*Clays and Clay Minerals*, Vol. 25, pp. 102–104. Pergamon Press 1977. Printed in Great Britain

# THE INFLUENCE OF HYDROXYL ORIENTATION, STACKING SEQUENCE, AND IONIC SUBSTITUTIONS ON THE INTERLAYER BONDING OF MICAS

R. F. GIESE, JR.

Department of Geological Sciences, State University of New York at Buffalo
4240 Ridge Lea Road, Amherst, NY 14226, U.S.A. and
Wave Propagation Branch, Terrestrial Sciences Laboratory, Air Force Cambridge
Research Laboratories, Hanscom Air Force Base, Bedford, MA 01731, U.S.A.

(*Received* 22 *December* 1975; *and in final form* 21 *November* 1976)

**Abstract**—Hydroxyl orientation has a major influence on the strength of the ionic interlayer bonding in micas because of the strong repulsion between the hydrogen and the interlayer cation (IC). In order to determine if other factors also influence the magnitude of the interlayer bond energy, the effect due to the varying H–IC distance, as one finds, for example, between a dioctahedral and a trioctahedral mica, must be removed. This can be done by calculating the bond energy as a function of the H–IC distance; a plot of which is a smooth curve with a minimum energy for the minimum H–IC distance. If there are no other factors which substantially contribute to the interlayer bonding energy, such curves for all micas should be superimposed. If, however, the curves are not superimposed but fall into groups with common attributes (stacking sequence, ionic substitutions, etc.) the energy separations between groups of curves indicate the influence of these other factors.

The results of such calculations for four dioctahedral micas ($2M_1$ muscovite, 3T muscovite, and two 1M muscovites) and four trioctahedral micas ($2M_1$ biotite, 1M phlogopite, $2M_2$ lepidolite and a 1M MgIV mica) indicate that these curves are at higher energy for dioctahedral than for trioctahedral micas and this energy increase is due to the filling of the octahedral sites. The dioctahedral micas are arranged in terms of energy as $1M \geq 3T \gg 2M_1$ while the order for the trioctahedral micas is $1M \geq 2M_1 \cong 2M_2$. In addition, the calculated energies suggest that the distribution of the layer charge between the octahedral and tetrahedral sheets affects the strength of the interlayer bond such that the greater the charge on the octahedral sheet, the stronger the interlayer bond.

## INTRODUCTION

Since the interlayer bonding of micas arises principally from the electrostatic attraction between the interlayer cation and the layer charge, one might expect that all micas with the same charge would have identical bonding energies. Apparently, this is not the case, as shown by the very different interlayer cation exchange properties of muscovite and phlogopite. The difference between these two micas has been explained in terms of the hydroxyl orientations which, in a trioctahedral mica, results in a much shorter H–IC distance and thus a greater repulsion (weaker interlayer bond) between the silicate layer and the potassium (Giese, 1975a). Other factors also may be important as indicated by the calculated bond energies for talc (4.1 kcal/mole) and pyrophyllite (6.5 kcal/mole) which do not have layer charges or interlayer cations (Giese, 1975b). These might include the nature of the layer stacking (polytype), the distribution of the layer charge between the tetrahedral and octahedral sheets, the number of vacant octahedral sites (with dioctahedral and trioctahedral micas being the extremes) and structural distortion such as tetrahedral rotation.

## METHOD

The procedure used for calculating the interlayer ionic bond strengths for sheet silicates has been described elsewhere (Giese, 1974). However, it is not very useful to compare the bond strengths calculated in this manner for a dioctahedral and a trioctahedral mica because the difference in energies is due primarily to the different hydroxyl orientations, as already mentioned. A more useful comparison would be between two micas which have identical hydroxyl orientations. A difference in interlayer bond strength for these must be due to factors other than the repulsion between the interlayer cation and the hydroxyl hydrogen. In the case of dioctahedral and trioctahedral micas, this means that one cannot use the real OH orientations but theoretical ones.

In the IM micas (space group C2/m) the hydroxyl group lies on a mirror plane which passes between the M2 sites and bisects the M1 site. The hydrogen must lie on a circle centered on the hydroxyl oxygen with a fixed radius (assumed to be 0.97 Å). With these restrictions, the minimum H–IC distance for all micas will be about 3 Å. By rotating the OH in either direction away from the minimum in increments of 10° one can calculate the interlayer bond energy as a function of the H–IC distance. A rotation of 90° in either direction corresponds to an H–IC distance of about 4.5 Å and this value was chosen as the maximum separation. For micas which do not have such a symmetry plane, the same general orientation has been used with a pseudo-mirror plane passing through the hydroxyl oxygen, the M1 site and the



https://doi.org/10.1346/CCMN.1977.0250205 Published online by Cambridge University Press

interlayer cation. Plotting the interlayer bond energy vs the OH orientation (or, as done here, the H–IC distance) will yield a smooth curve with the minimum energy corresponding to the orientation with minimum H–IC distance. This curve is characteristic of the mica and a comparison of these curves for several micas is independent of the hydroxyl orientation. By examining a number of different mica structures with various stacking sequences, layer charge distribution and structural distortions, one can begin to relate these factors to the interlayer bonding.

## CALCULATIONS

The calculations presuppose an accurately refined crystal structure including the distribution of cations among the available sites. In order to simplify the interpretation of the resulting energies, only micas with potassium as the interlayer cation were used. The calculations assumed full ionic charges and in cases of ionic substitution, the electrostatic charge assigned to a cation was the weighted average of the various ions occupying the site. For each structure except one, a series of approximately 25 different hydroxyl orientations with maximum K–H distances of approximately 4.5 Å was used to compute the interlayer bond strength. The computing time for the 3T muscovite structure was sufficiently long that only 11 orientations were used. The crystal structures are listed in Table 1. All are accurate, single crystal X-ray or neutron diffraction refinements except 1M muscovite which was included in spite of the obvious unreliability of the refinement because it is the only available dioctahedral structure for the polytype. As a check on the results of the 1M muscovite calculations, an ideal structure was constructed using the DLS procedure (Villiger, 1969), as described elsewhere (Giese, 1975c).

## RESULTS AND DISCUSSIONS

The interlayer bond strengths are plotted in Figure 1 against the K–H distance. For all of the structures, as expected, the minimum K–H distances (OH normal or nearly so to (001)) corresponds to the minimum bond strength and the energy increases as the

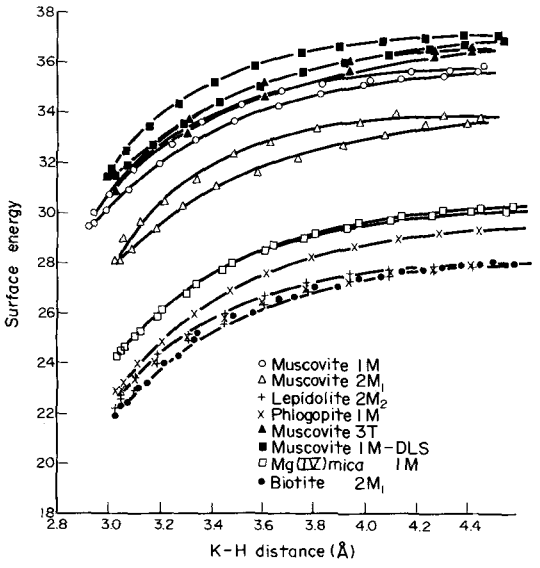



Figure 1. A plot of the surface energies (kcal/mole) for eight di- and trioctahedral micas vs the distance between the interlayer cation and the hydroxyl hydrogen.

K–H distance. All of the curves have the same shape and fall into two groups separated by approximately 4 kcal/mole. The higher energy group contains only dioctahedral micas and the lower group contains only trioctahedral micas. This agrees with the relative energies of talc and pyrophyllite and, therefore, is almost certainly true for all 2:1 layer silicates.

The interlayer bond energies for $2M_1$ muscovite and 1M phlogopite are 32.2 and 22.4 kcal/mole respectively (Giese, 1975a). As mentioned before, the difference between these two values, 9.8 kcal/mole, is the result of their very different hydroxyl orientations and possibly other factors. Figure 1 indicates that the vertical separation of the curves for these two micas is approximately 5 kcal/mole for all OH orientations. In view of the fact that all dioctahedral micas are at higher energies than the trioctahedral micas, it is reasonable to conclude that this energy is due to the manner in which the octahedral sites are occupied. The contribution to the 9.8 kcal/mole due to the different OH orientations can be estimated independently from the difference in bonding energy of

Table 1. The polytypes, tetrahedral and octahedral site charges and tetrahedral rotation angles (alpha) for the micas used in this study

| Mica | Polytype | Alpha | Charge | | Reference |
|---|---|---|---|---|---|
| | | | Tetrahedral | Octahedral | |
| Muscovite | 1M | 7.9 | 15.00 | 6.00 | Giese (1975c) |
| Muscovite | 1M | 7.9 | 15.00 | 6.00 | Soboleva *et al.* (1969) |
| Muscovite | 2M | 11.4 | 15.02 | 5.98 | Güven (1971) |
| Muscovite | 3T | 11.8 | 15.11 | 5.89 | Güven and Burnham (1967) |
| Biotite | 2M | 7.5 | 15.00 | 6.00 | Takeda and Ross (1974) |
| Phlogopite | 1M | 1.5 | 15.00 | 6.00 | Hazen and Burnham (1973) |
| Mg (IV) mica | 1M | 7.1 | 15.32 | 5.68 | Tateyama *et al.* (1974) |
| Lepidolite | 2M | 6.5 | 15.36 | 5.64 | Sartori *et al.* (1973) |

https://doi.org/10.1346/CCMN.1977.0250205 Published online by Cambridge University Press

a fluor- and a hydroxy-phlogopite. The sum of this energy, 5.2 kcal/mole (Giese, 1975a), and the 5 kcal/mole from Figure 1 is in good agreement with the total value of 9.8 kcal/mole. It is remarkable to observe that the occupancy of the octahedral sites plays as large a role as the OH orientation even though the latter is very much closer to the interlayer cation. This suggests that the distribution of the layer charge among the octahedral and tetrahedral sites may be very important in determining the expandability of phyllosilicates such as the smectites and vermiculite.

The differences between the micas in each of the two groups in Figure 1 are much smaller than between the groups. This, plus the fact that there are so few micas of each kind in the two groups, makes it more difficult to draw conclusions about the origin of the observed energy differences. Therefore, the following discussion should be considered to be tentative. In both groups, the 1M polytype has the largest or nearly the largest energy while the $2M_1$ and $2M_2$ (for trioctahedral micas) polytypes have the smallest energies. The unusual $Mg^{IV}$ mica with the layer charge distributed among both the tetrahedral and octahedral sheets has the largest energy of the trioctahedral micas, as does the 3T muscovite among the dioctahedral micas. The implication is that burying the (−) layer charge partly in the octahedral sheet increases the strength of the interlayer bonding. The relation between the site of the negative layer charge and the strength of the interlayer bonding is surprising. One would expect that separating the interlayer cation and the site of the layer charge would weaken the electrostatic attraction between them. A possible complicating factor is that the change in layer charge distribution is due to ionic substitution which also changes the dimensions and interionic distances of the tetrahedra and octahedra. These dimensional changes may have a large influence on the interlayer bond energy and may in fact be more important than the change in the layer charge distribution.

The data presented here do not allow one to estimate the influence of structural distortions of the silicate layer, such as tetrahedral rotation, because of the small number of structures involved and, in the case of tetrahedral rotation, the small variation in $\alpha$ in the structures studied.

## CONCLUSIONS

Interlaying bond strengths have been calculated for four dioctahedral and four trioctahedral micas for a variety of OH orientations with H–IC distances between 3.0 and 4.5 Å. For each mica the energies form a simple curve with the smallest energy occurring at the shortest K–H distance when plotted against the K–H distance. For the micas, the curves lie at higher energies for the dioctahedral micas in agreement with previous work on talc and pyrophyllite. The energy relations resulting from differences in stacking sequence are less certain because of the small number of samples but the general relations are $1M \geq 3T \gg 2M_1$ for the dioctahedral and $1M \geq 2M_1, 2M_2$ for the trioctahedral micas. The distribution of layer charge between the tetrahedral and octahedral sheets also seems to affect the strength of the interlayer bonding; the larger the tetrahedral (−) charge, the weaker the interlayer bonding.

*Acknowledgements*—Part of this work was carried out while the author held an NRC Resident Research Associateship at the Air Force Cambridge Research Laboratories. Financial support was also provided by the AFCRL through Contract F19628-73-C-0030.

## REFERENCES

Giese, R. F. (1974) Surface energy calculations for muscovite: *Nature* **248,** 580.

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

Giese, R. F. (1975b) Interlayer bonding in talc and pyrophyllite: *Clays & Clay Minerals* **23,** 165.

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

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

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

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

Rothbauer, R. (1971) Untersuchung eines $2M_1$ Muskovits mit Neutronenstrahlen: *Neues Jahrb. Mineral. Monatsh.* **4,** 143.

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

Soboleva, S. V. and Zvyagin, B. B. (1969) Crystal structure of dioctahedral Al-mica 1M: *Soviet Physics—Crystallogr.* **13,** 516.

Takeda, H. and Ross, M. (1974) Dissimilarities in the crystal structures of 1M and $2M_1$ biotite polytypes co-existing in a rhyodacite lava flow: *GSA Ann. Meeting,* Miami Beach.

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

https://doi.org/10.1346/CCMN.1977.0250205 Published online by Cambridge University Press