THE CRYSTAL CHEMISTRY OF MONTMORILLONITE

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ABSTRACT

A modification of the Hofmann-Endell-Wilm structure is proposed in order to account for the thermochemical properties of montmorillonite. According to the new hypothesis, hydroxyl ions can occur in the tetrahedral layers as statistical substitutions in a manner analogous to the substitution of $(OH)_4$ for SiO_4 in the garnetoids.

The second high-temperature endotherm is interpreted as evidence of the occurrence of hydroxyls in tetrahedral configuration, whereas the hydroxyl water given off during the first high-temperature endotherm is liberated from the octahedral layer. If the silicon content of the structural unit decreases in the manner postulated, the amount of aluminum in tetrahedral coordination cannot be calculated without a knowledge of the hydroxyl content of the tetrahedral layers. This concept may explain unsuccessful calculations of the base-exchange capacity from analytical data.

Preliminary measurements on liberation of high-temperature water tend to substantiate certain portions of the hypothesis, but further data will be required in order to obtain confirmation. Sufficient reliable data probably are not available to permit rigorous calculation of structural formulas.

INTRODUCTION

Existing hypothetical structures of montmorillonite, as proposed by Hofmann, Endell and Wilm (1) and by Edelman and Favejee (2), have proven extremely useful in permitting further consideration of the isomorphism and crystal chemistry of montmorillonite and its close relative beidellite.* That both of these structures are somewhat imperfect, particularly when called upon to explain some of the observed data on clays of the montmorillonite-beidellite group, has been recognized by numerous investigators. It is the purpose of this paper to present a brief description of a new hypothetical structure for montmorillonite which, although different from either of these structural hypotheses, has some of the more attractive aspects of both.

One of the earlier difficulties that was visualized for the Hofmann-Endell-Wilm structure was the manner of adsorption of interstitial water. This difficulty has been largely overcome through the explanation offered by Hendricks and Jefferson (5). However, other incompatibilities exist between the experimental data and the Hofmann-Endell-Wilm structure, as mentioned by Grim (6, p. 241). Some of these discrepancies are more readily explained on the basis of the Edelman-Favejee structure but, here again, difficulties arise and a more adequate theoretical ex-

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* The term beidellite is used here in the same sense as in the works of Marshall (3) and Ross and Hendricks (4), i.e., for montmorillonite in which a significant amount of aluminum occurs in the tetrahedral layer.

planation is lacking. In the sections to follow, certain types of experimental data will be discussed and tentative explanations of these phenomena will be based on a new structural hypothesis.

The interpretations furnished here will not be substantiated by detailed considerations of data, but it is believed that the hypothesis will, nevertheless, prove useful as a starting point for further discussion at a later date of the crystal chemistry of montmorillonite and related substances. It should be emphasized, therefore, that this is a brief, preliminary statement of the hypothesis and its ultimate acceptability will depend upon further consideration of numerous different types of data.

ISOMORPHISM AND BASE EXCHANGE

The present hypothesis is predicated upon two statistical observations obtained from the numerous analytical data recorded in the literature, which have been excellently collated by Ross and Hendricks (4). These observations, stated succinctly are: (1) No regular increase in the base-exchange capacity accompanies replacement of silicon by aluminum (Si→Al) in tetrahedral coordination, even after substitution of Mg in the octahedral layer has been taken into account, and; (2) according to the calculations of Ross and Hendricks, there is an apparent increase in the amount of hydroxyl water with substitution of aluminum for silicon in tetrahedral coordination, although this increase is not regular.

If the existing structures were adequate to account for these conditions, a regular increase in the amount of base exchange occasioned by $Si^{+4} \rightarrow Al^{+3}$ would be expected, provided the integrity of normal oxygen and hydroxyl ions were maintained, because one additional unsatisfied negative charge would accompany each aluminum ion introduced in tetrahedral configuration. The available analyses give no straightforward indication of such a relationship.

With regard to the second premise above, existing structures make no provision for substitution of additional hydroxyl ions in a non-systematic manner although it has been pointed out by Ross and Hendricks (4, p. 52) that commonly the amount of water liberated above 300° C. is significantly in excess of the amount required by the Hofmann-Endell-Wilm hypothesis.

These generalizations, if valid, indicate that the amount of hydroxyl water of montmorillonite not only exceeds the amount required by the Hofmann-Endell-Wilm hypothesis but the excess amount is related in some way to the distribution of aluminum between octahedral and tetrahedral coordination, as calculated by Ross and Hendricks.

The hydroxyl content can be further considered in light of the thermal decomposition of montmorillonite and beidellite.

ENDOTHERMIC REACTIONS OF MONTMORILLONITE

As a basis for consideration of the structure of this mineral and its relatives, only the liberation of hydroxyl ions is of primary importance. Thus the low temperature endothermic reactions exhibited by montmorillonite (at temperatures below 300° C.) will be largely omitted from the present discussion. Most samples of montmorillonite exhibit two high-temperature endothermic reactions which begin and reach maxima within the approximate ranges of 500° to 750° and 800° to 900° C.

Other interpretations cannot be completely eliminated but, for the purpose of the present hypothesis, these two endothermic reactions are interpreted as activation temperatures required to rupture two different types of hydroxyl bonds within the structural framework of the mineral. Edelman and Favejee (2) have proposed a structure in which hydroxyl ions appear in both tetrahedral and octahedral coordination and this proposal will account for the observed liberation of water in excess of what is required by the Hofmann-Endell-Wilm structure. However, the proposal of Edelman and Favejee will not adequately account for variable amounts of hydroxyl water.

Preliminary experiments, which were designed to examine critically the mode of liberation of water, have led to certain tentative conclusions concerning the thermal decomposition of montmorillonite. Although the experimental results will not be presented here, the conclusions can be briefly summarized as follows:

(1) All of the adsorbed water can be removed at temperatures below 300° C. and, if sufficient time is allowed, at considerably lower temperatures for some montmorillonites.

(2) Approximately the amount of water required by the Hofmann-Endell-Wilm hypothesis is liberated during the temperature interval of the first high-temperature endotherm.

(3) Above the temperature interval of the first high-temperature endotherm, additional water is liberated and the amount seems to be related to the intensity of the second high-temperature endotherm.

Detailed interpretation of these preliminary experiments does not seem justifiable, but it seems probable that the octahedral layer loses hydroxyls during the first high-temperature endothermic reaction and thereby loses some of its structural organization although, judging from the experience of other investigators, its original condition can be partially restored by rehydration (7). During the second high-temperature endotherm hydroxyls are lost from the silica sheets and complete reorganization of the structure is effected during the exotherm which follows almost immediately.

Inasmuch as the occurrence of hydroxyl ions in the tetrahedral layers would require concomitant alteration of the quantities of other constituents within the tetrahedral layers in order to preserve electrostatic neutrality, it has been necessary to find a reasonable mechanism for the introduction of these hydroxyl ions.

THE STRUCTURE OF THE TETRAHEDRAL LAYER

The proposed hypothesis accepts the basic units of the three-layer structure of Hofmann, Endel and Wilm, including the arrangement of the tetrahedra with respect to the octahedral layer; it is concerned essentially with modification of the hexagonal sheet of Si_2O_5 groups, which occasionally contain Al substituting for Si.

In order to reconcile the existing data with a more complete structural picture, it is essential to draw analogies from other compounds which crystallize in aqueous environments at atmospheric temperatures. A particularly useful analogy is the isostructural series:

$Ca_3Al_2(SiO_4)_3$	high temperature
$Ca_3Al_2(SiO_4)_2(OH)_4$	intermediate to high
$Ca_3Al_2(OH)_{12}$	room temperature
$Ca_3Fe_2(OH)_{12}$	room temperature

which has been discussed by Flint, McMurdie and Wells (8), by Pabst (9) and by the writer (10, 11). It has been demonstrated in these studies that $(OH)_4$ has a stable configuration as discrete tetrahedra and 4H becomes equivalent electrostatically to Si in the garnetoid structures. There appears to be no fundamental factor prohibiting this type of tetrahedral configuration in silicate sheets. Extending these considerations to the tetrahedral layers of montmorillonite will permit:

$$n[Si_4O_{10}]^{-4} \rightarrow (n-1)[Si_4O_{10}]^{-4} + [Al_3O_6(OH)_4]^{-7} \qquad (A)$$

or,

$$n[Si_4O_{10}]^{-4} \rightarrow (n-1)[Si_4O_{10}]^{-4} + [Si_3O_6(OH)_4]^{-4}. \qquad (B)$$

These conditions are shown schematically in Fig. 1, where the $(OH)_4$ tetrahedra are shaded. In order to simplify the figure, only the coplanar oxygens with $z=0$ are shown.

It seems desirable to examine some of the principal consequences of this hypothesis:

(1) Hydroxyl ions may occur in the tetrahedral layer of montmorillonite, either substituting simply for Si_2O_5 groups (B) or in association with Al ions substituting for Si ions (A).

(2) Some of the apex hydroxyls of such $(OH)_4$ tetrahedra may be shared with the cations in octahedral coordination and this type of sharing would, in general, take place in the vicinity of Al→Mg.

(3) Although an increase in hydroxyl ions in the tetrahedral layer may

accompany Si→Al, this increase need not be a systematic increase because hydroxyls might enter this layer by mechanism (B).

(4) The sum of the Si+Al ions of the tetrahedral layers need not be constant, but $X+Y+Z/4=4$, if ions of the tetrahedral layers are represented by $(Si_XAl_YH_Z)O_{10}$.

In the description of the theoretical model, an attempt has been made to indicate the isomorphous substitutions in an explicit manner and to examine the precise consequences. Actually one would expect statistical substitutions where real crystals of montmorillonite are involved. Indeed, no greater regularity would be expected for the types of substitutions suggested here than would be expected for such substitutions as Al→Mg in the octahedral layer. Therefore, the association of one $(OH)_4$ group with three atomic replacements of the type Si→Al (Fig. 1) is an arbitrary device which is used merely for the purpose of clearly depicting a general situation. The more general thesis, then, is intended to cover even such statistical occurrences as O→(OH) within the tetrahedral layer; it is not restricted to the intimate association of four such hydroxyls. Nevertheless, in the present hypothesis it is fundamental that the ratio of hydroxyls to silicons in these layers is not constant and that the tetrahedral layer does not have the cristobalite arrangement as postulated by Edelman and Favejee (2).

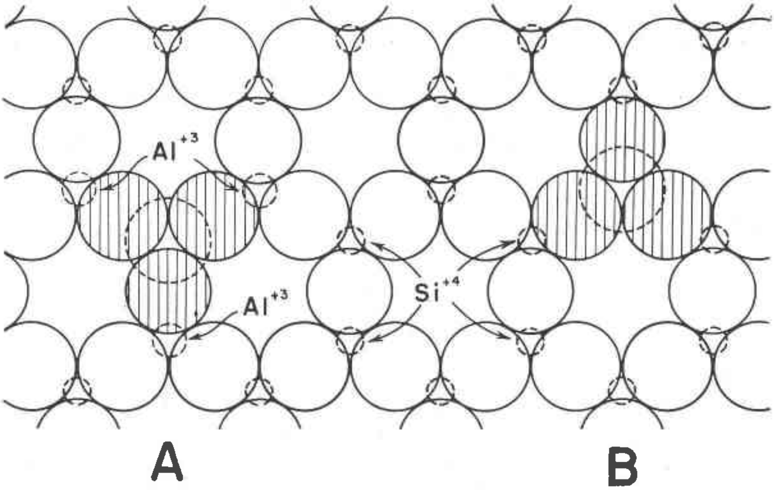

FIG. 1. Arrangement of tetrahedra in the basal plane of montmorillonite, showing the substitutions: (A) $[Si_4O_{10}]\rightarrow[Al_3H_4O_{10}]$ and (B) $[SiO_4]\rightarrow[H_4O_4]$. (NOTE: Only the oxygens with coordinates $z=0$ are shown. Hydroxyls with $z=0$ are shaded. The large dotted circles represent hydroxyls approximately 2.2 Å from the plane $z=0$.)

The general expression for the proposed isomorphous substitutions can be written:

$$n[\mathrm{Si_4O_{10}}]^{-4} \rightarrow (n-m)[\mathrm{Si_4O_{10}}]^{-4} + m[\mathrm{Si}_X\mathrm{Al}_Y\mathrm{H}_Z\mathrm{O}_{10}]^{-R} \qquad \text{(C)}$$

where $X+Y+Z/4=4$, and $R=X+2Y+Z/4=4+Y$. This expression is written in such a way as to preserve the original charge of the silica sheet except for the increase in negative charge which will accompany each Si→Al. Actually these negative charges may be partially compensated by addition of hydrogen ions, and thus it becomes essential to consider the ions of the octahedral layer, as well as the exchangeable bases, in order to obtain neutrality of charges.

THE CALCULATION OF STRUCTURAL FORMULAS

Ross and Hendricks (4) have made a contribution of great value and some of the assumptions applied to their calculations of mineral formulas are undoubtedly justifiable. However, their assumption of 10 oxygens and 2 hydroxyls per structural unit is incompatible with the present hypothesis. For the purpose of testing this hypothesis, it will be necessary to determine quantitatively the hydroxyl water which is associated with different types of bonding energies in order to permit allocation of these hydroxyls to appropriate positions within the structure. Likewise, the amount of Al in tetrahedral coordination will not be calculable until the amount of hydroxyl in the tetrahedral layers has been determined.

In addition to the usual analysis for non-volatile oxides and the precision determinations of water at appropriate temperatures, it will be necessary to determine the base-exchange capacity and the kinds and amounts of exchangeable bases. Although the base-exchange capacity may increase (beyond what is required by Al→Mg) with substitution of Al for Si in the tetrahedral layers, no satisfactory method exists for calculating the inverse relationship, i.e., the amount of this substitution from the base-exchange capacity.

In the present preliminary discussion, the correct procedures for accomplishing these calculations will not be considered. Indeed, it is highly questionable whether sufficient reliable data are available to permit unambiguous calculations of this sort.

CONCLUSIONS

It seems highly probable that the uncertainties and complexities of the montmorillonite structure will be resolved but, in order to accomplish this, analytical data of excellent quality will be required. Analytical data obtained on mixtures, e.g., containing feldspar or quartz, will be quite useless for this purpose and the results will continue to be misleading.

The hypothesis that hydroxyl ions can occur in the tetrahedral layers as substitutions for silicon-oxygen groups has been outlined in general terms. Some of the data which seem to require this modification of the Hofmann-Endell-Wilm structure are discussed, particularly with regard to base-exchange capacity and thermal behavior of these minerals. By this proposal the variable excess of high-temperature water above what is required by the Hofmann-Endell-Wilm hypothesis can be taken into account.

Preliminary thermochemical data tend to substantiate the hypothesis and permit interpretation of the second high-temperature endotherm of montmorillonite as an indication of the presence of hydroxyls in the silica sheets. It is suggested that these hydroxyls can occur in a manner analogous to their occurrence in garnetoids.

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