

DIFFERENTIAL THERMAL CURVES OF PREPARED MIXTURES OF CLAY MINERALS*

RALPH E. GRIM, *Illinois State Geological Survey, Urbana, Illinois.*

ABSTRACT

This paper presents differential thermal curves of clay minerals, of prepared mixtures of such minerals, and of some clay minerals diluted with inert materials.

Variations in the size and perfection of crystallinity of particles of kaolinite appear to be reflected in variations in the intensity of the thermal reactions characteristic of the mineral.

Thermal curves of many prepared mixtures show that the thermal reactions characteristic of the individual component minerals are not always discernible, particularly if the mixing is very intimate and if the components are poorly crystallized. Caution must be used in the identification of the clay minerals in mixtures, and quantitative evaluations are very difficult.

INTRODUCTION

The differential thermal method of analysis (3, 4) has been used widely and successfully to determine the clay mineral composition of clays, soils, and shales. In the course of extensive use of the method in the laboratory of the Illinois State Geological Survey, differential thermal analyses have been obtained for a wide variety of clay minerals, prepared mixtures of clay minerals, and various clay minerals diluted with inert materials. The object of the present paper is to present some results of this work which are pertinent in the use of the differential thermal procedure for clay mineral identifications.

KAOLINITE—INERT MIXTURES

In Fig. 1, curves *A*, *B*, and *E* are for closely similar amounts of three different kaolinites (K_1 , K_2 , K_3), whose monomineral identity has been checked by x-ray diffraction analyses. The kaolinites show significant differences, namely: (1) K_1 and K_2 show broad low-intensity initial endothermic reactions whereas K_3 shows no such reaction; (2) the intensity of the large endothermic reaction with a peak at about 600° C. is slightly greater for K_3 than for K_1 or K_2 ; (3) the intensity of the final exothermic reaction is much greater for K_3 than for either K_1 or K_2 ; and (4) the final exothermic reaction in K_3 is immediately preceded by a slight endothermic reaction whereas no such reaction is shown for K_1 or K_2 .

By way of explanation for the foregoing differences in the kaolinite curves, it should be noted that kaolinites K_1 and K_2 have a lower degree

* Published with the permission of the Chief, Illinois State Geological Survey, Urbana, Illinois.

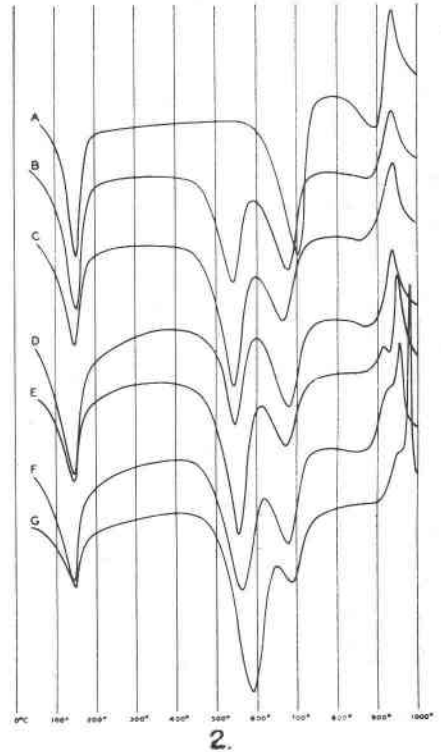
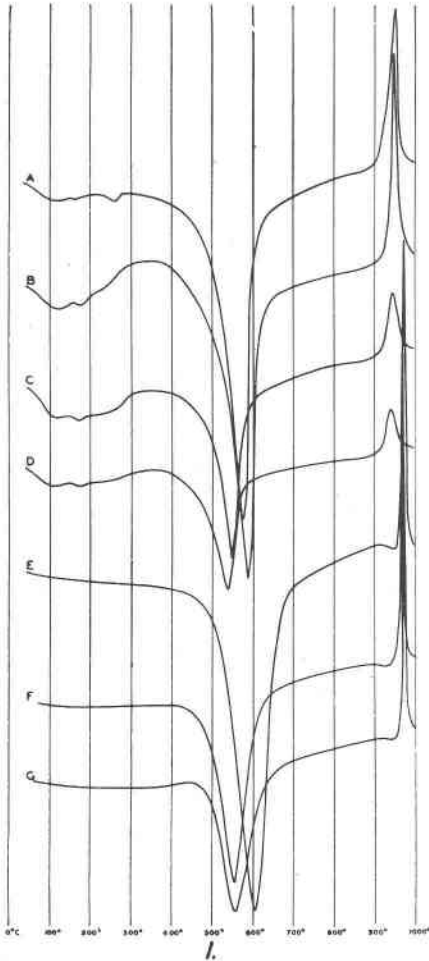


FIG. 1. Differential Thermal Curves

- A. Kaolinite, K₁, Vera, Washington, 0.522 g.
- B. Kaolinite, K₂, Anna, Illinois, 0.460 g.
- C. Kaolinite, K₂, Anna, Illinois, 0.370 g.
- D. Kaolinite, K₂, Anna, Illinois, 0.215 g.
- E. Kaolinite, K₃, Dry Branch, Georgia, 0.427 g.
- F. Kaolinite, K₃, Dry Branch, Georgia, 0.355 g.
- G. Kaolinite, K₃, Dry Branch, Georgia, 0.230 g.

FIG. 2. Differential Thermal Curves

- A. Sodium montmorillonite, M₁, Clay Spur, Wyoming, 0.628 g.
- B. Sodium montmorillonite, 0.536 g. and kaolinite, K₁, 0.268 g.
- C. Sodium montmorillonite, 0.425 g. and kaolinite, K₁, 0.425 g.
- D. Sodium montmorillonite, 0.518 g. and kaolinite, K₂, 0.259 g.
- E. Sodium montmorillonite, 0.424 g. and kaolinite, K₂, 0.424 g.
- F. Sodium montmorillonite, 0.514 g. and kaolinite, K₃, 0.257 g.
- G. Sodium montmorillonite, 0.408 g. and kaolinite, K₃, 0.408 g.

of crystallinity than K_3 . By lower degree of crystallinity is meant less perfect stacking of the units and perhaps distortion within the units. It is noteworthy also that kaolinites K_1 and K_2 have higher plastic and bonding properties than K_3 , characteristics that are probably related to the degree of crystallinity and which might be predicted from the thermal curves.

The differences in the final portion of the curves may be taken to mean that loss of (OH) from the kaolinite lattice for well crystallized sample K_3 is not accompanied by complete destruction of lattice which occurs with the final slight endothermic reaction at about 925–950° C., whereas in the case of the poorly crystallized samples K_1 and K_2 the kaolinite lattice is completely destroyed along with the loss of (OH).

Curves *C* and *D* are for the same kaolinite as K_2 , but the sample in the furnace was diluted with precalcined Al_2O_3 . Similarly curves *F* and *G* are for the same kaolinite as K_3 , but the sample in the furnace was also diluted with precalcined Al_2O_3 . The curves for reduced amounts of kaolinite show a proportionate reduction in the size of the thermal reactions. It is noteworthy that the final exothermic reaction for K_2 is reduced proportionately more than that for K_3 .

Curve *D* might be confused with some illite curves, whereas curve *G* for about the same amount of well crystallized kaolinite would not be so confused because of the absence of an initial endothermic reaction and the character of the final exothermic reaction. Also the curves show that an initial endothermic reaction does not always mean the presence of a clay mineral other than kaolinite.

KAOLINITE AND SODIUM MONTMORILLONITE (WYOMING BENTONITE) MIXTURES

Curve *A* in Fig. 2 is that of a sodium montmorillonite, M_1 , in Wyoming bentonite. Curves *B* and *C* are mixtures of this montmorillonite and kaolinite, K_1 of Fig. 1; curves *D* and *E* are similar mixtures with kaolinite, K_2 ; and curves *F* and *G* are similar mixtures with kaolinite, K_3 . The mixtures were prepared by mixing weighed amounts of minus 200-mesh material, then soaking in distilled water overnight, followed by 30 minutes agitation in a mechanical mixer. The mixture was then allowed to dry, soaked again in distilled water, stirred 30 minutes and dried. This procedure was repeated through four cycles.

The initial endothermal peaks of the mixtures are about proportional in size to the amount of montmorillonite in the mixture. However, this peak is slightly larger for mixtures containing kaolinite K_1 or K_2 (curves *B–E*) than for mixtures with kaolinite K_3 (curves *F–G*) because kaolinites K_1 and K_2 (unlike K_3) also have initial endothermic reactions.

The second endothermic peaks are also about proportional to the amounts of montmorillonite and kaolinite in the mixtures. In mixtures with kaolinite K_3 , because of the higher intensity of the thermal reaction for this kaolinite, the portion of the second thermal reaction due to montmorillonite appears to be reduced in size.

The final part of the curves are of considerable interest. In mixtures with kaolinite K_1 (curves *B* and *C*) the sharp final exothermic reaction for kaolinite is not obvious even in mixtures with 50 per cent kaolinite (curve *C*). It seems significant that a relatively small amount of kaolinite eliminates the third endothermic reaction for montmorillonite at about 900° C., and this may be a usable clue in recognizing the presence of kaolinite in such mixtures. In case of kaolinite K_2 , the final exothermic kaolinite peak does not show distinctly in mixtures with one-third kaolinite (curve *D*), but does show clearly when the amount of kaolinite is increased to 50 per cent (curve *E*). For mixtures with the well crystallized kaolinite, K_3 , even with as little as one-third kaolinite, the final part of the curve is a distinct combination of the montmorillonite and kaolinite curves.

The kaolinites with the lesser degree of crystallinity (K_1 and K_2) break down on agitation in water to smaller particle size than kaolinite K_3 , and as a consequence the clay minerals in mixtures with kaolinites K_1 and K_2 are probably more intimately mixed than with kaolinite K_3 . It follows that the final thermal reactions due to the formation of new phases may be misleading and must be interpreted with great caution, particularly when there is any reason to suspect a mixture of clay minerals. However, when the final reactions indicate a distinct mixture, the mixing is probably not very intimate and at least some of the components are probably well crystallized. Cailiere (1) and her colleagues have also shown recently the necessity for caution in the interpretation of the final reactions in the thermal curves of some clay minerals.

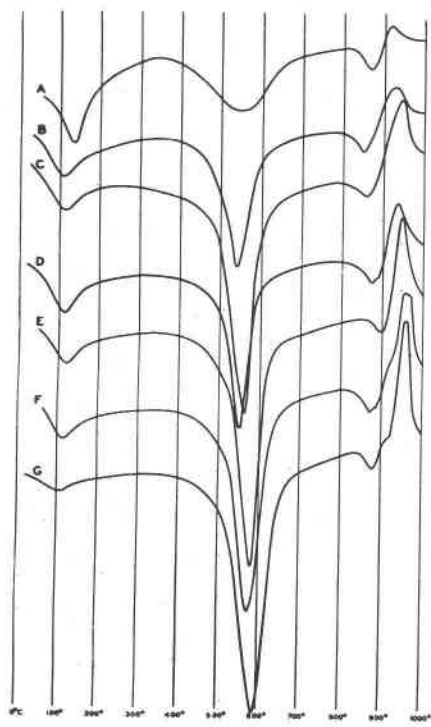
KAOLINITE AND ILLITE MIXTURES

Curve *A* in Fig. 3 is that of an illite, (2) I_1 , from an underclay of Pennsylvanian age from Grundy County, Illinois. Curves *B* and *C* represent mixtures of this illite and kaolinite K_1 ; curves *D* and *E* are for this illite plus kaolinite K_2 ; and curves *F* and *G* are for this illite plus kaolinite K_3 . The mixtures were prepared by the same procedure as used for mixtures reported in Fig. 2.

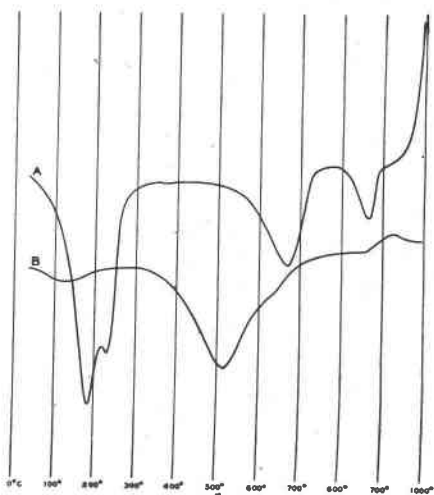
The initial endothermic peaks are roughly proportional to the amount of illite in the mixture. However, the curves (*B-E*) for mixtures with kaolinites K_1 and K_2 show slightly larger reactions than those (*F, G*) for

mixtures with kaolinite K_3 , because the former kaolinites themselves yield initial endothermic reactions.

The second endothermic peak for illite is at about the same temperature as the endothermic reaction for kaolinite. Because the intensity of this reaction is much less for illite than for kaolinite, the effect of replacing kaolinite by illite is to reduce the size of this peak. The size of this peak for a given amount of illite and kaolinite varies with the kind



3.



4.

FIG. 3. Differential Thermal Curves

- A. Illite, I_1 , Grundy County, Illinois, 0.504 g.
- B. Illite, I_1 , 0.504 g. and kaolinite K_1 , 0.252 g.
- C. Illite, I_1 , 0.371 g. and kaolinite K_1 , 0.371 g.
- D. Illite, I_1 , 0.518 g. and kaolinite K_2 , 0.259 g.
- E. Illite, I_1 , 0.371 g. and kaolinite K_2 , 0.371 g.
- F. Illite, I_1 , 0.502 g. and kaolinite K_3 , 0.251 g.
- G. Illite, I_1 , 0.363 g. and kaolinite K_3 , 0.363 g.

FIG. 4. Differential Thermal Curves

- A. Calcium montmorillonite, M_2 , Arizona, 0.749 g.
- B. Illite from Minford silt, I_2 , Ohio, 0.743 g.

of kaolinite. The relative amounts of kaolinite and illite could be estimated accurately only if the size of the reaction for the particular kind of kaolinite were known.

The final part of curve *B* shows that substitution of one-third of the illite with kaolinite K_1 causes little difference in the final thermal reactions for the illite. Curve *C* shows that substitution by 50 per cent kaolinite K_1 has little more effect. Unlike the mixtures with montmorillonite, the substitution of kaolinite does not tend to eliminate the third endothermic reaction for illite. It seems quite probable that as much as one-third of this kind of kaolinite might well go unidentified in mixtures of this kind.

In mixtures with one-third kaolinite K_2 , the final part of the curve does not clearly show a reaction for the kaolinite. In the mixture with 50 per cent kaolinite (curve *E*) the exothermic kaolinite reaction is evident.

In mixtures with kaolinite K_3 (curves *F* and *G*) the final part of the curve clearly shows the kaolinite reaction. The curves are distinct composites of the final part of the illite and kaolinite curves.

Apparently the final part of the curve is related to intimacy of mixing and degree of crystallinity of the kaolinite for illite mixtures as well as for montmorillonite mixtures.

MISCELLANEOUS MIXTURES OF CLAY MINERALS

Curve *A* of Fig. 4 was obtained from a calcium montmorillonite, M_2 , from a bentonite from Arizona. Curve *B* of Fig. 4 was obtained from an illite, I_2 , from the Minford silt from Ohio. Variations in the thermal curves for various members of the montmorillonite and illite groups have been presented (3).

Curve *A* in Fig. 5 is for a mixture of one-half sodium montmorillonite, M_1 , and one-half illite, I_1 , by the same wet mixing procedure. The second endothermic peak of both clay minerals shows intensities about proportional to the amount of each mineral in the mixture. The final part of the curve is very interesting in that it is that of the illite without any reflection of the montmorillonite. Again it is clear that the final portion of differential thermal curves must be interpreted with caution.

Curves *B*, *C*, and *D* of Fig. 5 are mixtures of equal amounts of illite, I_2 , and kaolinites K_1 , K_2 and K_3 respectively, prepared by the same wet mixing procedure.

The development of a double initial peak in curve for mixtures *C* and *D* is of interest and cannot be explained. An initial peak of this kind has been found in many natural clays without any satisfactory explanation.

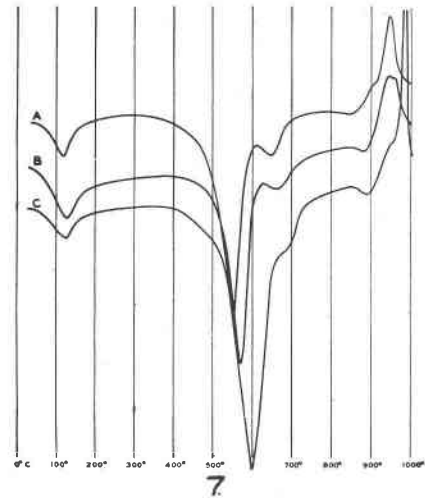
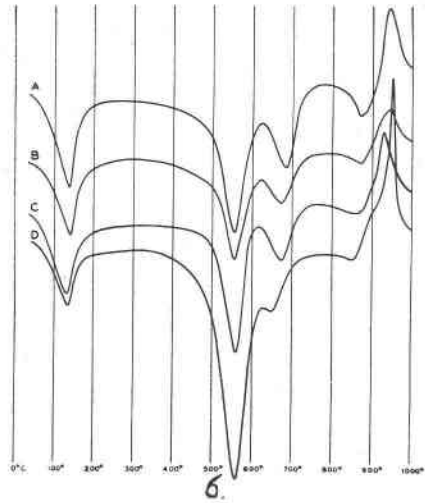
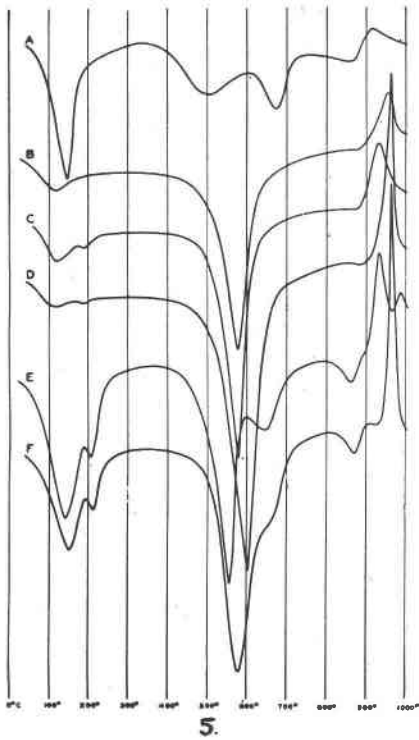


FIG. 5. Differential Thermal Curves

- A. Sodium montmorillonite, M_1 , 0.436 g. and illite, I_1 , 0.436 g.
- B. Illite, I_2 , 0.353 g. and kaolinite, K_1 , 0.353 g.
- C. Illite, I_2 , 0.350 g. and kaolinite, K_2 , 0.350 g.
- D. Illite, I_1 , 0.346 g. and kaolinite, K_3 , 0.346 g.
- E. Calcium montmorillonite, M_2 , 0.386 g. and kaolinite K_2 , 0.386 g.
- F. Calcium montmorillonite, M_2 , 0.363 g. and kaolinite K_3 , 0.363 g.

(See next page for description of figures 6 and 7.)

The second endothermic peak for the illite is completely masked by the kaolinite peak. Substitution of the 50 per cent illite for kaolinite does not affect the shape of the kaolinite peak, but does reduce the intensity of the reaction by an amount that depends on the kind of kaolinite.

The character of the final part of the curve varies with the kind of kaolinite mixed with the illite. In case of the well crystallized kaolinite K_3 (curve *D*) the kaolinite is distinctly shown whereas the illite is not. In the case of kaolinites K_1 and K_2 (curves *B* and *C*) the kaolinite is only faintly suggested. It would be easy to fail to identify the kaolinite in curves *B* and *C* purely on an evaluation of the final part of the curve.

Curves *E* and *F* of Fig. 5 are mixtures of equal amounts of calcium montmorillonite, M_2 , and kaolinites K_2 and K_3 , respectively, prepared by the same wet mixing procedure. All of the thermal reactions for the montmorillonite and for the kaolinite are shown by both curves. However, the kind of kaolinite causes distinct variations in the curve—the intensity and prominence of the montmorillonite thermal reactions are greatly reduced in mixtures with kaolinite K_3 as compared to those with kaolinite K_2 .

A comparison of the curves for the different montmorillonites and illites indicates that the kind of montmorillonite or illite also affects the character of the final peak in mixtures as well as does the kind of kaolinite.

Curve *A* of Fig. 6 represents a mixture of equal amounts of kaolinite K_1 , sodium montmorillonite, M_1 , and illite, I_1 , prepared by dry mixing. Curve *B* of Fig. 6 represents a similar mixture except that it was prepared by the wet mixing as described herein. If curve *B* were obtained for a clay of unknown composition it is likely that kaolinite would be unrecognized since it does not show in the final reactions and the endothermic reaction at about 550° C. might well be interpreted as the result of illite alone. In the curve for the dry mixture (curve *A*), the kaolinite

FIG. 6. Differential Thermal Curves.

- A. Kaolinite, K_1 , 0.223 g.; sodium montmorillonite, M_1 , 0.223 g.; illite, I_1 , 0.223 g., mixed dry
- B. Kaolinite, K_1 , 0.249 g.; sodium montmorillonite, M_1 , 0.249 g.; illite, I_1 , 0.249 g., mixed wet
- C. Kaolinite, K_2 , 0.262 g.; sodium montmorillonite, M_1 , 0.262 g.; illite, I_1 , 0.262 g., mixed wet
- D. Kaolinite, K_3 , 0.273 g.; sodium montmorillonite, M_1 , 0.273 g.; illite, I_1 , 0.273 g., mixed wet

FIG. 7. Differential Thermal Curves

- A. Kaolinite, K_1 , 0.450 g.; sodium montmorillonite, M_1 , 0.150 g.; illite, I_1 , 0.150 g.
- B. Kaolinite, K_2 , 0.468 g.; sodium montmorillonite, M_1 , 0.156 g.; illite, I_1 , 0.156 g.
- C. Kaolinite, K_3 , 0.471 g.; sodium montmorillonite, M_1 , 0.157 g.; illite, I_1 , 0.157 g.

would probably be identified since the endothermic peak at about 550° C. is rather large for illite alone and the exothermic peak at about 940° C. is suggestive of kaolinite. A comparison of curves *A* and *B* shows quite well the influence of intimacy of mixing on the thermal reactions of the clay minerals and particularly on the final reactions. When the mixing is very intimate, as much as one third kaolinite might well be missed, even though pure kaolinite gives exceedingly intense and distinct thermal reactions.

Curves *C* and *D* are for mixtures like curve *B* except kaolinite K_1 was replaced by kaolinite K_2 and K_3 respectively. Both mixtures were prepared by the wet procedure. In these curves the kaolinite would easily be spotted because of the size of the endothermic reaction at about 550° C. and because of the character of the final reactions. Kaolinite is much more distinctly shown in the curve *D* for the mixture with the well crystallized kaolinite than in curve *C*. In curves *C* and *D* the identification of illite would almost certainly be missed unless some information regarding the kind of kaolinite and therefore the intensity of the kaolinite reactions were available.

Curve *A* of Fig. 7 represents a mixture of 60 per cent kaolinite K_1 , 20 per cent of sodium montmorillonite, M_1 , and 20 per cent of illite, I_1 , prepared by the wet mixing procedure. Curves *B* and *C* of Fig. 7 represent similar mixtures except that kaolinite K_1 was replaced by kaolinite K_2 and K_3 , respectively. The presence of kaolinite is shown in each curve, but with considerable variation dependent on the kind of kaolinite. In such curves the presence of montmorillonite would be detected easily by the endothermic reaction at about 650–700° C. The presence of illite would probably be missed unless some information regarding the kind of kaolinite were available.

The writer is indebted to his colleagues Dr. W. F. Bradley for making the x-ray analyses and Mr. W. A. White for preparing the mixtures and running the thermal curves.

REFERENCES

1. CAILIERE, S., HENIN, S., AND TURE, L., Investigations of the differential thermal analysis of clays—significance and specificity of the phenomenon of recrystallization: *Compte rendu*, **223**, 383–384 (1946).
2. GRIM, R. E., BRAY, R. H., AND BRADLEY, W. F., The mica in argillaceous sediments: *Am. Mineral.*, **22**, 813–829 (1937); *Rept. Inv.* **44**, Ill. State Geol. Survey (1937).
3. GRIM, R. E., AND ROWLAND, R. A., Differential thermal analyses of clay minerals and other hydrous materials: *Am. Mineral.*, **27**, 746–760, 801–818 (1942); *Rept. Inv.*, **85**, Ill. State Geol. Survey (1942).
4. GRIM, R. E., AND ROWLAND, R. A., Differential thermal analyses of clays and shales, a control and prospecting method: *Jour. Am. Cer. Soc.*, **27**, 65–76 (1944); *Rept. Inv.* **96**, Ill. State Geol. Survey (1944).