

## NOTE

### THE STABILITY OF FLUORINE ANALOGUES OF KAOLINITE

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**Key Words**—Fluoride, Fluorine, Kaolinite, Structure.

#### INTRODUCTION

Hendricks (1938) pointed out that the superposition of layers in kaolinite is such that oxygens and hydroxyls of adjacent layers are able to form long hydrogen bonds and that presumably these are responsible and necessary for the stability of the structure. This has been accepted as the fundamental requirement for the existence of any structure based on a layer similar to that of kaolinite (Brindley, 1951; Newnham, 1961). That the long hydrogen bonds lead to a strong interlayer bonding was shown independently by Cruz et al. (1972) and Giese (1973). The latter work was particularly important in that it demonstrated that substitution of F<sup>-</sup> for OH<sup>-</sup> resulted in a weak repulsion between the layers, thus proving that the interlayer attraction is due solely to the hydrogen bonds. This is quite understandable since a fluoro-kaolinite would have a zero layer charge and neutral surfaces (the OH's which are directed away from the hydroxide surface of kaolinite present a positively charged surface). However, both pyrophyllite and talc also have no layer charge as well as neutral surfaces and yet these are stable and in fact have interlayer bond energies of several kcal/mole. The possibility therefore exists that a fluorine analogue of the kaolin layer might form a stable structure but for a different mode of stacking than that found in kaolinite. This would be of some theoretical interest in further elucidating the interlayer bonding properties of phyllosilicates, but also there may be some practical use as well. By expanding kaolinite, for

example, with hydrazine, and thus exposing the inner surfaces, it might be possible to actually replace the surface hydroxyls with fluoride ions yielding a new, stable structure. This will not have the same stacking as kaolinite since that is already known to be unstable, but another type of stacking. This contribution points out the limited number of possibilities for the new stacking which should make it possible to identify such a product.

#### CALCULATIONS

The calculations follow closely those reported earlier (Wolfe and Giese, 1972). The electrostatic potential energy is calculated as a function of the translation of one kaolin layer over the adjacent one in two dimensions. The perpendicular distance between layers,  $d_{001}$ , remains unchanged during this process. The results are presented in the form of a topographic map in which the  $x$  and  $y$  coordinates of a point represent the translation of the origin of the second layer with respect to that of the first. Since we are dealing only with one-layer structures, all subsequent layers will have identical translations. The elevation on the map corresponding to each  $(x, y)$  translation represents the potential energy for that particular superposition (stacking) of layers. It was shown earlier that the stable structures based on the kaolin layer are those whose translations lie inside closed energy depressions (Wolfe and Giese, 1972) and that these translations and only these may have a net attraction (interlayer bond) between layers (Wolfe and Giese, 1974).

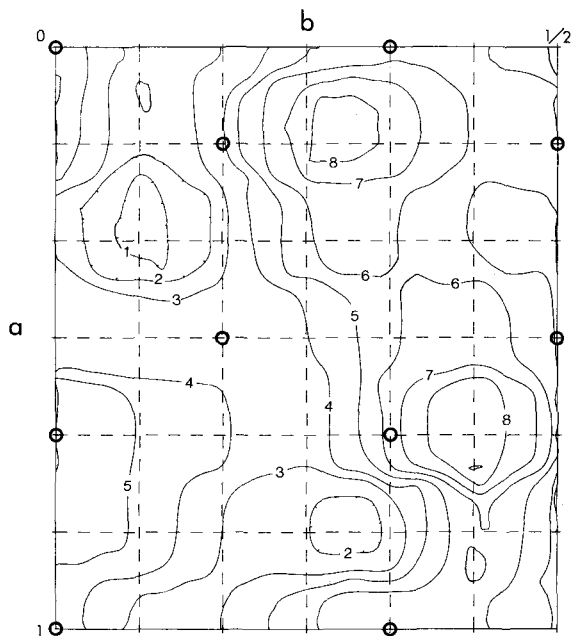


Fig. 1. Electrostatic potential energy surface for 1-layer fluoro-kaolinite. The grid represents shifts of the second layer relative to the first in units of  $a/6$  and  $b/12$  in the orthohexagonal cell. The contour interval is 1 kcal/mole.

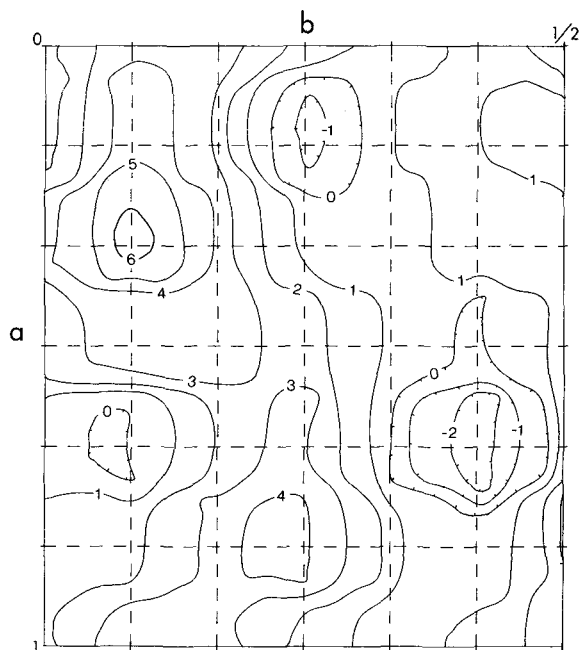


Fig. 2. Interlayer bond energies for 1-layer fluoro-kaolinite. Translations and contour interval are the same as in Figure 1.

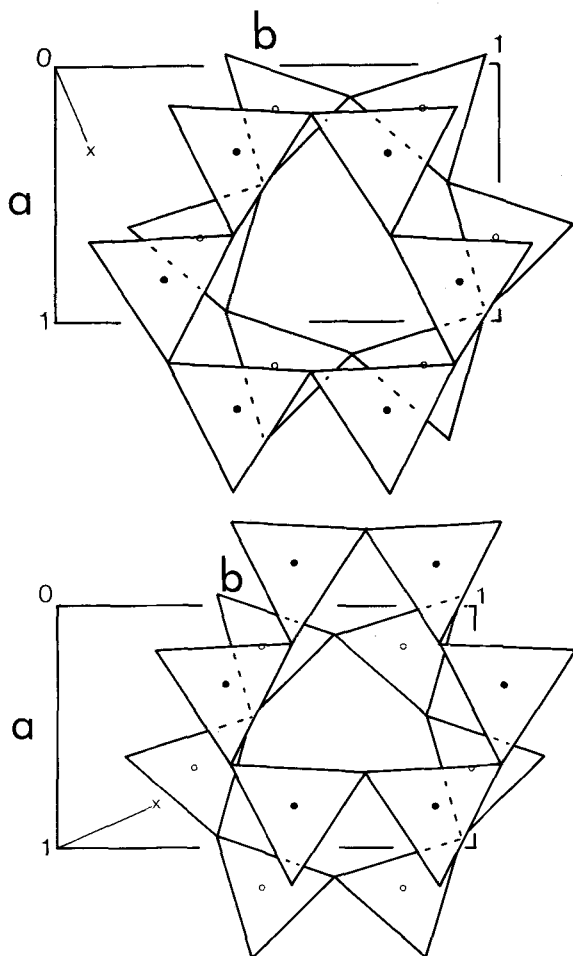


Fig. 3. Stable fluoro-kaolinite structures projected on (001). Shown are the bases of tetrahedra and octahedra in adjacent layers; open circles are Si and closed circles are Al. (a) Fluoro-kaolinite with origin of the second layer shifted by  $(a/3, b/12)$ ; (b) Fluoro-kaolinite with the second layer shifted by  $(-a/6, 3.5/12)$ .

The procedure for the fluoro-kaolinite was to take the crystal structure refined by Zvyagin (1967) and replace each of the hydroxyl oxygens with  $F^-$ . The potential energy map was computed in exactly the same way as before (Wolfe and Giese, 1972), but the interlayer bonding as a function of the translations has been done differently. Since the layers of the fluoro-kaolinite are neutral, the potential energy of the structure quickly reaches an asymptotic value as the increase in the distance between the layers exceeds  $3 \text{ \AA}$ . Therefore, the energy at a separation of  $9 \text{ \AA}$  ( $d_{001} = 16 \text{ \AA}$ ) minus the energy for the same structure with no change in the interlayer spacing ( $d_{001} = 7 \text{ \AA}$ ) is the total interlayer bond energy. It is this value which has been calculated rather than the slope of the energy versus change in interlayer distance as was done before (Giese, 1973; Wolfe and Giese, 1974).

#### RESULTS

The potential energy map (Figure 1) is based on calculations of the energy for translations in steps of  $a/6$  and  $b/12$  (indicated by dashed lines in the figure). There are two depressions;  $(a/3, b/12)$  and  $(-a/6, 3.5/12)$  with the former being somewhat deeper. The superpositions which give rise to hydrogen bonds between layers (Brindley, 1951), shown by open circles, do not coincide with either of the two depressions. The map showing interlayer bond energy (Figure 2) as a function

of the two-dimensional translations is almost exactly the same except that the topography is reversed (the convention adopted here is that a positive value indicates a net attraction between layers). The two depressions in the potential energy map have interlayer bond energies of 6.5 and 4.5 kcal/mole. These are similar to the energies for talc (4.2 kcal/mole) and pyrophyllite (6.2 kcal/mole) (Giese, 1975). The contribution of the van der Waals and repulsion energies are very difficult to assess but there seems little reason to suppose that these would be extremely different in a 2:1 structure compared to a fluorine substituted kaolinite. Therefore, the evidence presented here strongly supports the idea that the fluoro-kaolinite can exist as a stable phase.

#### DISCUSSION

Since in the fluorine analogue of kaolinite there is no possibility of an electrostatic attraction between the surface oxygens and fluorines, the interlayer bonding must result from attraction between the silicons of one layer and the  $F^-$  ions of the adjacent surface as well as the aluminum ions with the oxygen of the adjacent surface. For the two stable stackings (Figure 1) a projection of the crystal structure onto the (001) plane shows this to be correct (Figure 3). Both modes of stacking represent a compromise between the desirability of minimizing the Si...F and Al...O distances while maximizing the Si...Al distances between layers. There are many possible interlayer translations which will bring the surface fluorines and oxygens close to the cations in adjacent layers but repulsion due to Si...Si and Al...Al overlap between layers makes all but two of these unfavorable.

It is of some interest to note that in both stable superpositions, one fluorine atom is placed approximately in the middle of the ditrigonal ring of tetrahedra and thus does not participate in the interlayer bonding. Because this atom is relatively far removed from the silicon atoms, it seems to be a reasonable site for an OH group. Therefore, one could still expect these two stackings to be stable if only 2/3 of the surface hydroxyls were replaced by fluorine. In fact, as seen in Figure 3, the remaining surface OH would form a long hydrogen bond to the nearby oxygen of the adjacent surface thereby contributing to the interlayer bonding and stability of the structure.

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