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IMPLICATIONS OF HYDROXYL-OXYGEN JUXTAPOSITION IN LAYER SILICATES

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ABSTRACT

Observed (OH)—O directions in dickite and chlorite are used to formulate models for the orientation of monohydric alcohol molecules on montmorillonite surfaces. The *T*—O—*T* angle in layer silicates is related to the surface oxygen configuration and may be an important structural parameter. The free swelling of montmorillonites in water and the orientation of the hydroxyl group in muscovite are related to the clay organic complexes.

INTRODUCTION

Emerson (1957) proposed a model from which the basal spacings could be computed for methanol montmorillonite and single layer complexes. The calculations were based on the assumption that the organic molecules were oriented by directed bonds from the hydroxyl atoms of the alcohol molecules to the surface plane of oxygen atoms of the layer silicate. He suggested that two conditions must be met if an oxygen atom formed a bond with a clay surface oxygen atom; the O—H · · · O bond must be linear and, if the clay surface oxygen was already attached to two other atoms in the clay at the tetrahedral angle, then the O—H · · · O bonds would be expected to form at the remaining tetrahedral angles. In other words, the O—H · · · O bond would be oriented at 54°44′ to the normal to the silicate layer. It was suggested that the latter condition was satisfied exactly on the interlamellar surfaces of montmorillonite.

Examination of a layer silicate model reveals the basal (surface) oxygens are not bonded at the tetrahedral angle, therefore, Emerson's model cannot be entirely correct. The *T*—O—*T* (tetrahedral atom–basal oxygen-tetrahedral atom) angle is approximately 140° with tetrahedral rotations (α) equal to zero. The *T*—O—*T* angle and α are inversely related so that the theoretical maximum α ($=30°$) corresponds to the minimum *T*—O—*T* angle (equal to the tetrahedral angle). Brittle micas (Takeuchi, 1966) are notable among real crystals whose structures have been analyzed for their large α values ($\sim 20°$) and small *T*—O—*T* angles ($\sim 120°$). Most layer silicates, montmorillonites in particular (Radoslovich, 1962), are likely to show small values for α ($\sim$5–10°) and, consequently, *T*—O—*T* angles that do not closely approximate the tetrahedral angle. The apical oxygen-tetrahedral atom-basal oxygen angles closely approximate the tetrahedral angle but this angle is not directly relevant to the present discussion.

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Brindley and co-workers (Brindley and Ray, 1964; Brindley and Moll, 1965) have shown that chain molecules containing a single functional terminal group, such as hydroxyl or carboxyl, form complexes with montmorillonite with the organic molecules oriented at steep angles to the clay surfaces. Brindley and Ray have demonstrated that the basal spacings of the alcohol complexes can be related to the orientation of the organic molecules by considering the incremental spacing per carbon atom of the molecular formula. These investigators indicated that the molecular orientation suggested by their experimental data was consistent with the model proposed by Emerson. The agreement of these experimental data with a partially incorrect model suggested to us that a more acceptable model might be determined from alternative structural criteria.

RESULTS

An analysis of the (OH)—O directions in dickite provided a reasonable alternative to Emerson's model. Dickite was chosen because accurately-known atom positions were available (Newnham, 1961) and it is chemically pure which precluded the possibility that atomic substitutions, *e.g.*, aluminum for silicon, might affect the analysis. Adjacent layers are superimposed in kaolin minerals so that oxygen atoms and hydroxyl groups of contiguous layers are paired. O—H · · · O bonding has been suggested (Hendricks, 1938) as a consequence of the pairing and provides a reason for the polymorphism observed among kaolin minerals.

Pertinent computed structural data for dickite are shown in Table 1. Details concerning the calculations are given by McGuire (1968). The three independent oxygen-hydroxyl pairs are listed in column 1. Newnham's subscripts are used to designate the atoms. The angle between the (OH)—O directions and planes (called pointer planes) perpendicular to the Si—O—Si planes and including the oxygen atoms are given in column 2. All three (OH)—O lines very nearly lie in the pointer planes, the

TABLE 1. COMPUTED STRUCTURAL DATA FOR DICKITE. ATOM COORDINATES FROM NEWNHAM (1961)

Hydroxyl-oxygen pair	Angle between (OH)—O line and pointer plane[a]	Angle between (OH)—O line and *BIS*[a]	Angle between (OH)—O line and c^*
O_1—$(OH)_2$	2°	2°	15°
O_2—$(OH)_4$	7°	7°	17°
O_3—$(OH)_3$	3.5°	10°	16.5°

[a] See text for definition.

TABLE 2. COMPUTED STRUCTURAL DATA FOR CHLORITE. ATOM COORDINATES FROM LISTER AND BAILEY (1967)

Hydroxyl-oxygen pair	Angle between (OH)—O and *BIS*	Angle between (OH)—O line and c^*
O_1—$(OH)_6$	7.5°	13.5°
O_2—$(OH)_4$	10.5°	15.5°
O_3—$(OH)_5$	6.5°	16.5°

maximum deviation being 7°. (Computed angles are reported herein to the nearest half degree.) The angle between the (OH)—O directions and the lines (called *BIS* since the line bisects the Si—O—Si angle) defined by the intersection of a given Si—O—Si plane and its pointer plane is shown in column 3. The data indicate the (OH)—O directions and corresponding *BIS* directions are nearly coincident, the maximum deviation being 10°. A very regular disposition of the (OH)—O directions with respect to the normal to the (001) planes (c^*) is shown in the last column. These angles are $16 \pm 1°$.

If we assume the hydrogen atoms lie on the (OH)—O lines the data given in Table 1 indicate the hydrogen atoms are positioned very nearly as far away as possible from the two silicon atoms that are bonded to the basal oxygens. It would appear, therefore, that the (OH)—O directions can be rationalized on the basis of electrostatic considerations.

The muscovite data of Güven (1968) was analyzed in light of our results with dickite with a view toward predicting the hydroxyl orientation. The calculated direction of the line bisecting the Al—(OH)—Al angle and lying in the Al—(OH)—Al plane makes an angle of 30° with the *b*-axis projected onto the *ab* plane and an angle of 33° with c^* (away from the octahedral sites). Vedder (1964) on the basis of infrared evidence reported the OH group very nearly made an angle of 32° with the *b*-axis projected onto the *ab* plane and 74° with c^* *away* from the octahedral sites. We suggest the discrepancy between our calculations (for the angle between the OH direction and the c^* axis) and the observed angle is due to repulsion between the hydroxyl proton and the proximate potassium ion which causes the proton to take a position electrostatically balanced between the potassium and the two aluminum ions linked to the hydroxyl.

The mutual orientation of the hydroxyl planes in the brucite-like sheets and the basal oxygen planes of the talc-like layers in cholrite was analyzed (Table 2). The structural data of Lister and Bailey (1967) was used for the computations. The three (OH)—O directions lie within 10.5° of the corresponding *BIS* directions and the (OH)—O angles with

c^* are 15±1.5°. The accordance of the dickite and chlorite data indicates that the substitutions within the chlorite structure that create an electrostatic interaction between the positively-charged brucite-like sheets and the negatively-charged talc-like layers do not appreciably affect the (OH)—O directions.

DISCUSSION

Models depicting the orientation of the alcohol molecules in the long spacing complexes of Brindley and Ray consistent with an (OH)—O angle with c^* equal to 15° are shown in Figures 1 and 2. These models can be contrasted with those shown in Figures 2(b) and 2(c) in Brindley and Ray. The alcohol chain orientation is about 70° for the below-melting-point series (Fig. 1) and about 40° for the above-melting-point series (Fig. 2) very nearly the angles deduced by Brindley and Ray from their experimental data. Both models proposed by us picture alcohol molecules that are fully extended—a reasonable condition.

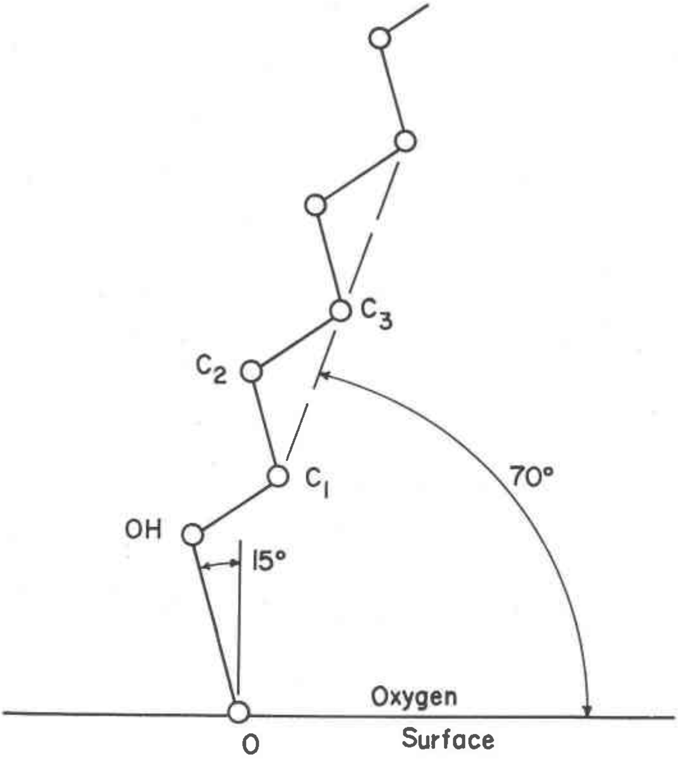

FIG. 1. Model for the below melting-point alcohol montmorillonite series of Brindley and Ray (1964).

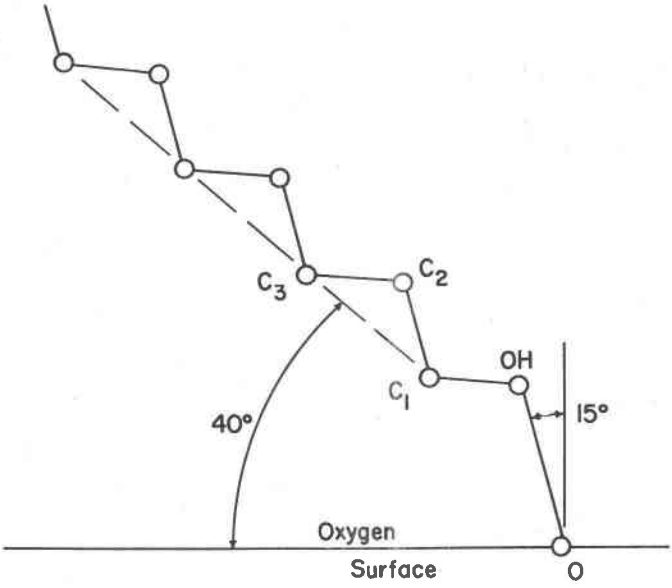

Fig. 2. Model for the above melting-point alcohol-montmorillonite series of Brindley and Ray (1964).

A model for the single layer alcohol-montmorillonite complexes (alcohol chain parallel to clay surface) consistent with the dickite-chlorite data is less satisfying and it is with some reservation that the model illustrated in Figure 3 is proposed. The basis for our reservation is that full extension of the alcohol molecules does not appear possible if we presume an angle between (OH)—O and c^* equal to 15°. The lack of full extension in our model of the alcohol molecule orientation was achieved by rotating the alcohol chain 180° about the (OH)—C_1 axis. Emerson achieved a flat-lying orientation by rotating the alcohol mol-

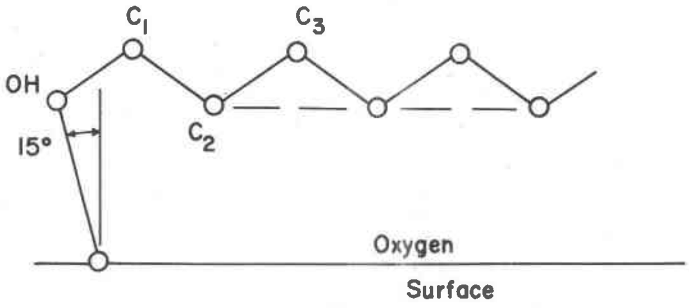

Fig. 3. Possible model for one-layer alcohol-montmorillonite complexes.

ecules 180° about their C_1—C_2 axes. Compare our Figure 3 with Emerson's model shown as Figure 2(a) in Brindley and Ray.

The relatively close approach of adjacent layers in the single layer complexes might suggest other factors would have a relatively larger influence in the clay-organic bonding scheme. Under these conditions the alcohol molecule orientation might be influenced less by (OH)—O orientation.

Although speculative two further points in partial defense of the model shown in Figure 3 may be made. (1) The proposed orientation allows exposure of the more negative end of the alcohol hydroxyl to the interlamellar space and, therefore, possibly better coordination with interlamellar cations. (2) The lack of long-spacing complexes of dihydric alcohols having terminal functional hydroxyl groups on both ends might be attributed to two (OH)—O interactions both fixed at 15° to c^*, either to the same montmorillonite layer or to adjacent layers for single layer complexes, thereby constraining the molecules into a flat-lying orientation. The latter presumption would seem to require a rather coincidental fit between the dimensions of the diol chains and the distances between surface oxygens in a given montmorillonite layer or on a particular mutual orientation of adjacent montmorillonite layers.

Another study related to the present discussion has been made by Davidtz and Low (1968). They reported that the free-swelling of sodium montmorillonites in aqueous suspension could be related to the configuration of the surface oxygens to which the adjacent water was hydrogen bonded. They concluded that a change in α produced a corresponding change in the lengths of and angles between hydrogen bonds in the water structure connected to the surface oxygens which changed the potential energy of the water between the clay layers and, thereby, the swelling of the clay. Their data and interpretation are in qualitative accord with our model for hydroxyl-oxygen juxtaposition in layer silicates. Associated with a change in α would be a corresponding change in the angle made by *BIS* with c^*. A corresponding change in the orientation of the water molecules immediately adjacent to the clay surface would be expected with a consequent change in the entire water structure proceeding outward from the clay surface.

Postscript. After submitting our report a paper by Alice M. Blount, I. M. Threadgold and S. W. Bailey entitled "Refinement of the Crystal Structure of Nacrite" which appeared in *Clays and Clay Minerals*, 1969, **17,** 185–194 became available to us. We have used their data to compute the angles pertinent to our communication. These are set forth in Table 3 and may be compared with the other results.

TABLE 3. COMPUTED STRUCTURAL DATA FOR NACRITE. ATOM COORDINATES FROM BLOUNT, THREADGOLD AND BAILEY (1969)

Hydroxyl-oxygen pair	Angle between (OH)—O and *BIS*	Angle between (OH)—O line and c^*
O_1—$(OH)_2$	15°	12.5°
O_2—$(OH)_3$	4°	14.5°
O_3—$(OH)_4$	10°	14.5°

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