latter structures provided a basis for extending such calculations to micas of different compositions, symmetry, and polytype modification. The problem was in supplementing structural data with estimations of the orientations of the OH-bonds and in studying their dependence on chemical composition, individual features of structures, and modes of stacking of the 2:1 layers.

Giese (1979) dealt with similar problems, paying most attention to trioctahedral micas. A series of dioctahedral structures with a minor deviation of the charge of the M2 site from +3, typical of muscovite, was also studied. The orientations of the OH-bonds of the structural hydroxyls in di- and trioctahedral micas are qualitatively different; in the former, the OHs are tilted, the angle between the (001) plane and the OH-vector ranging from 1° to 21° , while in the latter, the OHs are almost normal to the cleavage plane. Giese (1979) considered unit-cell parameters, the angle of tetrahedral rotation, and the mean charges of octahedral, tetrahedral, and interlayer sites as the most probable factors affecting OH-vector orientations. His regression analysis showed that in dioctahedral micas the only predictor is the charge distribution over the interlayer, tetrahedral, and *cis*-octahedral sites. He concluded that a crystallochemical formula of the compound is sufficient to predict the OH-bond orientation, the knowledge of details of the structure being not necessary.

However, the difference between the OH-orientations obtained from the regression equation and by the minimization procedure, from -10° to $+9^\circ$, appears to be still greater for some micas in which OH-orientations were calculated earlier (Bookin, 1979). The entire range of the inclination angles mentioned above being compatible with the displayed errors, the suggested regression equation is a crude description of the experimental data.

Such errors may be due to a certain methodological deficiency. In his study, Giese (1979) replaced the experimentally established distributions of cations over the crystallographic positions with those characteristic of micas of ideal composition. Formula units of these micas correspond to a single monovalent or divalent interlayer cation, four tetrahedral, and two or three octahedral cations for di- and trioctahedral structures, respectively. The compositions of natural micas commonly differ from the ideal formula. A structure may have a deficiency of interlayer ions and at the same time a restricted hetero- and/or homovalent cation substitution. The sum of the cations that usually occupy the octahedral sites is not always equal to two or three per formula unit, and extra cations may occupy either empty M1 octahedral sites or partially vacant interlayer positions. In addition, different cations may be distributed over geometrically equivalent sites in several modes which may alter the symmetry of the structure.

The results of such idealization may be seen in margarite (Guggenheim and Bailey, 1975, 1978). From their chemical analysis, the presence of Na and K in the interlayers results in a 1.9 charge instead of the ideal 2.0 charge for this position. The sum of the octahedral cations exceeds the required amount by 0.035, testifying only to partial vacancy of the *trans*-octahedral posi-

Table 1. Distribution of charges and orientation of OH-vectors in micas.

Sample	Mica	Polytype	Space group	IC	T1, T2	M2, M2', M1	ρ	ψ	Literature
1	Muscovite ¹	2M ₁	C2/c	1.00	2 × 3.75	2 × 3.00	15°	0°	Rothbauer, 1971
2	Muscovite	2M ₁	C2/c	0.89	2 × 3.79	2 × 2.97	15°	0°	Tsipursky and Drits, 1977
3	Muscovite	1M	C2	0.74 0.68	3.96, 3.80	3.00, 2.80, — 3.00, 2.80, 0.06	11° 20°	7° 7°	Zvyagin, 1979
4	Phengite	1M	C2/m	0.88 0.84	2 × 3.85	2 × 2.86, — 2 × 2.86, 0.04	11° 17°	0° 0°	Tsipursky and Drits, 1977
5	Celadonite	1M	C2	1.09	2 × 3.99	2.55, 2.40	-14°	8°	Tsipursky, 1979
6	Celadonite	1M	C2/m	0.93	2 × 3.99	2 × 2.57	-14°	0°	Zvyagin, 1979
7	Celadonite	1M	C2/m	0.99	2 × 3.93	2 × 2.64	-5°	0°	Ideal model
8	Glaucconite	1M	C2/m	0.83 0.79	2 × 3.91	2 × 2.71, — 2 × 2.71, 0.04	-6° 0°	0° 0°	Ideal model
9	Margarite	2M ₁	Cc	1.90	3.147, 3.847 3.908, 3.215	2 × 3.00, 0.07	20°	4°	Guggenheim and Bailey, 1978
10	Protolithionite	3T	P3 ₁ 12	1.02	3.86, 3.66	3.00, 1.52, 1.52	70°	60°	Pavlishin <i>et al.</i> , 1981
11	Biotite	1M	C2/m	0.98	2 × 3.71	2 × 2.34, 2.34	90°	—	Takeda and Ross, 1975
12	Biotite	2M ₁	C2/c	0.98	2 × 3.71	2 × 2.34, 2.34	85°	3°	

¹ The data for this mica coincide with those obtained by Giese (1979).

tion, which was confirmed by X-ray diffraction. According to the same data the Si and Al ordering in tetrahedra is almost perfect, but even the mean charges of the upper and lower tetrahedral sheets (3.497 and 3.562, respectively) differ from the ideal value of 3.500 used by Giese (1979).

Dealing with an unrepresentative series of idealized dioctahedral micas, Giese (1979) supplemented it with hypothetical minerals without charges in the interlayer sites. Because such compounds are not electrically neutral, their inclusion in the regression analysis does not seem to be justified.

These assumptions would have had no consequences in fitting regression equations, if one was sure that geometrical parameters (interatomic distances and angles) do not significantly affect the OH-bond inclination angle. However, the different values of the polar angles for the three muscovites and the paragonite calculated by Giese (1979) indicate the importance of the geometrical factors that can hardly be presented as a single parameter—the tetrahedral rotation angle. For these reasons, the orientation of OH-vectors in hydroxyls of natural micas of different compositions, polytypic modification, and symmetry were calculated by the method of minimization of electrostatic energy.

RESULTS OF CALCULATIONS

Table 1 lists the micas studied; their polytype modifications and space groups; their interlayer (IC), tetrahedral (T1, T2), and octahedral (M1, M2, M2') charges in valence units; their polar angles (ρ) between the OH-vector and the cleavage plane; and the absolute values

of pertinent azimuthal angles (ψ). The latter angles were measured relative to a plane normal to the cleavage plane that passes through the oxygen atoms of nearest hydroxyl groups (coinciding with the mirror plane in the 2:1 layers with ideal symmetry C2/m). The direction of the polar angle was considered positive when the proton occupied a position outside of the octahedral sheet; the direction of the azimuthal angle was described in each specific case. The references in the last column of Table 1 contain chemical compositions, unit-cell parameters, and coordinates of independent positions and their populations by atoms of different kind (or sizes of polyhedra). From these latter experimental data and from chemical analysis the mean charges of cationic and anionic crystallographic positions were calculated.

Table 1 also contains the results of calculations of the OH-vector orientations for glaucconite and celadonite ("samples" 7 and 8). Because direct experimental data for these minerals are not available, models of their structures were obtained by using the compositions and unit-cell parameters listed in Table 2 and the established regularities reported by Bailey (1966) and Drits (1975).

DISCUSSION OF RESULTS

From these data the possible factors that affect the orientation of the OH-bonds in micas can be analyzed.

Localization of uncompensated charge in the 2:1 layers

Giese (1979) considered the interaction of a proton with octahedral, tetrahedral, and interlayer charges. This consideration is extended here by examining mi-

Table 2. Chemical compositions and unit-cell parameters of celadonite and glauconite.

Sample ¹	Crystallochemical formula	a (Å)	b (Å)	c (Å)	β
7. Celadonite	(K _{0.82} Na _{0.17})(Si _{3.78} Al _{0.82})(Al _{0.16} Fe ³⁺ _{1.06} Fe ²⁺ _{0.14} Mg _{0.67})O ₁₀ (OH) ₂	5.22	9.05	10.12	100°44'
8. Glauconite	(K _{0.78} Na _{0.01})(Si _{3.65} Al _{0.35})(Al _{0.68} Fe ³⁺ _{0.79} Fe ²⁺ _{0.10} Mg _{0.43} Ti _{0.02})O ₁₀ (OH) ₂	5.24	9.08	10.14	100°48'

¹ From Table 1.

cas with other distributions of charges over non-equivalent positions.

Consider a set of K-containing micas: muscovite-2M₁, muscovite-1M, phengite-1M, glauconite, celadonite (Table 1). Assume that the unit cells of muscovite-1M, phengite-1M, and glauconite have four octahedral cations and vacant *trans*-positions, and that the extra two valence cations are localized in the interlayers. The transition from muscovite-2M₁ to celadonite reveals a sequential increase of positive cation charge in the tetrahedral sheets of the 2:1 layers and a decrease in the octahedral sheets. Whereas in both refined structures of the muscovite-2M₁, the OH-vectors are oriented identically (towards the vacant M1 octahedron at an angle of 15° to the cleavage plane), and the proton in the muscovite-1M and the phengite-1M moves toward the plane of the oxygens of octahedra ($\rho = 11^\circ$) in response to the increase of tetrahedral charge. The extreme case of charge distribution is realized in celadonite, where all tetrahedral sites are occupied by silicon and the octahedral sheet has the lowest charge. Such a distribution of charges leads to a qualitatively new pattern, with the OH-bond oriented towards the center of the octahedral sheet. Whereas the protons of muscovite occupy the hexagonal holes of the tetrahedral sheets, in celadonite the protons of the two hydroxyls of the *trans*-octahedron M1 lie inside the octahedron acting as a divalent octahedral cation. Celadonite ("sample" 7) and the glauconite ("sample" 8), with tetrahedral charges less than the maximum value, have an intermediate direction for the OH-bond, close to the oxygen plane of the octahedra. The OH-vector is similarly oriented in typical phengite-2M₁, in which the polar angle is 1°, according to Giese (1979).

The dependence of OH-vector orientations on the distribution of charges over the non-equivalent positions, considered by Giese (1979), is qualitatively the same. However, even the corrected¹ regression equation for dioctahedral micas gives very rough estimations of the polar angles for micas in which compositions differ considerably from those of muscovite (-34° and -24° for celadonite samples 5 and 6) or from those containing charges in *trans*-octahedral positions (+11°

for margarite) which runs counter to our results by 10°-20°.

Influence of structural distortions of polyhedra

Muscovite-2M₁ and paragonite-2M₁ have the same spatial distribution of charges. Replacement of interlayer K in muscovite by Na in paragonite leads to a decrease of unit-cell parameters, thinning of the interlayer space, and an increase of the ditrigonal rotation angle. Hence, the ρ angle of paragonite is 20° (Giese, 1979), i.e., 5° larger than that of muscovite. Similarly, it is interesting to compare the data obtained for muscovite-1M by Datta and Giese (1973) and those provided in the present paper. The first calculation based on the atomic coordinates of Soboleva and Zvyagin (1969) gave a polar angle of -1°. Our calculation of ρ for the same structure as reinvestigated by Zvyagin (1979) gave a much larger value of 11°. Similarly, a more precise determination of the dickite structure (Rozdestvenskaya *et al.*, 1981) has led to a divergence of approximately 5° between the OH-bond orientations obtained by Bookin *et al.* (1982), as compared to the calculations by Giese and Datta (1973) based on the results of the previous refinement of this mineral by Newnham (1961).

Thus, even the exact knowledge of the charge distribution cannot guarantee a reliable estimation of the OH-bond orientation if the structure is refined with insufficient precision.

Role of trans-octahedral and interlayer cations

Giese (1979) applied the model of micas with the ideal charge in the interlayer position and vacant *trans*-octahedron in his calculations. As mentioned above, in the muscovite-1M, phengite-1M, glauconite, and margarite samples studied here the sum of octahedral cations is 1-2% higher than that required for an ideal dioctahedral structure, whereas the interlayers have vacancies. Calculations show that the value of ρ depends considerably on the localization of these extra cations. Transfer of a small charge from the interlayer position to the M1 octahedron leads to an increase of ρ from 11° to 20° in the muscovite-1M, from 11° to 17° in the phengite-1M, and from -6° to 0° in the glauconite (see Table 1). The polar angle of 20° in margarite exceeds that obtained by Giese (1979) by almost 10° for the same reason. The cation density in the M1 octahedron was confirmed experimentally for the phengite-

¹ The equation for the dioctahedral micas listed by Giese (1979) is incorrectly printed in the paper (R. F. Giese, Department of Geological Sciences, State University of New York at Buffalo, Amherst, New York 14226, private communication, 1981).

1M (Bookin *et al.*, 1982) and for the margarite (Guggenheim and Bailey, 1975).²

Further influence of the increase of charge in the *trans*-octahedron may be illustrated by protolithionite, which has a general distribution of charges between the sheets of the 2:1 layer close to that of muscovite. Here, ρ increases to 70° due to a considerable charge in the M1 octahedron.

Cation densities for all octahedra in trioctahedral micas are approximately the same, and ρ is close to 90° (e.g., in biotites, Table 1). Similar angles in the same biotites were obtained by Giese (1979), in spite of the fact that the author used charge distribution which did not coincide with experimental data and that neglected the two-fold reduction of the amount of hydroxyls. The similarity of results demonstrates that in trioctahedral micas random distribution of heterovalent cations and vacancies, as well as specific polyhedra distortions, are the main factors influencing the OH-orientation, irrespective of the particular charges of the sites.

Significance of order-disorder in distribution of atoms

Even with similar composition, the 2:1 layers of micas can differ from each other in the distribution of the cations over equivalent positions. For example, for the phengite-1M and celadonite 6 samples in Table 1 the space group *C2/m* was determined, which reflects a statistical disorder in the distribution of cations. On the contrary, the muscovite-1M and celadonite 5 samples show an ordered distribution, accompanied by a decrease in symmetry and the appearance of two non-equivalent octahedral (M2 and M2') and tetrahedral (T1 and T2) positions in the unit cell. For a better estimation of the influence of cation distribution in micas of the same composition of 2:1 layers, an ordered structure can be artificially transformed into a disordered one by averaging the coordinates of the corresponding pseudo-symmetric sites (e.g., T1 and T2 in the micas with space group *C2*). Similarly, a disordered structure can be reconstructed into an ordered model in which there is a different charge density in the pseudo-symmetrical polyhedra as well as a difference in their dimensions and shapes.

For micas with space group *C2/m*, only one azimuthal orientation of the OH-vector is possible, e.g., one in which the OH-vector is in the mirror plane. In mus-

covite-2M₁, due to the disordered distribution of Si and Al in the tetrahedra, the symmetry of each separate layer remains high, and in such 2:1 layers, as well as in micas with space group *C2/m*, $\psi = 0^\circ$. The ordered cation distribution found in the celadonite 5 and muscovite-1M samples moved the OH-vector towards the *cis*-octahedron with the lower average cation charge. The azimuthal angle is 8° in celadonite 5 and 7° in muscovite-1M.

If the charges of the M2 and M2' octahedra are equalized in the celadonite and the experimental shapes and dimensions of the polyhedra remain the same, $\psi = 5^\circ$. On the contrary, if the shapes and dimensions of octahedra are averaged and the experimental distribution of octahedral cations remain the same, ψ is only 2°. Thus, the dimensions of the polyhedra affect the azimuthal angle of the OH-bond to a larger extent than the difference in charges localized in the octahedra. Therefore one can expect a divergence of ψ from 0° in micas where the adjacent *cis*-octahedra are occupied with identically charged cations but differ considerably in size.

It should be pointed out that the degree of *cis*-octahedra asymmetry in both of the ordered micas studied is not extreme. So far it is difficult to make any definite conclusions about the azimuthal angle when the two neighboring M2 and M2' sites have 2+ and 3+ valences, but the above estimations show that the azimuthal rotation may shorten considerably the distance between the proton and an oxygen ion of the vacant octahedron.

The OH-vector orientation in protolithionite is qualitatively different from that discussed above. Coincidence of cation composition in the *cis*-octahedron M2' and the *trans*-octahedron M1 leads to the formation of a pseudo-mirror symmetry plane in the distribution of octahedral charges that transects octahedron M2 instead of octahedron M1, as with dioctahedral micas. Therefore, the azimuthal angle is 60° for a symmetrical distribution of charges between M1 and M2' sites. The experimental localization of the proton in protolithionite gave an ψ angle of 72° (Pavlishin *et al.*, 1981), pointing to a larger charge in M1 *trans*-octahedron relative to M2'.

The OH-orientations in ordered margarite (Guggenheim and Bailey, 1978), as calculated by Giese (1979), contradict our data. In our calculations both of the independent hydroxyls are tilted to the (001) plane at about the same angles, and the effect of the ordering is displayed by an azimuthal rotation of OH-bonds by 4°. According to Giese the Si and Al ordering results in an additional OH inclination of $\pm 5^\circ$ as compared with the disordered margarite. Hydroxyls with smaller polar angles appear to be related to the lower charged tetrahedral sheet and vice versa, i.e., the supposed ordering effect dominates the above described repulsion of protons and the highly charged tetrahedra. We could not find any explanation for such discrepancy of the results.

² In the 1981 private communication, Giese made a supposition that because the population of the M1 sites is small, it does not play a significant role, because most of the hydroxyls are located next to vacant M1 octahedra, and the rest have orientations close to perpendicular. This supposition is not unlikely in so far as real fragments of structure are concerned; however, if a crystal is described in terms of the unit-cell concept, the location of hydrogen should be described in the same way, i.e., with its coordinates, mean-weighted over the whole crystal.

Another type of ion substitution that is common in micas is substitution of F^- for OH^- , which is especially common in Li-containing and trioctahedral micas. We calculated the OH-bond orientations in lepidolite- $2M_1$, where 76% of hydroxyls are replaced by fluorine ions. If the usual anionic framework is used (cf. Giese, 1979), $\rho = 58^\circ$. Anionic substitution was accounted for by changing the proton site charge for 0.24 and the (F,OH) site charge for -1.24 , which resulted in an increase of the polar angle of 11° . It is, however, quite insufficient for the calculated value to coincide with the experimental value of 151° (Swanson and Bailey, 1981). This discrepancy is due to the inadequacy of the assumption that OHs are distributed at random in respect to vacancies over the crystal. The supposition that OH-groups are situated preferably next to vacant *cis*-octahedral positions and fluorine ions are located in trioctahedral environment would perhaps yield the experimental OH-bond orientation. Such preference is experimentally observed when using spectroscopic methods that are not based upon the unit-cell concept (Sanz and Stone, 1979; Rausell-Colom *et al.*, 1979).

Effect of stacking sequence of 2:1 layers

Considerable attention to this problem (Datta and Giese, 1973; Mineeva *et al.*, 1978) has been associated with the relative stabilities of different polytypes. As mentioned above, the insufficient precision in atomic coordinates of the muscovite- $1M$ has resulted in the conclusion that the orientation of the OH-vector in this polytype essentially differs from that in the $2M_1$ and $3T$ polytypes (Datta and Giese, 1973). That calculation promoted the spreading of the opinion that the mode of stacking affects the OH-orientation (Swanson and Bailey, 1981; Rozdestvenskaya *et al.*, 1979). In the paper 1979, Giese reported that for the modelled muscovite- $1M$ structure, $\rho = 15^\circ$. Although the influence of the polytype modification on the OHs was not discussed in the above paper, the value given there makes the previous conclusion seen doubtful.

The results of the present work have enabled us to conclude that the mode of stacking sequence does not influence the OH-orientation. Comparative analysis of the data listed in Table 1 for the $1M$ and $2M_1$ polytypes of muscovite, does not reveal a significant difference in polar angles; the observed difference, in light of what has been mentioned above, can be attributed to differences in the chemical compositions of these micas. To investigate the influence of stacking sequence alone, excluding the effects of such factors as peculiarities of compositions and distribution of proxying ions, we have obtained models for the $1M$, $2M_1$, and $2M_2$ polytypes for each mica studied on the basis of the structure of an individual 2:1 layer, after it was refined experimentally. The orientation of the OH-bond appeared to be identical for all three polytypes. The latter is true, however, only in cases when the structure does not undergo great

distortions caused by the stacking sequence of 2:1 layers. From this standpoint very interesting results were obtained by Takeda and Ross (1975) for biotites- $1M$ and $-2M_1$. These micas have the same unit-cell parameters and identical chemical compositions of the structure as a whole and of the separate polyhedra. Nevertheless, the refinement of the crystal structures revealed a peculiar distortion of octahedral sheets of biotite- $2M_1$ as compared to biotite- $1M$. The orientations of the hydroxyls, calculated for these biotites differ from each other by 5° (see Table 1).

CONCLUSIONS

The obtained results strongly suggest that the geometry, the mean charges of *trans*-octahedral and interlayer sites, and the degree and mode of ordering of cations significantly affect OH-bond orientations. This means that in principle it is impossible to construct regressional equations permitting the prediction of proton positions on the basis of the minimum information about the formula unit. Only if all the factors listed above are considered can we hope to obtain an answer to the question. Moreover, at present it is hardly possible to construct a new equation including all known parameters, and it is necessary to minimize electrostatic energy in each specific case.

The mean OH-bond orientations may differ considerably from the orientations of the actual hydroxyls. It is also obvious that the chief influence on the position of the proton is exercised by its nearest neighbors. In mica, with heterovalent cation substitution, one can expect a wide variety of OH-orientations, resulting from different combinations in the arrangement of the nearest cations and vacancies relative to the hydroxyl examined. However, such calculations for the real specimens cannot be carried out just by formal variations of the charge in this or that position. In order to take into account the geometric factor, extremely precise coordinates of the specimen's atoms are needed.

Modelling of the nearest neighbor environment and accounting for the orientations of individual OH-groups in different heterovalent arrangements appear to be important factors in interpreting the γ -resonance spectra of celadonite (Bookin *et al.*, 1979) and nontronite (Besson *et al.*, 1981). It is possible that interpretation of the infrared spectra of clay minerals in the region of hydroxyl vibrations may also be made with due regard to these same factors, because the positions of the bands and the orientation of OH-groups are correlatable (Farmer, 1974).

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Резюме—Ориентации OH-векторов гидроксильных групп слюд разного состава, политипных модификаций и симметрии были рассчитаны методом минимизации электростатической энергии. Как оказалось, они сильно зависят от структурных особенностей слюд и даже слабые отклонения от диоктаэдрической периодичности могут внести поправки до 10° к величине полярного угла. Упорядочение катионов в октаэдрах приводит к повороту OH-связи в сторону октаэдра с меньшим зарядом и большими размерами. Для упорядочения в тетраэдрах этот эффект меньше. Вследствие этих факторов, а также зависимости положения протона от координат тяжелых атомов, такие расчеты могут давать правильные результаты только для хорошо уточненных структур. Различные политипные модификации слюд обнаруживают одинаковую ориентацию OH-векторов относительно осей отдельного слоя при условии, что последовательность наложения слоев не вносит специфических искажений структуры самих 2:1 слоев.

Resümee—Die Orientierungen der OH-Vektoren von Hydroxyl-Gruppen in Glimmern verschiedener Zusammensetzung, polytyper Modifikation und verschiedener Symmetrie wurden durch Minimierung der elektrostatischen Energie berechnet. Die Orientierungen werden sehr stark durch die Eigenheiten der Struktur beeinflusst, und sogar geringe Abweichungen von der idealen dioktaedrischen Abfolge können zu einer Abweichung von bis zu 10° vom Wert des polaren Winkels führen. Die Anordnung von Kationen in den Oktaedern führt zu einer Verdrehung der OH-Bindung gegen das Oktaeder mit der kleineren Ladung und den größeren Dimensionen. Dies stimmt weniger für Kationen in Tetraederlücken. Wegen dieser Faktoren und der Abhängigkeit der Wasserstoffposition von den Koordinaten von Schwermetallen können derartige Berechnungen nur dann verlässliche Ergebnisse liefern, wenn die Struktur mit großer Genauigkeit verfeinert wurde. Verschiedene Polytype von Glimmern zeigen die gleiche Orientierung der OH-Vektoren im Hinblick auf die Achsen einer einzelnen Schicht, wenn die Stapelfolge nicht zu spezifischen Verdrehungen der 2:1 Schicht führt. [U.W.]

Résumé—Les orientations de vecteurs-OH dans des groupes hydroxyles de micas de compositions différentes, les modifications polytypiques, et la symétrie ont été calculées par la méthode de minimisation de l'énergie électrostatique. Les orientations sont fortement affectées par les particularités des structures, et même de légères déviations de la périodicité dioctaédrale idéale peut introduire une correction de jusqu'à 10° à la valeur de l'angle polaire. Le rangement de cations dans les octaèdres mène à la torsion de la liaison OH vers l'octaèdre avec la charge plus basse et ayant les plus grandes dimensions. Ce dernier fait est moins vrai pour le rangement de cations dans les tétraèdres. A cause de ces facteurs, et de la dépendance de la position hydrogène sur les coordonnées d'atomes lourds, de tels calculs ne peuvent donner des résultats dignes de foi que si la structure a été raffinée avec beaucoup de précision. Des polytypes de micas différents exhibent la même orientation pour le vecteur-OH respectivement aux axes d'une couche séparée, si la séquence d'empilement n'introduit pas de distortions spécifiques dans la couche 2:1. [D.J.]