

# 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 alundum 12 inches long and 2 inches inside diameter, wound in the middle with 46 feet of coiled Kanthal A wire and surrounded

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

† Petrographer and Assistant Petrographer, respectively, Illinois State Geological Survey, Urbana, Illinois.

with 4 inches of refractory insulating brick. A heating rate of approximately  $10^{\circ}\text{C.}$  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  $1000^{\circ}\text{C.}$ , 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

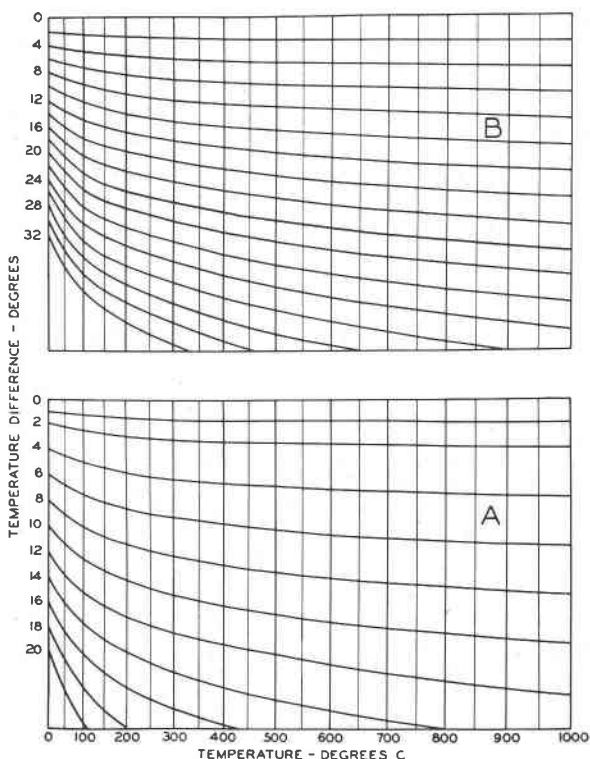


FIG. 1. Scales for determining the temperature differences recorded by the peaks of the thermal curves. Scale A—100 ohms series resistance; scale B—200 ohms series resistance.

dried at 90°C. for 12 hours and then were placed in a desiccator over a saturated solution of hydrous calcium nitrite ( $\text{Ca}(\text{NO}_2)_2 \cdot 4\text{H}_2\text{O}$ ) 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  $\alpha$  to  $\beta$  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  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, a spinel.

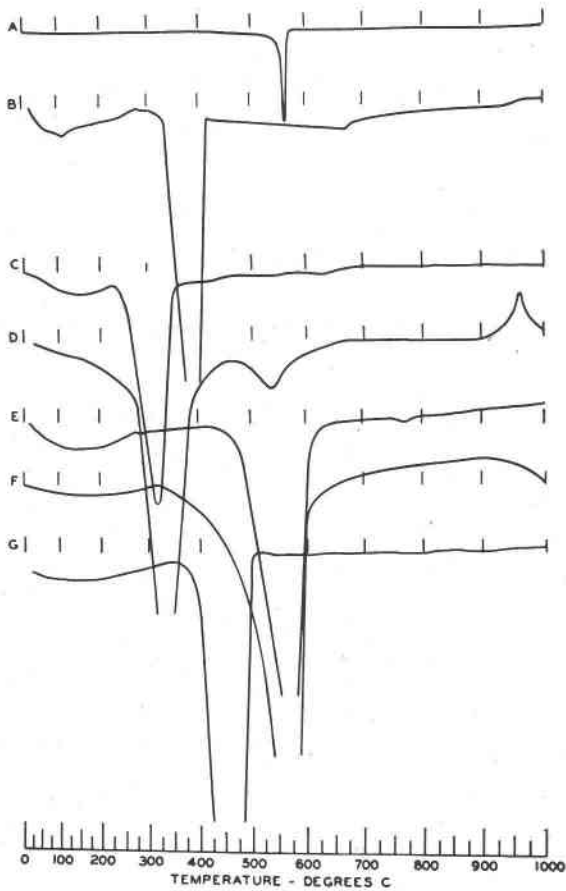


FIG. 2. Oxides and hydroxides.

- 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 Büsser 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  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. 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 2H<sub>2</sub>O 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 Al<sub>2</sub>O<sub>3</sub> · 2SiO<sub>2</sub> · 4H<sub>2</sub>O is designated hydrated halloysite, and the form Al<sub>2</sub>O<sub>3</sub> · 2SiO<sub>2</sub> · 2H<sub>2</sub>O is designated halloysite. The expression "a halloysite" is used when the particular form cannot be identified.

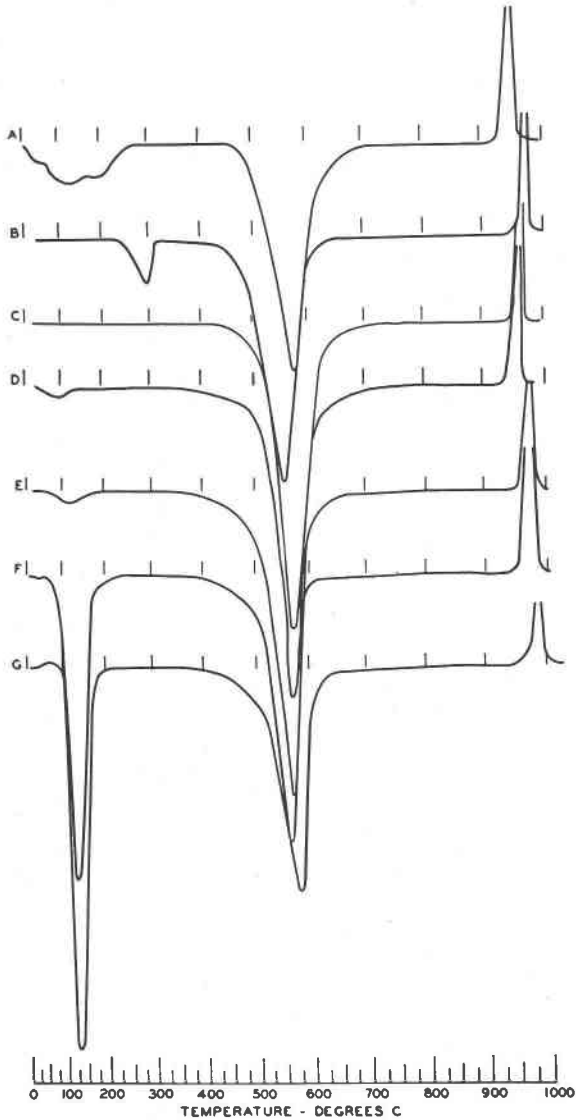


FIG. 3. Kaolinites and halloysites. Scale B.

- 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

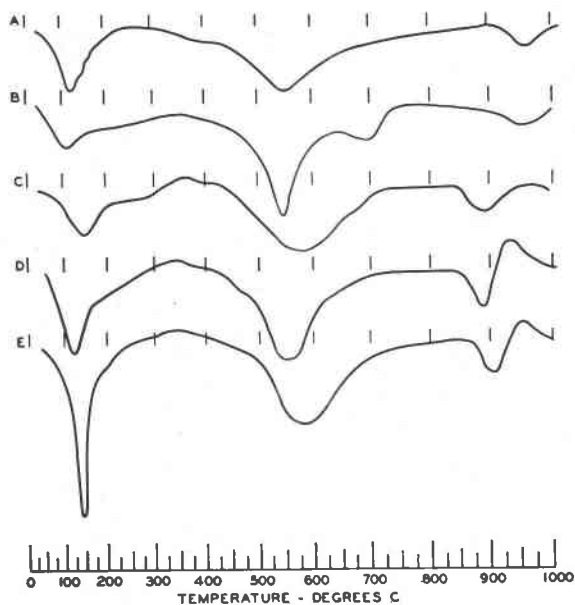


FIG. 4. Illites. Scale A.

- A. Glaucanite, University of Illinois collections.
- B. "Glimmerton," Sarospatak, Hungary, from U. Hofmann, University of Rostock, Rostock, Germany.
- C. Illite, purified from shale, Alexander County, Illinois.
- D. Illite, purified from underclay, Vermilion County, Illinois.
- E. Illite, purified from underclay, Grundy County, Illinois.

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-

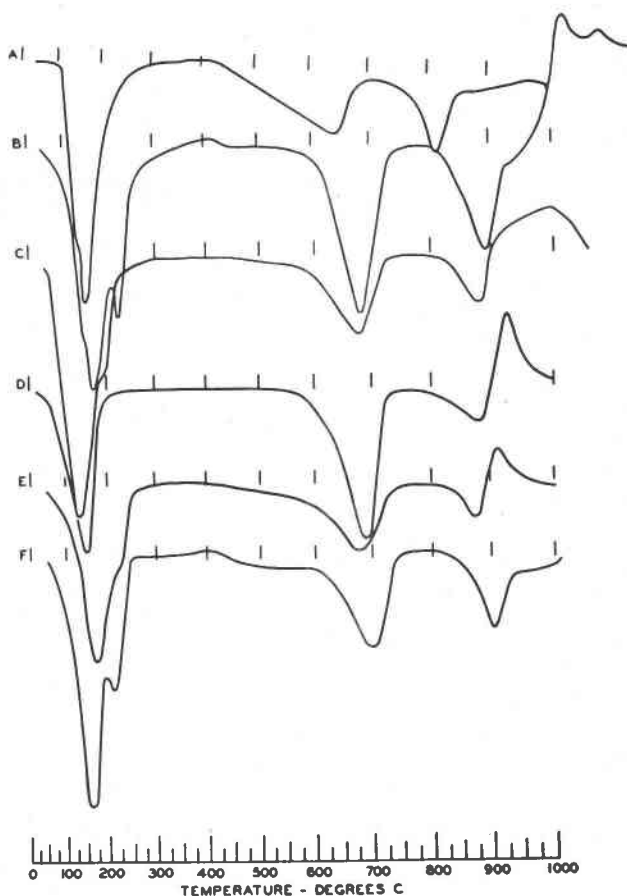


FIG. 5. Montmorillonites. Scale A.

- 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

(12, 8) 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 I. CHEMICAL ANALYSES OF MONTMORILLONITE

	5A	5B	5D	5E	5F
SiO <sub>2</sub>	50.30	66.02	64.32	64.17	52.09
Al <sub>2</sub> O <sub>3</sub>	15.96	19.97	20.74	17.14	18.98
Fe <sub>2</sub> O <sub>3</sub>	.86	.71	3.03	4.81	.06
FeO		.13	.46		
MgO	6.53	5.04	2.30	3.90	3.80
CaO	1.24	1.97	.52	1.48	3.28
Na <sub>2</sub> O	1.19	.12	2.59	.21	
K <sub>2</sub> O	.45	.09	.39	.48	
TiO <sub>2</sub>		.19	.14		
Ign. loss		6.51			
Total		100.75			
H <sub>2</sub> O+	}23.61	6.42	5.15	7.78	7.46
H <sub>2</sub> O-		11.89			14.75
SiO <sub>2</sub> /R <sub>2</sub> O <sub>3</sub>	5.12	5.15	4.83	5.40	5.05
SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	5.34	5.63	5.28	6.36	5.20

5A Otay, California. *Jour. Am. Cer. Soc.* 9, 88 (1926).

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 Tatatila, 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. (5B).

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.

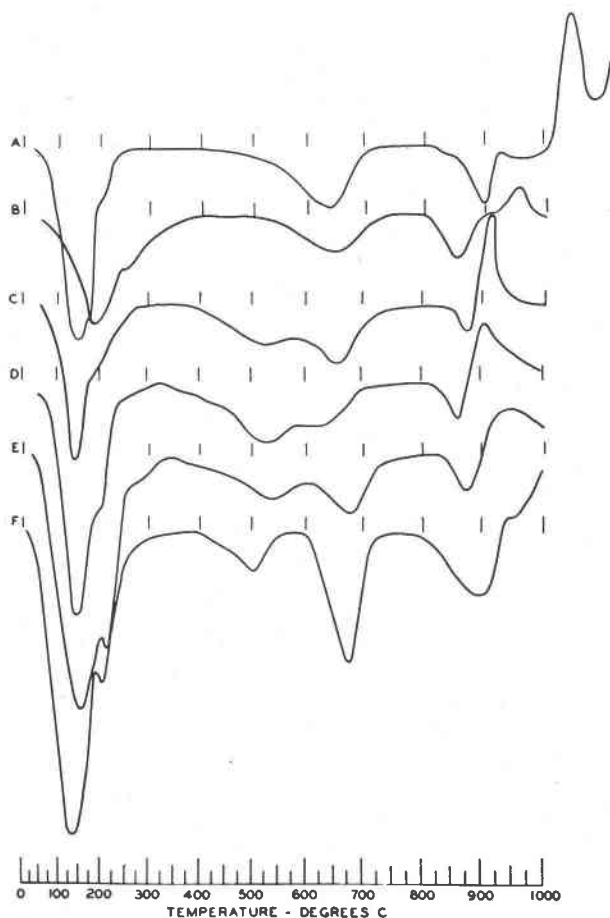


FIG. 6. Miscellaneous clays containing montmorillonite, Scale A.

- 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 birefringence 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

	6A	6C	6D	6E
SiO <sub>2</sub>	66.69	59.87	57.55	57.54
Al <sub>2</sub> O <sub>3</sub>	19.67	21.70	19.93	20.23
Fe <sub>2</sub> O <sub>3</sub>	1.01	6.86	6.35	5.60
FeO		.17	.95	.24
MgO	4.66	2.89	3.92	3.29
CaO	1.00	.95	1.94	2.92
Na <sub>2</sub> O		.09	.33	.89
K <sub>2</sub> O		.14	.59	2.10
TiO <sub>2</sub>		.27	.32	.66
Ign. loss	7.14	7.74	8.53	7.08
Total	100.17	100.68	100.41	100.55
H <sub>2</sub> O+		7.53	8.51	6.93
H <sub>2</sub> O-	10.73	6.07	7.43	5.51
SiO <sub>2</sub> /R <sub>2</sub> O <sub>3</sub>	5.58	3.90	4.10	4.12
SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	5.76	4.68	4.92	4.84

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 K<sub>2</sub>O 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 K<sub>2</sub>O 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.

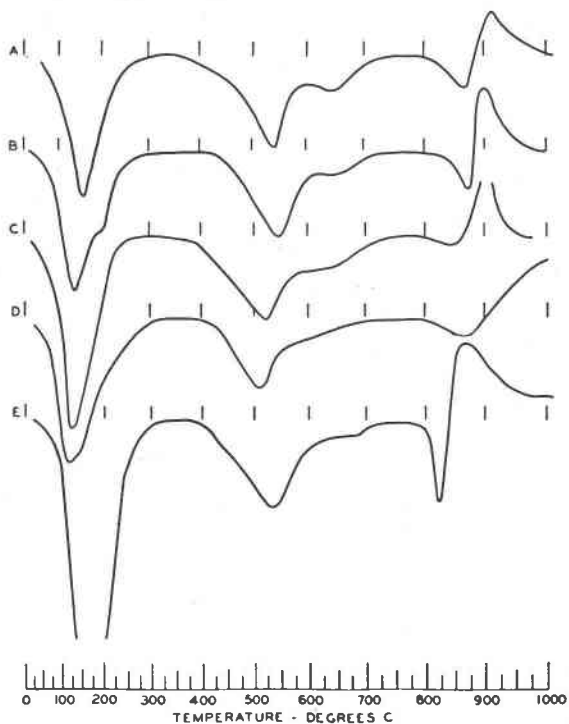


FIG. 7. Miscellaneous clays containing montmorillonite, Scale A.

- 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
- E. "Montmorillonite," Sierra de Guadalupe, Atzacapozalco, Mexico, U. S. Nat. Mus. 7591.

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 K<sub>2</sub>O content of the materials is not necessarily evidence against the illite interpretation.

TABLE 3. CHEMICAL ANALYSES OF MISCELLANEOUS CLAYS CONTAINING MONTMORILLONITE

	7A	7B	7C	7E
SiO <sub>2</sub>	62.91	60.13	56.99	50.44
Al <sub>2</sub> O <sub>3</sub>	19.47	21.57	22.70	16.26
Fe <sub>2</sub> O <sub>3</sub>	4.84	5.42	9.27	5.38
FeO	.22	.15	.31	
MgO	3.18	2.67	1.65	3.92
CaO	.25	1.58	.61	.72
Na <sub>2</sub> O	.04	.38	.25	
K <sub>2</sub> O	.63	1.02	.21	
TiO <sub>2</sub>	.58	.64	.38	.42
Ign. loss	8.20	7.00	8.29	
Total	100.32	100.56	100.66	
H <sub>2</sub> O+	7.97	6.76	8.07	6.30
H <sub>2</sub> O-	5.66	6.56	5.77	16.00
SiO <sub>2</sub> /R <sub>2</sub> O <sub>3</sub>	4.74	4.07	3.88	4.33
SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	5.44	4.73	4.26	5.25

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.

7E "Montmorillonite," Sierra de Guadalupe, Atzacapozalco, Mexico. Analyses from W. F. Foshag, U. S. Nat. Museum.

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.

(To be continued)