TEMPERATURE STABILITIES OF MONTMORILLONITE- AND VERMICULITE-GLYCOL COMPLEXES[1]

By

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ABSTRACT

Stabilities of Mg-, Ca-, and Na-montmorillonite- and vermiculite-glycol complexes are compared by heating experiments with the oscillating-heating x-ray powder diffraction method. In the course of expulsion of glycol from the 17A two-layer glycol complexes of the Mg-, Ca-, and Na-montmorillonites, a 14A one-layer complex is encountered which is substantially the same as the 14A one-layer vermiculite-glycol complex. One-dimensional Fourier methods are utilized for analysis of interlayer liquid distributions.

Direct observations of x-ray diffraction phenomena under dynamic conditions during the course of dehydration of monoionic montmorillonites reported at the Fourth National Clay Minerals Conference (Rowland, Weiss, and Bradley, 1956) indicated a transient intermediate hydration stage of about 11.5A, from which surprisingly close approach of water molecules to complex silicate layers was inferred.

The range of temperature of stability seemed too narrow for collecting data for analysis by Fourier methods, but two avenues of approach suggested themselves for obtaining supplemental information. These were the utilization of a higher boiling organic liquid as substitute for the water concerned, and the utilization of vermiculite as a better crystallized analogue of the silicate complex. Each approach afforded data sequences in the $00l$ series superior to those afforded by the water-montmorillonite systems. The degree of improvement is readily illustrated in the diffractometer registrations but, unfortunately, still falls far short of a quality that would be independently definitive.

Figure 1 illustrates the extent of the data available from the water systems from slides arranged as for the oscillating-heating technique. Records of the migrations of the several maxima were illustrated last year (Rowland, Weiss, and Bradley, 1956). The improved range in the $00l$ series from a similarly arranged ethylene glycol complex is illustrated in Figure 2. The glycol complexes are prepared by exposure of moderately well-oriented water system slides to ethylene glycol vapor in the oscillating-heating furnace.

Records of the position and intensity of first maxima from glycolated complexes are illustrated in Figure 3. For the monoionic montmorillonite complexes, transition from a 17A two-layer complex to a 14A one-layer complex is clearly depicted, and for the magnesium member, at least, a hopefully broad temperature range of stability is indicated for the one-layer complex. The ver-

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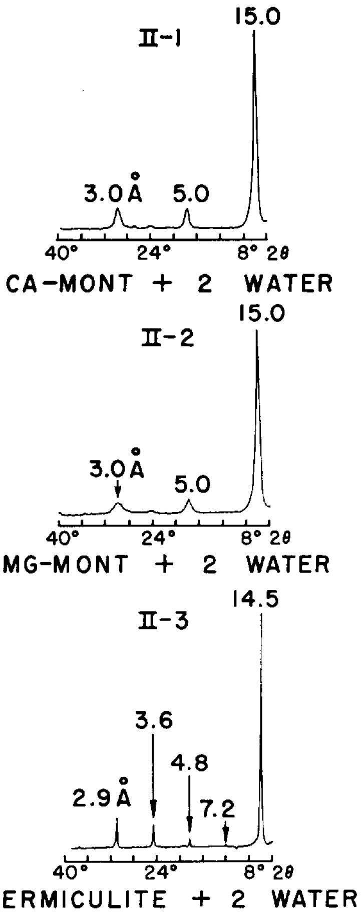

Figure 1. — Diffractometer traces of slides of monoionic montmorillonite preparations and natural vermiculite with limited degree of preferred orientation.

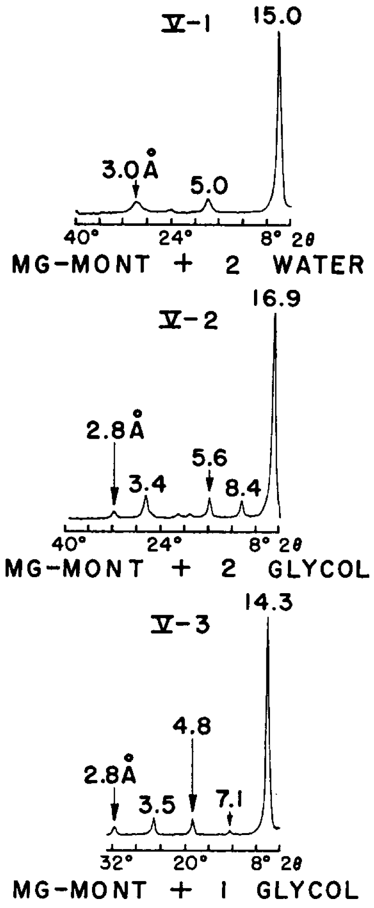

Figure 2. — Diffractometer traces comparing Mg-montmorillonite slide with the product of its glycolation through the vapor phase and the product while maintained in the camera at 130°C.

miculite record, for which no two-layer complex preparation is available for starting material, is seen to stabilize to an apparently fixed single-layer state through a range of about 150°C.

It is to be noted, however, that observed maxima (as in Figs. 1 and 2) reach only to sin θ/λ values of about 0.2. The observed intensities, reduced to relative F values, and supplied with appropriate signs, afford only the syntheses illustrated in Figure 4 (b and c). Comparison with the synthesis from a supplementary set of data extending to sin $\theta/\lambda = 0.3$ (Fig. 4a) indicates that neither the size nor the shape of the indicated electron density maxima is of

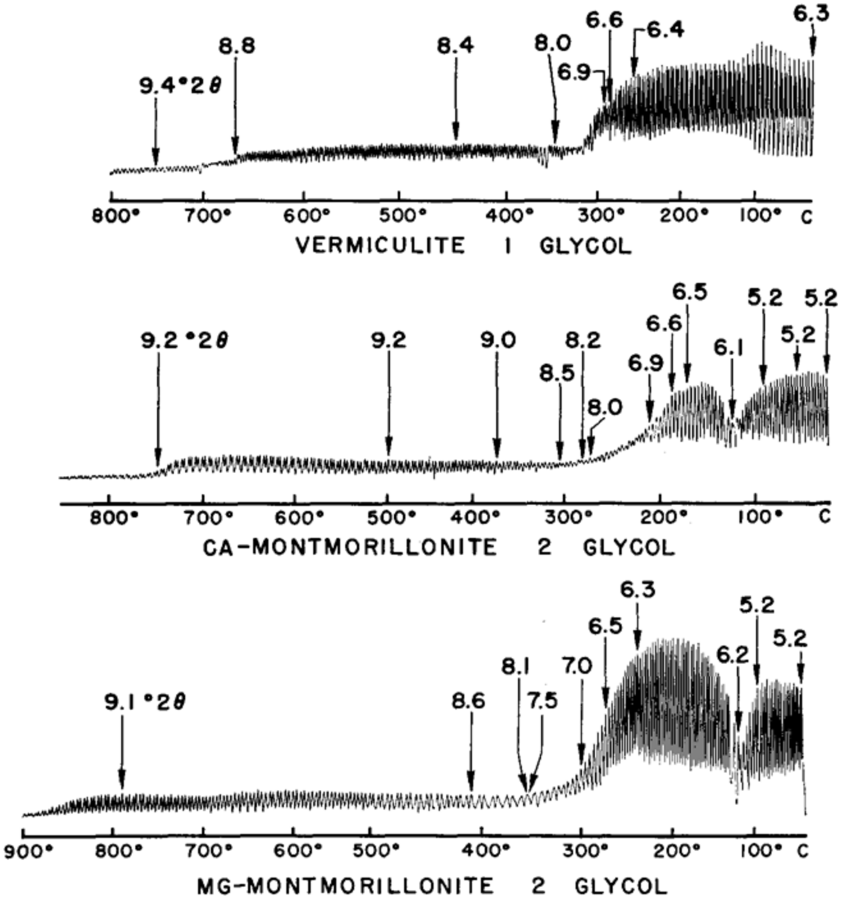

FIGURE 3. — Continuous records of the position and intensity of first-order maxima from vapor-glycolated products with increasing temperature.

desirable reliability for the short sequences. The faults of the trace 4*b* can probably all be ascribed to the poor resolution due to the shortness of the sequence, but the trace 4*c* indicates the additional defect that the small but appreciable evaporation of volatiles which took place during the collection of the data was enough to affect diffracting power deleteriously.

Collection of data at the moderate intermediate temperatures of interest in the dehydration and deglycolation of vermiculite afforded syntheses at the degree of resolution to be realized from short sequences which look hopeful, but still fail to inspire any confidence in possible interpretation of detailed mechanisms. The four separate syntheses of Figure 5 look very much alike through the silicate portion of the structure, but do not actually resolve atomic layers.

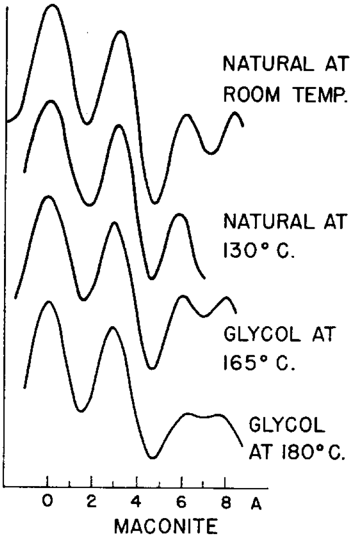

Figure 4. — One-dimensional syntheses of electron densities afforded by data from Mg-bentonite glycol complexes under static and dynamic conditions.

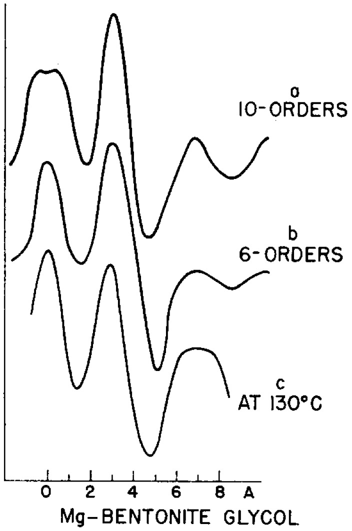

Figure 5. — One-dimensional syntheses of data afforded by fine-grained vermiculite aggregates under dynamic conditions.

Data of high quality have been available to Mathieson and Walker (1954) and to Grudemo (1954) for "single crystal" studies of the crystal structure of

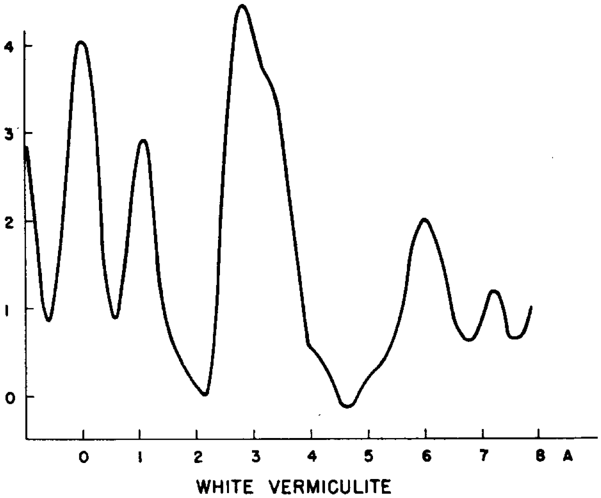

Figure 6. — One-dimensional synthesis for diffraction effects afforded by a single large cleavage flake of vermiculite (Cu radiation).

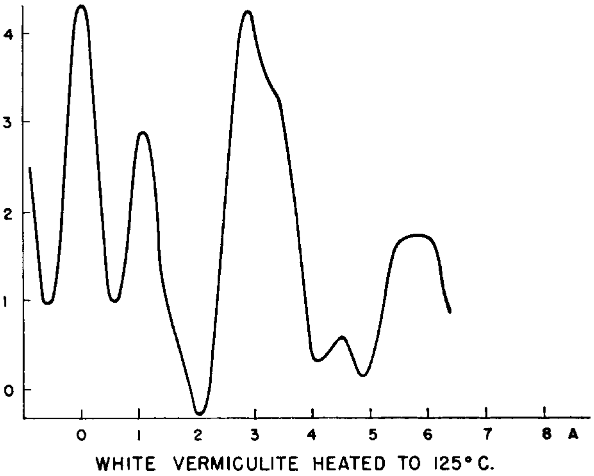

FIGURE 7. — A synthesis of composite data collected from the partially dehydrated portions of preheated large vermiculite cleavage flakes.

vermiculite. Large cleavage fragments afford data sequences with Cu radiation (filtered and unfiltered) up to 20 orders, from which well-resolved syntheses like that of Figure 6 may be realized. Details of octahedral and tetrahedral coordination are convincingly reproduced, and water and exchange ion levels are strongly indicated.

Because flakes of this quality react only slowly with atmospheric moisture, composite data can be collected by spectrometer methods from a sequence of unprotected heated flakes. The appearance of diffraction effects for the hydrated phase furnishes both a safeguard for the reliability of the dehydrated phase data and an internal standard. A synthesis so obtained from vermiculite heated to 125°C is illustrated in Figure 7. Octahedral and tetrahedral levels strongly resemble those of the unheated specimen. Previous inferences that exchange ions are relocated closer to the tetrahedral oxygen layers (Mathieson and Walker, 1954) and that residual water does not maintain the normal van der Waals distance from the silicate layer are confirmed. Even the wishful thought that some silicon could be active in binding this water could be accommodated. In the absence of more attractive hypotheses, little is to be gained by further discussion.

The hope that a stable single-layer vermiculite-glycol complexed crystal could be prepared for room-temperature observation was only partially successful. Large cleavage flakes were soaked for several days in ethylene glycol at 130° to 150°C, conditions demonstrated to remove about one-half of the natural water content in the absence of a solvent. It was erroneously presumed that the solvent would promote greater removal. The flakes were unmistakably modified, but reactions were clearly incomplete. The data are sufficiently extensive to raise some question whether organic liquid complexes are ever complete.

Detailed comparison of diffraction effects from a natural flake, a partially glycol-complexed flake, and a "fully" glycolated flake, as in Figure 8, establishes that the glycol reaction has shrunk the structure noticeably, and that scattering contributions from interlayer matter have modified the relative intensities of successive orders. It also strongly indicates that in no important case has the modification included a change of sign. This is perhaps most striking in the case of the sixth order, for which the vermiculite crystal model predicts different signs for an entirely water system and an entirely glycol

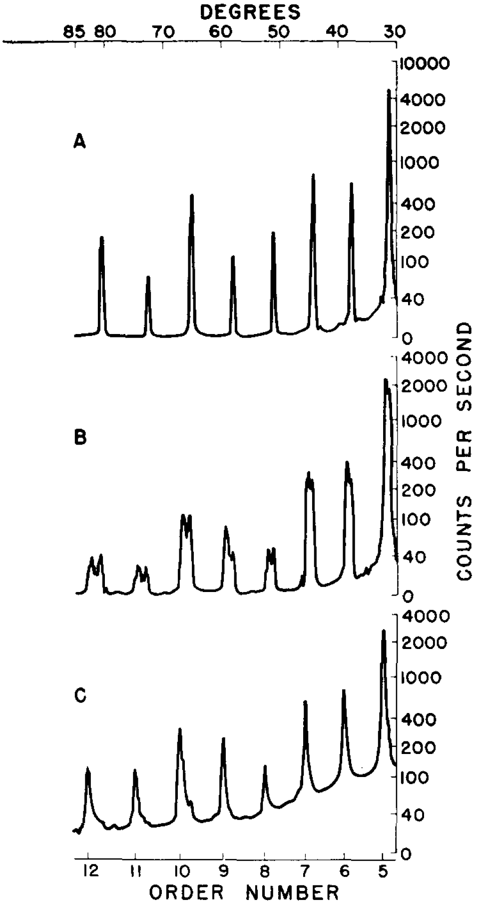

FIGURE 8. — Specimen diffractometer traces of (A) a natural vermiculite cleavage flake, (B) a glycolated product indicating modification of about 75 percent of the flake by glycol attack, and (C) an apparently nearly completely glycol-reacted flake, for which further analysis of the data established that actual completion is far less than the apparent.

TABLE I.—RELATIVE OBSERVED *F* COEFFICIENTS AND SIGNS FOR DIFFRACTION EFFECTS FROM VERMICULITE CLEAVAGE FLAKES

Order Number	Natural Crystal	Crystal Dehydrated at 130°C	Glycol Treated Crystal
1	+.47	+.40	+.43
2	—.10	—.26	—.07
3	—.32	+.34	—.30
4	+.52	+.60	+.61
5	+.79	—.43	+.69
6	—.31	—.38	—.37
7	—.37	+.09	—.38
8	—.19	+.47	—.19
9	+.16	+.26	+.33
10	+.38	+.20	+.39
11	+.15	+.09	+.25
12	+.25	+.17	+.27
13	+.05	+.44	+.07
14	+.14		+.17
15	+.14		+.18
16	+.19		+.21
17	+.12		+.06
18	—.04		—.05
19	—.11		—.07
20			+.08

system. With increasing resolution at higher angles, it also becomes apparent that diffuse scattering maxima exist between positions of respective equal orders. These are attributed to scattering from domains incompletely attacked, and constitute further evidence that respective amplitudes are of equal sign.

Relative *F* factors for the organic complex reduced from representative spectrometer traces are listed in Table 1, together with the signs based on the accepted natural model; the synthesis of the glycol-modified product is reproduced in Figure 9. It is clear that residual water is more important in the interlayer space than is the glycol.

In this light a return to the less well resolved dynamic observations on maconite can be seen strongly to indicate important amounts of residual water, decreasing with increasing temperature, and one is led to speculate that some water may still persist in the montmorillonite-glycol complexes from which there seems no hope to extend the range of diffraction observations sufficiently to reach an established conclusion.

Conclusions to be drawn from the present information are undesirably vague and speculative. Apparently, the projected thickness of the clay-organic complexes are controlled primarily by dimensions of the organic liquid molecules, subject only to minor modification by a tendency to assume stoichiometric proportions, so that complexes of clays of smaller *a* and *b* dimensions pack noticeably thicker than equal complexes on clays of larger *a* and *b* dimensions. Modifying this generality is the second principle that water is

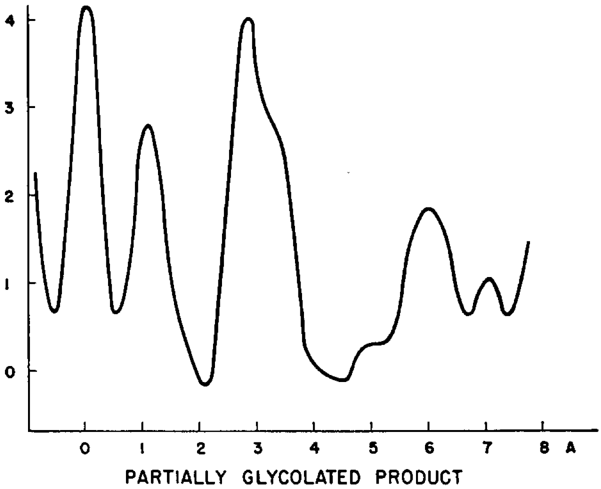

Figure 9. — One-dimensional synthesis for diffraction effects of the reaction product of glycol attack on a large vermiculite cleavage flake.

involved in the assemblages in quantities related to the abundance of water in the whole environment of the preparation and the disposition of space resultant from the tendency of the organic liquid to distribute itself in stoichiometric proportions at preferred sites in the silicate surfaces.

Under these conditions, it seems fair to say that useful qualitative conclusions are to be drawn from diffraction observations on complex crystallizations, but that intimate details on molecular scale must be reserved for high-grade single-crystal studies.

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