DIFFERENTIAL THERMAL ANALYSES OF CLAY MINERALS AND OTHER HYDROUS MATERIALS

By
RALPH E. GRIM AND RICHARDS A. ROWLAND

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November 24, 1942
DIFFERENTIAL THERMAL ANALYSIS OF CLAY MINERALS
AND OTHER HYDROUS MATERIALS.* PART 1.
RALPH E. GRIM AND RICHARDS A. ROWLAND†

Abstract

Differential thermal curves are presented for a large number of clay minerals and related silicates. The characteristics of the thermal curves of illites, kaolinites, and montmorillonites, and other clay minerals are discussed. The significance of the thermal data with regard to the lattice structures of the clay minerals, and to the changes they undergo when subjected to heat is considered. On the basis of these considerations certain clay mineral names are discredited.

Thermal curves are presented also for natural and artificial mixtures of clay minerals, and the use of differential thermal curves for identifying clay minerals and estimating their relative abundance in conjunction with x-ray, optical, and chemical methods is critically analyzed.

Introduction

The differential thermal method for studying minerals, based on the suggestions made by Le Chatelier (4) in 1887, has been developed and applied with considerable success to the study of clays by several investigators, notably Orcel (24), Cailliere (25), Norton (22), Wohlen (31), and Hendricks and his colleagues (13). Briefly, the method consists of heating a small amount of the substance at a constant rate up to 1000°C. or as close to fusion as is possible experimentally, and recording, by suitable devices, the endothermic and exothermic effects that take place in the material. The temperatures at which the thermal effects take place and their intensities are different for many minerals.

Differential thermal analyses have been published for many of the clay minerals, but unfortunately results of different authors have not always been in agreement. The present paper records additional analyses for many of these minerals and seeks to clarify some of the controversial points. Analyses are presented also for many additional materials that have not been studied heretofore by this method. Explanations are suggested for some of the thermal reactions based on changes that take place in the various minerals.

Apparatus and Analytical Procedure

The differential thermal analyses were made in a furnace consisting of a horizontal tube of alunum 12 inches long and 2 inches inside diameter, wound in the middle with 46 feet of coiled Kanthal A wire and surrounded

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with 4 inches of refractory insulating brick. A heating rate of approximately 10°C. per minute was obtained by placing a motor-driven variable transformer in the line.

The specimen holder was a nickel block one inch square and $\frac{5}{8}$ inch deep with four holes each $\frac{1}{4}$ inch in diameter and $\frac{3}{8}$ inch deep, mounted on an alundum cylinder that fit inside the furnace tube. The sample was placed in one of the holes of the specimen holder, and calcined aluminum oxide, which undergoes no thermal reaction up to 1000°C., was placed in the other three holes. A platinum-platinum 10 per cent rhodium thermocouple with the junction in one of the masses of aluminum oxide was attached to a reflecting galvanometer, and the furnace temperature was recorded photographically. A similar thermocouple was placed in another of the masses of aluminum oxide and attached to a potentiometer. The readings from the potentiometer were flashed onto the photographic record in order to evaluate the curve recording the furnace temperature.

A double junction difference thermocouple, consisting of two platinum leads joined by platinum 10 per cent rhodium wire, was placed with one junction in the sample and the other in the remaining mass of aluminum oxide. When the temperature of the sample was greater or less than that of the aluminum oxide, because of a thermal reaction, a potential difference was set up in the thermocouple. The difference thermocouple was attached to a second reflecting galvanometer and the temperature differences were recorded photographically on the same sheet used to record the furnace temperature.

By varying the series resistance in the difference thermocouple circuit, different vertical exaggerations can be obtained for the same temperature difference. Resistances up to 400 ohms were used, and on the diagrams (Figs. 2-14) scale $A$ represents 100 ohms and scale $B$ represents 200 ohms series resistance. Varying the resistance is important because the magnitude of the thermal reactions is very different for different minerals. Thus, a vertical scale designed for the thermal reactions of kaolinite may fail to show the thermal reactions of the micas because the intensity of the mica thermal reactions is about one-tenth that of kaolinite. In Fig. 1, the vertical scales used in most of the present work are given. By applying these scales to the figures that follow, the temperature difference represented by the peaks of each curve can be determined. The scales were constructed by measuring the swing of the galvanometer for known temperature differences.

All samples were ground to pass a 60-mesh sieve, and an attempt was made to pack each sample the same way in the specimen holder. The weight of the sample used was determined for each run. All of the ground samples, except those containing halloysites, were placed in an oven and
dried at 90°C. for 12 hours and then were placed in a desiccator over a saturated solution of hydrous calcium nitrite (Ca(NO₂)₂·4H₂O) which gives a relative humidity of 46 per cent at 30°C. (27). Each sample remained in the desiccator at least 24 hours before being placed in the furnace. This procedure was necessary so that the initial part of the analyses representing heat adsorption due to loss of adsorbed water would be comparable. X-ray* and optical studies were made of all the samples investigated and chemical analyses were made of many of them.

In order to obtain reproducible results great care was taken to pack all the samples the same way and to keep the positions of the thermocouple junctions constant (18). Since the initial portions of the differential thermal curves vary with slight changes in the rate of heating because

* All X-ray analyses were made by Dr. W. F. Bradley of the Illinois State Geological Survey. Dr. Bradley read the manuscript, and offered many helpful suggestions which are hereby gratefully acknowledged.
different room temperatures and humidities alter the starting rate of heating, this range is the least precise. Experience suggests that attempts to estimate quantitatively the mineral components of mixtures can hope for an accuracy of no more than 10 per cent. Experimental difficulties in attaining uniform packing, slight variations in heating rate, etc., prevent greater accuracy. Further, the weight of the sample used must be taken into consideration in qualitative as well as quantitative work.

**Experimental Results**

**Oxides and hydroxides**

Quartz shows an endothermic reaction (Fig. 2A) at about 565°C. corresponding to the transformation from the α to β form. The curve for quartz was obtained with great vertical magnification, using only 50 ohms resistance. The peak at 565°C. represents a temperature difference of only about 2°C. Some runs with quartz show a slight break in the curve at about 870°C., the transformation point of quartz to tridymite. Since all of the curves obtained for quartz do not show the break at 870°C., its significance is questionable.

Orcel (24) reported that goethite exhibited an endothermic reaction at about 450°C. and limonite at about 350°C. The curves presented here (Fig. 2B and C) show peaks at about 400°C. and 300°C., respectively. This apparent discrepancy is probably due to differences in the material studied. There are several forms (26, 30) of hydrated ferric iron oxide, and natural samples are apt to be unlike mixtures. The specific hydrates and their forms have not been precisely characterized and further work is necessary before their thermal reactions become well known. The limonite curve was obtained with 400 ohms resistance in the thermocouple circuit, and the goethite curve with only 100 ohms. Even with the increased resistance, the peak for limonite is larger than that for goethite, indicating that the thermal reactions of the various hydrates are of considerably different magnitude.

Gibbsite, according to Norton (22), Orcel (25), and Jourdain (15), shows an endothermic peak at about 350°C. and diaspore, according to Orcel (25) and Norton (22), exhibits an endothermic peak at about 550–575°C. The curves shown in Fig. 2 check these findings. The sample of gibbsite (2D) also contains some kaolinite which is responsible for the small endothermic reaction at 550°C. and the exothermic reaction at 950°C. Both curves were obtained with 100 ohms resistance. The endothermic reactions correspond to the dehydration of the minerals. According to Deflandre (6), diaspore upon dehydration develops a structure similar to corundum, and gibbsite, according to Bragg (2), dehydrates to böhmite and this in turn to γ-Al₂O₃, a spinel.
Fig. 2. Oxides and hydroxides.

A. Quartz, Ottawa, Illinois.
B. Goethite, El Paso County, Colorado.
C. Limonite, University of Illinois collections.
D. Gibbsite, Saline County, Arkansas.
E. Diaspore, Chester, Massachusetts.
F. Brucite, Brewster, New York.
G. Brucite, Lancaster, Pennsylvania.
The brucite curve (Fig. 2G) obtained with 100 ohms resistance, shows an endothermic reaction at 425–475°C, accompanying dehydration. According to Büssem and Köberich (3) brucite dehydrates to cubic periclase. Sample 2F, also listed as brucite, has optical properties like those of hydromagnesite (28), and therefore its differential thermal curve is probably not the characteristic one for brucite.

**Kaolinite and halloysite**

Many investigators have recorded the endothermic reaction of kaolinite at 550–600°C. as well as the abrupt intense exothermic reaction at 950–1000°C., and these findings are checked by the present work (Figs. 3A, B, C). The endothermic peak accompanies the dehydration of the mineral, and, according to Insley and Ewell (14), the exothermic reaction is associated with the formation of γ-Al₂O₃. Sample 3B contains gibbsite in addition to the kaolinite. The explanation for the peculiar initial endothermic peak of 3A is not known.

Hydrated halloysite* (halloysite of Mehmel (21), hydrated halloysite of Hendricks (11) shows the same thermal reactions (Fig. 3F, G) as kaolinite, with an additional sharp endothermic reaction at 100–150°C. accompanying the loss of 2H₂O and the transition to halloysite. After heating the mineral in an oven at 90°C. for several hours the initial endothermic peak is almost entirely lost and the curve (Fig. 3E) is like that of kaolinite. Attempts to develop the initial endothermic peak in kaolinite or halloysite by rewetting the material that had been dried were unsuccessful (3D and 3E). Norton (22) has suggested that halloysites show an additional endothermic peak at about 325°C. and that the endothermic peak between 500°C. and 600°C. takes place at slightly lower temperatures for halloysites than for kaolinite. These suggestions could not be checked, and the peak at 325°C. may represent some gibbsite in Norton’s material.

The differential thermal curves present no evidence that halloysite differs from kaolinite, or that hydrated halloysite differs from kaolinite, except by the presence of the initial endothermic peaks representing water lost at low energy levels. Loss of the swelling water from montmorillonite yields an endothermic reaction in the same low temperature region.

* In the present paper the halloysite minerals are designated according to the nomenclature suggested by Hendricks (11), i.e., the form with the composition Al₂O₃·2SiO₂·4H₂O is designated hydrated halloysite, and the form Al₂O₃·2SiO₂·2H₂O is designated halloysite. The expression “a halloysite” is used when the particular form cannot be identified.
Fig. 3. Kaolinites and halloysites. Scale B.

A. Kaolinite, Anna, Illinois.
B. Kaolinite, Spruce Pine, North Carolina.
C. Kaolinite, Dry Branch, Georgia.
D. Kaolinite, wetted and then dried at room temperature, Dry Branch, Georgia.
E. Halloysite, dried at 90°C., wetted, and then redried at room temperature, Djebel Debar, Algeria, from U. Hofmann, University of Rostock, Rostock, Germany.
F. Hydrated halloysite, Eureka, Utah.
G. Hydrated halloysite, Djebel Debar, Algeria.
Illites

Illites (Fig. 4) show endothermic peaks at 100–200°C., 500–650°C., and about 900°C., and an exothermic peak immediately following the third endothermic peak. The exothermic peak is not always very pronounced (Fig. 4A, B, C) and occurs in some materials slightly above the highest temperature (1000°C.) of most of the experiments. The endothermic peak at 500–650°C. accompanies the loss of most of the water from the lattice, and the third endothermic peak is interpreted as being associated with the final destruction of the illite structure. This is in accordance with the finding of Grim and Bradley (9) that the illite lattice is not destroyed when most of the water is lost from the lattice and that the breakdown of the structure comes at a higher temperature followed by the formation of spinel. The exothermic reaction following the third endothermic peak is probably associated with the formation of spinel.
The halloysites, kaolinite, and the illites all show an endothermic reaction between 500°C. and 650°C., but the reaction in kaolinite and the halloysites is sharper and has about ten times the intensity of the reaction in the illites. Because of this difference in reaction intensity the resistance in the galvanometer circuit must be varied for the different clay minerals. If the apparatus is set up to record a moderate galvanometer swing for the reactions in kaolinite, the reactions of illites may well go undetected. Perhaps this explains why several previous workers have failed to detect the characteristic thermal reactions of the illites.

The reason for the greater intensity of the endothermic reaction in the two-layer kaolinite-type lattice between 500°C. and 650°C. than in the three-layer mica-type lattice at the same temperature is not entirely clear. A partial explanation is that the reaction represents the loss of more water from the two-layer lattices than from the three-layer lattices, and that the reaction represents also destruction of the two-layer lattice, whereas the three-layer lattice is not destroyed until a higher temperature is reached and in a separate reaction. These facts, however, do not seem entirely adequate to account for the difference in intensity.

The illite curves are less regular and show more variation than the kaolinite curves. This is expected as illite represents a group of minerals and is not a specific mineral name. The final exothermic reaction is particularly variable, and frequently (see discussion of montmorillonite curves) takes place at a temperature above that usually attained in the furnace, i.e., 1000°C.

Sample 4B is representative of the type of clay mineral described by Maegdefrau and Hofmann (20) as "glimmerton" (mica-clay mineral). The thermal curve for sample 4B is like that of the illites with an additional endothermic peak at about 700°C. indicating that montmorillonite is also present.

The curve for the glauconite (4A) is quite like that of the illites. Additional glauconite samples must be studied before the significance of this similarity can be fully interpreted.

Montmorillonites

All of the montmorillonite samples represented by differential thermal curves in Fig. 5 yielded clear x-ray diffraction patterns showing the distinct lattice expansion characteristic of the mineral. The curves show an initial endothermic peak at 100–250°C., apparently representing the loss of water held between the basal planes of the lattice structure (i.e., swelling water). Hendricks et al. (13) have mentioned the dual character frequently shown by this montmorillonite peak and discussed its relation to the exchangeable base composition of the mineral. This initial peak
is larger and extends over a wider temperature range than the similar peak for illites, and it extends over a much wider temperature range than the initial peak for hydrated halloysite. The presence of this initial endo-

![Thermal analysis graph]

Fig. 5. Montmorillonites. Scale A

A. Otay, California.
B. Rideout, Utah.
C. Geisenheim, Germany, from K. Endell, Technische Hochschule, Berlin, Germany.
D. Upton, Wyoming.
E. Aberdeen, Mississippi.
F. Tatatila, Vera Cruz, Mexico, U. S. Nat. Mus. 101, 836.

thermic peak in these three clay minerals suggests that they all possess water other than pore water (which causes no thermal reaction above 100°C.) and lattice water (which is lost at a higher temperature). Studies
of the water relationships in montmorillonite suggest that this water is held on the basal planes of the unit cells and further that the water itself has distinctive properties. Such water would correspond to the “planar water” postulated by Kelley and his colleagues (16). It follows that other clay minerals, e.g., illites, can have some of this type of water without also having expanding lattice characteristics.

Montmorillonite yields a second endothermic peak between 600°C. and 700°C. corresponding to the loss of lattice water. The explanation for the slightly lower temperatures of the second and third endothermic peaks of the Otay sample (Fig. 5A) is not known.

<table>
<thead>
<tr>
<th>Table 1. Chemical Analyses of Montmorillonite</th>
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5B Rideout, Utah, Analysis made under the supervision of O. W. Rees, Ill. State Geol. Survey.
5D Upton, Wyoming, American Colloid Co. (1940).
5E Aberdeen, Mississippi, American Colloid Co. (1940).
5F Tatitila, Vera Cruz, Mexico, Analysis from W. F. Foshag, U. S. Nat. Museum.

There is no satisfactory explanation of why the second endothermic reaction corresponding to the loss of lattice water takes place about 100°C. higher in montmorillonite than in the illites. Both of them have three-layer lattices and about the same amount of lattice water, yet the one which is found in larger and more perfectly crystalline masses (8) and does not expand, i.e., the illites, loses most of its lattice water at the lower temperature.
Montmorillonite shows a third endothermic peak at about 900°C. corresponding to the final breakdown of the montmorillonite lattice. Grim and Bradley (9) have shown that this clay mineral, like illites, first loses most of its lattice water, and later at a higher temperature the structure is destroyed. This third endothermic peak appears to be characteristic of three-layer clay minerals since it is not shown by kaolinite and the halloysites.

The third endothermic reaction is followed by an exothermic effect probably accompanying the formation of spinel (9). A comparison of this peak with the chemical analyses given in Table 1 shows that this exothermic reaction takes place at a slightly lower temperature in samples 5D and 5E which have the highest iron content. Additional data support the conclusion that the exothermic reaction is closely related to the iron content. Samples with low iron content show the exothermic reaction above 1000°C. and hence it is not recorded unless the temperature is carried above 1000°C. (5F).

Previous workers (15, 22, 24, 25) have recorded that montmorillonite curves show three endothermic peaks, but except for the initial one, somewhat different temperatures for the reactions were recorded. The final exothermic reaction does not seem to have been detected before.

Miscellaneous clays containing montmorillonite

Differential thermal curves are shown in Fig. 6 for a miscellaneous group of samples known to contain montmorillonite. Curves 6A and 6F are like those of montmorillonite except that 6F contains additional material, probably brucite, which is responsible for the 500°C. endothermic peak. These samples (6A and 6F) yield excellent diffraction patterns of montmorillonite, and their accurately measurable optical properties are also those of montmorillonite. Sample 6A was heated to 1100°C. to confirm the presence of the final exothermic peak above 1000°C. in samples with low iron content.

Samples 6C, 6D, and 6E of Fig. 6 yield curves with endothermic peaks between 500°C. and 600°C. and also between 600°C. and 700°C. The latter peak indicates that these samples contain montmorillonite and the former peak shows the presence of some other clay mineral. Illites, kaolinite and the halloysites all give endothermic reactions between 500°C. and 600°C. The characteristics of the third endothermic peak and the final exothermic peak are more like those of the illites than those of kaolinites or the halloysites. The suggested interpretation of the curves is that these samples are mixtures of montmorillonite and illite, using illite, as originally defined (10), as a general term for clay minerals closely related to the micas.
Fig. 6. Miscellaneous clays containing montmorillonite, Scale A.

A. Acid activated bentonite, Jackson, Mississippi.
B. Metabentonite, High Bridge, Kentucky.
C. Bentonite, Saline County, Arkansas.
D. Bentonite, Pontotoc County, Mississippi.
E. Bentonite, Phillips County, Kansas.
F. "Montmorillonite," San Bernadino County, California.

X-ray diffraction analyses of samples 6C, 6D, and 6E yielded very poor patterns that are in accord with the interpretation that these samples are composed of more than one clay mineral. The presence of montmorillonite is shown definitely by the patterns, but other constituents cannot be identified. The optical values of the samples cannot be determined accurately—only a mean index of refraction and a suggestion
that the birefringence is moderately high. The character of the birefrin-
gence is in accord with the interpretation that illite rather than kaolinite
or a halloysite is mixed with the montmorillonite.

Table 2. Chemical Analyses of Miscellaneous Clays
Containing Montmorillonite

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<td>4.68</td>
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<td>4.84</td>
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</table>

Analyses made under the supervision of O. W. Rees, Ill. State Geol. Survey.
6A Acid-activated bentonite, Jackson, Mississippi.
6C Bentonite, Saline County, Arkansas.
6D Bentonite, Pontotoc County, Mississippi.
6E Bentonite, Phillips County, Kansas.

Chemical analyses (Table 2) of samples 6C, 6D, and 6E show that the
K₂O content of 6C and 6D is lower than would be anticipated if illite is
the additional clay mineral. However, the potash content of illites is
variable, and the chemical data are not believed to be strong evidence
against the presence of illite. Except for the low K₂O content, the chemical
data are in accord with the illite interpretation. In addition to clay
minerals, these samples contain some hydrated ferric iron oxide which
may account for the rise in the thermal curves between 400°C. and
500°C.

The differential thermal curve for the metabentonite sample (Fig.
6B) is like that of montmorillonite except that the second endothermic
peak is less abrupt. However, the x-ray pattern of the material is similar
to that of micas, and is particularly like the pattern for glauconite. The
reason for the apparent conflict between the thermal and x-ray data is
not clear, and the optical properties cannot be measured with sufficient
accuracy to offer additional evidence. This is the only sample of clay
studied so far in which an endothermic peak between 600°C. and 700°C.
did not indicate an expanding lattice mineral. It is further evidence, if any is needed, of the danger of identifying the constituents of a clay material on the basis of a single set of characteristics, whether they be thermal, optical, x-ray, or any other one.

![Graph](image)

Fig. 7. Miscellaneous clays containing montmorillonite, Scale A.

A. Fuller's earth, Twiggs County, Georgia.
B. Bentonite, Harris County, Texas.
C. Bentonite, Ouachita Parish, Louisiana.
D. "Montmorillonite," Glen Riddle, Pennsylvania, U. S. Nat. Mus. 103058

Differential thermal curves for an additional set of samples thought to contain montmorillonite are presented in Fig. 7. All the curves show a large endothermic peak at 500–600°C. and a smaller one between 600°C. and 700°C. The small peak indicates the presence of some montmorillonite, but the larger peak between 500°C. and 600°C. suggests that the principal constituent is either kaolinite, a halloysite, or illite. The character of the third endothermic peak and the final exothermic peak of samples 7A, 7B, 7D, and 7E suggests illite whereas this part of the curve for sample 7C suggests kaolinite or a halloysite.
X-ray patterns of all samples represented in Fig. 7 were poor and all that can be determined from them is that the samples contain a small amount of montmorillonite. Only a mean index of refraction can be determined for these samples. All of them except sample 7C appear to have a moderately high birefringence which is in accord with the suggestion that kaolinite or a halloysite is present in 7C whereas an illite is present in the other samples. Chemical analyses for most of these samples are given in Table 3, and as noted in discussing the previous group of samples the low K₂O content of the materials is not necessarily evidence against the illite interpretation.

<table>
<thead>
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<th>Table 3. Chemical Analyses of Miscellaneous Clays Containing Montmorillonite</th>
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<td>H₂O−</td>
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<td>SiO₂/R₂O₅</td>
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<td>SiO₂/Al₂O₃</td>
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</tbody>
</table>

Analyses 7A–C made under the supervision of O. W. Rees, Ill. State Geol. Survey.  
7A Fuller’s earth, Twiggs County, Georgia.  
7B Bentonite, Harris County, Texas.  
7C Bentonite, Ouachita Parish, Louisiana.  

The data here presented suggest that many bentonites and other materials previously thought to be composed entirely of montmorillonite, contain large and frequently dominant amounts of other clay minerals. Orcel (24) has noted the presence of kaolinite in some bentonites, but the fact that clay minerals other than montmorillonite are the dominant constituents in some of them has not been recorded. The evidence suggests that this other constituent is usually an illite, but that in some samples it may be kaolinite or a halloysite.
DIFFERENTIAL THERMAL ANALYSIS OF CLAY MINERALS AND OTHER HYDROUS MATERIALS. PART 2.

RALPH E. GRIM AND RICHARDS A. ROWLAND†

Materials that have been called beidellite

The samples represented by differential thermal curves in Fig. 8 have been classified as beidellite chiefly on the basis of their optical properties. Sample 8A has a curve like that of kaolinite, or a halloysite, because of the endothermic peak between 500°C. and 600°C., the sharp exothermic peak, and the absence of a third endothermic peak. The initial endothermic peak suggests hydrated halloysite rather than kaolinite, and the hump at 400°C. reflects the presence of a ferric iron hydrate. The trace of a peak between 600°C. and 700°C. indicates the presence of a small amount of montmorillonite. X-ray diffraction analysis checks these identifications, showing the dominant constituent to be a two-layer type clay mineral. The low silica-alumina molecular ratio shown by the chemical analysis (Table 4) is also in accord with this interpretation, but the K₂O content suggests that the sample also contains illite.

Under the microscope this sample (8A) appears to be homogeneous except for pigmented hydrated ferric iron oxide, and the optical properties can be closely approximated (γ = 1.580, γ − α = .025). It is clear that a study of the optical properties alone might lead easily to a misinterpretation of the composition of the sample. A correlation of optical, chemical, X-ray, and thermal data for this and other samples shows clearly that mixtures of clay minerals and hydroxides can be so closely intergrown that the obtainable optical data for the mixtures suggest homogeneity and a composition other than the actual one. This does not reduce the value of optical data in clay mineral work but it does mean that such data must be used with caution, particularly when the determinations are incomplete and approximate.

The differential thermal curves of samples 8B and 8C are closely alike, and they indicate the presence of a small amount of montmorillonite and a dominant amount of illite, kaolinite, or a halloysite. Because of the smallness of the third endothermic peak and the large size of the initial peak, hydrated halloysite is suggested as a prominent constituent. The X-ray diffraction patterns of these samples are very poor and indicate only that they contain a small amount of an expanding-lattice type clay mineral. The K₂O content shown by the chemical analyses (Table 4)

† Petrographer and Assistant Petrographer, respectively, Illinois State Geological Survey, Urbana, Illinois.
suggests that illite is an important constituent. It seems clear that these samples are mixtures of a halloysite and illite with a very small amount of montmorillonite. Only a mean index of refraction could be determined for the samples, and optical study alone would not disclose the true composition of the materials.

![Figure 8](image)

**Fig. 8.** Materials that have been called beidellite. Scale A.

B. Fairview, Utah.
C. Twin Falls, Idaho.
F. Nashville, Arkansas.

Sample 8D, crude material from the type beidellite locality, gave a curve similar to 8B and 8C and it is concluded that the material is primarily a mixture of a halloysite, illite and montmorillonite. The x-ray diffraction pattern of this material was very poor and indicated only the
presence of some montmorillonite. A differential thermal curve was also obtained for a sample in which an attempt was made to hand-pick homogeneous material. The curve for the hand-picked material was the same as the curve for the crude sample except that the size of the peak between 600° C. and 700° C. increased. An x-ray analysis of the hand-picked material showed more pronounced montmorillonite diffractions than did the crude sample. It seems clear that the material from Beidell, Colorado, even if purified by hand-picking, is a mixture and not a single species. Again, on the basis of optical properties alone, one might conclude that the hand-picked material was homogeneous.

The curve for sample 8E is similar to the curve for sample 8D except that the endothermic peak at 600–700° C. is more pronounced, indicating a greater proportion of montmorillonite. The curve for 8F is also similar except that the montmorillonite peak is still larger, indicating an even larger amount of this mineral. The diffraction pattern for sample 8E showed the montmorillonite lines more distinctly than in previous samples of this series, and the montmorillonite lines in the pattern for sample 8F were even more pronounced. The x-ray evidence is therefore in accord

### Table 4. Chemical Analyses of Materials That Have Been Called Beidellite

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<tr>
<th></th>
<th>8A</th>
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</table>

Analyses 8B, 8C and 8E were made under the supervision of O. W. Rees, Ill. State Geol. Survey.

8B Fairview, Utah.
8C Twin Falls, Idaho.
8E Wagon Wheel Gap, Colorado.
with the conclusions that samples 8E and 8F contain a relatively larger amount of montmorillonite than the other members of this series. Sample 8F appears under the microscope to be a mixture, whereas sample 8E has the appearance of a single species. The optical properties of 8E can be accurately determined \((\gamma = 1.560, \gamma - \alpha = 0.030 (\pm))\) and on these data alone one might easily conclude that the material was a single species and not a mixture.

The curves of all of the so-called beidellite samples show an endothermic hump or a suggestion of one at about 400°C to 500°C. This is in the temperature range of the endothermic reaction of hydrated ferric iron oxides, and this is believed to be the proper interpretation since optical study reveals the presence of some such material in these samples. However, the study of so-called "nontronite" and "chloropal" (samples 12A and 13D) suggests that some expanding-lattice type clay minerals, probably those containing ferric iron instead of aluminum, may show an endothermic reaction between 400°C and 500°C. It is possible, therefore, that the hump on the curves between 400°C and 500°C may reflect the presence of a trace of this type expanding-lattice clay mineral as well as ferric iron hydrate.

The data herein presented do not necessarily mean that beidellite is not a valid species. They do show that much of the material classed as beidellite, including that from the type locality, is actually a mixture of clay minerals and hydrated ferric iron oxide. Norton (22) presented curves for beidellite showing endothermic peaks between 500°C and 600°C and at 690°C, but failed to suggest that the curves indicated mixtures. Orcel and Caillere (25) and Jourdain (15) also presented curves for beidellite showing endothermic peaks between 550°C and 600°C, which they interpreted as due to kaolinite. It seems likely, on the basis of the present data, that the peak between 550°C and 600°C in many samples is due to illite whereas in others it reflects the presence of kaolinite or a halloysite.

**Prepared mixtures of montmorillonite and illite**

Orcel (24) and Norton (22) have published curves of prepared mixtures of kaolinite and montmorillonite, but synthetic mixtures of other clay minerals have not been studied previously.

Differential thermal curves for illites and montmorillonite show endothermic peaks at 100–250°C and about 900°C, and an exothermic peak following the 900°C endothermic peak. The substitution of one of these clay minerals for another in a mixture is not reflected in any of the thermal reactions at these temperatures. Thermal curves for montmorillonite show an endothermic peak at about 700°C and none between 500°C.
and 600°C., whereas illite curves show an endothermic peak between 500°C. and 600°C., and none at about 700°C. As shown in Fig. 9 the substitution of montmorillonite for illite in a mixture is clearly reflected quantitatively by the second endothermic peak.

![Graph showing thermal analysis of clay minerals](image)

**Fig. 9.** Prepared mixtures of montmorillonite (5D) and illite (4D). Scale A.

A. 90% montmorillonite, 10% illite.
B. 75% montmorillonite, 25% illite.
C. 50% montmorillonite, 50% illite.
D. 25% montmorillonite, 75% illite.
E. 10% montmorillonite, 90% illite.
F. 5% montmorillonite, 95% illite.

*Prepared mixtures of illite and kaolinite.*

Illites show endothermic reactions at 100–250°C. and at about 900°C. whereas kaolinite does not show a thermal reaction at either tempera-
ture. The substitution of illite for kaolinite in mixtures is indicated quantitatively by peaks representing these reactions in the curves as shown in Fig. 10. The final exothermic reactions are distinctive for each of these clay minerals so that the substitution of illite for kaolinite is indicated also by the portion of the curve showing these reactions. Both kaolinite and illites show endothermic reactions between 500°C and 600°C. However, the mixing of kaolinite and illite is reflected to some extent in the peak representing this reaction because of the much greater magnitude of the reaction for kaolinite than for illites.

Fig. 10. Prepared mixtures of illite (4D) and kaolinite (3C). Scale B.
A. 95% illite, 5% kaolinite.
B. 90% illite, 10% kaolinite.
C. 75% illite, 25% kaolinite.
D. 50% illite, 50% kaolinite.
E. 25% illite, 75% kaolinite.
F. 10% illite, 90% kaolinite.
Miscellaneous minerals

In order to obtain the necessary background for the interpretation of the differential thermal analyses of clays, differential thermal analyses were made of a large number of specimens of hydrous material. Many of these samples were obtained from the United States National Museum, and the authors are indebted to Drs. W. F. Foshag and E. P. Henderson for their kindness in supplying them. Differential thermal curves of these samples are presented in Figs. 11 to 14. In many samples the curves suggest that the species is not valid, but other characteristics of most of the samples require study before this point can be settled definitely.

The curve for muscovite presented in Fig. 11A shows a broad endo-
thermic reaction between 750°C. and 950°C., and small peaks from 300°C. to 400°C. which may or may not be significant. This curve does not agree with those published for muscovite by Orcel (24) and Norton (22). It is quite possible that all the muscovite curves so far published are not significant, because the coarse flakes permit only a small amount to be packed loosely in the specimen holder. Consequently inherent limitations of the differential thermal method are magnified and reproducible results are difficult to obtain.

The curve for talc (sample 11B) is in agreement with the curves for this mineral published by Orcel (24) and Norton (22).

The curve for the pyrophyllite sample from North Carolina (sample 11C) is believed to be significant for the mineral. The other sample of pyrophyllite (11D) is not pure, and its curve is less significant. The curve for sample 11C checks Orcel's (24) findings for pyrophyllite, but not Norton's (22).

Orcel (23) has published a large variety of curves for the chlorites but none of them is like that shown for chlorite sample 11E. A study of many chlorites, combining x-ray, thermal, and chemical analytical data, is needed before this group of minerals will be well understood.

Sample 12A, "nontronite" from San Luis, Potosi, Mexico, is shown by microscopic study to be composed of about thirty per cent quartz, ten per cent ferric iron hydrate, and the remainder a clay mineral that has the optical properties of nontronite. An x-ray diffraction analysis of the sample showed lines characteristic of clay minerals with an expanding lattice, in addition to lines for quartz and ferric iron hydrate. The differential thermal curve is not exactly like the curves of known materials, and is particularly characterized by an endothermic peak between 400°C. and 500°C. Since the relative amount of ferric iron hydrate in the sample is too small to cause this thermal effect, and quartz does not exhibit a thermal reaction at this temperature, it seems likely that it results from the clay mineral with the expanding lattice. These data suggest that iron-rich clay minerals of the expanding lattice type exhibit a second endothermic reaction about 200°C. lower than the aluminous variety. Some ferric iron hydrates show an endothermic reaction between 400°C. and 500°C., and it may be difficult to determine if a peak in this temperature interval has resulted from a clay mineral or a ferric iron hydrate.

The differential thermal curve of the "woody nontronite" (Fig. 12B) indicates a mixture of illite, montmorillonite, and a ferric iron hydrate or an iron-rich expanding-lattice type clay mineral. The optical characteristics of the sample ($\gamma = 1.535$, $\gamma - \alpha = .030$) can be measured accurately, and again on the basis of optical data alone the sample might easily be designated as a single homogeneous mineral.
The sample of white magnesium clay from near Hector, California, described by Foshag and Woodford (7), gives a unique curve (Fig. 12C). The curve is unlike the montmorillonite curves, suggesting that the material should not be classed in this group of clay minerals. Under the microscope, the sample seems to be a single species.
Bravaisite from the type locality yields a differential thermal curve (Fig. 12D) like that of the illites with an additional endothermic peak close to 700°C, suggesting the presence of a small amount of montmorillonite. The chemical composition of bravaisite (Table 5) and its optical properties \((\gamma = 1.552, \gamma - \alpha = .025 (-))\) are also similar to the illites.

**Table 5. Chemical Analyses of Illites and Bravaisite.**

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Analyses made under the supervision of O. W. Rees, Ill. State Geol. Survey.
4C Illite, purified from shale, Alexander County, Illinois.
4D Illite, purified from underclay, Vermilion County, Illinois.
12D Bravaisite, Noyant Allier, France.

The differential thermal curve for the smectite sample (Fig. 12E) is like that of montmorillonite. The presence of a small amount of illite is suggested by the endothermic hump between 500°C. and 600°C., and the exothermic reaction between 250°C. and 450°C. indicates the presence of organic material. This is in agreement with Kerr’s (17) conclusion that smectite is not a valid species because of its similarity to montmorillonite.

The curves for two samples labeled leverrierite (Figs. 12F and 12G) are like those of montmorillonite. The second endothermic peak of sample 12F occurs at a temperature slightly above that usually found for montmorillonite, but probably not too high for that identification. Sample 12F has the optical properties of montmorillonite, whereas sample 12G appears to be only faintly anisotropic with a mean index of refraction of about 1.470. On the basis of optical data the latter sample would be classed as allophane, illustrating again the caution necessary in identify-
ing clay minerals from a single criterion. The very low apparent birefrin-
gence of sample 12G is probably due to a random orientation of the clay
mineral particles mixed with some isotropic material. X-ray diffraction

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**FIG. 13.** Miscellaneous materials. Scale A.
C. Attapulgite, Quincy, Florida.
E. Volkonskoite, near Sverdlosk, U. S. S. R.
analyses of both samples gave good patterns characteristic of the expanding-lattice type clay minerals. Samples of leverrierite studied by Ross and Kerr (29) proved to be kaolinite, and de Lapparent (19) has described leverrierite as an intergrowth of kaolinite and mica. Clearly the term does not designate a valid mineral species.

The differential thermal curve for the sample of rectorite (Fig. 13A) is unique. Under the microscope the sample has the appearance of a halloysite with some additional hydrated ferric iron oxide which may be responsible for the slight endothermic hump in the curve at about 450°C.

The differential curve for the celadonite sample (Fig. 13B) is unique except that the three endothermic peaks are somewhat similar to the endothermic peaks of the illites. The optical properties of the sample are like those of glauconite. The sharp exothermic reaction at about 450°C. probably results from organic material.

Attapulgite gives a curve (Fig. 13C) unlike that of the other minerals studied and this supports the conclusion (1) that the material is a distinct species.

The differential thermal curve for the sample of "chloropal" (Fig. 13D) is much the same as the curve for the "nontronite" from San Luis, Potosi, Mexico. An x-ray analysis of the "chloropal" sample indicated that the prominent constituent has an expanding lattice. Therefore, this sample provides further evidence that certain clay minerals with an expanding lattice may show an endothermic peak between 400°C. and 500°C. The samples of expanding lattice material with the endothermic peak between 400°C. and 500°C. show two exothermic peaks between 800°C. and 1000°C., and they do not show a third endothermic peak. In all of these characteristics the curves are unlike those of the expanding-lattice material with an endothermic peak at 600° to 700°C.

The curve for the sample of volkonskoite (13E) is distinctive because it shows no endothermic reaction above 250°C., i.e., no thermal reaction corresponding to a loss of lattice water. Under the microscope the volkonskoite appears to be an amorphous substance with a pigmentary material distributed through it. The material is listed by Dana (5) as a chrome-bearing clay.

The sample labeled "allophane" from Bedford, Indiana, (13F) gave a curve suggesting a mixture of kaolinite or a halloysite because of the 525°C. endothermic and 950°C. exothermic peaks, gibbsite because of the 350°C. endothermic peak, and amorphous material. The 925°C. exothermic peak is difficult to explain but it is probably due to the amorphous material. This and other samples suggest that amorphous hydrous aluminum silicate materials show only a single endothermic reaction
Fig. 14. Miscellaneous materials. Scale A.
which occurs below about 250°C. Optical study of the sample indicates a mixture containing a considerable amount of kaolinite or a halloysite.

The sample of "allophane" from Iyo, Japan, gives a differential thermal curve (Fig. 13G) like that of a halloysite except that the exothermic reaction takes place at a lower temperature. The sample has the optical characteristics of a halloysite.

The sample of racewinite (14A) from the type locality appears under the microscope to be a mixture of amorphous material and carbonate, and this is the composition suggested by the curve. The endothermic peak between 750°C. and 875°C. is in the range in which carbonates show endothermic reactions,* and the endothermic reaction below 250°C. is in the range of the thermal reaction of amorphous material.

The sample of dillnite yielded a differential thermal curve (Fig. 14B) exactly like kaolinite, and the optical characteristics of the sample are identical with those of kaolinite.

The curve for the sample of severite (Fig. 14C) is also similar to the curve for kaolinite, except that the initial low temperature endothermic peak suggests the presence also of a halloysite. The optical characteristics of this sample are like those of a halloysite or kaolinite.

The miloschite sample gave a differential thermal curve (Fig. 14D) indicating the presence of kaolinite and/or a halloysite. The initial endothermic peak is broader than that for hydrated halloysite and probably indicates the presence of some amorphous material. Optical study of the sample shows material with the optical properties of a halloysite pigmented with amorphous material. Miloschite is listed by Dana (5) as a chromiferous clay.

The curve for the sample of clylyrite (Fig. 14E) is also like that for kaolinite and/or a halloysite. The optical characteristics of the sample are like those of a halloysite.

The differential thermal curve for the sample of cimolite (Fig. 14F) is unlike the other curves. An x-ray diffraction analysis shows the presence of alunite, but further study is required to determine if the curve is characteristic of alunite.

The curve for the sample of newtonite (Fig. 14G) suggests the presence of kaolinite and/or a halloysite because of the endothermic peak between 500°C. and 600°C. and the sharp exothermic peak at about 950°C. The endothermic peaks between 700°C. and 900°C. indicate the presence of additional material which cannot be identified. Under the microscope the sample has the optical characteristics of kaolinite. Ross and Kerr (29) have shown that samples of newtonite studied by them were actually kaolinite.

Summary and Discussion

Kaolinite and halloysite type clay minerals are characterized by a sharp endothermic reaction between 500°C. and 600°C., and by a very abrupt exothermic reaction at about 950°C. Hydrated halloysite shows an additional sharp endothermic reaction between about 100°C. and 200°C.

Illites give endothermic peaks between 100°C. and 250°C., 500°C. and 650°C., and at about 900°C. and an exothermic peak immediately following the third endothermic peak. Montmorillonite gives a curve similar to that for illites except that the initial endothermic curve is larger and the second endothermic reaction takes place at about 100°C. higher temperature (600° to 700°C.). For both of them the exothermic reaction shifts to a slightly lower temperature as the iron content increases.

The third endothermic reaction at about 900°C. has not been found in two-layer-lattice clay minerals, and seems to be characteristic of the three-layer types, i.e., illites and montmorillonite. Illites and montmorillonite are largely dehydrated in the temperature range of the second endothermic peak, but their lattice structure is not destroyed until a higher temperature is reached, and this is followed at once by the formation of spinel. It is believed that the third endothermic peak corresponds to the final destruction of the lattice and the exothermic reaction to the formation of spinel.

In the case of the three-layer clay minerals an endothermic peak between 500°C. and 600°C. seems to be characteristic of the non-swelling type (illites) and one between 600°C. to 700°C. appears to be characteristic of the swelling type (montmorillonite). No swelling material has been found to have an endothermic peak between 500°C. and 600°C. and only one example of a non-swelling material (metabentonite, sample 6B) has been found to have an endothermic reaction between 600°C. and 700°C. However, the sample of "nontronite" from Mexico (12A) and the sample of "chloropal" (13D) which gives a thermal curve similar to that of "nontronite," suggest that iron-rich expanding-lattice-type clay minerals may show their second endothermic peak at a lower temperature (400°C. to 500°C.) than that of the illites, and in the same temperature interval in which the endothermic reaction in some ferric iron hydrates takes place.

Kaolinite and halloysites require considerably more energy for dehydration than illites or montmorillonite. The temperature difference indicated for this reaction in kaolinite and halloysites is about ten times that of the other clay minerals. Because of this large difference, apparatus designed for kaolinite may not detect the thermal reactions of the other clay minerals unless special provisions are made to vary the vertical ex-
ageration of the record of the thermal reactions by varying the resistance in the galvanometer circuit of the difference thermocouple.

Pore water in the samples does not show in the thermal curves above 100°C. Montmorillonite, illites, and hydrated halloysite all show initial endothermic reactions below about 200°C. It is suggested from information regarding the structure of montmorillonite that this water is held on the basal planes of the unit cells and that it may have distinctive properties. It corresponds to "planar water" as defined by Kelley (16) and his colleagues. The thermal data suggest that certain clay minerals, e.g., illites, can have some of this type of water without also having an expanding lattice.

The thermal evidence indicates that many bentonites and other clays thought to be composed of a single clay mineral are actually mixtures of clay minerals probably closely intergrown. Many of the bentonites are mixtures of illite and montmorillonite; others are mixtures of kaolinite and/or a halloysite and montmorillonite. In some of these clays montmorillonite does not seem to be the dominant constituent. X-ray and optical data are in accord with these conclusions.

A series of samples that have been classed as beidellite, including material from the type locality at Beidell, Colorado, gave differential thermal curves indicating that they are not composed of a single species, but are mixtures of clay minerals. X-ray diffraction data are not opposed to this conclusion. Some of these mixtures yield optical data that suggest homogeneous material and so might easily lead to erroneous identifications. The sample from the Princess Mine, Namiquipa, Chihuahua, Mexico, is a particularly good example because x-ray and thermal data show definitely that it is a mixture primarily of kaolinite and/or a halloysite and a ferric iron hydrate, whereas its apparent moderately high birefringence and indices of refraction would not suggest this identification. This does not reduce the value of optical studies in clay mineral investigations, but it does emphasize the fact that trustworthy clay mineral identifications usually require the study of more than one set of properties. Undoubtedly the literature is full of clay mineral identifications that are inaccurate because they are based either on optical, x-ray, thermal, or chemical data, but not on a combination of several of these data.

Differential thermal analyses are presented for a series of additional miscellaneous hydrous minerals that were investigated primarily to provide a background for the clay mineral study. These samples were obtained mainly from the collection of the U. S. National Museum. Some of the salient conclusions from this work are as follows:

Attapulgite and the white magnesium clay mineral from Hector, California, each show distinctive differential thermal curves unlike that of
montmorillonite or any other clay mineral. Bravaisite from the type locality has the same thermal characteristics, optical properties, and chemical composition as the illites. A sample of celadonite also yielded a differential curve similar to that of the illites. A sample of smectite had the thermal properties of montmorillonite, which is further evidence for Kerr’s (17) conclusion that smectite is montmorillonite.

Two samples of leverrierite proved to be montmorillonite. Other samples studied before by Ross and Kerr (29) and by de Lapparent (19) have another clay mineral composition so that the term can have no standing as a specific mineral name.

A sample of volkonskoite appeared from its curve to be a mixture of amorphous material and a pigmentary material, perhaps chromic oxide. Similarly a sample of racewinite from the type locality seems to be a mixture of amorphous material and a carbonate.

One sample labeled allophane gave a differential thermal curve suggesting a mixture of gibbsite, amorphous material, and a halloysite. Another sample of allophane from another locality proved to be chiefly a halloysite.

Samples labeled respectively dillnite, severite, miloscite, and collyrite gave differential thermal curves exactly like that of kaolinite and/or a halloysite. Optical data confirm this classification of the material. A sample of newtonite also gave a differential thermal curve of the same type, but had in addition several small peaks indicating unidentified constituents.

Samples labeled cimolite and rectonite yielded differential thermal curves different from those of any other materials studied.

References


