# OSCILLATING-HEATING *X*-RAY DIFFRACTOMETER STUDIES OF CLAY MINERAL DEHYDROXYLATION[1]

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## ABSTRACT

With an oscillating-heating *x*-ray-diffraction technique the position and intensity of an *x*-ray diffraction maximum may be followed continuously while a powdered sample is heated at a regular rate of temperature rise (5° C. per minute). The sample is sedimented on a platinum slide mounted in a furnace designed to fit the horizontal shaft of the North American Philips X-ray Diffractometer. The diffractometer is set with the maximum to be followed at the center of one-half degree $2\theta$ oscillation. After heating and oscillating the tops of the recorded series of peaks indicate position and intensity. The bottoms represent the background which is very sensitive to position changes.

Typical oscillation-heating patterns of basal spacing maxima for Georgia kaolinite, a Vermont chlorite, a clinochlore, and sheridanite are presented. The kaolinite (001) remains constant at 12.32 $2\theta$ until it collapses at 525° C. The chlorites (002) shift from 12.55° $2\theta$ to 12.42° $2\theta$ and begin to collapse simultaneously with the intensity increase of the (001).

Sheridanite (001) increases abruptly at 575° C. and collapses at 850° C. after shifting from 6.28° to 6.49° $2\theta$. Clinochlore follows a similar pattern. The (002) collapses abruptly at 575° C. Vermont chlorite (001) begins the intensity increase at 600° C., is greatest at 780° C., begins to collapse at 840° C., and is collapsed at 910° C. after shifting from 6.28° $2\theta$ to 6.52° $2\theta$. The (002) collapse begins at 600° C. and is complete at 910° C. These differences may be related to the iron content of the brucite layer.

## INTRODUCTION

The *x*-ray diffraction technique described in this paper fills a gap in the available methods for distinguishing by *x*-ray diffraction between two similar but slightly different materials. It has long been the practice among investigators to apply the principle, "if it is solid, heat it, and if it is liquid, freeze it," to difficult diffraction problems. Stepwise heating often loses the beginning of phase changes, the fine detail of which is important to the final analysis. Actually, the real need is a method for obtaining a complete diffraction pattern instantaneously at any temperature; but for reasons of geometry and sensitivity of the registering devices for the scattered *x*-rays, such a method is not feasible presently. However, by oscillating the diffractometer over a sufficient number of diffraction maxima while the temperature is increased at a regular rate, a series of diagrams may be obtained which represent the diffraction pattern at any temperature within the range. This technique can be extremely useful with many materials. Here it has been applied to three

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chlorites and a kaolinite because of their importance in fine grained sediments. The chlorites, with the great intensity increase of the (001) maximum, make a most spectacular demonstration of the ability of the heating-oscillation technique to furnish a continuous record of changes in the diffraction pattern at every temperature within the range.

## Description of Apparatus

The diffractometer furnace and the oscillation technique were developed at the Shell Development Research Laboratory. Many of the details were adapted from a furnace built by Birks and Friedman (1947) at the U. S. Naval Research Laboratory.[4] The furnace, shown ready for mounting in Fig. 1, consists of a brass cassette enclosing a cylindrical nickel shield. Openings in the cassette and the shield are aligned for the passage of the *x*-ray beam. A platinum case fastened inside the nickel shield holds the furnace and the sample.

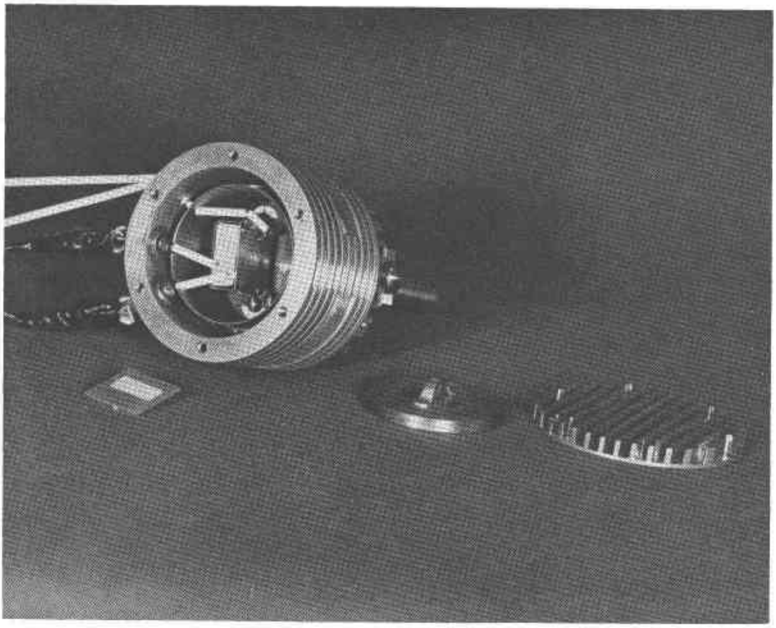

Fig. 1. Assembled view of heating-oscillating furnace.

The heating element consists of No. 30 *B* and *S* gauge 87 per cent platinum, 13 per cent rhodium wire which is wound on two-hole, one-

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[4] Birks, L. S., and Friedman, H., A high temperature *x*-ray diffraction apparatus: *Rev. of Sci. Instruments*, **18,** 578–580 (1947).

inch long alundum thermocouple tubes (*OD* $\frac{3}{64}$ inch). The coils are welded together in series and are mounted in alundum cement. The entire coil assembly, 1 inch by 1 inch by $\frac{1}{2}$ inch, is attached to the spindle of the diffractometer head by means of an insulating block. A parallel motion adjustment screw incorporated in the assembly allows alignment of the specimen.

## Experimental Procedure and Results

The sample is sedimented or smeared on a platinum plate on which a platinum 10 per cent rhodium thermocouple is welded. The mounted sample is placed in the holder over the furnace and a preliminary run is made at room temperature to locate the position of the diffraction maxima. The goniometer is then set to oscillate over the maximum to be scanned. The range of the oscillation is set to cover any possible shift in the position of the diffraction maximum and still be as short as possible. The oscillation limits are adjusted so that the backgrounds of the maximum through the upscale and downscale oscillations are at the same level on the chart. The temperature of the furnace is raised at a regular rate, while a record is made of changes in the height and position of the diffraction maximum.

This oscillation and heating technique permits the detection of slight changes in $2\theta$, because a small change in the position of the diffraction maximum is exaggerated on the tracing. When the maximum is at the midpoint of the upscale or downscale oscillation, there is a definite background height for this maximum; and since the oscillation is set over the upper portion of the maximum, a shift in $2\theta$ changes the height of the background. The background height is increased in one direction of oscillation and decreased in the other. These combined displacements of the upscale and downscale maxima emphasize any slight shift in position.

*Kaolinite, Bath, South Carolina.* The oscillation tracings of the first and second order basal diffraction maxima of a South Carolina kaolinite are shown in Fig. 2. The breakdown of the two maxima is abrupt at 525° C. There is only barely perceptible shift in the position of the 7 Å maximum toward larger spacing, but the effect is clearly apparent in the second order. Only trivial expansion and abrupt simultaneous disappearance are indicated. The abrupt breakdown of the basal diffraction maxima and the essentially steady position of the 7 Å spacing throughout the temperature range of its stability appear to be typical of kaolinite.

*Sheridanite, Sheridan County, Wyoming.* The oscillation tracings of sheridanite are shown in Fig. 3. The first-order basal diffraction max-

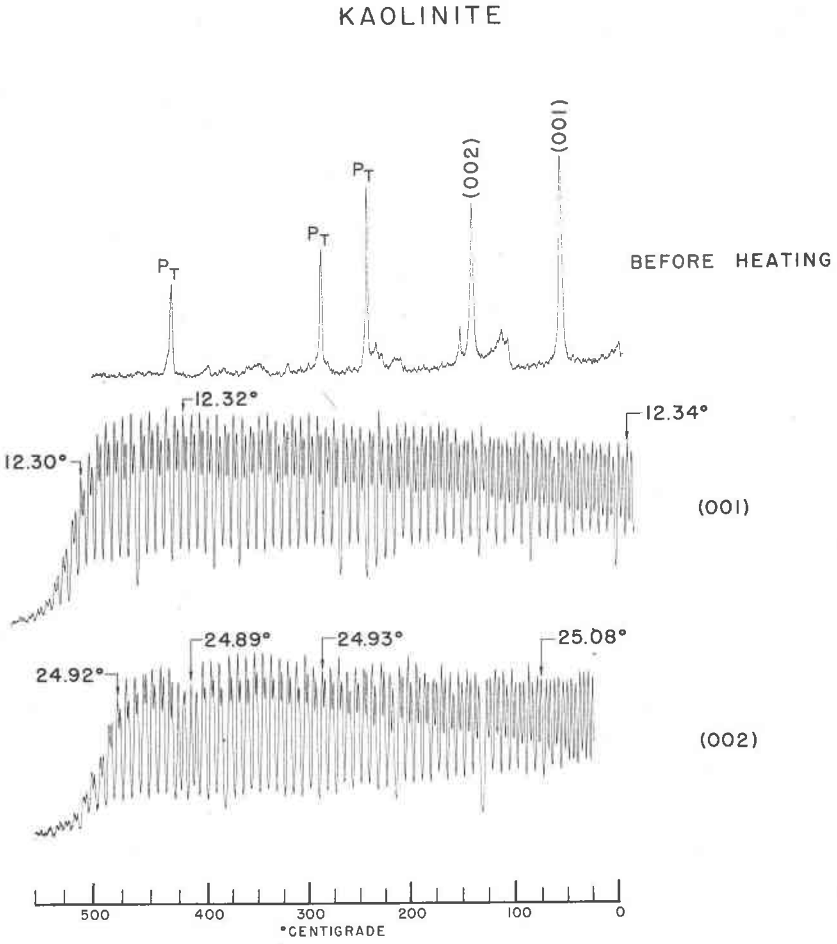

FIG. 2. Heating-oscillating patterns of the first and second order of the basal spacing of kaolinite.

imum (14 Å) increases in intensity abruptly near 575° C., the temperature at which there is the greatest decrease in the intensity of the 7 Å maximum. The position of the (001) diffraction maximum changes from 6.28° $2\theta$ to 6.49° $2\theta$ with the greatest shift between 600° C. to 850° C. On the (001) tracing of sheridanite, the background of the upscale maximum is lower than that for the downscale (the $2\theta$-angles are marked for the maximum on the travel of the geiger tube toward a higher angle) because the goniometer was set so that the position of the upscale maximum was nearer the low-angle limit of the oscillation. This setting compensated for the normal shift of the 14 Å maximum toward a larger angle and kept both the upscale and downscale maxima within the oscillation range. The divergence of the backgrounds is constant up to 600° C. Over a short temperature range, slightly above 600° C. to 620° C., the upscale and downscale backgrounds are at the same level, indicating that the maximum is at the center of the oscillation range. At 625° C. the backgrounds begin to diverge. This shift in the position of the maximum is greatest at the temperature of its decrease in intensity. At 850° C. the upscale position is only slightly below the upper limit of the goniometer oscillation. At higher temperatures this maximum disappears.

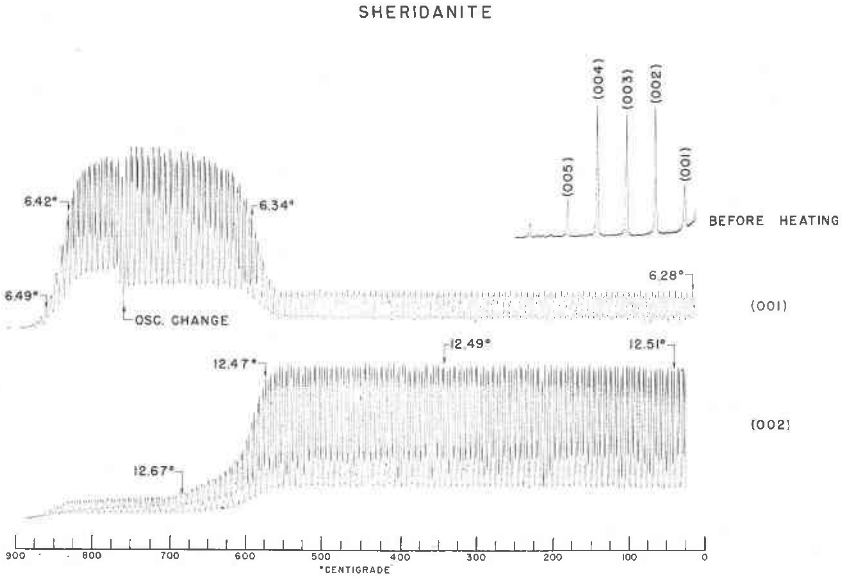

FIG. 3. Heating-oscillating patterns of two orders of the basal spacing of sheridanite.

During the oscillation over the (002) basal maximum of sheridanite, Fig. 3, the limits of the geiger tube travel were set so that the 7 Å maximum was close to the upper limit of the oscillation. This compensates for the migration of the maximum to smaller $2\theta$. The shift is from 12.51° $2\theta$ at room temperature to 12.47° $2\theta$ at approximately 580° C. and is greatest in the temperature range of the abrupt decrease in intensity of the maximum. The two backgrounds are at nearly the same level from 580° C. to the temperature at which the maximum collapses, indicating that the position of the maximum is nearly constant between 580° C. and 875° C. Characteristics of oscillation tracings of sheridanite are: the 7 Å and 14 Å maxima each finally collapse at the same temperature,

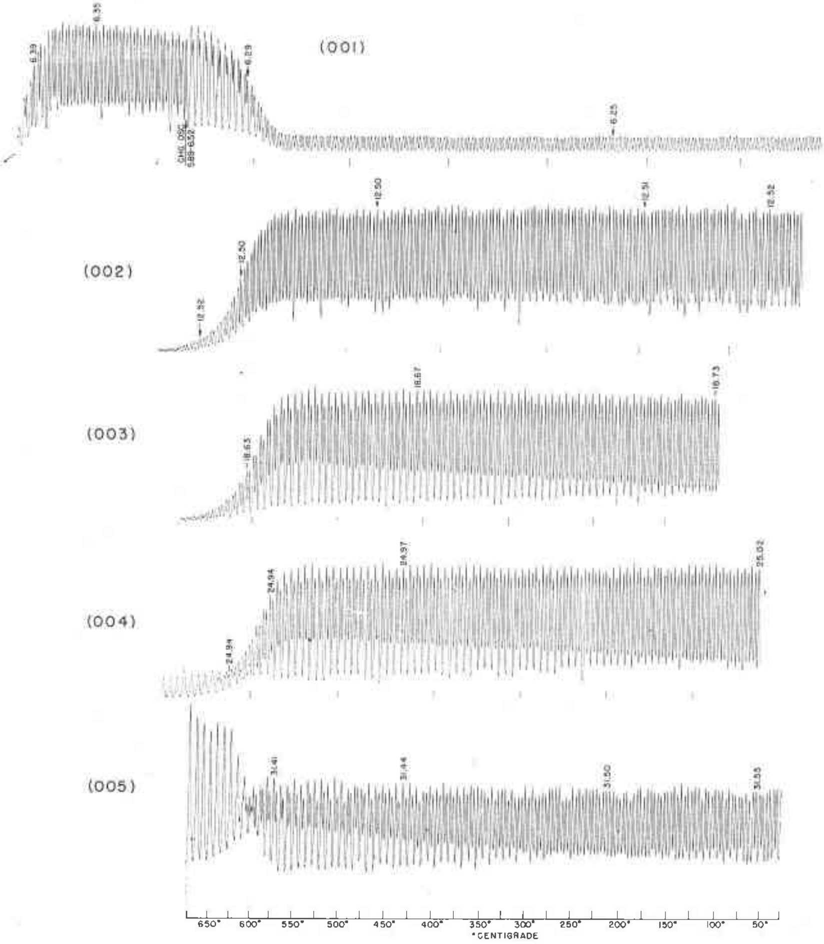

FIG. 4. Heating-oscillating patterns of five orders of the basal spacing of clinochlore.

the rise and fall in intensity of the 14 Å maximum is abrupt, and the 7 Å maximum after an initial abrupt collapse gradually declines until the final disappearance about 875° C.

*Clinochlore.* The oscillation tracings of the first, second, third, fourth and fifth orders (00*l*) basal diffraction maxima are shown in Fig. 4. The (001) maximum increases in intensity at 575° C., collapses at 850° C., and shifts toward a smaller spacing. The (002) and (003) maxima also shift, the (002) migrating toward a larger spacing, and the (003) shifting slightly toward a smaller spacing. The (002) and (003) collapse at 640° C., a temperature 210° C. below the collapse of the 14 Å max-

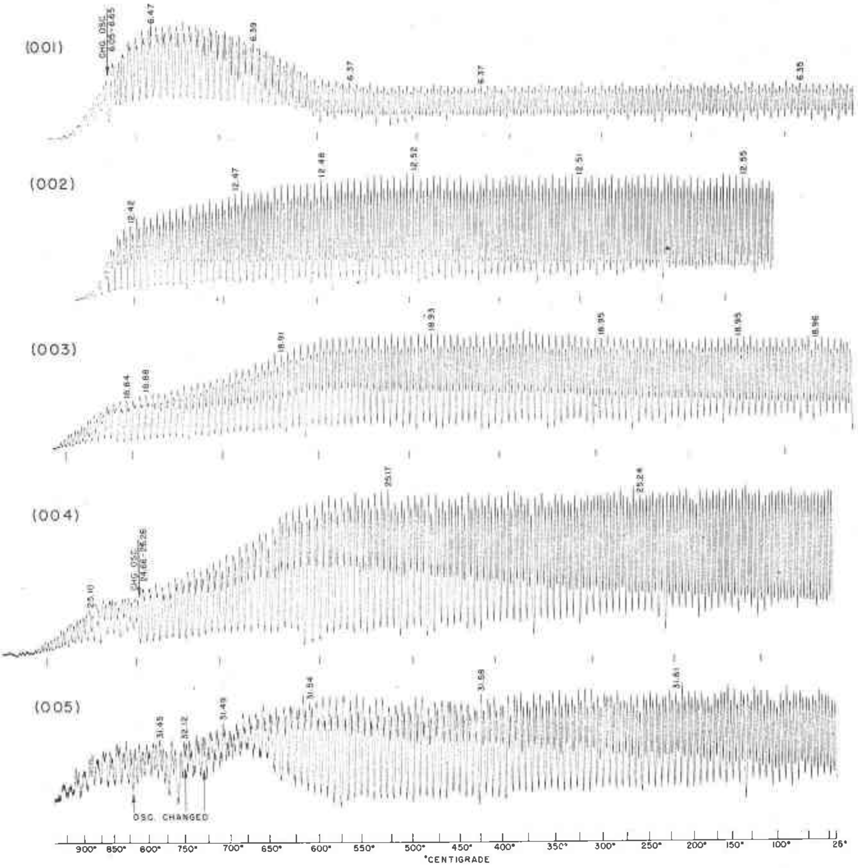

FIG. 5. Heating-oscillating patterns of the first five orders of the basal spacing of a Vermont chlorite.

imum. At this temperature the 14 Å (001) maximum is most intense. The abrupt collapse of these three maxima is characteristic of clinochlore.

The oscillation tracing of the (004) basal diffraction maximum shows a shift toward a smaller spacing and collapse at 575° C. and 24.9° $2\theta$. The behavior of the (005) basal diffraction maximum is similar to that of the (004). However a new maximum, formed at 570° C., which persists to 900° C., may be the result of the formation of olivine.

*Vermont Chlorite.* The oscillation tracings of the first, second, third, fourth and fifth orders of the (00*l*) basal maxima of a Vermont chlorite are shown in Fig. 5.

The (001) maximum begins a gradual increase in intensity at 600° C. which attains its greatest height at 780° C. It then decreases uniformly until its disappearance at 910° C. There is a shift toward a smaller spacing from 600° C. to 910° C.

The (002) maximum, which shifts slightly toward a larger spacing, begins a gradual decrease in intensity at 600° C., then the intensity decrease becomes more rapid at 580° C. At 680° C., the intensity decrease again becomes gradual and continues until the maximum disappears above 910° C.

The oscillation tracing of the (003) maximum indicates an almost constant spacing (18.95° $2\theta$) up to 600° C., after which there is shift to a larger spacing (18.84° $2\theta$). The gradual decline and disappearance of this maximum then follows the behavior of the (002) maximum.

The oscillation tracings of the (004) and (005) maxima shift slightly toward a larger spacing. The (004) from 25.25° $2\theta$ to 25.17° $2\theta$ and the (005) from 31.61° $2\theta$ to 31.54° $2\theta$. The initial break in intensity for each is at 600° C. On the (004) oscillation tracing, there is an indication of the development of a new maximum at 750° C. At the same temperature a definite new maximum at 32.1° $2\theta$ is developed on the (005) oscillation tracing. Both of these maxima disappear near 800° C. Above 800° C., another maximum at 31.25° $2\theta$ becomes evident on the (005) oscillation tracing. This may be attributed to the development of olivine.

## CONCLUSIONS

A composite drawing of a room temperature chlorite diffraction pattern and the outline of the heating-oscillation tracings for clinochlore and chlorite is shown in Fig. 6. The differences between these two chlorites may be summarized as follows:

1. The increase in intensity of the (001) maximum for the clinochlore is greater and more abrupt than that of the Vermont chlorite.

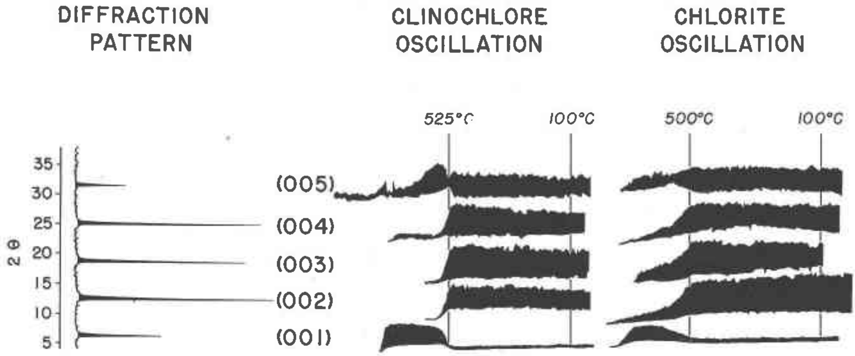

FIG. 6. Composite heating-oscillating pattern envelopes comparing the first five orders of the basal spacing of a clinchlore and a chlorite.

2. The (002), (003) and the original (004) and (005) maxima of the clinochlore collapse completely prior to the temperature of collapse of the (001) maximum.

3. At the temperature of the increase in intensity of the (001) maximum, all other basal diffraction maxima of the Vermont chlorite collapse only partially. The final collapse of all orders takes place at approximately the same temperature.

4. The intensity of the clinochlore maxima rises and decreases abruptly in contrast to the gradual rise and decrease in intensity of the Vermont chlorite.

5. The spacing shifts are greater for the Vermont chlorite than for the clinochlore. The collapse of the second, third, fourth, and fifth orders of the (00*l*) basal diffraction maxima of clinochlore occurs at a temperature below the temperature of collapse of the first order (001) basal diffraction maximum. The collapse of the first five (00*l*) basal orders of the Vermont chlorite takes place at the same temperature. Further distinctions may be made with regard to the amount of the decrease in intensity of the (002) maximum and the amount of increase in intensity of the (001) maximum. These may be seen by comparing the (002) oscillation and heating pattern of sheridanite, Fig. 3, and Vermont chlorite, Fig. 5.

The differences in the heating records of the different chlorite specimens may be explained on the basis of differences in their chemical compositions. It was established by Brindley and Ali[5] that the major factor in intensity alterations following heat treatments of chlorites was the expulsion of water from the brucite layer, with consequent rearrangement of the non-volatile brucite layer remnants. Structural formulae indicate that for complete dehydration water would be lost from the brucite layer and from the talc layer in the ratio of 3 mols to 1. The actual ratio may well be much higher, but could hardly be lower.

Augmented intensity in the first order is a consequence of the heat treatment having made the brucite layer differ from the brucite member of the talc layer by more than was the case before heating. The big factor is water loss, and any rearrangement is relatively ineffective.

Decline in intensity of the second order does not distinguish whether the reaction which took place was effective in the brucite layer, in the brucite member of the talc layer, or both. The decline only measures the magnitude of the reaction, and both water loss and rearrangement are effective in bringing the decline about. In a sense, a chlorite is a double-

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[5] Brindley, G. W., and Ali, S. Z., Thermal Transformations in Magnesian Chlorites: *Acta Cryst.*, **3,** 25–30 (1950).

unit structure, so that the responses of the even orders measure the reaction, and those of the odd orders locate it.

For the high magnesian compositions, the local reaction may be represented schematically as

$$Mg(OH)_2 \rightarrow MgO + H_2O,$$

in which event $\frac{1}{2}$ of the oxygen of the brucite layer is expelled. For compositions high in ferrous iron, roasting also oxidizes the iron. The comparable reaction, written as

$$Fe(OH)_2 + 1/2\ O\ (\text{atm.}) \rightarrow 1/2 Fe_2O_3 + H_2O$$

illustrates that only $\frac{1}{4}$ of the brucite layer oxygen is lost from the solid product. The same proportion obtains for the oxidized chlorites.

The lesser increase in 001 intensity for iron-bearing species is a reflection of this lesser loss of oxygen from the structure, and the lesser decline in 002 intensity indicates that the rearrangement which characterizes magnesian members is also inhibited.

Additional factors may be operative in modification of many chlorites by heat, particularly in instances in which some brucite layers are so abnormally hydrous that they collapse locally to talc in the course of the heating. Such collapse does not appear to have been extensive in these present instances.

The distinction and subgrouping of various definite types of chlorite is facilitated by the detailed information available from the oscillation-heating *x*-ray diffraction technique. The characteristics and differences among the three chlorites and the kaolinite which have been discussed are based upon an investigation by the oscillation-heating technique of many micaceous materials. The materials include montmorillonites, vermiculites and mixed-layer minerals in addition to chlorite and kaolinite.

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