

DIFFERENTIAL THERMAL ANALYSIS OF CLAY MINERALS AND OTHER HYDROUS MATERIALS. PART 2.

RALPH E. GRIM AND RICHARDS A. ROWLAND†

(Continued from page 761)

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 pigmentary hydrated ferric iron oxide, and the optical properties can be closely approximated ($\gamma=1.580$, $\gamma-\alpha=.025$). 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.

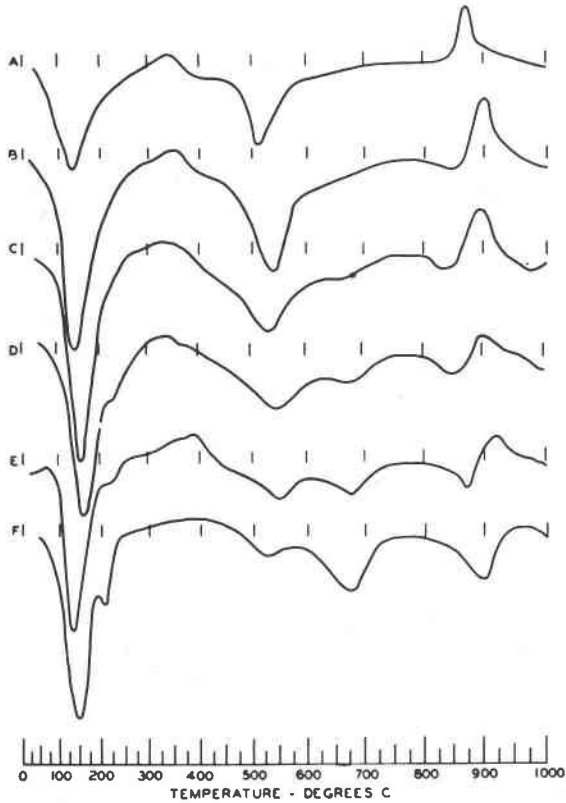


FIG. 8. Materials that have been called beidellite. Scale A.

- A. Namiquipa, Chihuahua, Mexico, U. S. Nat. Mus. No. R7595.
- B. Fairview, Utah.
- C. Twin Falls, Idaho.
- D. Beidell, Colorado, U. S. Nat. Mus. No. 93239.
- E. Wagon Wheel Gap, Colorado, U. S. Nat. Mus. No. 94963.
- 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

	8A	8B	8C	8D	8E	8F
SiO ₂	43.76	51.65	55.48	47.28	52.80	45.52
Al ₂ O ₃	27.88	26.40	20.83	20.27	25.66	27.52
Fe ₂ O ₃	6.42	5.53	7.76	8.68	6.47	2.80
FeO		.29	.15		.31	
MgO	1.23	2.48	3.23	.70	1.76	3.00
CaO	.90	1.36	1.45	2.75	2.11	.52
Na ₂ O	.30	.15	.40	.97	.06	
K ₂ O	1.18	1.88	2.19	tr	1.09	
TiO ₂	.30	.49	.88		.39	
Ign. loss		10.21	8.18		8.98	
Total		100.44	100.55		99.63	
H ₂ O+	7.67	10.08	7.47	19.72	8.70	19.60
H ₂ O-	10.59	5.99	7.15		7.26	
SiO ₂ /R ₂ O ₃	2.33	2.90	3.67	3.11	3.00	2.55
SiO ₂ /Al ₂ O ₃	2.66	3.32	4.53	3.96	3.49	2.81

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

8A Namiquipa, Chihuahua, Mexico. Analysis from W. F. Foshag, U. S. Nat. Museum.

8B Fairview, Utah.

8C Twin Falls, Idaho.

8D Beidell, Colorado. *Jour. Am. Cer. Soc.*, **9**, 94 (1926).

8E Wagon Wheel Gap, Colorado.

8F Nashville, Arkansas. *Jour. Am. Cer. Soc.*, **9**, 94 (1926).

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 ($\gamma=1.560$, $\gamma-\alpha=.030$ (-)) 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.

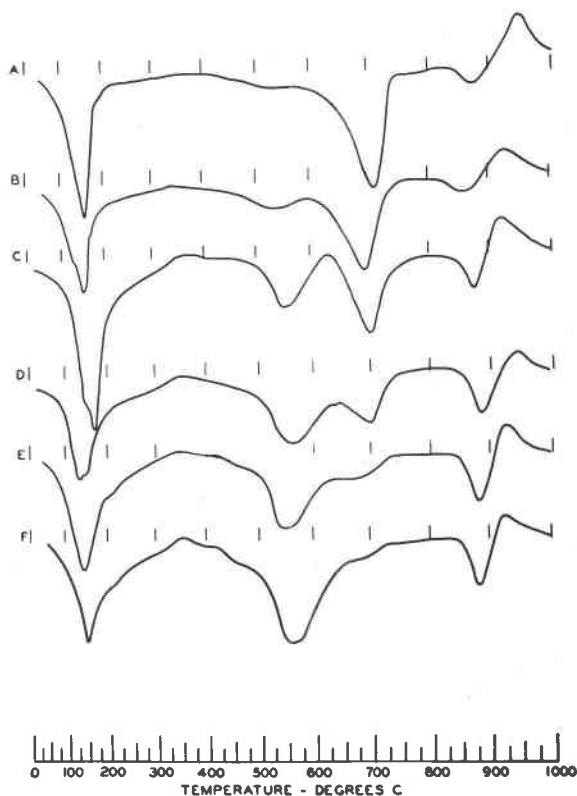


FIG. 9. Prepared mixtures of montmorillonite (5D) and illite (4D). Scale A.

- 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 in-

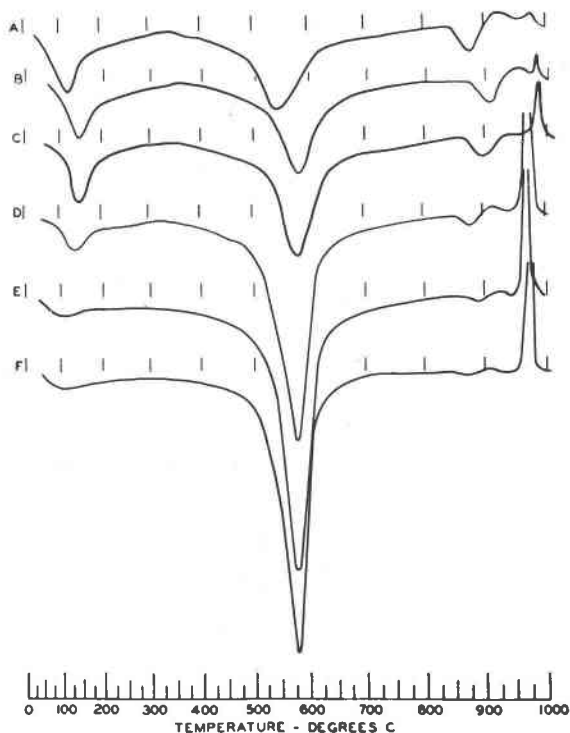


Fig. 10. Prepared mixtures of illite (4D) and kaolinite (3C). Scale B.

- 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.

dicated 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.

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

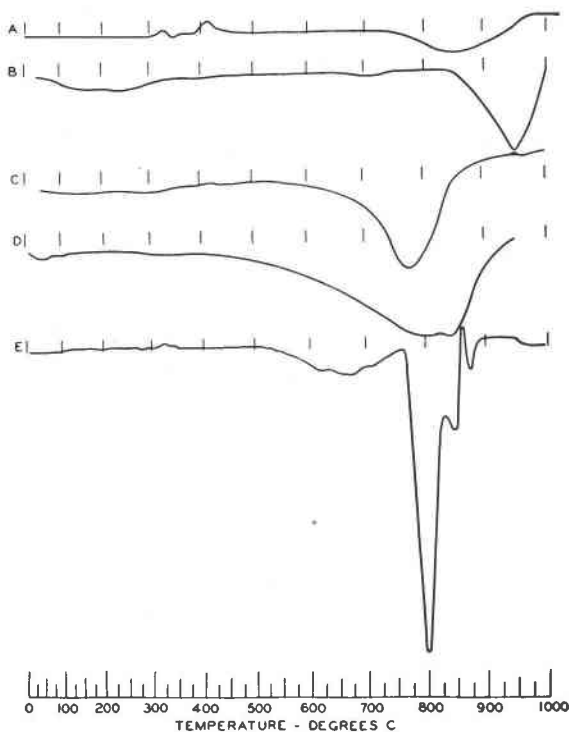


FIG. 11. Miscellaneous minerals. Scale A.

- A. Muscovite, University of Illinois collections.
- B. Talc, Vermont.
- C. Pyrophyllite, North Carolina.
- D. Pyrophyllite, Oreana, Nevada.
- E. Chlorite, Chester, Massachusetts.

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.

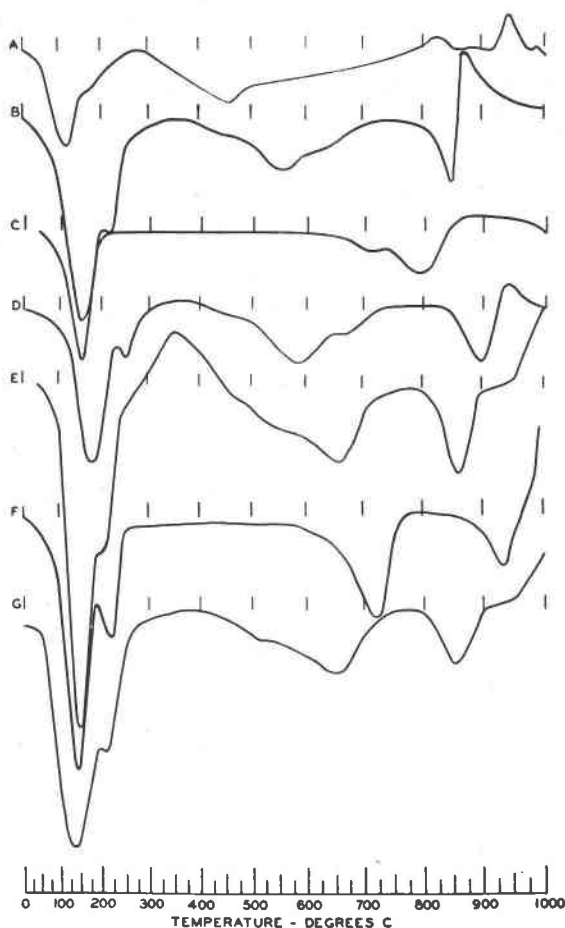


FIG. 12. Miscellaneous materials. Scale A.

- A. "Nontronite," San Luis, Potosi, Mexico, U. S. Nat. Mus. No. R6685.
- B. "Woody nontronite," Howard County, Arkansas.
- C. White Hector clay, Hector, California.
- D. Bravaisite, Noyant Allier, France, U. S. Nat. Mus. No. 4918.
- E. "Smectite," Cilly, Austria, U. S. Nat. Mus. No. 13098.
- F. "Leverrierite," April Fool Hill, Manhattan, Nevada, U. S. Nat. Mus. No. 3819.
- G. "Leverrierite," Salida, Colorado, U. S. Nat. Mus. No. 94962.

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.

	4C	4D	12D
SiO ₂	52.23	51.22	54.64
Al ₂ O ₃	25.85	25.91	26.29
Fe ₂ O ₃	4.04	4.59	1.51
FeO		1.70	0.38
MgO	2.69	2.84	3.03
CaO	0.60	0.16	1.40
Na ₂ O	0.33	0.17	0.12
K ₂ O	6.56	6.09	5.94
TiO ₂	0.37	0.53	0.45
Ign. loss	7.88	7.49	6.68
Total	100.55	100.70	100.44
H ₂ O+	7.88	7.14	6.61
H ₂ O-	1.13	1.45	4.28
SiO ₂ /R ₂ O ₃	3.13	3.02	3.41
SiO ₂ /Al ₂ O ₃	3.43	3.36	3.53

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 birefringence of sample 12G is probably due to a random orientation of the clay mineral particles mixed with some isotropic material. X-ray diffraction

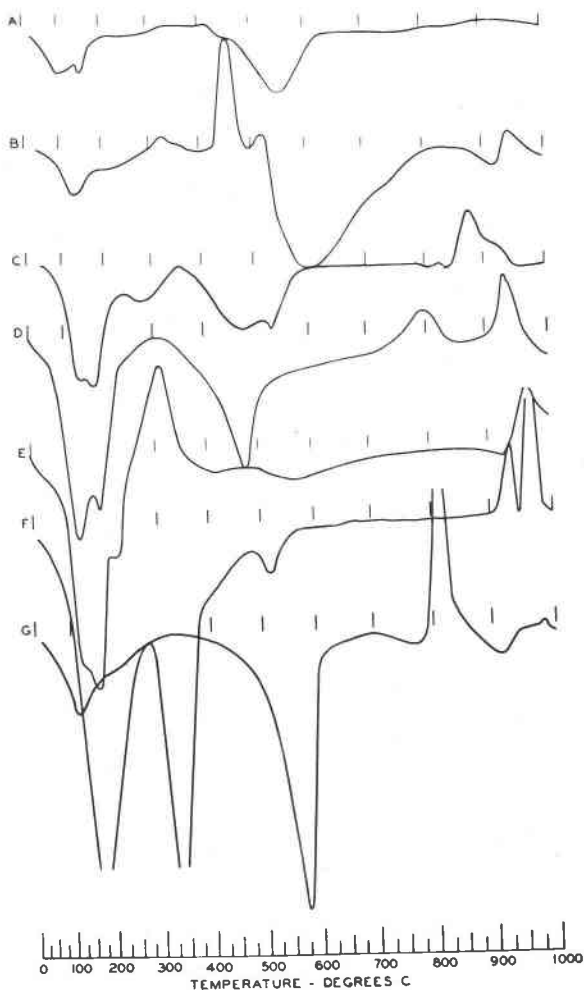


FIG. 13. Miscellaneous materials. Scale A.

- A. Rectorite, Garland County, Arkansas, U. S. Nat. Mus. No. 80607.
- B. Celadonite, Verona, Italy. U. S. Nat. Mus. No. 93080.
- C. Attapulgit, Quincy, Florida.
- D. "Chloropal," Hungary, U. S. Nat. Mus. No. 80644.
- E. Volkonskoite, near Sverdlosk, U. S. S. R.
- F. "Allophane," Bedford, Indiana, U. S. Nat. Mus. No. 95335.
- G. "Allophane," Iyo, Japan, U. S. Nat. Mus. No. 93052.

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

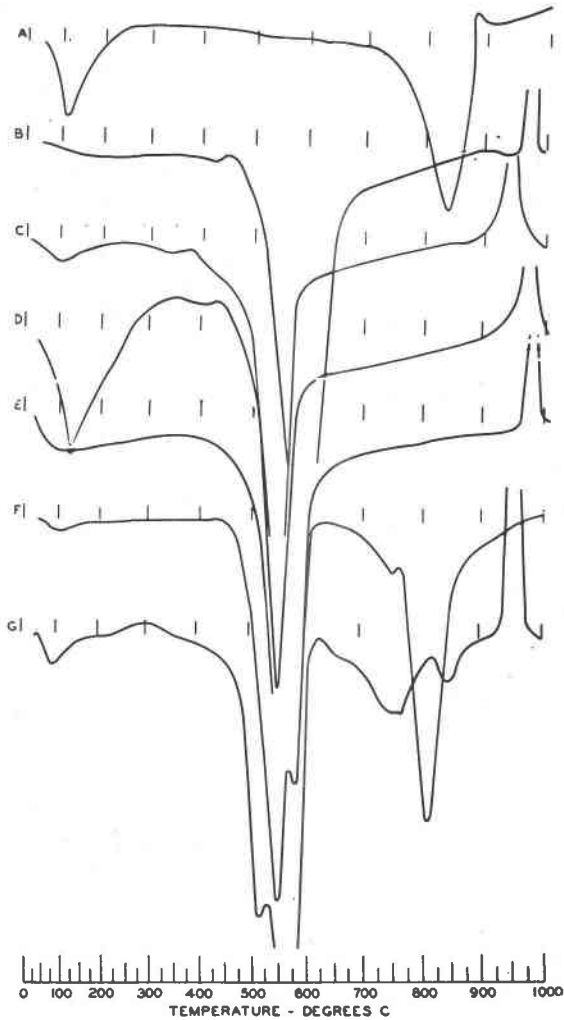


FIG. 14. Miscellaneous materials. Scale A.

- A. Racewinite, Bingham, Utah, U. S. Nat. Mus. No. R4759.
- B. Dillnite, Schemnitz, Hungary, U. S. Nat. Mus. No. R4795.
- C. Severite, Elko, Nevada, U. S. Nat. Mus. No. 13511.
- D. Miloschite, Rudniak, Serbia, U. S. Nat. Mus. No. 48649.
- E. Collyrite, Fichtelgebirge, Bavaria, U. S. Nat. Mus. No. R4793.
- F. Cimolite, Sverdlosk, U. S. S. R., U. S. Nat. Mus. No. R4765.
- G. Newtonite, Newton, Pennsylvania, U. S. Nat. Mus. No. R4760.

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 racewinitite (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 collyrite (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.

* Unpublished work by R. A. Rowland and F. L. Cuthbert: Illinois State Geological Survey, Urbana, Ill.

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-

aggeration 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:

Attapulgit 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 racewinitite 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, miloschite, 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 rectionite yielded differential thermal curves different from those of any other materials studied.

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