# THERMAL TRANSFORMATIONS OF PYROPHYLLITE AND TALC AS REVEALED BY X-RAY AND ELECTRON DIFFRACTION STUDIES*

*by*

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## ABSTRACT

Single crystal X-ray and electron diffraction studies were carried out to examine the thermal transformation sequences of pyrophyllite and talc, respectively. The results showed that both minerals transformed topotactically. No dehydroxylated talc phase was observed, while an anhydride of pyrophyllite was obtained at about 900°C. The presence of a distorted anhydride lattice of pyrophyllite tends to indicate a homogeneous mechanism for the dehydroxylation of pyrophyllite. In contrast, the diffraction features of heated talc together with the cell volume relationship between talc and enstatite suggest an inhomogeneous mechanism for this reaction.

## INTRODUCTION

In terms of the layer structure, pyrophyllite and talc are of the same type with one octahedral layer sandwiched between two tetrahedral layers. Much work has been done on the thermal transformations of these minerals mainly by differential thermal analysis. Using the thermal curves as reference, Bradley and Grim (1951) investigated the phase transformations of various clay minerals with a summarizing discussion concerning the mechanisms of these reactions. They attempted to find the structural (i.e. the topotactic) relationships between the original and the transformed phases and were successful for pyrophyllite, chrysotile and clinochlore.

More recently, Taylor and his co-workers (see Taylor, 1962) have contrasted two different approaches to the problem of dehydroxylation mechanisms. One is termed a "homogeneous" mechanism in which the loss of oxygens as water molecules is more or less uniform throughout a crystal. The other, which is called an "inhomogeneous" mechanism, involves the assumption that a countermigration of protons and other

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cations occur during dehydroxylation and that no oxygen is lost from those parts of a crystal where the topotactic transformation is taking place.

Thus far, all suggestions for the *mechanism* have been based mainly on such data as topotactic relationships, infrared spectra and differential thermal curves. There is no direct evidence for either of the mechanisms mentioned above. But the fact that pyrophyllite has its somewhat distorted anhydrous phase prior to the formation of mullite whereas the anhydride of talc has not yet been observed led us to think that there might be a difference between the dehydroxylation mechanisms of pyrophyllite and talc.

In interpreting the experimental data, various experimental conditions have to be taken into account. Crystal sizes, degrees of compaction, ambient gases, and rates of heating are all factors having considerable effects upon the entire processes of thermal decomposition and transformation. The present investigations deal with single crystals of pyrophyllite and talc under mild heat treatments in air, and were undertaken to see whether single crystal data would give further information concerning the mechanisms of thermal decomposition and transformation.

## EXPERIMENTAL PROCEDURES AND RESULTS

Pyrophyllite crystals, about 1 mm average size, were obtained from Goto Islands, Japan, and a massive talc from which small flakes of single crystals were cleaved came from Ishikawa, Fukushima, Japan. These specimens were placed on a platinum plate, heated to a predetermined temperature with a heating rate of approximately 100°C/30 min, held at that temperature for a certain length of time, and then quenched in air. The products were examined by either the X-ray or the electron diffraction method.

### Pyrophyllite

Several X-ray Weissenberg photographs for $(0kl)$, $(1kl)$, $(h0l)$, and $(h1l)$ were obtained from both the original and the heated specimens. To establish the topotactic relationship between these specimens, one and the same crystal was used throughout a series of heat treatments. The crystal was mounted, at first, on a thin glass fibre to obtain a diffraction pattern in the unheated state. Then, it was demounted from the specimen holder, heated at a certain temperature and again remounted to examine the

pattern after that particular temperature; it was assumed that the structural state after heating was retained by the quench treatment.

In electron diffraction work, one cannot use the same crystal after each heat treatment. Therefore, the topotactic relationship, if any, must be examined on a pattern which consists of reflections from both the unchanged and changed parts of the crystal. One can establish the relationship also by examining the crystal shapes of various single crystals in relation to the directions of crystallographic axes. Both methods were used in the present investigations. An electron diffraction pattern with the electron beam normal to the basal plane of pyrophyllite after heating at 1030°C is shown on Plate 1.

The experimental results can be summarized briefly as follows:

The anhydrous phase of pyrophyllite was obtained by heating a crystal at 900°C for 5 hr. Its Weissenberg patterns differed from those of the starting crystal in the intensity distribution of the reflections but the diffraction symmetry did not show any change for each corresponding layer-line pattern, and the lattice parameters remained almost unchanged.

The electron diffraction pattern, such as that in Plate 1, consists of both mullite and cristobalite reflections. Moreover, it does not represent any *single* reciprocal lattice plane but rather corresponds to an oscillation diagram of a crystal. The pattern shows that the mullite is an aggregate of small crystals with their $c$-axes lined up in the same direction corresponding to the $b$-axis of original pyrophyllite. Each crystallite rotates to

## P Y R O P H Y L L I T E

$$\vec{a}_p \ /\!/ \ \vec{a}_{anhyd.} \qquad \vec{a}_{anhyd.} \ /\!/ \ (110)_m \ /\!/ \ (110)_{crist.}$$

$$\vec{b}_p \ /\!/ \ \vec{b}_{anhyd.} \qquad \vec{b}_{anhyd.} \ /\!/ \ \vec{c}_m$$

$$(001)_p \ /\!/ \ (001)_{anhyd.} \qquad \vec{c}^*_{anhyd.} \ /\!/ \ (111)_{crist.}$$

## T A L C

$$\vec{a}_t \ (5.3 \ \text{Å}) \ /\!/ \ \vec{c}_e \ (5.2) \ /\!/ \ (110)$$

$$\vec{b}_t \ (9.1 \ \text{Å}) \ /\!/ \ \vec{b}_e \ (8.8)$$

$$\vec{d}_{001, t} \ (18.7 \ \text{Å}) \ /\!/ \ \vec{a}_e \ (18.2), \ \vec{c}^*_t \ /\!/ \ (111)_{crist}$$

FIGURE 1.—Topotactic relationships in the series of pyrophyllite–mullite and talc–enstatite.

some extent around its $c$-axis with respect to its neighboring crystallites. Bradley and Grim (1951) have also observed the same phenomenon.

The topotactic relationships are found as shown in Fig. 1, where the suffixes $ap$, $m$, and $crist.$ stand for anhydride, mullite, and cristobalite, respectively.

## Talc.

The same methods as in the pyrophyllite study were applied for talc and the topotactic relationships are given in Fig. 1. The suffixes $t$ and $e$ represent talc and enstatite, respectively.

As shown in Fig. 1, the $c$-axis of enstatite was found parallel with the $a$-axis of the initial talc. Along with this orientation, however, the transformation with the $c$-axis of enstatite parallel with either of two pseudo-$a$-axes of talc was observed in many cases with the result that the entire diffraction pattern appeared to be of high symmetry. It is not certain whether this is caused by an equal probability of the $a$- and pseudo-$a$-axes of talc being transformed to the $c$-axis of enstatite, or is due simply to the twinning which is frequently observed with the present specimens. This twinning also made it difficult to obtain a clear single crystal Weissenberg pattern.

In the early stage of enstatite formation, the axial angle between the $b$- and $c$-axes of enstatite was not exactly 90°. It became 90° upon further heat treatment. Therefore, the term "enstatite" is used in this article only for describing a magnesian silicate derived from talc and no attempt is made to distinguish between proto-enstatite, enstatite, and clino-enstatite. An electron diffraction pattern of enstatite from talc heated at 1000°C for 10 hr is given in Plate 2. When the specimen was heated for a shorter length of time at that temperature, the original talc pattern was still superimposed on the enstatite pattern.

With regard to cristobalite, difficulties were encountered in determining the cristobalite reflections on some of the enstatite pattern, partly because of the small number of reflections from cristobalite, but also because of the similarity of the periodicities of enstatite and cristobalite as projected on the $b$-$c$ plane of enstatite ($-$along the [111] of cristobalite). The existence of a cristobalite pattern superimposed on the enstatite pattern was, therefore, a little doubtful. A single crystal pattern of cristobalite, however, was obtained from some of the heated specimens, from which the orientational relationships were established between cristobalite, enstatite and talc. Plate 3 shows a cristobalite pattern from talc heated at 1200°C. The electron beam was normal to the basal plane of talc.

## DISCUSSION

The dehydroxylation and recrystallization processes of layer silicates take the following sequence in general:

Original →Dehydration (with no change in its original structure) →
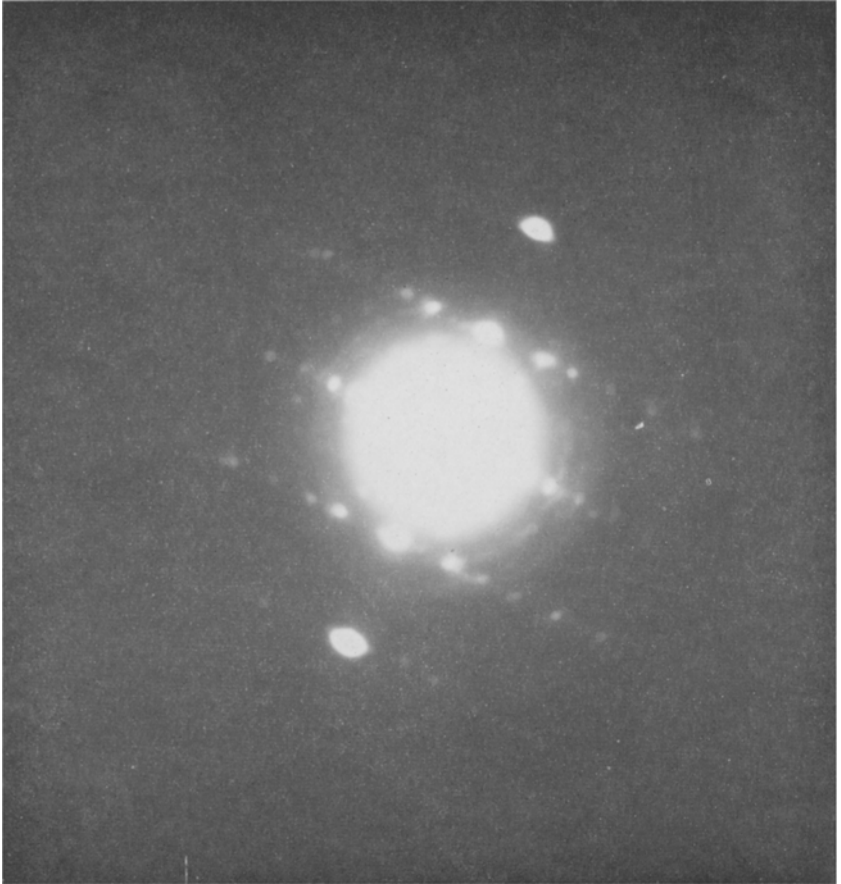
PLATE 1.—Electron diffraction pattern of pyrophyllite heated at 1030°C.
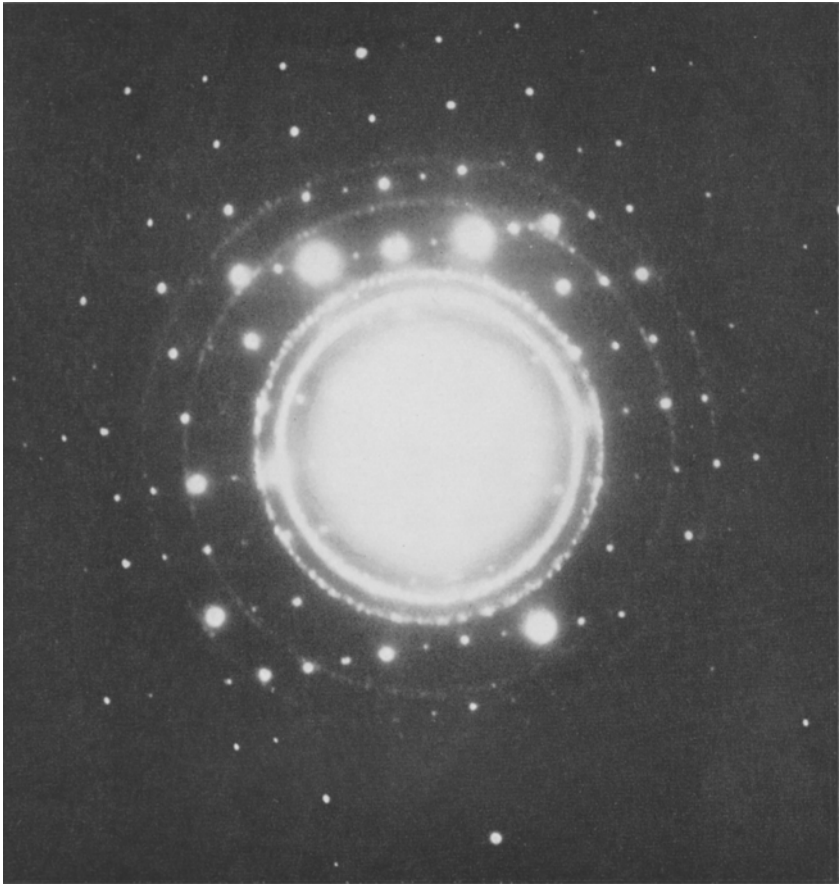
PLATE 2.—Electron diffraction pattern of talc heated at 1000°C.

PLATE 3.—Electron diffraction pattern of cristobalite from talc heated at 1200°C.

Dehydroxylation (with a change in the structure to various extends) →
Recrystallization.

It is not always true that dehydroxylation results in the formation of a definite anhydrous phase. As described in the previous chapter, pyrophyllite forms its anhydrous phase as a result of dehydroxylation, whereas an anhydrous form of talc cannot be obtained at its dehydroxylation stage.

In many cases, the entire sequence is a process in which the atomic reorganization is governed mainly by the diffusion of cations through the anion framework that has been less disturbed during the process. At the same time, one must admit that a great number of water molecules must be taken out of a crystal in the dehydroxylation process, and this may result in a drastic change of the entire anion framework of the crystal lattice, causing a random distribution of product crystals with respect to crystallographic directions of the starting crystal. To reconcile this with the topotactic formation of dehydroxylated products, Taylor and his co-workers (1962) have put forward a concept of inhomogeneous reaction in which a counter-diffusion of cations and protons is involved with little distortion of the anion-framework. Brindley (1961) also has described the same mechanism for the dehydroxylation of serpentine single crystals. In contrast, there is also much evidence, especially with aluminum silicates, for a lattice distortion during the dehydroxylation, which may suggest a direct interaction between two neighboring hydroxyl ions to form a water molecule. The present experimental results will, therefore, be discussed with an attempt to find out which approach is more feasible to explain the transformation sequences of pyrophyllite and talc.

The structure of pyrophyllite anhydride has not yet been worked out in detail, but the present experiments show that there is little change in the entire structural scheme at the stage of dehydroxylation to form an anhydrous phase. Only a lattice distortion has taken place to some extent, resulting in a change in X-ray diffraction intensities.

The subsequent step of transformation in which mullite is formed from the anhydride involves a further reorganization of oxygen frame-work. This is shown clearly in the "fibre" diagram as given in Plate 1. A re-organization of this kind become more understandable when the trans-formation is regarded in terms of chemical formulae as follows:

$$3(Al_4Si_8O_{22}) \rightarrow 2(3Al_2O_3.2SiO_2) + 20SiO_2$$
anhydride      mullite
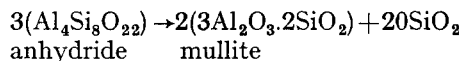
There is no *simple* relationship between the unit cells of anhydride and mullite. A great number of silicon ions must be discarded from the mullite parts. One can ask, therefore, where the potentiality for this reorganization comes from. Since the mullite formation is a direct result of the transforma-tion of anhydride, it certainly lies in the structure of anhydride.

In the original pyrophyllite structure, the hydroxyl ions are polarized by the large positive charges of adjacent aluminum ions. This differs from

the situation in magnesium silicates where the hydroxyl ions are not influenced to the same extent by magnesium ions, and on these grounds a difference may arise in the mechanisms of dehydroxylation of the aluminum and magnesium silicates. With highly polarized hydroxyl ions, the vibration of protons becomes more directional as the temperature is raised, and eventually an interaction between two neighboring hydroxyl ions may occur. The loss of oxygen ions on the surface or at the positions of lattice defects will provide opportunities for further diffusion of water molecules from the interior of the crystal. At the same time, the lattice framework will be slightly distorted by losing some oxygen ions. The infrared studies by Stubican and Roy (1961) and by Heller *et al.* (1962) precluded the presence of 4-fold coordination of aluminum in pyrophyllite anhydride, but does not exclude 5-fold coordination which might exist as a result of the process described above. The electrical neutrality is still retained in this case and the aluminum ions will remain near their original positions.

There is no direct evidence for this mechanism in the present experiments, but the existence of lattice distortion in the anhydride structure probably can be explained in this way.

The structural change from anhydride to mullite involves the expulsion of a large amount of silicon ions from those parts of the crystal where mullite is formed. The distorted open structure as assumed in the above discussion will provide enough space for these ion-migrations. As can be seen in the topotactic relationships the *c*-axis of mullite which is parallel with the direction of Al-octahedral chains in the structure runs parallel with the *b*-axis of pyrophyllite which is again the direction of Al-octahedral chains. This might mean that the reorganization of the oxygen framework in the anhydride structure with an increase in temperature is promoted without much difficulty because of the distorted open structure. At the same time, the re-packing of this kind will result in a fibre aggregate of the product crystallites rather than a single crystal of the product.

Contrary to the behavior of pyrophyllite, the thermal transformation of talc is characterized by the dehydroxylation and recrystallization being almost simultaneous reactions. A schematic representation of the reaction is as follows

$$Mg_6Si_8O_{20}(OH)_4 \rightarrow 6MgSiO_3 + 2SiO_2 + 2H_2O \uparrow$$
$$\text{(talc)} \qquad\qquad \text{(enstatite)}$$
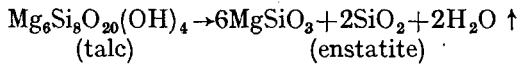
The unit cell relations indicate that one unit cell of talc transforms to one unit cell of enstatite as shown below:

Talc:        12Mg, 16Si, 48O, 8H
Enstatite:   16(=12+4)Mg, 16Si, 48O.

The number of oxygens shows no change in this schematic representation. This may imply that, during the dehydroxylation, no oxygen is lost in

those parts of talc where enstatite will be formed. It is in favor of the inhomogeneous mechanism.

The migration of protons from one oxygen to another disturbs the electrical neutrality. To make up for the loss of positive charge, a counter-migration of other cations will take place towards that region. The schematic representation given above shows that 8 protons are lost per unit cell of talc and 4 magnesium ions counter-migrate to form one unit cell of enstatite. This is exactly right to keep the charge balance. In other words, the mobilities of cations at the stage of dehydroxylation are increased by the unbalanced electric fields, and the dehydroxylation and recrystallization appear to be simultaneous reactions provided the process proceeds slowly enough to re-arrange the migrating cations. One of the justifications of this statement lies in that the anhydrous phase of talc has not been observed in either diffraction studies or in thermal analyses. This is in contrast to the case of pyrophyllite where there is no reason to see an increase in the ionic mobility.


## CONCLUSION


A homogeneous mechanism seems to be more feasible to explain the thermal transformation sequence of pyrophyllite, whereas the transformation of talc follows an inhomogeneous process. There is, however, no direct evidence for these mechanisms, and a further examination of the ionic mobility at the stage of dehydroxylation will be a powerful approach to the problem.

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