# ELECTRON DIFFRACTION AND MICROGRAPHIC STUDY OF THE HIGH-TEMPERATURE CHANGES IN ILLITE AND MONTMORILLONITE UNDER CONTINUOUS HEATING CONDITIONS*

*by*

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ABSTRACT

TRANSMISSION and diffraction electron micrographs were made of illite and montmorillonite to study the changes that take place as the clays were heated continuously to 1200°C.

In both of the clay minerals studied, expulsion of a highly fluid material occurred subsequent to dehydroxylation and prior to the development of the first-formed high temperature phases. It was hypothesized that this material represented the expulsion of constituents in the clay in excess of those needed for the formation of the first high-temperature phase. Electron diffraction indicates that the high-temperature phases that formed all developed with some preferential orientation, and were strongly influenced in their development by the structure of the original clay.

## INTRODUCTION

To DATE, only a few high-temperature investigations have been carried out on the clay minerals using the electron microscope, and none under continuous heating conditions. In this study, transmission electron microscopy and electron diffraction were utilized to determine the variations that occurred in illite and montmorillonite as they were heated continuously in the electron microscope to 1200°C. The high-temperature phases were examined from the viewpoint of the morphological changes that occurred when considered in the light of the structural changes taking place. In addition, oriented transformations of the high-temperature phases inherited from these clay minerals were also considered in detail.

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## MATERIALS AND METHODS

### *Samples Studied*

The samples used in this investigation were obtained from the clay mineral laboratory at the University of Illinois. The clays utilized for the study were as follows:

1. (a) Well-crystallized illite from Marblehead, Wisconsin.
   (b) Poorly-crystallized illite (Grundite) from Grundy County, Illinois, containing mixed layer clay, montmorillonite, and kaolinite.
2. Montmorillonite
   (a) Cheto, Arizona (bentonite).
   (b) Wyoming (bentonite).

### *Electron Microscope*

High temperature analyses were performed on a JEM-7 electron microscope equipped with a hot stage. The microscope was equipped with a five-lens, double-condenser system, and was operated at an accelerating potential of 80 kV. The microscope could be switched into selected area electron diffraction without modification simply by inserting a selector (field limiting) aperture and properly adjusting the lenses.

### *Hot Stage*

The hot stage consisted of a doubly wound tungsten wire coil mounted in the microscope in place of the regular specimen stage. The furnace was heated by resistance to a current supplied by a 12-volt storage battery.

The furnace temperature was measured from the current input, and was calibrated by means of a Pt–Pt, 10% Rh thermocouple. It was found that the furnace temperature could be determined with a maximum error of $\pm 15$°C after proper calibration.

*Sample preparation.*—The fraction of the clay with particles $<2\ \mu$ in diameter was separated by settling procedures and dilute suspensions of the $<2\ \mu$ fraction were prepared by placing about 0.5 g of clay in 50 ml of distilled water. A drop of this suspension was placed on a 200-mesh molybdenum electron microscope grid upon which a thin carbon film had previously been evaporated. When the water from the suspension had evaporated the grid was placed in the hot stage furnace for analysis.

After the first few test runs the following general procedure was established. A photograph was taken at room temperature and the furnace was then raised directly to 400°C (because no observable reactions occurred below this temperature). The temperature was then increased in 100°C increments to a maximum temperature of 1200°C. Except when reactions were observed to be taking place in a shorter interval, each temperature level was maintained for at least 30 min before photographs or diffraction patterns were taken in order to allow the temperature to stabilize and possible reactions to

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occur. Constant temperature levels of up to 3 hr were maintained where it was believed reactions were occurring or might occur.

## ILLITE

### *Results*

*Well-crystallized illite.*—No observed change takes place in illite until the temperature reaches about 700°C. At this temperature small spots of liquid begin to form within the outline of the clay platelets. These liquid spots begin developing beyond the temperature at which dehydroxylation should occur (475–600°C) and form within the range of the anhydride structure (600–850°C, Bohor, 1964). Plate 1 shows the development of these spots at 850°C.

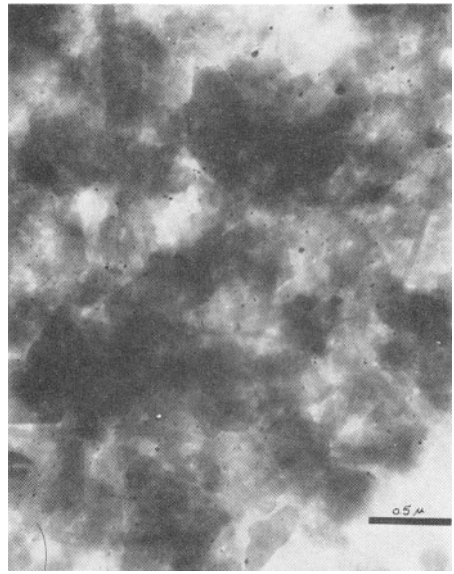



PLATE 1. Development of spots of liquid in well-crystallized illite at 850°C. Sample from Marblehead, Wisconsin.

All diffraction up to this point has been similar, and has produced patterns representing the *a–b* plane of illite essentially unchanged from room temperature (Plate 2). At 1000°C, no diffraction could be obtained from the clay and no further diffraction maxima were obtained until the appearance of spinel patterns at 1100°C.

After 40 min at 1150°C decomposition was occurring in the solid state in some areas (Plate 3*a*), and in these areas relatively intense spinel Debye rings were recorded with weaker mullite reflections. In other areas partial

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or complete melting has occurred (Plate 3*b*) and the diffraction patterns showed intense mullite development with occasional spinel rings present. By 1200°C complete fusion of the anhydride and spinel phases had taken place and mullite crystals were actively developing (Plate 4).

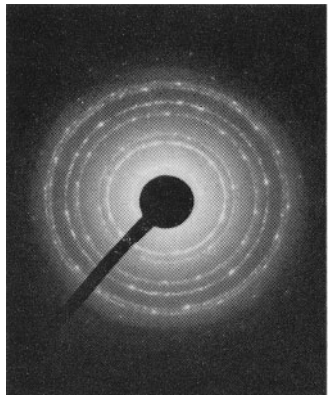


PLATE 2. Diffraction pattern of *a–b* plane of illite at room temperature. Sample from Marblehead, Wisconsin.

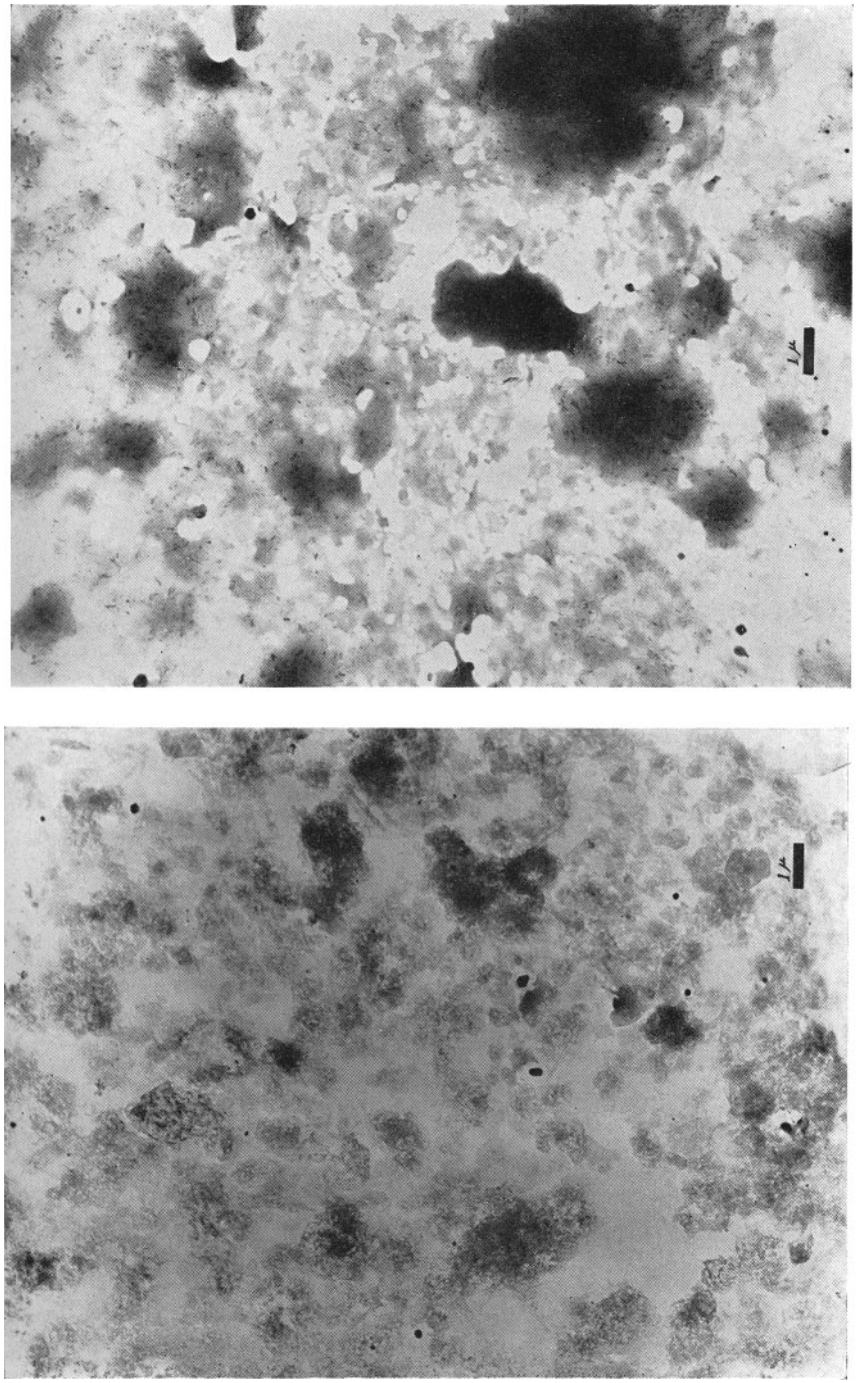
*Grundite.*—Slightly lower temperatures were obtained for reactions in the Grundite sample because of the poorer order and the presence of impurities. The liquid spots which first occurred in the well-crystallized illite at about 700°C were abundant in the Grundite at about 600°C, and it is obvious from the fusion of the foreign particles in Plate 5 that impurities contribute to the number of liquid spots.

Spinel was first detected on the diffraction patterns at 1000°C rather than 1100°C as in the well-crystallized Marblehead clay, and a small number of liquid spots are still present at 1000°C when the spinel was first detected in the diffraction patterns. No crystal development was observed at 1000°C, in contrast to the well-crystallized illite at this temperature.

## *Discussion*

A distinct broadening of the 440 ring of the spinel-type phase that develops from kaolinite at about 850°C was recorded by Comer (1961). This ring broadening indicated that there was preferred orientation of the [110] zones. The distinct orientation of the [110] of the spinel-type phase on the electron diffraction patterns of kaolinite is essentially absent from the patterns of the spinel phase in illite (Plate 6). The spinel phase developed in illite did show that the (111) plane was parallel to the *a–b* plane of illite similar to the orientation of the spinel-type phase in kaolinite as proposed by Brindley and Nakahira (1959) and confirmed by Comer (1961). The lack of orientation of the [110] may reflect the smaller particle size of the illite, for with a smaller

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(a) (b)

PLATE 3. Variation in decomposition of illite after 40 min at 1150°C. (a) Little or no fusion has occurred. (b) Fusion taking place and mullite crystals developing.

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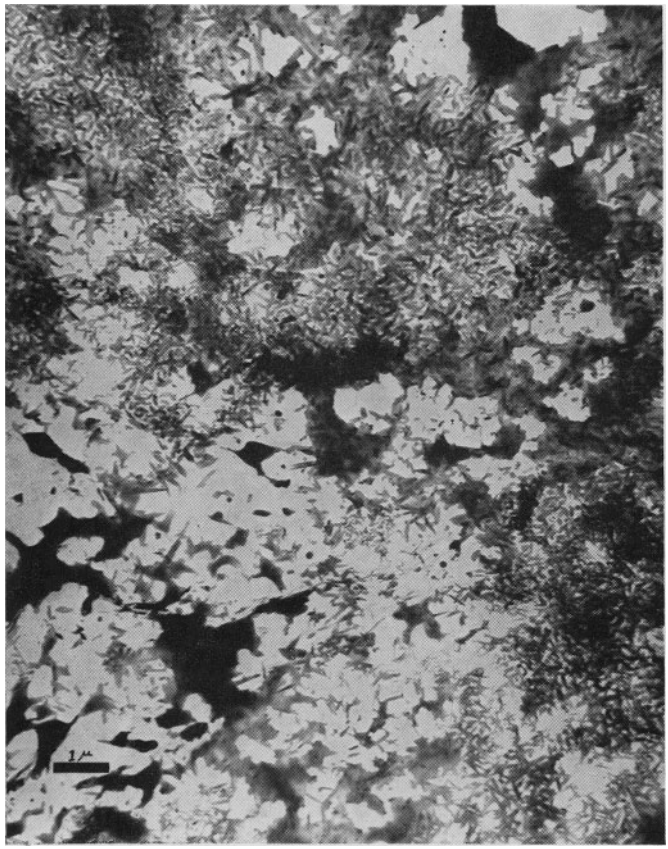



PLATE 4. Active development of mullite at 1200°C in well-crystallized illite. Sample from Marblehead, Wisconsin.

particle size the pattern would be obtained from a larger number of platelets and any orientation that might exist in any single platelet would be masked by the superposition of the patterns of other platelets in the vicinity.

The mullite phase in illite was found to be preferentially oriented with its *c*-axis lying in the (111) plane of the spinel phase (Plate 7), similar to the orientation found by Comer (1961) for the mullite phase in kaolinite.

It seems likely that the spots of liquid that develop in illite between 600°C and 850°C reflect the expulsion of material, probably siliceous, which must precede reorganization into the spinel phase. When the hydroxyl ions are lost at about 600°C, disruption of two silica tetrahedral layers takes place and some of the disrupted tetrahedra have to be removed in order to convert the anhydride into the spinel phase. This removal of these tetrahedral con-

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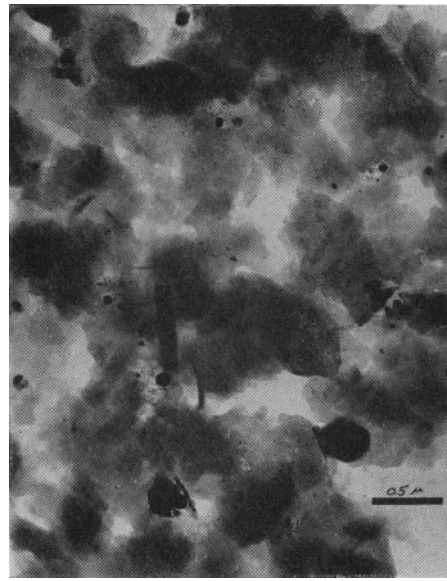



PLATE 5. Grundite clay at 800°C. Spots of liquid actively developing from the clay and foreign substances in clay. Sample from Grundy County, Illinois.

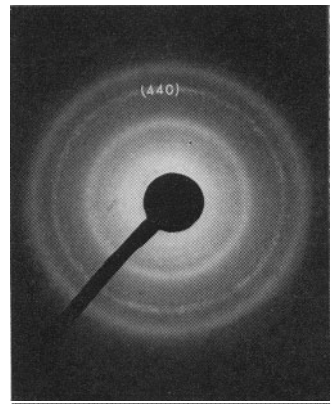



PLATE 6. Diffraction pattern showing spinel development in Marblehead illite at 1150°C. The 440 reflection of spinel is shown.

stituents probably is reflected in the formation of the droplets of material which can be observed in Plate 1.

This hypothesis of liquid or fluid expulsion of material from illite is also in keeping with data from DTA and X-ray investigations. The second endotherm in illite reflects the loss of the anhydride structure and this structural

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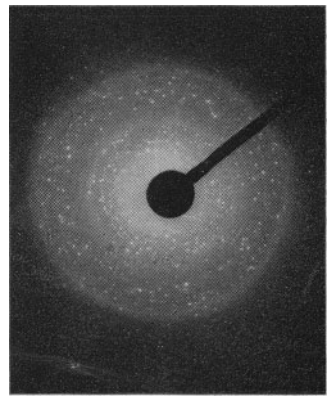


PLATE 7. Mullite diffraction array from Marblehead illite after 30 min at 1200°C.

loss occurs at the point of maximum liquid spot development ($\simeq$900–1000°C). It seems likely that the liquid spots that develop reflect the removal of the superfluous tetrahedral constituents just prior to total collapse of the structure and the subsequent reorganization into the spinel phase.

Another feature that seems to reinforce the idea of considerable reorganization in the illite anhydride is the loss of diffraction at 900–1000°C. This loss would be expected with the reorganization described above.

Because of the composite nature of the image in transmission microscopy it was impossible to tell whether the liquid spots that developed were moving along the substrate, through the clay, or between the individual platelets. The very rapid movement of the droplets suggests expulsion from the clay caused by the sudden reaction to non-equilibrium conditions in a certain small area. Once the liquid or fluid formed, it would quickly diffuse out of the clay and volatilize. When the spots remained for some time they were either being reinforced by other liquid spots moving into the same area, or were trapped in the clay, or between the clay and the substrate.

No investigator in the past has made any mention of the development of these so-called "liquid spots". In previous research the much longer heating periods, use of the replica technique, and heating the clay in air in the absence of a substrate to trap the liquid would have prohibited their observation.

## MONTMORILLONITE

### *Results*

*Cheto montmorillonite.*—The first change that occurs in Cheto montmorillonite is the appearance of spots of liquid at 600°C, similar to those observed in illite. These liquid spots continue to develop as the temperature is increased and reach a maximum at about 850°C (Plate 8). At 900°C there

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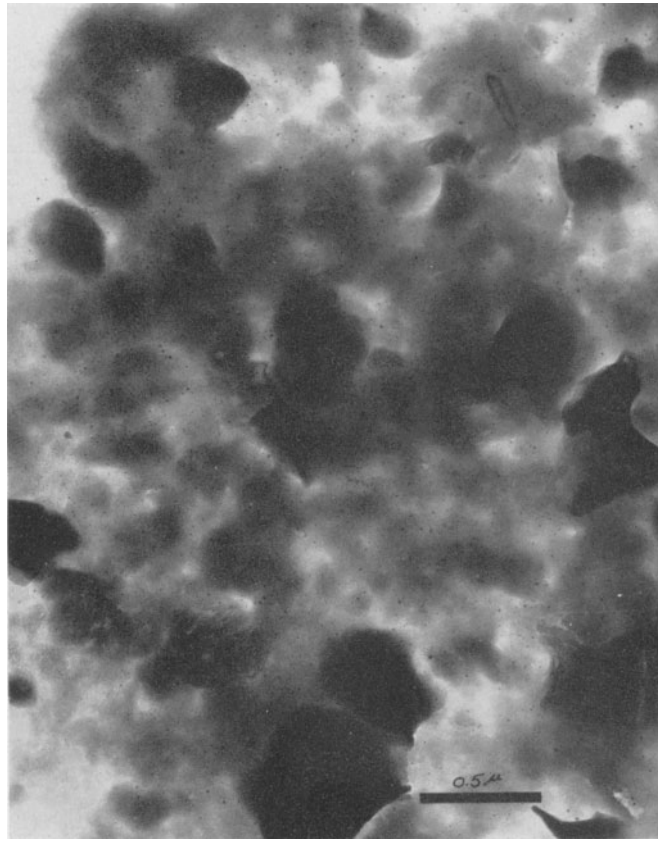



PLATE 8. Development of liquid spots in Cheto montmorillonite at 800°C.

is a considerable diminution in the number of liquid spots indicating that the development stage has been passed and volatilization is taking place.

At 1000°C crystallization has begun and by 1100°C the newly formed crystallites are about 0.5 $\mu$ in length (Plate 9). The micrograph obtained after about 35 min at 1200°C (Plate 10) shows the continuing growth of the crystals, many now exceeding 2 $\mu$ in length.

In general, the diffraction patterns obtained from the high temperature phases of the Cheto montmorillonite were quite poor, and those patterns that were obtained were badly scattered.

Although previous researchers (Grim and Kulbicki, 1961) have recorded $\beta$-quartz developing between 900°C and 1100°C in Cheto montmorillonite, no recognizable $\beta$-quartz diffraction patterns were recorded in the present study. Diffraction effects of montmorillonite were lost at 900°C as they were

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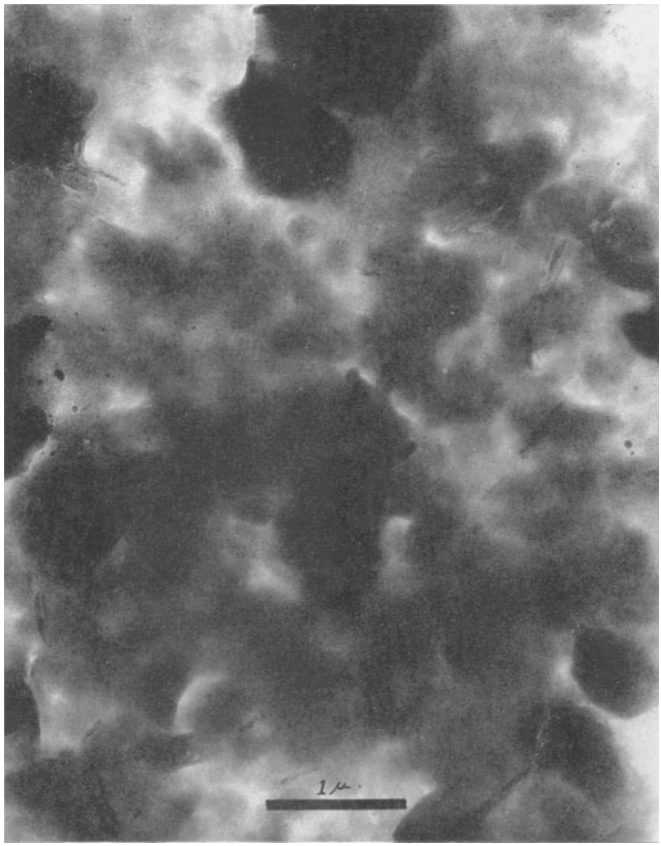



PLATE 9. Cristobalite crystals in Cheto montmorillonite at 1100°C.

in Grim and Kulbicki's study but the development of $\beta$-quartz which they observed at 950°C did not appear. No further diffraction occurred until the furnace temperature had reached 1000°C, but even at this temperature the reflections were so scattered that identification was very difficult. Readily recognizable patterns were not recorded until 1100°C was attained and cristobalite reflections began to appear.

Diffraction patterns obtained at 1100°C and 1200°C were all of cristobalite, although the patterns here were also somewhat scattered. The diffraction patterns indicate that the cristobalite crystals are oriented with their (111) plane parallel to the $a - b$ plane of the montmorillonite.

*Wyoming montmorillonite.*—Wyoming montmorillonite registered the same changes as Cheto montmorillonite up to a temperature of 1000°C.

Spots of liquid began developing at about 600°C and reached their maximum

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PLATE 10. Cristobalite crystals in Cheto montmorillonite after 35 min at 1200°C.

development at 800°C. Subsequently, the liquid began to volatilize and by 1000°C it had all disappeared.

The diffraction results up to 1000°C were also similar to the Cheto clay with the pattern of the *a–b* plane of montmorillonite persisting up to 800°C and with the diffraction effects disappearing at 900°C. No more patterns were observed until the furnace had been at 1000°C for about 1 hr. After this interval Debye rings of mullite began to appear. Examination of Plate 11 shows the faint prismatic development typical of the mullite phase.

Cristobalite was first recorded at 1100°C, both by diffraction and in the micrographs. Plate 12*a* and *b* shows the development of the two phases, mullite and cristobalite respectively, at 1200°C. The extensive development of cristobalite (Plate 12*b*) contrasts strongly with the short, poorly developed prisms of mullite (Plate 12*a*). This poor mullite development was predicted

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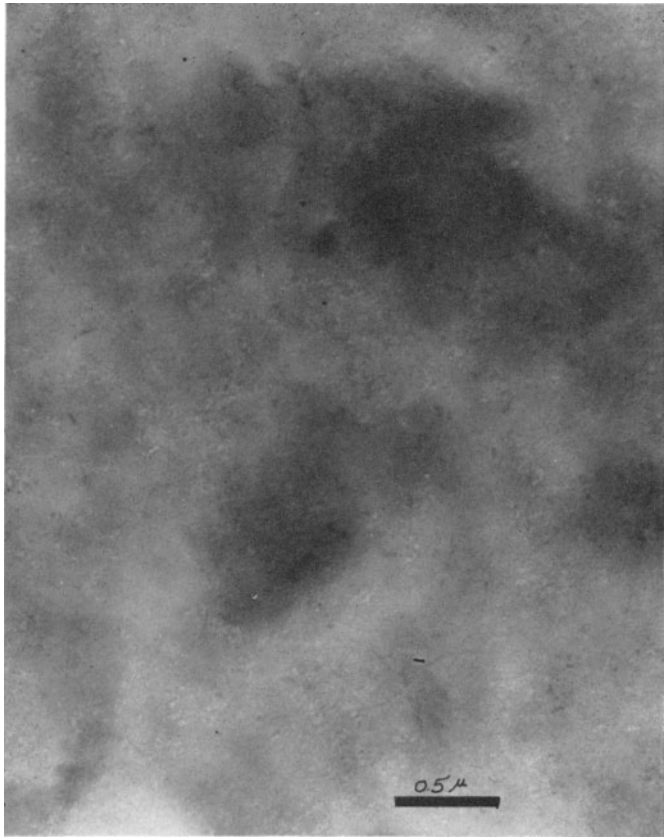



PLATE 11. Mullite crystallization in Wyoming montmorillonite at 1000°C.

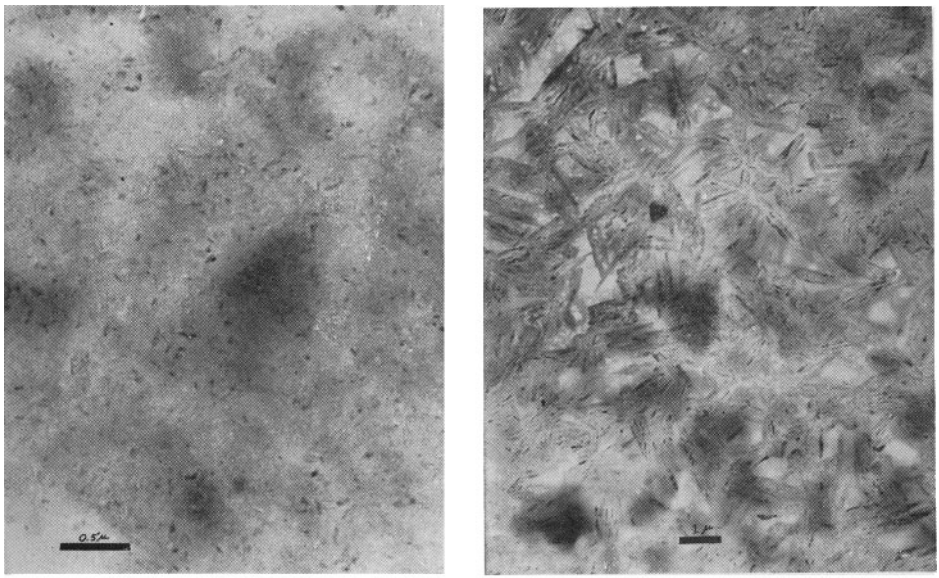
by Grim and Kulbicki (1961) and was attributed to the presence of magnesium in the clay which tended to block the development of mullite.

## *Discussion*

The structure of cristobalite, the principal high-temperature phase developing from montmorillonite, is a framework silicate composed of six-membered rings of silica tetrahedra. The entire cristobalite structure can be formed by connecting sheets of these six-membered rings and inverting alternate tetrahedra in the rings relative to their neighbors. It is then only necessary to connect these sheets together through the tips of the tetrahedra to complete the structure. Because both montmorillonite and the resulting cristobalite phase contain six-membered rings of silica tetrahedra it may be supposed that the transformation of montmorillonite to cristobalite involves the

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expulsion of the constituents of the octahedral layer, together with the proper arrangement of silica tetrahedral sheets which have, or develop, the tetrahedral inversions necessary for the cristobalite structure. Grim and Kulbicki (1961) have pointed out that some of the silica tetrahedra in montmorillonite may already be inverted, and the formation of cristobalite from montmorillonite would seem to provide strong support for this idea. If



(*a*) (*b*)

PLATE 12. Contrasts development of (a) mullite, and (b) cristobalite in Wyoming montmorillonite at 1200°C.

montmorillonite does contain inverted tetrahedra, the formation of cristobalite would require only the removal of ions from the octahedral part of the structure and then the joining of successive tetrahedral sheets; providing only that the pattern of tetrahedral inversion was similar to the pattern of inversions in cristobalite.

Grim and Kulbicki suggest that the presence of $\beta$-quartz in Cheto montmorillonite and its absence in Wyoming montmorillonite can be attributed to a larger number of tetrahedral inversions in the Cheto clay. Consideration of the arrangement of the tetrahedra in the $\beta$-quartz and cristobalite structures, and the fact that both clays produced cristobalite in solid state reactions, and at about the same temperature (at least in the present study) would seem to suggest the contrary. The cristobalite structure is formed from

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tetrahedral sheets with a regular pattern of alternating tetrahedral inversion, and $\beta$-quartz is likely a step in the process of inverting tetrahedra to produce this regular alternating pattern. Wyoming montmorillonite, on the other hand, may already have more inversions (perhaps even approaching the right number and arrangement) and thus does not form the intermediate $\beta$-quartz phase. The densely packed growth of cristobalite crystals grown in the Wyoming montmorillonite is considerably different from the widely spaced acicular development in the Cheto clay and would seem to suggest that the cristobalite forms more readily from the Wyoming clay.

Although Grim and Kulbicki (1961) were unable to detect any phase developing in Wyoming montmorillonite subsequent to the exotherm at 920°C, mullite crystals were observed at 1000°C in the present study. It seems likely that the exotherm at 920°C was caused by the nucleation of mullite, or a bond shift from face to edge shared octahedra in the octahedral chains preparatory to mullite nucleation.

The liquid spots developing in montmorillonite between 600°C and 900°C indicate that something is being expelled from the clay structure. In the area depicted in Plate 12*a* the high-temperature phase developing is mullite, and no cristobalite was found to be crystallizing here. Perhaps constituents such as MgO are removed which are unneeded to tend to block the formation of mullite. The poor development of mullite crystals could reflect the presence of tetrahedral inversions which would be detrimental to its formation.

A similar explanation can be proposed for those sections of the clay where only cristobalite crystals form, such as the area in Plate 12*b*. Here unneeded ions are expelled but cristobalite rather than mullite forms because the number of inverted tetrahedra is larger or more regular, and cristobalite can form more easily than mullite with these inversions.

One further factor that must be considered is why spinel does not develop with structural collapse of the montmorillonite anhydride as it does in illite. Again, this probably can be attributed to inverted silica tetrahedra in montmorillonite. If tetrahedral inversions are present in the viscous mass in which the high-temperature phases are developing, it would be easier to expell the octahedral constituents and form $\beta$-quartz or cristobalite, than to arrange all the tetrahedra in any given layer in one direction to form the spinel phase.

## CONCLUSIONS

The recurrence of similar orientation in the high-temperature phases in successive hot stage runs, and the repetition of similar orientation in high temperature phases of mullite in both illite and montmorillonite indicate that these clay minerals strongly influence the development of their high-temperature phases. This influence is reflected not only in preferential orientation, but also in the phase that develops as evidenced by the cristobalite development in montmorillonite.

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