# A GLYCOL–SODIUM VERMICULITE COMPLEX[1]

by

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## ABSTRACT

A complex of vermiculite with ethylene glycol was prepared by repeated boiling of a sodium-saturated cleavage flake in dry ethylene glycol. A stable product with a $c$ period of 12.9 Å afforded 15 terms for a one-dimensional Fourier synthesis. A model composed of glycol molecules with the plane of the zigzag normal to the silicate face is found to be consistent with the observed diffraction data. The complex apparently conforms to a stoichiometric ratio of two molecules per unit cell per layer of vermiculite.

The essentially iron-free vermiculite in the Texas Mines magnesite quarry near Llano, Texas, visited on the Sunday field trip of this Conference (Barnes and Clabaugh, 1961, p. 51) has a cation-exchange capacity approaching the level commensurate with the two charge per $a$-$b$ unit per layer level characteristic of the potash micas (Bradley and Serratosa, 1960, p. 262). Attempts to prepare a glycolated complex directly from the natural magnesium-saturated state resulted in an incompletely reacted product which retained an obvious significant residue of vermiculite hydration water (Bradley *et al.*, 1958, p. 353). The present product was prepared by pre-exchanging the natural $Mg^{2+}$ cations with $Na^+$, under which conditions actual determined $Mg^{2+}$ ion recovery is about 0.9 $Mg^{2+}$ per $a$-$b$ unit per layer. Suitable preparations are obtained from leaching in NaCl solutions of strength from 1 to 3 N. The Na-saturated products are subject to monitoring by diffraction as well as by chemical methods. Two one-dimensional Fourier syntheses from the respective 00$l$ sequences for two hydration states are reproduced in Fig. 1. At low relative humidities ($< ca.$ 40 percent R.H.) a single layer hydrate is stable in an 11.8 Å period. A projected resolution of the interlayer matter is indicated assuming that two of the water molecules in the plane are 5.6 Å from the origin, the other two in the plane 6.2 Å from the origin, and the two $Na^+$ ions in the 180° plane. At high relative humidities, or wet with excess liquid water, a two-layer hydrate is stable in a 14.8 Å period. Four or possibly somewhat more than four water molecules lie in each of the planes 5.9 and

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8.9 Å from the origin, with the two $Na^+$ ions again in the 180° plane. In each case the period is distinctly foreshortened with respect to the analogous periods for comparable hydration states of lesser charged montmorillonite layers in their Na-saturated forms.[1]
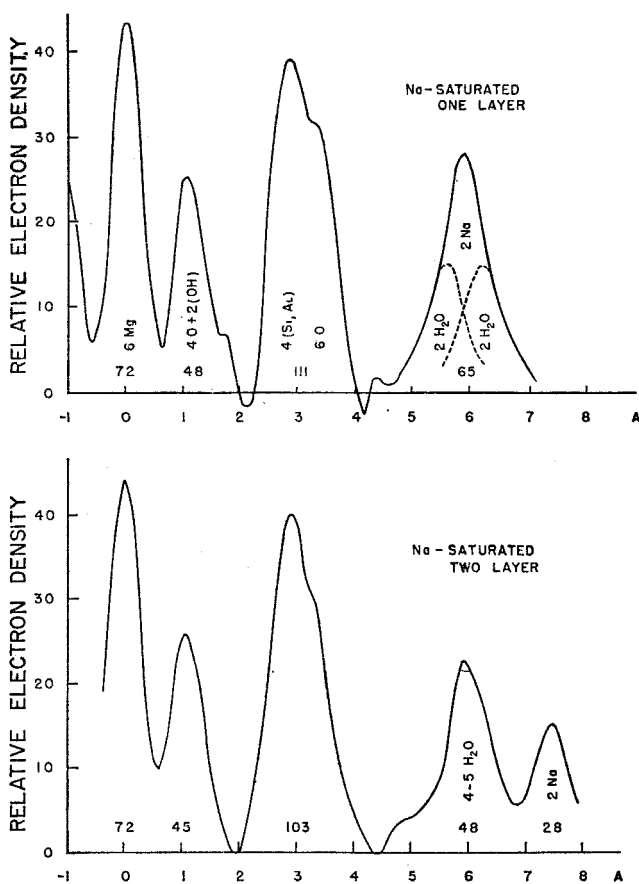


FIGURE 1.—One-dimensional syntheses from the 00*l* sequences of each of the two stable hydration states of Na-vermiculite. Upper, one water layer of 4 molecules; lower, two water layers of 4 or 5 molecules each. Numerals denote the relative planimeter areas under the major partially resolved features.

It is considered significant that the lower hydrate level conforms closely to a stoichiometric water content of four molecules per cell, matching the four positions per cell into which a water molecule could seat on one side or

[1] The existence of correlation between cation exchange capacities and diffraction periods of some synthetic montmorillonite products was noted by Prof. G. W. Brindley in discussions at the 7th National Clay Minerals Conference.
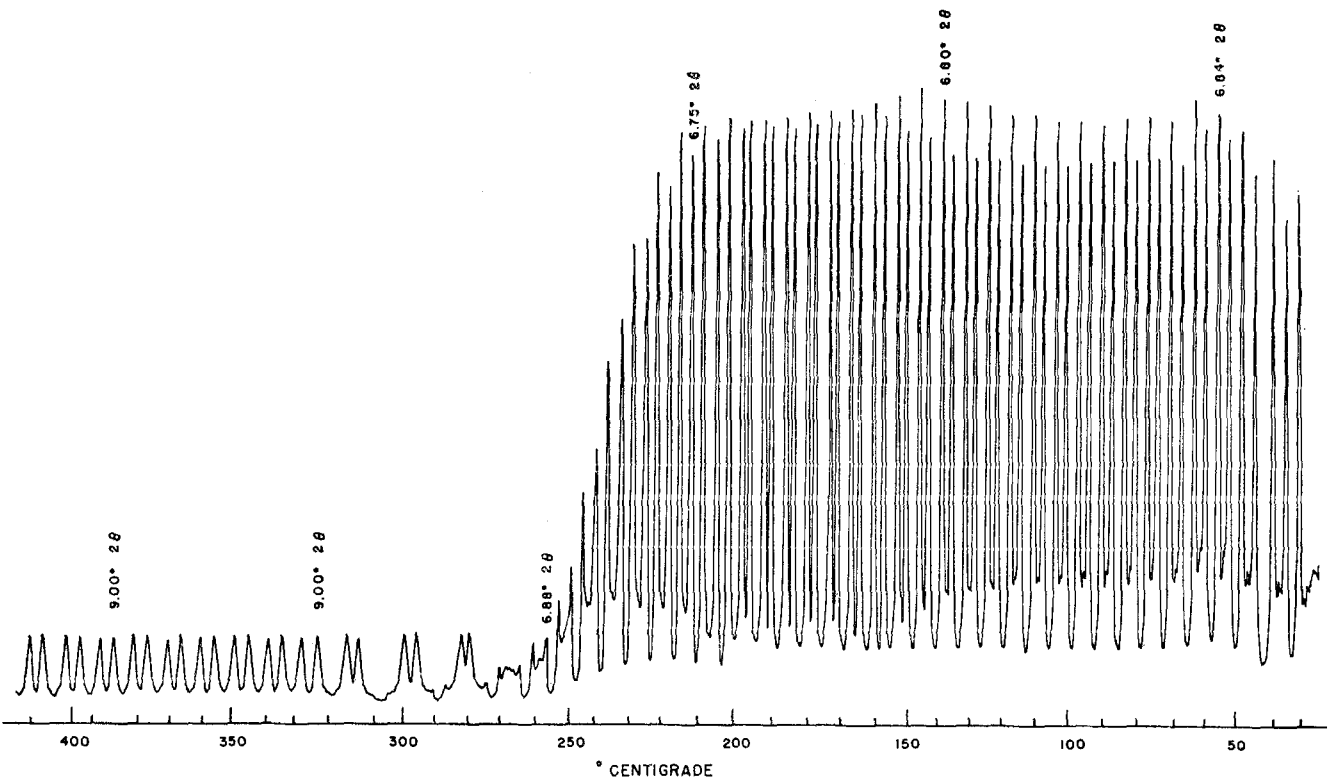
FIGURE 2.—Oscillating-heating diffractometer record of the position and intensity of the 001 diffraction feature of a glycol–vermiculite complex while raised from room temperature to 400° C. Diffraction angles are indicated above several representative maxima. (Cu Kα radiation.)

the other into the open hexagonal (trigonal) surface oxygen arrangement of the silicate skeletons. The higher hydrate can accommodate no more than four of its water molecules in such seats, stoichiometric restrictions do not apply to additional water, and determined total water contents range somewhat more than eight molecules per cell (up to nine or ten).

Repeated boiling of the Na vermiculite preparation with ethylene glycol was found to yield a final stable product from which, for all practical purposes, water was excluded, and which exhibited a well-defined diffraction periodicity of 12.9 Å. Inspection of a first order maximum by the oscillating-heating technique (Weiss and Rowland, 1956) afforded the record reproduced in Fig. 2. The preparation retains a stable maximum in both position and intensity while being raised through the boiling point of water and retains an apparently full complement of glycol up to temperatures somewhat above the boiling point of the glycol. This clearly differs from the incompletely reacted preparations previously described (Bradley *et al.*, 1958, p. 350).

The observed reduced relative $F$ coefficients from a diffractometer record of the 00$l$ diffraction sequence from one prepared vermiculite–glycol flake are compared with those of the two Na hydrate states in Table 1, and the corresponding one-dimensional synthesis for the glycol complex is reproduced in Fig. 3. The interlayer region includes two maxima for planes 6.0 and 6.9 Å from the origin, and the degree of similarity of the reproduction of the silicate skeleton to that shown in Fig. 1 supports the reality of the interlayer maxima.

TABLE 1.—RELATIVE VALUES OF $F$ REDUCED FROM OBSERVED INTENSITIES

|  | 2 water layers ($d_{001} = 14.8$ Å) | 1 water layer ($d_{001} = 11.8$ Å) | 1 glycol layer ($d_{001} = 12.9$ Å) |
|---|---|---|---|
| 1 | +0.49 | +0.28 | +0.39 |
| 2 | +0.12 | −0.13 | — |
| 3 | −0.25 | +0.12 | −0.17 |
| 4 | +0.36 | +1.00 | +1.00 |
| 5 | +1.00 | −0.36 | +0.32 |
| 6 | −0.06 | −0.35 | −0.61 |
| 7 | −0.44 | — | −0.35 |
| 8 | −0.22 | +0.46 | +0.32 |
| 9 | — | +0.30 | +0.56 |
| 10 | +0.59 | +0.27 | +0.37 |
| 11 | +0.17 | +0.09 | +0.27 |
| 12 | +0.40 | +0.18 | — |
| 13 | +0.17 | +0.21 | +0.27 |
| 14 | +0.08 | +0.16 | +0.39 |
| 15 | +0.23 | −0.04 | +0.28 |
| 16 | +0.21 |  |  |

As was true for the one-layer hydrate, steric considerations again require that stoichiometry be preserved. The molecular volume of ethylene glycol

in the pure liquid is about $72 \text{ Å}^3$, and van der Waals' cross-section for aliphatic chains is about $4 \text{ Å} \times 4.5 \text{ Å}$. Neither thickness could be accommodated in the measured interlayer clearance which is only about $3.7 \text{ Å}$ $(12.9 - 9.2)$, but two
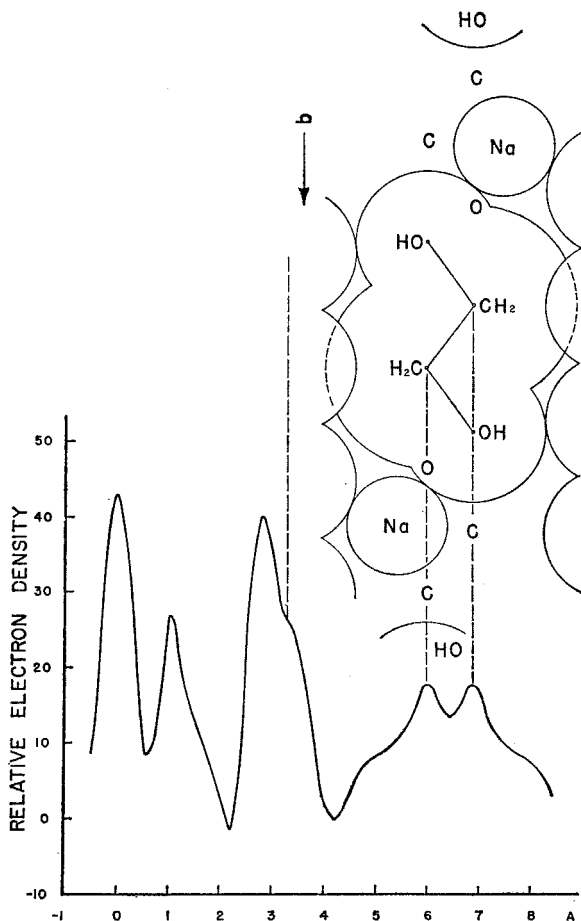


FIGURE 3.—One-dimensional synthesis from the $00l$ sequence of the glycol–vermiculite complex. The inset illustrates the packing aspect of glycol molecules and Na ions in the $bc$ plane. Auxiliary symbols C and O mark the position of next neighboring glycol molecules in planes $2.6 \text{ Å}$ above and below the plane illustrated. Each illustrated Na position is accompanied by an equally probable position on the other side of the constriction imposed by the indicated ethylene carbons of neighboring molecules, but the two options could not be filled simultaneously.

glycol molecules occupy less than the $165 \text{ Å}^3$ of clear volume per unit silicate skeleton layer. The same mechanism as was cited for the one layer hydrate does accommodate two glycol molecules per cell. The methylene groups, as

individuals, seat, one on one hand, the other on the other, into the open hexagonal surface oxygen arrangements. $CH_2$—O van der Waals' approaches, assuming a reasonable trigonal aspect of the "hexagonal" seat, are about 3.6 Å and OH—O glycol-to-surface approaches are 2.7–2.8 Å. The coverage per molecule on a single surface is only about 20 Å², leaving adequate interstitial space for the two $Na^+$ exchange ions. These ions have not been resolved in the synthesis, but are presumed to be associated with the rather high electron density flanking the glycol features about 5.5 Å and 7.5 Å from the origin.

A detailed schematic rationalization of volume relationships with the relative electron densities is inset in the Fourier sketch of Fig. 3. Linear strings of glycol molecules extend along $b$ (or a [110] analogue) in $c$-face centered array. Between pairs of alcoholic ends are dumbell-shaped interstices, in which either end of the bell could accommodate one $Na^+$ ion. A partition of ions between these sites, without crystallographic regularity, would afford the diffuse high electron density features on which the better resolved features seem to be superposed.

This analysis represents a preliminary appraisal to establish the need for and the prospect for success of a collection and analysis of three-dimensional data.

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