DEHYDRATION OF MONOIONIC MONTMORILLONITES[1]

By

R. A. ROWLAND

Shell Development Company, Houston, Texas

E. J. WEISS

The University of Texas, Austin, Texas

W. F. BRADLEY

Illinois State Geological Survey, Urbana, Illinois

ABSTRACT

The dehydration of sodium, potassium, lithium, hydrogen, calcium, magnesium, and manganese monoionic montmorillonites (prepared with ion-exchange columns) and a ver-miculite, was examined by the x-ray powder diffraction oscillating-heating method. The position and intensity of each of the first-order basal spacings were measured at intervals of 5° to 10° C from room temperature to 900° C. Position and intensity measurements were made for the first five orders of the basal spacing of the calcium montmorillonite up to 300° C and compared with computed intensities at these spacings. These data are presented as oscillating-heating x-ray diffraction diagrams showing the intensity change with tempera-ture, with important spacing shifts indicated, and as graphs showing the change in spacing with change in temperature.

Like vermiculite, calcium, magnesium, manganese, lithium, and hydrogen montmorillonite have an octahedral coordination of their exchange cation, and upon heating they also pass through two stable hydrates (ca. 14.5 A and 11.5 A). Montmorillonites of the two larger ions, sodium and potassium, have a regular one-water-layer configuration at 12.4 A, which is distinctly different from the 11.5 A hydrate of the smaller ions.

The foreshortened oxygen-oxygen approaches of the lower hydrate (11.5 A) may be ac-counted for by assuming that the exchange ions take up coordinate positions between silica-oxygen and water levels or, alternatively, that some of the silica tetrahedra are inverted.

INTRODUCTION

The oscillating-heating method of x-ray powder diffraction was described and the results of a study for making distinctions between different types of chlorites and for distinguishing chlorite from kaolinite were reported at the Third National Clay Mineral Conference (Weiss and Rowland, 1955). The apparatus, Figure 1, has been developed further and the technique has been ex-tended to a number of micaceous minerals. This method consists of oscillating the goniometer over a basal maximum while heating the sample at a constant rate of temperature rise. The position and intensity of the maximum is re-corded while the sample is heated. The present report is concerned with the dehydration of a montmorillonite (Wyoming bentonite) prepared in several monoionic forms by the method of Lewis (1953), and of a Macon County, North Carolina, vermiculite, "Jeffersite," from the American Museum of Nat-ural History, New York.

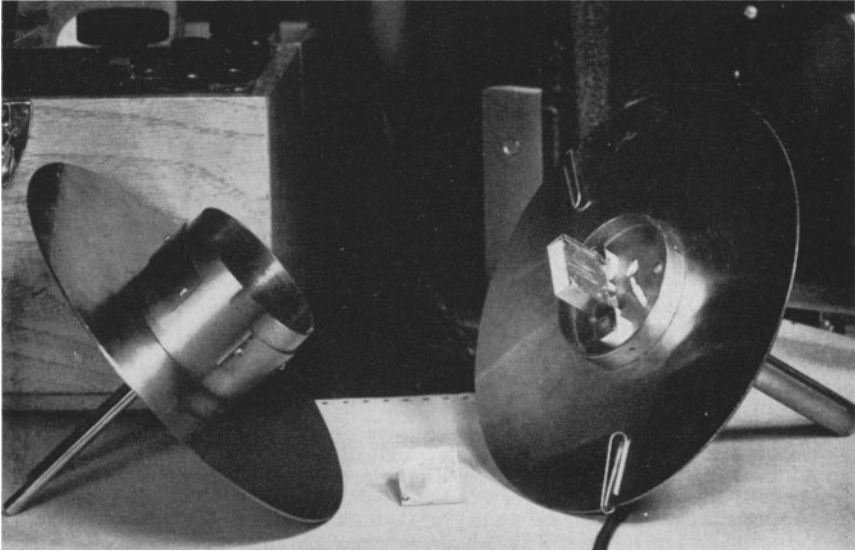For these fine-grained aggregates, only a limited number of orders are easily

---

FIGURE 1. — Oscillating-heating goniometer head showing furnace and thermocouple parts (right), platinum sample holder (center), and cover with beryllium windows and atmosphere control tubes (left).

surveyed at best, and the well-known shrinkage of the hydrated structures introduces such latitude of migration of the diffraction maxima that it is desirable to draw as heavily as possible on comparisons with more extensive data from better-crystallized materials. Especially valuable for the present instance is vermiculite, which permits close analogy with the montmorillonite preparations, and which has been the subject of recent independent detailed structural analyses by Mathieson and Walker (1954) and Grudemo (1954). It is, therefore, possible to choose a relatively limited number of ranges of diffraction angle through which to oscillate, and it becomes unnecessary to prepare separately the large number of specimens which would be required to survey completely the $00l$ reciprocal row line.

The dynamic conditions of observation of the dehydration of the various monoionic montmorillonites permit the discernment of a much closer parallelism between the montmorillonites and vermiculite than was possible when Méring (1946) examined prepared, partially dehydrated Ca-montmorillonites under static conditions.

The shape of the complex structure factor (here called form factor) along the $00l$ pole to montmorillonite layers is known to consist alternately of regions of high density in reciprocal space for which the form factor is positive, and regions of high density for which it is negative. The dynamic conditions sample this form factor normally at reciprocal lattice nodes for any specific fixed structure, and they sample it with reduced efficiency at weighted average positions between nodes when two or more structures coexist. Continuous records are available when the migration of sampling points, occasioned by shrinkage, does

not exceed the bounds of one of the high-density regions of a given sign. This is true in all cases for the first maximum.

EXPERIMENTAL

In Figures 2a, b, and c, are reproduced Cu Kα spectrometer traces from moderately well-orientated aggregates of the several starting materials and the records of the continuing drift of the several first maxima with temperature rise. Figures 3a and b are graphs of the change in 2θ with increasing temperatures. The first vermiculite maximum drifts from about $6.2°2\theta$ to about $7.5°2\theta$ with some loss of intensity until about 75° C, and then regains in intensity as it stabilizes near $7.6°2\theta$, and maintains its character until about 200° C. It then declines and drifts rapidly away to about $8.5°2\theta$, and eventually on to about $9.7°2\theta$. It was established by Mathieson and Walker (1954) that the stable condition around 100° C was a regularly crystalline lower hydrate with a c axis periodicity of about 11.8 A. The present data indicate nearer to 11.5 A at the temperature of stability. Other scans established that integrally spaced higher orders develop through this stable range.

Five of the montmorillonite preparations (Ca^{2+}, Mg^{2+}, Mn^{2+}, Li^+, and the H^+ clay in which it is presumed that substantial rearrangement to provide Al^{3+} exchange ions has occurred) share with the vermiculite the fact that their exchange ions are subject to octahedral coordination. In each of these except Li^+, the first-order maximum near $6°2\theta$ drifts with loss of intensity toward positions near $7.5°2\theta$ where they make slight temporary intensity gains and seem to attain a brief period of stability in a regular configuration. Li^+ which starts at $7.2°2\theta$ immediately gains in intensity and enters a brief period of stability. Supplemental scans again establish the simultaneous development of essentially regularly spaced higher orders.

From this stage each first maximum of these preparations declines more or less gradually in intensity as it drifts to positions characteristic of anhydrides with regular c axis periodicities between 9 and 10 A.

The two larger univalent ion preparations start, in the Na^+ clay, with a regular one-water-layer configuration which shrinks rapidly through a mixed assemblage to a paragonite-like anhydride, and in the K^+ clay, with a mixed assemblage less hydrous than one average full-water-layer which shrinks rapidly to a muscovite-like anhydride.

The vicissitudes encountered in following higher than first-order effects are illustrated in Figures 4 and 5 for Ca-montmorillonite preparations. In the upper scan (Fig. 4) the room temperature $17°2\theta$ maximum, in a region of negative form factor (Fig. 5b), diffuses with increasing temperature and moves off toward an 003 node for the 11.5-A hydrate. This node lies in a region where the form factor is positive (Fig. 5c) and the track is lost. The lower right scan (Fig. 4), beginning at $12°2\theta$ for the position of the 002 node of the 15-A hydrate, develops from diffuse scattering to an 002 node of the 11.5-A hydrate. The diffuse scattering of the 003 node could have been followed to the low-angle side to join this scan near $14°2\theta$ as a continuous record.

The high-density, positive form factor region near $30°2\theta$ (Fig. 5c and d) includes the fifth node for 15-A structures, the fourth node for 11.5-A, and the third node for the 9- or 10-A structures. In the lower left-hand record (Fig. 4)
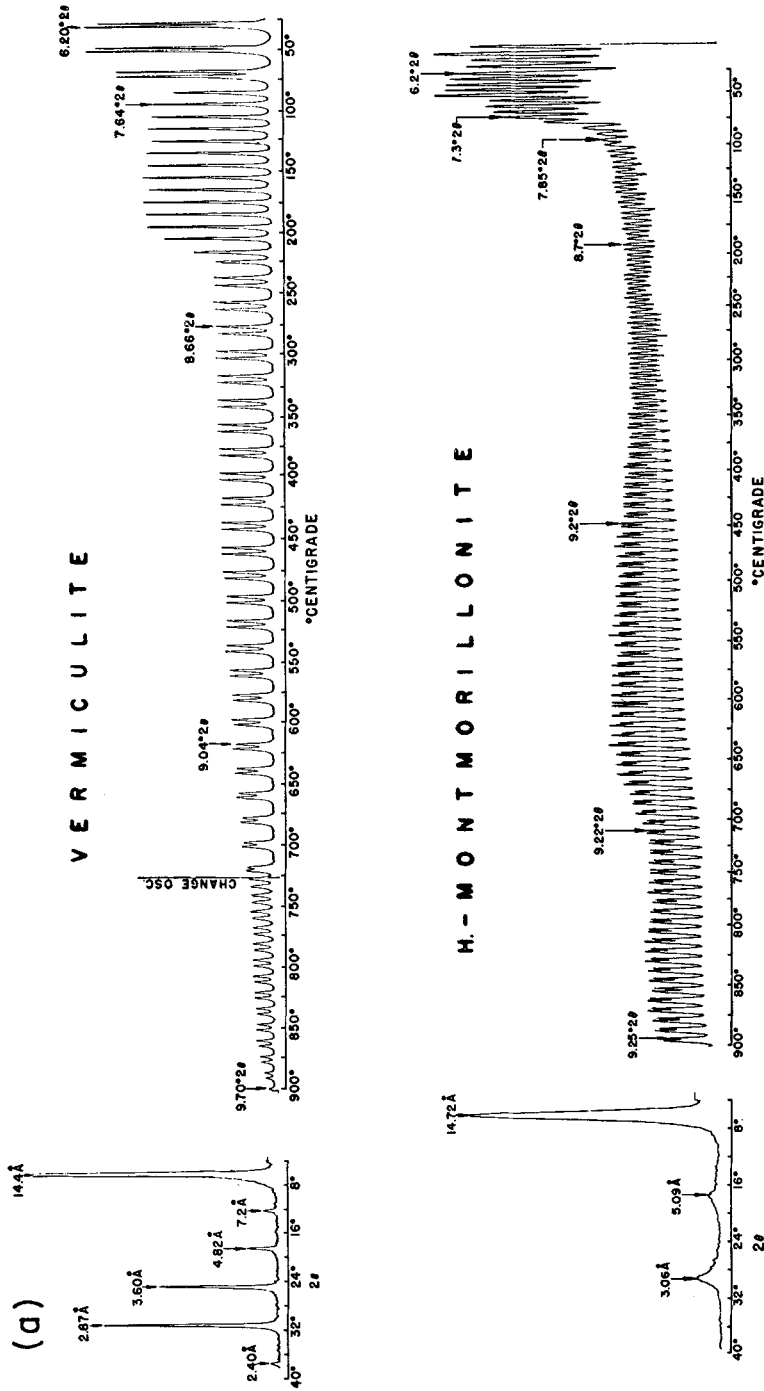
FIGURE 2.— (a). X-ray diffraction patterns and oscillating-heating x-ray powder diffraction diagrams of 001 for vermiculite and hydrogen montmorillonite from room temperature to 900° C at a rate of temperature rise of 5° C per minute.
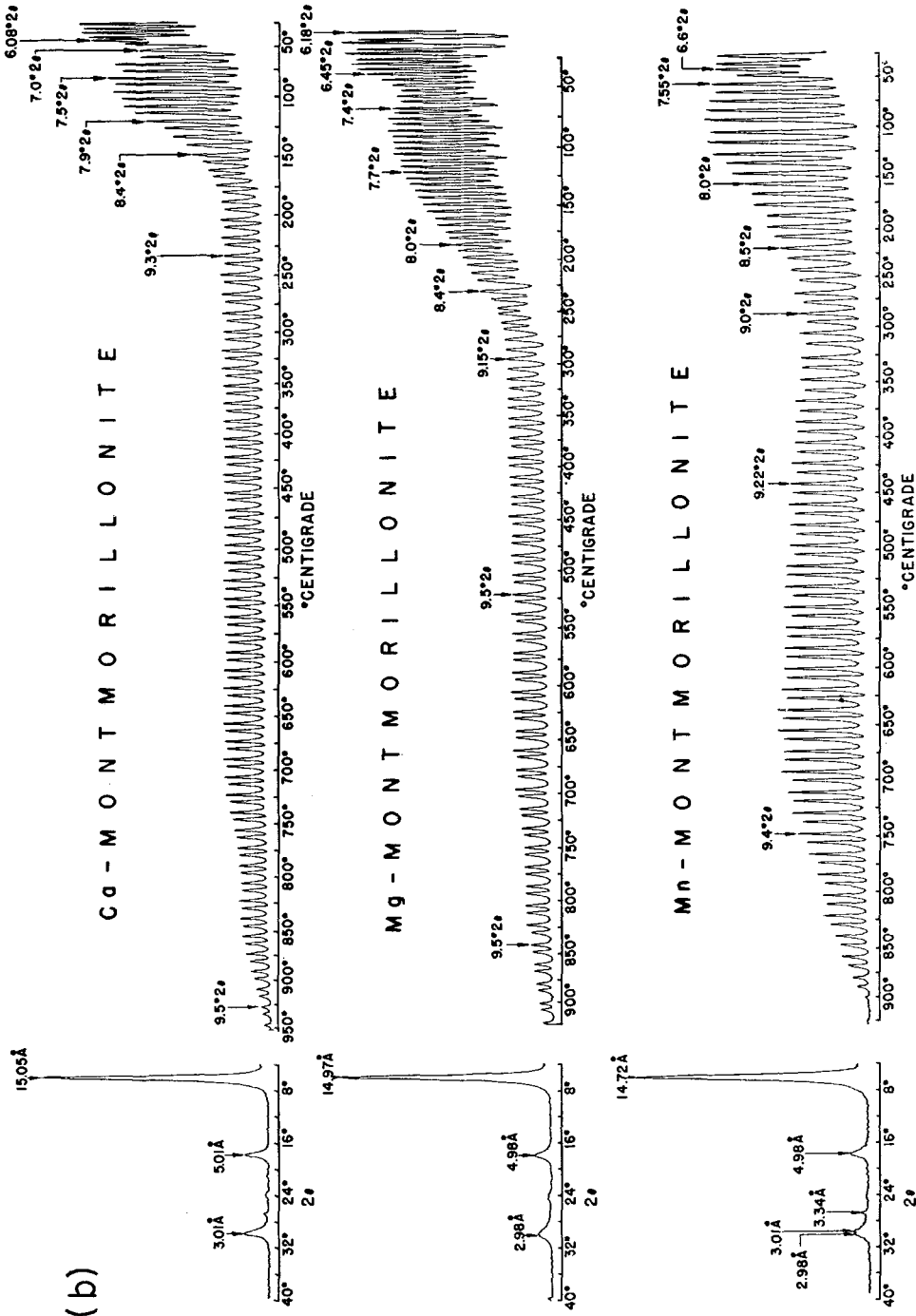
FIGURE 2.— (b). X-ray diffraction patterns and oscillating-heating x-ray powder diffraction diagrams of 001 for calcium, magnesium and manganese montmorillonite from room temperature to 900° C at a rate of temperature rise of 5° C per minute.
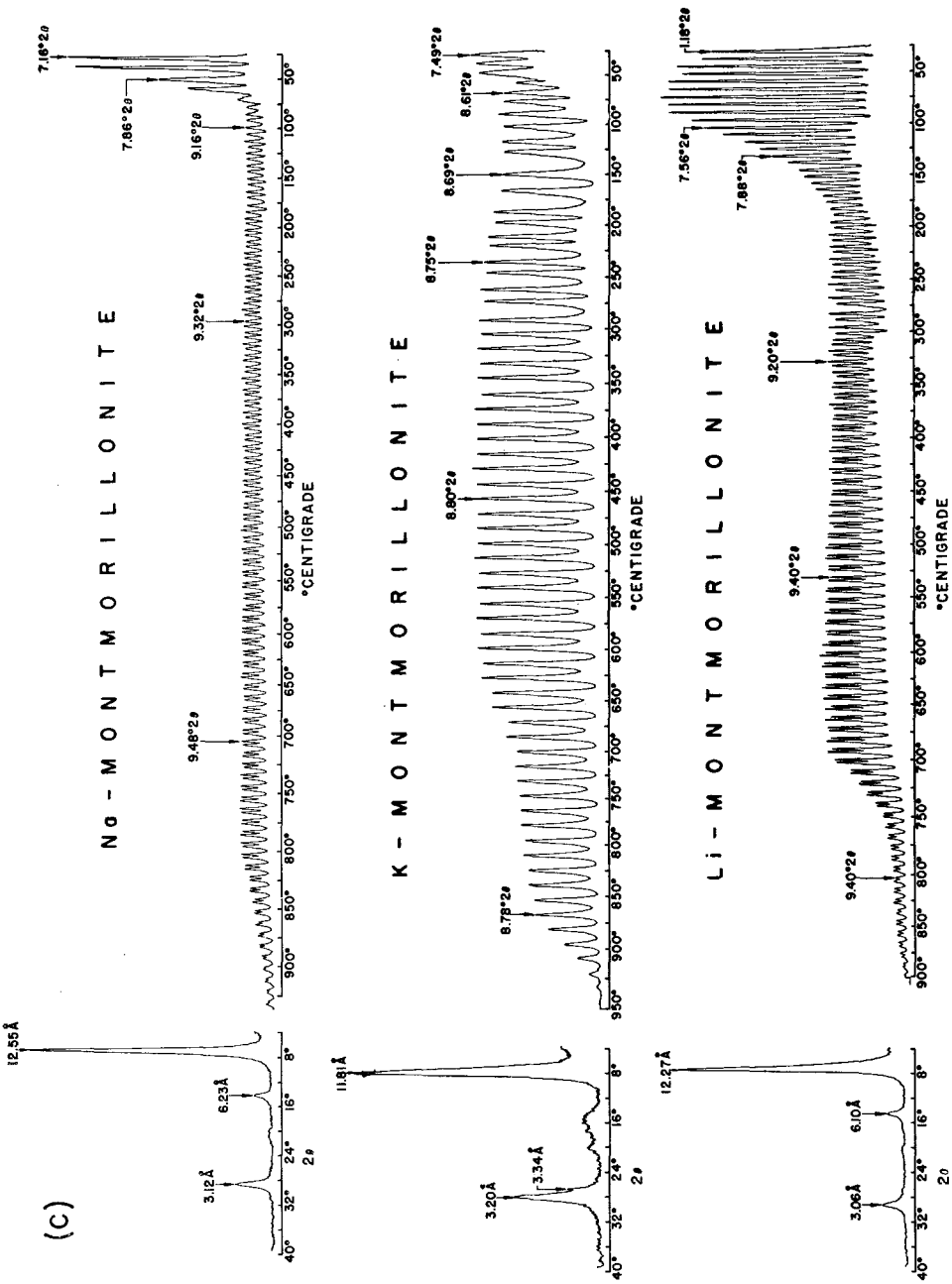
FIGURE 2. — (c). X-ray diffraction patterns and oscillating-heating x-ray powder diffraction diagrams of 001 for sodium, potassium, and lithium montmorillonite from room temperature to 900° C at a rate of temperature rise of 5° C per minute.
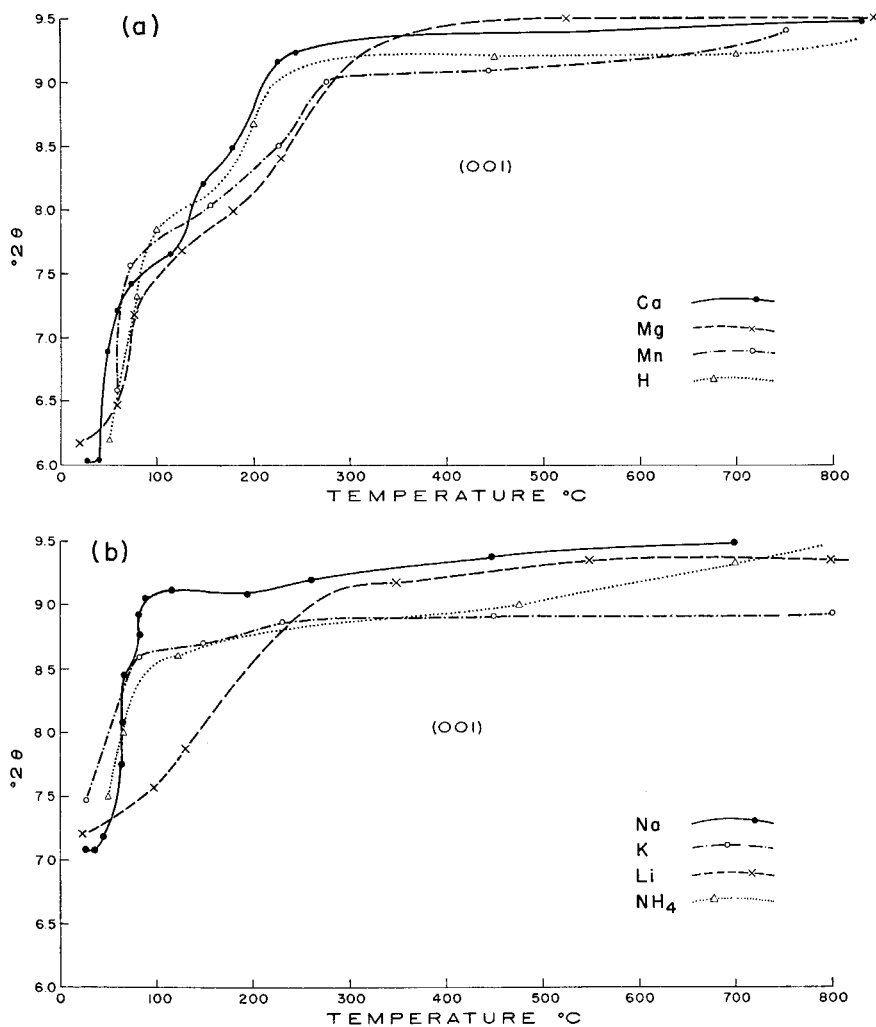
FIGURE 3. — (a). 001 spacing in degrees 2θ for calcium, magnesium, manganese, and hydrogen montmorillonite from room temperature to 800° C. (b). 001 spacing in degrees 2θ for sodium, potassium, lithium, and ammonium montmorillonite from room temperature to 800° C.

the maximum is seen successively to diffuse and migrate toward a higher angle, to sharpen in the stability range of the partial hydrate (about $30°2\theta$), then to diffuse and migrate toward a lower angle, and finally to sharpen and stabilize at a third node for an anhydrous structure.
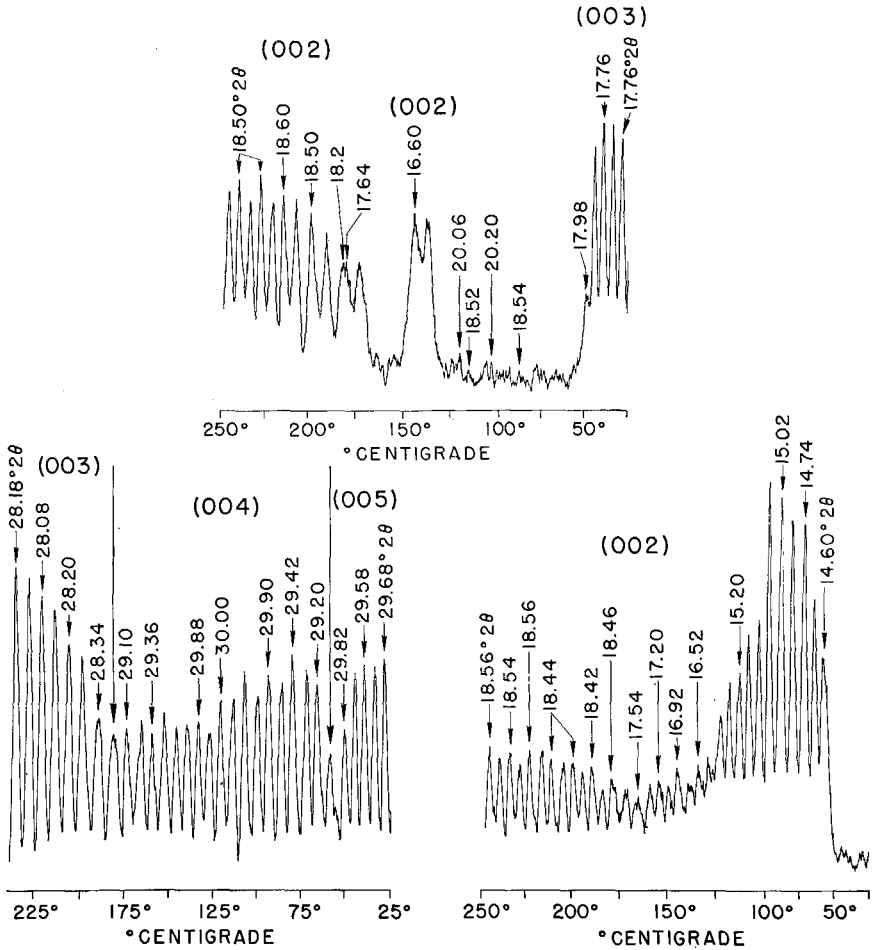
FIGURE 4. — Oscillating-heating diagrams in the 17° and 30°2θ range showing the interrelation of several orders.

DISCUSSION

The five cited preparations with octahedrally coordinating ions may therefore be said to be like vermiculite in the sense that they pass through a lower hydrate stage which is regular, with water content of the order of one layer per cell but distinctly different from the single-water-layer configuration characteristic of Na^+ montmorillonites. This difference is deserving of some speculative discussion.

The general features of the layer-lattice structures have been well established
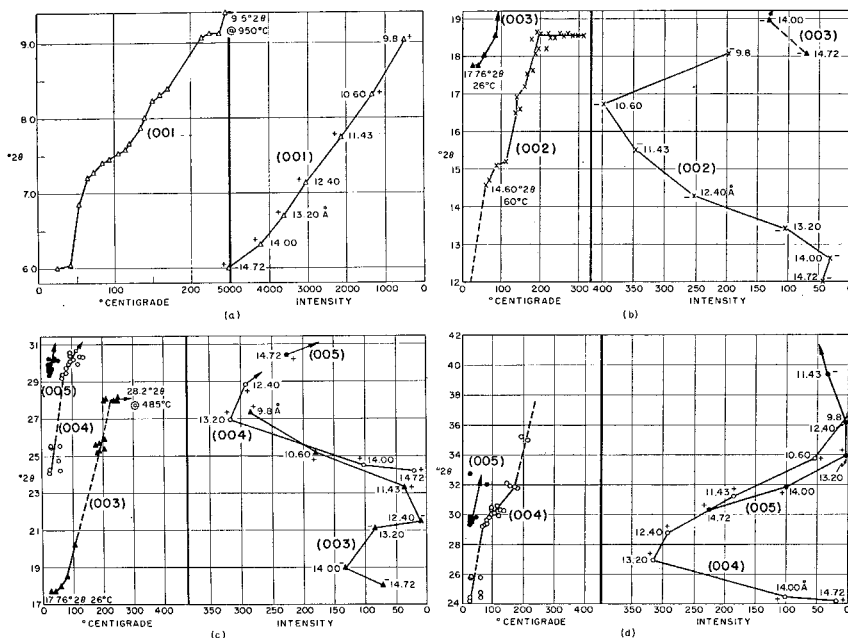
FIGURE 5. — Observed drift, with increasing temperature of the first five orders of a calcium montmorillonite (left) compared with computed intensities (F^2) for these positions (right). The $(+)$ and $(-)$ symbols are the sign of the structure factor (F).

from the early Pauling analyses, and from time to time are intimately confirmed. A most recent valuable study by current procedures is that of Pézerat and Méring (1954). In this present discussion the useful feature is the résumé of common effective thickness of various articulated layers in the direction normal to (001).

All reported instances for tetrahedrally or octahedrally coordinated layers are between 2.1 and 2.2 A for the projected oxygen-to-oxygen or hydroxyl levels, averaging closer to 2.2 A. Levels associated with hydrogen bonding or with van der Waals approaches of oxygen are more of the order of 2.8 A in thickness. The additional space in the mica schemes is that necessary to accommodate the alkalies in their larger coordination polyhedra.

Common complex thicknesses, equivalent to (001) periodicities, are approximately summations of the proper combinations of these increments. For the chlorites and vermiculites a period is made up of four primary bonded increments and two hydrogen bonded $(4 \times 2.2 \text{ A} + 2 \times 2.8 \text{ A} = \text{ca. } 14.4 \text{ A})$; for the single-water-layer configurations of montmorillonite, of three primary and two hydrogen bonded $(3 \times 2.2 \text{ A} + 2 \times 2.8 \text{ A} = \text{ca. } 12.4 \text{ A})$; and for the two-water-layer configurations of combinations of four and two with three and three (ranging from about 14.5 to 15.5A). It is also reported by Walker (1956, these

Proceedings) that vermiculite has the ability to imbibe sufficient water to approximate the three-and-three summation.

The first water loss from vermiculite is accompanied by shrinkage equivalent to one hydrogen-bonded layer thickness, and the shrunken period affords a sequence of higher orders indicative of crystalline regularity. This requires that the remaining water level be asymmetrically disposed, being articulated with its oxygen neighbors on one side into coordination polyhedra about some cation, but retaining a hydrogen-bonded or van der Waals relation with the oxygen neighbors on the opposite side (4×2.2 A $+ 2.8$ A $=$ ca. 11.6 A). A tentative conclusion to this effect was advanced by Mathieson and Walker (1954 a) who suggested that exchangeable magnesium ions assumed coordination positions between oxygen and water levels. The low population of exchangeable magnesium ions hardly seems adequate to so foreshorten so many oxygen-oxygen approaches.

An alternative possibility involves the Edelman-Favajee (1940) disposition of some silica tetrahedra. One analysis of a chloritic mineral in which the occurrence of some silica on the "wrong side" was clearly demonstrated was presented in 1953 at the Second National Clay Conference (Brindley and Gillery, 1954), and several other possibilities were discussed in 1954 at the Third National Clay Conference (Bradley, 1955). It seems possible that the conditions under which a few silicon ions can be activated to pass the barrier presented by a set of the three oxygens to which they are bonded may be considerably milder than is currently assumed.

The second shrinkage, continuing eventually to about 9.1 A (a lesser thickness at elevated temperature than that of talc at room temperature) is also suggestive that some primary bonding exists between each of the four remaining oxygen levels.

The present clays have lower base-exchange capacities, and fewer exchangeable ions, than vermiculite. That montmorillonites also should pass through a stage too foreshortened (somewhat less than 12 A, as compared with the 12.4-A characteristics of Na-montmorillonites) to accommodate van der Waals or hydrogen-bonded association on both sides of the single possible remaining water layer is too great an effect to be attributed to the coordination of exchange ions alone. From four to six octahedral ions per cell are utilized in coordinating the oxygen of the original skeletons into octahedra of 2.2-A height, and less than one-half ion per cell is available to pack the interlayer matter. The conclusion seems inescapable that some silicon occupants of tetrahedra of the original skeleton have been activated to accept one new neighbor from the residual interlayer water, thus taking up positions of the Edelman-Favajee structure. There would presumably be a compensating migration of some H ions into the skeleton, at the expense of the "water," to provide new hydroxyls at both levels.

Such activation of silica to recoordinate (apparently reversibly since this configuration is not easily preserved at room temperature) at the temperature of boiling water is a far more drastic concept than we like. It has come to attention before, however (Bradley and Grim, 1951, p. 192), that some montmorillonites knit through interlayer matter to form eventually cristobalite while others rearrange to form quartz. There seems to be reasonable hope that an entirely satisfactory unified concept of dehydrations eventually will emerge.

REFERENCES

Bradley, W. F., 1955, Structural irregularities in hydrous magnesium silicates: in Clays and Clay Minerals, Natl. Acad. Sci.—Natl. Res. Council Pub. 395, p. 94-102.

Bradley, W. F,, and Grim, R. E., 1951, High temperature thermal effects of clay and related minerals: Amer. Min., v. 36, p. 182-201.

Brindley, G. W., and Gillery, F. H., 1954, A mixed-layer kaolin-chlorite structure: in Clays and Clay minerals, Natl. Acad. Sci—Natl. Res. Council Pub. 327, p. 349-353.

Edelman, C. H.. and Favajee, J. Ch. L., 1940, The crystal structure of montmorillonite and halloysite: Z. Krist. (A), v. 102, p. 417-431.

Grudemo, A., 1954, X-ray examination of the structure of vermiculites: Proc. Swedish Cement and Concrete Res. Inst., no. 22, 56 p.

Lewis, D. R., 1953, Replacement of cations of clay by ion exchange resins: Ind. and Eng. Chem., v. 45, p. 1782-1783.

Mathieson, A. McL., and Walker, G. F., 1954, Crystal structure of vermiculite: Amer. Min., v. 39. p. 231-255.

——, 1954a, Crystal structure of normal and partially-dehydrated Mg-vermiculite (abstract): Acta Cryst., v. 7, p. 631-632.

Méring, J., 1946, The hydration of montmorillonite: Faraday Soc. Proc., v. 42B, p. 205-219.

Pézerat, H., and Méring, J., 1954, The influence of isomorphous substitution on the structural parameters of clays: Clay Minerals Bull., v. 2, p. 156-161.

Weiss, E. J., and Rowland, R. A., 1956, Oscillating-heating x-ray diffractometer studies of clay mineral dehydroxylation: Amer. Min., v. 41, p. 117-126.