HIGH-TEMPERATURE D.T.A. AND X-RAY DIFFRACTION STUDIES OF REACTIONS

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ABSTRACT

Several reactions which take place in clay minerals at elevated temperatures were investigated by D.T.A. and continuous high-temperature X-ray diffraction. The combination of these techniques was used to examine the energy changes and phase transformations that occur in kaolinite, halloysite, illite, and montmorillonite at temperatures up to 1450°C.

Diffraction data obtained from these minerals as they were heated are used to interpret the nature of the structural transitions, and new phase developments in two-layer type clay minerals are compared with similar developments in three-layer type clays.

Continuous diffraction is used to detect changes that take place in the firing history of a clay in which small amounts of chemical impurities or other mineralizing substances are present or have been added. Several chemical impurities were added to each of the clays to determine their ability to either enhance or retard structural transition and new mineral development upon firing. The effects which these additives have on predicted structural changes are illustrated and are interpreted in lieu of chemical and structural requirements.

INTRODUCTION

WITHIN the last decade, there has been an increased interest in the reactions which take place when clay minerals are heated to elevated temperatures. There are two principal reasons for this interest. First, by examining the phases that develop from a specific clay mineral it is possible to better understand the structure of the original mineral for it has been demonstated (Graf *et al.*, 1962) that structural inheritance is often a major factor in controlling new mineral development. Secondly, the industrial application of clays for specific purposes, such as in the ceramics industry, is dependent upon the thermal response of the clay material. If predicted thermal reactions and transformations can be catalyzed through the addition of small amounts of mineralizing components, it might be possible to lower the firing temperature of the products and also to provide a stronger coherent bond within the product through more complete development of some favorable new phase.

The transformations that occur in kaolinite, halloysite, illite, and montmorillonite have all been examined in recent years by continuous high-temperature X-ray diffraction and D.T.A. (Grim and Kulbicki, 1957 and 1961; Wahl, 1962). The action of certain impurities in changing the new phase development pattern of these four basic minerals will be expanded in this paper and the combined data from these researches will be used to interpret the mechanism of the transformation processes and the importance of primary structure.

EXPERIMENTAL PROCEDURE

The data to be presented for each of the four basic types of clay minerals were obtained in the clay minerals laboratory of the University of Illinois, and the apparatus and high-temperature diffraction and D.T.A. techniques used were identical. The diffraction furnace was originally described by Grim and Kulbicki in 1957 and was subsequently modified by Graf *et al.* in 1962 to allow a more effective heating program.

Samples and Treatment

All experimental data to be presented and compared were derived from the samples listed below and interpretations are based on X-ray thermal studies of these samples. Each material was first examined in its natural state and then re-examined after treatment with a variety of selected chemical additives.

Kaolinite—well-crystallized variety, McIntyre, Georgia
Kaolinite—poorly-crystallized variety with quartz impurity from Anna, Illinois
Halloysite—hydrated ($4H_2O$) variety from Eureka, Utah
Illite—Fithian variety from Vermillion County, Illinois, as used and described by Bohor (1959)
Montmorillonite—Cheto-type from near Otay, California
Montmorillonite—Wyoming-type from Crook County, Wyoming

X-ray Diffraction Data

All samples were monitored continuously as they were heated to 1400°C or above. The samples were repeatedly scanned at a speed of 2° two theta per minute for a traverse range which included some diagnostic reflections for the material and the new phases which were expected to develop. For all samples, this included the diagnostic (120) and (210) mullite reflections at 26.0 and 26.3° respectively and the (111) cristobalite reflection at 21.4° two theta. Also included in the range of traverse were the principal beta quartz and cordierite reflections which were reported for montmorillonite by Grim and Kulbicki (1961), and also a spinel reflection as reported by Bohor (1959).

Chemical Additives

Several chemical compounds (Mg, Fe, Bi, Ca, Li, K, and Na chlorides as well as lead acetate and phosphoric acid) were added to the halloysite and poorly-crystallized kaolinite samples so that comparisons could be made with reported results from similarly treated well-crystallized kaolinite. The impurities were added to the clays on a straight weight percentage basis. An amount equal to 5 per cent of the dry clay weight was normally used, but in certain cases other percentages were added to determine the effects of variable amounts.

HIGH-TEMPERATURE PHASE DEVELOPMENT

Well-crystallized Kaolinite

The D.T.A. curve of this material is shown in Fig. 1. Normal dehydroxylation is complete at about 600°C and is followed at 980°C by a sharp exothermic reaction which accompanies the formation of primary mullite

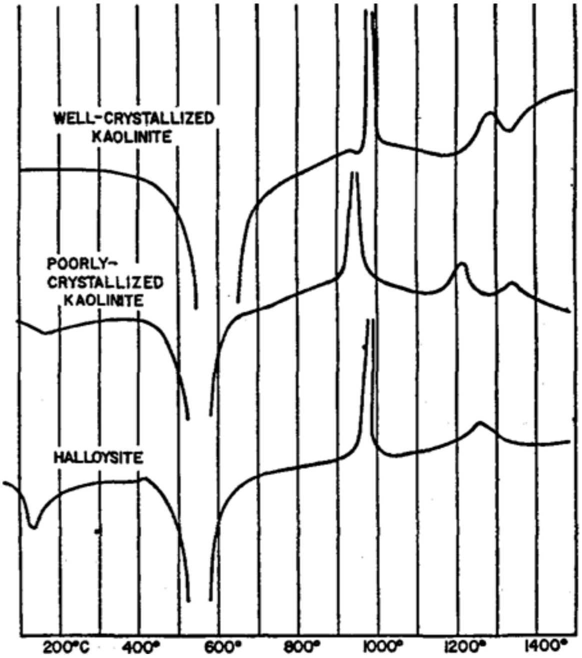

FIGURE 1.—Differential thermal curves of well-crystallized kaolinite, poorly-crystallized kaolinite, and hydrated halloysite.

crystallites. The beginning of a second exothermic reaction at approximately 1200°C represents the formation of what has been called secondary mullite (Wahl, 1962). This is followed at approximately 1350°C by a third exothermic reaction corresponding to the formation of beta-cristobalite.

Examination of this sample by continuous diffraction while it was heating showed the initial appearance of mullite on the diffractogram at 1180°C (Fig. 2). However, powder camera diffraction data from the same sample showed the definite presence of primary mullite crystallites in the heated material between 980 and 1180°C. Apparently the mullite is not in sufficient abundance to be detected on the diffractogram. The most significant quantitative development of mullite thus coincides with the second exothermic peak on the D.T.A. curve.

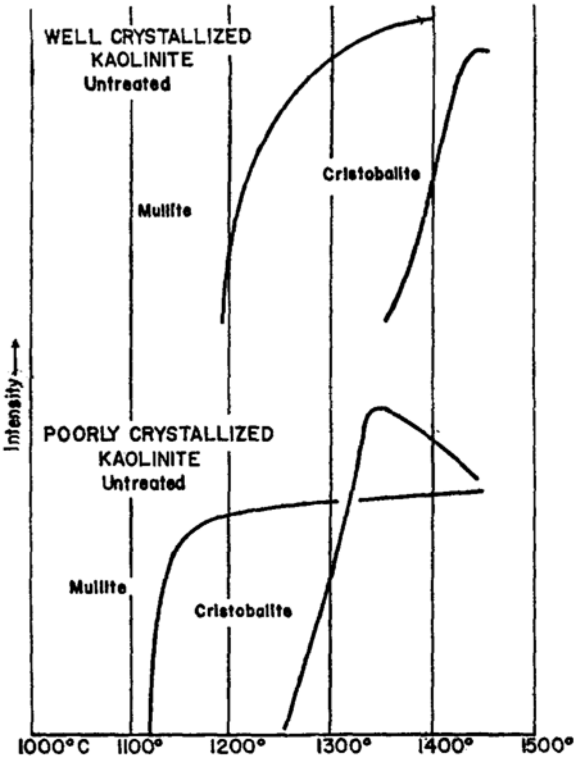

FIGURE 2.—Intensity of diffraction by high-temperature phases in heated well-crystallized and poorly-crystallized kaolinites.

The appearance of beta-cristobalite at 1350°C coincides with the third exothermic reaction on the D.T.A. trace.

Poorly-crystallized Kaolinite

The differential thermal curve for the poorly-crystallized variety of kaolinite shows an endothermic reaction of reduced intensity at 550°C (Fig. 1). Mullite nucleation at 950°C is of a lesser magnitude as indicated by a subdued exothermic peak and also by less intense mullite diffraction lines on powder camera patterns; however, there is no particular delay in the formation of secondary mullite as compared with that formed from well-crystallized kaolinite. In fact, secondary mullite begins to develop from the poorly-crystallized material at 1120°C (Fig. 2) as compared with the 1200°C necessary for well-crystallized kaolinite. Beta-cristobalite

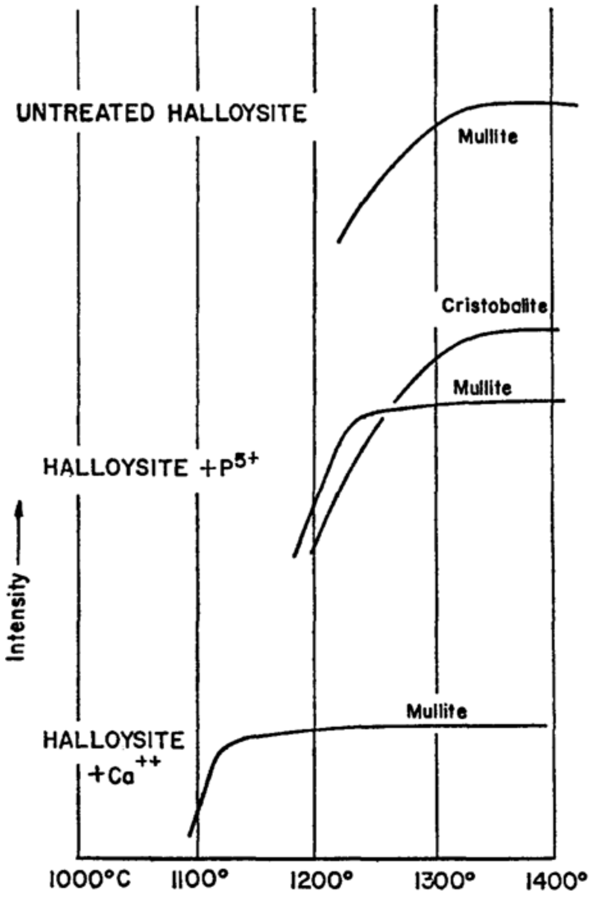

FIGURE 3.—Intensity of diffraction by high-temperature phases in heated halloysite, untreated and after the addition of P^{5+} and Ca^{++}.

from the poorly-crystalline material also appears on the diffractograms at a temperature which is approximately 80° below that at which the phase was first observed for the well-crystallized variety. The beta-cristobalite reflections which appear at 1250°C increase rapidly in intensity and reach a maximum at 1375°C. At higher temperatures this phase disappears through fusion.

Halloysite

The D.T.A. curve for halloysite is shown in Fig. 1 and is with one exception, similar to that of poorly-crystallized kaolinite up to 950°C. The noted exception is, of course, the increased intensity of the first endothermic reaction between 100–200°C which merely reflects the loss of adsorbed water from this hydrated form of the mineral.

No primary mullite crystallites could be definitely identified from powder camera patterns until the material had been heated to 1100°C, and this phase does not appear on the continuous-heating diffractogram (Fig. 3) until the second exothermic peak is reached at 1250°C.

Beta-cristobalite did not form from this variety of halloysite, even when heated to 1400°C.

EFFECTS OF IMPURITY ADDITIVES

Well-crystallized Kaolinite

An earlier work (Wahl, 1962) describes in detail the effects of twenty-two different impurity additives on the phase transformations which occur

TABLE 1.—THE EFFECTS OF IMPURITY ADDITIVES ON THE FORMATION TEMPERATURES OF SECONDARY MULLITE AND BETA-CRISTOBALITE AS DEVELOPED FROM WELL-CRYSTALLIZED KAOLINITE

Additive	Amount	Effect on formation temperature of secondary mullite	Effect on formation temperature of beta-cristobalite
$FeCl_3$	5%	Lowered 50°	Lowered 100°
$MgCl_2$	5%	Lowered 50°	Lowered 100°
$Pb(C_2H_3O_2)_2$	5%	Lowered 100–150°	Lowered 150–175°
$BiCl_3$	5%	Lowered 150–175°	Lowered 50°
$CaCl_2$	5%	Lowered 200–225°	Lowered 200°
LiCl	5%	Lowered 150°	Prohibited phase
KCl	5%	Lowered 100°	Prohibited phase
CsCl	5%	Lowered 50°	Prohibited phase
NaCl	5%	None	Prohibited phase
H_3PO_4	5%	None	Lowered 175–200°

when well-crystallized kaolinite is fired. It was found that the presence of certain ions can significantly lower the temperatures at which both secondary mullite and beta-cristobalite develop. The results of this earlier investigation are summarized in Table 1 and will be compared with data on the firing history of similarly treated poorly-crystallized kaolinite and halloysite.

It should be noted from the previous study of well-crystallized kaolinite that the nucleation of primary mullite at 980°C was not affected by the presence of mineralizing ions. Only the subsequent formation of secondary mullite was changed by the presence of the additives.

Poorly-crystallized Kaolinite

The thermal history of poorly-crystallized kaolinite can also be changed by the presence or introduction of chemical additives. These changes are not necessarily of the same nature, nor are they as pronounced, as those observed from well-crystallized kaolinite.

Only those additives which had a significant effect on the phase transformations of well-crystallized kaolinite were added to the poorly-crystallized variety. These are listed in Table 2 along with their effects on phase mineral development. Of the additives effective for the well-crystallized kaolinite, only Mg^{++}, Bi^{++}, and Na^{+} influenced the development and growth of secondary mullite from poorly-crystallized kaolinite. Magnesium and bismuth ions lower the temperature of secondary formation of this phase by 50–100°C, and sodium increases the formation temperature by 50°C.

The alkaline additives Li^{+} and Na^{+} do not have the same influence on secondary mullite development that they produced in the ordered variety

TABLE 2.—THE EFFECTS OF IMPURITY ADDITIVES ON THE FORMATION TEMPERATURES OF SECONDARY MULLITE AND BETA-CRISTOBALITE AS DEVELOPED FROM POORLY-CRYSTALLIZED KAOLINITE

Additive	Amount	Effect on formation temperature of secondary mullite	Effect on formation temperature of beta-cristobalite
$FeCl_3$	5%	None	Lowered 50°
$MgCl_2$	5%	Lowered 50–100°	Lowered 50°
$Pb(C_2H_3O_2)_2$	5%	None	Lowered 50°
$BiCl_3$	5%	Lowered 50–100°	Lowered 250°
$CaCl_2$	5%	None	Lowered 100°
LiCl	5%	None	Prohibited phase
NaCl	5%	Raised 50°	Prohibited phase
H_3PO_4	5%	None	Lowered 200–400°

of kaolinite. Li^+ produces no reduction in the temperature at which mullite first appears on the diffractogram and the addition of small amounts of Na^+ retards the growth of secondary mullite by 50°C.

As indicated in Table 2, the temperature at which beta-cristobalite forms from poorly-crystallized kaolinite is readily effected by the addition of certain chemical impurities. Data obtained by both continuous heating diffraction and D.T.A. analyses show that the following ions all lower the temperature at which beta-cristobalite begins to form. Listed in order of their effectiveness (the extent to which they lower the development temperature is given in parentheses) these are Mg^{++} (50°C), Fe^{++} (50°C), Ca^{++} (100°C), Bi^{+++} (250°C), and P^{5+} (200—400°C). A comparison of data in Tables 1 and 2 shows that these elements, with the exception of Bi^{+++}, lower the temperature a smaller amount for poorly-ordered than well-ordered kaolinite.

The alkaline ions prohibited the development of beta-cristobalite from the poorly-crystallized variety of this mineral—the same result that was observed for well-crystallized kaolinite.

Halloysite

The sequence of phase changes in halloysite, both before and after the addition of impurities, was not studied in as great detail as were the changes observed in kaolinite. This mineral was only treated with P^{5+} and Ca^{++} for these additives both had a pronounced effect on the two varieties of kaolinite.

The addition of P^{5+} to halloysite causes the formation of secondary mullite at 1190°C as compared with its development at 1220°C in the untreated material (Fig. 3). Equally significant is the development of beta-cristobalite from halloysite treated with this ion. Cristobalite did not form from the untreated halloysite, but crystallized at 1200°C when the phosphorous ion was added. This phase grew steadily until maximum development was reached at 1330°C.

The addition of the calcium ion to halloysite lowered the initial temperature of secondary development to 1100°C (Fig. 3). As in the untreated material, however, there was no beta-cristobalite crystallization.

PREVIOUS HIGH-TEMPERATURE STUDIES OF THREE-LAYER CLAY MINERALS

The development of high-temperature phase minerals from 38 different montmorillonites was examined in detail by Grim and Kulbicki (1961). Also, Bohor (1959) studied new phase development from five illites, both before and after chemical treatment. Each of these studies utilized the continuous heating diffraction technique and many experimental observations were supported by differential thermal analyses to 1400°C. Results from both investigations are presented here so that an overall comparison can be made between the sequence of phase development from two-layer and three-layer type clay minerals.

Montmorillonite

Grim and Kulbicki reported significant differences in the phases developed from two different aluminous dioctahedral montmorillonites, namely the Cheto and Wyoming types. Differential thermal analysis curves and summarized continuous diffraction data representing the phase development indicated on these D.T.A. patterns are shown in Figs. 4 and 5 for representative samples of each of the two montmorillonite types.

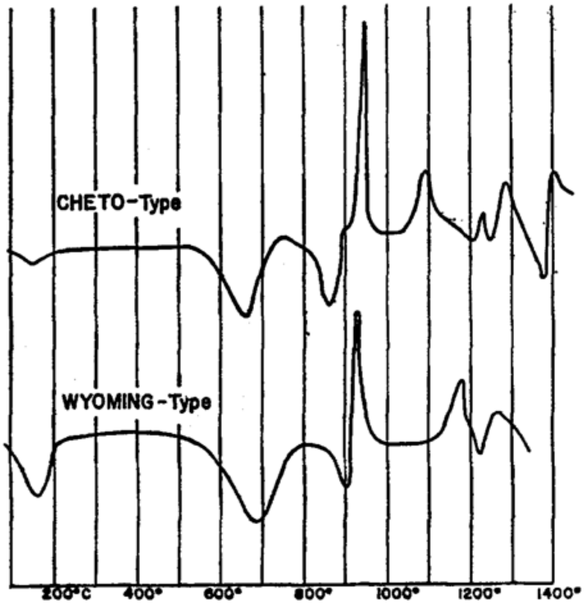

FIGURE 4.—Differential thermal curves of Cheto-type and Wyoming-type montmorillonites (after Grim and Kulbicki, 1961).

It should be noted that the intense exothermic peak at about 950°C in both sample types was not accompanied by detectable crystalline beta-cristobalite until a temperature of approximately 1100–1150°C was reached. In the Cheto-type material, the formation of beta-quartz was observed at 1020°C, but no similar crystalline phase developed from the Wyoming variety. This formation of beta-quartz was interpreted to indicate the

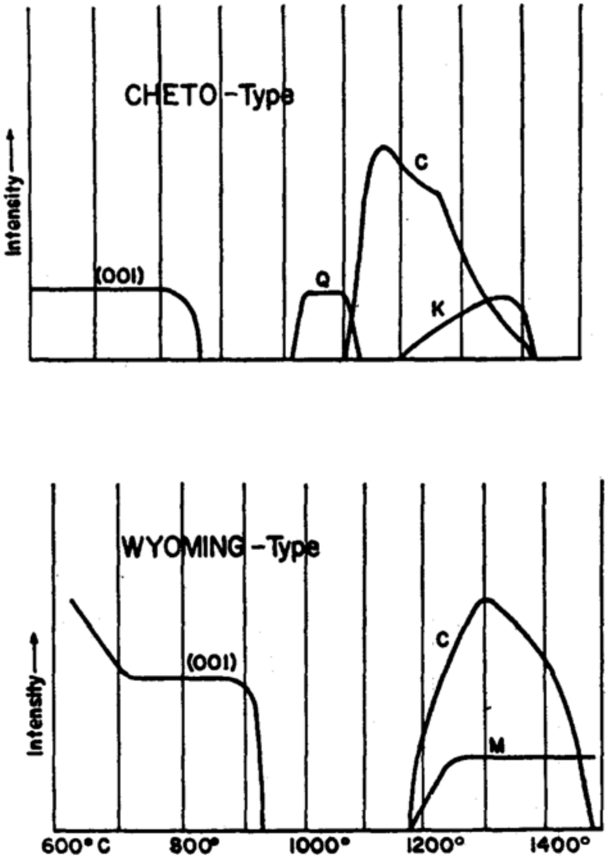

Figure 5.—Intensity of diffraction by high-temperature phases in heated Cheto-type and Wyoming-type montmorillonites. Q–Beta-quartz; C–Beta-cristobalite; M–Mullite; K–Cordierite (after Grim and Kulbicki, 1961).

presence of some inverted tetrahedral units, thus favoring the formation of this mineral. The authors pointed out that there was no difference in the composition of the tetrahedral positions in these two types of montmorillonite.

The nucleation stage of phases which occur above approximately 1200°C were found to be closely dependent upon the structure of the original mineral. For example, the arrangement of the magnesium ions in the octahedral layer of the Cheto-type was such that the formation of cordierite was favored and this crystalline phase was first observed at 1200°C (Fig. 5). Mullite formed from the Wyoming montmorillonite at approximately this same temperature (Fig. 5) and its development was preferred in the presence of a reduced concentration of Mg^{++} ions. Nontronite and iron-rich montmorillonites were found to yield only cristobalite at elevated temperatures and it was concluded that iron apparently in substantial amounts blocks the development of any crystalline phase" (Grim and Kulbicki, 1961, p.1369).

Illite

The new phase development in illites when heated was investigated by Bohor (1959) who worked with five different varieties of this mineral. Although he observed the appearance of a spinel and forsterite at approximately 1000°C and of mullite at 1100°C, when Fithian illite was heated, only a small amount of each of these newly-formed crystalline materials developed and all had disappeared through fusion by 1250°C. He concluded that phase development was, in general, quite poor in all of the illites examined because of the high potassium content. The addition of certain ionic impurities did show, however, that the formation of mullite could be either enhanced or repressed. He reported that beryllium and stannous ions facilitated the formation of mullite immediately following the collapse of the mica anhydride at 1000°C; whereas, potassium, sodium, and lithium all had a repressive effect on mullite development. No beta-cristobalite formed from any of the illites used in his study.

DISCUSSION

The realignment of ions which follows structural collapse in all clay minerals as indicated by an endothermic reaction between 900–1000°C on the D.T.A. curves is controlled to a large extent not only by the type and perfection of the original structure of the mineral, but by the presence of extraneous ions in the system, which can either enhance or retard the degree of rearrangement to form new minerals. The sharp exothermic reaction which usually follows structural collapse as in the case of kaolinite, montmorillonite and halloysite, probably represents a shift in bonding from face-sharing octahedral units to more stable edge-sharing units which normally exist in high-temperature structures. Accompanying this shift in bonding in well-crystallized kaolinite, primary mullite crystallites can be detected by powder camera diffraction; however, the mullite only becomes more abundant with continued heating, a factor which appears necessary to facilitate further reorganization of component ions. In poorly-crystallized kaolinite and halloysite, less primary mullite formation accompanies this structural rearrangement. Consequently more poorly-ordered uncombined alumina remains in the system to later combine with free silica-forming secondary mullite. On the basis of observed data, it is suggested that the abundance of this poorly-ordered material facilitates a faster recombination with silica on continued heating. The appearance of secondary mullite is represented by the second exothermic reaction at about 1150°C on the thermal curve for poorly-crystallized kaolinite as compared with the same reaction for well-crystallized kaolinite at 1250°C.

This second part of the two-stage formation of mullite, i.e., migration of cations into proper positions to facilitate crystal growth, was also observed by Grim and Kulbicki for Wyoming-type montmorillonites.

The formation of beta-cristobalite never precedes the formation of mullite in the two-layer type clay minerals. Its appearance usually coincides with maximum mullite development, thus suggesting that the initial nucleation of this phase represents the combination of excess silica that is left over after nearly complete mullitization has occurred.

In the case of halloysite, no beta-cristobalite formation was observed, thus suggesting that uncombined alumina still remained in the system at 1400°C or the organization of the silica was such as to make the transition to beta-cristobalite too difficult. With the addition of phosphorous, however, increased mullite growth was observed in this same material and subsequent beta-cristobalite development occurred.

The pattern of formation of beta-cristobalite in the three-layer type clay minerals is quite different from that in the two-layer type clays. Because of the close proximity of the silica tetrahedral layers of adjacent montmorillonite particles, these units might be expected to reorganize more readily thus forming a polymorph of silica. This was observed on heating Cheto-type montmorillonites which showed beta-quartz formation at 1020°C. This particular variety of montmorillonite was thought to already contain some inverted tetrahedral units which would speed the development of this phase. Even without the inversion of any tetrahedra, the close proximity of similar structural units in Wyoming-type montmorillonites appears to facilitate the earlier formation of a silica phase (beta-cristobalite) which first appears with mullite. It should be emphasized, however, that as in the case of the two-layer minerals, maximum development of this phase is not obtained until mullitization is complete.

In the case of illite and for kaolinite and montmorillonite samples treated with potassium, there is no cristobalite formation, for the size of the potassium ion effectively blocks the movement of other ions to desired positions within the mullite structure. In a similar manner, potassium limits the maximum development of secondary mullite by prohibiting ionic migration in the heated material.

The influence of cations such as potassium, thus plays a significant role in the development of new phases from clays. As opposed to the alkaline elements which in general retard phase mineral growth, certain other cations have a definite mineralizing effect in promoting the formation of high-temperature phases. In general, the mineralizing ions have a more pronounced influence upon transformations in two-layer clay minerals than upon those in minerals with three-layer structures.

There appears to be no invariable correlation between the effects of a mineralizing ion and its valence nor does there appear to be any definite association between observed effects and the ionic radii of added impurities. The influence of many mineralizing ions is probably the consequence of catalytic chemical activity in that the presence of certain ions in the chemical systems causes a sufficient lowering of the melting temperature of the heated mixture thus allowing the initial crystallization of phase minerals to occur at temperatures below those normally considered essential.

In some cases, larger ions may effectively block structural rearrangement of component ions as was mentioned in the case of potassium. At the same time, it must be remembered that the alkaline ions also facilitate the formation of glass by lowering the fusion temperature.

The effectiveness of phosphorus in lowering the temperature at which cristobalite forms from the two-layer minerals can be attributed to the substitution of this ion for silica in the cristobalite structure. Such a substitution is indicated by a measurable increase in the amount of cristobalite that forms from both types of kaolinite when treated with this ion and also by the development of cristobalite from halloysite, a mineral which formed no beta-cristobalite when fired in the untreated state. The effects of phosphorous on the formation of beta-cristobalite from three-layer clay minerals has not yet been investigated in detail, but it is expected that this element should also promote cristobalite development from these minerals.

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