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DIFFERENTIAL THERMAL CURVES OF PREPARED MIXTURES OF CLAY MINERALS

BY

RALPH E. GRIM

REHYDRATION AND DEHYDRATION OF THE CLAY MINERALS

BY

RALPH E. GRIM AND W. F. BRADLEY

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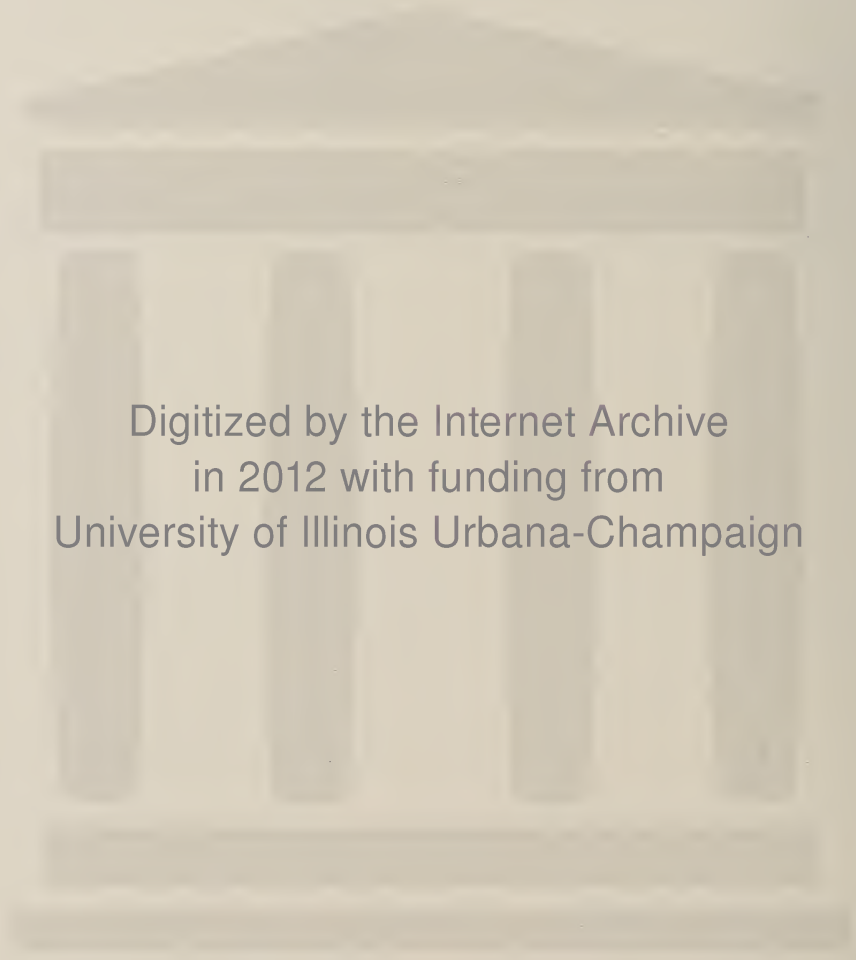RUBY D. FRISON, *Technical Assistant*

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DIFFERENTIAL THERMAL CURVES OF PREPARED
MIXTURES OF CLAY MINERALS

BY
RALPH E. GRIM

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 figure 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 ex-

othermic 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 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
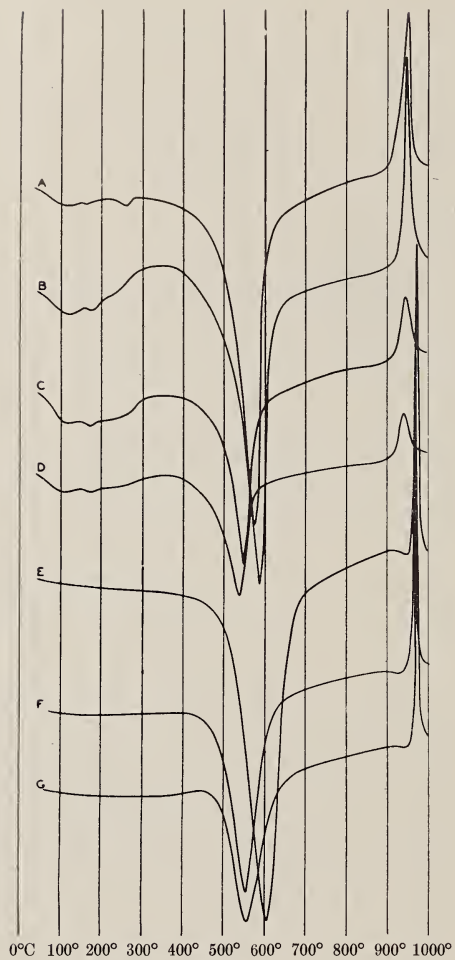
0°C 100° 200° 300° 400° 500° 600° 700° 800° 900° 1000°
Fig. 1

0°C 100° 200° 300° 400° 500° 600° 700° 800° 900° 1000°
Fig. 2
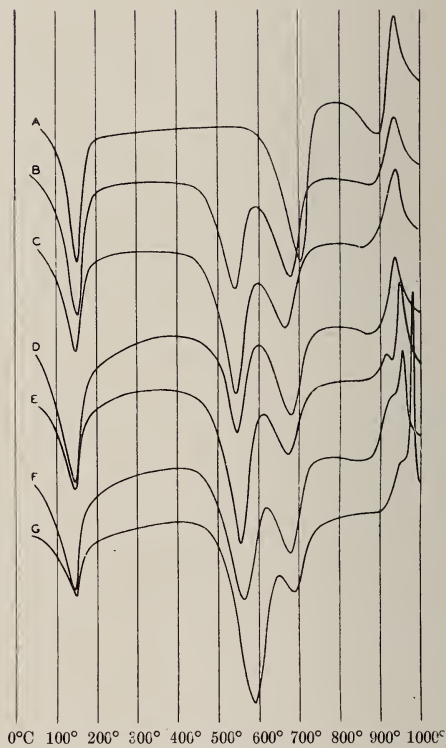
Fig. 1. Differential Thermal Curves
A. Kaolinite, K_1, Vera, Washington, 0.522 g.
B. Kaolinite, K_2, Anna, Illinois, 0.460 g.
C. Kaolinite, K_2, Anna, Illinois, 0.370 g.
D. Kaolinite, K_2, Anna, Illinois, 0.215 g.
E. Kaolinite, K_3, Dry Branch, Georgia, 0.427 g.
F. Kaolinite, K_3, Dry Branch, Georgia, 0.355 g.
G. Kaolinite, K_3, Dry Branch, Georgia, 0.230 g.

Fig. 2. Differential Thermal Curves
A. Sodium montmorillonite, M_1, Clay Spur, Wyoming, 0.628 g.
B. Sodium montmorillonite, 0.536 g. and kaolinite, K_1, 0.268 g.
C. Sodium montmorillonite, 0.425 g. and kaolinite, K_1, 0.425 g.
D. Sodium montmorillonite, 0.518 g. and kaolinite, K_2, 0.259 g.
E. Sodium montmorillonite, 0.424 g. and kaolinite, K_2, 0.424 g.
F. Sodium montmorillonite, 0.514 g. and kaolinite, K_3, 0.257 g.
G. Sodium montmorillonite, 0.408 g. and kaolinite, K_3, 0.408 g.

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 figure 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 figure 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 parts of the curves are of con-siderable 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 figure 3 is that of an illite, I_1, from an underclay of Pennsylvanian age from Grundy County, Illinois (2). 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 figure 2.
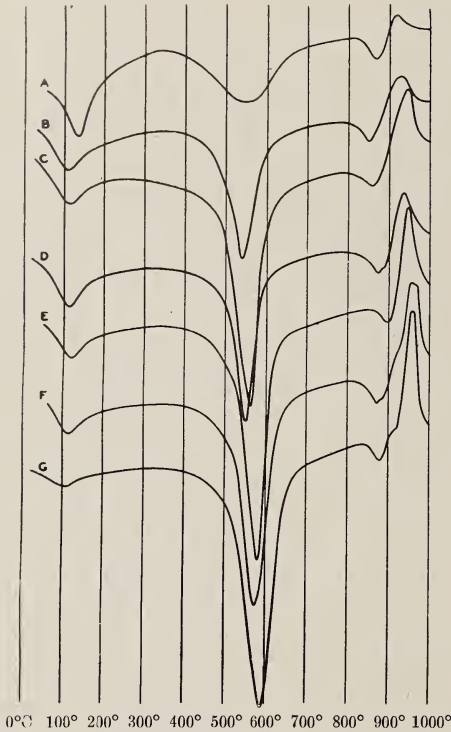
0°C 100° 200° 300° 400° 500° 600° 700° 800° 900° 1000°   0°C 100° 200° 300° 400° 500° 600° 700° 800° 900° 1000°

Fig. 3   Fig. 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.

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 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 sub-

stitution 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 figure 4 was obtained from a calcium montmorillonite, M_2, from a bentonite from Arizona. Curve B of figure 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 figure 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 figure 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.

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 figure 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 figure 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 figure 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 would probably be identified since the endothermic
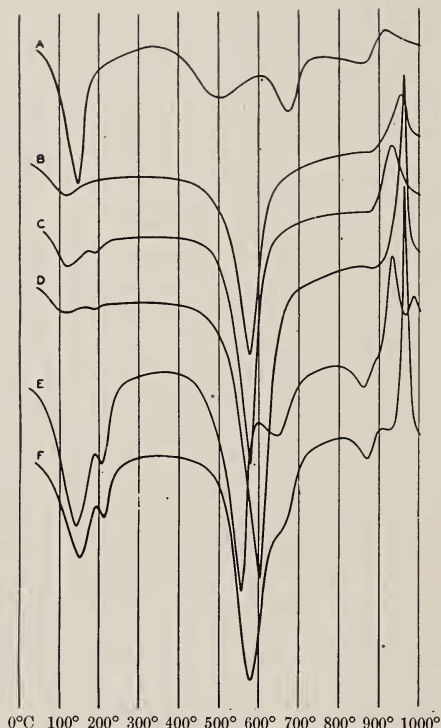
0°C 100° 200° 300° 400° 500° 600° 700° 800° 900° 1000°

FIG. 6

0°C 100° 200° 300° 400° 500° 600° 700° 800° 900° 1000°

FIG. 5

0°C 100° 200° 300° 400° 500°   700° 800° 900° 1000°

FIG. 7

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.

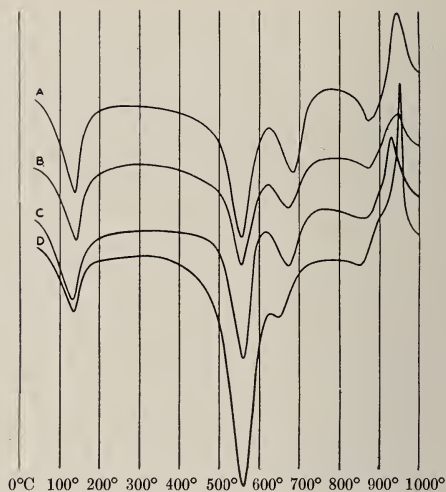F. Calcium montmorillonite, M_2, 0.363 g. and kaolinite K_3, 0.363 g.

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

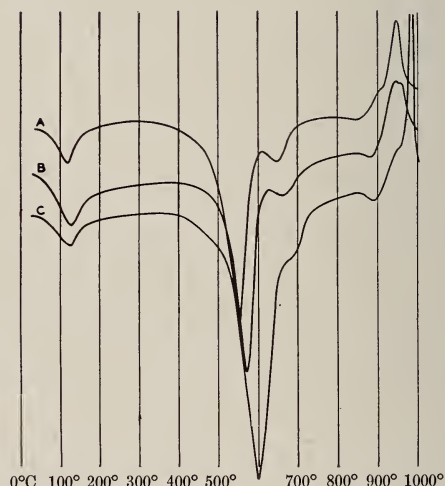D. Kaolinite, K_3, 0.273 g.; sodium montmorillonite, M_1, 0.273 g.; illite, I_1, 0.273 g. mixed wet

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.

peak 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_2 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 figure 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 figure 7 represent similar mixtures except that kaolin-

ite 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 W. F. Bradley for making the x-ray analyses and W. A. White for preparing the mixtures and running the thermal curves.

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REHYDRATION AND DEHYDRATION OF THE CLAY MINERALS

BY

RALPH E. GRIM AND W. F. BRADLEY

ABSTRACT

Certain clay minerals, particularly the illites and montmorillonites, regain some hydroxyl water as well as adsorbed water on standing at room temperature after being dehydrated by heating to temperatures as high as 800°C. The removal of the recombined hydroxyl water may take place at slightly lower temperature than the original hydroxyl water.

Experimental data are presented showing the rehydration and loss again of the rehydration water together with a discussion of the structural significance of rehydration.

INTRODUCTION

In the course of the study of the character and properties of the clay minerals as revealed by differential thermal analyses, it was found that certain of the clay minerals apparently rehydrate after being dehydrated by heating to temperatures as high as 800° C. The rehydration includes both the picking up of adsorbed water and the recovery of actual lattice water hydroxyl groups. In the latter case removal of the recombined hydroxyl water may take place at a slightly lower temperature than did the removal of the original hydroxyl water. Dehydration and rehydration are important in considering the properties and the structure of the clay minerals, and may be of practical significance in the utilization of clays. The purpose of the present paper is to present some preliminary work on these matters.

PROCEDURE

About 5 grams of minus 60-mesh material of various clay minerals were heated to temperatures up to 800°C. The samples were heated rapidly to the top temperatures and held there for at least one hour. After heating, the samples were allowed to cool to room temperature (25° to 30°C.) and kept in open dishes, but protected from dust, in the laboratory until they were studied.

The method of study was that of differential thermal analysis (1). This method is satisfactory because dehydration is accompanied by an endothermic reaction. Thermal curves, therefore, indicate any rehydra-tion, the temperature at which the rehydrated water can be removed, and something of the energy involved.

EXPERIMENTAL RESULTS

Montmorillonite.—Figure 1 presents thermal curves for a sodium montmorillonite from Wyoming bentonite, obtained on samples which had remained in the laboratory for various periods of time following heating to 500°C., 600°C., and 800°C. for one hour.

Curve B shows that a considerable amount of adsorbed water is picked up in 13 days by material heated to 500°C. This temperature is not high enough to affect the (OH) lattice water.

Heating to 600°C. for one hour (curves C-F) removes the (OH) lattice water as well as the adsorbed water. Following heating to this temperature, there is a very slow gradual pickup of adsorbed water so that a small amount is shown at the end of 268 days. Likewise there is a very slow gradual regaining of (OH) lattice water, and of great interest is the dual character of the endothermic reactions corresponding to the removal of this rehydrated water. Apparently the regained water is of two kinds or forms in the lattice. Some of this water is removed at about the same temperature as the original dehydration, and the other at about 150°C. lower temperature. Both kinds or forms of water are regained at about the same rate.

The samples heated to 800°C. (curves G–H) show no pickup of adsorbed water

0°C 100° 200° 300° 400° 500° 600° 700° 800° 900° 1000°   0°C 100° 200° 300° 400° 500° 600° 700° 800° 900° 1000°

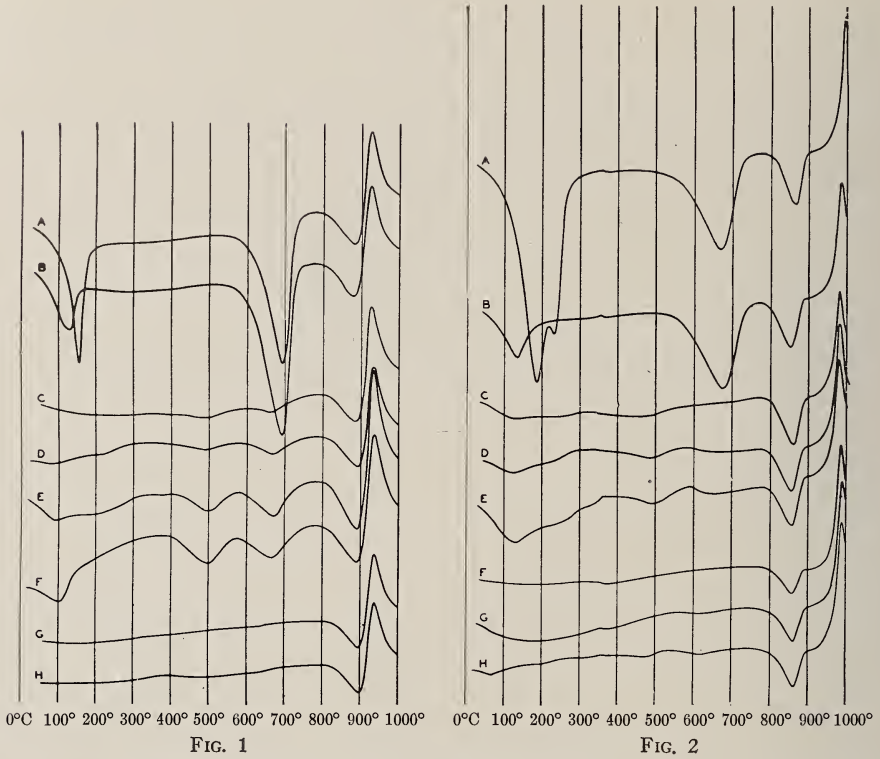Fig. 1   Fig. 2

Fig. 1.   Differential thermal curves of sodium montmorillonite, bentonite, Clay Spur, Wyoming.

A. Not heated.
B. Heated 500° C. for 1 hour, curve run after standing   13 days.
C.   "   600° C. " 1   "   ·   "   "   "   "   11   "
D.   "   600° C. " 1   "   "   "   "   "   68   "
E.   "   600° C. " 1   "   "   "   "   "   146   "
F.   "   600° C. " 1   "   "   "   "   "   268   "
G.   "   800° C. " 1   "   "   "   "   "   76   "
H.   "   800° C. " 1   "   "   "   "   "   268   "

Fig. 2.   Differential thermal curves of calcium montmorillonite, bentonite, Arizona.

A. Not heated.
B. Heated 500° C. for 1 hour, curve run after standing   13 days.
C.   "   600° C. " 1   "   "   "   "   "   14   "
D.   "   600° C. " 1   "   "   "   "   "   68   "
E.   "   600° C. " 1   "   "   "   "   "   145   "
F.   "   800° C. " 1   "   "   "   "   "   73   "
G.   "   800° C. " 1   "   "   " · "   "   145   "
H.   "   800° C. " 1   "   "   "   "   "   272   "

and only a faint trace of (OH) lattice water regained after 268 days.

The thermal reactions at about 875° to 950°C., corresponding to the destruction of the montmorillonite lattice and the development of new phases (2), are unchanged in samples heated to 600° C. In the 800°C. sample, the only effect is a very slight reduction in the intensity of the reactions.

Figure 2 shows thermal curves obtained on samples of a calcium montmorillonite from an Arizona bentonite, which had remained in the laboratory for various periods of time following heating to 500°, 600°, and 800°C. for one hour.

The curves show that this calcium montmorillonite has the same rehydration characteristics as the sodium montmorillonite shown in figure 1, except that the rehydra-

tion following heating to 600°C. (curves C–E) seems to be a little slower. The calcium montmorillonite that was heated to 800°C., after standing for 272 days (curve H), definitely shows some pickup of adsorbed water and of (OH) lattice water.

Illite.—Differential thermal curves for an illite (3) purified from an underclay of Pennsylvanian age found near Fithian, Illinois, are presented in figure 3. The curves show that after heating to 600°C. (curves B–D) some pickup of adsorbed water and (OH) lattice water is very rapid. Apparently a considerable portion of both kinds of water is taken up quickly and further amounts are taken up at a slow gradual rate. The curves show also that loss of the rehydrated (OH) water begins at a lower temperature (400°C.) than that of the original (OH) water (475°C.).

On standing after heating to 800°C. (curves E–H) there is a gradual regaining of adsorbed water and (OH) lattice water. The similarities of the curves for 147- and 275-day standing periods suggest that after a certain amount of rehydration takes place, any further pickup of water is slight and very slow.

The final part of the curve, showing reactions corresponding to destruction of lattice and the formation of a new phase, is unchanged by the dehydration and rehydration.

The curves for the illite purified from the Grundy County, Illinois, clay presented in figure 4 shows that this sample has the same general rehydration properties as those of the previously considered illite. The rehydration of the Grundy County illite appears to be slower and without any suggestion of a lowering of the temperature required to remove the water gained on rehydration.

The rehydration characteristics of an illite from the Minford silt of Ohio are shown in figure 5. The adsorbed water is picked up slowly and gradually on material heated to 600°C. so that after 217 days (curve L) there appears to be more adsorbed water than there was in the original sample. Adsorbed water is picked up also after heating to 800°C. (curve M).

The curves show a slight regaining of (OH) lattice water after heating to temperatures as high as 800°C. The amount of (OH) water regained is small—considerably smaller than the previously considered illites. There is no indication that the samples heated to 500°C. (curves B, C) regained more water on rehydration than the sample heated to 800°C (curve M.)

In some of the Minford silt samples, illite occurs associated with a chlorite. Although no chlorite was apparent by x-ray diffraction or optical examination of the sample used in this study, it is not unlikely that the variations of these curves from those of the other illites are nevertheless due to the admixture of undetected chlorite.

Halloysite and kaolinite.—The kaolinite represented by curve B in figure 6 is rather poorly crystallized, whereas that represented by curve C is very well crystallized (4). The curves for these two kaolinites show pronounced differences (*a*) in the intensity of the reactions, (*b*) in the presence of an initial endothermic reaction in the poorly crystallized kaolinite, and (*c*) in the presence of a slight endothermic reaction at about 930°C. in the well crystallized sample.

The thermal curve D in figure 6 shows that after heating to 600°C. there is a very slight pickup of adsorbed water by the halloysite sample, but in the light of the known highly porous condition of halloysite aggregates, it is probable that this represents merely adsorbed rather than crystalline water. There is also a suggestion of the regaining of a trace of (OH) lattice water.

Curve E for the poorly crystallized kaolinite suggests the pickup of a trace of adsorbed water, but there is no positive indication of the regaining of any (OH) water.

The well crystallized kaolinite (curves F and G) shows a distinct pickup of a very small amount of (OH) lattice water after heating to 600°C.

The final part of the curves are substantially unchanged by heating to 600°C. It is significant that the halloysite and well crystallized kaolinite which show an endo-

0°C 100° 200° 300° 400° 500° 600° 700° 800° 900° 1000°   0°C 100° 200° 300° 400° 500° 600° 700° 800° 900° 1000°
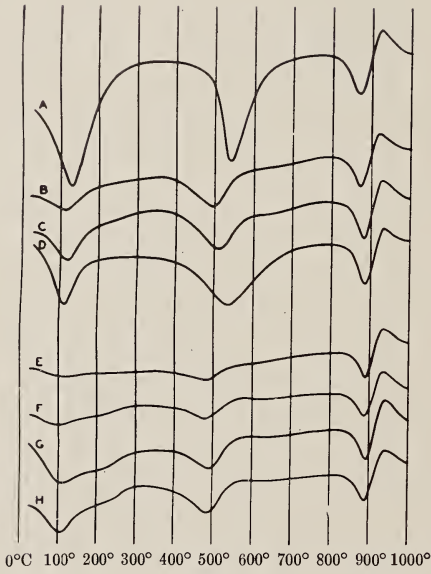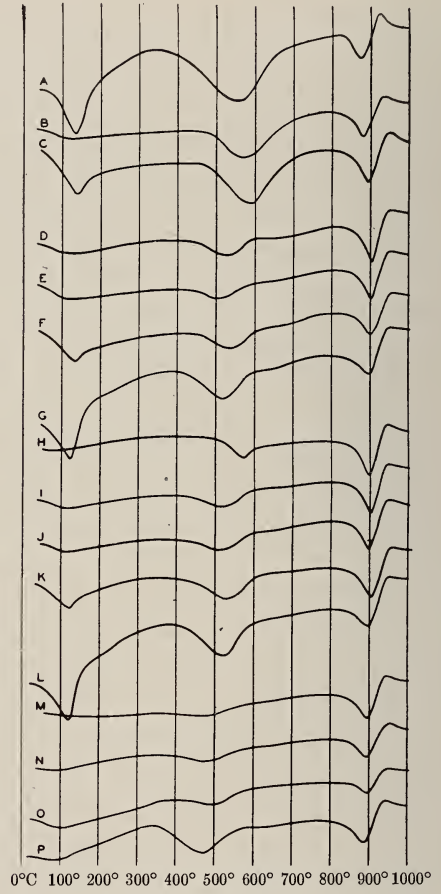
Fig. 3   Fig. 4

Fig. 3.   Differential thermal curves of illite, Fithian, Illinois.

A. Not heated.
B. Heated 600° C. for 3 hours, curve run after standing   2 hours.
C.   "   600° C. " 1 "   "   "   "   "   1 day.
D.   "   600° C. " 1 "   "   "   "   "   70 days.
E.   "   800° C. " 1 "   "   "   "   "   13 "
F.   "   800° C. " 1 "   "   "   "   "   70 ."
G.   "   800° C. " 1 "   "   "   "   "   147 "
H.   "   800° C. " 1 "   "   "   "   "   275 "

Fig. 4.   Differential thermal curves of illite, Grundy County, Illinois.

A. Not heated.
B. Heated 450° C. for 1 hour, curve run after standing   7 days.
C.   "   450° C. " 1 "   "   "   "   "   55 "
D.   "   550° C. " 1 "   "   "   "   "   4 "
E.   "   550° C. " 1 "   "   "   "   "   17 "
F.   "   550° C. " 1 "   "   "   "   "   55 "
G.   "   550° C. " 1 "   "   "   "   "   221 "
H.   "   600° C. " 1 "   "   "   "   "   1 "
I.   "   600° C. " 1 "   "   "   "   "   9 "
J.   "   600° C. " 1 "   "   "   "   "   17 "
K.   "   600° C. " 1 "   "   "   "   "   53 "
L.   "   600° C. " 1 "   "   "   "   "   223 "
M.   "   800° C. " 1 "   "   "   "   "   12 "
N.   "   800° C. " 1 "   "   "   "   "   70 "
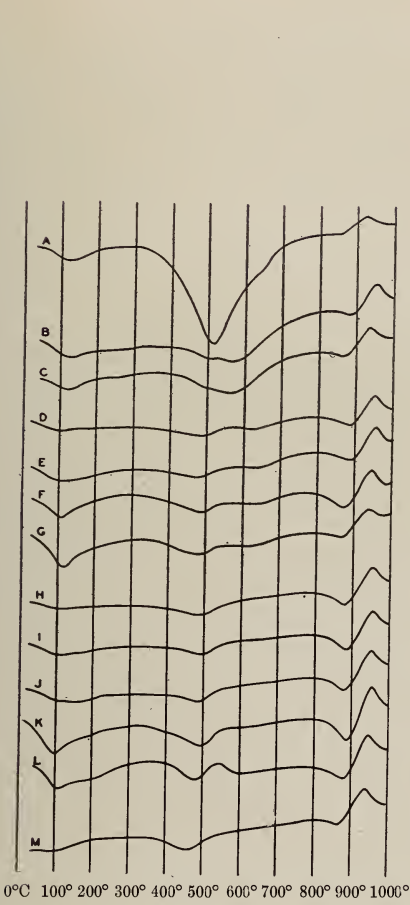O.   "   800° C. " 1 "   "   "   "   "   146 "
P.   "   800° C. " 1 "   "   "   "   "   278 "

0°C 100° 200° 300° 400° 500° 600° 700° 800° 900° 1000°

FIG. 5

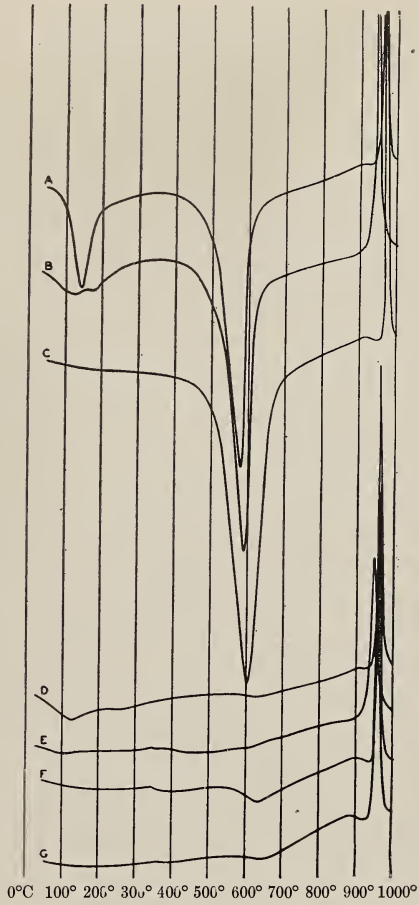0°C 100° 200° 30ʋ° 400° 500° 600° 700° 800° 900° 1000°

FIG. 6

FIG. 5.   Differential thermal curves of illite from Minford silt, Ohio.

    A. Not heated.
    B. Heated 500° C. for 1 hour, curve run after standing 14 days.
    C.   "   500° C. " 1 "   "   "   "   "   163 "
    D.   "   550° C. " 1 "   "   "   "   "   2 "
    E.   "   550° C. " 1 "   "   "   "   "   16 "
    F.   "   550° C. " 1 "   "   "   "   "   52 "
    G.   "   550° C. " 1 "   "   "   "   "   218 "
    H.   "   600° C. " 1 "   "   "   "   "   2 "
    I.   "   600° C. " 1 "   "   "   "   "   7 "
    J.   "   600° C. " 1 "   "   "   "   "   16 "
    K.   "   600° C. " 1 "   "   "   "   "   52 "
    L.   "   600° C. " 1 "   "   "   "   "   217 "
    M.   "   800° C. " 1 "   "   "   "   "   6 "

FIG. 6.   Differential thermal curves of kaolinites and halloysite.

    A. Halloysite (partially hydrated form), Eureka, Utah. Not heated.
    B. Kaolinite, Anna, Illinois, not heated.
    C. Kaolinite, Dry Branch, Georgia, not heated.
    D. Halloysite heated 600° C. for 1 hour, curve run after standing 70 days.
    E. Kaolinite, Anna, Illinois, heated 600° C. for 1 hour, curve run after standing
        70 days.
    F. Kaolinite, Dry Branch, Ga., heated 600° C. for 1 hour, curve run after standing
        70 days.
    G. Kaolinite, Dry Branch, Ga., heated 600° C. for 3 hours, curve run after standing
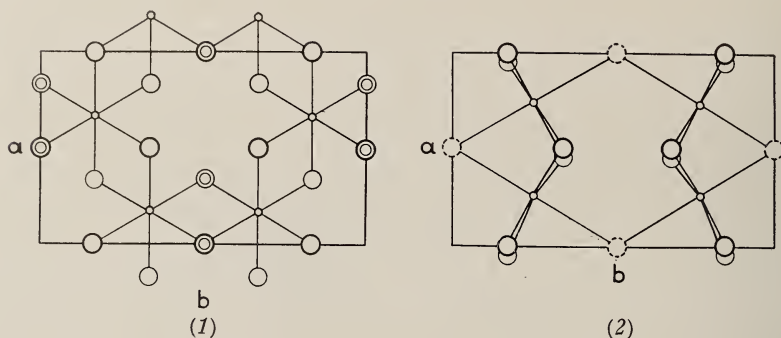   7 days.

FIG. 7.—Schematic representation of the configurations in the layers of octahedral coordination (*1*) before and (*2*) after condensation of the (OH) lattice water of the three-layer silicates. Large circles represent oxygen, double circles hydroxyl, and small circles aluminum or magnesium.

thermic reaction at about 920–930°C. show some regaining of (OH) lattice water, whereas the poorly crystallized kaolinite which shows no final endothermic reaction also shows no regaining of (OH) lattice water.

DISCUSSION OF RESULTS

Quite a surprising number of common minerals, not otherwise so obviously related, are based upon variations of a single characteristic assemblage of oxygen and hydroxyl ions coordinated about various combinations of particular cations. This structural unit, with the proportion of 20 oxygen ions to 4 hydroxyl ions, is encountered in the crystallizations of the micas, talc, pyrophyllite, the chlorites, the montmorillonite group minerals, the illites and probably several others.

For the better crystallized examples of this structural type the hydroxyl water is not very readily removed by firing, and any approach to equilibrium conditions at a given temperature is so slow that they do not lend themselves to thermal analysis. For the two fine-grained groups, however, the illites and the montmorillonites, the thermal expulsion of this water has become a well-known diagnostic feature in numerous thermal analysis studies, and it has been generally noted that the illites lose this water at about 100–150°C. lower temperature than do the montmorillonites.

It has been remarked before (5, 6) that this type of fundamental structural unit is able to survive the abstraction of its hydroxyl water with only moderate readjustment, but detailed analysis has not been attempted.

In connection with a related study of heat effects (6), occasion has arisen to examine several montmorillonites after ignition to temperatures just above those necessary to remove the hydroxyl water. X-ray diffraction diagrams obtained from such material are found to be consistent with effects to be anticipated from the relatively simple layer rearrangement illustrated in figure 7. The two packed layers of octahedrally coordinated ions are merely shifted from the packed position to one of direct apposition, with each pair of hydroxyl ions being replaced by a single residual oxygen ion set between two hydroxyl positions.

It is noted that the described arrangement affords a reasonably adequate disposition for four octahedrally coordinated cations per unit cell per layer as in a heptaphyllite type, but would demand a highly unreasonable sequence of shared coordination octahedron faces for an octaphyllite type mineral. Neither the 500°–700°C. endothermic peak nor the characteristically modified diffraction diagram is observed for the one certain example of octaphyllite clay (the "hectorite") which was available in the study referred to above.

The quantity of hydroxyl water taken into recombination by these montmorillonites amounts to only about one-fourth the original hydroxyl water and does not afford any clear cut x-ray diffraction inference, but

in the light of the anhydrous configuration illustrated, it seems reasonable to assume that only a small part is recombined into the original configuration, with an additional significant amount attaining only some other bonding of lower energy.

The nature of the micas is such that they do not afford even the limited data that are obtainable from the montmorillonites. The pairing of layers in the muscovite structure, which is presumably also present in illites, reduces the natural β angle so nearly to 90° that such a shift as the one described for montmorillonites results in too slight an effective shift for the double layer to be clearly observable in the diffraction diagrams. For this same reason, however, we can feel that the more intimate association of adjacent layers not only permits easier abstraction of the interior hydroxyl water, as evidenced by the lower temperature of the endothermic reaction, but also promotes the reversibility of the recombination and reabstraction of such water.

The structural unit upon which the crystallization of the kaolinite minerals is based is less stable and does not survive the loss of its (OH) water as a conventional crystal. Some degree of order does persist however, the state being commonly designated as "metakaolin." The thermal curves for the two-layer clay minerals indicate that a noticeable amount of (OH) lattice water rehydration takes place for the halloysite and the well crystallized kaolinite, but that none takes place in the poorly crystallized kaolinite. It is significant that the samples showing rehydration also show the small endothermic reaction at about 930°C. Although not well shown by the curves presented herein, differential thermal analyses

of a very large number of kaolinites have shown that when the endothermic peak at about 930°C. is present, there is also a definite upward slope to the curve between the endothermic peak at about 600°C. and the 930°C. peak, and that when the 930°C. endothermic reaction is not present the curve is horizontal between the 600°C. endothermic peak and the final exothermic reaction. The best interpretation of the foregoing observations seems to be that in the case of at least some halloysites and in well crystallized kaolinites, the structural remnant which makes up the "metakaolin" retains sufficient regularity to recombine at least minor amounts of (OH) water, and that some of this structure persists even up to about 930°C.

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