Clays and Clay Minerals, Vol. 28, No. 2, pp. 81–86, 1980.

HYDROXYL ORIENTATIONS AND INTERLAYER BONDING IN AMESITE

R. F. GIESE, JR.

Department of Geological Sciences, State University of New York
4240 Ridge Lea Road, Amherst, New York 14226

Abstract—The hydroxyl orientations in the $2H_2$ polytype of amesite, $Mg_2Al(SiAl)O_5(OH)_4$, have been determined by minimizing the electrostatic potential energy as a function of OH orientation. The angles, ρ, between the hydroxyls and (001) vary between 81.5 and 88.8°. All surface hydroxyls form hydrogen bonds with oxygens of the adjacent layer. The OHs tend to tilt away from the higher charged Al^{VI} ions, and the spread in ρ values is due to variations in the positions of the receptor oxygens. The inner hydroxyls noticeably weaken the interlayer bonding. The substitution of Al in both T and M sites creates a dipolar layer charge and the resulting attraction between layers forms an important part of the interlayer bonding. The $2H_2$ polytype of amesite has substantial interlayer bonding even with all surface hydroxyls replaced by fluorine. This is not true for a composition of $Mg_3Si_2O_5(OH)_4$ where a similar F for OH substitution destroys all interlayer bonding as in kaolinite.

Key Words—Amesite, Fluorine, Hydroxyl orientation, Interlayer bonding, Serpentine.

INTRODUCTION

The interlayer bonding (ILB) in 2:1 phyllosilicates was at one time discussed solely in terms of the attraction between the negative layer charge and the positive interlayer cation. It is known that many other factors are also important. Hydroxyl orientation, the octahedral site occupancy (tri- or dioctahedral), and polytype have been identified as contributing to the interlayer bonding. The existence of a layer charge is not necessary in order to have an electrostatic interlayer bond as shown for the neutral-layered talc and pyrophyllite (Giese, 1975). Doubtless, as more work is completed, other factors will be uncovered.

By comparison with 2:1 layer structures, 1:1 structures are simpler, and their interlayer bonding has received much less attention. Of this group, by far the most work has been done with kaolinite. It was recognized very early that the asymmetric nature of the layer with oxygens on one surface and hydroxyls on the other provides the opportunity for hydrogen bond formation. Much subsequent work was devoted to determining the OH orientations before this hypothesis could be tested. Because, in the kaolin-group minerals, ionic substitutions are very minor, the question of the possible role played by substitutions never arose. Recent work has in fact substantiated the earlier ideas about hydrogen bonding and, while the OH orientations vary considerably among the minerals kaolinite, dickite, and nacrite, the resulting ILB for all three is of comparable magnitude (Giese, 1973).

The trioctahedral 1:1 structures have received less attention probably because there was little question about the OH orientations which were assumed to be normal to (001). At the same time there was no accurate structure determination of a well characterized 1:1 trioctahedral structure with which to work. In spite of this, an attempt was made by Wolfe and Giese (1974) to determine the OH orientations of an idealized structure. The hydroxyls were found to be nearly normal to (001) as predicted. However, on examination of the ILB of this structure, several unexpected results were found, particularly when various ions were substituted in the tetrahedral and octahedral sites. It was not clear at the time whether the results were real or an artifact due to the idealized structure. The results reported here completely substantiate the correctness of the previous work.

Recently, a refinement of the structure of amesite has appeared (Hall and Bailey, 1979). Amesite is an excellent structure for the purpose of studying the ILB because extensive substitution of both tetrahedral and octahedral sites occurs and the substitutions are highly ordered. These features allow one to examine three aspects of the structure: (1) OH orientations, (2) the effect of ordered T and M sites on OH orientations, and (3) the role played by the substitutions in the ILB. The hydroxyl orientations and the ILB are treated in separate sections below.

HYDROXYL ORIENTATIONS

Hydroxyl orientations have been determined using the electrostatic energy minimization method as described elsewhere (Giese and Datta, 1973; Giese, 1979). The amesite of Hall and Bailey (1979) has a $2H_2$ structure with extensive Al substitution for Si and Mg. The observed structural formula closely approximates the ideal composition $Mg_2Al(SiAl)O_5(OH)_4$ used for the present calculations. The $2H_2$ polytype has two unique

Copyright © 1980, The Clay Minerals Society

https://doi.org/10.1346/CCMN.1980.0280201 Published online by Cambridge University Press

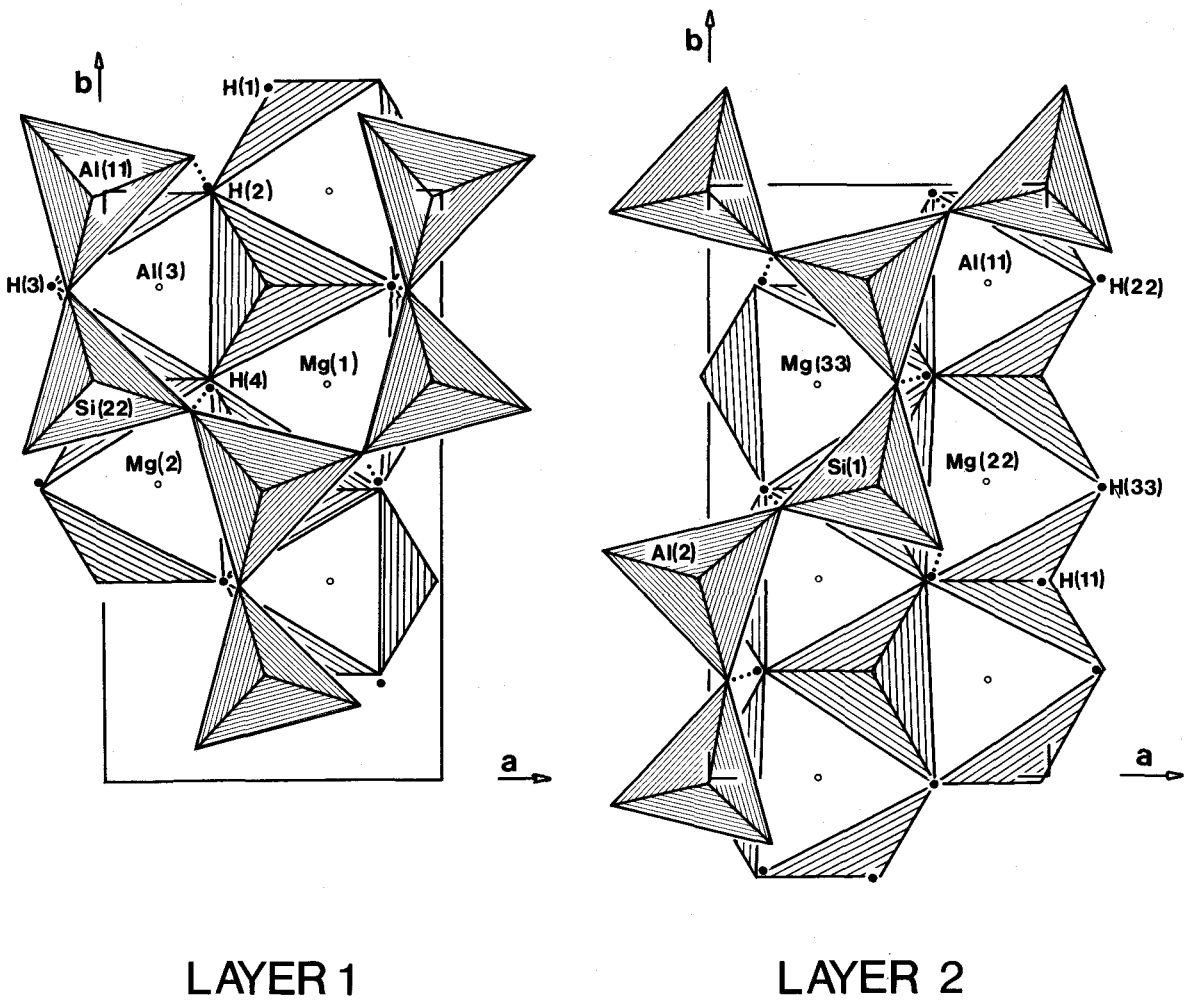


Figure 1. Projections of the amesite structure onto (001) for the two independent layers. The tetrahedral sheets are shown superimposed over the adjacent octahedral sheets. Hydrogens are indicated by solid circles and hydrogen bonds by a line of dots. The nomenclature is identical with that of Hall and Bailey (1979).

layers with a total of 8 hydroxyls. This is the largest number of hydroxyls to be refined to date by the electrostatic energy approach. To treat such a large number of variables would require lengthy computations; however two simplifying features allow a substantial reduction in computing time. First, the hydroxyls of the two layers are sufficiently far from each other that the interaction of an OH in one layer with one in an adjacent

Table 1. Hydrogen fractional positional parameters, hydroxyl orientations, and the hydrogen bonding environment for the hydroxyls of amesite.

Layer		x	y	z	ρ	O(H). . .O (Å)	H. . .O (Å)	O–H. . .O	Receptor
1	H(1)	0.492	0.170	0.096	82.4°				—
	H(2)	0.317	0.007	0.377	82.4°	2.81	1.85	172.6°	O(33)
	H(3)	0.356	0.340	0.375	88.5°	2.73	1.77	168.8°	O(44)
	H(4)	0.824	0.166	0.376	81.5°	2.83	1.86	170.5°	O(55)
2	H(11)	−0.011	0.329	0.595	82.3°				—
	H(22)	0.668	0.341	0.875	82.3°	2.76	1.79	171.7°	O(5)
	H(33)	0.671	−0.013	0.877	88.5°	2.80	1.85	167.0°	O(4)
	H(44)	0.153	0.180	0.876	83.0°	2.83	1.86	171.5°	O(3)

https://doi.org/10.1346/CCMN.1980.0280201 Published online by Cambridge University Press

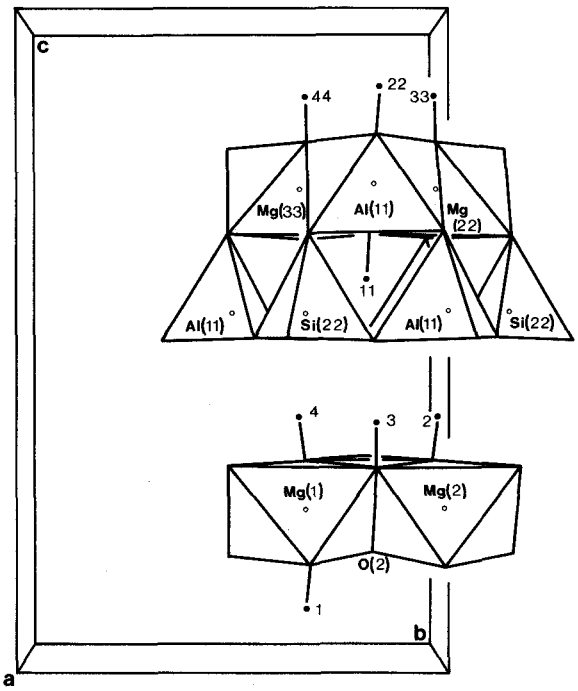


Figure 2. A perspective view of part of the amesite structure looking down the *a* axis.

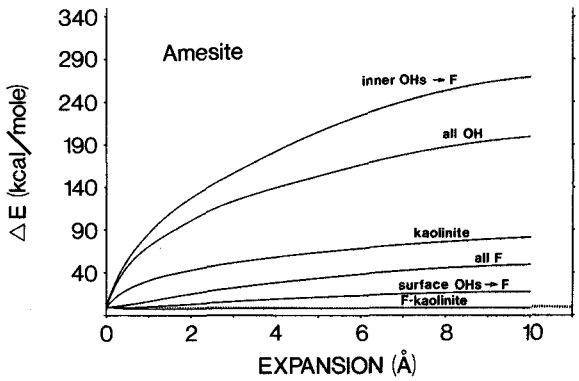


Figure 3. The change in potential energy of amesite and kaolinite as a function of the increase in the interlayer space. The horizontal dashed line represents the zero value of energy change.

layer can be neglected. Second, the inner hydroxyl, in practice, has little effect on and in turn is little affected by the other three surface hydroxyls of its layer. Therefore, amesite can be treated as two separate problems of 4 OHs each and of these 4, only 3 interact to the extent that they need be refined in an iterative manner. The starting model had all 8 OHs oriented normal to (001) and directed away from the plane containing the coordinating M sites. The inner hydroxyl was located first and held fixed in its minimum energy orientation while the 3 surface hydroxyls were refined. This required three cycles of refinement for each layer.

The orientations of the OHs are nearly normal to (001) as indicated by the earlier study of Wolfe and Giese (1974). Table 1 gives the fractional positional parameters of all 8 hydrogens, the angle ρ between the OH and (001), the O(H). . .O and H. . .O distances, and the O–H. . .O angle where hydrogen bonding is indicated. All of the surface hydroxyls are involved in nearly linear hydrogen bonds as will be discussed below and, as suggested by the similar H. . .O distances, to about the same degree.

Figure 1 shows the relevant parts of the structure projected onto (001); Figure 2 is a perspective view of the structure looking down the *a* axis. It is clear from the figures as well as from the ρ values in Table 1 that the deviations from perpendicularity of all the hydroxyls are small but significant. It has been shown for the kaolin-group minerals as well as for the 2:1 phyllosilicates that the factors which determine OH orientation are (1) occupancy of the M sites as well as the charges of the M cations, (2) availability of an appropriate acceptor atom, and (3) suitable placement of cations other than the coordinating M cations (Giese and Datta, 1973; Giese, 1979). The first factor determines the orientation (perpendicular) in a trioctahedral structure unless the difference in charge among the three sites is extreme. All surface hydroxyls of amesite have oxygens in the neighboring sheet which are in positions where, geometrically, hydrogen bonds can form. The inner hydroxyls, H(1) and H(11), are far from any other anions so that the possibility of hydrogen bonding does not arise. The third factor exerts little influence on the surface hydroxyl orientations in amesite.

When viewed in detail, the deviations of the hydroxyls from 90° are easily explained in terms of the previously described factors. The inner hydroxyls are the simplest since no hydrogen bonding exists. These hydroxyls lie in a large cavity surrounded by atoms distributed in a highly symmetrical arrangement, and they tend to cancel each other. Figure 1 shows that OH(1) is tilted away from the high-charge M site, Al(3), and lies close to the plane containing the shared edge of the other two M sites, Mg(1) and Mg(2). The interpretation that the asymmetry of the M site charges is the principal cause for the tilt of 7.6° is hard to resist. Examination of OH(11) in the second layer (Figure 1) shows a similar situation. The magnitude of these tilts is in very good agreement with some earlier work done on a 1M biotite with two divalent ions and one trivalent ion in the octahedral sites (Giese, unpublished).

The other hydroxyls fall into two categories; those with ρ values between approximately 81° and 83° and those with values near 90°. All 6 of these hydroxyls are involved in hydrogen bonding as is shown below. The positions of the acceptor oxygens vary and, in one

https://doi.org/10.1346/CCMN.1980.0280201 Published online by Cambridge University Press

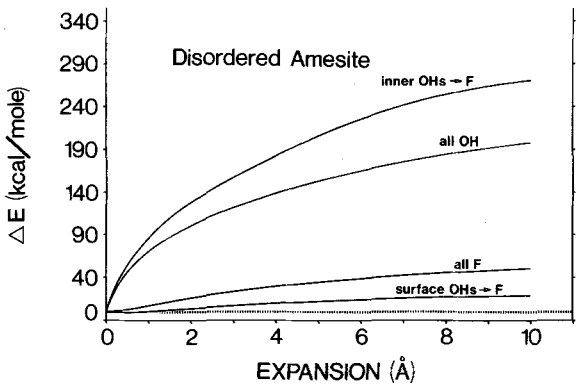


Figure 4. The change in potential energy of "disordered" amesite as a function of the increase in the interlayer space. The disordering results from assigning average cation charges to the T and M sites of the amesite structure.

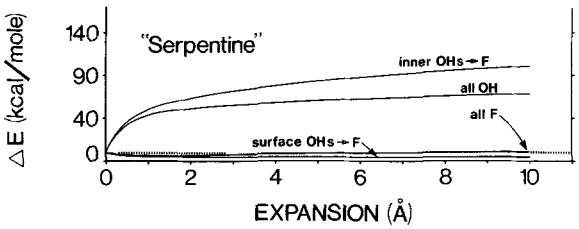


Figure 5. The change in potential energy of "serpentine" as a function of the change in the interlayer space. The "serpentine" is based on the amesite structure but with +2 charges on the M sites and +4 charges on the T sites.

group (81° to 83°), the acceptor and the coordinating Al are on opposite sides of the hydroxyl oxygen. The repulsion of the Al tends to tilt the OH away from the Al site, coinciding with the direction of closest approach of the acceptor. The acceptor atoms of the second type (near 90°), OH(3) and OH(33), are positioned over the Al containing sites as viewed in a (001) projection. The OH has the tendency to tilt toward the Al in order to shorten the H. . .O distance, but this increases the Al. . .H repulsion. The result of these conflicting forces is an OH which is more nearly perpendicular to (001) than the other OHs. The placement of the T cations in one layer over the OHs in the surface of the adjacent layer is never such that the T cations interfere markedly with the desired OH orientations. This is very different from the kaolin-group minerals where the T sites apparently strongly influence the OH orientations, particularly for hydroxyls which are not involved in the hydrogen bonding.

INTERLAYER BONDING

The ILB has been examined in a large number of phyllosilicates (Giese, 1978). The deviations of the ρ values of amesite from 90° are not sufficient to justify examining the ILB as it is influenced by ρ. Of much more interest, however, is the change in the ILB as a function of cation substitution. To study this aspect, three model structures were used: (1) a normal amesite as described in the previous section, (2) a "disordered" amesite with average charges on the T and M sites corresponding to complete long-range disorder, i.e., 3½ on the T sites and 2⅓ on the M sites, and (3) a "serpentine" of composition $Mg_3Si_2O_5(OH)_4$. All three used the structure data of amesite and differed only in the distribution of the cation charges.

For these three structures, the contribution of the individual hydroxyls to the ILB was evaluated by substituting selectively F for OH and comparing the resulting ILBs. The following situations were examined: (1) the normal structure with all hydroxyls present, (2) the inner OH only replaced by F, (3) the surface hydroxyls only replaced by F, and (4) all hydroxyls replaced by F.

The results of these calculations are summarized in Figures 3–5 in the form of changes in potential energy as a function of increase in the separation of the layers. By comparing the curves, it is clear that the ILB of amesite and "disordered" amesite are nearly identical and that both greatly exceed the ILB of the "serpentine." For each structure, the sequence of curves is the same; they vary only in vertical displacement. Surprisingly, the strongest ILB for each of the three occurs when the inner OH is replaced by F. This result is completely different from the dioctahedral structures (Giese, 1973) where the inner OH has no influence on the ILB. The difference between the two structure types is due first to the different OH orientations: vertical for the trioctahedral and in the (001) plane for the dioctahedral structures. The perpendicular orientation in amesite brings the hydrogens much closer to the atoms of the adjacent layer. Second, the stacking of the layers is also very different. Amesite has a stacking such that the inner hydroxyls are directed toward oxygens of the next layer which are shared by three octahedra and one tetrahedron. These two oxygens [O(22) for H(1) and O(2) for H(11)] lie below the surface of the hydroxyl sheet in the plane of oxygens shared by the octahedral and tetrahedral sheets. The attraction of the oxygen and hydroxyl hydrogen will be weak due to the large distance between them [6.03 Å for H(11). . .O(2)]. Counteracting this attraction is the repulsion from the three hydrogens of nearby surface hydroxyls [3.54 to 3.67 Å about H(11)], the three octahedral cations [5.30 to 5.37 Å about H(11)], and the tetrahedral cation directly opposite the inner OH [7.79 Å for H(11). . .Al(2), see Figure 2]. It is clear from the ILB curves in Figures 3–5 that the repulsion terms are much larger than the attraction. The inner OHs in amesite, therefore, weaken substantially the ILB.

Substitution of F for surface OHs also greatly weak-

https://doi.org/10.1346/CCMN.1980.0280201 Published online by Cambridge University Press

ens the ILB for amesite and "disordered" amesite indicating that they are a major, but not the only, factor in determining the ILB. Even with all the surface hydroxyls replaced by F, there remains a substantial attraction between the layers due to the dipolar layer charge, (−) on the T sites and (+) on the M sites.

When all hydroxyls are replaced by F, the ILB is increased compared to the situation in which the surface OHs only are replaced. This is due to the destabilization of the ILB by the inner OHs referred to above.

Figure 3 shows, in addition to the curves for amesite, ILB curves for kaolinite and F-kaolinite, that is, kaolinite with all of the hydroxyls replaced by F. In general, the substituted trioctahedral structures have a stronger ILB than kaolinite. This increase means that the exchange of F for surface OHs which results in a near zero ILB for kaolinite has a much less dramatic effect on the trioctahedral structures, and that these structures retain significant interlayer bonding. On the other hand, the kaolinite and "serpentine" curves are very similar.

CONCLUSION

The hydroxyl orientations for the $2H_2$ polytype of amesite determined by minimizing the electrostatic potential energy are nearly perpendicular to (001). The ordered substitution of Al for Mg in the M sites results in tilts away from perpendicularity of approximately 7.6°. Superimposed upon these tilts is the influence of the receptor oxygens in the adjacent layer. Placement of these oxygens perturbs some of the OH orientations by several degrees.

In amesite, the ILB is due to the dipolar charge of the 1:1 layer resulting from Al substitution in T and M sites as well as the interlayer hydrogen bonding. The latter predominates over the former. The inner hydroxyls contribute in a negative sense to the ILB, mainly because there seems to be repulsion between the inner-hydroxyl hydrogen of one layer and the surface-hydroxyl hydrogens of the adjacent layer, as well as between the M cations of the adjacent layer. Selective replacement of these hydroxyls by halide would substantially increase the ILB.

ACKNOWLEDGMENTS

Professor S. W. Bailey kindly supplied the author with a preprint of the paper on the structure of amesite. Financial support was provided by the National Science Foundation through grant EAR7804561.

REFERENCES

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

Giese, R. F. (1975) Interlayer bonding in talc and pyrophyllite: *Clays & Clay Minerals* **23,** 436–438.

Giese, R. F. (1978) The electrostatic interlayer forces of layer silicate minerals: *Clays & Clay Minerals* **26,** 51–57.

Giese, R. F. (1979) Hydroxyl orientations in 2:1 phyllosilicates: *Clays & Clay Minerals* **27,** 213–223.

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

Hall, S. H. and Bailey, S. W. (1979) Cation ordering pattern in amesite: *Clays & Clay Minerals* **27,** 241–247.

Wolfe, R. and Giese, R. F. (1974) Hydroxyl orientation and interlayer bonding in trioctahedral 1:1 phyllosilicates: Program and Abstracts, 23rd Clay Minerals Conf., Cleveland, Ohio, p. 66.

(Received 30 October 1979; accepted 4 December 1979)

Резюме—Определялись ориентации гидроксила в $2H_2$ политипном аиезите, $Mg_2Al(SiAl)O_5(OH)_4$, с помощью минимизации электростатической потенциальной энергии как функции ориентации OH. Углы, ρ, между гидроксилами и (001) изменяются в пределах 81,5 и 88,8°. Все поверхностные гидроксилы формируют водородные связи с кислородами примыкающего слоя. OH имеет тенденцию отклоняться от выше заряженных ионов Al^{VI}, и разброс величин ρ происходит в результате изменений в расположении рецепторных кислородов. Внутренние гидроксилы заметно ослабляют межслойные связи. Замещение Al в местах T и M создает биполярный слойный заряд и образующееся в результате этого притяжение слоев включает существенную часть межслойных связей. $2H_2$ политипный амезит имеет значительные межслойные связи даже со всеми поверхностными гидроксилами, замещенными флюоритом. Другая картина наблюдается для состава $Mg_3Si_2O_5(OH)_4$, где подобная замена OH на F уничтожает все межслойные связи как в каолините. [N. R.]

https://doi.org/10.1346/CCMN.1980.0280201 Published online by Cambridge University Press

Resümee—Die Hydroxyl-Orientierungen des $2H_2$-Polytyp von Amesit, $Mg_2Al(SiAl)O_5(OH)_4$, wurden durch Minimierung der elektrostatischen Potentialenergie als einer Funktion der OH-Orientierung bestimmt. Die Winkel, ρ, zwischen den Hydroxylen und (001) variieren zwischen 81,5° und 88,8°. Alle Oberflächen-Hydroxyle bilden mit der benachbarten Silikatschicht Wasserstoffbrücken. Die OHs tendieren dazu, sich von den höher geladenen Al^{VI}-Ionen wegzuneigen und die Streuung der ρ-Werte beruht auf den Unterschieden in der Lage der Rezeptorsauerstoffe. Die inneren Hydroxyle schwächen deutlich die Zwischenschichtbindung. Die Substitution von Al auf den T- und M-Plätzen verursacht eine dipolare Schichtladung. Die daraus resultierende Anziehung zwischen den Lagen bildet einen wichtigen Beitrag zur Zwischenschichtbindung. Der $2H_2$-Polytyp von Amesit hat eine beträchtliche Zwischenschichtbindung selbst dann, wenn alle Oberflächenhydroxyle durch Fluor ersetzt sind. Das gilt nicht für eine Zusammensetzung von $Mg_3Si_2O_5(OH)_4$, wo eine ähnliche Substitution von OH durch F jegliche Zwischenschichtbindung zerstört, genauso wie es bei Kaolinit der Fall ist. [U.W.]

Résumé—Les orientations hydroxyles du polytype $2H_2$ d'amésite, $Mg_2Al(SiAl)O_5(OH)_4$, ont été déterminées en minimisant l'énergie potentielle électrostatique en fonction de l'orientation d'OH. Les angles ρ compris entre les hydroxyles et (001) varient entre 81,5° et 88,8°. Tous les hydroxyles de surface forment des liens d'hydrogène avec les oxygènes de la couche adjacente. Les OH tendent à pencher à l'écart des ions Al^{VI} plus fortement chargés, et l'étendue des valeurs de ρ est due aux variations dans les positions des oxygènes récepteurs. Les hydroxyles intérieurs affaiblissent remarquablement les liens intercouches. La substitution d'Al dans les sites M et T crée une charge de couche dipolaire et l'attraction résultante entre les couches forme une partie importante des liens intercouche. Le polytype $2H_2$ d'amésite à des liens intercouches substantiels, même avec tous les hydroxyles de surface remplacés par la fluorine. Ceci n'est pas vrai pour une composition de $Mg_3Si_2O_5(OH)_4$ où une substitution semblable de F à OH détruit tous les liens intercouches comme dans la kaolinite. [D.J.]

https://doi.org/10.1346/CCMN.1980.0280201 Published online by Cambridge University Press