

ON THE DIFFERENTIATION OF VERMICULITES AND SMECTITES IN CLAYS

By G. F. WALKER.

C.S.I.R.O., Division of Industrial Chemistry, Melbourne, Australia.

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ABSTRACT

Certain of the criteria used for distinguishing vermiculites in clays from smectites are critically examined, and attention is drawn to the urgent need for further research in this field. Difficulties inherent in the differentiation are heightened by the common occurrence of interlayer contamination in the naturally occurring minerals.

INTRODUCTION

The frequency during recent years with which vermiculites have been reported as constituents of clays requires that general agreement should be reached among clay mineralogists on methods of distinguishing them from the structurally-similar smectites. (The name "smectite" (Brown 1955) is used herein to designate the montmorillonite group of minerals). At the present time, this agreement is lacking and the current literature as a consequence shows evidence of increasing confusion. In particular, identifications are frequently based on inadequate criteria. The present article attempts to establish more clearly the nature of the problem involved and to explore possible solutions.

CHARACTERISTICS OF THE GROUPS

Clay vermiculites and smectites may be either dioctahedral or trioctahedral. Chemical data on pure clay vermiculites are entirely lacking so that the chemical differences between them and the smectites cannot be defined accurately at the present time. Macroscopic vermiculites (trioctahedral), however, always show a greater degree of Al^{3+} for Si^{4+} substitution (Walker and Cole 1957) than the smectites while, in other respects, their structural formulae are rather similar.

Structurally, both groups consist of triphormic silicate layers with interleaved sheets of water molecules carrying exchangeable cations. The intensity distribution of the basal reflexions on the X-ray diagrams has been invoked in certain instances for diagnostic purposes, but it is doubtful if an effective distinction between the clay

minerals can be made on this basis alone, as may be demonstrated by reference to the Fourier transforms of the triphormic $\text{Si}_4\text{O}_{10}(\text{OH})_2^{6-}$ skeleton, and of ideal dioctahedral (pyrophyllite-type) and trioctahedral (talc-type) layers (Fig. 1). Calculations indicate that substitution of Al^{3+} for Si^{4+} in tetrahedral positions has little effect on the transforms; hence, differences in the relative intensities of the basal reflexions of expanding triphormic lattices depend largely on the interlayer distance, the nature of the interlayer material, and the composition of the octahedral portion of the silicate layer. Only very minor differences are therefore likely to appear in the basal intensity distributions of corresponding members of the vermiculite and smectite groups if their degree of hydration is similar, *e.g.*, between a trioctahedral magnesium-vermiculite with double sheets of interlayer water and a similarly-hydrated magnesium-saponite.

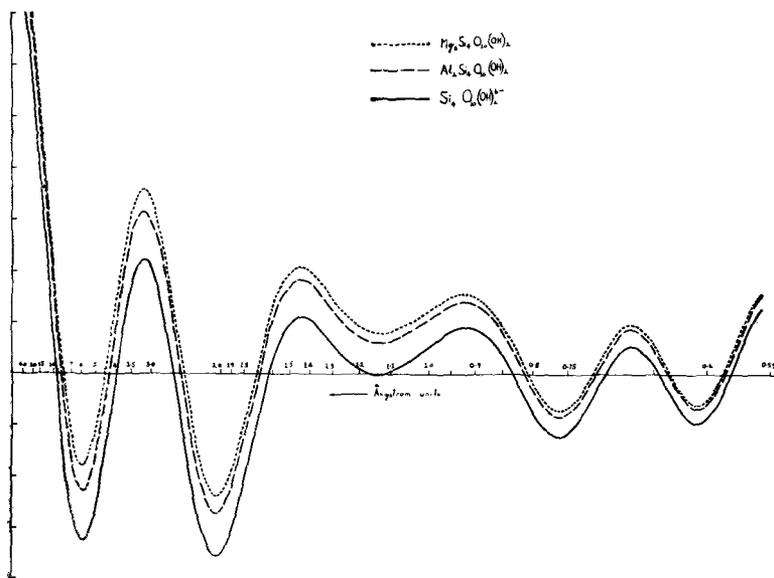


FIG. 1.—Fourier transforms of triphormic silicate layer skeleton and of ideal dioctahedral and trioctahedral layers.

It is probable that the line profiles of the non-basal reflexions on the X-ray diagrams of clay vermiculites tend to be more symmetrical than those of the smectites, so that the reflexions can be indexed (hkl) rather than (hk). This feature indicates a tendency towards greater regularity in the stacking sequence of the silicate layers in clay ver-

miculites. Weiss, Koch and Hofmann (1955), however, have drawn attention to a saponite and a beidellite which show poorly-developed (*hkl*) reflexions, so that observations of the nature of the non-basal reflexions can only be regarded as of limited value for diagnostic purposes. A similar conclusion must apply to particle size although, as Weaver (1956) has suggested, it appears that clay vermiculites tend to be of larger size than smectites. It should be noted, however, that the nature of the interlayer cation may be of importance since calcium- and magnesium-smectites tend to be of larger size than sodium-smectites (*e.g.*, Vedeneva and Rateev 1955).

In both groups, the basal spacing is influenced by the nature of the interlayer cations and by the interlayer water content. There is a tendency, however, for macroscopic vermiculites, even if reduced to clay size, to expand less than smectites with a given interlayer cation; hence, a magnesium-vermiculite takes up a maximum of two sheets of interlayer water molecules ($d_{ool}=14.8 \text{ \AA}$) whereas a magnesium smectite may take up three or even four sheets ($d_{ool}\sim 18-21 \text{ \AA}$). Saturation with large monovalent ions, moreover, causes the vermiculite lattice to contract to between 10 and 12 \AA (Barshad 1948, 1950), and Walker (1949a) suggested saturation with NH_4^+ ($d_{ool}\sim 11 \text{ \AA}$) as a means of distinguishing vermiculites in clays from smectites. It has not been established, however, that this test, or others based on the use of large monovalent ions, are universally valid.

The tendency for vermiculites to expand less than smectites also appears to be generally true of complexes with organic molecules (Walker 1950; Barshad 1952). This difference in behaviour is probably related, not simply to a particle size effect but, more particularly, to the surface charge density and hence the interlayer cation population of the minerals. Reference to the literature suggests that the layer charge per $\text{O}_{10}(\text{OH})_2$ unit of structure in the smectites may range from about 0.4 to about 0.6 (*e.g.*, Foster 1951; Osthaus 1953; Weiss, Koch and Hofmann 1955), whereas most vermiculites appear to fall within the range 0.6-0.8 (*e.g.*, Barshad 1952, 1954; Weiss, Koch and Hofmann 1955; Walker and Cole 1957). The cation exchange capacity data of different authors, however, are difficult to compare, and the limits of layer charge quoted above can only be regarded as approximations. A low exchange capacity value, moreover, recalculated by Barshad (1954) for the vermiculite component of a vermiculite-chlorite would, if included, extend the lower limit of the vermiculite range considerably,

and indicate that the ranges of layer charge covered by the groups overlap. On the other hand, Weiss, Koch and Hofmann (1955) consider that there is a continuous gradation in layer charge between the groups, and suggest that the groups should be defined by reference to a value of about 0.55 equivalents per $O_{10}(OH)_2$ unit.

Removal of interlayer water from both groups causes a 9-10 Å basal series to develop on the X-ray diagrams, representing diffraction from the triphormic silicate layer. Walker (1955), using macroscopic crystals, has shown that during removal of interlayer water from a hydrated vermiculite lattice a series of partially-hydrated phases develop, *e.g.*, for magnesium-vermiculite, the normal 14.4 Å phase is replaced successively by phases with basal spacings of 13.8 Å, 11.6 Å and 20.6 Å (11.6 Å and 9 Å alternating) before the "dehydrated" 9 Å phase is attained. More recent studies by the writer suggest that magnesium-smectites also develop a series of partially-hydrated phases. Rowland, Weiss and Bradley (1955) have also drawn attention to analogies in the dehydration behaviour of a macroscopic vermiculite and a montmorillonite, and have identified a partially-hydrated phase with a basal spacing at about 11.5 Å in magnesium-vermiculite and in montmorillonite saturated with Ca^{2+} , Mg^{2+} , Mn^{2+} , Li^+ or H^+ . The close resemblance between the low-temperature peak systems on the differential thermal curves of air-dried magnesium-smectites and macroscopic magnesium-vermiculites has been emphasized by Walker and Cole (1957). Since magnesium-smectites may take up larger quantities of interlayer water than magnesium-vermiculites, however, differences in the first low-temperature peak are observable under the appropriate conditions. For a similar reason, differences may also appear in the low-temperature peak systems of specimens saturated with cations other than Mg^{2+} . These considerations call for the exercise of caution in the use of dehydration methods, but indicate that such methods may be invoked in certain circumstances to aid in the differentiation of the groups.

THE GLYCEROL TEST

The ability of smectites to complex with double sheets of glycerol molecules and so give a basal spacing of ~ 18 Å (MacEwan 1944, 1946) has led to the adoption in many laboratories of glycerol treatment as a standard procedure for the identification of these minerals. In applying the test, MacEwan (1951) recommends that the presence of large monovalent ions in interlayer positions be avoided since

these may inhibit the lattice expansion and lead to the formation of single-sheet glycerol complexes ($d_{001} \sim 14 \text{ \AA}$) with some specimens (see also Barshad 1950). So far as is known, however, all smectites saturated with Mg^{2+} give double-sheet glycerol complexes. (Twelve Mg-saturated smectites examined in the writer's laboratory were found to conform to this rule).

The existence of triphormic soil-clay minerals which form single-sheet glycerol complexes has been reported. Such minerals were originally labelled "clay vermiculites" because of their resemblance, for example with respect to the glycerol reaction, to macroscopic vermiculites developing in the same soils (Walker 1947, 1949, 1950a), and apparently-similar minerals have been found in a variety of soil-clays (e.g., Jackson et al. 1952; Brown 1953; Rolfe and Jeffries 1953; Hathaway 1954; Rich and Obenschain 1955). Tests made on macroscopic magnesium-vermiculites have shown that single sheets of glycerol molecules are taken up ($d_{001} = 14.28 \text{ \AA}$, Walker 1950) and Barshad (1950) has found that a coarsely-powdered sample and a $< 0.25 \mu$ fraction of the Macon Co. magnesium-vermiculite both imbibed single sheets of glycerol. Barshad (1950) further reported that the Macon Co. vermiculite saturated with a number of different cations gave a 14.3 \AA complex with glycerol.

In the present study, the reaction of vermiculites with glycerol at room temperature was further investigated using four well-characterized macroscopic magnesium-vermiculites. These specimens, which come from Kenya, Nyasaland, West Chester and Macon Co. respectively, are the purest available to the writer in adequate quantity, and are listed in order of increasing layer charge. Reduction of particle size by dry grinding was rejected because of uncertainties as to the chemical identity of the product with the original mineral. Samples were therefore pulverised in water in a macerator, which may be less damaging than grinding, and a series of fine fractions obtained by centrifuging the product. From these tests it was ascertained that no $\sim 18 \text{ \AA}$ peak developed on the diffraction diagrams nor was the 14.3 \AA peak appreciably displaced towards lower angles with decreasing particle size, although the finest fractions gave no basal reflexions whatsoever, suggesting that the platelets were approaching unit cell thickness. (In all the tests reported herein, the organic complex was formed at room temperature by immersing in the liquid one end of a quartz specimen tube containing the powdered sample. Liquid entered the tube by capillary action and saturated the sample, leaving an excess of liquid in contact with the specimen).

The effect of replacing the interlayer Mg^{2+} by other cations was studied on samples of these vermiculites filed to pass a 300 meshes B.S. sieve. Since the presence of large monovalent ions in interlayer positions tends to contract the vermiculite lattice, the formation of glycerol complexes tends to be inhibited. Replacement by Ca^{2+} , Sr^{2+} or Ba^{2+} , however, revealed that stable single-sheet or double-sheet glycerol complexes formed, depending apparently on the layer charge of the specimen and its interlayer spacing at the time of its treatment with glycerol. Thus, a high layer charge and low hydration state tends to restrict the glycerol complex to single sheets, and conversely for double sheets. (Details of these results will be published at a later date). Reduction of particle size led to no differences in response to glycerol treatment apart from a more rapid attainment of equilibrium (minutes for clay-size fractions). After resaturation of the Ca^{2+} , Sr^{2+} and Ba^{2+} samples with Mg^{2+} , single-sheet glycerol complexes again formed even if the sample was fully hydrated; the response to glycerol treatment, therefore, is not conditioned by the leaching procedure. So far as the experimental results on the Macon Co. vermiculite overlap with those of Barshad (1950), there is no disagreement; it is clear, however, that generalizations based on this single specimen are not warranted.

In view of the foregoing it is evident that the glycerol test should only be applied to homo-ionic samples. (The same applies when internal surface areas are measured by means of glycerol retention (or ethylene glycol retention, q.v.)) For normal identification purposes, pretreatment with Mg^{2+} would seem to be the simplest procedure. Development of a double-sheet glycerol complex would then indicate a smectite, and a single-sheet complex a vermiculite. Limited tests subsequently made on three other vermiculites (batavite, Palabora vermiculite and Young River chloritic vermiculite) gave concordant results. The *universal* validity of the test as a means of distinguishing vermiculites from smectites, however, cannot be regarded as established until a greater range of vermiculites and smectites has been examined.

Clay vermiculites which behave similarly have been examined in this laboratory. Other clay specimens, however, fail to expand under conditions where the macroscopic minerals do. Such behaviour is explicable if the charge of these "clay vermiculites" is assumed to be very high. On the other hand, it may be that interlayer contaminants (cf. Discussion) interfere with the lattice expansion of these specimens. It has not been possible to obtain an unequivocal answer to

this question from the limited range of specimens in the writer's possession.

THE ETHYLENE GLYCOL TEST

Ethylene glycol is also used extensively for the identification of swelling minerals and, like glycerol, forms a complex with smectites in which double sheets of the liquid are taken up, giving a basal spacing in the region of 17 Å (Bradley 1945). The glycol test, however, is not generally regarded as a means of distinguishing *between* vermiculites and smectites, and Bradley (1950) has pointed out that some vermiculites imbibe double sheets of glycol while others do not. Clay vermiculites which expand to about 17 Å on glycol treatment have been reported by Bradley (1945a, 1950), Weaver (1956) and others. On the other hand, Hathaway (1954) has described specimens which fail to expand with ethylene glycol (or with glycerol).

Of the four powdered macroscopic magnesium-vermiculites (<300 mesh B.S.S.) referred to previously, three showed no displacement of the basal reflexion when treated with glycol. The Kenya specimen, however, which has the lowest layer charge of the four, gave spacings in the region of 15 Å (irrational), but neither continued immersion in glycol up to 16 days nor reduction of particle size produced evidence of further penetration in this specimen, although some magnesium-vermiculites give a 14.3 Å complex with ethylene glycol, therefore, displacement of the basal reflexion towards higher spacings can occur with other specimens (apparently those of relatively low layer charge). The effect was subsequently confirmed by tests on the Young River chloritic magnesium-vermiculite which gave a ~16 Å spacing with glycol. (The proportion of chloritic material present and hence the exchange capacity of the vermiculite component in this specimen is not known accurately). Replacement of the interlayer Mg^{2+} by Ca^{2+} , Sr^{2+} or Ba^{2+} led to the displacement of the basal spacings of all the vermiculites tested to between 15.6 and 16.4 Å (rational) on subsequent glycollation. These spacings are rather lower than the ~17 Å usually reported for the glycol-smectite complex, although perhaps too close to be of general value for diagnostic purposes. It is interesting that the smaller spacings are obtained from vermiculites of high exchange capacity suggesting that the thickness of the double-sheet glycol complex may be a function of layer charge.

Clay vermiculites which respond to glycol treatment in similar

fashion to the macroscopic minerals have also been examined. As with glycerol, however, ethylene glycol fails in some instances to expand other specimens even after saturation with Ca^{2+} , Sr^{2+} or Ba^{2+} .

DISCUSSION

In dealing with natural clays, which are often mineralogically complex, it is seldom practicable to gauge accurately the chemical composition or exchange capacity of a single constituent. On the other hand, swelling ability can be readily tested in the presence of other minerals, provided the entry of the swelling agent is not inhibited by amorphous coatings on the particles or by interlayer contaminants (*viz.*, organic matter, brucitic or gibbsitic material, etc., occurring as "islands" in the interlayer regions). Unfortunately, "contaminated" structures appear to be rather common in the natural clays. It would appear that such structures may be justifiably characterized as having a "vermiculitic" or a "smectitic" matrix only if the swelling behaviour is not affected by the contaminant, or if the contaminant can be removed without harming the silicate layers. It is doubtful if strict fulfilment of these conditions is always possible.

It seems likely that the presence of interlayer contaminants could influence the shrinkage characteristics of the lattice and so prevent or retard lattice contraction on K^+ or NH_4^+ saturation. Rich and Obenschain (1955) have suggested that the presence of non-exchangeable aluminium in the interlayer regions of dioctahedral clay vermiculites can inhibit lattice contraction, and have shown that vigorous treatments (*viz.*, boiling in $\text{N NH}_4\text{F}$ for 5 minutes or N KCl plus 0.1 N HCl for 48 hours) cause the basal spacing to be displaced to near 10 \AA . Contraction of the hydrated lattices on heat treatment may also be delayed and rendered partial by the presence of interlayer contaminants (*e.g.*, Brown 1953, Hathaway 1954). On the other hand, the ability of clay mineral lattices to expand beyond about 14 \AA is not necessarily prevented by the presence of an interlayer contaminant (brucitic material) as may be shown by reference to the work of Stephen and MacEwan (1951) and Grim and Johns (1953). It cannot be assumed, however, that this is a general rule, and further work is required before the influence of the amount and nature of different interlayer contaminants can be fully assessed.

The present communication is primarily concerned with the differentiation of the uncontaminated minerals and, even here, the difficulties may be very considerable. If the groups are considered to

grade continuously into one another as the interlayer cation population changes, any dividing line between them must be an arbitrary one. Moreover, it is uncertain whether different swelling tests will be critical at one and the same time. Thus "intermediate" minerals may exist which behave as typical smectites to one test and as vermiculites to another. It seems unwise, therefore, to select any single test as a final criterion in the present state of our knowledge. The problem of differentiation, moreover, is further complicated if mixed-layering or lateral mixing of vermiculite and smectite layers occur. Such mixed structures seem likely to occur in natural clays if they can arise from relatively small variations in the population density of the interlayer cations.

The fundamental similarity of smectites and vermiculites is such that the question naturally arises as to whether a distinction should be made at all, or whether the limits of the smectite group should be extended to include all swelling triphormic clay minerals and the name "vermiculite" reserved exclusively for the macroscopic minerals. The question of treating vermiculites as smectites has already been raised (*e.g.*, Roy and Romo 1954, Weaver 1956), but the incomplete nature of the evidence makes it appear inadvisable at this stage to attempt to reach final conclusions. It will be evident from the present article that various criteria which have been used for making the distinction between the clay minerals are invalid, and that misidentifications are therefore likely to have been made. Under the currently accepted system of nomenclature, swelling clay minerals which behave more like macroscopic vermiculites than like smectites may be justifiably labelled "clay vermiculites." On the other hand, it may be that a clear distinction between "clay vermiculite" and "smectite" is not always possible. It would seem that structures of this kind are best characterized by detailed descriptions of their properties rather than by labels. To be effective, however, such characterization implies a prior and thorough understanding of the differences between the groups, and it is apparent that this has not as yet been achieved.

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