HIGH TEMPERATURE THERMAL EFFECTS OF CLAY AND RELATED MATERIALS*

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Abstract

A selected series of clay minerals and related silicates are examined by thermal, optical, and *x*-ray diffraction methods with a view toward establishing the significance of the various observed thermal effects. The heating range for the thermal curves is extended to 1300°C, and the study of specimens so fired is supplemented by the examination of the various materials after firing to several intermediate temperatures.

Detailed hypotheses are presented for the mechanisms of several of the structural changes observed as new phases are developed, and the influence of types of structures upon the nature and rapidity of such changes is discussed.

Introduction

The widespread interest in the use of thermal analyses for clays and related hydrous minerals has suggested the desirability of investigation of the nature of the various phase changes which cause the individual heat effects observed for the commoner types of materials to which thermal analyses are being applied.

Using the thermal curves as reference, the method of approach employed in this study has been simply to prepare portions of each of the specimens being investigated, fired to various intermediate temperatures below and above each prominent thermal effect, and to examine the resultant suites of specimens by *x*-ray diffraction and, where possible, by optical methods.

Initial developments of several of the high temperature phases are characterized by such small particle size that *x*-ray diffraction lines are noticeably broadened. In this condition particles are not resolvable microscopically, and one cannot even observe an average index for any single phase unmodified by refractivities of the matrix. In these circumstances, one is forced to rely entirely on the *x*-ray diagrams. It has further become apparent that not all of the materials encountered have been subjects of adequate prior description in the literature. To attempt to suitably characterize each of these somewhat variant phases is beyond the scope of this study. Instead, it seems desirable to interpose a short series of general remarks about each of the types which have not been found to be strictly correlative with standard literature descriptions—such as ASTM catalogues. Other phases, for which we are aware of no great latitude in diffraction characteristics, will simply be referred to without comment.

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THE PHASES

The three-layer anhydrides.

The altered diffraction effects observed from pyrophyllite after moderate ignition have been described by Thilo and Schünemann (1), and the observation of a similar phenomenon in the course of ignition of several montmorillonites and illites was previously remarked by the present authors (2). Consideration of the present and several other moderately fired montmorillonites suggests the following interpretation.

The removal of hydroxyl water, which is correlative with endothermal peaks around 500–700° and with increases of 0.1–0.3 Å in c-axis periodicities, involves the expulsion of about one-sixth of the oxygens of the octahedrally coordinated portion of the structure. This correlation is apparently confined to heptaphyllite type members.

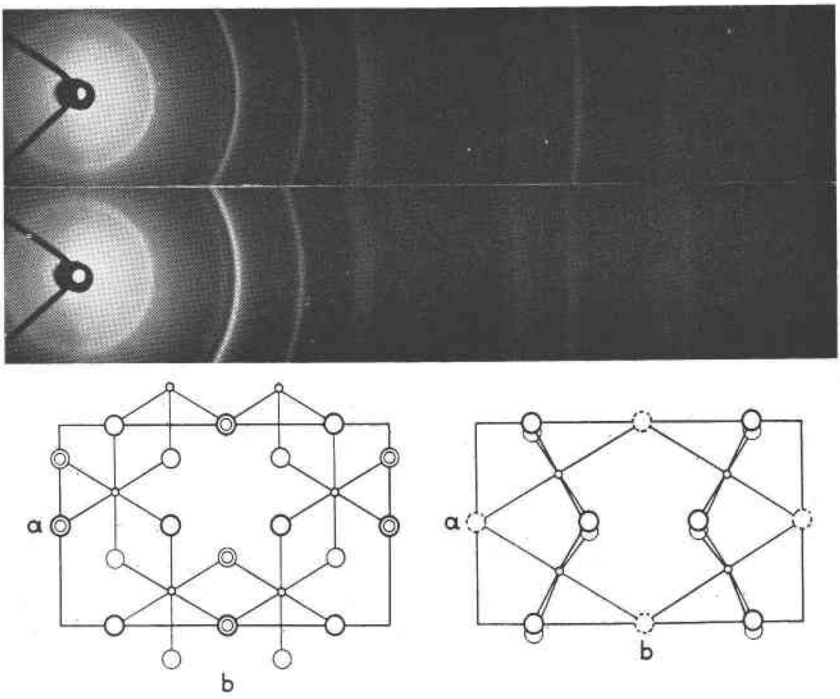

FIG. 1. The probable rearrangement in the heptaphyllite type clays upon loss of hydroxyl water. The diffraction diagrams illustrate the Tatatila montmorillonite after heating to 550° (upper) and 725° C. (lower). The schematic sketches represent the arrangement within an octahedral layer before and after dehydroxylation.

An idealized rearrangement of the octahedral layers which adequately accounts for the meager data observable is illustrated in Fig. 1. It represents merely the lifting of the adjacent oxygen layers out of the packed position, with the immediate consequences that the vertical height is increased and the intensity of the 4.5 Å diffraction line is augmented. A diagram of a typical dehydroxylated specimen is compared with its normal dry state in Fig. 1.

TABLE 1. THE ANHYDRIDE OF THE TATATILA MONTMORILLONITE IGNITED TO 725° C.

Indices as orthohexagonal	*d* in Å	Observed relative intensity	Calculated relative intensity for idealized scheme of Fig. 1
001	9.7	m	2
002	4.85	m	2
110,020	4.48	ss	18
003	3.22	s	10
200,130	2.59	m	4
	2.5	diffuse m	
220,040	2.23	m	2
	2.1	diffuse w	
005	1.93	w	1
240,150	1.72	w	2
	1.67	diffuse m	
330,060	1.51	m	2
	1.49	diffuse w	
400,260	1.31	w	3
420,350	1.25	w	1

In Table 1 are summarized the diffraction data for the rearranged material. Prismatic reflections conform more nearly to hexagonal relations, their relative intensities are clearly altered, and in addition several diffuse scattering maxima are apparent at positions where better crystallized related minerals have strong pyramidal reflections.

The idealized scheme of Fig. 1 involves shared pairs of octahedral coordination faces for a heptaphyllite, and is probably unstable. Application of the same scheme to an octaphyllite type would demand sharing of three such pairs of faces, presumably impossible. For the magnesian clay from Hector, and for talc, the only two certain octaphyllites examined, no rearranged anhydride was observed.

THE SPINEL TYPE OXIDES

The spinel crystallization is well known, and it has even been possible to make useful correlations between composition and cell dimensions within limited systems (3). Under the uncertain conditions of composition under which new phases develop in fired clays, however, the present authors have not attempted to search out any possible indication of composition. Indeed, as these spinel phases first appear, *x*-ray diffraction lines are notably diffuse and it is probably more true that rather than having any particular composition, the phase is merely an irregularly constituted assemblage of small cations, some octahedrally coordinated and others tetrahedrally coordinated, with only the oxygen packing actually approaching crystalline regularity. These spinels are not particularly refractory, however, and they grow rapidly to a clearly crystalline powder affording a clean diffraction diagram. No noticeable difference in relative intensities is observed between the diffuse and the sharp patterns, although cube edge parameters may change somewhat (with changing composition), and no erratic appearances of new lines have been remarked.

The character of the spinel type mixed oxides is thus in marked contrast to that of γ-Al_2O_3, a phase which has from time to time been described as a spinel-like structure. γ-Al_2O_3 also is probably some mixed arrangement of tetrahedrally and octahedrally coordinated aluminum ions, but the clean spinel type alumina material has been obtained only in the presence of a lithium mineralizer, and this clean material is actually a lithium aluminate.

The γ-Al_2O_3 normally observed upon ignition of gibbsite or boehmite varies markedly in character with the temperature of ignition at which it is formed (4), and the variations are much more profound than mere particle growth. Additional lines appear erratically, and probably of greater significance, the degree of diffuseness is unequal for different sets of lines, thus suggesting a distinct anisotropy, at least in the habit of the crystallites, and probably in the actual structure.

The apparent significance of these structural implications will be referred to again under discussion of the energy relationships inferred from the thermal curves for several individual specimens.

QUARTZ

Quartz has traditionally been looked upon as a phase of relatively fixed composition and invariant behavior. The cryptocrystalline synthetic products which have been found to result from firing of many montmorillonites at about 1000° C exhibit surprising vagaries with respect to their apparent relation to the high-low inversion. Synthesized quartz in the present study, when observed at room temperature, is found to exist in some cases as α-, in others as β-modification (in one case apparently intermediate).

In the absence of any criterion for the diffraction effects of the high form at room temperature, some attention must be given to the validity of its identification. Analyses of the material free from the matrix in which it is grown are not available. Either the α- or the β-quartz however makes the normal slow transition to cristobalite at more elevated temperatures.

Table 2 lists the observed reflections for the quartz which is developed in the montmorillonite from Otay, California, upon ignition to 1000° C.

TABLE 2. SYNTHETIC β-QUARTZ AT ROOM TEMPERATURE

$a_0=5.11$ $c_0=5.37$ $u=.21$

Indices	*d* in Å	Observed relative intensity	Calculated relative intensity for powder diagram
100	4.43	m	20
101	3.42	sss	140
110	2.55	m	9
111		—	.2
102	2.30	w	2
200	2.22	m	4
201	2.045	m	4
112	1.85	ss	30
202	1.71	w	2
121	1.57	s	10
122	1.421	s	8
301			1.5
203	1.393	s	11
302	1.292	m	5
104		—	.5
220	1.277	m	5
123	1.225	w	4
131	1.196	m	5
114	1.190	w	3
132	1.113	ww	2
400	1.105	ww	1
105	1.044	ww	2
223			1

The observed a_0 and c_0 values represent reasonable extrapolations of the thermal expansion data of Jay back to room temperature (5). The apparent best estimate of the oxygen parameter is based mainly on the near equality of 121 and 122. It is probably sufficiently reliable to interpret in terms of dimensions within the structure. It is thus shown that the O-O approach of the unbonded oxygen atoms across the 00*l* open channels increases from 3.46 to 3.73 Å with falling temperature. An obvious explanation of the failure to invert would be the trapping of occasional extraneous ions in these channels.

Recent analyses of lithium aluminum silicates would suggest that lithium could be such an ion. Magnesium also is of suitable size. Neutrality would have to be maintained by inclusion of some aluminum.

CRISTOBALITE

Carefully prepared low-cristobalite is apparently a normal, well-organized crystal. The fine-grained manifestation resulting from syntheses in heterogeneous matrices are however noticeably variable (possibly even in composition (6)) and of uncertain inversion character. In addition there exist the opaline silica materials which are clearly subcrystalline, but seem to be based upon the cristobalite crystallization. Such materials gradually become typical cristobalite without any important sudden energy effects upon ignition to sufficiently high temperatures. In the discussion to follow, no attempt is made to evaluate the quality of a cristobalite. The point is merely made that it is unlikely that poorly organized manifestations of such a crystal would be involved in any of the striking energy effects which provide the major features in a thermal analysis curve. The apparently abnormal instances of rapid evolution of cristobalite will be referred to later.

MULLITE

Mullite powder diffraction diagrams have been studied in meticulous detail by Rooksby (7), but the data are not correlated with the actual crystallization. It is probable that the sillimanite structure should be regarded only as a schematic representation, from which the pertinent observation to be made is that mullites are based upon centered chains of alumina coordination octahedra extending parallel to *c* and sharing two opposed edges. Details, such as the orientation of chains and the population of interchain cation positions are probably variable in moderate degree. No significance is attached to variations in crystals from separate sources in this study.

THE MAGNESIUM META-SILICATES

Studies of the preparation and polymorphism of magnesium metasilicates (8) have indicated that the crystallization processes are probably too slow to provide energy effects identifiable in thermal analysis curves of already crystallized phases. It does appear to be true that the crystallization of enstatite from amorphous hydrous magnesium silicates involves exothermal effects.

Enstatite and clinoenstatite are normal, well-crystallized phases and are observed in the firing of several high magnesian minerals. The $MgSiO_3$ which is formed in the firing of several typical montmorillonites is comparable with the "mesoenstatite" of Thilo and Rogge. This material is probably to be looked upon as a rudimentary nucleation rather than as a normal crystallization.

The structural relations of the layer silicates and the pyroxenes are such that projections onto the respective orthohexagonal axes are approximate equivalents. In the imperfectly developed diffraction diagrams of the fired montmorillonites the lines which appear are only those which relate to the pseudohexagonal nature. In fact, they constitute an identification of $MgSiO_3$ only in the sense that they correspond with equivalent lines which appear in better and better crystallized materials of higher magnesian content for gradations up to and including the typical enstatite crystallization obtainable from tremolite asbestos.

THERMO-CHEMICAL GENERALITIES

The method of thermal analysis is inherently an expression of the response of systems to nonequilibrium conditions. If thermal effects are to be apparent in the difference couple traces, it is required that reactions involving appreciable energy transfer be accomplished in a limited time. Endothermal reactions involving the crystallization of a new phase are of quite variable nature. Without going into quantitative aspects, which in most cases would be impossible for want of data, the following statements can be accepted. The rapid evolution of a hard, dense phase will afford a sharp exothermal effect. Sufficiently hard and dense crystals may, but need not, show broad exothermal effects in development over ranges of 50 to 100° C. Soft, irregularly constituted phases certainly cannot evolve detectable energy in slow development, and probably do not in moderately fast precipitation.

The simplest types of reactions, to which one would naturally like to look for standards by which to judge crystallization energy effects, do not present the features as resolved peaks. For example, for ignition of pairs like calcite and magnesite, where lime is softer than periclase, it is only apparent that following the decarbonation effect the return of the MgO temperature to the furnace temperature is more abrupt than that of the CaO. Similarly, for a set like brucite, hydrated lime and gibbsite, after dehydration the curves are respectively, abrupt, intermediate and gradual. For diaspore, which goes to the α- rather than the γ-oxide, the return is again abrupt.

The kind of reaction that does appear to produce a single sharp exothermal effect identifiable separately on a curve is the kind for which substantial articulated units present in the structure of the starting material condense without significant rearrangement into the crystals of the new phase. Probably the clearest instance of this sort is the crystallization of forsterite (H=6–7, G=3.21–3.33) from clinochlore or from chrysotile. The latter case especially has attracted attention before, and can be discussed in some detail.

The Thermal Synthesis of Forsterite

The justification for projecting forsterite into a clay mineral study is that the syntheses may be accomplished from mineral specimens of far more perfect crystal development than that of the respective clay mineral analogues. Thus, there are available for study both chrysotile, which can be fired as a fibre, and high magnesium chlorites (clinochlore), which can be fired as cleavage lamellae. For each of these the crystal structures are known in sufficient detail to afford direct correlation between the natural phase and the synthetic forsterite. Each also exhibits an exothermal feature correlated with the development of the new phase.

Monochromatic pinhole diffraction diagrams taken through a fired flake of clinochlore and through a fired chrysotile fibre are reproduced in Fig. 2. Specialized orientation conditions for the new phase are readily apparent in each case. The chlorite flake affords three sets of strictly parallel grown forsterite aggregates mutually related to each other by rotations of 120° about *a*. The diagram amounts to three superposed preferred orientation diagrams each approximately along *a* for each of the three parallel grown sets. The latitude of deviation of *a* from the pole of the flake appears to be no greater than that normally introduced into flakes like chlorite or vermiculite by roasting them at lower temperatures where a layer silicate structure is preserved.

The chrysotile diagram, originally fibrous about *c*, now affords superposed forsterite rotation diagrams about the poles [011], [020], [311], and [320]. The spots belonging to the [011] and [020] rotations are the clear, symmetrically shaped ones in layer lines of form, respectively $k+3l=0$, 1, 2, etc., and $k=0$, 1, 2, etc. Spots for the other rotations are weaker and are elongated parallel with the rotation axis. In Fig. 2 are illustrated the respective structural relations between the natural crystals and the fired product. It is seen that at the level of octahedrally coordinated Mg ions the transition from the old to the new phase requires no chaotic disintegration followed by reconstitution of a new assemblage, but simply the freedom of a few Mg ions to migrate to the nearest equivalent interstice.

The chance that so extensive articulated assemblies carry from the

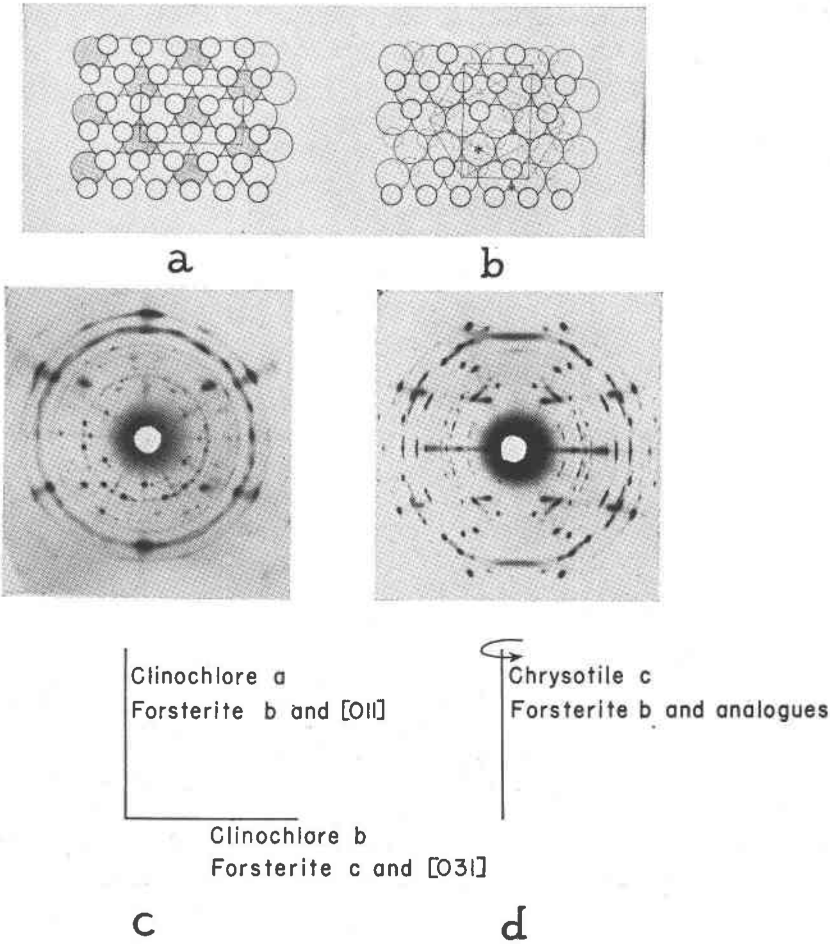

FIG. 2. The relationship of corresponding octahedrally coordinated levels in (*a*) clinochlore or chrysotile and in (*b*) forsterite. The diffraction diagram (*c*) represents a view along *c* for clinochlore or *a* for the forsterite growths. The diagram (*d*) is the synthetic fibrous forsterite product. In each case sufficient diffraction features of the respective unreacted starting materials show in the diagrams to mark the relative orientation before and after firing.

one structure to the other by other than lineal descent is remote. It seems therefore to be inferred that the stability of the brucite arrangement of octahedra is such that in the expulsion of water from its derivatives, it is the silica rather than the magnesia coordination which is disrupted. This is an apparently significant difference between octaphyllite and heptaphyllite octahedral arrangements.

The Synthesis of Quartz

The synthesis of quartz from a crystalline silicate under the conditions of rapid temperature rise maintained in analysis is a matter of some concern. The quartz phase not only develops suddenly at temperatures of the order of 1000° C, the development being correlative with a sharp exothermal effect, but the crystallites are even subject to moderate grain growth in soaking periods of a few hours, before eventually transforming into cristobalite. The further complication that the quartz so synthesized on cooling to room temperature inverts in some cases and in others does not is probably less a surprise than is the synthesis itself.

The original concept of the layer silicates was drawn from observations of the dimensional compatibility of brucite and the cristobalite-tridymite type of tetrahedral layer. Probably one should think that, if a quick crystallization of silica were to occur at all, the modification should be one of those forms, but that does not seem to be the case.

Being granted that a structural inheritance can be traced from an old to a new phase in a particular instance, it seems reasonable to test whether any inheritance can be postulated that might govern the transition from linked layers to quartz in this instance.

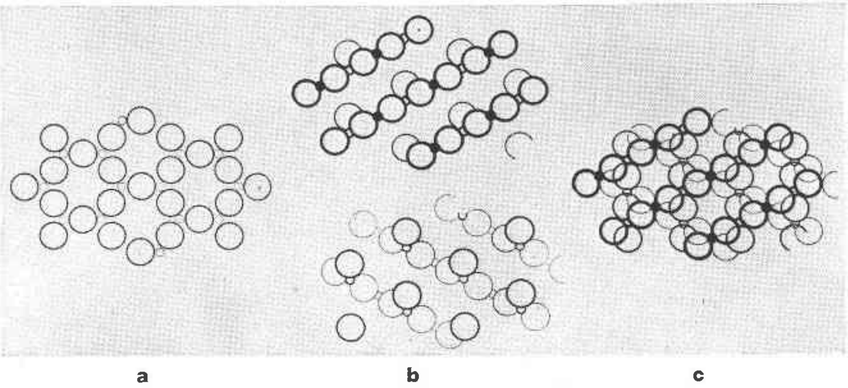

Fig. 3. The articulation of tetrahedrally arranged montmorillonite surfaces to form quartz.

a. A montmorillonite surface.
b. Two distorted arrangements of *a*.
c. A superposition of the two levels *b*.

In Fig. 3 are sketched two sets of linked tetrahedra, representing adjacent montmorillonite surfaces, in which oxygens are partitioned into two kinds. Suitable articulation of these pairs actually does simulate the quartz arrangement of height equivalent to one complete unit cell and the new grouping effects a localized gain in density of the order of about 10%.

This postulation of the articulation of montmorillonite surfaces into the quartz arrangement is a consequence of extended clean clay mineral surfaces. To articulate two such surfaces into a segment of the cristobalite structure would require the introduction of additional oxygen between surfaces to complete the coordination of any silicons which might provide valence bonds between layers.

Acid activated clays retain considerable quantities of $SO_4^=$, presumably on layer surfaces. These materials fire directly to cristobalite with a prominent exothermal effect around 1000° C. It is presumed that the presence of these interlayer sources of oxygen can condition the direct, energy-releasing articulation into cristobalite for such materials, even though in their natural condition they would fire to quartz.

MULLITE FROM PYROPHYLLITE

The synthesis of mullite from pyrophyllite appears to offer an example intermediate in facility of the synthesis and in clarity of the structural inheritance. Through the temperature range in which mullite is demonstrated to form there is no prominent exothermal feature, but only a broad ill-defined effect. There is again, however, a clear predisposition in the orientation of the synthesized mullite needles from which a structural relation may be deduced.

Figures 4*a* and *b* are illustrative diagrams. The (*a*) diagram is the monochromatic pinhole diffraction effect from a subparallel splinter aggregate of a fibrous pyrophyllite. Axial relations for the aggregate are sketched below. The (*b*) diagram is the resultant fired product. It consists of three superposed rotation diagrams for mullite, as rotated about *c*. Each diagram is 120° from the other two, and the three mullite *c* axis traces are parallel with the original pyrophyllite poles [020], [110], and [$1\bar{1}0$].

The structural implications are reminiscent of those deduced for the forsterite synthesis. In the octahedrally packed layers in pyrophyllite, the orientation of each octahedron with respect to *b* and its analogues is precisely that of the orientation of each alumina octahedron with respect to *c* in the coordinated strings which extend along the center and corners of the mullite cell. In the absence of an actual analysis of the configuration in the octahedrally coordinated portion of the anhydride of pyrophyllite, one cannot follow the precise redistribution of aluminum ions among the apparently undisturbed octahedra. It does seem justifiable to conclude, though, that the octahedra are undisturbed and that the building of mullite strings, in this case without sharp exo-

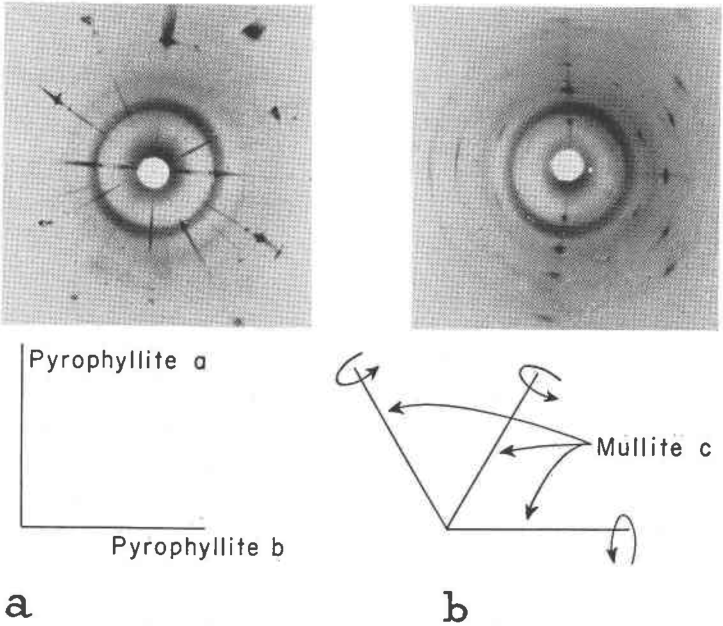

FIG. 4. Pyrophyllite and mullite.

a. Subparallel splinter aggregate of pyrophyllite. The three oxygen ion chain directions of the octahedral layer are horizontal and at the two 120° rotation positions in the plane of the film.

b. The mullite developed by firing splinter *a*. The three *c*-axis rotation diagrams demonstrate that all *c*-axes lie in and only in the three chain directions of *a*.

thermal effect, is merely less readily accomplished than the building of the same chains in kaolinite, which does afford a sharp exothermal effect.

THE THERMAL CURVES

The latitude of variation in the actual thermal analysis curves observed for the number of different minerals to be considered is such that they have not been set in order with respect to any particular generality.

The several groups of curves are simply reproduced in Figs. 5–10 without individual comment. In supplement a skeletal tabulation of respective constitutions at pertinent points in the firing sequence is arranged as a synopsis of the data in Table 3.

DISCUSSION

On a number of occasions, thermal curves of this sort have been reproduced for which it has been clearly established that prominent endothermal effects in two ranges around 100–250° C and around 400–700° C

TABLE 3. GENERAL SUMMARY OF FIRING PRODUCTS FROM VARIOUS CLAYS

High alumina	900° C	1000° C	1100° C	1200° C	1300° C
Kaolinite		mullite (1)		mullite (1) cristobalite (2)	
Endellite		mullite (1)		mullite (1) cristobalite (2)	
Diaspore	α-Al_2O_3 (1)				
Gibbsite	γ-Al_2O_3 (1)	α-Al_2O_3 (1)			
Bauxite (Kaolinite & gibbsite)					
Montmorillonite group					
Otay, Calif.		β-quartz (1) enstatite (3)	cristobalite (1) β-quartz (1) enstatite (2)	cristobalite (1) cordierite (1)	cristobalite (3) cordierite (1) periclase (3)
Tatatila, Vera Cruz		β-quartz (2)			cristobalite (1) mullite (2) cordierite (2)
Upton, Wyo.	spinel (1)	spinel (1) α-quartz (2)	spinel (2) cristobalite (1)		mullite (2)
Cheto		β-quartz (1) anorthite (?) (3)	β-quartz (1) cristobalite (3) anorthite (?) (3)		cristobalite (1) cordierite (1)
Palmer, Ark.		spinel (1)	spinel (1) quartz (3)	cristobalite (1) spinel (1) mullite (1)	
Sierra de Guadalupe		spinel (1)	cristobalite (1) spinel (1)	cristobalite (1) spinel (1) cordierite (2)	cristobalite (1) cordierite (1)
Harris Co., Texas		spinel (2) cristobalite (3)	cristobalite (1) spinel (1)	cristobalite (1) spinel mullite (2)	cristobalite (1) mullite (2)
Pontotoc Co., Miss.		spinel (1) α-quartz (2)	cristobalite (1) spinel (1)		cristobalite (2) cordierite (2)
Beidell, Colo.					mullite cristobalite
Fairview, Utah				mullite (1) cristobalite (1)	mullite (1)
Wagon Wheel Gap	spinel (2)	cristobalite (1) mullite (3) spinel (2)			cristobalite
Woody Nontronite					mullite cristobalite spinel

Parenthetic numbers signify: (1) important, (2) moderate, and (3) minor.

are related respectively to loss of molecular and hydroxyl water. In the present discussion, attention will be confined to reactions which follow the second water loss.

The three-layer anhydride phase, present between the 400–700° reaction and the subsequent endothermal effect about 200° higher, is not

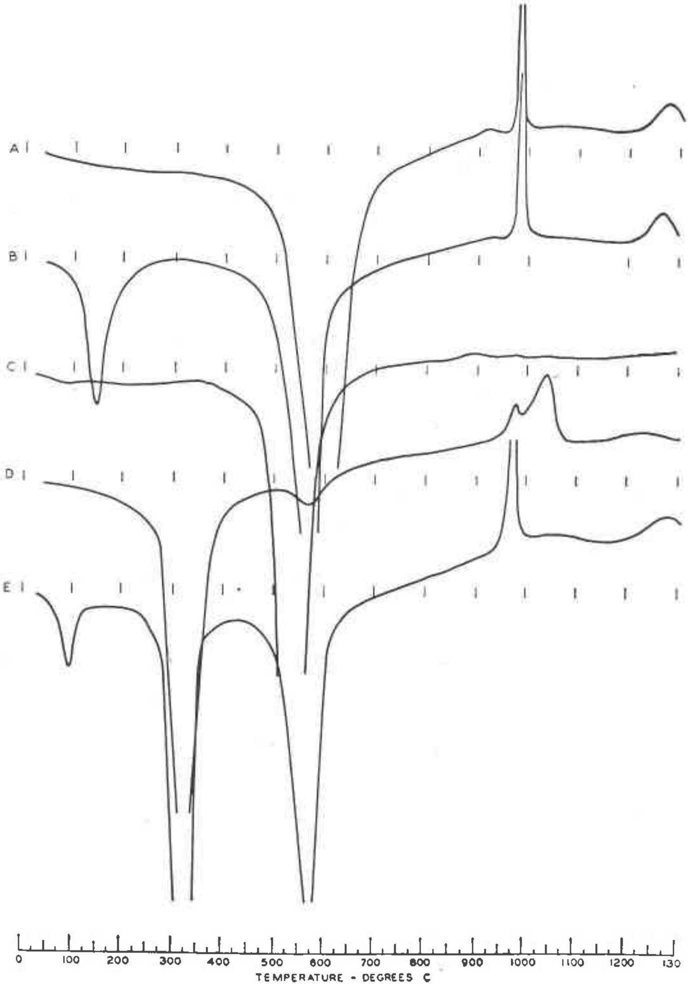

FIG. 5. Miscellaneous hydrous minerals.

A. Kaolinite, Dry Branch, Georgia.
B. Endellite, Eureka, Utah.
C. Diaspore, Chester, Massachusetts.
D. Gibbsite, Saline County, Arkansas.
E. Bauxite (Gibbsite and Kaolinite), Irvington, Georgia.

strictly anhydrous. Additional water losses of the order of one-half to one per cent are readily demonstrated in weight vs. temperature curves, but the magnitude of the loss is too small to hope that its significance might ever be deduced from diffraction data. Nor does it seem justified in the absence of an instantaneous weight record to speculate on whether the amount of water loss under analysis conditions is commensurate with the indicated energy effect.

Beyond the temperature of water losses, over-all compositions of the separate systems are not subject to change (ignoring instances of reducible iron oxide content). The problem is thus not to account for the simplicity of a curve, but to account for its complexity. There seems to be no reason to expect that a system would attempt to approach equilibrium by successive reactions. It is here that the role of structural inheritance becomes apparent. Predisposition to crystallize as a phase which "doesn't belong" affords starting material for a subsequent reaction, with a possible subsequent energy effect.

Probably in no case does the intensity of an inheritance energy effect or the estimated abundance of that phase in the diffraction diagram bespeak the entire content of that chemical component. In general, though, it appears to be true that great abundance of such a phase correlates with greater intensity for subsequent effects in the same system. For those curves which show two prominent exothermal effects in the high temperature range then, it is indicated that the first is a consequence of the coordination scheme of the natural mineral and the second is a consequence of its chemical composition.

Perusal of the various three-layer clay mineral curves brings out that separate thermal traces tend to differentiate themselves into two separate types, those which present an *S*-shaped feature (as Fig. 6*c*, 7*a*, 7*c*, 8*d*), and those which exhibit a distinct shoulder (as Fig. 6*a*, 6*b*, 6*d*). Each presumably represents an energy absorption followed by energy evolution, the two effects being simply unresolved for the former case. In terms of phase development, however, the separate types are clearly differentiated. Clays of the *S*-shaped curves contain proportions of spinel type oxides, following this reaction, which are proportional to the observed magnitude of the thermal effect. The second group, in which crystallization seems to be somewhat delayed, are those in which the first prominent new phase to appear is quartz. The new phase is thus seen to develop in the one case from the octahedral region in the clay, and in the other case from the tetrahedral. It is perhaps to be noted that the trace depicting crystallization of forsterite (based on the octahedral portion) from chlorite is an exaggeration of the *S*-shaped type.

In the comprehensive tabulation of montmorillonite group analyses included in the recent survey by Ross and Hendricks (9) corresponding specimens in the two studies fire to quartz if they appear in Ross and Hendricks table with Si^{++} population near 4.00, and fire first to spinel if there is substantial substitution of Al^{+++} in tetrahedral coordination. It is inferred that regularity in the composition of the tetrahedral scheme endows it with ability to maintain its unity under conditions which disorganize substituted layers.

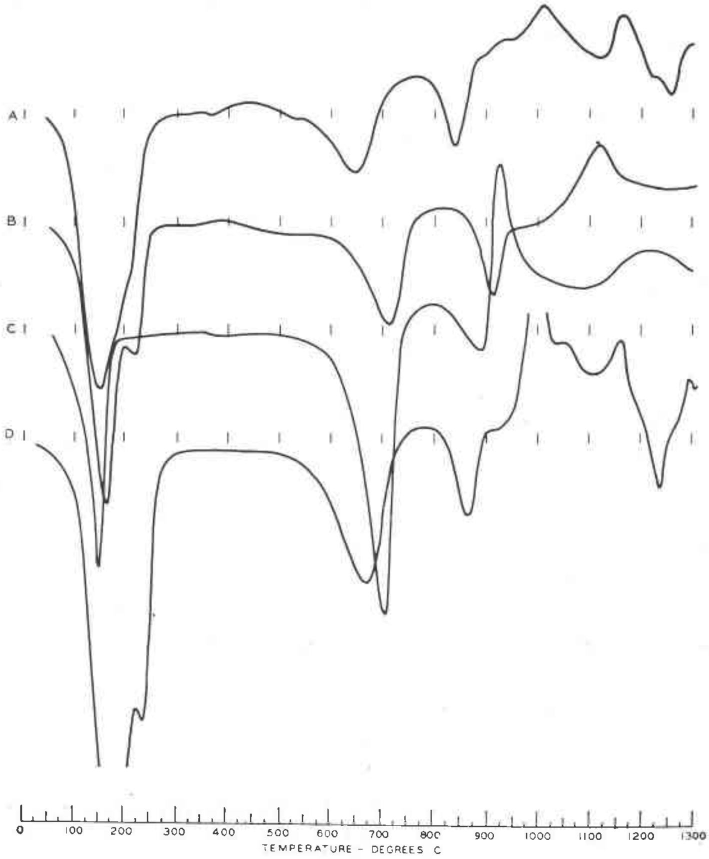

FIG. 6. Montmorillonite.

A. Otay, California.
B. Tatatila, Vera Cruz, Mexico, U. S. Nat. Mus. 101,836.
C. Upton, Wyoming.
D. Chambers, Arizona.

Clays of either type, which have undergone either of the foregoing syntheses, may show an additional fairly prominent reaction near 1200° C. The new phase encountered here seems to be either mullite or cordierite with about equal frequency. One reaction having already taken place

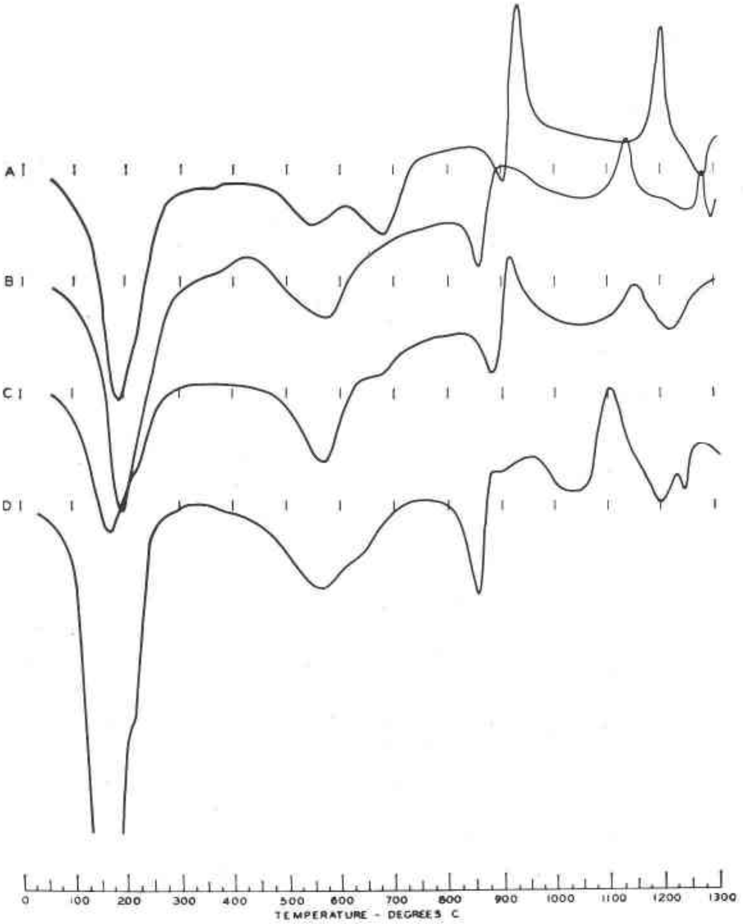

FIG. 7. Montmorillonite Group Clays.

A. Palmer, Arkansas.
B. Sierra de Guadalupe, Atzoopozalco, Mexico, U. S. Nat. Mus. 7591.
C. Harris County, Texas.
D. Pontotoc County, Mississippi.

there is no reason to believe that either of these crystallizations are inheriting characteristics from the starting material. They seem to be predetermined only by the chemical composition of the system, and have in common only the properties of density and hardness which would indicate that both would evolve heat in formation from the respective raw materials present.

The spinel forming specimens all develop more or less cristobalite around 1000° or 1100° C., without going through the quartz inter-

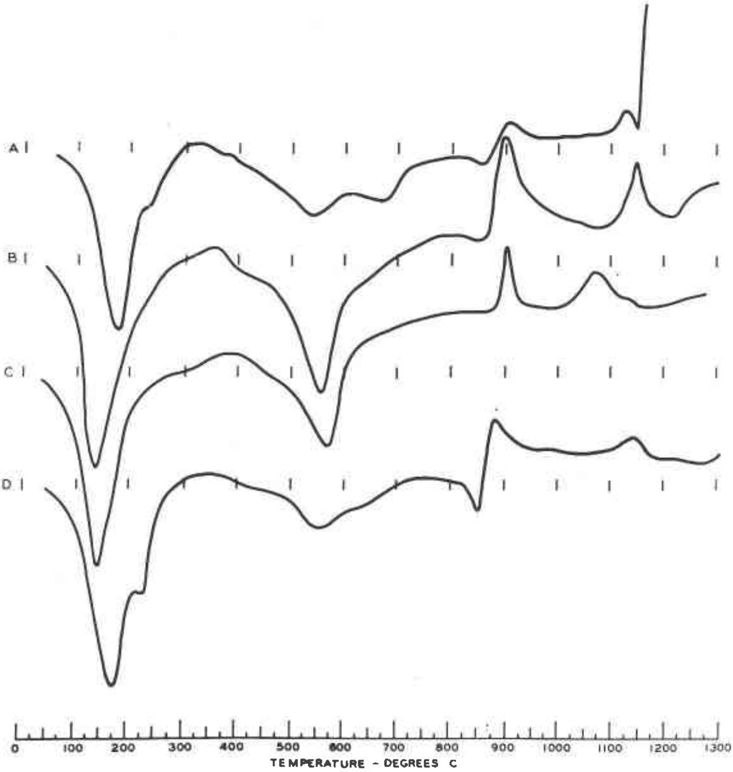

FIG. 8. Materials Often Called Beidellite.

A. Beidell, Colorado, U. S. Nat. Mus. 93239.
B. Fairview, Utah.
C. Wagon Wheel Gap, Colorado, U. S. Nat. Mus. 94963.
D. Nontronite, Howard County, Arkansas.

mediate stage. No separate feature appears in the curves to indicate any energy effect associated with the growth. Since this is true also of opal fired alone, it is assumed that any exchange involved is not picked up by the method. Cristobalite is actually effectively somewhat less dense than the condensed layer configuration, and might even require an energy input to crystallize under the analysis conditions.

SUMMARY

1. Endothermal effects up to 900–1000° C are normally occasioned by the expulsion of some volatile constituent.

2. Exothermal effects of moderate magnitude may, when they immediately follow endothermal effects, be evidenced merely in the more abrupt return of the test specimen to reference temperature.

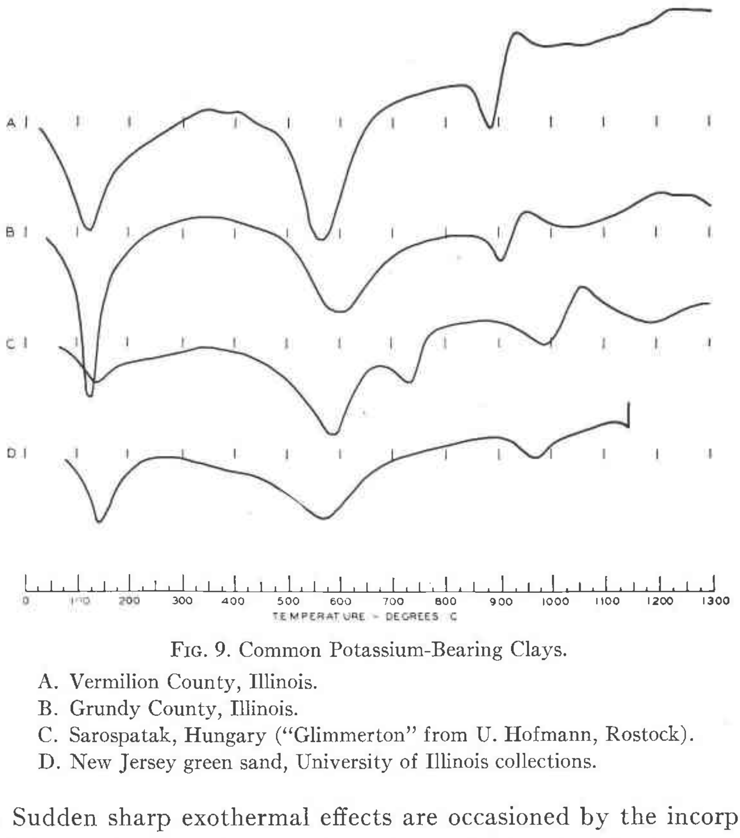

FIG. 9. Common Potassium-Bearing Clays.

A. Vermilion County, Illinois.
B. Grundy County, Illinois.
C. Sarospatak, Hungary ("Glimmerton" from U. Hofmann, Rostock).
D. New Jersey green sand, University of Illinois collections.

3. Sudden sharp exothermal effects are occasioned by the incorporation into new phases of large articulated units from reactant structures without catastrophic rearrangements within the units.

4. Secondary exothermal effects may be observed for crystallization of phases whose development is conditioned only by the chemical composition of the system.

NOTE

Since the preparation of this article, Roy and Osborn (10) have stabilized high quartz at room temperature with lithium, and Brindley and Ali (11) have analyzed the mechanism of forsterite growth in fired chlorite flakes.

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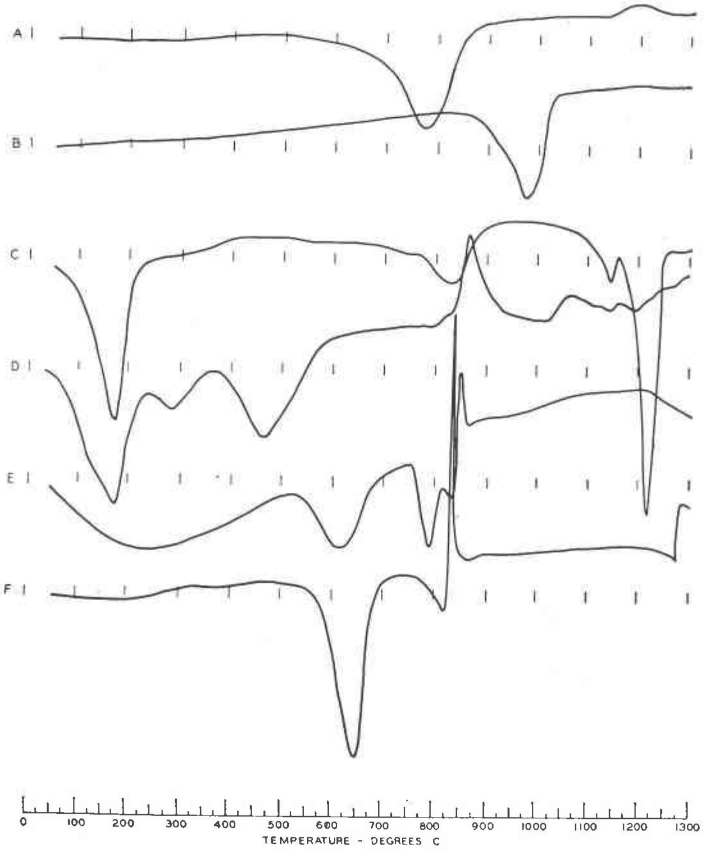

FIG. 10. Miscellaneous Related Minerals.

A. Pyrophyllite, North Carolina.
B. Talc, Vermont.
C. Hectorite, Hector, California.*
D. Attapulgite, Quincy, Florida.
E. Prochlorite, Chester, Vermont.
F. Clinochlore, Brewster, New York.

* The unique feature near 1200° is the inversion to clino-enstatite under the mineralizing influence of fluorine in the natural clay.

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