HIGH-TEMPERATURE PHASES FROM KAOLINITE AND HALLOYSITE*

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ABSTRACT

A selected group of kaolinite and halloysite clays of varying structure and impurities are examined by differential thermal and *x*-ray diffraction methods to establish the significance of the various observed thermal effects. The heating range for the thermal curves extends to 1350° C. and the study of specimens is supplemented by the firing of materials to intermediate temperatures.

Interpretations are given for the cause of the various thermal peaks, and the reasons for lack of agreement in the literature are discussed. The complete firing sequence for kaolinite and halloysite is described.

INTRODUCTION

Kaolinite-type clays are so widely used in the manufacture of ceramics that many investigators have studied the sequence of phase changes in kaolinite during its firing. The investigators have differed, however, regarding the phase changes observed and also their interpretations as to cause of the thermal reactions. The author therefore examined phase changes in kaolinite and halloysite under controlled firing conditions.

The results of this study show that the disagreements in previous reports may be accounted for by the fact that materials of different degrees of crystallinity, morphology, and purity show different sequences of phase changes at high temperatures.

Differential thermal analysis is a laboratory method which is especially useful in studying high-temperature reactions in clays because the deflections in the curve graphically represent changes in phase within the material. This method analyzes substances under nonequilibrium conditions, and corroborating *x*-ray data must therefore be obtained under similar conditions, by air-quenching samples at the desired temperatures. If samples are "soaked" thermally, equilibrium conditions are approached; differences are then observed in phases and temperatures of formation between soaked samples and air-quenched samples.

All thermal curves for kaolinite and halloysite show two significant features below 1000° C.: (1) a prominent endothermic reaction between 500° and 600° C. which can be correlated with the absorption of energy that results from loss of hydroxyl groups; (2) an intense exothermic

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reaction just below 1000° C. which has been attributed to the crystallization of either mullite or what has been called γ-Al_2O_3.

The firing product at temperatures between the two prominent thermal peaks is referred to as "metakaolin" and "pro-mullite." The theory (Insley and Ewell (1)) which correlates the exothermic peak with γ-Al_2O_3 implies that an intimate mixture of amorphous alumina and amorphous silica is formed after the lattice is dehydrated, and that γ-Al_2O_3 is an intermediate step in the formation of mullite.

The mullite hypothesis (Comeforo, Fischer, and Bradley (2)) postulates that when hydroxyl groups are expelled, the noncrystalline compound which is formed possesses some residual structure. On further heating, the noncrystalline compound collapses into crystalline mullite nuclei which are then free to grow normally. γ-Al_2O_3 is considered incidental and not a step in the major reactions of the firing process.

Selection of Kaolinite Samples

Kaolinite is known to vary in degree of crystallinity because of random displacement of structural layers by multiples of $b_0/3$; transitional types range from well crystallized to poorly crystallized. The diffraction diagrams of poorly crystallized kaolinite (similar to Brindley's (3) fireclay material) contain fewer reflections than those for well crystallized material. The degree of crystallinity should be known before kaolinite samples are fired, because the results of firing may vary at certain temperatures according to variation in crystallinity.

Different sequences of phase changes during firing may also develop depending upon the type of impurity in the clay. For this reason, the impurities associated with the clay, both kind and quantity, are even more important than crystallinity. Coarse particles can be removed by fractionation, and the finer impurities can usually be detected by *x*-ray methods. Cations which cause fluxing may be detected by chemical analysis.

A micaceous impurity, apparently intergrown with kaolinite, is often observed; it is probably related genetically or diagenetically to the kaolinite. (Kaolinites which contain mica that can be observed in diffraction patterns are not discussed here.) Particularly important are poorly crystallized kaolinites in which the micaceous material is not detected in powder diffraction patterns but in which it appears as an anhydride after the kaolinite is dehydrated.

Powder diffraction patterns of unfired kaolinite and kaolinite fired to 800° C. are shown in Fig. 1. The unfired clay shows no effects of mica, but at 800° C. the anhydride shows clearly. A few anatase lines are also present.

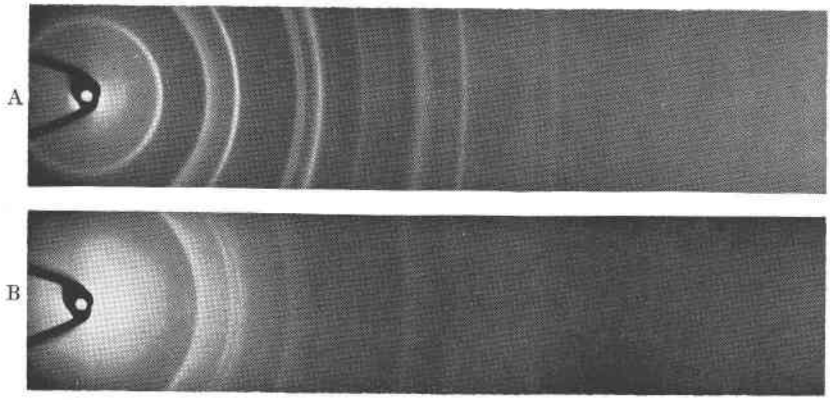


Fig. 1. *X*-ray powder diffraction photographs of mica-bearing, poorly crystallized kaolinite. A. Unfired clay. B. Fired to 800° C.

Undetected mica and other impurities probably caused some of the differences previously reported in the phase changes during firing and shown in thermal curves for kaolinite. Thus it is important to determine not only the degree of crystallinity, but also the kind and amount of impurities, detrital, intergrown, and chemical.

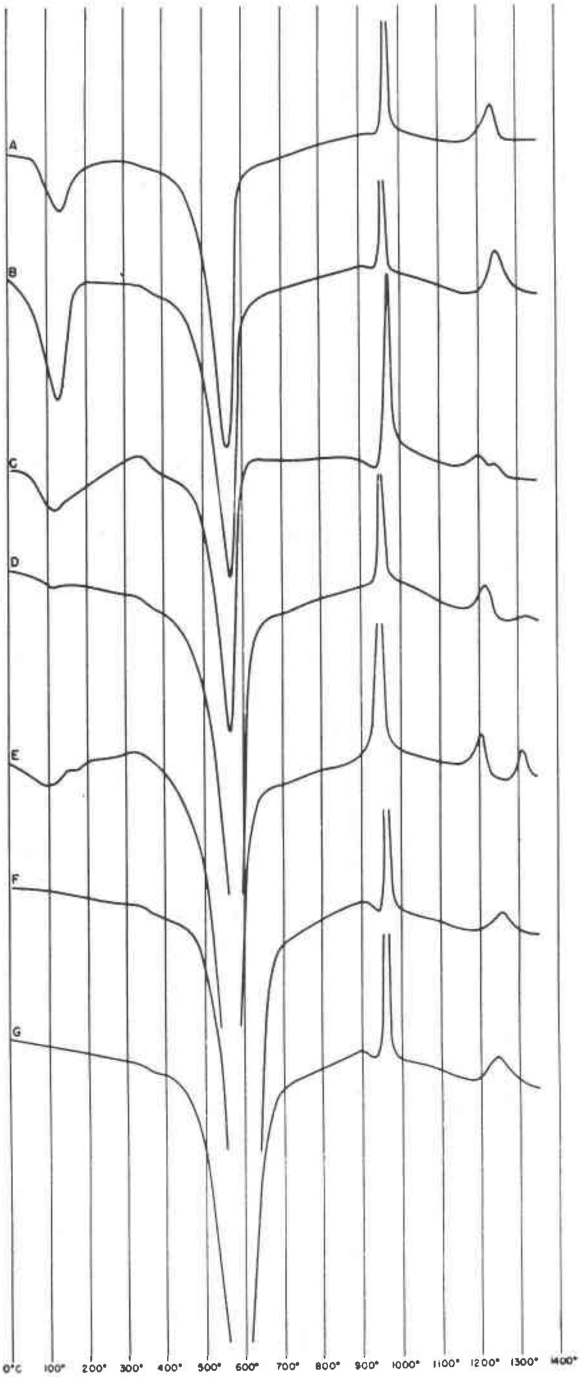
This study investigates the phase changes of mica-free, well crystallized kaolinite and mica-free, poorly crystallized kaolinite, mica-bearing, poorly crystallized kaolinite, and halloysite. No studies were made with kaolinite whose diffraction patterns showed visible mica, although such mica would be expected to cause additional effects on the thermal curve and firing sequence.

Experimental

Samples studied were mica-free, poorly crystallized kaolinite from Mt. Savage, Maryland; mica-bearing, poorly crystallized kaolinite from Anna, Illinois, and Sayreville, New Jersey; mica-free, well crystallized kaolinite from Dry Branch, Georgia, and Lewistown, Montana; halloysite ($4H_2O$) from Bedford, Indiana, and halloysite ($2H_2O$) from Mica, Washington.

The degree of crystallinity of the kaolinites and the physical impurities in all samples were determined by *x*-ray diffraction. The kaolinites contained minor anatase as an impurity, and the Illinois and Maryland clays contained a small amount of fine-grained quartz. The Maryland clay contained a small amount of an unknown impurity. The halloysites were free from impurity.

Thermal curves for all samples were run to 1350° C. and rerun for reproducibility checks. Samples were heated in the thermal furnace at a


A
B
C
D
E
F
G
0°C
100°
200°
300°
400°
500°
600°
700°
800°
900°
1000°
1100°
1200°
1300°
1400°

rate of about 10° C. a minute to significant portions of the thermal curve below 1000° C. and also to 1000°, 1100°, 1150°, 1200°, 1250°, 1300°, and 1350° C. The air-quenched samples were then examined by *x*-ray powder diffraction analysis.

Thermal curves are shown in Fig. 2. The phases for fired samples are listed in Table 1. Thermal curves and phases for both examples of each of the three pairs of clay types are identical except for the effects of quartz in the Illinois clay.

THE THERMAL CURVES

There is no reason to expect that $b_0/3$ shifts in the lattice structure of kaolinite should be reflected in the shape of the thermal curve. The principal features cited by Grim (4) as thermal differences between well and poorly crystallized kaolinite at temperatures below 1000° C. are as follows: (1) The poorly crystallized kaolinites have broad low-intensity initial endothermic reactions whereas the well crystallized kaolinites do not; (2) the intensity of the large endothermic reaction at about 600° C. and the final exothermic reaction are much greater for the well crystallized varieties; (3) the final exothermic reaction for well crystallized kaolinite is immediately preceded by a slight endothermic reaction whereas no such reaction is shown for poorly crystallized kaolinite. Other features may also be observed: the 600° C. endothermic peak is higher in temperature and occurs over a greater temperature range for well crystallized varieties; the exothermic slope of the curve between 600° and 900° C. is greater for well crystallized kaolinite, and the final exothermic peak is higher in temperature.

The smaller particle size of poorly crystallized kaolinite readily accounts for most of the differences except (3) above and the slope between 600° and 900° C. The important difference is the presence or absence of the small endothermic reaction which precedes the final exothermic peak. In Fig. 2 the peak is present in both mica-free, well crystallized kaolinite and mica-free poorly crystallized kaolinite and therefore cannot be related to the structure of the clay. The peak is absent in mica-bearing kaolinites because mica suppresses the peak. Absence of this peak indicates that the material is not pure.

Thus it appears that previous interpretations have been made on

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FIG. 2. Differential thermal curves of kaolinite and halloysite. A. Halloysite ($2H_2O$), Mica, Washington. B. Halloysite ($4H_2O$), Bedford, Indiana. C. Mica-free poorly crystallized kaolinite, Mt. Savage, Maryland. D. Mica-bearing poorly crystallized kaolinite, Sayreville, New Jersey. E. Mica-bearing poorly crystallized kaolinite, Anna, Illinois. F. Mica-free well crystallized kaolinite, Lewistown, Montana. G. Mica-free well crystallized kaolinite, Dry Branch, Georgia.

TABLE 1. PHASES AND OBSERVED RELATIVE INTENSITIES FOR KAOLINITE AND HALLOYSITE FIRED UNDER NON-EQUILIBRIUM CONDITIONS

Temperature	800° C.	Exothermic peak ca. 950° C.	1000° C.	1100° C.	1150° C.	1200° C.	1250° C.	1300° C.	1350° C.
Mica-free well-crystallized kaolinite	metakaolin	amor. silica	amor. silica	amor. silica	amor. silcia	amor. silica	?		
		γ-Al$_2$O$_3$ *m*	γ-Al$_2$O$_3$ *m*	γ-Al$_2$O$_3$ *m*	γ-Al$_2$O$_3$ *m*	γ-Al$_2$O$_3$ *m*	γ-Al$_2$O$_3$ *w*		
		mullite* *w*	mullite *w*	mullite *w*	mullite *mw*	mullite *m*	mullite *ms*	mullite *s*	mullite *vs*
Mica-free poorly-crystallized kaolinite	metakaolin	amor. silica	amor. silica	amor. silica	amor. silica				
		γ-Al$_2$O$_3$ *m*	γ-Al$_2$O$_3$ *m*	γ-Al$_2$O$_3$ *m*	γ-Al$_2$O$_3$ *m*				
		mullite *w*	mullite *w*	mullite *m*	mullite *m*	mullite *ms*	mullite *ms*	mullite *ms*	mullite *s*
							cristobalite *ms*	cristobalite *s*	cristobalite *vs*
Mica-bearing poorly crystallized kaolinite	metakaolin	α-SiO$_2$ *s*	α-SiO$_2$ *s*	α-SiO$_2$ *s*	α-SiO$_2$ *s*	α-SiO$_2$ *w*	α-SiO$_2$ *vw*		
	α-SiO$_2$† *s*	anhydride *m*							
	anhydride *m*	γ-Al$_2$O$_3$ *m*	γ-Al$_2$O$_3$ *m*	γ-Al$_2$O$_3$ *m*	γ-Al$_2$O$_3$ *m*				
					mullite *vw*	mullite *ms*	mullite *ms*	mullite *ms*	mullite *s*
							cristobalite *ms*	cristobalite *s*	cristobalite *vs*
Halloysite	metakaolin	amor. silica	amor. silica	amor. silica	amor. silica	amor. silica			
		γ-Al$_2$O$_3$ *m*	γ-Al$_2$O$_3$ *m*	γ-Al$_2$O$_3$ *m*	γ-Al$_2$O$_3$ *m*	γ-Al$_2$O$_3$ *m*	γ-Al$_2$O$_3$ *vw*		
						mullite *w*	mullite *ms*	mullite *s*	mullite *vc*

* Intensities of diffraction lines are not proportional to amounts.

† Not present in Sayreville, New Jersey, kaolinite.

impure materials, and there is no significant difference in the thermal curves for poorly crystallized and well crystallized kaolinite except for the effects caused by particle size.

Additional evidence for the presence of mica is indicated by the small endothermic reaction at about 700° C. which is present only in mica-bearing, poorly crystallized kaolinite. The reaction is caused by the dehydration of the micaceous intergrowth, and the peak indicates the presence of the anhydride. The peak is 150° C. higher than that observed for illite (5); dehydration at higher temperatures is evidence that there are muscovite-crystallization clay-micas intimately associated with kaolinite whose physical properties and composition differ from those of the original illite materials.

Above 1000° C., well crystallized kaolinite and halloysite show one exothermic peak at about 1250° C.; the poorly crystallized kaolinites show two distinct peaks. Mica-bearing varieties have peaks at about 1200° and 1300° C., and the mica-free clay has peak temperatures at about 1200° and 1240° C. The significance of the peaks is discussed below.

Characteristics of the halloysite thermal curve are: (1) there is a large initial endothermic peak at about 100° C.; (2) the large endothermic peak near 600° C. occurs at approximately the same temperature as the similar peak for poorly crystallized kaolinite but is reduced in intensity; (3) the peak for halloysite returns to base line faster than it departs, whereas well crystallized kaolinites show about equal rates of speed; (4) the exothermic slope above 600° C. is similar to the slope for mica-bearing, poorly crystallized kaolinite; (5) the small endothermic reaction at about 950° C. is less intense than it is for well crystallized kaolinite; (6) the exothermic reaction below 1000° C. is less intense than it is for well crystallized kaolinite; (7) the curve above 1000° C. is similar to that of well crystallized kaolinite, and the peak at 1250° C. is greater in intensity.

SEQUENCES OF PHASE CHANGE

For kaolinite and halloysite, the development of high-temperature phases depends on the type and amount of impurities as well as the crystallinity and morphology of the clay.

(1) *Mica-free kaolinite.*—Diffraction patterns of well and poorly crystallized kaolinites are identical up to 1000° C., which indicates that neither structure nor impurities exerts influence below this temperature. Diffraction patterns made after loss of hydroxyl groups are characterized by a broad diffuse asymmetrical reflection at about 4.3 a.u. as well as at least two weaker bands at higher diffraction angles which could not be measured. These reflections are attributed to the noncrystalline com-

pound of metakaolin (2). As the samples were mica-free, there was no anhydride structure. The 960° C. exothermic peak coincides with the formation of mullite, γ-Al_2O_3 and amorphous silica; the amount of γ-Al_2O_3 formed is less than that of mullite. The amount of mullite observed in diffraction patterns depends upon the crystallinity of the clay; diffraction intensities are greater in well crystallized varieties. The low-temperature mullite nuclei are greatly elongated along the *c*-axis and grow slowly, mostly in lateral directions, with increase of temperature (2). The 960° C. exothermic peak also coincides with a decrease in intensity of the 4.3 a.u. band.

Above 1000° C. the temperatures at which phases form apparently depend on impurities. The 1200° C. exothermic peak for poorly crystallized kaolinite and the 1250° C. peak for well crystallized kaolinite are correlated with a second generation of mullite from γ-Al_2O_3 and amorphous silica. γ-Al_2O_3 diffraction lines and the reduced 4.3 a.u. band retain their intensities until the start of the thermal peak; their disappearance at the peak is accompanied by a sharp increase in intensity of mullite diffraction lines. The higher-temperature mullite crystals do not exhibit the pronounced elongation of the low-temperature nuclei.

After mullite has formed from γ-Al_2O_3 and amorphous silica, the remaining silica crystallizes to form cristobalite. The process is indicated by the small exothermic peak at temperatures higher than the upper mullite thermal peak. For well crystallized varieties cristobalite does not form within the temperature range studied and therefore no exothermic peak was observed. The reaction evidently occurs at temperatures above 1350° C. (6). On the other hand, poorly crystallized kaolinite formed cristobalite at about 1240° C. and the thermal peak is therefore present.

(2) *Mica-bearing kaolinite.*—The sequence of high-temperature phases is greatly affected by mica. Diffraction patterns made after loss of hydroxyl groups indicate the presence of a crystalline three-layer anhydride. No micaceous impurity could be detected in powder diffraction diagrams or by petrographic analysis of unfired samples, but diffraction effects from well-oriented aggregates revealed a small amount of micaceous material. For powder diagrams, the anhydride is apparent only after the kaolinite structure is destroyed by firing. Analytical data indicate 0.53 and 0.60 per cent K_2O for the Illinois and New Jersey clays respectively, not unreasonable figures for small amounts of mica.

As powder *x*-ray and petrographic methods may not detect small amounts of mica, they may not necessarily be accurate methods for establishing purity of kaolinite.

The anhydride structure persists to the 950° C. exothermic peak, and only γ-Al_2O_3 and amorphous silica is observed in diffraction patterns at this temperature. The destruction temperature is about 100° C. higher than those observed by Grim and Bradley (5) for the original illite materials and is probably related to the different mode of origin of the two micaceous materials. No mullite phase was observed at the 950° C. peak.

The 1200° C. thermal peak is related to second generation mullite formation from γ-Al_2O_3 and amorphous silica. The typical sequence again occurs, mullite diffraction lines appear at the peak where γ-Al_2O_3 lines and 4.3 a.u. band disappear. The excess silica, converted to cristobalite at about 1300° C., is represented by a small thermal peak. Cristobalite does not form until all γ-Al_2O_3 has been used up in mullite formation. The mullite peak at 1200° C. is about 50° C. lower in impure kaolinites. There is evidently a relationship between the peak temperatures for mullite and cristobalite. Whenever the mullite peak is formed at about 1200° C. the cristobalite peak occurs within the temperature range studied (1240°–1320° C.). But for pure clays the mullite peak occurs at about 1250° C. and no cristobalite peak is present up to 1350° C.

(3) *Halloysite.*—The firing sequence for halloysite is identical with that of pure kaolinite up to the 960° C. exothermic peak. For halloysite, γ-Al_2O_3 and amorphous silica are observed in diffraction patterns at this temperature, similar to mica-bearing, poorly crystallized kaolinite. γ-Al_2O_3 and the 4.3 a.u. band disappear as mullite is formed at the 1250° C. exothermic peak. The larger size of the upper halloysite mullite peak as compared to that for well crystallized kaolinite is evidently caused by the crystallization of a greater amount of mullite at 1250° C. Thus the observed firing sequence for halloysite and poorly crystallized micaceous kaolinite is similar, the second mullite peak for halloysite being about 50° C. higher. As with well crystallized kaolinite, no cristobalite is formed up to 1350° C., and the excess silica remains amorphous.

THE DEHYDRATED STATE

There are two possibilities for the structure of kaolin-type minerals after loss of hydroxyl groups: (1) an intimate mixture of amorphous alumina and amorphous silica; (2) an amorphous compound of alumina and silica (metakaolin). The evidence of the 4.3 a.u. and related bands in diffraction patterns implies that a noncrystalline compound is formed because these bands are more prominent than those observed from truly amorphous solids (2). It has been demonstrated by Brindley (7) that single crystal photographs of dehydrated nacrite show a coordinated structure and not an amorphous mixture. The metakaolin structure has been interpreted by Comeforo, Fischer and Bradley (2) as "coordinated strings of alumina octahedra, with only some buckling of the silica layer to provide the additional oxygen necessary to complete the arrangement."

The diffraction effects of such a structure would be identical with those to be expected from amorphous silica (8). In metakaolin the silica is confined to the structure, but at temperatures following the major exothermic peak, the compound has been destroyed and amorphous silica exists with γ-Al_2O_3. The decreased intensity 4.3 a.u. band here indicates that amorphous silica is present.

THE MAJOR EXOTHERMIC PEAK

The phases at the major exothermic peak for pure kaolinite show that although γ-Al_2O_3 and amorphous silica are always present, mullite is the dominant phase. Experiments which have shown only γ-Al_2O_3 at the prominent peak have evidently used mica-bearing kaolinite. As shown in Table 1, only γ-Al_2O_3 is present in diffraction patterns at this temperature for mica-bearing varieties.

The formation of a hard dense phase such as mullite more readily explains the large evolution of energy than does a subcrystalline compound such as γ-Al_2O_3. The early mullite crystals are asymmetrical and strongly suggest that "long strings of alumina coordination octahedra are carried over directly from the one structure to the other" (2). As the earlier mullite formation is determined by the structure of the original kaolinite, any possibility of an intermediate phase such as γ-Al_2O_3 is eliminated.

The formation of mullite from the collapse of the metakaolin structure cannot use up all alumina, as shown by the formation of γ-Al_2O_3 at the peak. An excess of silica is also indicated by the decreased intensity 4.3 a.u. band. Thus the formation of mullite directly from the metakaolin phase leaves the remaining silica and alumina as separate oxides in the form of amorphous silica and γ-Al_2O_3. The phases at the exothermic peak for clean kaolinites should always show the three phases: mullite, γ-Al_2O_3, and amorphous silica. There is no amorphous alumina phase which forms γ-Al_2O_3, so that the γ-Al_2O_3 for the first formation of mullite is an accompanying phase and not an intermediate phase.

The growth of mullite nuclei is predisposed by the structure of the clay mineral fired. Two factors must be taken into consideration: (1) the degree of order in the stacking of the layers; (2) the morphology of the crystal lattice. The amount of mullite detected at the exothermic peak decreases as the structure becomes more random, and the thermal peak decreases in intensity. The $b_0/3$ shifts in kaolinite evidently cause the development of smaller mullite nuclei with resultant decrease in thermal intensity.

For halloysite, the effect of morphology is pronounced. In the dehydrated kaolinite structure, coordinated alumina and silica layers are of much greater lateral extent than in the halloysite metakaolin phase. Breakdown of the kaolinite structure affords little opportunity for the alumina from one sheet to combine with alumina from other sheets to form γ-Al_2O_3 except at the edges of the layers. In halloysite, the smaller dimensions of the layers permit much greater interaction of alternate alumina layers resulting in a decreased particle size of the primary mullite nuclei. Mullite nucleation could hardly be expected to pass any grain boundary and thus might well consist of too few units to afford recognizable *x*-ray diffraction effects. The mullite nuclei are too small to be registered by *x*-ray diffraction, and γ-Al_2O_3 is the only crystalline phase actually observed. This results in a decreased intensity of the thermal peak although the formation of mullite may well be the cause for the effect.

For mica-bearing kaolinite, the effect of the intergrown micaceous anhydride may also inhibit the size of early mullite crystals, so that only γ-Al_2O_3 is revealed in diffraction patterns and in reduced intensity of the thermal peak.

Primary mullite forms directly from the metakaolin structure at the major exothermic peak and is observed in diffraction patterns of mica-free kaolinite but not in mica-bearing kaolinite or halloysite. Thus it appears that morphology and impurities determine whether or not mullite will be detected in diffraction patterns at the major exothermic peak.

Although the alumina phase at the major exothermic peak is called γ-Al_2O_3 in this study, there are differences between it and γ-Al_2O_3 formed in the firing of aluminum hydrates. The diffraction lines of alumina from kaolin-type minerals are symmetrical reflections, whereas those of aluminum compounds are asymmetrical. The kaolin-type alumina phase more nearly resembles a spinel structure than does pure γ-Al_2O_3. Furthermore, the size of the unit cell is slightly larger than that of pure γ-Al_2O_3.

SECONDARY MULLITE AND CRISTOBALITE

As has been shown, formation of primary mullite coincides with the formation of γ-Al_2O_3 and amorphous silica. The latter phases persist until the second exothermic reaction, at temperatures between 1200° and 1250° C., depending on the type of clay fired. The disappearance of the diffraction lines of the silica and alumina phases at this point and the accompanying increase in amount and sharpness of symmetrical mullite lines indicates that a second generation of mullite has been accompanied by growth of the primary mullite nuclei. The higher temperature mullite forms from γ-Al_2O_3 and amorphous silica, and the alumina is now an intermediate phase in mullite formation. In halloysite and mica-bearing kaolinite, the early crystallites do not develop until the reaction between γ-Al_2O_3 and amorphous silica takes place. The 1250° C. mullite thermal peak for halloysite is more intense than the similar peak for well crystallized kaolinite, and the 1200° C. mullite peak for mica-bearing kaolinites is more intense than the similar peak for mica-free, poorly crystallized kaolinite. This indicates a sudden growth of primary crystallites as well as crystallization from γ-Al_2O_3 and amorphous silica for those clays which show no mullite in diffraction diagrams at the major exothermic peak.

The amorphous silica which remains after formation of secondary mullite forms cristobalite at the exothermic peak above the second mullite peak. Within the temperature range used, cristobalite peaks were observed only in impure specimens. The upper mullite peak is 50° C. lower in the impure poorly crystallized kaolinites, and the cristobalite peak is well below 1350° C.

The presence or absence of mullite in diffraction patterns at the major exothermic peak is not related to formation of secondary mullite at 1200° or 1250° C. Primary mullite is observed only for mica-free kaolinites, but the poorly crystallized variety forms secondary mullite at 1200° C. and the well-crystallized clays at 1250° C.

The organization of the unfired clay does not explain the difference in temperature for the second mullite peak. The clay with the highest degree of order in the stacking of structural units (well-crystallized kaolinite) and that with the lowest degree of order (halloysite) both have upper mullite peaks at 1250 ° C.

The variation in temperature may therefore be caused by impurities. Physical impurities such as quartz will not cause any lowering in temperature of peaks. It is thus possible that potassium and other fluxing elements present in mica and other impurities may be the cause for the variation.

In general, presence of fluxing impurities lowers the temperature of formation of secondary mullite and cristobalite, and it is possible that increase in mica could cause further changes limited by the fluxing action of potassium.

When the secondary mullite peak occurs at about 1200° C. and the cristobalite peak below 1350° C. the inversion of small amounts of quartz to cristobalite is always accompanied by the crystallization of cristobalite from amorphous silica. If large amounts of quartz impurity are present (amount unknown), no inversion occurs within the temperature range studied, nor does crystallization from amorphous silica take place. The thermal curve then shows only one peak at about 1200° C.

For clays where the mullite peak occurs at about 1250° C., no cristobalite peak is formed regardless of how much quartz impurity is present.

Although the formation of cristobalite from the crystallization of amorphous silica and the inversion of quartz occur at the same temperature, the thermal effect observed is caused only by amorphous silica crystallization. The inversion from quartz is an endothermic reaction and is not apparent because of the greater amplitude of the crystallization effect.

Equilibrium Firing Conditions

The phase sequences reported above represent changes during firing under non-equilibrium conditions at a constant heating rate. If samples are soaked or the rate of heating is varied, phases occur at different temperatures from those under the experimental conditions reported here. Thus micaceous, poorly crystallized kaolinite, which shows only γ-Al_2O_3 at 1100° C. when air-quenched, shows a complete mullite pattern with minor cristobalite after it soaks for 4 hours at 1100° C. Under this condition, mullite forms at temperatures 100° C. less than when air-quenched; and cristobalite forms at 200° C. less. Cristobalite, not observed in well crystallized, mica-free kaolinite at 1350° C. under non-equilibrium conditions, can be developed at lower temperatures by soaking. Prolonged firing, therefore, lowers the temperatures at which phases form and decreases the total temperature interval in which a complete firing sequence occurs. Only under non-equilibrium conditions can the phases be investigated without confusion.

The development of phases is directly dependent upon 4 factors: rate of heating, nature of equilibrium conditions, amount and type of impurity, and structure. The lack of agreement in the literature as to the sequence and interpretation of phase changes is due to the failure to control some or all of the four variables.

Summary

Thermal curves for kaolinite and halloysite to 1350° C. are dissimilar enough for precise identification. The essential differences between the thermal curves of well and poorly crystallized kaolinites to 1000° C. are the effects principally of decreased particle size.

After dehydration, an amorphous compound of silica and alumina (metakaolin) forms, which persists to the major exothermic thermal peak, then collapses to form mullite nuclei, γ-Al_2O_3, and amorphous silica. The amount and size of the mullite nuclei depend upon the morphology, structure and purity of the fired material. Mullite formation causes the principal evolution of energy. γ-Al_2O_3 is not an intermediate step in mullite formation at this temperature.

The development of phases at higher temperatures is controlled principally by fluxing impurities. Secondary mullite occurs at about 1200° C. for impure clays and at about 1250° C. in clean samples; it forms from γ-Al_2O_3 and amorphous silica. At this point γ-Al_2O_3 is an

intermediate step in mullite formation. The silica which remains forms cristobalite between 1240° and 1320° C. in impure clays and probably above 1350° C. in pure clays. Fluxing impurities tend to lower the temperature of thermal peaks for mullite and cristobalite.

Variation in amount and type of impurities, rate of heating, degree of equilibrium reached during firing, and structure of the clay all affect the sequence and temperature of phase formation. Failure to standardize firing conditions is a primary cause of lack of agreement in the literature as to the firing sequence of kaolinite and halloysite.

The phases observed in diffraction diagrams are as follows:

	Lattice dehydration	Major exothermic peak	Mullite thermal peak	Cristobalite thermal peak
Mica-free well crystallized kaolinite	metakaolin	mullite$\gg\gamma$-Al_2O_3	1250° C.	none present to 1350° C.
Mica-free poorly crystallized kaolinite	metakaolin	mullite$>\gamma$-Al_2O_3	1200° C.	1240° C.
Mica-bearing poorly crystallized kaolinite	metakaolin, mica-anhydride	γ-Al_2O_3, mica-anhydride	1200° C.	1300° C.
Halloysite	metakaolin	γ-Al_2O_3	1250° C.	none present to 1350° C.

The effect of heat on kaolin-type materials may be expressed as follows:

Above 600° C.	$\underset{\text{kaolin}}{Al_2O_3\cdot 2SiO_2\cdot 2H_2O}\rightarrow\underset{\text{metakaolin}}{Al_2O_3\cdot 2SiO_2}+2H_2O$
950°–980° C.	$Al_2O_3\cdot 2SiO_2\rightarrow\underset{\text{primary mullite}}{3Al_2O_3\cdot 2SiO_2}+\underset{\substack{\text{gamma}\\\text{alumina}}}{\gamma\text{-}Al_2O_3}+\underset{\substack{\text{amorphous}\\\text{silica}}}{SiO_2}$
1200°–1250° C.	$\gamma\text{-}Al_2O_3+SiO_2\rightarrow\underset{\text{secondary mullite}}{3Al_2O_3\cdot 2SiO_2}+\underset{\text{amorphous silica}}{SiO_2}$
1240°–1350° C. (?)	$SiO_2\rightarrow\underset{\text{cristobalite}}{SiO_2}$

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