

HIGH-TEMPERATURE PHASE DEVELOPMENT IN ILLITIC CLAYS

by

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ABSTRACT

Five illitic clays were treated with various inorganic cations and heated to over 1400°C in a high-temperature X-ray diffraction furnace.

The illite lattice undergoes dehydroxylation from 475–600°C, and the resulting anhydrides begin to disappear at 850°C. The major high-temperature phases formed from untreated illites are β -quartz (1000–1300°C), spinel (1000–1400°C), and mullite (1150–1400 + °C). Minor amounts of cordierite, kalsilite, feldspar, corundum, iron oxide and forsterite may also occur with various adsorbed cations at temperatures above 1000°C. β -cristobalite was never observed in any of the runs, contrasting strongly with its prominent development among the high-temperature phases of montmorillonite.

Certain adsorbed cations act as repressors of high-temperature phase development, while others seem to have the opposite effect. The order of decreasing repressive effect— $K^+ > Na^+ > Li^+ > Ca^{+2} > Mg^{+2} > Be^{+2} > Sn^{+4}$,⁴—also represents the sequence of increasing electronegativity and ionic potential of these cations. It is postulated that the degree of electronegativity and ionic potential of the adsorbed cations is proportional to the rapidity and degree of mullite crystallization, because of the influence of these factors in ion transfer and reaction product removal in the critical liquid phase at the clay mineral surface.

INTRODUCTION

THE high-temperature X-ray diffraction technique has been shown to be very useful in the study of montmorillonites (Kulbicki, 1958), kaolinites (Grim and Kulbicki, 1957; Wahl, 1958) and silica–alumina mixtures (Wahl, Grim and Graf, 1961). The author applied this technique to some illitic clays as part of a thesis study (Bohor, 1959). The samples used were selected for the amount and kind of illite mixed-layering they contained, and not for their purity with respect to illite. Consequently, the presence of various amounts of kaolinite, chlorite and montmorillonitic clay minerals introduce an unknown factor into the interpretation of these results.

Illites present a special case among the clay minerals in that most of the interlayer cations are “fixed” potassium, which are no longer readily exchangeable for other cations in solution. Thus, the cation-exchange capacity is low, and sites are present both on edges and between layers. Any influence of exchange cations on the phase developments should be

basically important in natural reactions (metamorphism), because this small amount of cations is surely available to clay minerals in the natural environment.

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TECHNIQUES

The high-temperature equipment and techniques used are similar to those described by Grim and Kulbicki (1957) and Kulbicki (1958). In essence, the equipment consists of a platinum-wound ceramic furnace installed on an X-ray diffractometer. The sample is sedimented on a small platinum slide and placed in the furnace, where it is heated to over 1400°C at a predetermined rate (usually 50°C per minute). The heating rate is set by a combination of motor-driven and manual variable rheostats. Kulbicki found this furnace design to have low thermal mass and a very small temperature gradient between the sample surface and the measuring thermocouple.

The diffractometer counter is either manually set at angles corresponding to the main diffraction lines of the phases being studied, or allowed to scan the entire angular diffraction range (0–52°, 2 θ) of the furnace.

SAMPLES AND TREATMENT

Five different samples of illitic clays were investigated:

Minford—A glaciolacustrine (Pleistocene) silt from Minford, Ohio.

Purington—A marine shale (middle Pennsylvanian) from Illinois.

TABLE 1.—PER CENT COMPOSITION AND CATION-EXCHANGE CAPACITY (<0.5 μ Fraction)

	Minford	Purington	Grundite	Jackson	Fithian
Illite	55	60	56	62	62
Mixed layers	18	27	31	29	31
Kaolinite	20	9	11	4	5
Chlorite	5	0	0	3	0
Montmorillonite	TR	4	TR	TR	TR
C.E.C. (meq/100g)	16	18	15	17	13

Grundite —Trade name for a modified shale or clay, lower Pennsylvanian in age, from Grundy County, Illinois.

Jackson —A modified Pennsylvanian marine shale from Jackson County, Illinois.

Fithian —An underclay (Pennsylvanian) from Fithian, Illinois.

The illitic portions of all of these clays are dioctahedral. Some auxiliary data on these samples are listed in Table 1.

Portions of the $<0.5\mu$ fraction of the clays were treated with normal solutions (chloride or nitrate) of K, Na, Li, Ca, NH_4 , Mg, Be, and Sn^{+2} . Not every clay was saturated with this entire series of cations.

After two days in these solutions the exchanged clays were washed several times in distilled water, sedimented on to small platinum slides, and run in the high-temperature diffraction furnace.

RESULTS

Intermediate Temperature Phases

Phase developments of only the illite lattice were observed in the temperature range 25–1000°C. The initial effect of heat upon all the oriented samples in the furnace is to sharpen and intensify the basal peaks due to expulsion of interlayer water. These changes begin almost immediately upon applying current to the furnace element and are usually completed at 150°C. Along with these effects the basal intensity maximum of illite shifts to around 10 Å as its associated hydrated mixed-layers collapse.

No significant further change occurs until a temperature of 475°–500°C is reached. At this temperature the basal reflections change intensity and spacing. The 001 maximum decreases in intensity to approximately its original intensity before the application of heat; the 003 peak, however, increases in intensity. These changes are the result of the abstraction of octahedra oxygens and protons in the amount of one water molecule per unit cell.

The mica-anhydride is completely formed at around 600°C and persists without change up to about 850°C. Here the structure begins to become disarranged and the basal reflection intensities decline steeply to zero in the range 1000° to 1080°C. The nature of the adsorbed cation seems to have only a minor effect on the stability of the anhydride. In the samples saturated with Li^+ , the decrease in intensity begins at a temperature slightly lower than 850°C; with K^+ or Na^+ the anhydride basal reflections retain their maximum intensities up to about 880°C.

High-temperature Phases

Major phases.—Only three crystalline phases occur in these high-temperature runs with enough frequency and intensity to be designated as

major phases typical of illitic clays; these are mullite, spinel and β -quartz, in order of general abundance. Of these three phases, only mullite shows enough significant variation in development with different adsorbed cations to be worthy of extra attention. Some characteristics of the other phases will be mentioned, however.

Figures 1 and 2 are generalized diagrams of the development of phases in these illitic clays above 1000°C. The diagrams for the untreated clays and

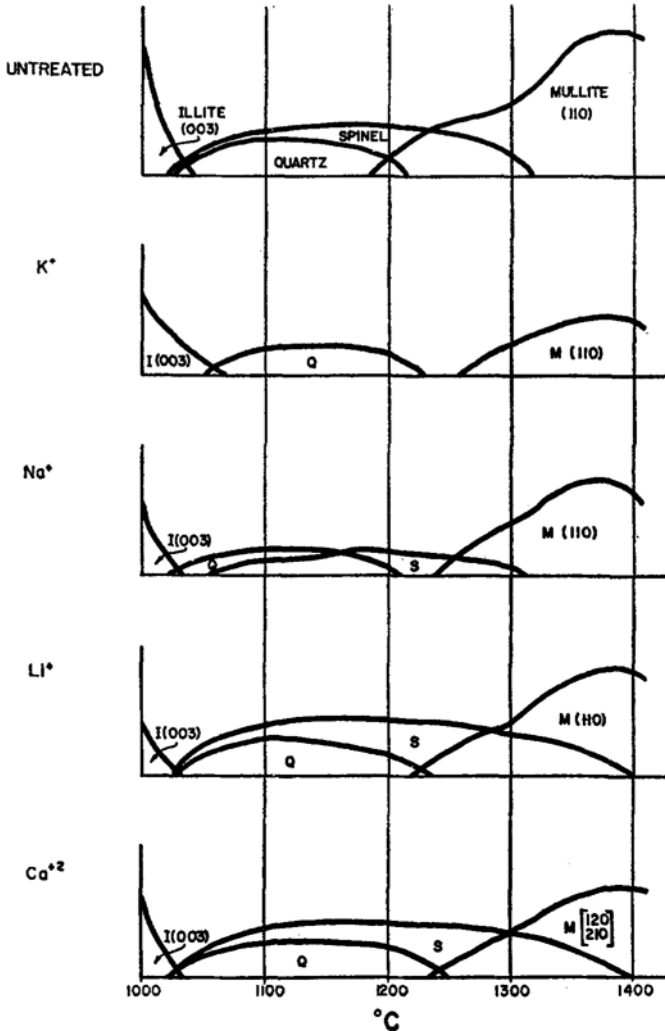


FIGURE 1.—Generalized illite phase development—repressive cations.

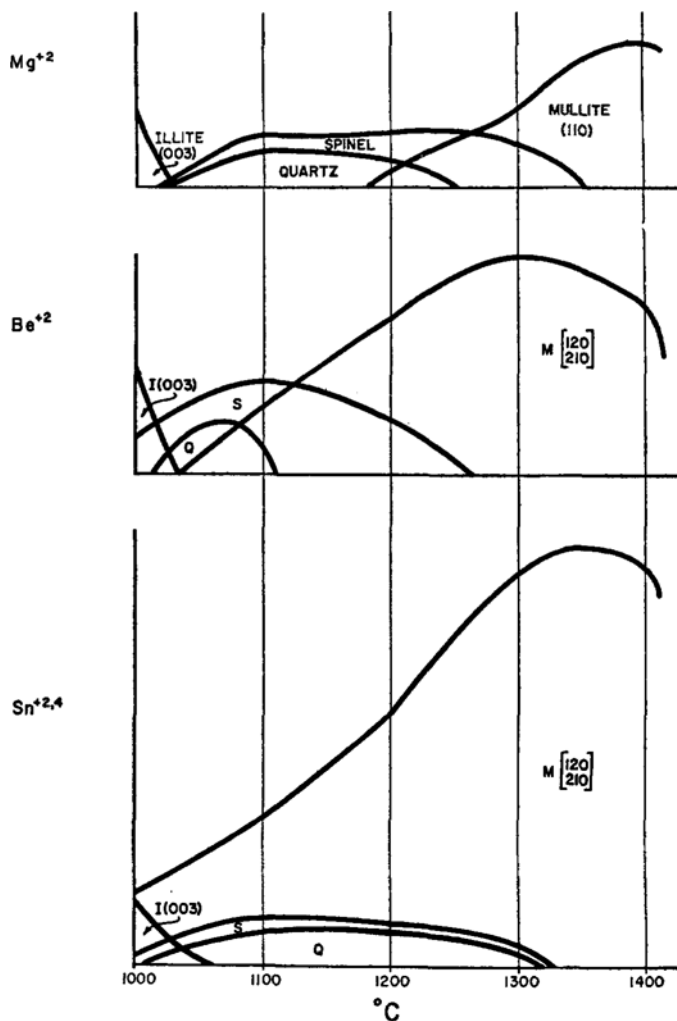


FIGURE 2.—Generalized illite phase development—expressive cations.

those saturated with K^+ , Na^+ , Li^+ , and Ca^{+2} are shown in Fig. 1. These saturating cations are called repressive because they inhibit high-temperature phase development, especially mullite, to some degree less than that displayed by the natural, untreated clay. Figure 2 shows the phase diagrams of clays saturated with the expressive cations (Mg^{+2} , Be^{+2} , $Sn^{+2,4}$), so named because they cause greater phase development than occurs in the unexchanged clay. The diagrams represent the average

behavior of all five different clay samples saturated with that particular cation; any noteworthy departure from this average behavior in individual samples will be mentioned below. Usually, however, no important differences were noted between the five different clays studied.

The NH_4^+ saturated samples are not represented by a diagram, in the interest of simplicity, because of its almost exact correspondence to the Mg^{+2} diagram. Both the NH_4^+ and Mg^{+2} phase developments are very similar to that of the natural untreated clays; hence, the former can just barely be considered expressive cations.

Because the diagrams of Figs. 1 and 2 shows phases only in the temperature range 1000–1450°C, the intensities of the illite anhydride basal reflection peaks are not shown in full. These usually amount to four or five times the height of the mullite development shown by the untreated clay. The 003 peak of the anhydride persists to slightly over 1000°C; 001 disappears just under 1000°C.

Immediately following, or concomitant with, the disintegration of the anhydride structure, spinel begins to form. Spinel has been observed in almost every run, indicating either that chlorite is present to some degree in all the samples, or that there is an appreciable amount of Mg^{+2} or Fe^{+2} substituting for Al^{+3} in the octahedral layers of the illites. The spinel phase shows its greatest intensity in those samples saturated with exchangeable Mg^{+2} , but not to the degree anticipated by the ion-exchange capacity of the clays. The appearance of spinel in the samples whose exchange positions are saturated with other ions presupposes that Mg^{+2} or Fe^{+2} also are present as substituting octahedral ions in the illites, or as constituents of a magnesian component.

When the spinel phase first appears at around 1000°C, its diffraction peaks are diffuse and exhibit maxima representing two different cube-edge parameters—those of Mg-rich and Fe-rich spinel. Because all the samples probably contain some percentage of iron oxides, the spinel's intensity maxima tend to move toward the greater (Fe) spacing with increasing temperature, reflecting a substitution of Fe for Mg in the spinel structures as the Fe_2O_3 phase dissolves and is incorporated into the spinel lattice. The spinel usually persists to 1350°C and sometimes exists even at the end of the run, which usually occurred between 1400° and 1450°C.

Spinel was formed in all of the samples run, except the potassium-exchanged clays. Potassium, sodium and calcium seem to inhibit spinel formation to a greater degree than the other exchangeable cations.

β -quartz is developed in the majority of the samples, but its quantity is never very great. The X-ray patterns are not very clear in the range where the quartz is developed (1000°–1200°C) and the crystallinity of the quartz is too poor, or its grain size too minute, to result in definitive patterns for identification. It appears, however, that the β - or high modification of quartz develops simultaneously with the spinel phase, both becoming apparent immediately upon the destruction of the illite-

anhydride lattice. It should be stated here that the spinel and quartz may possibly have begun forming at a slightly lower temperature than indicated, as no phases other than the mica-anhydride were investigated below 1000°C. The presence of the illite basal peaks below this temperature makes identification of these other phases difficult, if not impossible, because the illite maxima occur at almost the same spacings as the major spinel and quartz peaks.

The specific saturating cations do not seem to affect the β -quartz phase in any consistent manner. Sodium does appear to have the greatest repressive action on quartz formation though, as the Jackson and Purington sodium-clays have no quartz phase at all; Fithian shows little β -quartz development with any adsorbed cation.

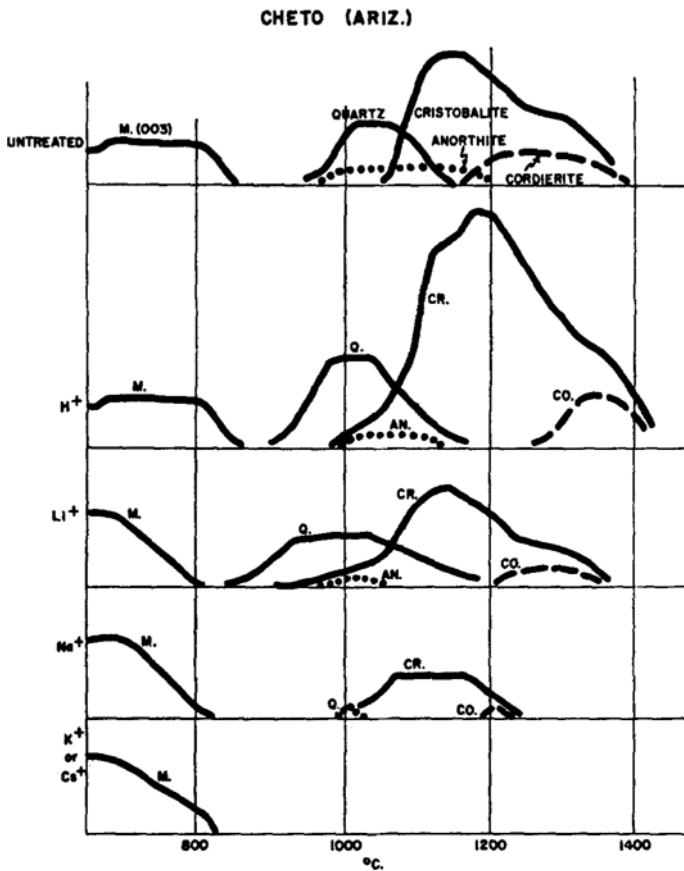


FIGURE 3.—Cheto (Ariz.) montmorillonite high-temperature phases—
from Kulbicki (1958).

Regarding the action of various cations on the β -quartz phase of montmorillonite, inspection of Kulbicki's curves (1958, Fig. 6, p.163) of the Cheto clay, treated with various concentrations of NaCl in solution and then heated, reveals that sodium represses quartz greatly in this clay too. The large expressive effect of lithium on quartz shown with the montmorillonites is not repeated in the illites, however.

A very interesting feature of these illitic samples is that cristobalite was never positively identified in any run, indicating that no inversion of the synthesized quartz takes place within the temperature range investigated. This is in direct contrast to the silica phases developed by firing montmorillonite (Fig. 3), which shows great development of β -cristobalite in most runs (Kulbicki, 1958). Any cristobalite developed in the illitic clays is therefore probably derived from montmorillonitic impurities. The presence or absence of cristobalite at high temperatures thus seems to be a reliable criterion for distinguishing between illite and montmorillonite.

Mullite is by far the most important and abundant phase crystallizing from illites at high temperatures. But, even so, the amount formed is usually far less than the major phases of fired montmorillonites (quartz and cristobalite), as shown in Fig. 3.

Mullite formed from every illitic sample, but not in equivalent amounts or at the same temperature. The Minford samples generally showed larger mullite developments than the other clays, possibly because of larger amount of kaolinite impurity. Potassium, sodium, calcium, and lithium as exchangeable ion complements caused little mullite to form, regardless of the clay sample (Fig. 1). Because these are the cations (except for lithium) usually present on natural illites, the untreated samples also showed rather small amounts of mullite at high temperatures. The mullite in all the samples of Fig. 1 began forming at about 1150°C, and usually did not begin melting until the furnace's peak temperature was reached.

With Be^{+2} and $\text{Sn}^{+2,4}$ as the exchange cations, mullite showed considerable enhancement in all the clays. Be and Sn were not exchanged onto all of the clays, but in those where they were used, mullite reached its greatest and earliest development. Immediately following the initiation of structural rearrangement (loss of diffracted X-ray intensity) in the anhydride (900°C), these ions caused discernable mullite to begin forming. Generally, these mullite peaks began decreasing in intensity due to fusion before the limiting temperature of the furnace was reached (1425°–1450°C).

As indicated on the diagrams, the mullite varied in preferred crystallographic orientation with different exchange cations. In well-oriented clays, such as those saturated with monovalent cations, the 110 reflection is enhanced. When Be or Sn are the exchange cations, however, the orientation is poorer, and the 120–210 doublet reflects with the greatest intensity. All of the mullite developed from Grundite samples showed this doublet reflecting with the highest intensity. These variations thus seem to depend on the original degree of preferred basal orientation of the clay sample

and, of course, this in turn is influenced by the exchange cations charge, size, and degree of hydration. All the enhanced reflections indicate, however, that the mullite is developing with its *c*-axis parallel to the clay's *a*- or *b*-axes.

Minor phases.—In addition to the major high-temperature phases mullite and spinel, a number of other minor phases developed in the samples when they were heated above 1000°C. These phases are generally of little consequence and their presence is probably due to migration of cations from the interior of clay mineral lattices to their edges, where they may combine with excess silica, adsorbed cations, and non-clay mineral impurities. Therefore, the same minor phases should not be found in runs of different clays, or even in runs of the same clay with different exchangeable cation populations. None of the minor phases attained any great magnitude in any run, nor was any one phase universally present in all of the runs. Most of these minor phases have their most intense and diagnostic peaks occurring in the vicinity of strong peaks belonging to the major phases and platinum (from the slides). Because of this interference and the small amounts of the minor phases developed, only tentative identifications were usually possible.

Cordierite, forsterite, corundum, γ -alumina, feldspar, kalsilite, and a form of iron oxide were the minor phases identified at one time or another in the runs. Cordierite develops in the range 1300–1400°C, and forsterite from 1100–1200°C; the presence of these phases in clays not specifically treated with magnesium shows the presence of either structural Mg in the illites, or chlorite as an impurity. Corundum sometimes is noted between 1040–1080°C; γ -alumina has been tentatively identified in a few patterns between 1100°C and 1350°C. Feldspar is a commonly occurring phase, usually appearing around 1050°C and melting into glass about 1300°C. Kalsilite, a feldspar-like phase, was observed in several runs in the lower range of feldspar crystallization temperatures. Its composition is near that of leucite or sanidine. Some form of iron oxide developed in all the clays except Grundite.

Figure 4 is another way of diagrammatically illustrating the phases

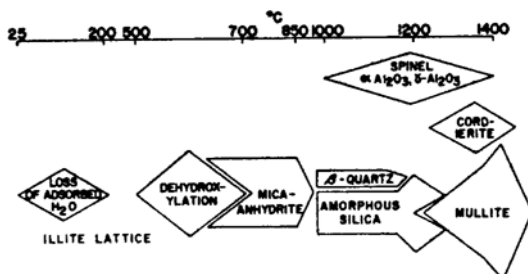


FIGURE 4.—Schematic representation of generalized high-temperature phase development in illitic clays.

formed by rapidly heating these illitic clays, and their general amount and persistence. The temperature scale is non-continuous, but the phases do not change between the breaks. The amorphous (glass) phase should probably be more prominent; Brindley and Maroney (1960, p.515) report 60 per cent glass in a similar mixture of clay minerals soaked for 2 hr at 1300°C. The cordierite phase is relatively exaggerated to indicate its persistent occurrence; its representation here should be considered to include other minor phases developing in the range 1250–1400°C, such as feldspars. Likewise, the representation of the development of spinel and alumina phases should also include iron oxide, forsterite, kalsilite and corundum.

Other worker's data support the phase developments reported here. Brindley and Udagawa (1960) fired and quenched a mixture of kaolinite and quartz similar to the Minford sample (except for the quartz) and reported the same phases— β -quartz, iron spinel, and mullite. Brindley and Maroney (1960) also experimented with various ratios of kaolinite and muscovite mixed with 15 per cent quartz. They found that when more than 20 per cent mica was present in the mixture, no cristobalite was formed in the high-temperature phases. Also, the phases mullite and β -quartz decreased as the per cent of mica in the unfired mixture was increased.

DISCUSSION

Consideration of these results leads to two rather inter-related points requiring discussion: (1) Why are these particular high-temperature phases developed from illitic clays, and (2) why do certain adsorbed cations inhibit while others encourage the development of these phases, especially mullite? No ultimate answers will be proposed to these questions here, but some solutions based on this and other supporting data are suggested.

We can start by making a simplifying assumption that the minor phases are controlled mainly by impurities and occasional structural and compositional anomalies in the clay. Their low intensities and general lack of reproducibility argue for this assumption. Crystallization of these minor phases probably takes place at the edges of clay mineral layers where ion migration into and out of the lattice is greatest. Some of the later crystallizations are undoubtedly melt reactions dependent on over-all composition.

The most striking distinction between the crystallization mechanisms of the major and minor phases is structural inheritance. Whereas the minor phases probably bear little or no relationship structurally to the original clay lattice and depend mostly on over-all composition for their existence, the major phases develop topotaxially and bear definite relationships to the clay. This is especially so in the case of mullite. The enhancement of reflections lacking a *c*-axis index indicates that the mullite prisms develop

with this axis parallel to the basal surfaces of the clay crystals. This topotaxial relationship has been reported earlier from X-ray data on fired kaolinite, and confirmed by electron micrographs (Comeforo, Fischer and Bradley, 1948); it has likewise been reported to occur in the three-layered clay mineral pyrophyllite (Bradley and Grim, 1951, p.192).

Johns (1953) has related the development of mullite from kaolinite to this clay's original crystallinity. The structure of mullite is thought to consist of chains of edge-sharing Al-O octahedral groups parallel to the *c*-axis. These chains are cross-linked laterally by Si and Al ions coordinated tetrahedrally; also, each Al in a chain is coplanar (in the *a-b* plane) with an Al counterpart in the other chains.

Johns points out that the major change accompanying the mullitization of kaolinite involves minor redistribution of octahedrally coordinated oxygen ions in the alumina coordination chains. Such redistribution results from the transformation of chains composed of octahedral units sharing pairs of coordination faces (metakaolin) to chains of edge-sharing octahedra (mullite).

Recently, Brindley and Nakahira (1959) have proposed the existence of an Al-Si spinel phase, intermediate between metakaolinite and mullite. This spinel phase also shows strong structural inheritance from metakaolin, and can be easily modified to the mullite crystallization scheme with a minimum of rearrangement. These authors point out that the entire reaction sequence metakaolin—Al-Si spinel—mullite involves a continuous loss of silica by diffusion of silicon ions, certain crystallographic rearrangements within the oxygen structural framework, and a redistribution of aluminum ions.

This very cogent delineation of the reactions and phase sequences of fired kaolinite is entirely a structural interpretation and applies only to the kaolinite layer sequence O-Si-O-Al-O-Si . . .; therefore, it is not a feasible explanation of reactions in the three-layered clays. The extra silica tetrahedral layer in illites precludes direct condensation to an Al-Si spinel phase from the anhydride, or to mullite either.

Another crystallographic obstruction to a simple transformation of illite anhydride to spinel or mullite is layer stagger. As Johns (1953) indicates, *any n b/3* translation in kaolinite will result in one-half of the alumina octahedra in adjacent layers losing their mutual parallel alignment. Because this stagger or glide translation takes place *between* layers in kaolinite, it does not affect the orientation of the constituent ions of any layer. In micas and other similar three-layer clay minerals, however, layer stagger occurs *within* unit layers (Fig. 5) and direct condensation to a spinel or mullite crystallization becomes very difficult to imagine.

Alternatively, mullite can be considered to form from illite by the process of "reconstructive transformation" (Kingery, 1960, p.136), in which original structural relationships are completely altered by the breaking of interatomic bonds. Nucleation and growth can then take place in the solid

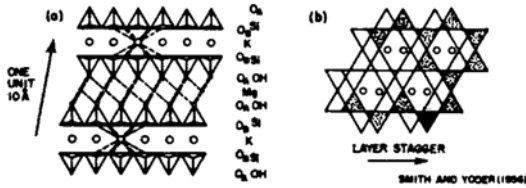


FIGURE 5.—Layer stagger in the micas.

state; this can be speeded by the presence of vapor or liquid phases, or by the addition of mechanical energy. Ion transfer takes place within crystals by diffusion, bringing aluminum ions to the surface boundaries where reorganization into mullite occur. Some silicon ions probably move in the opposite direction into the crystal centers as a balancing reaction; thus mullite nuclei form and grow on a silica substrate.

Mullite certainly does not seem to grow at the expense of the β -quartz and spinel phases. The origin of these two major phases is problematical, but their development simultaneously with the anhydride's collapse indicates a release of a portion of the clay's alumina and silica at that point, and its rapid reorganization into quartz and spinel. The intensities of these phases do not seem to be functions of the amount of clays other than illite either.

The second point deserving discussion is the role of the exchangeable cations. The results of firing the five clay samples exchanged with various cations show little influence of the adsorbed cation on the quartz and spinel phase developments, except that K, Na, and Ca seem to inhibit them slightly. The influence of adsorbed cations on mullite development, however, is striking. The adsorbed cations Be and Sn consistently enhance the amount of mullite formed and lower its formation temperature. The apparent sequence of decreasing inhibition of mullite phase formation— $K > Na > Li > Ca > NH_4 > Mg > Be > Sn$ —is also the sequence of increasing electronegativity of these cations (Table 2). These values of electronegativity and ionic potential are taken from Green (1959, Table 2). No value of electronegativity is given for Sn^{+2} , but other tables of electronegativity place its value near that of Cr^{+3} ; it definitely is more electronegative than Be^{+2} and Mg^{+2} . No values are listed for the NH_4^+ ion either.

Ringwood (1955) has pointed out the significance of electronegativity in controlling trace element distribution during magmatic crystallization. Electronegativity is defined as the power of an atom in a molecule to attract electrons to itself.

Ringwood (1955, pp.243-246) also discusses the affinity of cations in melts for anions, such as oxygen. This, he says, is controlled by the ionic potential (cation charge divided by ionic radius). Cations having low ionic

TABLE 2.—ELECTRONEGATIVITY AND IONIC POTENTIAL

Cation	Ionic Radius (Å)	Ionic Potential	Electronegativity (kilocalories/gram-atom)
K ⁺	1.45	0.69	100
Na ⁺	0.97	1.03	118
Li ⁺	0.68	1.47	125
Ca ⁺²	0.99	2.02	137
Mg ⁺²	0.66	3.03	0.74
Sn ⁺²	0.93	2.15	
Be ⁺²	0.33	6.06	210
Sn ⁺⁴	0.71	5.63	235
Si ⁺⁴	0.40	10.00	270

potentials do not tend to form oxygen tetrahedra in competition with silicon, and they exist only in holes between silica tetrahedra as "network modifiers". Cations with high ionic potentials do compete vigorously with silicon for the available oxygen anions, and actually enter silicate networks; accordingly, they are called "network formers".

These two concepts of electronegativity and network forming or modifying tendencies can now act as pegs on which to hand our hypotheses about the role of adsorbed cations in high-temperature phase development of illites. Their action certainly cannot be ascribed to fluxing, as the alkali and alkaline earth cations, which repress formation of high-temperature crystalline phases the most, are usually considered the best fluxing agents and greatly enhance fusion and glass formation.

Heterogeneous reactions, leading to nucleation and crystal growth in regenerative transformation, require three processes to be followed: (1) material transfer to the reaction interface, (2) reaction at the phase boundary, and (3) in some cases diffusion of products away from the reaction site (Kingery, 1960, p.331). Mullite seems to follow these heterogeneous reactions, so that an analysis of these three steps may reveal the role of the adsorbed cations.

Considering the first step, material transfer to the reaction interface takes place by solid state diffusion in the case of phase transformation in clay minerals within the temperature range 1000–1400°C, and the adsorbed cations cannot affect this. Secondly, glass and liquid probably form on the clay crystal surfaces because of the location of adsorbed fluxing cations at these interfaces, but this layer of melt is not very thick. Free silica and alumina, liberated when the anhydride rearranges at 1000°C, also contributes to this liquid phase. The most repressive cations have already been stated to provide the greatest fusion and liquid formation, so that the observed effects on mullite formation cannot be correlated with relative fluxing action. The presence of this liquid phase is probably indispensable, however, for speeding up the reaction rate at this boundary under the non-equilibrium conditions of the rapid heating schedule employed. The more

electronegative adsorbed cations may contribute here by virtue of their competition with the silicon ion for O^{2-} . This competition may cause a more rapid breakdown of the silica tetrahedral layer, releasing the substituting Al^{+3} ions for mullite nucleation. This breakdown may also speed up the transfer of diffusing ions into the liquid phase.

Finally, the expressive adsorbed cations act as complex formers in a silicate melt (as has been described earlier), such as the one postulated to exist on clay mineral surfaces at these high temperatures. Thus they help remove the product from the reaction site and thereby promote further reaction. The removal of silica (the product) has already been shown to be necessary in the case of kaolinite mullitization, and is even more vital in the three-layer clays, where silica is in great excess. This may be the key to unblocking the chain of reaction so that rapid and early nucleation and growth of mullite can occur in the high-temperature transformation of illite.

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