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# THE EFFECT OF PARTICLE SIZE ON THE THERMAL PROPERTIES OF SERPENTINE MINERALS

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ABSTRACT

The effects of particle size of chrysotile and platy serpentine on the differential thermal and thermal gravimetric analyses have been investigated. It was found with DTA that decreasing the particle size decreased the starting and peak temperatures of the endothermic or dehydroxylation reaction and that the peak height of the exotherm was considerably increased although the peak temperature was not appreciably changed. As the chrysotile particle size decreased the endothermic peak temperature decreased from a maximum of 710° C. with no grinding, to a minimum of 670° C. when it was finely ground. When chrysotile samples from several sources were ground following a standard procedure, the DTA thermograms obtained were quite similar. TGA also showed the dehydroxylation (weight loss) occurring at lower temperatures when the samples were ground. The results indicate that if comparison between serpentine samples is the objective of a DTA-TGA study, the sample preparation is of utmost importance, otherwise differences noted may not be true differences but due to variations in particle size between samples. Data obtained with chrysotile and platy serpentine on a thermal increment diffractometer are given. DTA-TGA were also obtained on a brucite-carbonate sample indicating particle size has a similar effect on its endothermic reactions but it is not as large as those noted for the serpentine minerals.

## INTRODUCTION

The literature contains many references to the thermal properties of the serpentine minerals, particularly chrysotile, with much of the reported data having been obtained using differential thermal and thermal gravimetric analyses. The two principal reactions with the serpentine minerals are a broad endotherm between 600° C. and 720° C. due to dehydroxylation of the mineral and an exothermic peak about 810° C. usually ascribed to the formation of olivine or forsterite. The reported results with chrysotile indicate wide differences of starting and peak temperatures for these reactions and these differences appear to be greater than the variations normally obtained due to the use of different equipment, varying size of samples, etc.

When the present DTA study of chrysotile was started, it was observed that the peak temperature for the endotherm was not constant and that occasionally shoulders occurred during the endothermic reaction suggesting the possibility that another reaction was taking place. The peak temperature for the exotherm remained fairly constant but the height and sharpness of the peak varied from run to run with the same sample. An investigation into the cause for this lack of reproducibility revealed that the particle size had a considerable effect on the endothermic and exothermic reactions for both chrysotile and platy serpentine; when

a standard grinding procedure was followed reproducible results were obtained.

## Description of Equipment and Sample Preparation

### *Differential Thermal Analysis*

The DTA unit, manufactured by the Robert L. Stone Co., Austin, Texas, utilizes the dynamic gas principle where a gas can flow through the sample and inert reference material during a run (Stone and Rase, 1957). Nitrogen was used as the flowing gas in all the tests reported. The temperature rate increase was approximately 10° C. per minute and the inert used was alundum. The Inconel sample holder is 1.5 inches in diameter by $\frac{5}{8}$ inch thick and the two cavities for the sample and inert are $\frac{1}{4}$ inch diameter by $\frac{3}{8}$ inch deep. Platinum-platinum, 10% rhodium thermocouples were used for both the differential and reference temperature thermocouples. The thermocouples were calibrated from time to time with quartz.

The differential temperature recording system contains an amplifier which is designed for adjustable range within wide limits. After grinding, the exothermic peak height of chrysotile became so large that the sensitivity of the amplifier output had to be decreased at about 750° C. to keep the recorder from running off scale during runs. In general the portion of the curve below 750° C. was run at ten times the sensitivity as that above 750° C. when ground samples of chrysotile were being run.

The chrysotile samples were obtained from crudes longer than one-half inch. The ends of the fibers were cut off with scissors and discarded to minimize contamination from the wall rock. The standard grinding procedure was as follows: A 210 mg. sample was weighed and split approximately into halves. Each half was ground in a Wig-L-Bug using a stainless steel vial with two pestles; every thirty seconds the grinding was stopped and the sample was scraped from the sides and ends of the vial to minimize packing. After grinding each half for a total of 180 seconds, the two halves were mixed and placed in the DTA holder. Approximately 500 to 550 mg. of $Al_2O_3$ were used as the inert.

The chrysotile samples that were not ground were pulled apart with tweezers and packed carefully around the thermocouples in the sample holder. This required great care and it is doubtful that packing from run to run was the same. When the sample was finely ground no difficulty in packing the sample around the thermocouple was experienced. Approximately 170 mg. could be packed in when the sample was unground.

### *Thermal Gravimetric Analysis*

The gravimetric analyses were run on a Chevenard thermobalance (Duval, 1953) converted electronically for graphic recording by Gordon

and Campbell using a system similar to that described in their paper (1956). A Moseley Autograph X–Y recorder was used to plot the temperature-weight loss curves. A heating rate of 5° C. per minute was used with a one-gram sample, unless otherwise noted. A Spex Mixer/Mill was used for grinding the larger chrysotile and platy serpentine samples required for TGA.

*Thermal Increment Diffractometer*

The thermal increment diffractometer studies were run by Mr. William A. Bassett. The unit used has been described by Bassett and Lapham (1957). For the runs reported, copper radiation produced at 40 kilovolts and 17 milliamperes was used. While the temperature was being increased at a rate of approximately 10° C./minute, the goniometer was oscillated over one of the prominent peaks with an oscillating range of 2° $2\theta$. The heating was stopped and scans were made at temperatures which seemed significant.

The chrysotile specimen was ground to a fine powder in a Wig-L-Bug and the platy serpentine was ground in a mortar and pestle. The samples were prepared for the thermal increment diffractometer by sedimenting the powder onto a platinum-rhodium plate in distilled water. The water was drawn off and the specimen allowed to air dry. The plate with the layer of powder was then mounted on the heating element of the instrument. This method of preparation permitted a considerable degree of preferred orientation of flaky and fibrous minerals.

## Test Results

*DTA-TGA*

The effect of particle size on the DTA of chrysotile was investigated by varying the time of grinding. The peak temperatures and heights of the reactions are given in Table I and the results of a microscopic examination of the ground samples in Table II. As the grinding time increased, the fiber lengths and widths decreased resulting in a decrease in the peak temperature for the endotherm from 710° C. in unground fiber carefully pulled apart with tweezers to a minimum of 670° C. with finely ground fiber; increased grinding time from 180 to 420 seconds did not decrease the endothermic peak temperature any further. The particle size did not change appreciably the peak temperature for the exotherm, but the sharpness and heights increased as grinding time increased.

Figure 1 shows the thermograms obtained with samples ground for different lengths of time. Included is a curve of a mixture of chrysotile half unground and half ground for 180 seconds resulting in two endothermic peaks.

After a standard procedure of grinding for 180 seconds was adopted,

TABLE I. EFFECT OF PARTICLE SIZE OF CHRYSOTILE ON DTA PEAK TEMPERATURES AND HEIGHTS OF EXOTHERMIC AND ENDOTHERMIC REACTIONS

| Grind. Time | Peak Temp., °C. | | Ratio Peak Hts. Exoth./Endoth. |
|---|---|---|---|
| Seconds | Endoth. | Exoth. | |
| 0 | 710 | 816 | 0.1 |
| 15 | 698 | 816 | 1.2 |
| 30 | 697 | 814 | 4.3 |
| 60 | 671, 693 | 813 | 11.3 |
| 90 | 671 | 812 | 12.0 |
| 180 | 670 | 812 | 13.7 |
| 420 | 671 | 812 | 11.4 |

Sample: Lake Asbestos of Quebec, Black Lake, P. Q.

extremely good reproducibility was obtained with the DTA. A number of chrysotile crude samples from other mines in Quebec gave very similar thermograms, as shown in Fig. 2.

The use of nitrogen as the dynamic gas flowing through the sample and reference resulted in a decrease of about 20° C. in the peak temperature of the endotherm compared to when no gas was used. The sweeping out of the products of reaction by the gas may be a contributing factor in obtaining good reproducibility.

Samples of ground and unground chrysotile were run on the thermobalance and the curves obtained are given in Fig. 3. The loss of weight due to dehydroxylation starts at a much lower temperature with the ground samples compared to one consisting of gross bundles of fiber. The small weight loss above 750°, the "high" temperature water, was still present after grinding.

TABLE II. MICROSCOPIC EXAMINATION OF GROUND CHRYSOTILE

| Grind. Time | Size of Bundle or Particle | | Approx. Avg. Size | |
|---|---|---|---|---|
| Seconds | Lengths | Widths | Length | Width |
| 15 | 100–5,500 | 40–900 | 3,000 | 400 |
| 30 | 30–4,000 | 10–600 | 2,000 | 150 |
| 60 | 20–2,000 | 8–200 | 1,200 | 50 |
| 90 | 10– 800 | 6–100 | 400 | 30 |
| 180 | 8– 160 | 4– 80 | 70 | 20 |
| 420 | 4– 60 | <3– 30 | 30 | 9 |

Sample: Lake Asbestos of Quebec, Black Lake, P. Q.

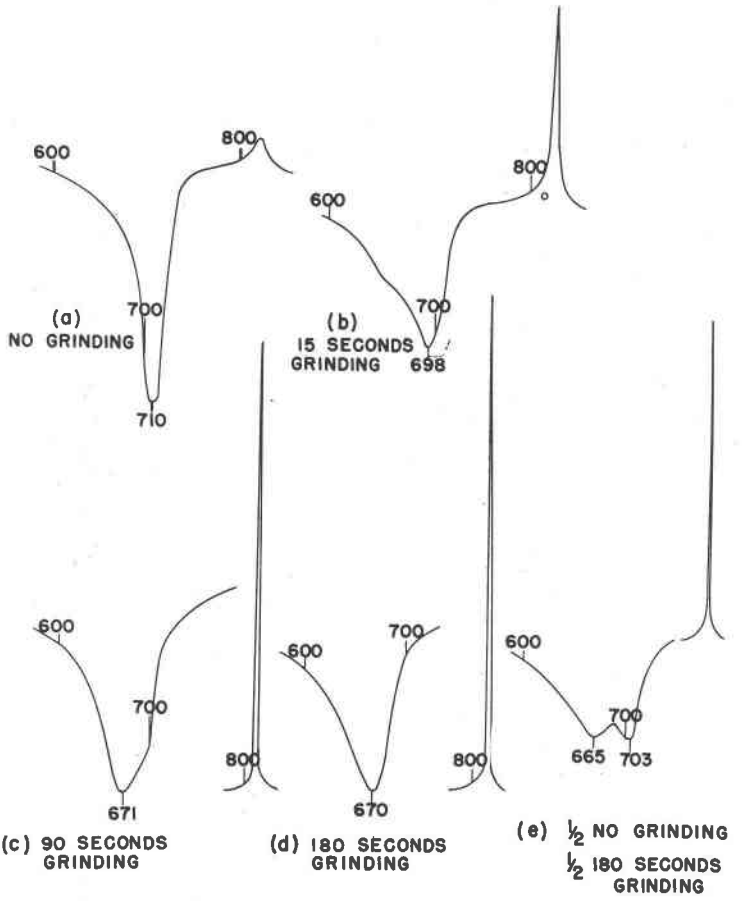


FIG. 1. Differential thermal analyses of chrysotile asbestos samples ground in Wig-L-Bug for varying lengths of time.

Platy serpentine was also run on the DTA and TGA and behaved in a very similar manner to chrysotile as indicated by the TGA curves in Fig. 4. In the DTA, grinding the sample resulted in a decrease in the starting and peak temperatures of the endotherm, and an increase in the peak height of the exotherm.

A 35×65 mesh sample of brucite containing carbonate was also run and the TGA curves are shown in Fig. 5. Decreasing the particle size reduced slightly the temperature at which the endothermic reactions in the DTA and weight losses in the TGA started for both brucite and carbonate. However, the effect was not as pronounced as those noted with

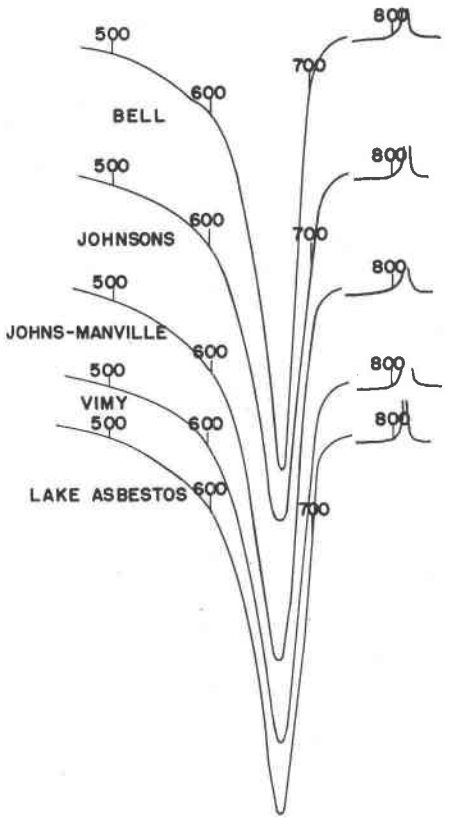


FIG. 2. Differential thermal analyses of chrysotile samples from various sources. Samples were prepared following a standard procedure of grinding for 180 seconds in Wig-L-Bug.

chrysotile. The TGA curves obtained with the brucite-carbonate sample also include a run at a temperature rate increase of 10° C. as well as the usual 5° C. per minute. The higher rate shifted the starting temperatures for the weight losses to higher values. The results indicate that the particle size had less effect on the starting temperatures of the breakdown of the $Mg(OH)_2$ and carbonate than did the rate of temperature rise.

*X-Ray Data*

Unground samples of chrysotile were heated to 350°, 500°, 775°, 870°, and 1100° C., allowed to cool to room temperature, and then $x$-ray patterns obtained on the Picker unit. The samples heated to 350° and 500° C. did not show any change from a standard unheated chrysotile; the 775° C.

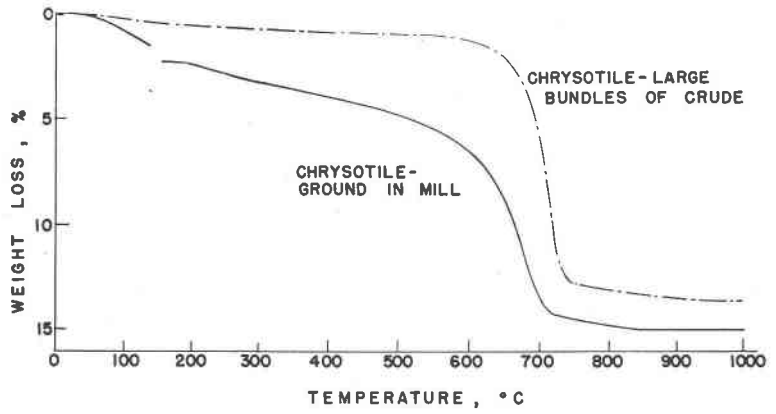


FIG. 3. Thermal gravimetric analyses of ground and unground chrysotile from the Lake Asbestos of Quebec mine, Black Lake, P. Q. Thermograms very similar to the lower one were obtained when ground chrysotile samples from Asbestos and Thetford, P. Q., were run. Heating rate was 5° C./min.

sample was amorphous with some unidentified lines; and the 850° and 1100° C. samples yielded sharp and well defined patterns of olivine.

Ground samples of chrysotile and platy serpentine were run on the thermal increment $x$-ray diffractometer. The temperature was raised at a rate of approximately 10° C. per minute and the goniometer oscillated over a prominent peak. The intensity of certain peaks vs. temperature for chrysotile and platy serpentine is plotted in Fig. 6. Table III contains data on chrysotile obtained from scans taken at 25°, 325°, and 515° C.,

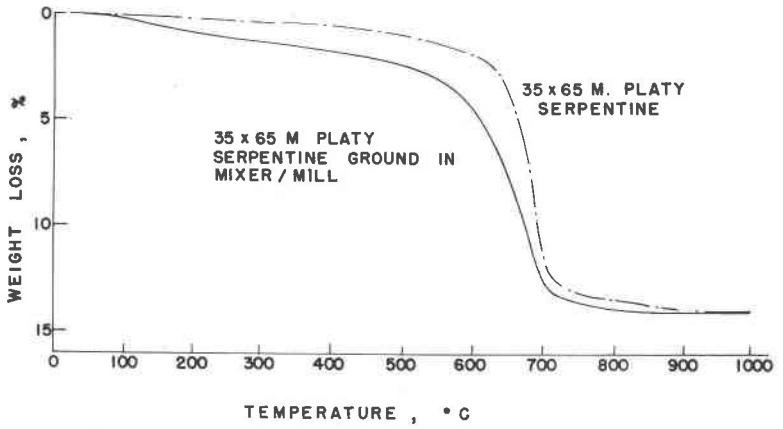


FIG. 4. Thermal gravimetric analyses of platy serpentine from Lowell, Vermont; heating rate was 5° C. per minute.

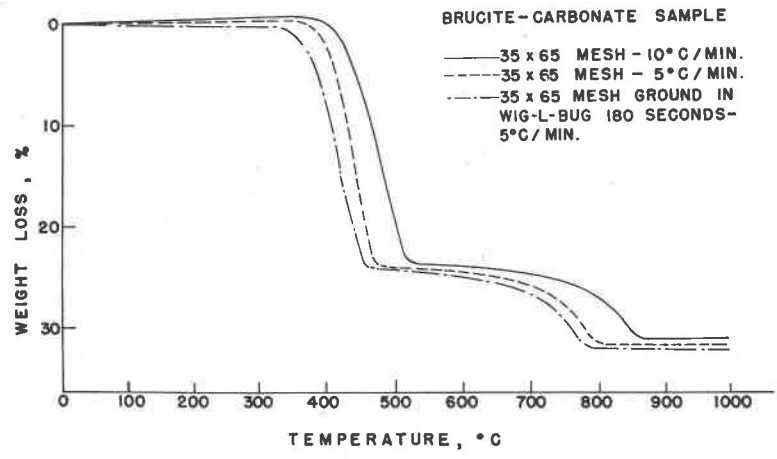


FIG. 5. Thermal gravimetric analyses of a brucite sample containing carbonate from Luning, Nevada.

and indicates that no major changes take place in chrysotile throughout this temperature range. However, the decrease in the 2.45 Å may be significant and should be more thoroughly investigated.

The *x*-ray data indicate that chrysotile and platy serpentine showed little change until 475° C., above which the intensity of the 7.3 Å reflec-

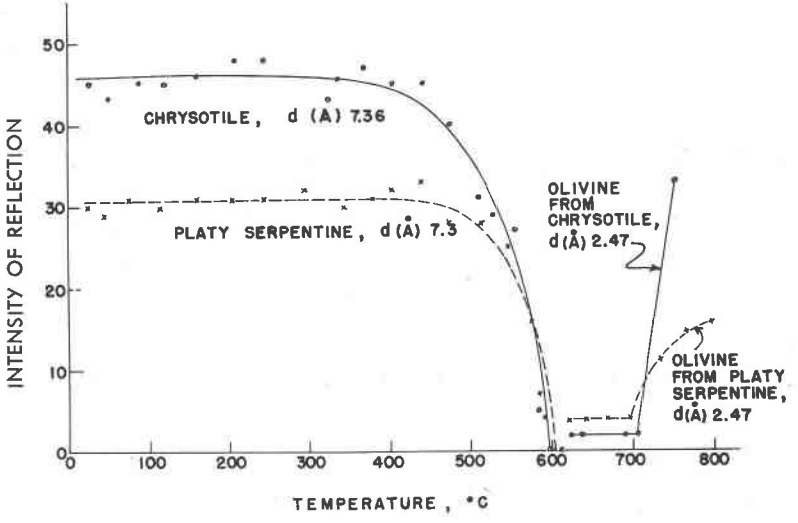


FIG. 6. Effect of temperature on reflection intensities of certain peaks of chrysotile and platy serpentine obtained on the thermal increment diffractometer.

TABLE III. THERMAL INCREMENT DIFFRACTOMETER *X*-RAY DATA ON CHRYSOTILE

| 25° C. | | 325° C. | | 515° C. | |
|---|---|---|---|---|---|
| *d*(Å) | Intensity | *d*(Å) | Intensity | *d*(Å) | Intensity |
| 7.36 | 100 | 7.36 | 100 | 7.36 | 100 |
| 4.50 | 20 | 4.50 | 24 | 4.50 | 25 |
| 3.668 | 80 | 3.675 | 80 | 3.67 | 65 |
| 2.561 | 16 | 2.561 | 20 | 2.59 | 13 |
| 2.453 | 30 | 2.447 | 30 | 2.47 | 13 |

Sample: Lake Asbestos of Quebec, Black Lake, P. Q.

tion begins to decrease until it disappears about 600° C. when both become amorphous. In addition a slight expansion of the platy serpentine occurs above 400° C. Although weak olivine lines were noted at lower temperatures, they do not become prominent until about 740° C. The olivine produced by heating both samples appeared to be near the magnesium rich or chrysolite end of the isomorphous series chrysolite-fayalite.

## DISCUSSION

That particle size can alter the shape and position of peaks in the DTA of some minerals has been recognized for some time. Smothers and Chiang (1958) and Mackenzie (1957) discuss this to some extent and give many references to investigations of various minerals where the effect of particle size on the thermal properties has been reported. There have been numerous publications on the DTA and TGA of serpentine minerals, but the effect of particle size has not been noted although Sabatier (1950) investigated this effect in the chlorites. Attempts have been made to identify the source of chrysotile samples (Pundsack, 1955; Woodrooffe, 1956) or to differentiate between fiber and matrix (Kalousek and Muttart, 1957; Lyon and Tuddeham, 1959) by means of DTA or TGA. Since the particle size has such a large effect on both reactions and the thermograms for chrysotile and platy serpentine are so similar, the sample preparation becomes of utmost importance if the objective of the study is comparison between samples. The DTA curve with half ground and half unground chrysotile resulting in two distinct endotherms (Fig. 1*e*) shows clearly the difficulty involved since such a pattern would normally be interpreted as being caused by two reactions, possibly leading to the conclusion that two minerals were present.

Pundsack has suggested that the ratios of endothermic to exothermic peak heights and areas vary depending upon the source of the chrysotile

sample. However, the ratios of exothermic/endothermic peaks given in Table I indicate the dependence of this ratio on the grinding time or particle size since it varied from 0.1 with no grinding to over 13 with 180 seconds in the Wig-L-Bug. When crudes from various sources were prepared using a standard grinding procedure, no appreciable differences in ratios were obtained between the samples tested. It should be noted that when the tests with the DTA were run in duplicate, varying the length of time in the Wig-L-Bug, reproducibility was poor with insufficient grinding. The peak temperatures for the main endotherm and the position of the shoulders varied as did the peak heights of the exothermal reaction with two samples ground for the same length of time. However, samples ground very fine gave excellent reproducibility.

The TGA results obtained with the serpentine minerals (Fig. 3 and 4) indicate the difficulty in determining the starting temperature for the dehydroxylation. Comparison of TGA results obtained with samples from various sources as Woodrooffe (1956) has done is complicated by the fact that some of the differences noted may be due to particle size variations between samples. With granular material it may be possible to grind and screen the sample to produce a closely sized product giving reproducible results; however, preparing chrysotile samples having similar particle size or surface areas presents a more difficult problem.

The decrease in the starting temperatures for dehydroxylation when the serpentine minerals are ground may be caused simply by the smaller particle size producing a greatly increased surface area making it easier for the $OH^-$ to leave the crystal. However, grinding may have altered the bond energy distribution of the particles (Stone, 1954) and thus some of the bonds usually broken by high temperatures in a large particle may have been broken or altered in grinding. The TGA curves substantiate the decrease in temperature for dehydroxylation noted in the DTA when the sample is ground. This eliminates the possibility that the DTA results were due solely to differences in conductivity or porosity between the ground and unground samples packed in the holder.

The thermal increment diffractometer data indicate a striking similarity between chrysotile and platy serpentine. Below 500° C. both minerals undergo only minor changes. Above 500° C. the changes noted were due to the dehydroxylation of the samples and correspond to the endotherm obtained in the DTA. The removal of the OH ions leaves a chaotic arrangement of magnesium, iron, silicon, and oxygen which recombine to form olivine at about 740° C.

The increased peak height of the exothermic reaction of the serpentine minerals noted in the DTA may be due to the finer size and more intimate mixture of the ground sample causing the reaction to occur over a

much shorter temperature range and resulting in a much sharper reaction. However, the chrysotile structure and the reactions taking place on heating are not yet completely understood. There are indications that it may be in the form of tubes (Turkevich and Hillier, 1949; Bates, *et al.*, 1950; Noll and Kircher, 1950) with plugs of water blocking the ends (Young and Healey, 1954) and amorphous appearing material surrounding the tubes (Bates, 1958; Comer, 1959). There is a small, but reproducible weight loss occurring about 800° C. (Woodrooffe, 1956; Kalousek and Muttart, 1957) that is not completely understood, but which was not eliminated by grinding. The formation of enstatite as well as olivine on heating has been reported (Calliere, 1936; Strelov, 1953). Although the exothermic reaction at 812° C. is normally ascribed to the formation of forsterite or olivine, the thermal diffraction data show that formation of olivine starts at about 740° C. Pundsack (1956) has noted the formation of forsterite below 800° C. It would appear from the above that the thermal reactions occurring in the serpentine minerals may be more complicated than usually assumed and that further study is necessary for a better understanding of the reactions taking place.

## Acknowledgments

The author is indebted to Mr. William A. Bassett for running the tests on the thermal increment diffractometer at Columbia University and interpreting the results; to Mr. Robert Haagensen of ASARCO for the microscopic study of the ground chrysotile samples; and to Dr. Max L. Hollander of ASARCO for his helpful suggestions and assistance.

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