

# EFFECT OF HEAT ON VERMICULITE AND MIXED-LAYERED VERMICULITE-CHLORITE<sup>1</sup>

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## ABSTRACT

The position and intensity of the first- and second-order basal spacings of vermiculite and mixed-layered vermiculite-chlorite were measured at intervals of 5° C. to 10° C., while the samples were heated at a rate of 5° C. per minute to 900° C. These data are presented as oscillating-heating *x*-ray diffraction diagrams showing the intensity change with temperature, with important spacing changes indicated, and as graphs showing the change in spacing with change in temperature.

The (001) of vermiculite remains at 14.4 Å to 80° C. On losing one water layer at 80° C., the (001) shifts to 11.5 Å with one-third intensity decrease. At 215° C., the spacing shifts to 10.3 Å, and the intensity decreases about one-half. Above 215° C., the spacing gradually decreases to 9.6 Å at 850° C. At 900° C., the maximum disappears. The weak (002) behaves like the (001).

The intensity of an orthochlorite (001) (14.2 Å) remains constant to 575° C., where it rapidly quadruples, and shifts to 13.8 Å, where it remains to 675° C. The maximum disappears abruptly at 825° C. The (002) (7.1 Å), several times as intense as the (001), remains constant to 575° C., then rapidly disappears as the (001) intensity increases.

A vermiculite from Nottingham, Connecticut, a chlorite-vermiculite mixed-layer material, combines the low-temperature intensity and spacing shifts of vermiculite and the 500° C. intensity increase of chlorite on a reduced scale.

The (001) (14.2 Å) of jefferisite, Westchester County, Pennsylvania, a chlorite-vermiculite mixture, behaves like vermiculite. The (002) behaves like the (002) of chlorite.

## INTRODUCTION

The *x*-ray diffraction powder patterns and oriented aggregate diagrams for chlorites and vermiculites have the positions of the prominent orders of the basal spacing in common, beginning with the first order at approximately 14 Å (Fig. 1). The principal difference in the patterns is that the 14-Å maximum for vermiculite is more intense than any of the succeeding orders, while the intensity of the 14-Å maximum of chlorite is not the strongest, and the relative intensities of the other orders vary considerably. In the interstratification of chlorite and vermiculite, either as mixtures or mixed layers, it is nearly impossible to determine the components until both are relatively abundant. Hendricks and Jefferson (1938) emphasized the virtual impossibility of distinguishing a relatively small number of chlorite layers in a vermiculite by means of *x*-ray dif-

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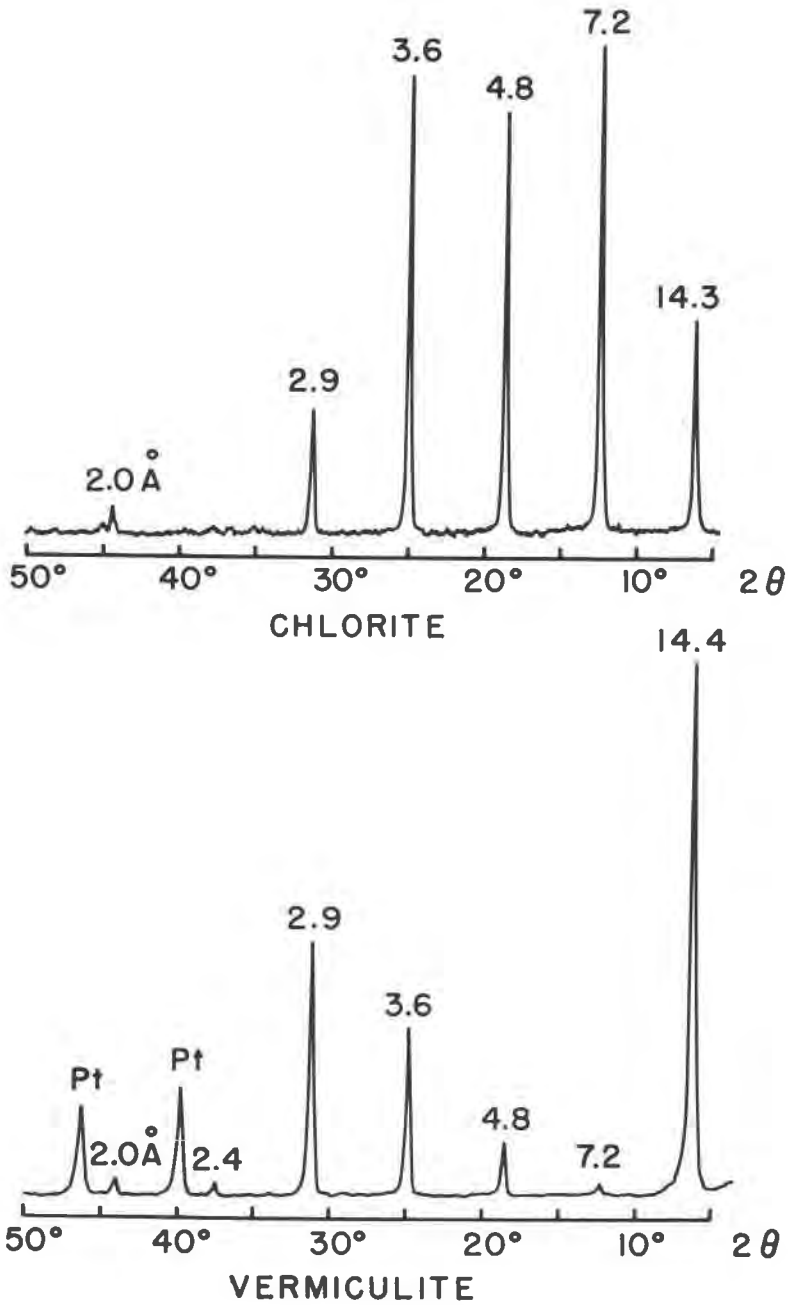


FIG. 1. X-ray diffraction powder diagrams of oriented flakes.

fraction powder patterns. Mixtures or mixed layers of vermiculite-chlorite are probably a common occurrence in nature, and Lippman (1954) and Bradley and Weaver (1956) have described a regular 1:1 mixed-layered chlorite-vermiculite occurring in sediments of clay size. Chlorite and vermiculite have been reported frequently as common constituents of soils and shales.

The effect of heat on vermiculite and mixed-layered vermiculite-chlorite and the accompanying stages of dehydration have been reported from *x*-ray diffraction powder patterns of materials heated and sealed in capillaries (Barshad, 1950). However, the temperature of the changes in the diffraction pattern has been indefinite as a result of the difficulty in determining the correct temperature to which the material must be heated to best illustrate a change in spacing or intensity.

The structural schemes of vermiculite and chlorite are very similar. The principal difference is the abundance and environment of the interlayer magnesium cations. The interlayer organization of chlorite resembles that of brucite, and the structure is fixed in spacing. The interlayer magnesium in vermiculite is less abundant, is associated with water, and the water is probably arranged octahedrally. Gruner (1934), from chemical and *x*-ray diffraction data, defined vermiculite specifically as a mineral. He showed that some materials classified as vermiculite were mixed-layer mica-vermiculite structures and he described hydrobiotite as a mica-vermiculite mixed layer in various ratios.

G. F. Walker (1951) considered the interlayer water in vermiculite as "bound water" and "unbound water." He found that about one-half the water is removed at 110° C. because on heating a sample to 110° C. and immediately sealing it in a capillary the *d* (001) spacing is 11.8  $K\alpha$  units, a collapse equal to one layer of water. Walker lists the thickness of water layers of a vermiculite saturated with various cations. The variation in thickness associated with the different cations suggests strongly that the hydration of the cation is the controlling influence on the *c* spacing.

Barshad (1950) has shown that, with bivalent cations, the basal spacing is that expected from a double layer of water and, with monovalent cations, it is as with a single layer of water. Certain monovalent cations, however, apparently require no interlayer water; for example, potassium, rubidium, and cesium.

These observations, in general, comply with the limitations imposed by the ionic radii of the cations on their coordination and the accumulation of water.

It is not intended to discuss details of the configuration of the water layers except to show that more than one condition exists, and that mag-

nesium, the common cation in natural vermiculites, dehydrates in two steps. The stages of dehydration of vermiculite are well known and the existence of vermiculite-chlorite mixtures and mixed-layered material have been documented.

#### EXPERIMENTAL METHOD

The difficulty in the study of vermiculite or a mixture of vermiculite and another material has been the rapid dehydration of vermiculite after it has been heated up to temperatures of as much as 500° C. This difficulty has been overcome by the oscillating-heating method, which enables the measurement of the position and intensity of the interplanar spacings while the sample is heated at a rate of 5° C. per minute from room temperature to 900° C. With the same apparatus, the complete diffraction pattern may be obtained at any temperature within this range. The oscillating-heating method gives detailed information on the temperature and the change in spacing and intensity at the time of dehydration.

The oscillating-heating diagrams are obtained by using a furnace which is mounted on the Norelco Diffractometer in place of the standard sample holder. Many details of the *x*-ray diffractometer furnace were adapted from a furnace built at the U. S. Naval Research Laboratory by Birks and Friedman (1947). The device consists of a cylindrical stainless steel shell with beryllium windows for the passage of the *x*-ray beam. The shell is attached to a spindle which fits the Norelco *x*-ray diffractometer. Within the shell, a platinum-13-per cent-rhodium wire heating element encased in a refractory is positioned in a platinum-13-per cent-rhodium holder. The specimen is sedimented on a platinum plate which lies on top of the heating element. The sample is set at the correct position for diffraction by means of adjusting screws.

Because the plate upon which the sample is sedimented is platinum, the exact temperature at the surface of the platinum plate and its contact with the specimen can be measured by welding the platinum-rhodium lead of a thermocouple in the center of the sample holder. The temperatures measured are those obtained at the lower surface of the sample and may be slightly higher than the temperature of the surface of the specimen. The thickness of the specimen sedimented is almost negligible, so it is unlikely that a large temperature gradient exists from the top of the sample to the position of the thermocouple. The rate of temperature rise is controlled by a Leeds and Northrup Rate Controller, and the temperature of the sample is read directly on a Leeds and Northrup potentiometer.

Four samples, a pure vermiculite, an orthochlorite, a chlorite-vermicu-

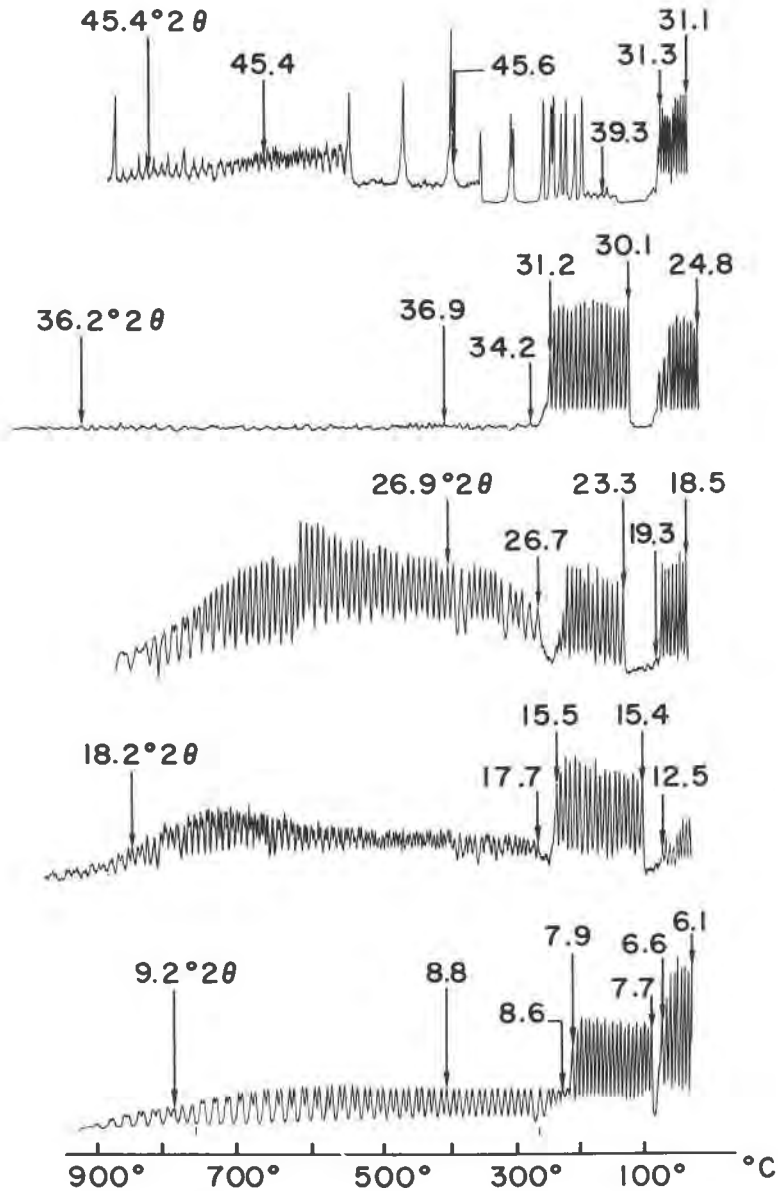


FIG. 2. Oscillating-heating diffraction powder diagrams of vermiculite. From bottom to top the first through fifth orders of (001).

lite mixed layer, and a chlorite-vermiculite mixture, have been chosen to illustrate the power of the oscillating-heating  $x$ -ray diffraction powder method. Cu  $K\alpha$  radiation was used.

#### VERMICULITE

The oscillating-heating  $x$ -ray diffraction powder diagrams of the first five orders of the basal spacing of a vermiculite from Macon County, N.C. (United States National Museum R-4620) are shown in Fig. 2.  $X$ -ray diffraction powder patterns at room temperature, 100° C., and 300° C. of this vermiculite (Fig. 3) show the position to which the basal orders have shifted and the relative intensity of the maxima at these

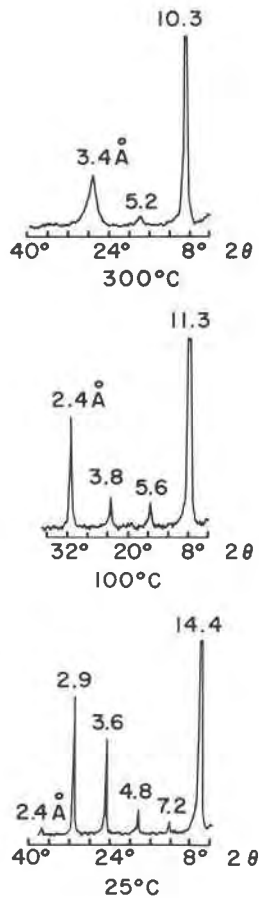


FIG. 3.  $X$ -ray diffraction powder diagrams of oriented flakes of vermiculite obtained at 25° C. (bottom), 100° C. (middle), and 300° C. (top).

temperatures. The temperature of these shifts and the intensity changes are shown in the oscillating-heating diagrams of Fig. 2. A plot of the change of spacing with temperature is shown in Fig. 4. Because the complex structure factor for vermiculite is alternately positive and negative (Mathieson and Walker, 1954), continuous scans of maxima in ordinal sequence reduce to zero intensity at the positions of sign changes. Mathieson and Walker's signs are indicated in the margin, and the approximate positions of pertinent sign changes are indicated by open

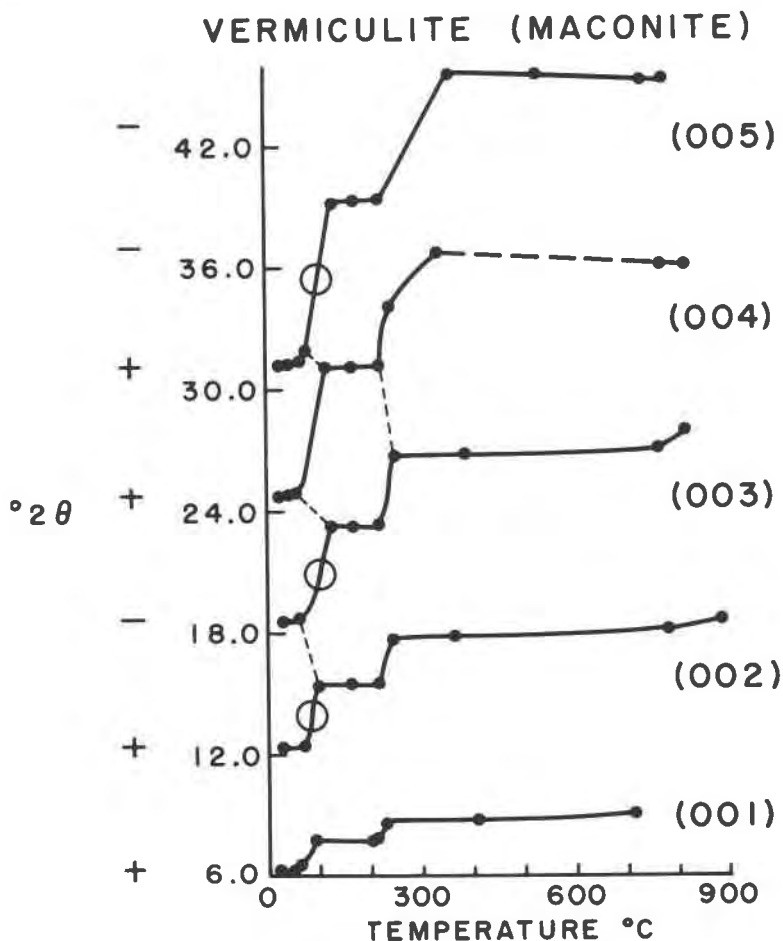


FIG. 4. Temperature versus  $2\theta$  of the first through fifth orders of (001) for vermiculite. Signs for structure factor are indicated at the left. The circles represent approximate positions of pertinent sign changes. Dashed lines indicate trends of diffuse maxima on dehydration.

circles in Fig. 4. Dashed connections indicate the trends of diffuse maxima from mixed configurations within a region of given sign during transitions from one to another of successive hydrates.

The  $x$ -ray diffraction powder pattern of vermiculite, Fig. 3, at 25° C. shows the first five integral orders of (00 $l$ ) beginning at 14.4 Å. At 100° C., there are four integral orders of (00 $l$ ) beginning at 11.3 Å. At 300° C., there are three nearly integral orders of a 10.3-Å spacing. The most obvious shifts in intensity are the increase and decrease of the second maximum. On oscillating-heating diagrams, Fig. 2, a record of the temperature of the changes in intensity and spacing, 14.4-Å (6.14° 2 $\theta$ ) maximum at the bottom, declines in intensity at 80° C. This is followed by a less intense plateau which ends with another abrupt decline in intensity at 215° C. Between 215° C. and 725° C., there is little change in intensity. There is another decline at 725° C. and the maximum disappears at 900° C. The spacing between 25° and 80° C. is fairly constant, 14.4 Å to 13.3 Å (6.14°–6.62° 2 $\theta$ ). The decreases in intensity at 80° C. and 215° C. are accompanied by shifts in the spacing from 13.3 Å to 11.5 Å (6.62°–7.72° 2 $\theta$ ) and from 11.2 Å to 10.3 Å (7.89°–8.59° 2 $\theta$ ) respectively. From 215° C. up to the temperature of collapse of the maximum (900° C.) 9.6 Å (9.21° 2 $\theta$ ), the shift in spacing is gradual. The oscillating-heating patterns of the second- and third-order maxima follow the decreases in intensity of the first maximum except in the range between 75° C. and 125° C. where maxima are migrating through positions of zero amplitude in the structure factors. There are some differences in intensities of the maxima, such as the increase in intensity of the second in the negative field. The three successive third orders all tend to be equally intense. The fourth maximum also follows the changes in intensity of the first maximum and, like the second and third maxima, is very weak between 75° C. and 125° C. Above 225° C., the maximum again becomes very weak. The fifth maximum is identical with the others with regard to the temperature at which changes in intensity take place. Above 125° C., the maximum is very weak and also is obscured by the presence of platinum lines from the specimen holder. Computed values of the intensity of the second through fifth maxima indicate that the expected intensity between 80° C. and 125° C. is too weak to be recorded by this  $x$ -ray diffractometer.

Two stages of dehydration of vermiculites are well shown when the data from the oscillating-heating diagrams are plotted as in Fig. 4. The spacing is nearly constant from 25° C. to 80° C. and from 100° C. to 215° C. The changes in spacing are abrupt and sharp with only a slight decrease in spacing towards the end of each stage of dehydration. Walker (personal communication) has pointed out that there is a shift in spacing



at a temperature lower than 80° C. from 14.8 Å to 14.4 Å. So trivial and so transient a state is not readily observed by the present method.

## LEUCHTENBERGITE

The oscillating-heating x-ray diffraction powder diagram and the x-ray diffraction pattern of leuchtenbergite (U. S. National Museum No. R-4520) from Montana are shown in Fig. 5. A graph of  $2\theta$  versus

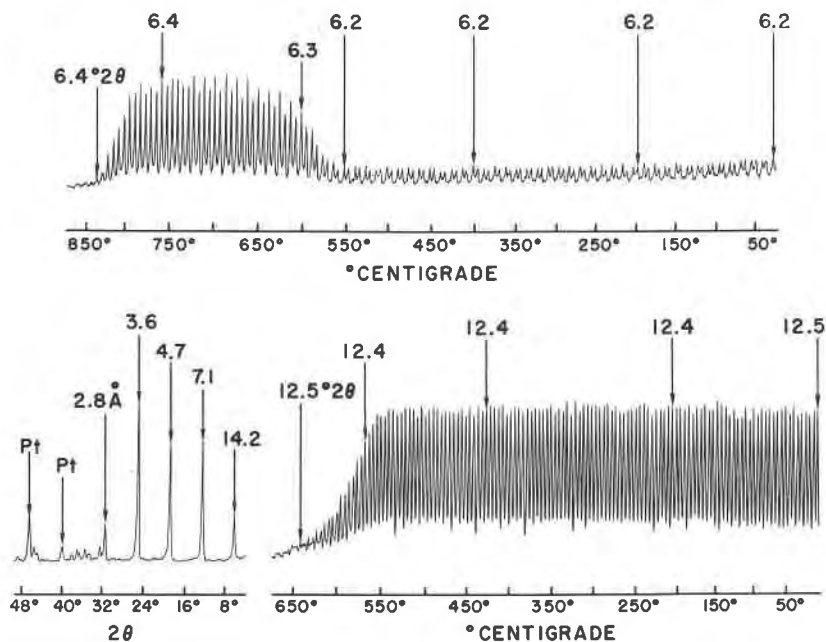


FIG. 5. Oscillating-heating diagrams of first and second basal orders of leuchtenbergite. X-ray diffraction powder diagram of oriented flakes, lower left.

temperature for the first and second basal maxima of leuchtenbergite is shown in Fig. 6.

Unlike vermiculites, the chlorites do not undergo a water loss at low temperatures. However, the first-order basal diffraction maximum of chlorites increases very rapidly in intensity at about 575° C. This is accompanied by an equally rapid decrease in intensity of the second-order basal maximum. A shift in spacing from 14.2 Å to 13.8 Å ( $6.22^\circ 2\theta$  to  $6.35^\circ 2\theta$ ) accompanies the rapid increase in intensity. Any migration of the position of the second order is clearly less than would exactly correspond to the first order ( $12.41^\circ 2\theta$  to  $12.48^\circ 2\theta$ ). The rapid increase in intensity of the first order and the rapid drop-off of intensity of the

second order have been attributed to the reorganization of the inter-layer "brucite," and the changes in basal spacing and intensity occur simultaneously (Brindley and Ali, 1950) for the first and second order of orthochlorites, such as clinoclors and leuchtenbergite. In other chlorites, the changes are less abrupt and may extend over a range of temperature (Weiss and Rowland, 1956).

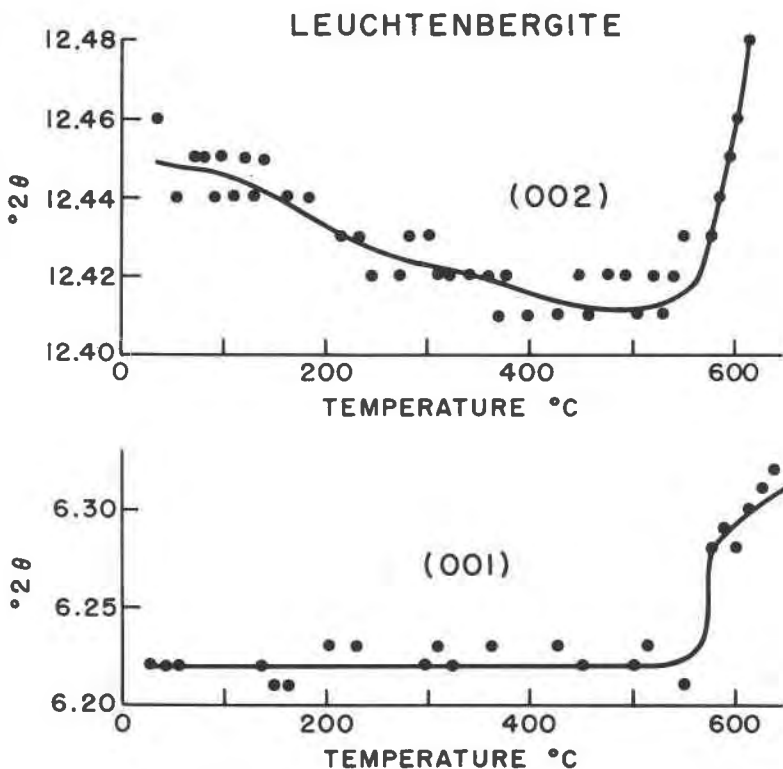


FIG. 6. Temperature versus  $2\theta$  of first and second basal maxima of leuchtenbergite.

#### VERMICULITE-CHLORITE MIXED LAYER

The oscillating-heating  $x$ -ray diffraction powder diagrams of the 14-Å and 7-Å maxima and the  $x$ -ray diffraction powder pattern of the prominent basal maxima of a vermiculite from Nottingham, Chester County, Pennsylvania (Harvard Museum No. 102186) are shown in Fig. 7. The relative intensities of the maxima are not like those for a pure vermiculite or for a chlorite. The low-temperature changes on the oscillating-heating diagram of the 14-Å maximum are characteristic of vermiculite. However, the spacing shift is not at all like a vermiculite. At 525° C., the

maximum increases in intensity, which is characteristic of chlorite. This basal maximum (001) has the characteristics of both chlorite and vermiculite. This is also evident in the 7.2-Å oscillating-heating diagram. This combination may be explained by mixed layering. The 14-Å maximum shifts from 14.4 to 13.9 Å ( $6.13^\circ 2\theta$  to  $6.34^\circ 2\theta$ ) at  $100^\circ$  C. Between  $525^\circ$  C. and  $750^\circ$  C., the shift is from 13.9 to 13.6 Å ( $6.36^\circ 2\theta$  to  $6.50^\circ 2\theta$ ). The differences in spacing are indicative of a vermiculite-chlorite mixed-layer material containing appreciable chlorite.

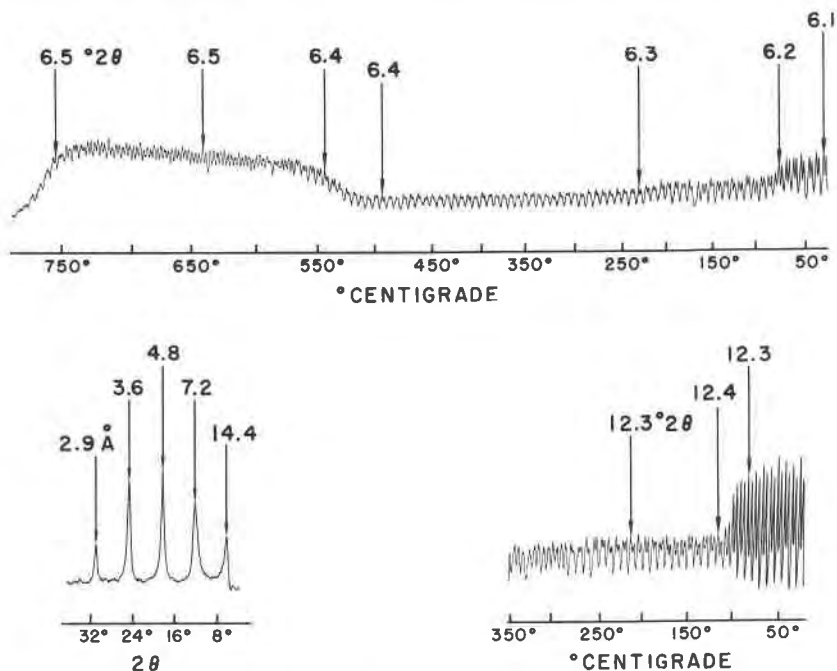


FIG. 7. Oscillating-heating diagrams of first and second basal orders of Nottingham vermiculite. X-ray diffraction powder diagram of oriented flakes, lower left.

Plots of  $2\theta$  versus temperature for the first- and second-order basal maxima are presented in Fig. 8. A comparison of these plots with Fig. 6 and Fig. 4 shows the effect of a combination of chlorite and vermiculite in each of the two basal maxima.

#### VERMICULITE-CHLORITE MECHANICAL MIXTURE

The oscillating-heating x-ray diffraction diagrams and the x-ray diffraction powder pattern of jefferisite from Westchester County, Pennsylvania (American Museum, New York) are shown in Fig. 9. Jefferisite is a trade name applied to vermiculite. Gruner (1934) examined material

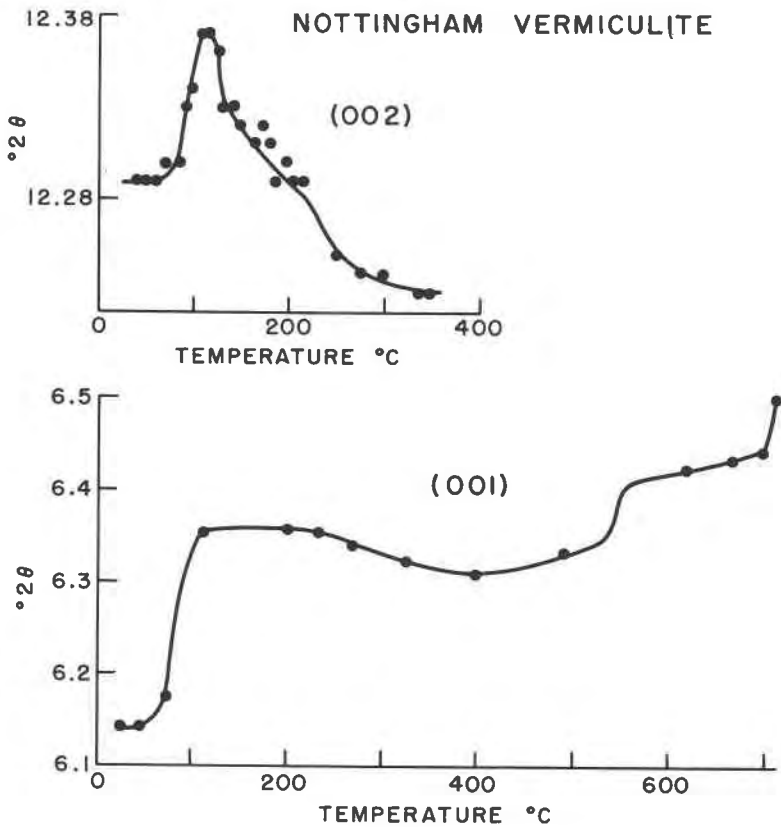


FIG. 8. Temperature versus  $2\theta$  of first and second basal orders of Nottingham vermiculite.

from Brinton's quarry, Westchester, Pennsylvania, which consisted of mixed vermiculite-mica layers. Walker (1951) reports no contamination by mica layers in the vermiculite sample he examined from Westchester, Pennsylvania, and he lists the relative intensities of the first five orders of the basal spacing as being 10, 2, 0.5, 6, and 4. The present jefferisite is obviously a different material than Walker studied. Walker also reported that at  $200^{\circ}\text{C}$ . and  $500^{\circ}\text{C}$ . the vermiculite he examined still had a strong maximum at  $14\text{ \AA}$ . The relative intensities of the first five orders of the basal spacing as reported by Walker do not agree with the spacing reported here for a pure vermiculite. For example, the relative intensities of the Macon County vermiculite shown in Fig. 3 are 10, 0.5, 1, 3, and 6. The relative intensities of the basal maxima of jefferisite indicate that another material is contaminating the vermiculite. Also the  $3.63\text{-\AA}$  maximum is broad, which indicates the presence of another basal

maximum overlapping the 3.63-Å spacing. The oscillating-heating *x*-ray diffraction diagrams indicate that this material is a mechanical mixture of vermiculite and a chlorite. The diagram for the 14-Å maximum (Fig. 9 top) shows intensity losses and spacing changes at temperatures similar to those for a pure vermiculite. An oscillation over only this maximum would indicate that the material is a pure vermiculite. However, the oscillation over the 7-Å spacing is typical of a chlorite rather than a

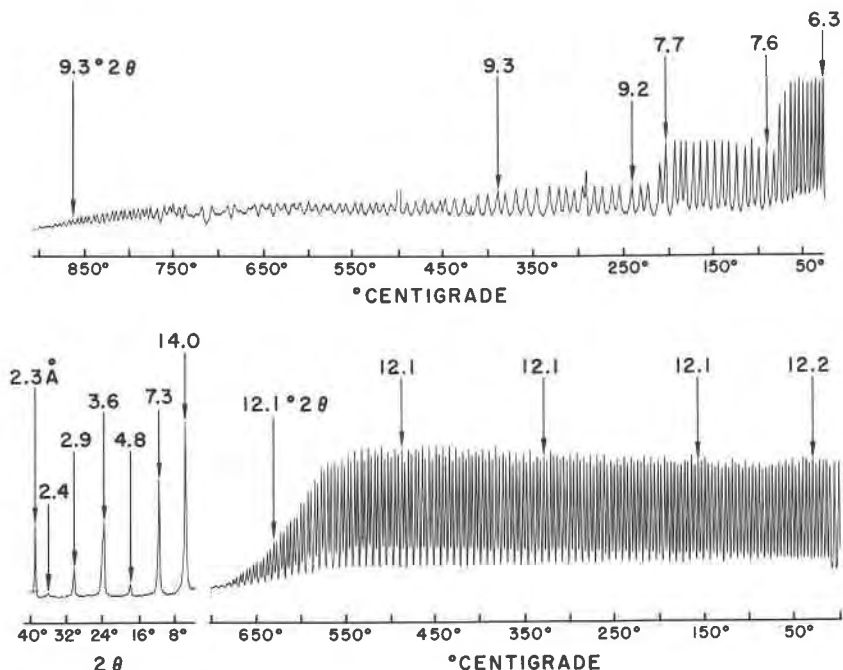


FIG. 9. Oscillating-heating diagrams of first and second basal orders of jefferisite. X-ray diffraction powder diagram of oriented flakes, lower left.

vermiculite. The shift is toward a slightly larger spacing rather than a collapse to a 4.8-Å spacing. The decrease in intensity does not take place until approximately 550° C. and the maximum is not lost entirely until a temperature 660° C. is reached. The second-order basal maximum of a pure vermiculite follows the temperatures of decrease in intensity and the integral shifts of the first-order basal spacing. It is apparent that this jefferisite 7-Å maximum results from packets of a substantial number of contiguous chlorite layers. The temperature versus  $2\theta$  data, Fig. 10, for the jefferisite oscillating-heating diagram confirms the presence of vermiculite in segregated packets of layers in the (001) curve and chlorite, rather than vermiculite, in the (002) curve.

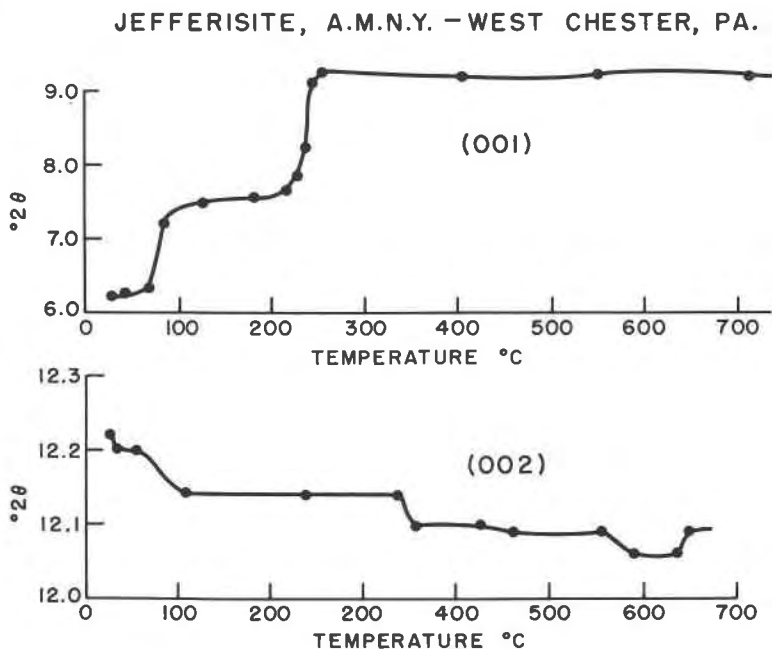


FIG. 10. Temperature versus  $2\theta$  of first and second basal orders of jefferisite.

#### SUMMARY

X-ray powder diagrams obtained by the oscillating-heating method have been used to demonstrate the temperature at which changes in interplanar spacing and intensity of the basal orders of pure vermiculite and chlorite take place. The differentiation between interstratified layers of vermiculite and chlorite and a mechanical mixture of vermiculite and chlorite also have been shown by the oscillating-heating method.

A pure vermiculite is characterized by two marked low-temperature intensity changes and another slight change, all of which are the result of dehydration. The dehydration at 80° C. is accompanied by a change in spacing of approximately 2.9 Å and the loss in intensity at 215° C. is accompanied by a further change in spacing of 1.1 Å. The shift in spacing at 80° C. is comparable to the thickness of one water layer. The structural implications have been discussed separately by Mathieson and Walker (1954) and by Rowland, Weiss, and Bradley (1956). For description purposes, it is sufficient to note that all orders of the basal spacing of vermiculite shift integrally with the first-order spacing, and the oscillating-heating method shows changes in intensity for these basal orders at any given temperature between 25° C. and 800° C.

The only apparent difference between a chlorite and vermiculite as indicated by *x*-ray diffraction powder patterns of oriented aggregates is the relative intensities of the diffraction maxima. The order of relative intensities for vermiculite is as follows: The first-order basal spacing is very strong, the second-order basal spacing is very weak, and each succeeding basal spacing increases in intensity until the fifth order which is about one-half as intense as the first order. Any variation in the relative intensities of the vermiculite maxima indicates the presence of a contaminant. This contaminant may be in the form of a mechanical mixture, or it may be extraneous layers interstratified with the vermiculite. Variations in the relative intensities of chlorite, as recorded by *x*-ray diffraction powder diagrams, may differ considerably without the presence of any contaminant in the form of a mixture or interstratified layers. The substitution of iron in the octahedral sites may reduce the intensity of the first-, third-, and fifth-order basal spacings greatly, even to the extent that the first-order spacing may be extinguished almost completely and still the material would be classified as a chlorite (Weiss and Rowland, 1956).

The oscillating-heating *x*-ray diffraction powder diagrams of most chlorites show no low-temperature intensity losses. The intensity is constant from 25° C. to 550° C. At 550° C. there is an abrupt increase in intensity of the first-order basal maximum accompanied by a slight shift in spacing. This intensity increases continuously up to approximately 600° C. and the maximum collapses near 800° C. The total shift in spacing of the first-order basal maximum of chlorite is approximately 0.4 Å. The diagram of the second order of the basal spacing also is different from that of a vermiculite. There is no decrease in intensity until approximately 550° C., and in the case of the leuchtenbergite, the maximum collapses at approximately 600° C. There is very little shift in spacing of this second-order basal maximum.

The *x*-ray diffraction powder pattern of mixtures of the two different minerals which share the same angular positions of diffraction maxima but make differing intensity contributions, as do chlorite and vermiculite, tends toward a pattern with each maximum having equal intensity. Where the *x*-ray diffraction powder diagrams obtained at room temperature give a series of relative intensities for the basal spacings that are not typical of a vermiculite or of a chlorite, the sample may be a mechanical mixture or it may be a mixed layering of vermiculite-chlorite. It has been observed that if the material is mixed-layered, the basal maxima oscillating-heating diagrams will have characteristics between vermiculite and chlorite. This is the case with the Nottingham vermiculite which has the two low-temperature intensity losses due to

the dehydration of the vermiculite layers as well as the rise in intensity at 525° C. which is typical for chlorite layers. Also, the extent of collapse of the 14-Å spacing is greater than for chlorite alone and less than for vermiculite alone. The oscillating-heating *x*-ray diffraction diagram of the 7-Å spacing has the low-temperature dehydration for vermiculite and then a constant intensity up to the temperature of the collapse of the maximum. The shift in spacing of the Nottingham material is more like chlorite than vermiculite. Mechanically mixed cases are demonstrated by following separately maxima that are characteristic of one or the other pure component.

*X*-ray diffraction powder diagrams obtained by the oscillating-heating method clearly show differences between vermiculite, chlorite, and mixtures of these two materials. The temperatures of the stages of dehydration and the shifts in spacing at these stages of dehydration are well defined on the diagrams. The possibility of inconclusive results because of the rapid dehydration of vermiculite layers is avoided by the oscillating-heating method of *x*-ray analysis.

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*Manuscript received April 23 1956*