

## Interlayer bonding in I Ib chlorite

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### Abstract

The interlayer bond energy of a I Ib-4 chlorite has been calculated as a function of layer charge, the site of the charge and the selective replacement of hydroxyl groups by fluoride ions. Long hydrogen bonds between the hydroxide sheet and the adjacent oxygens are strong and by themselves sufficient to create a stable structure. Coupled substitutions giving the 2:1 layer a negative charge and the hydroxide sheet a positive charge increase substantially the interlayer bond energy.

### Introduction

For quite some time there has been interest in the nature of the interlayer bonding in layer silicates and how the bonding relates to interlamellar expansion, cation exchange and weathering. Numerous qualitative explanations have been proposed to explain the observed variations in expansion and weathering characteristics. The most common explanation is based on the total layer charge resulting from ionic substitution in the various structural sites of the layer (Brindley, 1966). The quantitative estimation of the interlayer bond energies (ILBE) began with a study of the kaolin minerals (Giese, 1973) and has been extended to the neutral charge structures, talc and pyrophyllite (Giese, 1975a), and more recently to a large number of silicate and non-silicate layer structure materials (Giese, 1978). The approach to calculating the ILBE is based on an examination of the potential energy, in the ionic formulation, as a function of the interlayer separation which is treated as a variable. Giese (1980) found that the relative energies needed for a given separation of the layers, particularly for small changes in the vicinity of the equilibrium separation, were different for different types of layer

structure. The differences between groups of phyllosilicates were particularly evident for talc and pyrophyllite (zero layer charge) on one hand and the presumably more strongly bonded micas (layer charge of  $-1$ ). For very small increases in separation, talc and pyrophyllite required more energy than the micas. This observation correlates better with the observed expansion properties of these minerals than does the layer charge.

At the time that this work was done, an attempt was made to include as many diverse layer structures as possible in order to give a clearer idea of the influence on the ILBE of such factors as layer charge, stacking type, structural deformations and the nature of the layer itself. The chlorites were omitted from the study because at that time a structure refinement of a chlorite which included the hydrogen positions was not available. The hydrogens are large contributors to the ILBE as seen, for example, in the kaolins (Giese, 1973) and amesite (Giese, 1980). The nonhydrogen structures of several chlorites were known, but to determine the OH orientations from electrostatic energy calculations was considered to be too large a task. Since then two studies have appeared which describe refinements of a I Ib-4 chlorite including the hydrogen positions (Phillips *et al.*, 1980; Joswig *et al.*, 1980).

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It has been assumed that a positively charged interlayer octahedral sheet is necessary in chlorites for there to be a substantial ILBE (Droste *et al.*, 1962; Bailey, 1966, 1975). In this view, the charged hydroxide sheet plays the same role as the positively charged interlayer cations in micas. The chlorites are more complex because the OH's forming the surfaces of the hydroxide sheet are available for the formation of long hydrogen bonds. If the hydrogen bonds indeed are strong, a positive charge on the hydroxide sheet may not be necessary for stability of the structure. Variations in ionic substitution and hence layer charge in the hydroxide sheet may account for the observed differences in the physical and chemical properties of variously substituted chlorites.

To explore the role of the hydrogen bonding and the layer charge on the various parts of the chlorite structure, we have undertaken a series of calculations of the ILBE as a function of 1) the positive charge on the hydroxide sheet, 2) the crystallographic site of this charge and 3) the substitution of a nonpolar entity such as F for the OH groups. These calculations also give us some means of comparing chlorites with the other layer structures which have already been studied.

The calculations used the IIB-4 chlorite structure of Phillips *et al.* (1980). In this structure the inner hydroxyl of the 2 : 1 layer is OH(1) and the hydroxyls of the hydroxide sheet are OH(2), OH(3) and OH(4). The octahedral sites are M(1) and M(2) in the 2 : 1 layer and M(3) and M(4) in the hydroxide sheet. As a reference point, the structure with neutral charged layers (both 2 : 1 and hydroxide) has +2 species in all the M sites. The refinements of Phillips *et al.* and Joswig *et al.* agree that the +3 species preferentially go into M(4). Substitution of a +3 for a +2 ion in any of the M sites is balanced by Al for Si substitution in the T sites. Our model for this replaces the +4 charge on the T sites with a charge of +3.75 representing a disordered substitution. Our method of calculation is described in detail elsewhere (Giese, 1974) and is based on a modified version of the computer program of Baur (1965). The potential energy of the crystal structure is first computed for the normal structure and compared with the energies for related structures which contain the identical interatomic distances and angles within the silicate layer but an increased separation between the layers. This process mimics the macroscopic events which take place when a phyllosilicate is cleaved. By definition, the differ-

ence between the equilibrium energy and that for infinitely separated layers is the surface energy. In practice, separation of the silicate layers by distances varying between 3 and 10 Å often gives energies which approach an asymptotic value (equivalent to an infinite separation). We varied the interlayer separations from 0.01 Å to as much as 100 Å. The difference between the equilibrium structure and one which has been expanded as described above is the ILBE for the distance in question. The structure was split parallel to (001) with the plane passing between the hydroxyls for the hydroxide sheet, H(2), H(3) and H(4) in the notation of Phillips *et al.* (1980), and the adjacent oxygens of the 2 : 1 layer, O(2) and O(4). The effects of a positive charge on the hydroxide sheet and of the hydrogen bonding on the ILBE were examined by carrying out the following sets of calculations of energy as a function of changes of separation; 1) neutral layers, 2) trivalent ions in M(4) and 3) trivalent ions in M(1). Next we examined the effects of the hydrogen ions by replacing individual hydroxyl groups with a single negative (-1) ion on the oxygen sites (equivalent to a fluoride ion) for both neutral structures and those with trivalent cations in M(4). All calculations assumed full ionization for the atoms.

The magnitude of the ILBE has been shown to be strongly influenced by the net charge on each layer. Even for phyllosilicates such as the micas which have a non-zero layer charge, a net charge of zero can still exist if the interlayer cations are distributed in a regular and equal manner on each of the layer surfaces as the layers are separated (Giese, 1978). For such distributions of the interlayer cations and for structures with a truly neutral layer charge (talc and pyrophyllite), the asymptotic energy upon separation is reached for small separations, on the order of 7 Å. This is similar to what has been observed for the polar layer structures, kaolinite and cronstedtite (Giese, 1978) and for amesite (Giese, 1980). The bulk of the calculations were finished before the appearance of the refinement of a similar chlorite by Joswig *et al.* (1980). Their hydrogen positions determined from the neutron diffraction data are very similar to those determined from X-ray diffraction by Phillips *et al.*

### Results and discussion

The results of the calculations are summarized in Figures 1-3 in the form of log-log plots of the change in potential energy referred to the energy of the equilibrium structure as a function of the in-

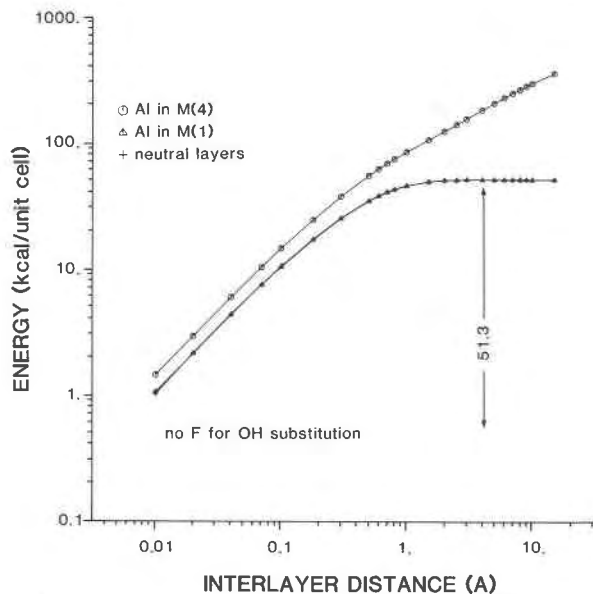


Fig. 1. A log-log plot of the change in the electrostatic energy as a function of the increase in interlayer separation for a IIB-4 chlorite with various cation substitutions. All hydroxyls are present.

crease in the interlayer separation. Figure 1 shows the ILBE curves for the neutral layer cases of no substitution and a trivalent cation in M(1). These are identical for separations greater than  $0.05\text{\AA}$  and give a total ILBE of  $51.3\text{ kcal/mole}$ . This value is comparable with ILBE's already calculated for di- and trioctahedral micas and demonstrates the importance of the interlayer hydrogen bonds in the chlorite structure. Placement of the trivalent cation in M(4) rather than M(1), balanced by tetrahedral substitutions, leads to charged layers and dramatically increases the ILBE to values near those found for margarite and cronstedtite (Giese, 1978). Substantial stabilization of the structure would be expected by locating trivalent cations in the M(4) site. The same conclusion may be reached by calculating the total electrostatic energy of unexpanded structures with a +3 charge, one site at a time, in M(1) through M(4). In this manner, one finds that the order of stability of trivalent cations follows the order  $M(4) > M(3) \gg M(1) > M(2)$ . This result agrees with the empirical observation that IIB chlorites tend to have trivalent ions concentrated in the M(4) sites (Steinfink, 1958; Phillips *et al.*, 1980; Joswig *et al.*, 1980).

Figure 2 shows the results of the selective F for OH substitution for neutral layer chlorites. These

potential energy curves illustrate the contribution each OH group makes to the ILBE (Giese, 1973). As one would expect (compare Fig. 1), replacing OH(1) causes little change in the ILBE ( $51.3$  vs.  $50.6\text{ kcal/unit cell}$ ) and only slightly increases the short-range interlayer energies. The hydroxyls of the hydroxide sheet play a larger role in the interlayer bonding as shown by the greater decreases in the ILBE when they are substituted by F. OH(4) contributes about half the total ILBE for the neutral layer case. Replacing all hydroxyl groups with fluorine in the neutral layer case results in a net electrostatic repulsion between the layers. This latter observation is in complete agreement with the results of similar calculations for the kaolin minerals (Giese, 1973) and for amesite (Giese, 1980).

The effects of the F for OH substitution in chlorites with a trivalent cation in the M(4) site are much less pronounced (Fig. 3) than for the neutral layer case. However, the short-range energies are significantly reduced by the substitution. Selective replacement of either OH(2), OH(3) or OH(4) has little effect, even on a short-range basis, but complete replacement (hydroxyls 1 through 4) or the replacement of the hydroxide hydroxyls (2 through 4) reduces the short-range attraction. A chlorite with trivalent cations in M(4) and all hydroxide hydroxyls replaced by fluorine actually has the smallest short-range attraction of all the arrangements studied with the exception of the neutral F-chlorite which has a repulsion between layers. Only at separations greater than about  $0.8\text{\AA}$  does the

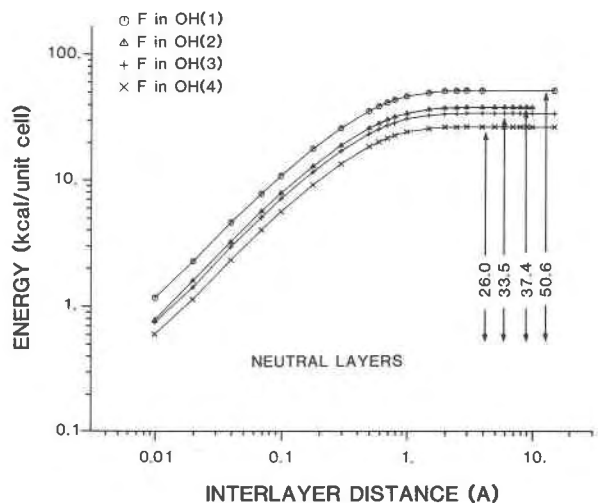


Fig. 2. A plot similar to Fig. 1 for neutral layer structures with differing F for OH substitutions.

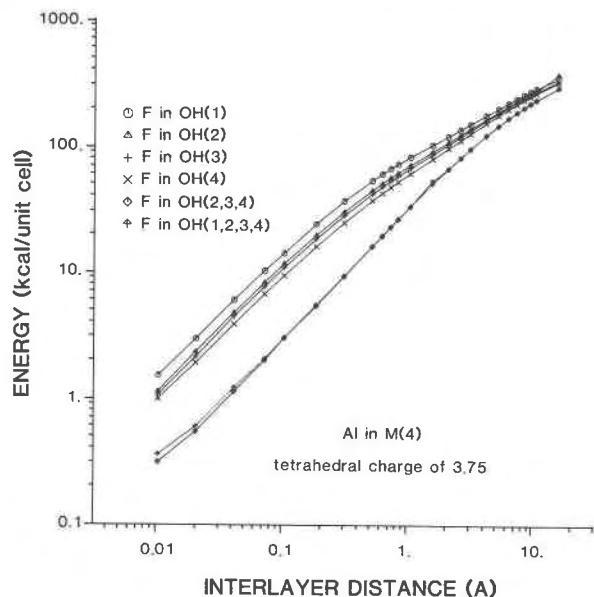


Fig. 3. A plot similar to Fig. 1 for chlorites with charged 2:1 layers and hydroxide sheets and various F for OH substitutions.

effect of the attracting charged layers begin to dominate the ILBE. It should be noted that the energies calculated for very small expansions of the equilibrium structure do not represent the real energies which exist in the mineral because the contributions of repulsion and van der Waals energies have not been included. Recent work on talc and pyrophyllite (Alcover and Giese, 1980) indicate that these contributions are important. This does not prevent one from using the electrostatic calculations only in a comparative manner rather than as a measure of absolute energies. At separations of 3–5 Å and larger, the van der Waals and repulsion terms are negligible.

### Conclusions

From the results of the calculations it is apparent that a positive charge on the hydroxide sheet is not necessary for the existence of the chlorite structure. Although a charged hydroxyl sheet increases the interlayer bond strength, the ILBE of a neutral layer chlorite is substantial and is comparable with that of the micas. This suggests that a chlorite of lizardite composition, *i.e.*,  $Mg_6Si_4O_{10}(OH)_8$ , is possible. The sizeable ILBE is due to long H-bonds between the layers. As Joswig *et al.* (1980) noted, it is the hydrogen bonding which produces an angular deviation of the OH dipoles away from the normal to the layer. However, because the presence of a charged

interlayer so dramatically increases the ILBE, large changes in physical and chemical properties with small changes in the chemistry of the hydroxide sheet are to be expected. For example, significant variations in crystallinity and resistance to weathering would arise through small changes in the charge on the hydroxide sheet. It is noteworthy that of the ten chlorites examined by Phillips *et al.* (1980), the three with the highest hydroxide charge showed no streaking of the  $k \neq 3n$  reflections. However, other factors such as the mechanism of crystal growth may be more important in determining the degree of crystallinity. A low charge chlorite would be expected to weather more readily than one with a large interlayer charge. Similar arguments have been advanced to explain weathering of trioctahedral *versus* dioctahedral micas (Giese, 1975b) except that in the case of the micas the variation in the ILBE is due to OH orientation rather than a variable charge on the material between the 2:1 layers.

Giese (1978) showed that the observed expandability of a particular layer structure correlated well with the relative energies needed to expand the equilibrium structure by 0.01 Å. This criterion appears to predict expansion behavior better than the layer charge, at least within the same mineral group. For a separation of 0.01 Å, chlorite stability is ordered, beginning with the most weakly bonded, in the sequence: 1) charged hydroxide sheet with all interlayer OH's replaced by F, 2) neutral hydroxide sheet with individual OH groups replaced by F, 3) charged hydroxide sheet with individual OH's replaced by F, 4) neutral hydroxide sheet with all OH's present, 5) a charged hydroxide sheet with all OH's present.

One might expect F for OH replacement to affect the weathering and alteration of chlorites, but other factors such as octahedral composition and iron oxidation are probably equally important. It is observed that natural chlorites have negligible fluorine contents in contrast with, for example, the micas (Deer *et al.*, 1962). Our calculations suggest that, in contrast to the trioctahedral micas where F for OH substitution has a great stabilizing influence, a similar substitution in chlorites has little advantage and may result in a weakening of the ILB.

Although variations in the interlayer charge and F for OH substitution cause substantial changes in the ILBE, the bonding will seldom become weak enough to cause rapid expansion. As noted above, the total neutral-layer ILBE is close to that calculated for muscovite and phlogopite while the ILBE for the

charged hydroxide sheet is similar to the values found for margarite and cronstedtite. In addition, the short range separation energies for all of the hydroxy chlorites are comparable to the strongly bonded layer structures, Group I of Giese (1978), consisting of kaolinite, margarite and cronstedtite. However, if substantial F for OH substitution takes place or appreciable dehydroxylation of the hydroxide sheet occurs, expansion may be possible.

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