REACTIONS OF EXPANDING-LATTICE CLAY MINERALS WITH GLYCEROL AND ETHYLENE GLYCOL

By G. F. WALKER

C.S.I.R.O., Chemical Research Laboratories, Melbourne, Australia.

ABSTRACT

Under certain circumstances, both glycerol and ethylene glycol form interlayer complexes with vermiculites resembling those formed with the smectites. The rate and degree of complex formation are related to the surface charge on the silicate layers, to the type of interlayer cation present and to crystal size. With glycerol, but not with ethylene glycol, the hydration state of the mineral immediately prior to complex formation is of some importance.

INTRODUCTION

The ability of smectites to imbibe double sheets of interlayer glycerol ($d_{00l}=17\cdot7$ Å) and ethylene glycol ($d_{00l}=17$ Å) molecules respectively was reported by MacEwan (1944, 1946) and Bradley (1945a). Bradley (1945b, 1950) further noted that certain vermiculites expanded to form double-sheet interlayer complexes with ethylene glycol whereas other specimens failed to do so. MacEwan (1951), referring to unpublished work by G. Brown, later indicated that smectites could form single-sheet glycerol complexes ($d_{00l}=14$ Å) if large monovalent cations occupied the interlayer positions, and Barshad (1950) arrived at a similar conclusion. Barshad (1950) also found that a vermiculite from Macon Co., when saturated with H^+, Li^+, Na^+, Mg^{2+}, Ca^{2+} or Ba^{2+} gave single-sheet glycerol complexes ($d_{00l}=14\cdot3$ Å), and Walker (1951) reported the formation of single-sheet glycerol complexes with Mg-vermiculites. More recently, during an attempt to evaluate the criteria currently employed for the differentiation of vermiculites and smectites in clays, Walker (1957) observed the formation of double-sheet glycerol and glycol complexes with vermiculites saturated with cations other than Mg^{2+}. Since identifications of expanding-lattice clay minerals are frequently based on X-ray diffraction measurements of changes observed in the c-direction of the unit cell when the organic liquids are added to the clays, a more detailed study of these reactions was undertaken and is

reported herein.   In the past, the usual practice has been to consider the mineral a smectite if a double-sheet glycerol complex is formed, and vermiculite if a single-sheet complex is formed.   The position with regard to ethylene glycol is less clear, but some workers seem to have assumed that both organic liquids behave in a similar fashion and hence that a double-sheet ethylene glycol complex excludes the possibility of vermiculite.

<center>EXPERIMENTAL</center>

Observations were made chiefly on powdered vermiculites ($<$ 300 mesh B.S.S.) produced by filing large flakes selected from well-characterized macroscopic specimens, care being taken to exclude material suspected of biotitic, chloritic or other contamination.   So that the influence of crystal size could be assessed, a number of tests were made on single flakes of approximate dimensions 1 mm $\times$ 1 mm $\times 0 \cdot 1$ mm and, in some instances, on fractions of $< 1\mu$ equivalent spherical diameter, collected by sedimentation after breaking down large flakes in water in a macerator.   Saturation with various cations was effected by leaching with neutral 4N chloride solutions followed by water washing till chloride-free.

Oriented samples were prepared for examination with an X-ray diffractometer in which the specimen mount was attached to a heating coil, allowing the temperature of the sample to be adjusted as required.   Arrangements could also be made to pass air at selected humidity values over the samples during diffraction.   The organic liquids were added either by means of a spray or a dropping-tube, sufficient liquid being used to make the powder visibly moist. Powders were also packed into quartz capillaries for X-ray photographic examination; one end of the tube containing the powder was placed in the liquid and the tube allowed to fill by capillary action; samples in tubes were in contact with a large excess of the organic liquid.   Since the ethylene glycol and glycerol tests on clay minerals are normally applied in an open atmosphere, no attempt was made to render the organic liquids anhydrous for these experiments.

The basal spacings of vermiculites saturated with different cations vary, depending on the degree of interlayer hydration.   Prior to the addition of the organic liquid, therefore, samples were equilibrated in air at fixed relative humidities, selected so that the lattice would contain either single sheets or double sheets of interlayer water molecules (Table 1); "mixed-layer" states, in which both single sheets and double sheets of interlayer water coexist in different parts of the

sample and which are particularly liable to occur when Li^+, Na^- or Ba^{2+} occupy interlayer cation positions, were thereby avoided.

The surface charge on the silicate layers was estimated from cation exchange capacity measurements.   Since the exchange capacities of vermiculites vary somewhat depending on the method used, the values of layer charge quoted can only be regarded as approximations. They serve nevertheless to indicate the *relative* values of the different specimens, and also suggest that the range of layer charge covered

TABLE 1—Basal spacings, in Angstrom units, of vermiculite containing various interlayer cations; A, single sheets of interlayer water; B, double sheets of interlayer water.*

Phase	Li^+	Na^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
A	12·3	12·3	11·6	12·0	12·1	12·3
B	14·9	14·8	14·4	14·9	15·0	14·8

approximates that covered by the vermiculite group as a whole (Walker 1957).   The source of the vermiculites used and their estimated layer charge in equivalents per $O_{10}(OH)_2$ unit of structure are as follows:

Young River, West Australia	0·6
Nyasaland	0·6
Kenya	0·65
West Chester, Pennsylvania	0·7
Macon Co., North Carolina	0·8

ETHYLENE GLYCOL COMPLEXES

The majority of the < 300 mesh powder samples expanded when treated with ethylene glycol, equilibrium usually being attained within a few hours (Table 2).   Mg-saturated samples were the most

TABLE 2—Maximum observed basal spacings, in Angstrom units, of powdered vermiculites in ethylene glycol.

	Li^+	Na^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
Young River	16·1	16·3	16·3	16·2	16·1	16·2
Nyasaland	16·1	16·2	15·5	16·1	16·1	16·2
Kenya	16·2	16·3	15·2	16·1	16·2	16·2
West Chester	16·1	16·1	14·3	16·1	16·1	16·2
Macon Co.	16·0	14·8	14·3	15·6	15·6	16·0

*Other double-water-sheet lattices may occur under different conditions; Mg-vermiculite, for example, forms 13·8 Å and 14·8 Å lattices both of which contain double sheets of interlayer water as well as the 14·4 Å lattice which is stable under normal conditions of temperature and pressure (Walker 1956).

reluctant to expand, and both the West Chester and Macon Co. specimens failed to show any expansion beyond 14·3 Å after immersion in an excess of liquid for several weeks at room temperature. The Young River specimen, on the other hand, expanded to 16·3 Å in a few hours and showed a nearly integral series of higher orders indicating considerable regularity throughout the crystal lattice. Intermediate values were observed with the Nyasaland and Kenya specimens, the reflexions in both instances being irrational and somewhat diffuse.

With Li^+, Na^+, Ca^{2+}, Sr^{2+} and Ba^{2+} in interlayer positions, expansions to the vicinity of 16 Å (approximately rational) were observed for four of the five vermiculites. The Macon Co. vermiculite, which has the highest layer charge of the five, expanded much more slowly than the others and failed altogether to expand when interlayer Na^+ was present. The Ca^{2+} and Sr^{2+} forms of this vermiculite, moreover, did not expand beyond about 15·6 Å (irrational), which is significantly lower than the spacings of the other vermiculites. (The accuracy of measurement of these spacings is estimated to be ± 0.15 Å). The original hydration state of the minerals had no observable effect on the rate or degree of expansion with ethylene glycol.

Samples prepared from $< 1\ \mu$ fractions gave similar expansions but reached equilibrium much more quickly, usually within a few minutes of treatment. Flakes 1 mm square, on the other hand, were reluctant to expand, particularly those of the higher layer charge vermiculites. Thus, the basal reflexion of the Macon Co. specimen gave little indication of displacement after several weeks in glycol, irrespective of the type of interlayer cation present, while the other vermiculites with the exception of the West Chester Mg-vermiculite gave irrational or nearly rational spacings of between 15 and $16\frac{1}{2}$ Å. These results suggest that the rate and degree of expansion are related to the layer charge of the vermiculites, and also imply that the charge varies within a single crystal, some portions taking up more glycol than others.

The glycol-smectite spacing of 17 Å (Bradley 1945a) is somewhat greater than the ∼16 Å values obtained with glycol-vermiculite, and this may be ascribed tentatively to the higher layer charge of vermiculites (see Discussion). The glycol-smectite complex is usually considered to consist of double sheets of interlayer glycol molecules, and a unidimensional Fourier synthesis reported below suggests that this may also be true of glycol-vermiculite. Heating the 16 Å glycol-vermiculite complex to 80°C tends to produce a diffuse and

irrational reflexion at about $13\frac{1}{2}$ Å, apparently representing a lattice containing single sheets of glycol molecules, and further heating to 300°C causes a further reduction in spacing accompanied by darkening of the crystals due to the decomposition of the interlayer glycol.

STRUCTURE OF THE GLYCOL-VERMICULITE COMPLEX

In spite of the reluctance of ethylene glycol to complex with the larger crystals, a few flakes formed regular complexes after several weeks immersion in glycol. A unidimensional Fourier synthesis was made on one such flake of approximate dimensions 1 mm $\times$ 1 mm $\times$ 0·1 mm taken from the Kenya specimen.   The strongly scattering Ba^{2+} was used as the interlayer cation in the hope that its position along the z-parameter could be unambiguously determined.   The first to the nineteenth orders inclusive and the twenty-fourth order of the basal series $(d_{00l}=16\cdot28$ Å) were recorded on moving-film
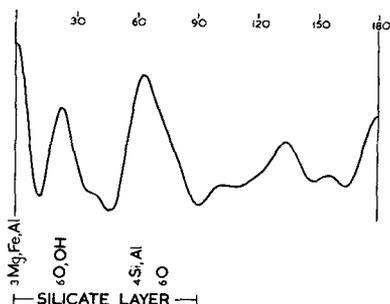

FIG. 1—Electron-density distribution normal to (001) of Ba-vermiculite (Kenya) complexed with ethylene glycol; $d_{00l} = 16\cdot28$ Å.

photographs using Mo Kα radiation.   A pack containing five films interleaved with tin-foil to increase the inter-film ratio was used for the estimation of the 00l intensities.   The signs of the observed structure amplitudes were calculated on the assumptions of centro-symmetry and of a silicate layer similar to that deduced by Mathieson and Walker (1954) and Mathieson (1958) for the Kenya Mg-vermi-culite.   No assumptions whatsoever were made regarding the contents of the interlayer region.

The resulting electron density distribution (Fig. 1) shows that the interlayer region contains a strong central peak, presumably due to the Ba^{2+} ions, with a more diffuse region of scattering on either side due to the glycol molecules.   The data are not sufficiently extensive

to allow the partial resolution of the tetrahedral Si, Al atoms from the surface oxygens of the silicate layer, such as was observed in the Mg-vermiculite analysis referred to above. Further, difference syntheses failed to eliminate amplitude waves in the silicate region of the curve, hence the smaller peaks in the interlayer region cannot be regarded as unambiguous. Provisional attempts at a solution based on asymmetric structures were unsuccessful. It follows that a much more detailed analysis would be needed to allow the precise orientation of the glycol molecules to be deduced. Nevertheless the indications, so far as they go, are consistent with the view that double sheets of glycol molecules are interleaved with the silicate layers and that the interlayer cation occupies a position midway between silicate layers.

Examination of the h0l and h3l spectra enables the β angle to be measured and suggests that the mutual stacking arrangement of the silicate layers is the same as that in the normal hydrated phase ($d_{00l} = 14 \cdot 36$ Å) of Mg-vermiculite (Mathieson and Walker 1954), where triads of oxygens from opposing silicate layer surfaces are related octahedrally. Since the normal hydrated (double-water-sheet) form of Ba-vermiculite also shows this stacking sequence, it can be inferred that the entry of glycol molecules does not involve a lateral displacement of the silicate layers with respect to one another but simply an increase in the c-dimension of the lattice.

GLYCEROL COMPLEXES

The reaction with glycerol was in general slower than with ethylene glycol, several days being required in some instances to attain maximum expansion with < 300 mesh powders. Diffractometer samples tended to expand less than those in tubes, and many of them gave diffuse reflexions or bands rather than sharp basal reflexions. The figures listed in Table 3 indicate expansion maxima observed

TABLE 3—Maximum observed basal spacings, in Angstrom units, of powdered vermiculites in glycerol.

	Li^+	Na^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
Young River	14·2	14·8	14·3	17·6	17·6	17·6
Nyasaland	14·2	14·8	14·3	17·6	17·6	17·6
Kenya	14·3	14·8	14·3	17·6	17·6	17·6
West Chester	14·3	14·8	14·3	17·6	17·6	17·6
Macon Co.	14·3	14·8	14·3	14·3	15·8	14·3

from a number of trials, and refer largely to data obtained photo-graphically from the tube samples which were in contact with a large excess of glycerol. Higher orders, where these could be measured, normally failed to provide an entirely rational series and an accuracy of no more than $\pm$ 0·2 Å can be claimed for the data.

None of the Li^+ or Mg^{2+} samples expanded beyond 14·3 Å; the 14·9 Å Li-vermiculite lattice containing double sheets of interlayer water in fact contracted to 14·3 Å and remained at this value, which is that of the single-sheet glycerol complex (Walker 1951). The fully hydrated Na-vermiculite lattice likewise contracted to 14·3 Å on treatment but reverted to 14·8 Å subsequently, a reversible transition which could be controlled by adjusting the humidity of the air in contact with the sample. With the exception of the Macon Co. vermiculite, specimens saturated with Ca^{2+}, Sr^{2+} or Ba^{2+} expanded to a maximum of about $17\frac{1}{2}$ Å, which is close to the 17·7 Å spacing of the glycerol-smectite complex. The latter is usually considered to consist of double sheets of interlayer glycerol molecules, but the lack of an entirely rational series of orders prevented structural examina-tion of the $17\frac{1}{2}$ Å glycerol-vermiculite complex.

The original hydration state of the lattice is of significance in the reaction with glycerol since, if single sheets of interlayer water are present, addition of glycerol gives a 14·3 Å spacing which tends to be stable under normal atmospheric variations. Passage of satur-ated water vapour at 30°C however caused expansion to 16·0 Å of all samples saturated with Ca^{2+}, Sr^{2+} or Ba^{2+} except those of Macon Co. The 16·0 Å lattice, which shows an approximately integral series of higher orders, has not been structurally examined, but its sensitivity to changes in humidity suggests that the interlayer con-figuration may consist of single sheets of glycerol together with single sheets of water molecules. Reversion to 14·3 Å or further expansion to $17\frac{1}{2}$ Å occurs when dry air is passed over the samples in the pre-sence of excess glycerol. Free energy differences between the 14·3 Å, 16 Å and $17\frac{1}{2}$ Å glycerol complexes are clearly small, a point which it may be of interest to illustrate further by reference to the $< 1 \mu$ fraction of the Kenya Sr-vermiculite. On adding glycerol to the 15·0 Å lattice, diffractometer measurements showed immediately a slight shift towards higher spacings, and in 10 minutes a diffuse 15-17 Å band had developed which remained without further change in the laboratory atmosphere (24°C, 50% RH). A sharp 16 Å reflexion, obtained on passing moist air over the sample, was followed by a sluggish reversion to the 15-17 Å band, which apparently

contains 14·3 Å and 17½ Å as well as 16 Å components.   Heating at 30°C or passing dry air over the sample slowly developed the 17½ Å lattice, whereas heating at 150°C in the presence of excess glycerol produced the 14·3 Å lattice.   Although both 14·3 Å and 17½Å phases when developed tended to remain stable in the laboratory atmosphere, rapid reversion to 16 Å occurred when the relative humidity exceeded about 90 per cent.

The 17½ Å glycerol complexes can be readily destroyed by washing with water; similarly interlayer glycerol can be replaced by ethylene glycol (or vice versa) simply by treatment with a large excess of liquid.   When the 17½ Å glycerol complex obtained with Ca^{2+}, Sr^{2+} or Ba^{2+} in interlayer positions is washed with water, resaturated with Mg^{2+} and again treated with glycerol, no expansion beyond 14·3 Å is observed.   The influence of the cation is therefore a real one, and the ability of the lattice to expand with glycerol is not simply a result of the cation-replacement process.

In general, < 1 μ fractions and < 300 mesh samples behaved similarly, with the former attaining equilibrium more rapidly. Macroscopic flakes, on the other hand, failed almost entirely to expand even after several months immersion in glycerol.

Hydrogen and Aluminium Vermiculites

Expanding-lattice layer silicates containing interlayer H^+ are notoriously difficult to prepare in homo-ionic form because of the tendency for the H^+ ions to attack the silicate layers, with the partial occupation of interlayer positions by Mg^{2+}, Al^{3+} and other cations displaced from the interiors of the silicate layers.   A similar difficulty arises in the case of saturation by Al^{3+} because of the low pH values of the salt solutions.   For this reason, results obtained with H- and Al-vermiculites are not listed in the Tables.   Nevertheless, because of the likelihood of the naturally-occurring minerals in clays having a proportion of interlayer H^+ or Al^{3+}, it was felt that some attempt should be made to assess the effect of these ions on the glycerol and glycol reactions.   After treatment with $AlCl_3$ solution, none of the vermiculite samples expanded beyond about 14 Å in the presence of glycerol or ethylene glycol.   Pretreatment with 0·1N or 0·01N HCl, moreover, failed to produce expansions in any of the samples with glycerol.   With ethylene glycol, on the other hand, the acid-treated vermiculites of low layer charge (Young River, Kenya and Nyasaland) expanded to the region of 16 Å, samples treated with 0·1N HCl expanding more rapidly than those treated with the weaker acid.

DISCUSSION

Cation exchange capacity measurements of smectites and vermiculites, which have been frequently reported in the literature, suggest that both groups extend over a range of layer charge, with the highest values of the smectites approaching the lowest values of the vermiculites. The data, however, which are usually expressed as milliequivalents per 100 grams of "air-dry" material and do not specify the interlayer water content, do not allow direct comparisons to be made with precision. (Different exchange values, moreover, may be obtained from a single specimen depending on the method of determination). Weiss, Koch and Hofmann (1955) have suggested that the critical value of layer charge dividing the groups is about 0·55 equivalents per $O_{10}(OH)_2$ unit of structure, and the indications of the present study are consistent with a value in this region or perhaps slightly higher (see below).

It has been pointed out that macroscopic vermiculites show an appreciably higher degree of Al^{3+} for Si^{4+} substitution than the smectites (Walker and Cole 1957). There are, however, no chemical data available for clay vermiculites, and chemical analysis is in any event of little value for diagnostic purposes except perhaps with the very rare mono-mineralic clays. Similar objections apply to a variety of other methods which have been considered diagnostic (Walker 1957). We are thus forced to the position of distinguishing clay vermiculites from smectites by reference to their swelling characteristics alone. If the groups grade into one another with respect to layer charge, the question as to where the dividing-line occurs becomes essentially one of terminology and of the criterion selected to make the differentiation. Since different tests may give different answers, it seems necessary to select a single criterion and to define the groups by reference to it.

On this basis, the present study indicates that a clay vermiculite pretreated with Mg^{2+} should not expand beyond about $14\frac{1}{2}$ Å with glycerol. This is close to the spacing of the normal hydrated Mg-vermiculite lattice, which is stable at ordinary temperatures and pressures, so that no appreciable displacement is involved. Mg-smectites, on the other hand, according to Barshad (1950), Walker (1957) and others, expand to about 17·7 Å on glycerol treatment. Moreover, on this basis, tests with the Groschlattengrün Mg-saponite, a small quantity of which was kindly provided by Professor Hofmann, clearly allocate this mineral to the smectite group. This saponite which, according to Weiss, Koch and Hofmann (1955), has a layer charge of 0·57 equivalents per $O_{10}(OH)_2$ structural unit, is

therefore very close to the vermiculite values reported herein. From these data, it seems reasonable to infer that the Mg^{2+} plus glycerol test provides a valid criterion for distinguishing the groups.

The greater reluctance of the vermiculites to expand with glycerol and ethylene glycol compared with the smectites may be ascribed to the greater electrostatic attraction operating between the silicate layers in the former group. The role of the interlayer cation, however, is less easy to understand and no explanation consistent for both glycerol and ethylene glycol can be offered. Whereas with glycol, the original hydration state of the lattice appears to have no influence on the final complex, this is not true of the glycerol complexes. In the latter, single-water-sheet lattices tend to give single-sheet glycerol complexes while double-water-sheet lattices may give double-sheet glycerol complexes when Ca^{2+}, Sr^{2+} or Ba^{2+} occupy interlayer cation positions. The overriding effect of layer charge, however, restricts the expansion of the Macon Co. specimen even when saturated with these cations. In general, lattice expansion occurs more readily with ethylene glycol than with glycerol, presumably because of the higher dipole moment of the former (Wesson 1948).

The influence of crystal size shows up in both the glycerol and glycol series as a slowing down of the rate of complex formation with increasing size. Furthermore, although there is little difference in the final spacing obtained as between $< 1\ \mu$ and < 300 mesh material, the 1 mm square flakes frequently failed to attain the same degree of expansion as the powders.

Treatment with ethylene glycol caused all specimens containing interlayer Li^+ or Ba^{2+} to expand to about 16 Å and similar values were observed with interlayer Na^+, Ca^{2+} and Sr^{2+} except for the specimen of highest layer charge (*viz.*, that from Macon Co.). In the Mg^{2+} series particularly (Table 2) the effect of increasing layer charge in restricting lattice expansion is clearly seen. The observed rates of expansion of these complexes were also related to the layer charge of the various specimens, those of low charge expanding more quickly than those of high charge. The Macon Co. specimen expanded most slowly, and failed in all cases to develop a rational series of higher orders, indicating that double sheets of glycol had not penetrated into all of the interlayer regions of the crystals. One may infer, therefore, that vermiculites of still higher layer charge would expand at a slower rate and to a smaller extent than the Macon Co. specimen or perhaps not at all; and such materials seem to exist in clays (*e.g.*, Walker 1957).

The results described herein raise the possibility of eventually developing a series of tests using glycerol, ethylene glycol and perhaps other liquids in combination, to obtain a measure of the layer charge of expanding-lattice triphormic minerals occurring in clays. Information of this type is likely to be of more value in studies of diagenesis, etc., than the mere ability to assign a mineral to one or other of the groups. Before such a project can be successfully undertaken, the possible effect of interference with lattice expansion characteristics by interlayer contaminants will have to be better understood.

The implications of the results reported here extend beyond the distinction of smectites from vermiculites to the mixed-layer minerals, particularly the "montmorillonite-illite" minerals so frequently found in the natural clays. In many instances, estimates as to the relative proportions of the montmorillonite and illite components are based on the amount of expansion observed when ethylene glycol or glycerol is added, no note being taken of the interlayer cation present. It will be evident that the presence of a vermiculitic mineral either as a unique entity or as a component of a mixed-layer system may be an equally valid interpretation of a basal spacing which is displaced to a higher value on treatment with one of the organic liquids. The combined Mg^{2+} plus glycerol treatment seems to offer the prospect of lessening difficulties of this kind.

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