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DIFFERENTIAL THERMAL ANALYSIS

Its Application to Clays and Other

Aluminous Minerals

By

SIDNEY SPEIL, LOUIS H. BERKELHAMER, JOSEPH A. PASK
AND BEN DAVIES

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CONTENTS

ILLUSTRATIONS

DIFFERENTIAL THERMAL ANALYSIS

Its Application to Clays and Other Aluminous Minerals [1]

PREFACE

Differential thermal analysis has been developed to meet a need for a method of determining the nature and character of certain minerals and mineral mixtures not revealed by either chemical analysis or X-ray patterns.

The investigations of Le Chatelier (*32*) [2] as far back as 1887 disclosed the principle upon which the present method of differential thermal analysis is based; but apparently the practical value of this early research work was not recognized for many years, and only since 1934 has definite progress been made toward developing a semiquantitative method applicable to clays and other aluminous minerals.

Briefly, the differential thermal analysis method is based upon the fact that the application of heat to many minerals causes certain physical and chemical changes that are reflected in endothermic and exothermic reactions. By comparing the change in temperature of a mineral heated at definite rate with that of a thermally inert substance (Al_2O_3) heated under the same conditions a curve or pattern is obtained which is characteristic of the particular mineral under examination.

A differential thermocouple is used to measure the difference in temperature between the mineral being tested and the check sample, and an ordinary thermocouple is employed to record the rate of temperature rise of the chamber in which the samples are placed.

Although the differential method of thermo-analysis can be applied to a variety of minerals, its use in determining the nature and characteristics of the broad group of minerals classed as "clay" has received particular attention by members of the technical personnel of the Bureau of Mines.

Much remains to be done before this method is perfected and enough data are accumulated to permit positive, rapid identification of mixtures made up of various proportions of different minerals, but characteristic patterns have been obtained for most of the individual hydrous minerals and for a number of mineral mixtures.

For the convenience of those interested in the development of this relatively new method of identifying and evaluating such materials, the three following reports pertaining to the differen-

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[1] Work on manuscript completed May 1944.
[2] Italic figures in parentheses refer to items in the Bibliography at the end of this paper.

tial thermal analysis of hydrous minerals have been assembled in a single technical paper:

> Applications of Thermal Analysis to Clays and Aluminous Minerals, by Sidney Speil.
>
> An Apparatus for Differential Thermal Analysis, by Louis H. Berkel-hamer.
>
> Thermal Analysis of Clay Minerals and Acid Extraction of Alumina from Clays, by Joseph A. Pask and Ben Davies.

The apparatus employed in the experiments described in the first and last reports was similar to that used by Norton (*37*). The second report gives a detailed description of an improved but simple and inexpensive apparatus developed by the personnel of the Bureau of Mines.

It is hoped that these reports will not only help others make use of this method of evaluating clays and other aluminous minerals but invite further work in this promising field of research.

APPLICATIONS OF THERMAL ANALYSIS TO CLAYS AND ALUMINOUS MINERALS [3]

By SIDNEY SPEIL [4]

INTRODUCTION

In the study of clays and related minerals, the analytical techniques commonly employed in mineral analysis are not always applicable. The X-ray examination of a clay sample usually will show the major constituents, but often minor clay impurities will not be detected because of line broadening and the similarity of the main lines of clay-mineral diffraction patterns. The petrographic analysis of clay minerals with clay particles as small as a few microns is usually difficult. With still smaller particles, a gross effect often is noted in which a mixture of several constituents gives the appearance of a single constituent with the mean optical characteristics of the mixture (15). The electron microscope has recently been used to study clay-particle shapes of various aluminosilicates (25, 26); however, this method has not yet been sufficiently explored. The chemical method in which a mineralogical analysis is calculated from the oxide chemical analysis has been discussed by Wilson (51) and others, and many of the shortcomings have been pointed out. It should also be recognized that the variable alkali and alkaline earth content of bentonites makes it inaccurate to assign these basic elements arbitrarily to feldspar or mica in any clay that contains appreciable bentonite.

As an alternative process, the thermal analysis method was selected. Starting with the original work of Le Chatelier (32), this was developed into a semiquantitative method by Granger (11), Orcel (40), Jourdain (29), Norton (36, 37), and Grim (15). Hendricks (19, 23) has used the differential thermal method in studying the hydration of montmorillonite. Insley and Ewell (27) have studied the thermal decomposition of the kaolin minerals. The essential step in the process is determination of the temperature at which any thermal reactions take place in the sample being studied and the magnitude of these thermal effects. The determination is most simply carried out by heating two specimens at a constant and equal rate, one the clay sample and the other a thermally inert substance, and noting any temperature differences between the two by means of a differential thermocouple. The applications and limitations of this method to the study of various clays, bauxites, and aluminous minerals will be discussed in this paper.

ACKNOWLEDGMENTS

This investigation was made under the general supervision of O. C. Ralston, principal chemical engineer, Bureau of Mines, Washington, D. C., and Hewitt Wilson, supervising engineer, Bu-

1

reau of Mines Electrotechnical Laboratory, Norris, Tenn.   Acknowledgment is made to H. R. Shell, assistant chemist, for chemical analyses and to the following for supplying samples of pure minerals:

EXPERIMENTAL TECHNIQUE
APPARATUS

The test apparatus used was similar to that described by Norton (*37*).   The samples are put into laterally positioned holes in a nickel block so that each will receive equal heat treatment.   This block is supported within a small inside-wound crucible furnace equipped with replaceable heating units (Arthur Thomas 5768, type 82).   By insulating the furnace with aluminum foil, the required rate of temperature rise can be easily attained from a 115-volt power supply controlled by a Variac voltage regulator.   This type of furnace reduces the thermal lag between the heating elements and the nickel block.   The measuring thermocouple, placed in the nickel block, also acts as the controlling thermocouple for a three-position, program-controller unit.   The two junctions of a platinum-to-platinum, 10-percent-rhodium differential thermocouple were placed centrally in the two specimen cavities, one of which contained calcined γ alumina, which is thermally inactive up to 1,000° C.   The temperature difference between the two junctions was then recorded photographically by reflecting a vertical line source of light from an L. & N. type-P galvanometer onto a sheet of bromide paper rotating behind a horizontal slit.   At every 50° C. interval, as indicated by the control thermocouple in the nickel block, a signal light was flashed automatically, giving a direct temperature scale on the record.   The galvanometer suspension and reflection distance from the galvanometer mirror to the photographic sheet were chosen to give appreciable deflections for the small thermal effects of bentonites.

In addition, two series resistances were used to change the sensitivity of the galvanometer system, depending on the type of sample being investigated.   The furnace is shown in figure 1 and the control and recording system in figure 2.

PROCEDURE

Samples were ground to minus 100-mesh and placed in a desiccator over anhydrous magnesium perchlorate for 24 hours before being placed in the test cavity in the nickel block.   They were not dried in an oven, since the higher temperature would very markedly affect the initial portion of the peak for many of the fine-grained minerals containing absorbed water.   By initially packing material on each side of the thermocouple, forcing it under the couple wire, and then packing the balance of the sampler over the wire with a tightly fitting plunger, it was almost invariably pos-

sible to pack the 0.35-gram specimen into the cavity without mov-
ing the thermocouple junction from its central position.

The specimen and standard cavities were covered with a nickel
shield and a thin sheet of insulating brick to eliminate direct ra-
diation effects through the top of the sample. The furnace was
warmed slightly before the start of the test to minimize the initial
thermal lag and then slid over the stationary nickel block in its
refractory holder. The external resistance of the thermocouple
circuit was set at the value appropriate for the type of specimen
being studied. The sensitivity was also varied during some runs
to magnify certain sections of the curve more than others. The
furnace was brought to 1,000° C. or slightly higher in some cases
(for example, with talcs) at the rate of 12° C. per minute in all
cases except for five special runs made to study the effect of tem-
perature rise.

THERMAL CURVE

If a record were made of water loss vs. temperature for pure
kaolinite under equilibrium conditions—that is, by allowing the
clay to remain at a constant temperature and attain equilibrium
before each water-loss determination was made—we would obtain
a curve similar to the top curve of figure 3 (39), which indicates
that the reaction is not instantaneous. On the other hand, the
thermal analysis curve is a dynamic and not a static or equilibrium
record of thermal reactions occurring within the sample being
studied. On the thermal analysis record, this dehydration and
decomposition reaction would appear to extend over a longer tem-
perature range because the actual temperature of the sample con-
tinues to rise during the reaction. A downward deflection of the
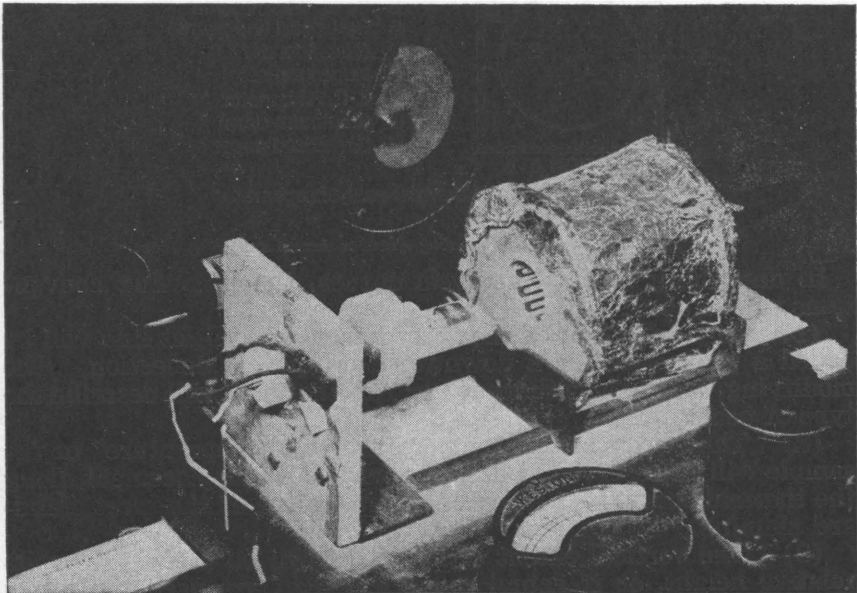
FIGURE 1.—Thermal analysis furnace and specimen holder.

curve indicates an endothermic reaction, while an upward deflec-
tion is caused by evolution of heat by the specimen.
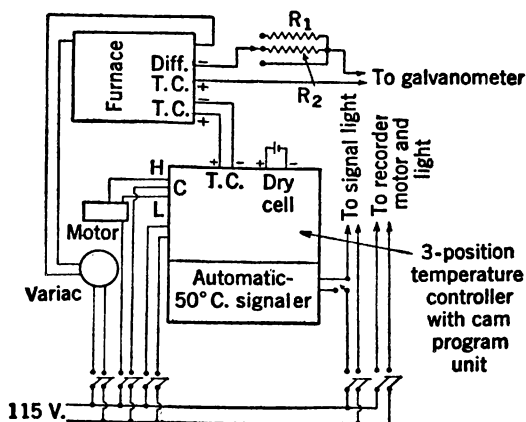
Wiring diagram for thermal analysis apparatus

B Vertical line source
C Horizontal line source
D Galvanometer
E Horizontal slit
F 1-R.P.H. motor
G Aluminum drum
H Sensitized paper

SECTION A-A
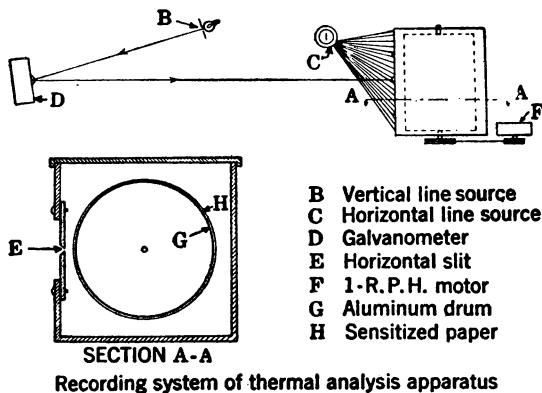
Recording system of thermal analysis apparatus

FIGURE 2.—Wiring diagram and recording system of thermal analysis apparatus.

In describing thermal analysis curves, the following conven-
tions will be used:

(1)   Any deflection of the record from a straight line will be
called a peak, whether a downward or upward deflection.   The
modifying words "endothermic" or "exothermic" will describe the
type of peak.

(2)   The words "actual temperature" or "temperature" of the
sample will be reserved to describe horizontal displacement along
the thermal curve, that is, actual temperature of the inert stand-
ard alumina.

(3)   The vertical extent of the peak will be described by its
relative height, or if actual numerical data are used the terms
"differential temperature" or "ΔT" will be employed.

(4)   The area of a peak will be that area included by the actual curve and a line joining the two points where the deflection starts and ends (points *a* and *c* of fig. 3, lower curve).
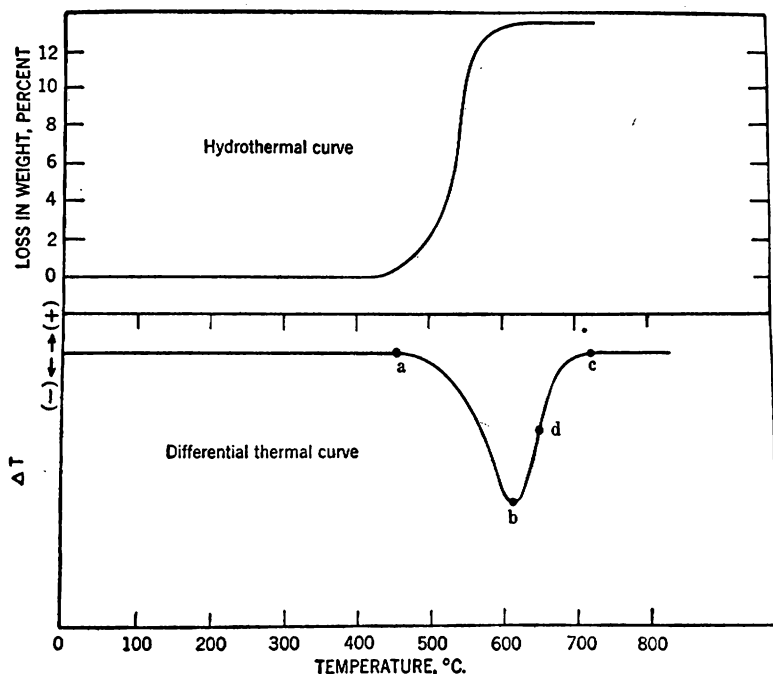
FIGURE 3.—Hydrothermal and thermal analysis curves of kaolin.

As the thermal curve is a differential function, we need consider only those thermal effects that do not occur simultaneously and equally in the specimen and in the standard alumina.   Assuming that the two samples are heated equally, normal heat input from the furnace may be neglected in analyzing the thermal analysis curve.   Therefore, two opposite thermal effects must be considered—the heat of the thermal reaction and the differential heat inflow from the nickel block to the specimen which, in the case of an endothermic reaction, is at a lower temperature than the standard.   An exothermic reaction will lead to a higher temperature in the sample than in the standard alumina and will be indicated by an upward deflection of the curve.   The decomposition of kaolin, indicated by the valley *abc* of figure 3, lower curve, may be used as an example of an endothermic reaction.   At point *b* the slope of the thermal curve equals that in the normal part of the curve. The temperature differential between the two thermocouples is not changing, and therefore the resultant heat input into each cavity must be the same.   Thus at this point the rate of heat absorption by the chemical reaction must equal the rate of differential heat conductivity into the clay specimen.   The rate of heat absorption then continues to decrease more rapidly than the equalizing heat input falls, and at some point *d* between *b* and *c* the reaction ceases.   However, this point cannot be established

exactly, and measurements are therefore made using the more definitely established points a and c as limits.

Under static conditions, the heat effect would cause a rise in temperature of a specimen consisting of kaolin and any thermally inert substance given by:

$$T = \frac{M \; (\triangle H)}{M_0 \cdot C},$$

wherein M = mass of reacting kaolin,
H = specific heat of reaction,
M_0 = total mass of specimen,
C = mean specific heat of specimen.

However, we must also take into account the heat flow from the nickel block toward the centers of the two sample cavities.

For any point between a and c (fig. 3, lower curve), the simplified equation for the thermally active constituent is:

$$M \int_a^x \frac{dH}{dt} \; dt \; + \; g \cdot k_1 \int_a^x (T_0 - T_1) dt = (T_0 - T_1) \; M_0 \cdot C_1,$$

and for the inert sample is:

$$g \cdot k_2 \int_a^x (T_0 - T_2) \; dt = (T_0 - T_2) M_0 \cdot C_2,$$

wherein t = time,
g = geometrical shape constant,
k_1 = conductivity of the specimen,
k_2 = conductivity of the standard alumina,
T_0 = temperature of the control couple in the nickel block,
T_1 = temperature at the center of the sample,
T_2 = temperature at the center of the standard alumina;

letting
$$C_2 = C_1 + \triangle C,$$
and
$$K_2 = k_1 + \triangle k,$$
gives the combined equation:

$$M \int_a^x \frac{dH}{dt} dt - g \cdot k_1 \int_a^x (T_2 - T_1) \; dt - g \cdot \triangle k \int_a^x (T_0 - T_2) \; dt =$$
$$M_0 \; (T_2 - T_1) \; C_1 - M_0 \; (T_0 - T_2) \triangle C.$$

As $T_2 - T_1 = \triangle T$ = temperature indicated by the differential thermocouple, the equation can be considerably simplified by assuming that the terms containing $(T_0 - T_2)$ and either $\triangle C$ or $\triangle k$ are small in comparison with the other terms. By using a and c as integration limits, we get:

$$M \int_a^c \frac{dH}{dt} dt - g \cdot k_1 \int_a^c \triangle T \; dt = \triangle Tc \cdot M_0 \cdot C_1;$$

but
$$\triangle Tc = 0, \text{ by definition of point } c,$$
and
$$\int_a^c \frac{DT}{dH} dt = \triangle H,$$

so we finally get the relation:

$$\frac{M \; (\triangle H)}{g \cdot k_1} = \int_a^c \triangle T \; dt.$$

The last expression is proportional to the area enclosed by the straight line *ac* and the curve *abc* if the scale deflection is a linear function of the temperature.   This area can be measured easily by using a planimeter.   In the limits of practical application, the linearity holds within ± 3 percent.   The total heat effect equals

5° C. / min.

8 ° C. / min.

12° C. / min.

16° C. / min.

20° C. / min.

600 °C.
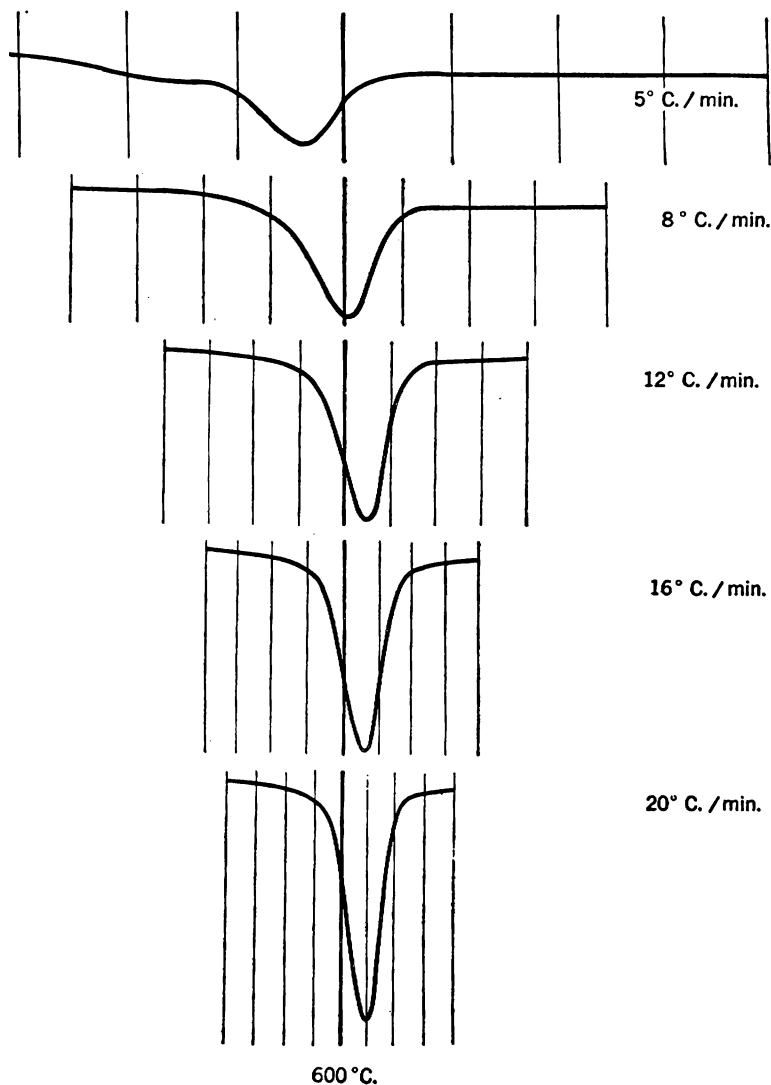
FIGURE 4.—Effect of rate of temperature rise on thermal curve of Pioneer (Ga.) kaolin.

the product of the specific heat of reaction and the mass of reacting material.   It is proportional, therefore, to the percentage of reacting material in a given weight of sample.   Although the derivation of this relation does not take into account the temperature gradient in the sample itself and also neglects the differential terms, it does serve as a basis for using the thermal area as a

measure of mineral percentage. Using this approximate equation, the area under the curve is a measure of the total heat effect; and if the conductivity is constant, the area under a peak should be proportional to the amount of thermally active material present. In the nonrigorous derivation, the area is considered to be independent of the specific heat. However, this factor will actually affect the shape of the peak and may also affect the area slightly.

EXPERIMENTAL RESULTS
RATE OF TEMPERATURE RISE

The mathematical derivation is not confined to any specific rate of temperature rise; therefore, the area should be independent of the rate of temperature rise, except for the effect of variation of second-order differential quantities with rate of temperature rise. A series of experiments was conducted on a Georgia kaolin to check this assumption. The thermal analysis curves obtained are shown in figure 4 and the data from them in table 1. On this figure the heavy vertical line is at 600° C., and each line represents a 50° C. interval.

TABLE 1.—*Effect of rate of temperature rise on the thermal analysis curve*

Rate of rise, °C. per min.	Area, mm.²	Position of peak, °C.	Return to zero deflection, °C.
5	6,030	575	620
8	6,030	605	700
12	1,100	625	700
16	6,160	630	740
20	6,200	650	750

Table 1 shows that the areas are equal within 3 percent, although there seems to be a slight tendency for smaller areas with low heating rates. This variation is, however, within the experimental error of the method. The slower the run, the lower and broader the peak when plotted on the time scale used in making the thermal analysis record, because the differential heat inflow into the specimen tends to keep the temperature differential low. The apex of the peak and the return to zero deflection occur at a lower actual temperature on the record with slow heating. These results are due primarily to the dynamic character of the test. The actual peak temperature is the point where the differential heat input equals the rate of heat absorption, and therefore

$$\triangle T_{(peak)} = \left(\frac{dH}{dt} \right)_{(peak)} \cdot \frac{M}{g \cdot k_1}.$$

A high rate of heating will cause $\frac{dH}{dt}$ to increase because more of the reaction will take place in the same interval of time, and therefore the height at the apex or the differential temperature $\triangle T_{(peak)}$ will be greater. As the return to the zero line is a time function as well as a temperature-difference function, the return to the zero line will occur at a higher actual temperature with more rapid heating.

STANDARD THERMAL CURVES

Norton (*36, 37*) and Grim (*15*) give thermal curves of many pure mineral types. Most of these have also been analyzed in this laboratory, but only the curves of those minerals essential to the study of common clays and kaolins will be discussed here. The sensitivity scale of each curve in this report is indicated on the individual figures. The distance between two vertical lines corresponds to a 50° C. interval, the first line representing an actual temperature of 50° C. Scale C, with the largest external resistance, gave an average deflection of approximately 1 centimeter for 0.037 millivolt. As the resistance of the thermocouple circuit changes with temperature, the ratio between different scales was determined by using the ratio of the total thermocouple circuit resistances with the furnace at 600° C. and the various external resistances in circuit. Actually the scale calibration is a curve and not a straight line; but an average straight line has been assumed, and average values of the calibration for the temperature range used are given in table 2. All areas mentioned in this report are based upon scale A unless otherwise noted.

TABLE 2.—*Comparison of galvanometer deflection scales*

Scale:	Average value of $\triangle T$ for 1 cm. deflection, °C.
A	2.2
B	3.05
C	6.1

KAOLIN MINERALS

These include the minerals kaolinite, dickite, anauxite, nacrite, halloysite, and allophane. The chemical analysis and origin of the minerals are given in table 3. Figure 5 shows the thermal analysis curves of this group. All kaolin minerals are characterized by the sharp exothermic peak at 980° C. corresponding to the transformation of amorphous alumina to γ alumina. The kaolinite curve, with an endothermic peak at 625° C., agrees in general with the curves obtained by Norton, Grim, and Jourdain. The anauxite peak at 600° and the dickite peak at 680° are similar to Norton's curves for these materials. Samples of these minerals from other localities gave identical peaks. It is virtually impossible to differentiate between kaolinite and anauxite upon the basis of thermal analysis alone. The halloysite curve is similar to that published by Grim and shows an adsorbed water peak and another endothermic peak at 590° C. It differs from Norton's curve in not having a peak at 310°, which may have been caused by a gibbsite impurity in Norton's sample. The halloysite curve obtained by Jourdain has a very broad endothermic peak extending over the temperature range from 100° to 450° C., which does not agree with the results found by other investigators. The allophane curve of figure 5 shows the characteristic broad endothermic peak from 120° to 270° C. due to loss of adsorbed water in addition to the high-temperature exothermic peak near 980° that characterizes the kaolin group. The small peak near 520° is

probably caused by a slight halloysite impurity, while that at 805°
may be due to the presence of some carbonate.   The record does
not show the 600° exothermic peak of Norton's allophane curve,
but the last curve of figure 5 is quite similar to Insley's curves for
the coprecipitated hydrogels corresponding to $Al_2O_3.2SiO_2$ or
$Al_2O_3.SiO_2$ (*27*).   When studying fine-grained clays it is desirable
not to oven-dry the sample, since this procedure may completely
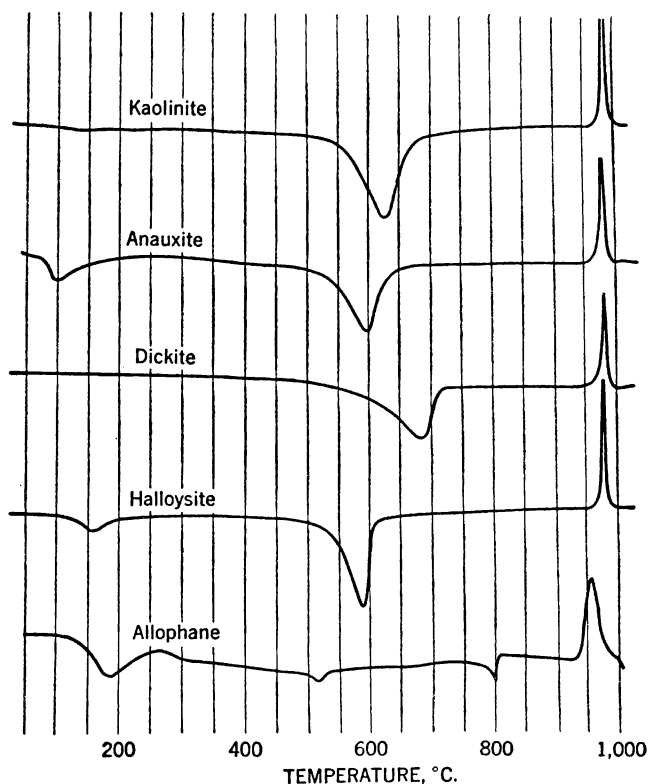
FIGURE 5.—Thermal curves of kaolin minerals, scale C.

destroy or weaken the low-temperature thermal reactions, which
often give very useful information.

MONTMORILLONITE AND RELATED MINERALS

The three-layer-lattice minerals include the illites (*16*) as well
as the various isomorphic forms of the montmorillonite type in
which magnesium and iron partly or entirely replace aluminum
ions.   The curves of different montmorillonite specimens are va-
riable both in regard to decomposition temperatures and magni-
tude of thermal effects.   The records for several typical minerals
listed in table 3 are reproduced in figure 6, which is made to scale
A because of the small thermal effects associated with this lattice
type.   In general, this group is characterized by three endo-

TABLE 3.—Chemical analyses of standard minerals [1]

No.	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	H_2O (−110°)	Ignition loss	Total
1	45.20	39.47	0.24	1.53	0.18	0.10	————	————	0.11	13.84	100.67
2	64.26	18.08	2.63	2.20	.65	.86	————	————	2.41	7.96	99.05
3	44.91	40.64	.13	.18	.33	.17	————	————	.03	14.61	101.00
4	43.74	40.82	.30	.00	.00	.00	————	————	2.43	14.93	102.22
5	28.54	27.61	.40	.00	3.52	2.01	————	————	24.66	14.06	100.80
6	60.26	21.50	3.76	.22	.00	2.50	2.67	0.43	3.53	5.34	100.21
7	53.84	17.64	3.94	.26	2.20	4.45	.10	.23	11.47	6.69	100.82
8	51.19	15.13	.86	.16	1.00	7.19	.73	.12	15.80	7.57	99.75
9	64.29	16.23	.43	.18	1.15	2.17	.74	5.91	8.94	5.57	100.25
10	52.71	22.24	6.16	.82	.31	2.42	.33	.50	3.08	6.15	100.13
11	55.98	2.18 [2]	————	————	.0	24.96	————	————	8.73	6.27	96.12
12	45.69	1.13	36.30	.00	2.33	.00	.00	.17	8.50	6.28	100.40
13	3.45	60.17	2.72	2.46	————	————	————	————	————	31.20	100.00
14	.5	84.8	.1	.0	————	————	————	————	————	14.2	99.6
15	45.94	33.15	5.14	.38	.00	.89	.58	10.17	.00	4.18	100.43
16	65.69	28.00	.13	.00	.00	.08	————	————	1.02	5.92	100.84
17	63.32	.23	.64	————	.01	30.83	————	————	.00	5.00	100.02
18	98.24	.97	.0	————	.0	.0	————	————	.03	.09	99.33
19	1.19	————	2.96 [3]	————	————	.63	————	.19	.08	31.20	99.03
20	————	————	83.63	————	————	————	————	————	.46	12.80	96.89
21	————	————	.1	(FeCO₃ = 84.7 ; MnCO₃ = 16.8)			————	————	.09	————	————

[1] H. R. Shell, analyst. [2] R_2O_3. [3] Calculated as carbonates.

KEY TO TABLE 3

1 Kaolinite_____Gordon, Ga.
2 Anauxite_____Franklin, N. C.
3 Dickie_____Chihuahua, Mexico
4 Hallosite_____Eureka, Utah
5 Allophane_____Hillsboro, Ohio
6 Montmorillonite_____Upton, Wyo.
  Do_____Smith County, Miss.
8 Montmorillonite "otaylite"_____Encinatas, San Diego County, Calif.

9 Mortmorillonite_____East Texas
10 Illite_____Grundy County, Ill.
11 Magnesium-montmorillonite_____Hector County, Calif.
12 Nontronite_____Hungary (Chloropal)
13 Gibbsite_____Arkansas (selected nodules)
14 Diaspore_____Chester, Mass.

15 Muscovite_____Chester County, Pa.
16 Pyrophyllite_____Staley, N .C.
17 Talc, Talladega, Ala._(flotation concentrate)
18 Quartz_____Potter's flint
19 Brucite_____Luning, Nev.
20 Goethite_____Oregon Furnace, Md.
21 Siderite_____Lodenstein, Saxony

thermic reactions, the last of which is followed by an exothermic reaction.   The first peak usually extends from 100° to 300° C., corresponds to the loss of adsorbed or "planar" water, and often consists of a doublet rather than a single peak.   The second deflection usually occurs slightly above 700° C., but its position is not as definite as in the case of kaolins.   The position of the third peak,
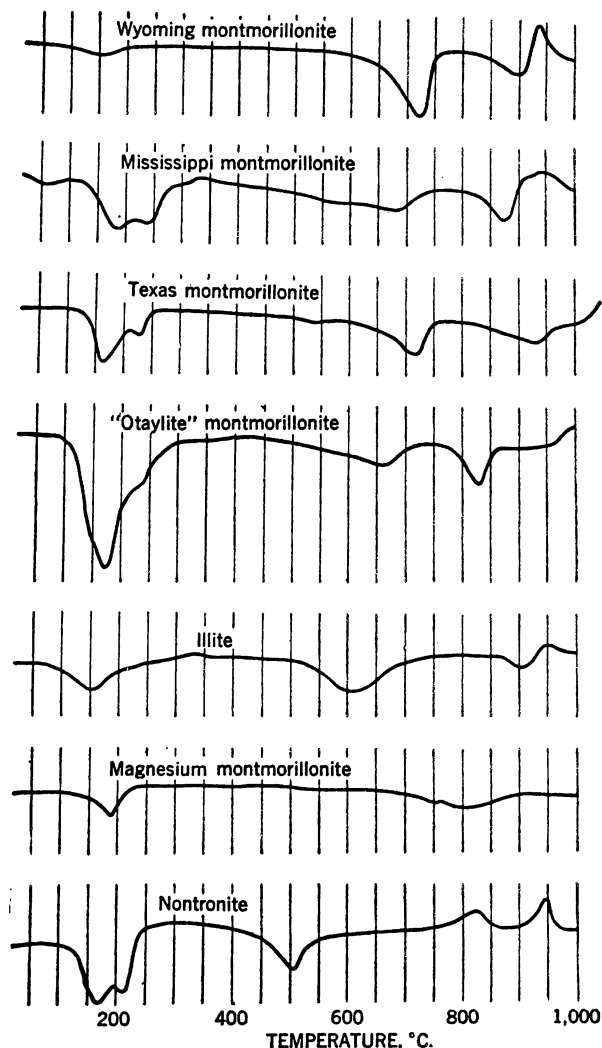
FIGURE 6.—Thermal curves of three-layer-lattice minerals, scale A.

at which the lattice is presumably completely destroyed, is still more variable.   It occurs at 840° in the Otay (Calif.) minerals and ranges up to 930° for the Texas montmorillonite.   Grim first noted the final exothermic peak and observed that its position de-

pends on the iron content (*15*).   The lower the iron content, the higher the temperature at which this peak occurs.   Thus relatively iron-free, white Texas montmorillonite does not show the exothermic peak until 1,050° C.   Although the curves of the various montmorillonites are not identical, they are of the same general type as those reported by Grim,

The curve of illite, a three-layer-lattice mineral, is characteristic and shows the same three endothermic peaks as montmorillonite.   It is distinguished from the latter because its second peak occurs at approximately 600° C.   It can be differentiated from kaolin by the high exothermic peak of the latter at 980° C.   The curve for magnesium montmorillonite agrees with those shown by Grim and Norton.   It is quite different from the usual curve for a three-layer-lattice mineral because it has only two peaks, a low-temperature one and a double peak at 750° and 800°.   From its thermal curve alone, magnesium montmorillonite would not ordinarily be classed as belonging to the montmorillonite group of minerals, and it does actually differ somewhat from the other members of its ionic lattice substitution (*20*).   The sample of nontronite, a three-layer-lattice mineral with iron replacing alumina, also has a different curve from that of the usual aluminosilicate mineral.   As with the magnesium-substituted mineral, there are only two endothermic reactions, the second occurring at 500°C.   The curve is also characterized by two distinct high-temperature exothermic peaks at 810° C. and 950° C., respectively.

ACCESSORY MINERALS
HIGH-ALUMINA MINERALS

When more alumina is present in a clay than corresponds to the theoretical proportions of pure kaolinte, it is usually due to the presence of some form of hydrated aluminum oxide.   There are two aluminous minerals with which we are mainly concerned in American bauxites and high-alumina clays—diaspore ($Al_2O_3.H_2O$)
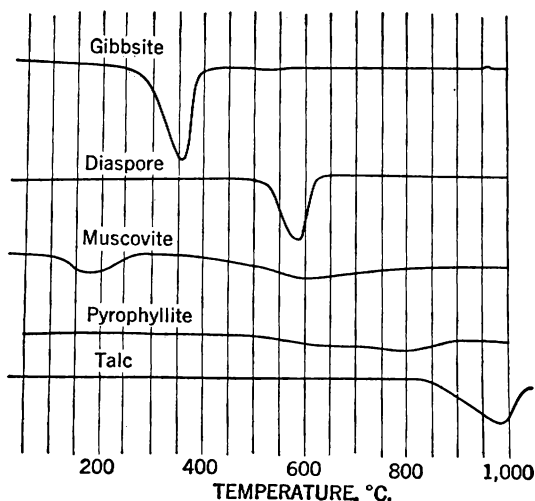
FIGURE 7.—Miscellaneous thermal curves: Gibbsite and diaspore, scale C; others, scale A.

and gibbsite ($Al_2O_3.3H_2O$). The former is attacked very slowly by a caustic soda solution and is therefore an undesirable form in an aluminum ore if used in the Bayer process of alumina extraction despite its higher alumina content (5). The curve for gibbsite (fig. 7) shows a decided absorption peak at 360°, agreeing exactly with Norton's curve but differing from Jourdain's, which had its peak near 500° C. A slight kaolin impurity is apparent in the gibbsite from the corresponding kaolin peaks. The peak on the diaspore curve occurs at approximately 580°, which agrees with Grim's curve but is at a slightly higher temperature than that noted by Norton. The diaspore used was a very pure sample and was practically free of silica, as shown in table 3. The curve can be easily differentiated from that of kaolin, since diaspore shows no heat evolution near 980°.

MISCELLANEOUS MINERALS

The muscovite curve has a very broad, shallow peak with a minimum near 600°. This agrees well with Norton's curve but not with Grim's. The curve of muscovite is variable, however, and is not distinct enough to have much value for determining this mineral in any clay mixture. The curve for crystalline pyrophyllite agrees roughly with that shown by Grim, although the peak in figure 7 is not as definite and covers a broader range. Actually the pyrophyllite structure is the basic lattice from which the montmorillonites are formed by ionic substitution, but its thermal and physical properties are very different from those of montmorillonite.

Similarly, the talc lattice (17) is the basis of the magnesium montmorillonite lattice, whose curve has already been presented in figure 6. The talc curve presented in figure 7 is that of a pure flotation concentrate and has an endothermic peak at 990°. Other talcs studied gave curves resembling those of Ewell (9) and Grim, respectively, often having small peaks at 550°.
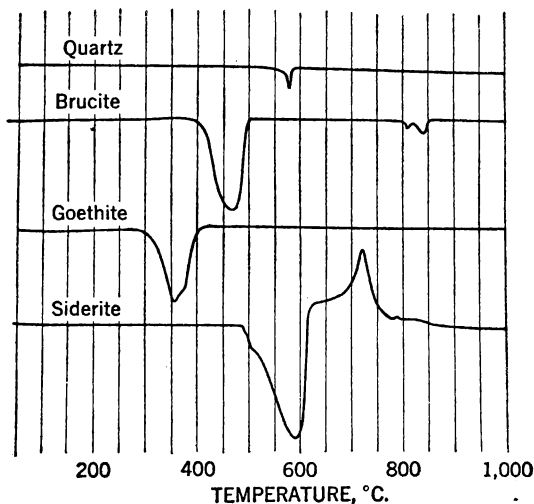
FIGURE 8.—Miscellaneous thermal curves: Quartz, scale A; others, scale C.

The inversion point of quartz from the alpha to the beta form at 575° is shown in the quartz curve of figure 8, using scale A. Because of the small amount of energy associated with this thermal effect, it is usually obscured by the kaolin peak unless quartz is the predominating constituent in an impure clay. Brucite has a single endothermic reaction at 460° corresponding to the decomposition of the $Mg(OH)_2$ lattice. The curve agrees with Norton's results and with Grim's curve for Lancaster (Pa.) brucite. The small endothermic doublet at 810° to 850° probably is caused by a carbonate impurity. The goethite peak in figure 8 agrees approximately with Norton's curve for this mineral. The hydrated ferric oxide decomposes at a lower actual temperature than the corresponding aluminum compound, diaspore. An analogous behavior of the complex silicate structure is shown by the iron silicate, nontronite (fig. 6), which has its endothermic effect at a lower actual temperature than montmorillonite. An increase of iron content similarly lowers the actual temperature at which the exothermic reaction of montmorillonite occurs. Siderite, $FeCO_3$, has a characteristic diagram that differs definitely from other thermal curves. A strong absorption of heat at 590° C. is followed by what seems to be a doublet exothermic peak. The presence of appreciable siderite in a kaolin mixture would markedly affect the kaolinite endothermic peak, since the change from heat absorption to heat evolution in the siderite curve occurs at the endothermic peak of the kaolin curve.

QUANTITATIVE ANALYSIS OF MIXTURES

In the preceding section the thermal analysis diagrams most commonly encountered in clay and kaolin analyses have been presented. Norton (*37*) has studied the application of thermal analysis to quantitative mineralogical determinations with good results. Grim (*15*) has presented semiquantitative diagrams showing mixtures of illite and kaolinite, and illite and montmorillonite. From the approximate derivation presented earlier in this paper, a quantitative relation would be expected for mechanical mixtures whose thermal conductivity did not differ appreciably from that of the mineral used as a reference.

GEORGIA KAOLIN-QUARTZ

Because one of the commonest impurities observed in kaolin is free quartz, the curves for a series of mixtures using minus 200-mesh "potter's flint" and a Georgia kaolin are shown in figure 9 and the calibration curves derived from these in figure 10. For the 980° exothermic peak, the relationship between area and percentage of kaolin is practically linear. The endothermic area shows a nearly straight line relationship. Silica impurities in clays vary considerably in physical structure and particle size. These factors presumably would change the conductivity of the specimen to some extent and thus alter the observed relationship between area and percentage of kaolin. The variation of the endothermic peak minimum temperature for figure 9 is shown in table 4.
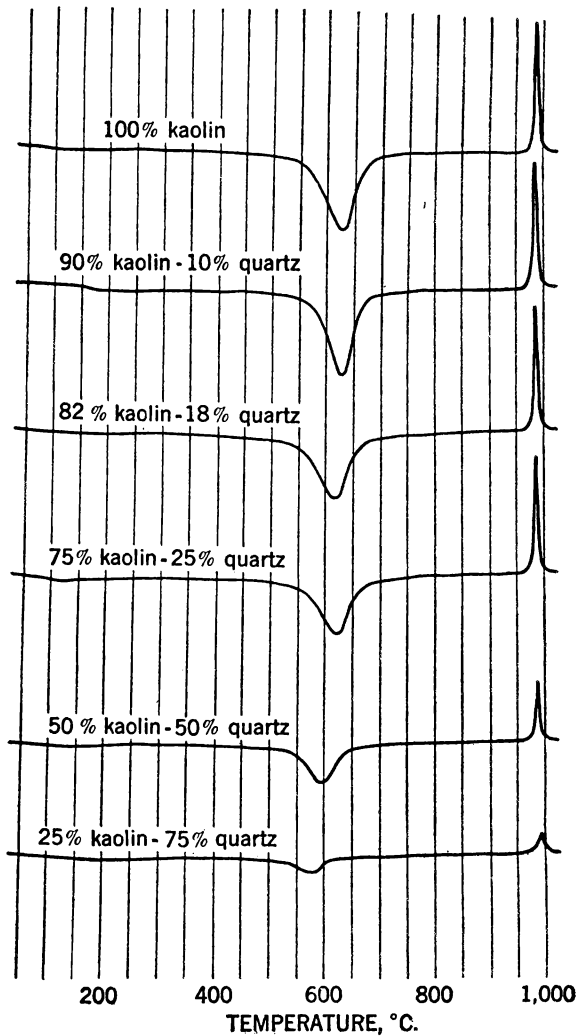
FIGURE 9.—Differential thermal curves of Pioneer (Ga.) kaolin and quartz mixtures, scale C.

TABLE 4.—*Effect of kaolin concentration on kaolin thermal peak position*

	Endothermic peak, °C.			Endothermic peak, °C.
100	625		75	615
90	625		50	595
82	625		25	580

The peak of the thermal curve occurs at the point where the rate of heat absorption equals the differential heat inflow to the kaolin. Therefore, this gradual shift of the absorption minimum with decreasing thermal effect is to be expected. Very small amounts of impurities in a substance will be indicated therefore by a peak that may differ from its normal position by as much as 50°C.
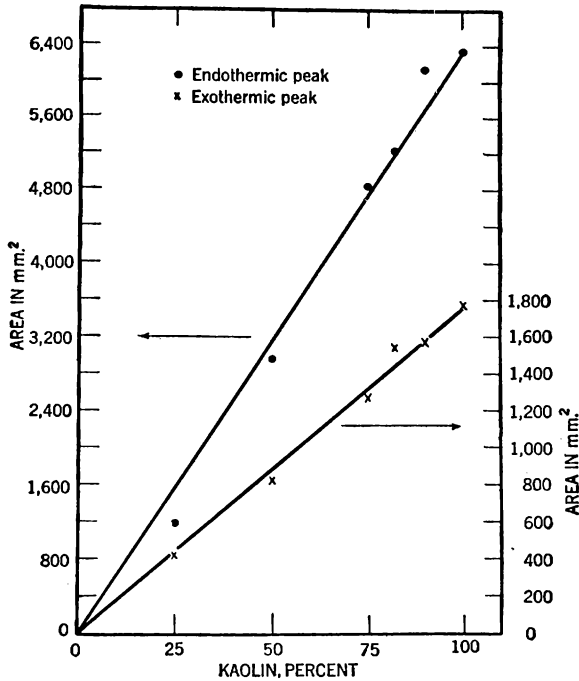
FIGURE 10.—Calibration curves for Pioneer (Ga.) kaolin and quartz mixtures.

GEORGIA KAOLIN-DIASPORE

Another complicating effect of this peak-temperature shift is noticeable in studying the diaspore-kaolin series where the two endothermic peaks nearly coincide. These results are presented in figure 11. There are two general methods of approach for the analysis of such an overlapping peak system. The combination peak may be divided graphically into its two components and each determined separately. The alternative procedure would be to determine the kaolin content, using the measured area of the 980° exothermic peak, subtract an area corresponding to this kaolin content from the total endothermic heat effect, and then attribute the remainder of the endothermic area to diaspore. The variable position of the peak for each mineral makes graphical resolution uncertain for any pronounced overlapping such as occurs in figure 11, which represents a series of synthetic mixtures of kaolin from Gordon, Ga., and diaspore from Mexico, Mo. The second alternative method was used in an attempt to analyze this series, and the results are tabulated in table 5. A linear relation was assumed for the variation of area with percentage of each constituent and the areas were assumed to be additive. This mixture is difficult to analyze quantitatively by the thermal method, yet the results give fair agreement with the known composition. The average deviation of the calculated percentage from the true value was 4 percent, and the maximum was 8 percent. In some instances where the two peaks can be easily differentiated, graphical analysis of the doublet may give better results.
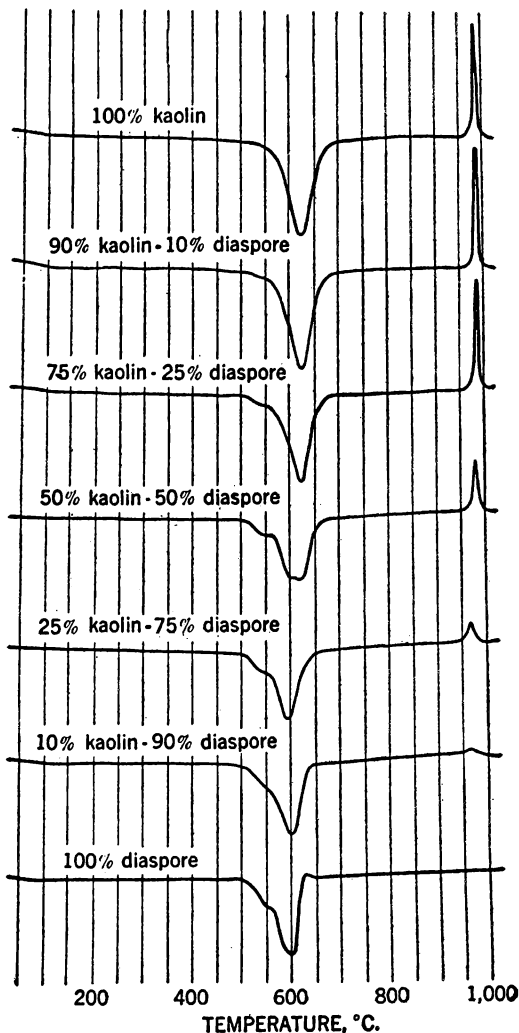
FIGURE 11.—Differential thermal curves of Gordon (Ga.) kaolin and Missouri diaspore mixtures, scale C.

TABLE 5.—*Thermal analysis of kaolin-diaspore mixtures*

Actual composition, percent [a]		Calculated endothermic areas, mm.[2] [b]			Measured areas, mm.[2] [b]				Calculated composition, percent	
Kaolin [a]	Diaspore [c]	Kaolin	Diaspore	Total	Total [a]	Kaolin [a]	Diaspore [a]	980° [d]	Kaolin	Diaspore
100	0	6,100	--------	6,100	6,100	6,100	---------	1,560	100.0	--------
90	10	5,500	485	5,985	5,985	5,520	330	1,410	90.5	7.0
75	25	4,580	1,210	5,790	5,880	4,880	1,000	1,250	80.0	20.6
50	50	3,050	2,425	5,475	5,350	3,180	2,170	810	52.0	45.0
25	75	1,520	3,640	5,160	5,050	1,800	3,250	460	29.5	67.0
10	90	610	4,370	4,980	5,200	560	4,640	145	9.2	95.0
0	100	-------	4,850	4,850	4,850	--------	4,850	------	------	100

[a] Endothermic peak.
[b] Areas based on curves which would be obtained with scale A galvanometer sensitivity.
[c] Kaolin from Gordon, Ga.; low-iron diaspore from Mexico, Mo. (silica impurity).
[d] Exothermic peak.

KAOLIN-BENTONITE

A third series was studied using mixtures of two thermally active constituents, Edgar plastic kaolin and Texas montmorillonite, whose peaks do not overlap. The thermal curves are shown in figure 12. The results presented graphically in figure

100% kaolin

80% kaolin - 20% bentonite

60% kaolin - 40% bentonite

40% kaolin - 60% bentonite

20% kaolin - 80% bentonite

100% bentonite

200   400   600   800   1,000

TEMPERATURE, °C.
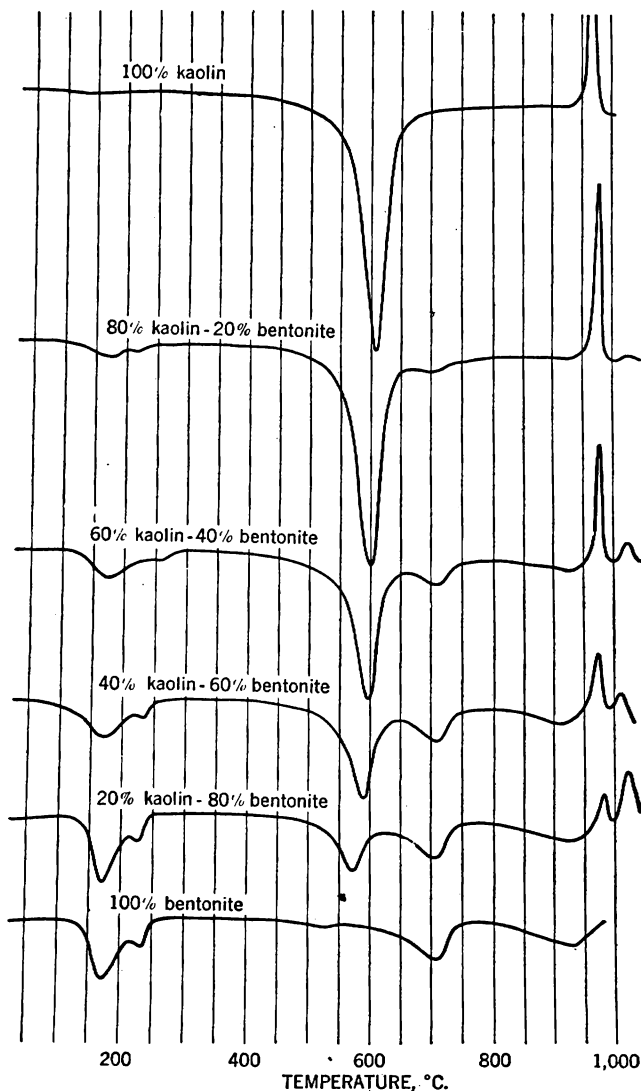
FIGURE 12.—Differential thermal curves of Edgar (Fla.) plastic kaolin and Texas montmorillonite mixtures, scale A.

13 indicate a linear relationship between peak areas and percentage of the corresponding mineral, except for the adsorbed water doublet at 100° to 250° C. This peak depends considerably on the treatment of the sample before thermal analysis and therefore

is not well-adapted to quantitative determinations. The experimental results show an average deviation of approximately 4 percent and a maximum deviation of almost 10 percent.
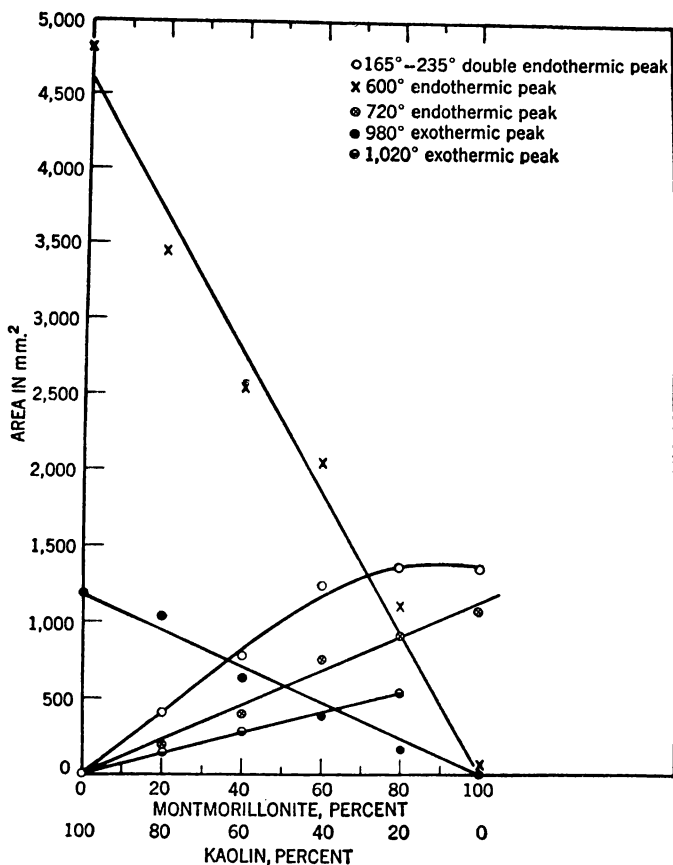
FIGURE 13.—Calibration curves of Edgar (Fla.) plastic kaolin and Texas montmorillonite mixtures.

CHARACTERISTIC THERMAL PEAKS

Table 6 summarizes the characteristic peaks for identification of the minerals whose thermal curves have been presented.

PARTICLE SIZE

DIFFERENTIAL THERMAL CURVE

From the above results and those of Norton, it would appear that the thermal analysis method is capable of giving nearly quantitatively the mineral compositions of clay mixtures. But other disturbing factors, such as particle size of the clay, must be considered. Van Nieuwenberg and Pieters (49) stated that the finer particles of clay decomposed at a lower temperature. Their

TABLE 6.—*Characteristic thermal peaks of minerals*

Mineral	Temperature, °C.	Scale A area, min.² [a]	Mineral	Temperature, °C.	Scale A area, min.² [a]
Kaolinite	620 [b] 980	6,100 1,560	Illite	605 900 [b] 940	1,625 [d] [d]
Anauxite	600	4,600			
Dickite	.690	4,900	Magnesium-montmorillonite	[e] 775–800	445
Halloysite	175 585	[c] 4,250			
			Nontronite	505 [b] 815	1,225 450
Allophane	200 [b] 980	[c] 1,060			
			Gibbsite	365	8,400
Montmorillonite (Texas)	165–235 725 940 [b] 1020	1,350 1,070 480 [c]	Diaspore	570	5,200
			Muscovite	[f] 600	[c]
			Pyrophyllite	[f] 3ʋ0	[c]
			Talc	980	1,800
			Quartz	580	170
Montmorillonite (Mississippi)	185–240 600–680 865 [b] 945	2,200 [c] [c] [c]	Brucite	465	7,000
			Goethite	3ϟ5	2,530
			Siderite	585 [b] 735	[d] 10,300 [d] 8,000

[a] Area may be changed to degrees C × seconds by multiplying by 2.36.
[b] Exothermic peak.
[c] Area indefinite.

[d] Peaks merge.
[e] Doublet.
[f] Very broad.

statement was based upon comparison of kaolinite and dickite, whose particle sizes differed; but since these minerals also have different lattice structures, the evidence is not conclusive. A series of different particle-size samples of kaolin was made from the same base material. Their respective differential thermal curves are recorded in figure 14. To obtain these samples a fraction of Pioneer (Ga.) kaolin 5 to 20 microns in size was prepared by sedimentation. Part of this was ground in an automatic agate mortar with a small amount of tetrasodium pyrophosphate solution and a 1- to 5-micron fraction was thus obtained. The latter was then ground further, and successive fractions were obtained by repeated centrifugal sedimentation and grinding. It was difficult to pack the 0.35-gm. sample of the finer fractions into the test cavity in the nickel block.

The data from the thermal analysis curves are tabulated in table 7.

TABLE 7.—*Effect of particle size on differential thermal curve of kaolin, scale C.*

Fraction, microns	Area of adsorbed water peak, mm.²	Area of endothermic peak, mm.²	Temperature of endothermic peak, °C.	Area of exothermic peak, mm.²
5–20		1,900	610	525
1–5		2,080	625	550
0.5–1	40	1,590	618	470
0.2–0.5	280	1,465	614	440
0.1–0.2	360	1,110	605	430
0.05–0.1	750	725	580	430

The low-temperature peak due to loss of absorbed water became so increasingly apparent with lesser particle size that it would be
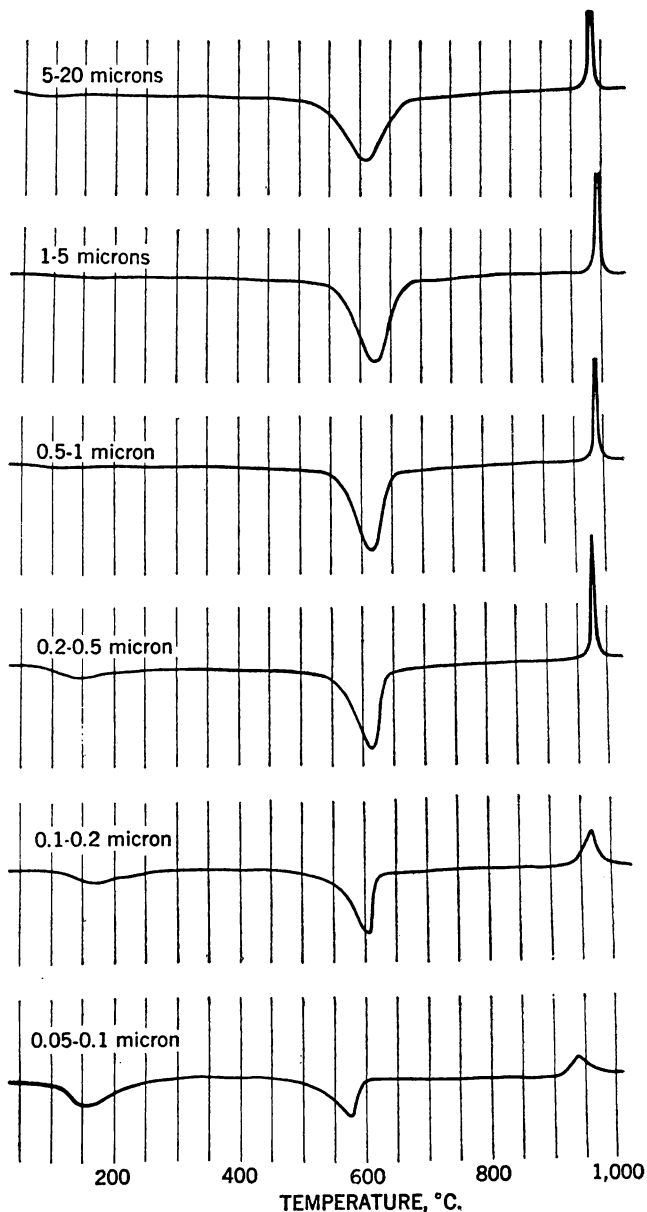
FIGURE 14.—Effect of particle size on thermal analysis curves of ground Pioneer (Ga.) kaolin, scale C.

difficult to differentiate, upon the basis of the thermal curve alone, between the finest fraction of kaolin and a sample of halloysite. The low-temperature thermal effect is caused by removal of adsorbed water. A decrease in particle size increases the area of surface and therefore the volume of adsorbed water. No particle-size or surface-area determinations were made on the fractions,

but the specific area approximately doubles with each successive fraction so the increase in area of the first peak is of the same order of magnitude as the increase in surface area.

The areas of the other two peaks decreased appreciably with decreasing particle size except for the interval between the 5- to 20-micron and the 1- to 5-micron fractions. The sharpness of the endothermic peak increased as the particles became smaller, indicating that these smaller grains may have dehydrated more uniformly. The finer the particle size, the lower the actual temperature for the decomposition peak, again with the exception of the 5- to 20-micron to 1- to 5-micron interval. Upon the basis of the differential thermal curves, it would be almost impossible to state definitely whether this decreased peak temperature is due to lower decomposition temperature or merely to a smaller thermal effect, as in the case of the previously mentioned shift of peak temperature with decreasing kaolin content for synthetic two-component mixures. It was decided, therefore, to determine the temperature of dehydration under equilibrium conditions.

HYDROTHERMAL CURVES

Water-loss curves were also made on this same kaolin series of varying particle size. One-gram samples were dried at 110° and then weight-loss measurements were made at 20° intervals from 300° to 600°. The five fractions were heated simultaneously and held at each temperature for 15 minutes. The results of this experiment are shown in figure 15. The smaller-particle-size fractions show a water loss at the lowest temperature. This lowering of decomposition temperature is also indicative of the greater surface energy of the finer-particle-size material and
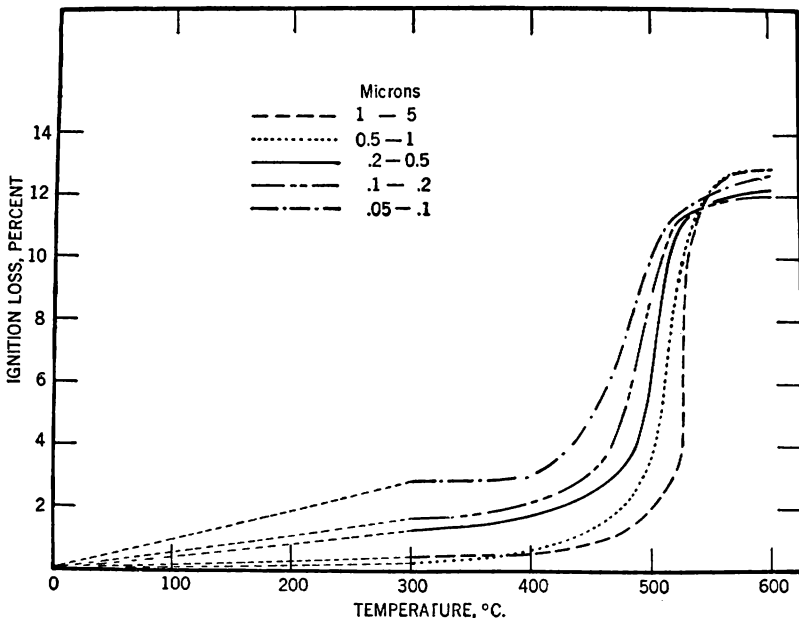
FIGURE 15.—Effect of particle size on thermal decomposition of ground Pioneer (Ga.) kaolin.

agrees with the observation that the dissociation pressure of silver carbonate, Iceland spar, and mercuric oxide decidedly increases when the particle size is decreased to 1 micron (47). The coarsest fraction shows a greater water loss than the others at the highest temperature, and this loss occurs over a smaller temperature range than would be expected from the differential thermal diagram. The initial water loss in the range from 110° to 300° probably occurs below 150°, but since no data were obtained in this portion of the curves, the dotted lines joining 0° and 300° are not significant. This initial water loss corresponds to the low-temperature peak of the differential thermal curves.

The preceding discussion on the effect of particle size leads to a further consideration of standards for thermal analysis. Not only do the kaolins differ in particle size, but even relatively pure kaolinites differ appreciably in their $SiO_2 : Al_2O_3$ ratio. Ross and Kerr (43) list a group of selected pure kaolinites whose $SiO_2 : Al_2O_3$ ratio ranges from 2.02:1.00 to 1.85:1.00.

These kaolins might be expected to show different thermal effects upon the basis of atomic structural differences due to varying $SiO_2 : Al_2O_3$ ratios. In the case of bentonitic materials, the problem is still more complex. Clay having the idealized montmorillonite lattice practically never occurs in nature. There is always more or less replacement of the alumina by magnesium or by ferric iron, and sometimes alumina is present in the tetrahedral coordination usually reserved for silica (12, 20). Montmorillonites contain varying amounts of alkalies and alkaline earths as shown by the analyses in table 3, yet all of these samples are properly classified as montmorillonites The end members of these isomorphic replacement series have quite distinct curves, as exemplified by the curves of magnesium montmorillonite in figure 6, but the intermediate substitutions associated with the usual bentonitic materials would be expected to influence peak temperature and area. The use of a standard bentonite as a basis for quantitative determinations of bentonite in a clay is therefore open to question. Qualitative, and in many cases semiquantitative ($\pm$ 10 percent), determinations are feasible. It appears moreover that the use of a comparison differential thermal peak for any mineral such as kaolinite is justified only when the standard mineral approximates the physical condition in which the mineral is present in the specimen being studied. This statement is substantiated by a comparison of the curves for Zettlitz kaolin (fig. 16) and Gordon (Ga.) kaolin (fig. 5), both of which are relatively pure, as shown in table 8.

TABLE 8.—*Comparison of Zettlitz and Gordon (Ga.) kaolin*

	Zettlitz	Gordon
SiO_____percent__	46.90	45.20
Al₂O₃_____ do____	37.40	39.47
Fe₂O₃_____ do____	.65	.24
SiO₂ : Al₂O₃_____	2.11 :1	1.95 :1
Position of endothermic peak_____°C.____	615	620
Area of endothermic peak_____mm.²__	5,450	6,100
Area of exothermic peak_____ do____	1,365	1,560

The calibration series made with two-component systems and previously discussed do indicate the applicability of the method to the study of mixtures whose prime constituents can be obtained and used as standards. This is particularly the case in the study of bauxites where pure gibbsite nodules may be selected from the material and used as a standard. The method may also be very useful in studying the variations of clay deposits encountered during prospecting or actual mining. Where intermediate quantities of a mineral are present in a mixture, the error in the calculated mineral percentage which would be caused by the use of an incorrect standard will not usually be more than ± 5 percent.

COMMERCIAL CLAYS
KAOLINS

Despite its limitations, the thermal analysis method is useful in studying the clays that are commonly used in the ceramic and other fields. Differential thermal records were made of many kaolins, and several typical curves are reproduced in figure 16.

Putnam (Fla.)

No Karb (Ga.)

Pioneer (Ga.)

Thomas (Ala.)

Peerless (S. C.)

Sparks (N. C.)

Zettlitz (Czech.)

Newport (Tenn.)

200   400   600   800   1,000

TEMPERATURE, °C.
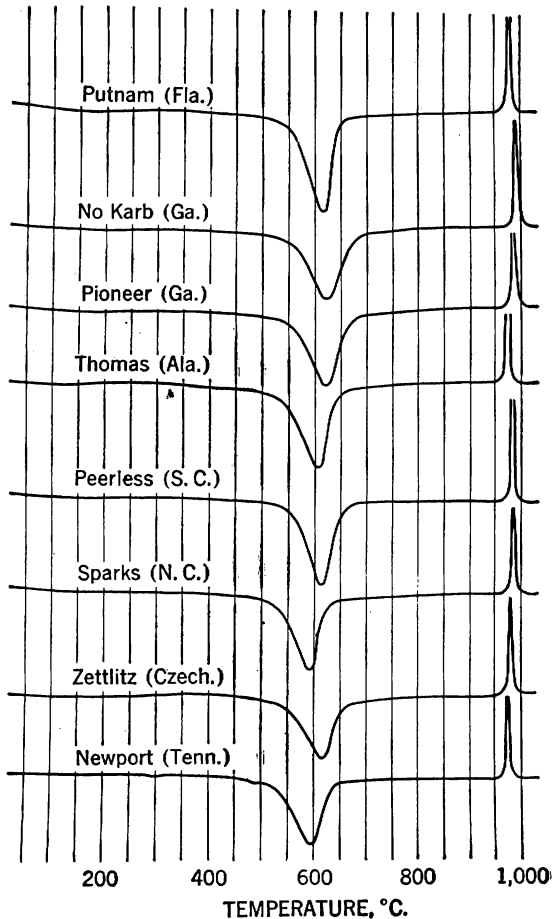
FIGURE 16.—Thermal analysis curves of typical kaolins, scale C.

These curves are characterized by the kaolinite peaks, and there is no indication of the presence of montmorillonite. The finer-size kaolins, such as Putnam (Fla.) kaolin and Thomas (Ala.) kaoiin, are marked by a relatively steep slope after the peak, while the coarsest clay, No-karb, returns more gradually to the zero deflection line. The kaolin obtained from a prospect pit near Newport, Tenn., is very plastic and gave a test for montmorillonite when treated with benzidine (22). The fact that thermal analysis gives no indication of the presence of montmorillonitic material substantiates the belief of Hauser and Leggett (18) who suggest that the benzidine test is not reliable to definitely confirm the presence of montmorillonite.

The areas of the peaks for various typical kaolins are included in table 9.

TABLE 9.—*Thermal data for typical kaolins*

Name of clay	Location of deposit	Peak temperature, °C.	Endothermic area, mm.²	Exothermic area, mm.²
Sparks	North Carolina	595	5,650	1,380
Putnam	Florida	615	7,250	1,480
Thomas	Alabama	610	6,150	1,500
Zettlitz	Czechoslovakia	615	5,450	1,370
Peerless	South Carolina	615	6,070	1,550
Pioneer	Georgia	620	6,350	1,760
No-karb	do	615	6,400	1,690
Gordon	do	620	6,100	1,560
Mean value			6,190	1,530
Max. deviation from mean___percent			6.6	7.5
Aver. deviation from mean___ do.			17.0	14.5

All of these clays are comparatively pure kaolins, so the discrepancies obtained cannot be attributed to varying kaolinite content alone. Nor is it a question of particle size, since the Alabama and Florida as well as the Zettlitz are fine-grained kaolins.

Unrefined kaolin crudes show relatively smaller peaks, and approximate kaolinite percentages can be obtained by using the mean value given in table 9 as the basis for a linear percent kaolin vs. peak-area relationship. The other constituents of a crude kaolin, such as feldspar, mica, or quartz, are not determined by the usual thermal analysis except as inerts.

BALL CLAYS

Ball clays constitute an important class of ceramic clays. In general, they are less pure than the kaolin and quite often are accompanied by some organic matter. They are very plastic and usually of finer grain size than the kaolins. A few representative curves for ball clays are given in figure 17. The ball clays usually show a broad exothermic peak with its maximum near 400° owing to the combustion of organic matter. The low-temperature peak near 150° C. is more pronounced than in the case of kaolins, indicating a finer grain size with more adsorbed water. Tennessee No. 5, Tennessee No. 9, and C. and C. ball clays from western Kentucky and Tennessee have low-temperature exothermic
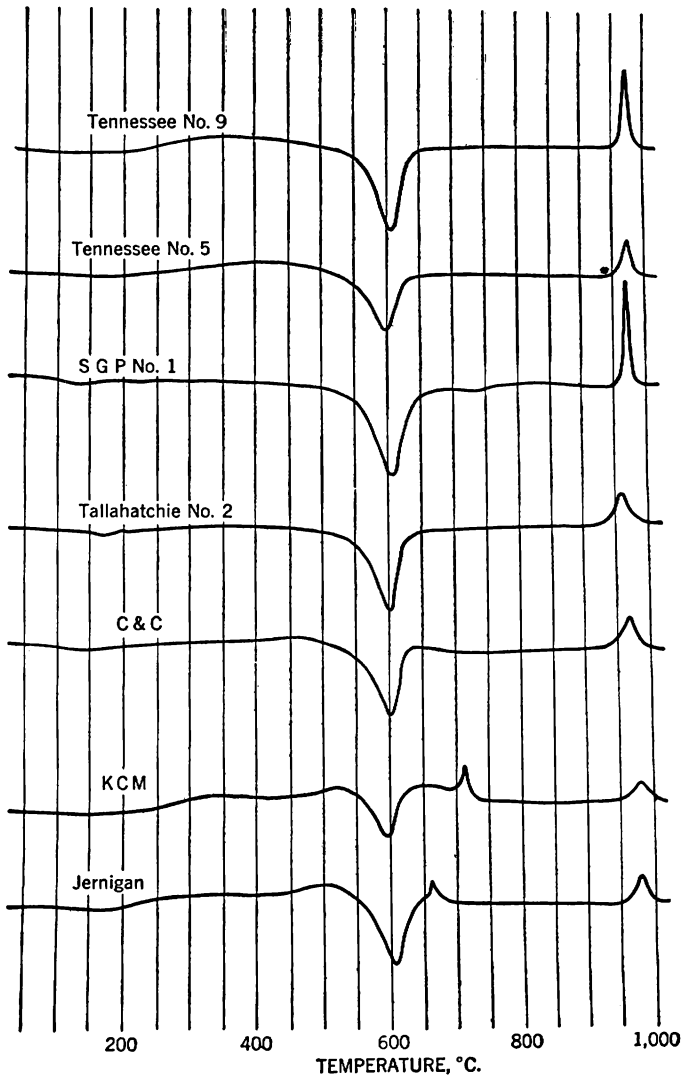
FIGURE 17.—Thermal analysis curves of typical ball clays, scale C.

peaks because of varying organic contents, as well as the char-
acteristic kaolin peaks. ' The curves for the light-firing, weak
No. 1 S.G.P. ball clay and the extremely plastic Tallahatchie
(Miss.) ball clay indicate some bentonitic content, with probably
more than 5 percent in the sample from the latter location.   The
two final curves, KCM and Jernigan, are more complex, having,
in addition to the kaolin and organic-matter peaks, another exo-
thermic peak at 710° in the case of KCM ball clay and one at 660°
in the Jernigan curve.   These additional peaks do not correspond
to any of the standard minerals and may be due to the presence of
bituminous or similar organic material with a relatively high

combustion temperature. The areas of kaolin peaks can be used to give the approximate kaolinite contents noted in table 10.

TABLE 10.—*Approximate kaolinite contents of typical ball clays*

Clay:	Producer	Approximate kaolinite content, percent
Jernigan	Spinks Clay Co	65
K. C. M.	Ky.-Tenn. Clay Co.	65
Tenn. No. 5	do	70
Champion and Challenger	Spinks Clay Co.	70
Tenn. No. 9	Ky.-Tenn. Clay Co.	80
Tallahachie	Tallahachie (Miss.) Clay Co.	80
No. 1 S. G. P.[1]	Ky.-Tenn. Clay Co.	90

[1] This ball clay fires to a near white color far lighter than the usual ball clay but is likewise lower in plasticity. It is quite similar to certain kaolins such as Thomas (Ala.) kaolin.

These values for kaolinite content are at the best only accurate to within ± 5 percent; but in three cases where the Al_2O_3 content was determined, the agreement is fair if all Al_2O_3 is attributed to kaolinite (and montmorillonite when found thermally). This correlation is shown in table 11.

TABLE 11.—*Alumina contents of typical ball clays*

Clay:	Al_2O_3, percent Chemical	Thermal [1]
Tennessee No. 5	30.8	28.0
Tennessee No. 9	29.4	31.5
S. G. P. No. 1	37.8	36.5

[1] Calculated from kaolinite content.

FRACTIONATION OF GEORGIA KAOLINS

In analyzing any clay, common practice is to use a single representative sample of all particle sizes. Both Norton (*38*) and Grim (*14*) have stressed the desirability of fractionating a clay so as to concentrate various minor components and thereby facilitate study of the clay. The fractionation of a clay by sedimentation alone is a different process from preparing different-particle-size fractions of the same mineral constitution by grinding a coarse fraction as described previously. To illustrate the application of the combined fractionation and thermal analysis procedure, Pioneer (Ga.) kaolin was split into several particle-size fractions by means of a Sharples supercentrifuge using tetrasodium pyrophosphate as a dispersant, and differential thermal records were made. The curves are presented in figure 18, and the numerical data are summarized in table 12.

TABLE 12.—*Thermal analysis of fractionated Georgia kaolin*

Fraction, microns	Kaolinite, percent	Bentonite, percent	Inert material, percent
> 20	80		[1] 20
5–20	90		[1] 10
1–5	100		
0.5–1	95		[1] 5
0.2–0.5	90	10	
0.1–0.2	85	15	
0.05–0.1	55	45	
< 0.05	30	70	

[1] By difference.
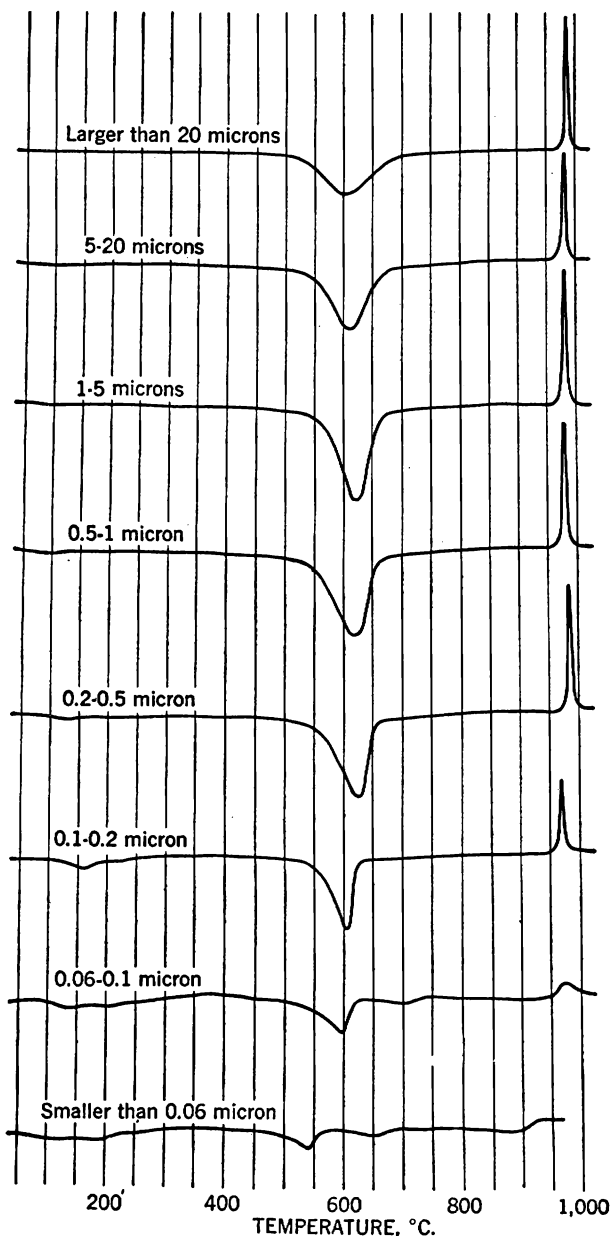
FIGURE 18.—Thermal analysis curves of fractionated Pioneer (Ga.) kaolin, scale C.

The coarse fractions are predominantly kaolinite, with small percentages of inert material, presumably free silica. The indicated excess silica content of approximately 5 percent for the entire clay is probably high. As the particle size decreases, increasing amounts of montmorillonite appear. The mineral percentages for the finer fractions are very approximate and based upon the particle-size results shown in table 7.

As only a small quantity of the entire clay content is finer than 0.2 micron, the montmorillonite content of the whole clay is less than 2.0 percent, but additions of 2 to 5 percent may greatly enhance the plastic properties of kaolin (50). Many clays with abnormally high plasticity may possess a small bentonite content which is not detectable when the total clay sample is analyzed thermally, by X-ray diffraction, or petrographically.

PACIFIC NORTHWEST KAOLINS

The clays of western Oregon and southwestern Washington are beginning to play an increasingly important role as ceramic raw materials. A great deal of consideration is being given to certain of them as a source of alumina, utilizing the cheap electric power available from the Bonneville Dam. These clays have been studied mainly from the geological viewpoint, and the most comprehensive data on their occurrence are summarized by Wilson and
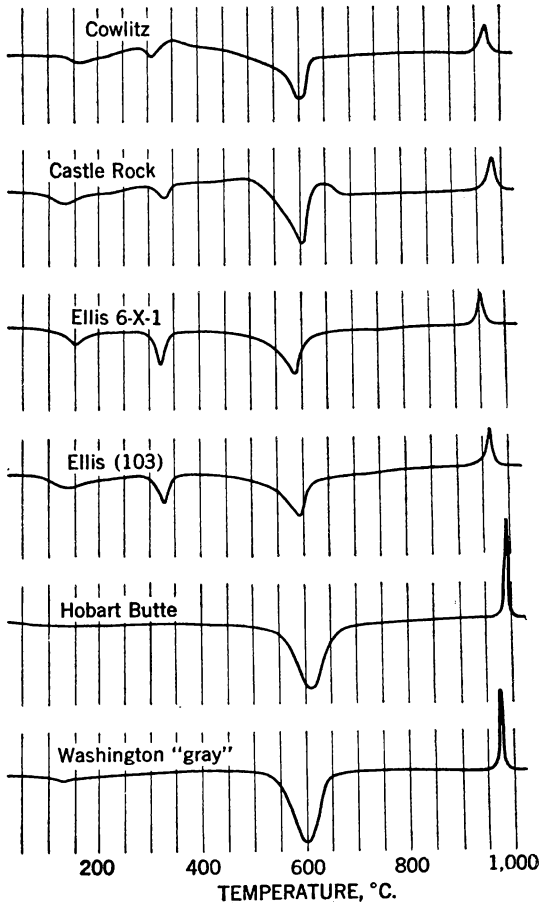
FIGURE 19.—Thermal analysis curves of high-alumina Pacific Northwest clays, scale C.

Treasher (*52*, *53*) and Glover (*10*).   The commercial deposits
range from the three-layer-type Willamina (Oreg.) black clay to
the siliceous kaolin of Hobart Butte, Oreg.   An important subdi-
vision of the kaolinitic clays consists of clays that contain appre-
ciable amounts of the aluminous mineral gibbsite.   The peaks of
goethite (345°) and gibbsite (365°) occur at nearly the same
temperature; consequently, the two minerals are difficult to dis-
tinguish thermally when present in small quantities.   Compari-
son of the chemical and thermal analyses in table 13 indicates
that the samples with the highest Fe_2O_3 content have no peak near
320°.   Those samples whose curves show this peak have compara-
tively low Fe_2O_3 contents.   For this reason, the peak is attributed
to gibbsite rather than to goethite.   In figure 19 the peak occur-
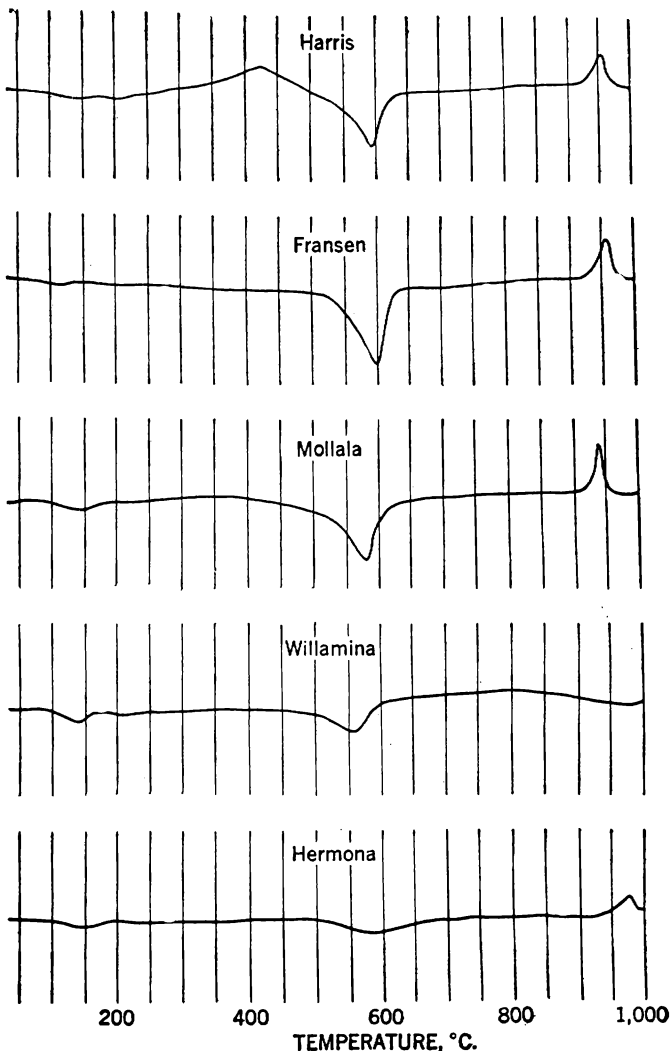
FIGURE 20.—Thermal analysis curves of several North Pacific Coast clays, scale C.

ring near 320° in some of the curves indicates the presence of this mineral desirable in alumina extraction. Table 13 gives the results of the thermal analyses as well as the Al_2O_3 and the SiO_2 contents determined chemically. Those clays whose thermal records show definite gibbsite contents, such as the Ellis or Castle Rock deposits, have an $SiO_2:Al_2O_3$ ratio less than 2.0. Those clays with high bentonite contents show the high $SiO_2:Al_2O_3$ ratios characteristic of this mineral and also excess silica as indicated by the chemical analysis. Exact quantitive determination of the montmorillonite content of these cannot be made from thermal data alone. Many of the samples which are predominantly kaolins also contain some mineral of the three-layer lattice type, as exemplified by montmorillonite. In the small quantities indicated by the thermal results, it is virtually impossible to determine whether any of the iron oxide is contained in a lattice structure such as that of nontronite.

TABLE 13.—*Analyses of Pacific Northwest kaolins*

| Clay | State | $SiO_2:Al_2O_3$, chemical | Al_2O_3, percent | | Kaolin | Bentonite | Gibbsite |
			Chemical [1]	Thermal			
Cowlitz [2]	Washington	1.97	36.0	28.5	60	5	5
Castle Rock (A) [3]	---do-------	1.96	34.8	34.0	70	5	7
Ellis (6–x–1) [3 4]	Oregon------	1.73	36.0	32.0	50	5	15
Ellis (103) [3 4]	---do-------	1.86	36.2	30.0	55	5	10
Hobart Butte [4]	---do-------	2.40	34.5	35.5	90	---------	---------
Washington Gray [5]	Washington	2.14	36.7	35.0	85	5	---------
Harris [2]	---do-------	3.35	26.3	26.0	60	10	---------
Fransen (1d) [4]	Oregon------	2.77	31.3	28.0	70	---------	---------
Mollala [4]	---do-------	2.30	33.1	29.0	70	5	---------
Willamina [4]	---do-------	6.5	19.4	---------	------	[6] High	---------
Hermona [3]	California	8.20	15.3	---------	25	do.	---------

[1] H. H. Shell, analyst.
[2] Sample from Joseph Pask, University of Washington.
[3] Sample from Gladding-McBean Co., Los Angeles, Calif.
[4] See ref. 53.
[5] Sample from Sheldon Glover, Washington Division of Mines, Olympia, Wash.
[6] Thermal analysis indicates high illite.

TABLE 14.—*Chemical analyses of Pacific Northwest kaolins*[1]

Clay	Moisture loss H_2O–110°	Ignition loss	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Total
Cowlitz	2.59	14.88	41.88	36.04	1.98	2.42	0.40	0.5	100.7
Castle Rock (A)	3.34	16.49	40.20	34.79	1.78	2.47	.40	.4	99.9
Ellis (6–x–1)	5.91	16.05	36.20	35.96	3.35	1.87	.56	.4	100.3
Do. (103)	4.99	15.28	39.74	36.20	1.96	1.78	.62	.5	101.1
Hobart Butte	.41	12.57	49.58	34.53	.29	2.80	.00	.7	100.9
Washington Gray	1.0	13.4	46.1	36.7	.4	2.5	.2	.0	100.3
Harris	2.62	12.15	52.18	26.33	3.92	1.21	1.24	.52	100.2
Fransen (1d)	1.20	12.02	51.22	31.34	2.92	1.82	.00	.4	100.9
Mollala	3.26	12.73	44.98	33.09	3.03	1.92	.44	.5	99.9
Willamina	.32	4.43	70.40	19.41	.19	1.02	1.00	.58	97.4
Hermona	2.45	6.70	74.46	15.34	.23	.13	.56	.7	100.6

[1] H. R. Shell, analyst.

Comparison of the alumina as determined thermally and chemically shows fair agreement but with thermal values consistently low. Part of this difference is due to the presence of alumina in minerals not determined by the thermal method. In addition, the large deviations observed in the thermal areas of kaolins in

table 9 give rise to the possibility that the average kaolin area from that table is not correct for these clays.   The thermal method does not always give the alumina content quantitatively but is very useful to obtain a preliminary classification and a semi-quantitative mineral analysis.

BAUXITES

North American bauxites usually consist of a mixture of dia-spore, gibbsite, kaolinite, quartz, and other minor minerals. Chemical analysis does not give enough data to permit determination of the mineralogical composition of these ores.   Differential thermal analysis finds, therefore, a very useful field of application in the mineralogical study of bauxites and high-alumina clays
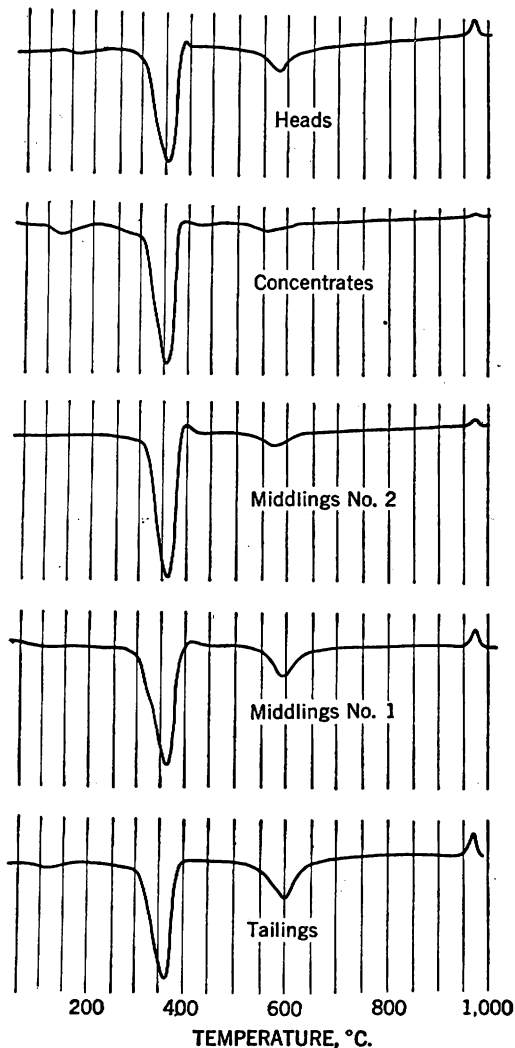
Figure 21.—Thermal analysis curves of bauxite flotation products, scale C.

(*36*).   In the flotation purification of bauxites (5), it is not always possible to get a complete picture of the progress of the beneficiation by chemical analysis alone.   The thermal curves for a series of flotation products are given in figure 21.   The method of rationalizing a mineralogical analysis which was adopted is as follows: The amount of accessory minerals, such as ilmenite, goethite, and siderite, was calculated from the available chemical analysis.   The gibbsite and kaolinite contents were determined thermally by using the 360° C. and 980° C. peaks, respectively.

TABLE 15.—*Calculated mineralogical analyses of bauxite beneficiation products from chemical and thermal data, percent* [1]

Fraction	Weight	Gibbsite [2]	Kaolinite [2]	Diaspore [2]	Quartz	Siderite [3]	Ilmenite [3]	Goethite [3]	Total
Heads___	_____	67.0	18.2	5.0	.8	3.5	4.4	0.7	99.6
Concentrates__	34.6	76.8	4.3	2.7	2.0	7.2	5.3	1.2	99.5
Middlings No. 2__	29.9	77.0	11.0	.3	2.7	3.0	4.5	.5	99.0
Middlings No. 1	14.9	59.5	20.2	11.3	3.5	.8	3.7	.7	99.7
Tailings__	20.6	51.3	25.5	12.9	6.0	.5	3.5	.5	100.2
	100.0								

CALCULATED DISTRIBUTION OF COMPOSITE HEADS SAMPLES

Fraction	Weight	Gibbsite [2]	Kaolinite [2]	Diaspore [2]	Quartz	Siderite [3]	Ilmenite [3]	Goethite [3]	Total
Concentrates__		26.5	1.5	.9	.7	2.5	1.8	.4	34.3
Middlings No. 2___		22.9	.3.3	.9	.8	.9	1.3	.2	30.3
Middlings No. 1___		8.9	3.0	1.7	.5	.1	.6	.1	14.9
Tailings		10.6	5.3	2.6	1.2	.1	.7	.1	20.6
Composite [4]		68.9	13.1	6.1	3.2	3.6	4.4	.8	100.1

[1] Chemical data supplied by L. H. Berkelhamer, Southern Experiment Station, Bureau of Mines, Tuscaloosa, Ala.
[2] From thermal data.
[3] From chemical data.
[4] Compare with distribution in heads above, with which the composite should agree.

The endothermic peak at 600° C. was corrected for kaolinite, and the remaining area was attributed to diaspore.   The silica in the bauxite which is not required by kaolinite was assumed to be free quartz.   As the sum of the mineral percentages usually differed from 100 percent, the minerals—except for those determined directly from chemical analysis, such as goethite, etc.—were corrected by a simple ratio to make the total 100.   Despite these assumptions, the comparison in table 15 between the calculated composite sample and the analyzed heads was encouraging.   The main discrepancy between the heads and the composite of the products exists in the total kaolinite and quartz, the errors for these two having opposite trends.   As the quartz percentage depends on the thermally determined kaolinite value the error probably lies in the latter determination.   The alumina content derived from thermal methods checks well with that from chemical analysis as shown in table 16.   In addition, the gibbsitic alumina checks well with the alumina available for extraction by the Bayer method as determined by treatment of the bauxite with hot caustic solution.   The method of rationalization described above utilizes

some chemical data because of the limitation of the thermal method to minerals which show definite thermal reactions. The thermal method alone does give, as stated before, a semiquantitative picture of the mineral constitution of the bauxite ore.

TABLE 16.—*Alumina content of bauxite beneficiation products, percent*

	Hydrous alumina [1]	Alumina from gibbsite (thermal)	Total Al₂O₃ (chemical) [2]	Total Al₂O₃ (thermal) [2]
Heads_____	43.6	44.0	53.6	54.7
Concentrates_____	48.3	50.0	55.2	53.8
Middlings No. 2_____	47.1	50.8	56.7.	55.2
Middlings No. 1_____	40.8	39.0	55.3	55.9
Tailings_____	33.8	33.6	52.8	53.0

[1] By autoclave digestion with caustic soda.
[2] Included all Al₂O₃, hydrous and silicate.

MISCELLANEOUS SAMPLES

A few miscellaneous samples that have been submitted for thermal analysis are included as further illustrations of the application of the method. The curves are shown in figure 22. The thermal curve of "montmorillonite" from Alzcapozales, Mexico, indicates only a minor amount of this mineral. The major constituent is illite, as shown by the large peak at 550° C. and the lack of an exothermic peak at 980° C. Another misnamed sample is the "beidellite" from San Diego, Calif. This material is essentially a fairly pure montmorillonite. The slight dip at 400° is probably due to the presence of iron oxides, and optical examination of this mineral led to an incorrect identification, as noted by Grim (*15*). The thermal analysis of a sample from Bedford, Ind., called "allophane" shows the presence of a large amount of gibbsite, approximately 40 percent, with a small halloysite or kaolinite admixture which causes the peak at 530° C., and allophane with the characteristic single low-temperature endothermic peak and high-temperature exothermic reaction. The fuller's earth has the characteristic curve of attapulgite, which indicates that this substance is structurally unique (*4*) rather than being a mixture of the more common clay minerals. In contrast to the fuller's earth, the curve of the typical Georgia bleaching clay in figure 22 indicates a mixture of montmorillonite and some other mineral, probably illite, since no 980° C. exothermic peak is present.

CONCLUSIONS

1. The thermal analysis method is quantitatively applicable (± 5 percent) to the determination of the mineral constitution of mixtures whose prime constituents can be obtained and analyzed individually to establish standard peak areas.

2. The thermal analysis method is applicable to the semiquantitative (± 10 percent) or qualitative study of the mineral constitution of natural clays and other aluminosilicate formations. However, the use of petrographic, X-ray, or chemical analysis in
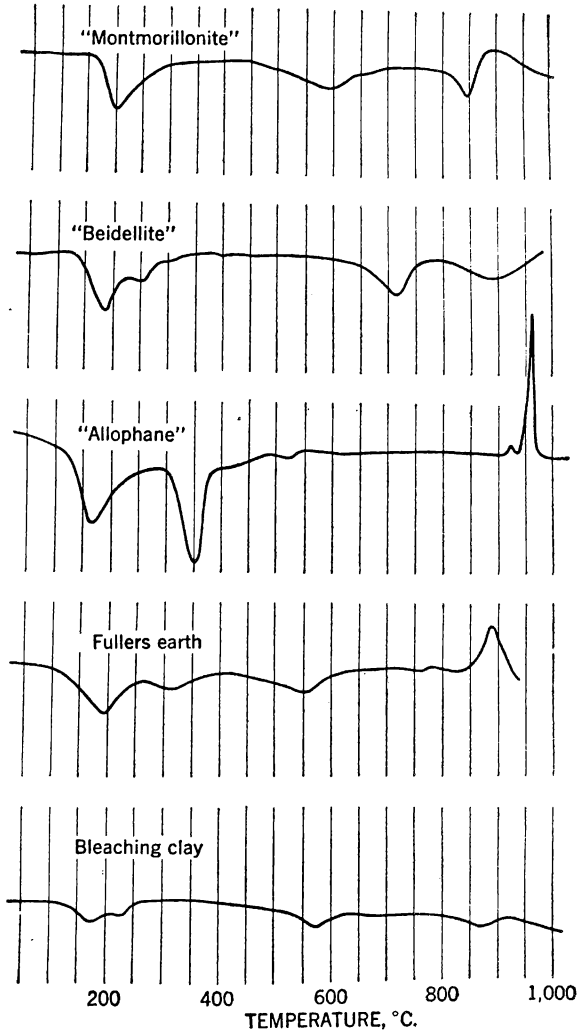
FIGURE 22.—Miscellaneous thermal analysis curves, scale A.

addition to thermal studies is recommended whenever feasible to increase the validity of the mineral analysis.

3. The thermal analysis method is applicable to the study of bauxite ores and particularly to the progress of bauxite ore beneficiation because the aluminum-containing minerals not amenable to solution in the Bayer process—diaspore and kaolinite—can be easily distinguished from the desirable gibbsite by thermal methods.

4. The peaks of various samples of montmorillonite may differ either in position or total area, making quantitative determination of montmorillonite in a mixture uncertain.

5. Decrease of particle size or increase of surface in kaolin, as

by fine grinding, decreases the reaction energy associated with the differential thermal peaks and lowers the temperature at which the endothermic decomposition of kaolin occurs.

6. Because of the dynamic character of the differential thermal method, the thermal peak of any mineral is displaced toward lower temperatures as the area of the peak becomes smaller.

7. The fractionation of clay into different particle sizes and the subsequent study of each fraction individually are advocated when a complete mineral investigation of any one clay is desired.

8. Change of rate of temperature rise from 5° to 20° C. per minute affects the position and shape of the thermal peak but does not noticeably change the area associated with the thermal effect. However, it is recommended that all determinations be made at a constant rate, as has been done in this work.

9. Certain clays occurring in western Oregon and southwestern Washington vary widely in mineral composition, ranging from pure kaolinite through admixtures of kaolinite with gibbsite, montmorillonite, and illite to fairly pure specimens of three-layer-lattice minerals.

10. Commercial kaolins and ball clays were found to be predominantly kaolinite. The organic content of the latter is shown by an exothermic peak in the thermal curve. The finer the grain size the more pronounced is the initial 150° C. low-temperature endothermic peak due to the larger amount of adsorbed water on the increased surface.

AN APPARATUS FOR
DIFFERENTIAL THERMAL ANALYSIS [1]

By Louis H. Berkelhamer [2]

INTRODUCTION

The method of differential thermal analysis as suggested by Le Chatelier (*32*) in 1887 has come to the fore of more recent date as an outstanding means of studying the constitution of various substances, particularly clays, soils, and miscellaneous hydrous materials (*2, 15, 21, 23, 30, 35, 36, 37, 41*). The literature ably discusses the applications and results obtained but has paid too little attention to specific details of construction of the apparatus. A knowledge of the apparatus is important to an experienced research man and is of extreme usefulness to the novice who ventures into this field of analysis. Further, it is generally acknowledged that the variations in design and conditions of operation are essential causes for differences in characteristic temperatures as reported by various investigators. A step forward in eliminating such differences is publication of the details of construction and operation of a simple, inexpensive apparatus that has proved useful at the Southern Experiment Station of the Bureau of Mines, United States Department of the Interior, working in cooperation with the University of Alabama, Tuscaloosa, Ala.

ACKNOWLEDGMENTS

The work described was performed at the Southern Experiment Station, Tuscaloosa, Ala., W. H. Coghill, supervising engineer. Acknowledgment is made to Homer S. Hardman, senior general mechanic, who constructed parts of the apparatus under the supervision of Gaines T. Adams, foreman general mechanic.

DIFFERENTIAL THERMAL METHOD

The differential thermal method of analysis detects and indicates the thermal effects that accompany the loss of water, decomposition, or changes in crystal structure that may occur when a substance is heated. The procedure, in brief, is one in which a sample being analyzed is set adjacent to a sample of a thermally inert material and both are heated at a fairly rapid and same constant rate of temperature rise. A temperature of 1,000° C. is usually reached, or as close to fusion as is allowed by the materials of construction of the equipment. A differential thermocouple is used to measure the difference in temperature between the two

samples, and a regular thermocouple measures the rate of temperature rise.   Temperatures may be recorded intermittently by the operator, using a potentiometer, or continuously recorded by the use of a reflecting galvanometer and photographic recorder. Plotting of the data or use of the photographic recorder arrangement results in a curve that indicates the differential temperature at any point along the rate of heating.   If the sample being studied undergoes any changes during heating, such as liberation of water or change in crystallinity, it is evidenced by the differential temperature readings.   These appear as peaks, endothermic or exothermic, as the case may be, on the differential thermal analysis curve.   The peaks are characteristic for most thermally active minerals and materials; and, as in X-ray diffraction, a mixture will give a superimposition of characteristic effects of individual components.

DESIGN OF APPARATUS

The apparatus designed and constructed for differential thermal analysis was patterned in general after that of Norton (*37*) but also utilized suggestions made by others (*15, 21, 35*).

The details of construction are self-evident in figures 23, 24, and 25.   Photographs of the apparatus (figs. 26, 27, and 28) augment the drawings.   In brief, the equipment consists of a tubular furnace arranged on horizontal slides and a stationary holder for a sample block (figs. 23, 26, and 27).   The rate of temperature rise in the furnace is controlled by a variable transformer (Variac) driven by a motor (figs. 23 and 28).   The differential thermocouple coming from the sample block leads to an ice junction and then joins in series with a variable resistance and a reflecting galvanometer (figs. 23 and 25).   A housing encloses the galvanometer (figs. 25 and 28) and is open at one end to receive the recorder (figs. 24 and 27).   The recorder contains a roll of photostat paper which moves slowly by a horizontal slit opening in the recorder face.   The travel of the paper is controlled by a combined recorder-drive and furnace-control mechanism (figs. 23 and 28).   A vertical slit of light is trained upon the reflecting galvanometer mirror by means of a lamp (fig. 25).   This slit of light intersects the horizontal slit opening on the recorder face when reflected and traces a point of light on the moving photostat paper.   The rate of temperature rise in the furnace is measured by a thermocouple leading from the sample block to an ice junction and then to a portable potentiometer.   The 50° C. intervals of temperature rise are flashed onto the photostat paper by means of a push-button and flash-bulb arrangement (figs. 25 and 28).

RECORDER

The recorder was designed to accommodate a 350-foot roll of 11-inch-width photostat paper (grade R, Photostat Corporation, Rochester, N. Y.).   The paper is also available in 13-, 14-, 15-, and 18-inch widths, and if desired, the recorder and accompanying enclosing housing box can be redesigned for the larger paper,

FIGURE 26.—Sample block with holder and furnace.

FIGURE 27.—Recorder, furnace, and sample-block holder set-up.

To 110 v. power

Switch box

To furnace

Variac,
type 200-C
115 v. 5 a.

2-jaw
coupling

Coupling
and shaft

Pointer on
Variac knob

$7'' \times 3\frac{1}{4}'' \times 1''$

200:1
Boston
reductor,
type LA-200

Split cast-iron
pillow block,
Boston PPB-16

$\frac{9''}{32} \times \frac{1}{2}''$, 2-hole porcelain insulators, $\frac{5''}{32}$ bore

$\frac{5''}{32}$ round double-bore, $\frac{3''}{64}$ porcelain insulators

18-8 stainless-steel sample
block (from 1" shaft)
and cover

Thermocouples
to ice-filled
vacuum bottle

$\frac{1}{4}''$ diam.

2"

1"

$\frac{11''}{32}$

$\frac{1''}{2}$ $\frac{1''}{2}$

$\frac{3''}{8}$

$\frac{11''}{16}$

$\frac{3''}{32}$

C

B

C

22-gage Cr-Al-Cr
differential
thermocouple

22-gage Cr-Al
thermocouple

1"

$\frac{11''}{16}$

$\frac{3''}{32}$ diam. porcelain insulator, $\frac{1''}{32}$ bore

B

$\frac{7''}{32}$

$\frac{9''}{32}$ $\frac{9''}{32}$

$\frac{11''}{64}$ diam.

SECTION C-C

SECTION B-B

Details of sample block and thermocouple set-up

Bodine motor,
type NCI 12R
$\frac{1}{70}$ hp. 1650 r.p.m.
110v. .23 a.
with 300:1
reductor

Spur gear,
Boston ND-144
meshing with
Boston
ND-24B,
gear ratio
6:1

6"

Recorder
drive

$14\frac{1}{2}''$

Details of recorder drive and furnace control

$8\frac{1}{2}''$ diam. $\times \frac{3}{8}''$ transite

$8\frac{1}{4}''$ O.D. $\times \frac{3}{16}'' \times 8''$ steel shell

$2\frac{1}{8}''$ layers rammed refractory
or shaped B & W K-30

2" diam. $\times \frac{7}{8}''$
B & W K-30

To variable
transformer

Powdered
Sil-O-Cel fill

A

Drill $\frac{1}{2}''$

Drill $\frac{3}{32}''$

$\frac{1}{4}'' \times 10''$ tie bolts

$\frac{1}{4}''$ bolt and wing-nut
for wiring

$4'' \times 8'' \times \frac{1}{8}''$ back and front
steel end plates notched as
indicated; holes in back plate
drilled oversize for adjustment

$\frac{3}{4}''$ rods fastened to base
at ends with slide stops

4" diam. steel flange with $2\frac{1}{2}''$ diam. neck, 2" bore;
drill 4 oversize holes for $\frac{1}{4}''$ bolts to allow position
adjustment

2" O.D. $\times \frac{1}{8}''$ steel tube

9"

B & W K-30
refractory plug

$3\frac{1}{4}''$ $5\frac{3}{8}''$

2" angle

2" $3\frac{1}{4}''$ 23" $1\frac{3}{4}''$

30"

$1\frac{1}{2}''$

$11\frac{1}{2}''$ 6" $1\frac{1}{2}''$

9"

A

2" I.D. $\times \frac{3}{8}'' \times 3\frac{3}{4}''$ alundum core wound with
6 turns coiled Nichrome alloy V (44' B & S No. 20 on
arbor) wire and coated with alundum cement

SECTION A-A

FIGURE 23.—Construction details of furnace, sample block with holder, recorder drive, and furnace control.

SECTION D-D

Brass bushing $1\frac{1}{2}"$ diam.
$\frac{5}{8}"$ bore, running fit

Brass set collar $1\frac{1}{8}"$
diam. x$\frac{3}{8}$"$\frac{5}{8}$"bore

$\frac{5}{8}"$ steel shaft

Brass flange
2" diam. x$\frac{3}{16}$",
$\frac{5}{8}"$ bore running fit

Wood construction unless otherwise indicated

Accommodates 350' roll of 11" photostat
paper obtained from Photostat Corporation

4-8" square doors; hinged at back;
catch-locks; with tapered closing fit;
door cracks on inside of box covered
by light-seal edging.

SECTION B-B

$\frac{1}{4}"$ screws, shank threaded to receive wing-nuts
for 10 slots and holes shown on front pieces

Thin rubber gasket glued
to edge, facing front pieces

$\frac{1}{2}"$ diam. steel rod
covered with rubber
tubing, mounted for
rotation against 1"
diam. wood rod

Cover with felt
or velvet to
bring paper
in contact
with edge of
slit on front
pieces

SECTION A-A

SECTION C-C

$\frac{1}{4}$" x $\frac{1}{2}$" slot

Thin metal strips
to give sharp edge

$\frac{1}{4}$"hole

FRONT PIECES
To fasten on front with wing-nuts

FIGURE 24.—Construction details of recorder for differential thermal analysis.

All wood construction, lumber dressed to $\frac{3}{4}$" thickness; all outside joints made lightproof

FIGURE 25.—Construction details of housing for galvanometer and recorder.

FIGURE 28.—Recorder drive and furnace control and box housing for galvanometer and recorder.

using the same basic design given in figures 24 and 25. (In this instance, it would be advisable first to obtain a spool upon which the paper is purchased and make dimension changes accordingly.) Two items not shown in the details of figure 24 are shown in figure 27. First are the rubber gasket flaps *A*, which are tacked on around the recorder face as shown and act as a light seal when the recorder is placed in the open end of the housing box. Second are the hooks and eyes *B*, that are placed on both the recorder and housing as shown and are used to tie the recorder in place with the housing.

An empty photostat-paper spool is necessary to act as a take-up connected to the recorder drive.

FURNACE

Construction of the furnace, as shown in figure 23, gives very uniform heating and with the control described allows a rate of heating of 11° to 12° C. per minute (90 minutes for a run from room temperature to 1,000° C.) with a slight lag in rate up to 50° C. Close reproducibility of this construction is readily possible, as evidenced by an instance wherein the refractory core and furnace winding were replaced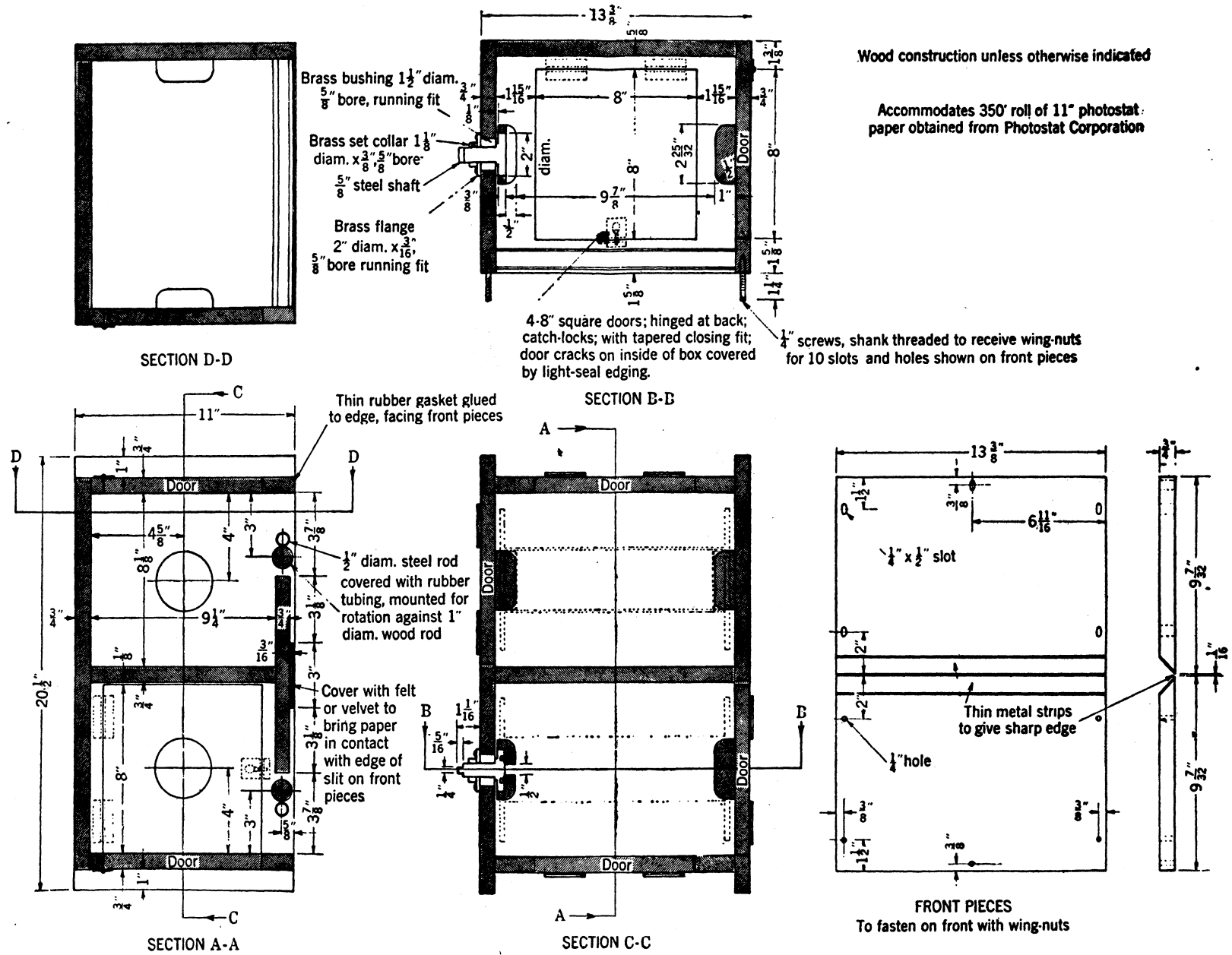 with a resulting change in heating rate of approximately ½° to 1° C. per minute (100 minutes for room temperature to 1,000° C. run). Individual runs on the furnace have varied by only approximately ± 2 minutes in total time for the run. Most of this variation occurred in the early part of a run, depending on changes in room temperature and in the heat content of the furnace at the start of the run.

SAMPLE BLOCK

Whereas according to the literature a nickel sample block appeared to be preferred, necessity forced the use of 18–8 stainless
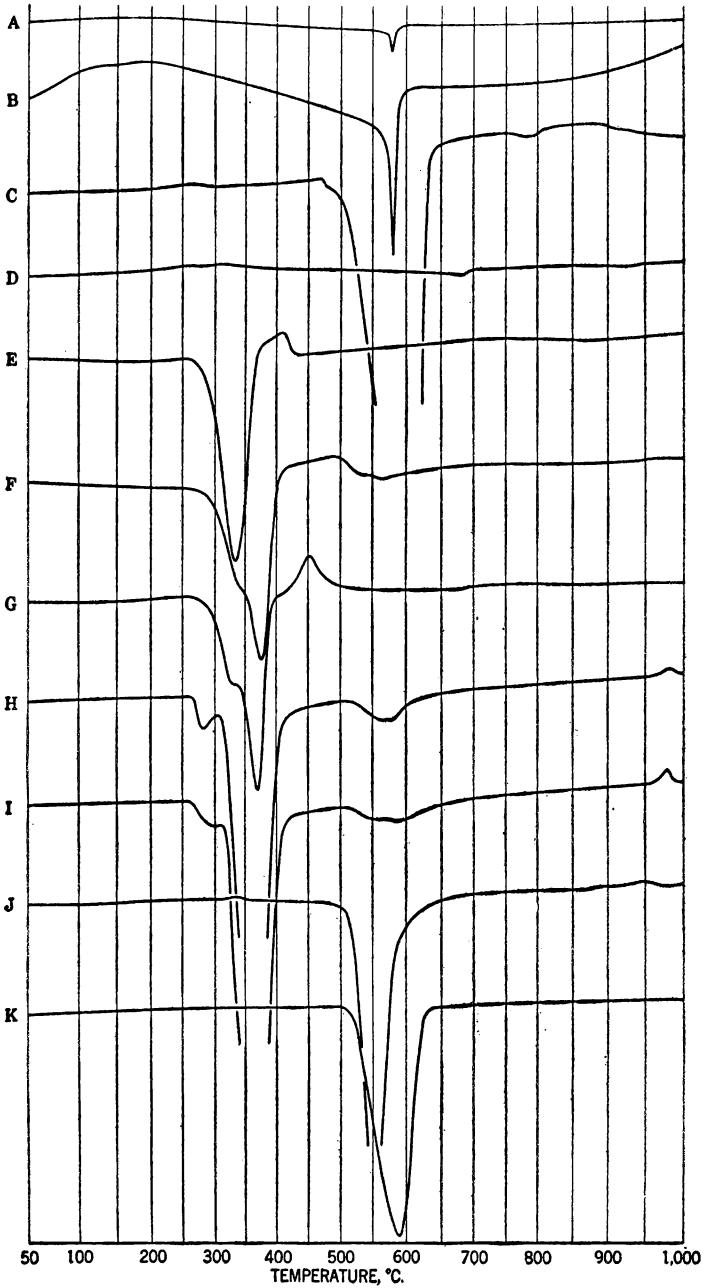
FIGURE 29.—Curves for oxides; carbonate; hydrated oxides (600 ohms resistance for all but B, which is 50 ohms): A and B, Quartz, potter's flint; C, siderite, Connecticut; D, fibrous crystalline hematite, Alabama; E, goethite, Alabama; F, limonite, Alabama; G, lepidocrocite, U. S. National Museum, Washington, D. C.; H, gibbsite, Wilkinson County, Ga.; I, bauxite concentrates (gibbsite), Saline County, Ga.; J, diaspore, Missouri; K, diaspore, Chester, Mass.

steel, and it has given admirable results.   Although slight scaling was apparent with use, the effect on results was not apparent. In fact, four different sample blocks, made to the same specifications, showed negligible differences in results, as evidenced by the rate of heating and the peak temperatures on the thermal curves of various standard samples.

THERMOCOUPLES

Chromel-alumel thermocouples (B. & S. gage No. 22) are used in preference to platinum-platinum 10 percent rhodium.   Chromel-alumel thermocouples, developing a little more than four times the voltage of platinum-platinum 10 percent rhodium for the same temperature, are more sensitive.   Excellent thermocouple life has been obtained despite the fineness of the wire.   Replacements have been made only on account of burn-outs due to temperatures accidentally exceeding 1,100° C.   Replacements of the differential couple affect only to a small extent the base line[3] of a thermal curve, and this in turn can be controlled by proper placement of the thermocouple hot-junction beads in the sample holes. It has been found that the size of the beads on the differential couple controls to a large extent the slope of the base line of a differential thermal curve.   Once the bead sizes are equalized, small changes in position of the couple in the same hole have only slight effect on the slope of the base line.   In any instance, the effect on peak temperatures for the thermal curves of standard samples is negligible.

Norton's method (*37*) of ascertaining the rate of temperature rise of the specimen by means of a separate thermocouple embedded in the center of the sample block is followed (fig. 23).   The thermocouple, so placed, indicated (fig. 29) a peak temperature of about 578° C. for the alpha-beta inversion point of quartz, which is a reasonably accurate figure (573° and 575° C. figures are usually cited in the literature) (*46*).   This peak temperature, as well as peak temperatures for kaolinite and various other samples, have been repeatedly obtained in trials with different sample blocks, thermocouples, and furnace windings.

FURNACE CONTROL AND RECORDER DRIVE

The furnace control and recorder drive (fig. 23) are constructed in one unit.   The recorder drive rotates at a speed which results in curves extending across approximately 25 inches of photostat paper, as shown in figures 29, 30, and 31.   The power for the variable transformer (Variac) and the motor drive is controlled from the same power switch, so that both can be turned on and off at the same time.   A supplementary toggle switch controlling the output of the Variac permits the recorder drive to operate in the absence of the power to the furnace.   A good precaution is the installation of a red signal light across the load end of the power switch.

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[3] The base line of a thermal curve for a sample would be the curve obtained for the same sample after it had been calcined at 1,000° C.
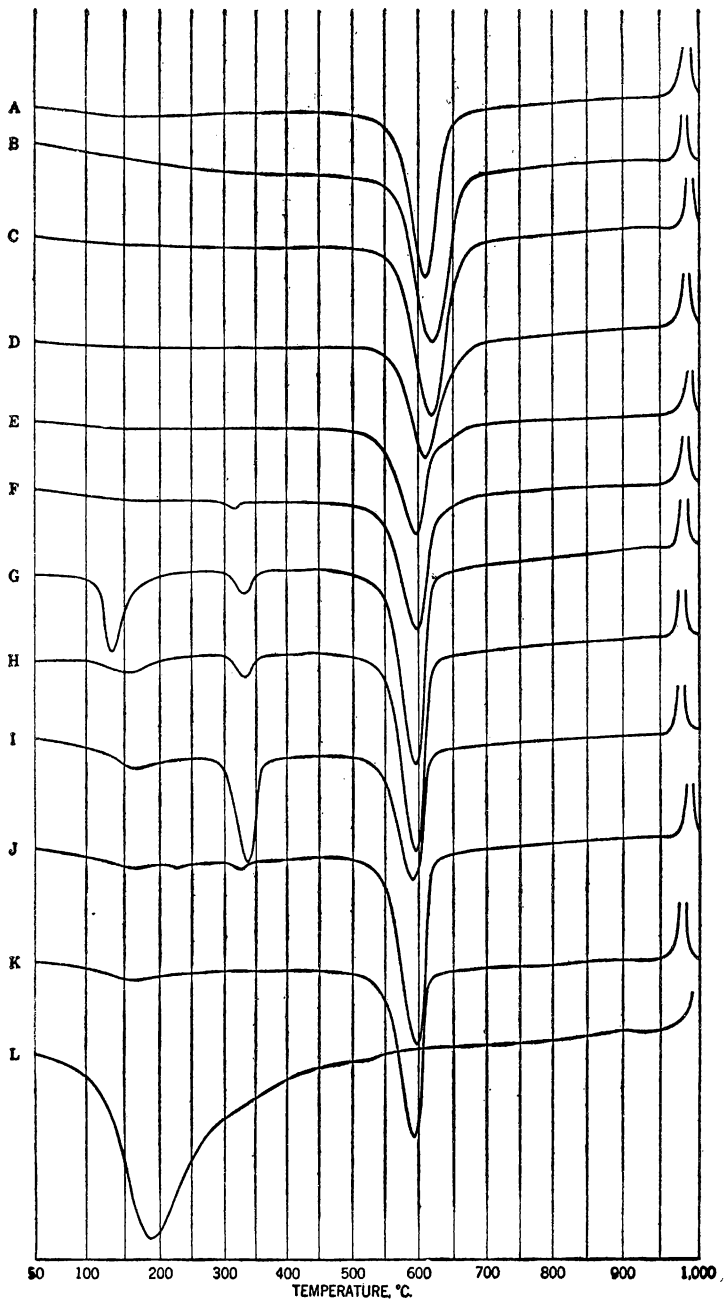
FIGURE 30.—Curves for kaolinite and halloysite clays; allophane (600 ohms resistance): *A*, Kaolin, Florida (E. P. K.); *B*, kaolin, Gordon, Ga. (M. & M.); *C*, kaolin, South Carolina (Peerless No. 1, R. T. V.); *D*, kaolin, Delaware (Milford, U. C. M.); *E*, kaolin, North Carolina (Miller, U. C. M.); *F*, kaolin, North Carolina (Kamee, Inc.); *G*, endellite (hydrated halloysite), Eureka, Utah, as received, not dried; *H*, endellite (hydrated halloysite), Eureka, Utah; *I*, halloysite, white, Bedford, Ind.; *J*, halloysite, white, Rome, Ga.; *K*, halloysite, Brazos County, Tex. (from C. S. Ross, Geological Survey); *L*, allophane, Hart County, Ky. (from C. S. Ross, Geological Survey).
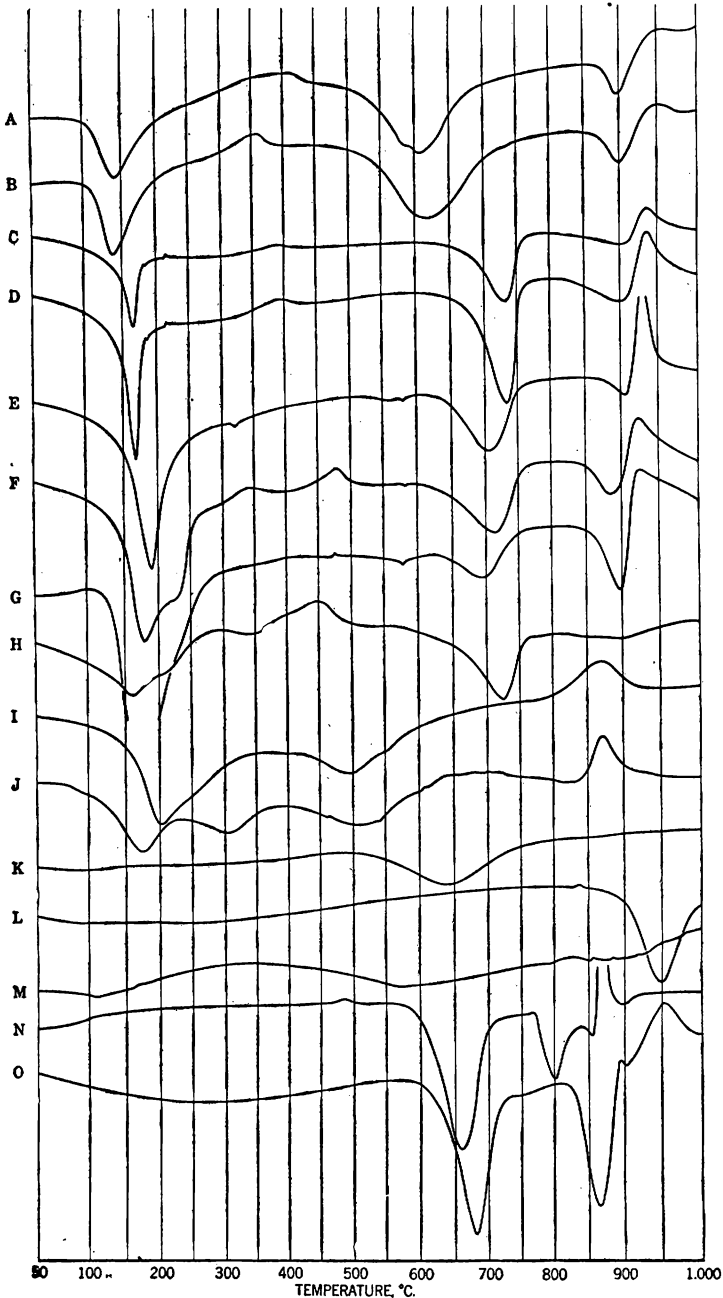
FIGURE 31.—Curves for illite and montmorillonite clays; nontronite; hydrated magnesium silicates; micaceous minerals (200 ohms resistance for all but C, which is 400 ohms: A, Illite, purified from underclay, Vermilion County, Ill, (from R. E. Grim, Illinois State Geological Survey); B, illite, puried from underclay, Grundy County, Ill. (from R. E. Grim, Illinois State Geological Survey); C and D, bentonite, 300 Volclay, Wyoming (American Colloid Co.); E, bentonite, near Little Rock, Ark.; F, bentonite, Panther Creek, Aberdeen, Miss. (American Colloid Co.); G, bentonite, Laurel, Miss.; H, bentonite, white, Pontian, Italy; I, nontronite, Sandy Springs, N. S.; (from C. S. Ross, Geological Survey); J, meerschaum, New Mexico; K, pyrophyllite, North Carolina; L, talc, Providence, R. I.; M, muscovite, Spruce Pine, N. C.; N, prochlorite, Chester, Vt.; O, sheridanite, near Sheridan, Wyo.

LIGHT SLIT AND GALVANOMETER CONNECTIONS

The slit of light projected onto the galvanometer mirror is obtained by use of a large cover glass coated with photographic opaque paint and properly mounted in the tube of the illuminating device shown in figure 25. The slit is made by running the edge of a sharp razor blade across the opaque paint surface. Setting the lamp approximately 1 meter from the galvanometer mirror gives a good, sharp image of the reflected slit of light. The image is conveniently viewed by its projection on a strip of tracing paper placed across the open end of the housing box at approximately the position of the slit opening in the face of the recorder.

When the apparatus is assembled (fig. 27), the connections of the differential thermocouple to the reflecting galvanometer are so made that deflections of the galvanometer are always in the direction of the warmer of the two sample holes in the sample block (fig. 23). This connection can be tested by touching either of the differential thermocouple beads with a warm match head.

THERMALLY INERT HOLE

The lower sample hole, as seen in figure 23 (plan view), or the hole closest to the operator, is packed with calcined alumina (−100-mesh), which acts as the necessary thermally inert material. To facilitate packing without harm to the insulating refractory plug in which the sample block is set, a small wood support is shaped to slip under the plug and take up the shock and jar due to packing. A small piece of transparent cellulose tape is kept over the top of the calcined-alumina-filled hole whenever the apparatus is not in use or during cleaning or filling of the other sample hole.

OPERATION

All samples were ground to pass 100-mesh and dried for 15 to 24 hours at 65° C. before testing.[4] A 0.50- to 0.75-gram sample was weighed and carefully tamped and packed into place in the testing hole (upper hole, plan view of sample block, fig. 23). The blunt end of a small glass stirring rod (sharp edges removed) was handy for this purpose, as well as a rounded pointed end for packing around the thermocouple. Care was taken to get as dense a packing as possible and to fill the hole completely. The top was slicked off with a spatula; and the remaining sample was weighed, giving by difference the amount used for analysis. Experience showed that the technique of packing could be developed to repeat sample weights for the same material. The stainless-steel cover was then placed over the sample holes, after the cellulose tape was removed from over the calcined-alumina-filled hole. A small level was placed on the covered sample block and the refractory plug holding the sample block rotated slightly until

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[4] Sample treatment is not a point in question in this paper; other workers (2, 15, 21, 23, 30, 35, 36, 37, 14) have seen fit to treat their samples otherwise. Except for halloysites, it has not been found to be of any advantage, in work for identification purposes, to treat a sample other than as stated above.

the block was horizontal.   The level was removed and the furnace moved on the slides to engage the refractory plug.   The resistance in series with the differential thermocouple was then adjusted. This adjustment is important since it controls the sensitivity of the galvanometer.   Such control is necessary, as pointed out by Grim and Rowland (15), because the thermal reactions of the various minerals differ in magnitude.   The reactions for kaolinite are much greater than for montmorillonite or illite, which in turn are much greater than for quartz and muscovite.   This is evident in figures 29, 30, and 31.   The effect of change in series resistance on the thermal curve of a material is brought out by comparison of curves A and B in figure 29 and C and D in figure 31.

With the series resistance adjusted, the illuminating device for the galvanometer was turned on and adjustment made to the galvanometer mirror so that the zero point was in the right place to allow all of the anticipated curve to record on the photostat paper.

Before going further, the recorder box was loaded with the roll of photostat film.   When a new roll was used, the loading was performed without recourse to a darkroom.   The roll was placed in the upper compartment of the recorder box (fig. 24), the film seal broken, and the film leader pulled out a few feet between the wooden and the rubber-coated steel rolls.   The top half of the recorder front piece was put in place, and the top screws were tightened but the bottom ones left loose.   The leader was pulled under this front piece until the paper appeared past the slit edge. Then the bottom screws of the top front piece were tightened, the leader was torn off, and the paper continued between the bottom two rolls and then thumb-tacked onto the empty spool in the bottom compartment.   The bottom front piece was then put on, allowing approximately 1 millimeter between the top and bottom slit edges.   The empty spool in the bottom compartment engaged the recorder drive by means of a small guide screwed into one end of the spool.   After the doors were closed, the exposed paper was taken up on the empty bottom spool by turning the small recorder drive shaft from the outside with a crescent wrench.   Care was taken to insure that the paper was flush against the slit edges at all times; otherwise, broad diffuse images of the record resulted.

The loaded recorder box was placed in the open end of the housing box, caution having been taken to keep the light seal flaps (A, fig. 27) on the outside, and then the hooks and eyes (B, fig. 27) were locked to tie the recorder to the housing.   The drive shaft on the recorder was then advanced until it was in position to mesh with the drive-shaft notch on the drive and furnace-controlling unit (fig. 23).   This also brought fresh paper into the position of the recorder slit.   The recorder-drive and furnace-control unit was then moved into position so that it engaged the recorder drive shaft on the recorder box.

The set screw engaging the large spur gear onto the shaft that turns the Variac dial was loosened, and the indicator of the Variac was set to slightly "before 60," according to the calibrated face. The set screw was tightened, and after making sure that the tog-

gle switch controlling the output of the Variac was on the "off" position, the main power switch was turned on. When the Variac dial indicator reached 60, the toggle switch was flipped on and the push button on the side of the housing box pushed to flash the starting line onto the photostat paper. Intervals of 50° C. were subsequently flashed onto the photostat paper as the rise in temperature of the sample was indicated by the portable potentiometer. Experimental trials showed that a proper schedule of heating rate was maintained if the Variac was always started at 60 volts output, being raised slowly according to the speed furnished by the design of the furnace control drive (fig. 23). At the end of a run to 1,000° C., the voltage output was approximately 130.

After reaching 1,000° C. the power was shut off and the recorder-drive and furnace-control unit removed by sliding back from the recorder box. A one and one-quarter advance turn was made on the drive shaft from the recorder box before it was removed from the housing box to bring the exposed paper around to where it was completely on the bottom take-up spool of the recorder. The recorder was taken into the dark room, the take-up spool removed after severing the continuous length of paper, and the record subsequently processed. A dark red safe light (Wratten Series 2) can be used without fogging the photostat paper; development time is 1 minute, or less if desired, in the developer, followed by 15 to 20 minutes in the fixing solution and a 30-minute wash.

Approximately 2 hours were required for a run, including preparation. One run was made the first part of the morning. In about 1½ hours after the run was completed, the furnace was shifted back from the sample-block holder and cooled for about 1 hour and then with an air blast for about 1½ hours until room temperature was reached (or reasonably close thereto). This allowed for a second run to be made during that same day.

APPLICATION

Some of the results obtained with the apparatus described are shown by the thermal curves of figures 29, 30, and 31. In all tests, except where otherwise indicated, the sample was dried at 65° C. for 15 to 24 hours, bottled and stoppered, and kept in a desiccator.

Comparison of the results with those of other workers must be carefully made, inasmuch as not all have used the same rate of heating. Since the endothermic and exothermic peaks are a function of both time and temperature, lower rates of heating will cause peak temperatures to be low as compared to higher rates of heating. The rates given by Norton (37) and Grim and Rowland (15) are close to that for the apparatus described in this paper, and their values may be used in comparison.

OXIDES; CARBONATE; HYDRATED OXIDES

Quartz (fig. 29, A and B) gave an endothermic peak at about 578° C. which represents the alpha to beta quartz inversion.[5]

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[5] The subject of the differential thermal analysis of quartz is treated more fully in a separate publication, Bureau of Mines Report of Investigations 3763.

This agrees favorably with values of 573° and 575° C. cited by Sosman (46). This peak temperature was found to be the same for numerous tests on four varieties of quartz tested. None of these quartz samples showed any traces of transformation of quartz to tridymite at 870° C., as Grim and Rowland (15) reported for some of their runs on quartz. Their value of 565° C. for the alpha-beta inversion-peak temperature indicates that probably their samples were heated at a little slower rate than those reported herein.

A sample of siderite (fig. 29, C) gave an endothermic reaction of extremely large magnitude occurring between approximately 500° and 630° C. with a peak temperature estimated to be approximately 600° C.

Hematite (fig. 29, D) gave only very minor irregularities in its curve, this being of no present significance except perhaps due to some impurity.

According to Norton's curve (36), goethite gives an endothermic peak temperature of approximately 425° C., whereas on Grim and Rowland's curve (15) the peak occurs at about 400° C. The curve presented here (fig. 29, E) shows an endothermic peak at about 335° C. accompanied by a small exothermic reaction at a peak temperature of approximately 415° C.

Limonite, on the other hand, shows a double endothermic reaction, according to Norton's curve (36), with peak temperatures of about 330° and 375° C. On Grim and Rowland's curve (15) a single peak is shown at a peak temperature of about 325° C. The limonite curve presented here (fig. 29, F) shows a double endothermic reaction with peak temperatures of approximately 335° and 375° C., followed by a small exothermic reaction with a peak temperature at about 490° C. and subsequently a very small endothermic peak at about 565° C. If Norton's goethite curve is in error, then it appears that in his limonite curve, as well as the one presented here, the sample is really a mixture; that is, the 335° C. peak of goethite is superimposed on the 375° C. peak of limonite. Of course, this also presupposes that Grim and Rowland's values for both goethite and limonite are in error, the limonite possibly being really goethite and vice versa. The very small endothermic peak at about 565° C. on the curve shown in figure 29, F, may be due to contaminating siderite. The goethite and limonite used in this work (fig. 29, E and F) were checked optically to corroborate the results obtained thermally.

The curve for lepidocrocite (fig. 29, G) is practically the same as that for the sample of limonite (fig. 29, F) with a slight shift of the double peak points to approximately 330° and 370° C. There is an absence, however, of the very small endothermic peak at about 565° C. and a shift in the small exothermic peak to about 450° C. This exothermic reaction, although not at the exact same peak temperature, is common to all three hydrates of iron oxide and occurs within a relatively small temperature range; it may be due to the presence of organic matter.

Gibbsite, according to Norton (37), has a distinctive endother-

mic reaction at a peak temperature of approximately 360° C., preceded by a small endothermic reaction at about 275° C. peak temperature. Grim and Rowland's curve (15) for gibbsite indicates a peak temperature of about 330° C. The sample of gibbsite represented by the curve of figure 29, H, gave a distinctive endothermic peak at about 365° C., immediately preceded by a small endothermic peak at about 280° C. This agrees well with Norton's data. At present there is no explanation for the small 280° C. endothermic peak. A similar double peak for gibbsite has been published by Pask and Davies (see page 64), although their peak temperatures are much lower owing to their very low rate of heating. The other peaks present on the curve of figure 29, H, are due to the known presence of small amounts of siderite and kaolinite and/or halloysite. The curve for a highly gibbsitic bauxite concentrate (fig. 29, I) was substantially the same as for the gibbsite just described (fig. 29, H).

Norton (37) gives an endothermic peak temperature of 550° C. for diaspore, and Grim and Rowland's (15) curve shows a peak temperature of about 575° C. Using samples from the same source as each of these workers, good checks were obtained, a sample from Missouri giving an endothermic peak at about 550° C. (fig. 29, J) and one from Massachusetts giving a peak temperature of about 585° C. (fig. 29, K). The discrepancy cannot be explained at present.

KAOLINITE AND HALLOYSITE CLAYS; ALLOPHANE

The endothermic peak accompanying the dehydration of kaolinite and the exothermic peak associated with the gamma-alumina formation reaction of kaolinite have been well-established. Norton (37) has given peak temperatures of 610° and 980° C., respectively, for these, whereas Grim and Rowland (15) cite the ranges of 550° to 600° C. and 950° to 1,000° C., respectively. Figure 30 shows curves for six kaolins tested. Florida (A), Georgia (B), South Carolina (C), and Delaware (D) kaolins all gave endothermic peak temperatures of about 610° to 620° C. Two North Carolina kaolins (E, F) gave endothermic peak temperatures of about 595° C.[6] All the kaolins showed an approximate 980° C. exothermic peak.

The halloysites (fig. 30, G, H, I, J, K) showed characteristics similar to kaolinite. The large endothermic peak temperatures ranged from about 590° to 595° C., and the exothermic peak was approximately 980° C. for each. In addition, they all indicated additional endothermic peaks at about 320° to 335° C. and at approximately 135° to 160° C. The latter was quite pronounced in a sample of endellite (1), or hydrated halloysite, which was tested as received (fig. 30, G) instead of after the usual drying at 65° C. The large size of the initial peak in endellite checks with Grim and Rowland's (15) results on a similar sample. Although drying at 65° C. reduced the magnitude of this peak (fig. 30, H), its presence was still apparent, accompanied by a slight upward shift

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[6] Two other North Carolina kaolins (Harris Clay Co., Spruce Pine, N. C.), not shown in figure 30, gave endothermic peak temperatures of about 605° and 610° C.

in peak temperature, and it was characteristic of all the halloysites. This peak appeared in the Pask and Davies (see pages 64 and 65) curves for halloysites and might be due to the presence of small amounts of endellite or even allophane (fig. 30, *L*). The sample of halloysite used by Norton (*37*) has since been classified as endellite (*1*). The peaks occuring in the range of 320° to 335° C. (fig. 30, *G, H, I, J*) have been recognized by other workers (*30*, and have been attributed by some (*15*; see also page 65) to be due to the presence of gibbsite.

The data on the principal endothermic peak in the neighborhood of 600° C. for kaolinites and halloysites deserve special consideration. Norton (*37*) claimed that this peak occurred at slightly lower temperatures for halloysite. Grim and Rowland (*15*) did not confirm this. The data of Kelley and Page (*30*), as well as those of Pask and Davies (see page 63), do confirm Norton's statement. The curves of figure 30 substantiate the difference cited by Norton. Undoubtedly in the pure samples of kaolinite and halloysite the differences in the principal endothermic peak are real. The observations of Kelley and Page (*30*) were that for halloysites contaminated with kaolinite (revealed by electron microscope), the temperatures for the endothermic reaction were higher. They contended that for mixtures of halloysite and kaolinite it was probable that the peak occurred somewhere between that for pure kaolinite and pure halloysite. 'In this light it would appear that the North Carolina kaolins (fig. 30, *E, F*) were contaminated with halloysite. The Kamec kaolin (fig. 30, *F*) even showed a small endothermic peak at about 320° C. which corresponds to those observed in the halloysites. This is not surprising, since Ross and Kerr (*42*) have stated that halloysite is very commonly associated with kaolinite in some kaolin deposits, especially residual deposits derived from pegmatites.

Allophane (fig. 30, *L*) shows a large, broad endothermic reaction with a peak temperature at about 185° C. which checks Norton's data (*37*). The gamma-alumina reaction occurs at a slightly higher peak temperature, about 990° to 995° C., as compared with the other kaolin minerals.

ILLITE AND MONTMORILLONITE CLAYS; NONTRONITE; HYDRATED MAGNESIUM SILICATES; MICACEOUS MINERALS

Two samples of illite obtained from Grim (Illinois State Geological Survey) gave curves (fig. 31, *A, B*) which checked the data of Grim and Rowland (*15*) very well. Endothermic peaks appeared at about 140° C., 610° to 620° C., and 900° C., followed by a slight exothermic peak at about 950° C. An important factor is that the thermal data for illite and the samples subsequently described were obtained with 200 ohms resistance in series with the differential thermocouple and the reflecting galvanometer. This increase in sensitivity of the galvanometer is a necessary and important consideration in detecting minerals of these groups because of the much smaller magnitude of their reactions as compared with the kaolin group and hydrous oxide group of minerals.

The four montmorillonite samples (bentonites), *D, E, F*, and *G*

in figure 31, checked in general the curves and data given by Grim and Rowland (15), except that the peak temperatures of their curves are slightly lower than those shown in figure 31. This has been noted consistently in the comparisons of other minerals and is undoubtedly due to their use of a slower rate of heating. Three endothermic reactions occurred at peak temperatures of about 170° to 190° C., 695° to 730° C., and 885° to 905° C., followed by an exothermic peak at about 925° to 935° C. This last exothermic peak has been described by Grim and Rowland (15) as sometimes occurring above 1,000° C., the same being true for the similar illite exothermic reaction. Of special interest was the detection of the presence of quartz in montmorillonites E, F, and G (fig. 31) by the small, sharp endothermic peak at about 578° C., characteristic of the alpha-beta quartz inversion.

A sample of a white Italian bentonite (6) gave the thermal curve in figure 31, H. The curve was quite irregular compared to the other bentonites, showing only two of the described characteristic peaks for montmorillonite, the first and second endothermics.

Nontronite (fig. 31, I), a member of the montmorillonite group, showed three broad reaction peaks. The first two were endothermic, with peak temperatures of about 200° and 500° C.; and the third was exothermic, with a peak temperature of about 870° C.

A sample of meerschaum (fig. 31, J), a hydrated magnesium silicate also called sepiolite, gave a curve that strikingly resembled that for the nontronite sample shown in figure 31, I. The only essential difference was a shift of the first endothermic peak to about 175° C. and the addition of another endothermic peak at about 305° C.

Pyrophyllite (fig. 31, K) gave a curve showing one broad endothermic reaction at a peak temperature of about 640° C. The occurrence of a single peak checks Grim and Rowland (15), but their peak temperature is much higher (about 775° C.). The sample used for the curve of figure 31, K, was hand-picked from large crystals and checked optically.

A sample of talc (fig. 31, L) checked the results given by Grim and Rowland (15) showing one endothermic reaction at a peak temperature of about 950° C.

A sample of hand-picked muscovite gave a more or less irregular curve (fig. 31, M) showing only extremely broad peaks with very indefinite peak temperatures. The data of other workers are similar, and as yet no verified characteristic peaks and temperatures have been established.

The curves for two chlorites, prochlorite and sheridanite, are shown in figure 31, N and O. The prochlorite (fig. 31, N) curve, from temperatures of 750° to 1,000° C., checked very well a similar portion of a curve given by Grim and Rowland for chlorite (15). The large endothermic peak at about 660° C. in figure 31, N, however, is shown only as a shallow, broad peak by Grim and Rowland (15). There was a striking similarity in the curves of figure 31, N and O, except for shifts in peak temperatures.

DISCUSSION

The data obtained with the apparatus described herein did not check completely with any one set of data presented by previous workers. For some samples, good checks were obtained against Norton's data (*36, 37*), and for others agreement has been found with Grim and Rowland (*15*). In most instances the general shape of the curves, if not the peak temperatures, agreed with those published by most workers. The discrepancies in peak temperatures, as given by different workers for various samples (sometimes samples obtained from similar sources), have been attributed to the differences in the rates of heating used during the thermal analysis. Other factors generally cited as important for obtaining reproducible results are constant methods of packing the sample, placement of the thermocouple in the sample block, and preparation of samples. Although no complete investigation has been made to evaluate the relative importance of all responsible factors, the author believes that the rate of sample heating coupled with accurate temperature measurement of the sample are the most important factors. The design described in this paper appears to be satisfactory in these respects. Although it is agreed that the peak temperatures of a differential thermal curve do not necessarily represent a reaction temperature, they are measurable points and reproducible to within a few degrees despite small variations of such factors as sample packing and sample preparation.[7] Thus if a peak temperature agrees with a known, reasonably constant, and dependable reaction temperature, such as the alpha-beta quartz inversion temperature (573° C. and 575° C., cited in literature) (*46*), all peak temperatures for the recorded reactions of different samples should be reasonably accurate. Samples of different varieties of quartz have given a reproducible peak temperature of about 578° C. for the alpha-beta inversion despite small variations in factors such as sample packing, etc., and it is believed that for all the samples tested and reported herein, the new equipment has made it possible to obtain data more reliable than those previously published in the literature.

SUMMARY

Design, construction, and operation details have been given for an apparatus for differential thermal analysis. This apparatus is simple and inexpensive and has proved itself in more than 250 runs. Curves were reproducible, despite changes in sample block, thermocouples, or furnace winding. Application of the apparatus has been described, using as examples the curves of typical minerals easily detected by the method. Table 17 lists, for some minerals, characteristic identification peaks considered more reliable than those previously given in the literature.

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[7] Low-temperature peaks (below 200° C.) may be affected seriously by sample preparation, but the diagnostic value of these peaks is very limited.

TABLE 17.—*Characteristic peak temperatures, in degrees centigrade, and magnitude of reaction*

Mineral	Endothermic peak			Exothermic peak	
	Large	Medium	Small	Medium	Small
Quartz			578		
Siderite	600				
Lepidocrocite Goethite	} 330–335				
Limonite	375				
Gibbsite	365				
Diaspore	550–585				
Kaolinite	610–620			980	
Endellite	{ 135–160 590–595	}		980	
Halloysite	590–595			980	
Allophane	185			990–995	
Illite		{ 140 610–620 900	}		950
Montmorillonite		{ 170–190 695–730 885–905	}		925–935
Nontronite		{ 200 500	}		870
Pyrophyllite		640			
Talc		950			

APPENDIX

The following is a list of the more important parts purchased during construction of the apparatus for differential thermal analysis, accompanied by the approximate price.

1 Variac (variable transformer) 115 volts, 5 amp., 0–135 output voltage, Type 200–CM (General Radio Co., Cambridge, Mass.) _____ $17.50

1 Bodine motor, Type NCI–12R, 1/70 hp., 1650 r.p.m., 110 volts, 0.23 amp., with 300:1 reductor (Bodine Electric Co. Chicago, Ill.) _____ 25.00

1 Boston reductor, Type LA 200 (200:1 reduction) (Boston Gear Works, Inc., North Quincy, Mass.) _____ 12.00

1 spur gear, Boston ND–144 _____ 5.75

1 spur gear, Boston ND–24–B _____ 1.30

1 split cast-iron pillow block, Boston PBB–16 _____ .70

1 No. 2239C L. & N. Type P reflecting galvanometer with 1-meter focal length lens (Leeds & Northrup, Philadelphia, Pa.) _____ 25.00

1 No. 2099 L. & N. illuminating device _____ 15.00

Grade R photostat paper, 350-foot roll of 11-inch width (Photostat Corporation, Rochester, N. Y.) _____ 11.40

Developing and fixing powders (Photostat Corporation), per package _____ .30 and .15

The following important items were at hand but may be obtained if necessary from indicated firms:

Portable potentiometer, L. & N. Type 8657–C.

Nichrome alloy V furnace wire, B. & S. No. 20 (Driver-Harris Co., Harrison, N. J.).

Chromel-alumel thermocouple wire, 22 gage (Hoskins Mfg. Co., Detroit, Mich.

Calibrated resistance box (at least in steps of 50 ohms to 1,000 ohms) or Tubular rheostat (a box such as No. 82784 by Central Scientific Co., Chicago, Ill., should be satisfactory).

THERMAL ANALYSIS OF CLAY MINERALS AND ACID EXTRACTION OF ALUMINA FROM CLAYS [1]

By Joseph A. Pask [2] and Ben Davies [3]

INTRODUCTION

Because of the greatly expanding need for aluminum, the Bureau of Mines has carried on an extensive program during the last few years for investigating high-alumina clay deposits of the western United States and methods of recovering from clays the high-grade alumina needed for the aluminum industries. Attention was confined chiefly to processes based on the use of sulfuric acid or sulfates, since methods of this type seem to offer the best possibilities for immediate commercial development.

Clay deposits vary considerably in alumina content and to a greater extent in their percentage of extractable alumina. Determination of the mineral composition is of primary importance, since the alumina can be completely extracted from certain minerals only, namely, those of the kaolinite type. The purpose of this report is to correlate the solubility of various clays and other alumina-bearing minerals with mineralogical composition. As it is not always possible to identify minerals by either chemical or X-ray analysis, thermal analysis was used for positive identification. The purpose of this study was to supply supplementary information regarding the various clay minerals, to be used in connection with other investigations on the development of acid processes for extraction of alumina from clays.

SCOPE

Chemical and thermal analyses of a number of known clay minerals were examined to determine the characteristics by which they may be identified. The available or acid-soluble alumina content and the percentage extraction were determined by a method developed by the Bureau of Mines, United States Department of the Interior. Identical tests were made on selected samples from some clay deposits in the Pacific Northwest. A pressure-digestion method was used on several samples with good success and offers possibilities for further study.

Free silica is one of the most common impurities in clay, and thus its effect on the solubility of alumina is of interest. An experimental trial was made to test this point.

ACKNOWLEDGMENTS

CLAY MINERALS

The common clay minerals of major importance have been classified into three groups: Kaolinite, illite, and montmorillonite (*12, 20, 33, 43*). Other clay minerals, such as attapulgite, hectorite, cimolite, and rectonite, have been described in literature but are of minor importance and have not been included in this study. Alumina hydrates, feldspar, and micas occur as mixtures with clay minerals. Pyrophyllite is similar to montmorillonite in structure but is seldom associated with clays.

All these minerals are crystalline and, except for a few, occur in flat, flake-shaped particles. Two main structural units are present in their atomic lattices. The alumina or aluminum hydroxide sheet consists of two layers of closely packed oxygens or hydroxyls between which aluminum atoms are embedded in such a position that they are equidistant from six oxygens or hydroxyls to form a network of the composition $(OH)_8Al_4O_4$. Actually, only two-thirds of the possible aluminum positions are occupied in this unit, which is the gibbsite structure. The second unit consists of a sheet of tetrahedral silica (SiO_4) groups, which when linked to form a continuous hexagonal network has the composition Si_4O_{10}.

KAOLINITE GROUP

Kaolinite, dickite, nacrite, halloysite, endellite, and anauxite are generally considered members of the kaolinite group. The crystal structure is called the 1:1 lattice type. The unit cell thus consists of a gibbsite sheet and a single tetrahedral silica sheet, which are held together by the valence bonds of four oxygens that occur commonly in both layers.

Kaolinite, dickite, and nacrite have the formula $(OH)_8Al_4Si_4O_{10}$ or $Al_2O_3.2SiO_2 2H_2O$. The structures differ by a slight shift or rotation of the sheets as they are placed above each other. Nac-

rite has the most completely stable stacking of layers, while dickite and then kaolinite have a lesser degree of organization. Kaolinite occurs commonly, and clays containing it are those sought as a source of alumina. Dickite and nacrite are not abundant and seldom are found in clay deposits.

Halloysite (1), also called meta-halloysite (34), is chemically similar to kaolinite, but the sheets in the structure are superimposed in a less orderly manner, resulting in further stresses that are probably responsible for the growth of small, lath-shaped instead of platelike particles, as revealed by the electron microscope (1).

Endellite (1), which was referred to as halloysite by Mehmel and has also been called hydrated halloysite, carries an additional amount of water to have the formula $(OH)_8Al_4Si_4O_{10}.4H_2O$. According to Hendricks, the structure consists of kaolinite-type layers alternating with single sheets of water molecules. A continuous series between endellite and halloysite is expected, since the latter forms upon drying of the former at 50° C.

Anauxite has the formula $(OH)_8Al_4Si_4O_{10}.SiO_2$ or $Al_2O_3.3SiO_2.-2H_2O$. The excess silica is suggested by Hendricks to be present in the kaolinite structure as neutral silica layers with the composition SiO_2 or possibly $4SiO_2.H_2O$, alternating with kaolinite-type layers in irregular sequence. Thus, a series between kaolinite and anauxite is possible, with varying excess silica content as indicated by Ross and Kerr's work on these minerals.

Theoretical compositions of minerals of the kaolinite group are shown in table 18. Oxides other than alumina and silica in the chemical analyses are due primarily to impurities, since appreciable isomorphous substitution of other ions for Al^{+++} and Si^{++++} is considered improbable because of the nature of the structure. Hendricks and Alexander (21) state that if iron oxide combined with silica exceeds 2 percent Fe_2O_3 or if more than 1 percent of nonexchangeable potassium or magnesium is determined, clay minerals other than those in the kaolinite group are present.

TABLE 18.—*Theoretical compositions of minerals of kaolinite group*

	Al_2O_3	SiO_2	H_2O
Kaolinite, dickite, nacrite, halloysite	39.5	46.5	14.0
Endellite	34.7	40.8	24.5
Anauxite	32.0	56.6	11.4

ILLITE GROUP

Illite (16) has been suggested as a group name rather than as a specific mineral name for clay materials similar to the white micas. In the past, minerals of this group have been referred to by clay technologists as "hydrous mica," "micalike clay mineral," "sericitelike mineral," "glimmerton," "potash-bearing clay mineral," "Ordovician bentonite," and "bravasite."

The general formula $(OH)_4K_yAl_4(Si_{8-y}Al_y)O_{20}$ with y varying from 1 to 1.5, has been proposed. The structure is similar to that for muscovite and is essentially a 2:1 lattice type consisting of two silica sheets and one gibbsite. About 15 percent of the Si^{++++} positions are replaced by Al^{+++}, represented by Al^y in the formula, and the resulting excess charges are satisfied chiefly by K^+ ions between the silica sheets of two successive units. Also replacement of Al^{+++} in the gibbsite sheet is possible. Illite thus forms a complex series of minerals, whose detailed structures are not yet completely known.

Theoretical compositions of the suggested end members of the illites, when y equals 1 and 1.5 and assuming no substitutions for Al^{+++}, are listed in table 19. The formula for muscovite, obtained when y equals 2, is also included. Generally, isomorphous

TABLE 19.—*Theoretical compositions of minerals of illite group*

	Al₂O₃	SiO₂	K₂O	H₂O
Illite, $y = 1$ $K_2O.5Al_2O_3.14SiO_2.4H_2O$ _____	33.6	55.4	6.2	4.8
Illite, $y = 1.5$ $3K_2O.11Al_2O_3.26SiO_2.8H_2O$ _____	36.1	50.2	9.1	4.6
Muscovite, $y = 2$ $K_2O.3Al_2O_3.6SiO_2.2H_2O$ _____	38.4	45.3	11.8	4.5

substitions of Fe^{+++}, Fe^{++}, and Mg^{++} for Al^{+++} lower the alumina content to about 25 percent.

MONTMORILLONITE GROUP

The montmorillonite group includes minerals that are similar to illite but do not have K^+ between the silica sheets because of charges set up by the substitution of Al^{+++} in the Si^{++++} positions. The structure of these minerals is thus of the 2:1 lattice type, consisting of two silica sheets and one gibbsite.

The formula for the structure suggested by Hofmann, Endell, and Wilm (24) is $(OH)_4Al_4Si_8O_{20}.nH_2O$ or $Al_2O_3.4SiO_2.H_2O.nH_2O$. The nH_2O is held between the silicate layers and varies with the humidity of the atmosphere, causing corresponding expansion of the lattice which characterizes this group. Edelman and Favejee (8), on the other hand, have proposed the possibility of a rearrangement in the silica sheets. According to their scheme, the formula for the mineral structure becomes $(OH)_{12}Al_4Si_8O_{10}.nH_2O$ or $Al_2O_3.4SiO_2.3H_2O.nH_2O$.

The mineral montmorillonite generally has partial replacement of the Al^{+++} in the gibbsite sheet by Mg^{++} and/or Fe^{+++}. If the substitution of magnesium is complete, the mineral saponite is derived; or if ferric iron, nontronite.

Theoretical compositions of the two suggested structures for montmorillonite with no substitutions for Al^{+++} and no nH_2O are shown in table 20. With these limitations, Hofmann's for-

TABLE 20.—*Theoretical composition of minerals of montmorillonite group*

	Al₂O₃	SiO₂	MgO	Fe₂O₃	H₂O
Montmorillonite (Hofmann)	28.3	66.7			5.0
Saponite (Hofmann)		63.4	31.9		4.7
Nontronite (Hofmann)		57.5		38.2	4.3
Montmorillonite (Edelman)	25.6	60.6			13.8

mula corresponds to that for pyrophyllite, which does not have an expanding lattice or clay properties. Compositions for saponite and nontronite are also listed. Commonly occurring isomorphous substitutions of Fe^{+++}, Fe^{++}, and Mg^{++} for part of the Al^{+++} lower the alumina content for montmorillonitic clays to about 20 percent.

BEIDELLITE

Beidellite has been classified as a separate clay mineral by Larsen and Wherry (*31*), since it had properties characteristic of homogeneous materials and determinable optical constants. According to Marshall (*33*), the structure is similar to montmorillonite, but substitutions of Al^{+++} for Si^{++++} occur in the silica sheet. Maximum substitution of aluminum results in the approximate proposed formula $(OH)_4Al_{4.34}(Si_{6.34}Al_{1.66})O_{20}$ or $Al_2O_3.2.11SiO_22H_2O$. The theoretical composition becomes: Al_2O_3 38.5, SiO_2 47.9, and H_2O 13.6 percent. Common isomorphous substitutions of Fe^{+++} and Mg^{++} for Al^{+++} in the gibbsite lower the alumina content to about 32 percent.

Recently the validity of the species as presented has been open to question. Grim (*15*) believes that beidellite may be a mixture of several clay minerals. The authors believe that this mineral is an interlayer mixture. Discussion relative to this point will be presented later.

ALLOPHANES

Allophanes or allophanoids include all noncrystalline solid solutions of silica, alumina, and water. According to Salmang (*44*) the range of compositions is $Al_2O_3.0.3-1.3SiO_21.8-8.5H_2O$. Small amounts are thought to be present in practically all clays. They originally had been identified by their solubility in hydrochloric acid. This, however, is insufficient, since other clay minerals also have been determined to have partial solubility in acid solutions. The compositions of the end members are presented in table 21.

ASSOCIATED NONCLAY MINERALS

The hydrous alumina minerals are gibbsite or hydrargillite, alpha alumina trihydrate ($Al_2O_3.3H_2O$, with 65.3 percent of alumina), boehmite, alpha alumina monohydrate, and diaspore, beta alumina monohydrate ($Al_2O_3.H_2O$, with 85.0 percent of alumina), and cliachite (an amorphous variety). All these types, in various amounts, have been found in bauxites and certain clays. Gibbsite and boehmite have been produced synthetically, according to cor-

respondence with G. H. Wagner of Aluminum Ore Co., and verified by the similarity in X-ray patterns with those of the naturally occurring minerals. Chemical analyses of diaspore generally show a small amount of silica as an impurity. Cliachite (*3*) has been identified in the Missouri diaspore deposits.

TABLE 21.—*Theoretical composition of allophanes*

	Al₂O₃	SiO₂	H₂O
Al₂O₃.0..3SiO₂.1.8H₂O_____	66.9	11.8	21.3
Al₂O₃.0..3SiO₂.8.5H₂O_____	37.3	6.6	56.1
Al₂O₃.1.3SiO₂.1.8H₂O_____	48.0	36.8	15.2
Al₂O₃.1.3SiO₂.8.5H₂O_____	30.6	23.4	46.0

Muscovite is similar to illite, but 25 percent of the Si^{++++} positions are replaced by Al^{+++} instead of about 15 percent, resulting in a larger number of K^+ between the silicate sheets. Pyrophyllite has the same composition as montmorillonite of the Hofmann structure without any expanding lattice water. Orthoclase feldspar has the composition $K_2O.Al_2O_3.6SiO_2$.

Other minerals that occur commonly in clays as impurities are quartz, calcite, pyrite, hematite, limonite, goethite, and leucoxene. Carbonaceous matter of various types is also present.

TEST MATERIALS

REFERENCE MINERALS

The reference clay minerals studied in this investigation included kaolinite, dickite, anauxite, four halloysites, two montmorillonites, illite, and beidellite. The nonclay minerals were gibbsite, boehmite, diaspore, muscovite, pyrophyllite, biotite, and orthoclase. The sources are listed in table 22.

The samples containing anauxite and illite required purification. The anauxite particles were interspersed in a sandstone crushed to free the grains. The minus 20-, plus 60-mesh fraction was subjected to heavy mineral separation. The portion with a density between 2.495 and 2.530 was then taken to be a representative sample. Anauxite has a density of 2.52 and quartz of 2.65. A liquid between these values would be expected to separate the two minerals, but on application poor results were obtained. Chemical analyses of the selected fraction showed an excess of silica beyond the theoretical amount, which may be due to chloritic material or to quartz that still was not completely removed.

The illite was present in a Grundy County (Ill.) underclay. Grim stated that the minus 1-micron fraction consisted mainly of this mineral. The clay was dispersed, and the desired fraction was obtained by controlled sedimentation.

CLAY SAMPLES

A number of samples from local clay deposits in the Pacific Northwest were selected. These included five from the Castle Rock (Wash.) region (*10*) about 10 miles north of Kelso; two from the Hobart Butte deposit in Oregon (*53*) about 35 miles

south of Eugene; four from the Molalla (Oreg.) region (*53*) about 30 miles south of Portland; one from the Harris clay mine (*10*) about 7 miles east of Renton, Wash.; and one from Bend, Oreg.   One sample from the Ione formation in California also was examined.

TEST METHODS
CHEMICAL ANALYSES
Chemical analyses of the test samples were made by the standard fusion method and in most cases included only SiO_2, Al_2O_3, Fe_2O_3, TiO_2, and ignition loss.   The difference between the summation and 100 percent mainly represented the alkalies and alkaline earths.   All analyses were made in the laboratories of the Northwest Experiment Station of the Federal Bureau of Mines.

THERMAL ANALYSES
Thermal analysis as a research tool for the study of clays was first suggested by Le Chetalier in 1887 but has not received a great deal of attention until more recent years.   The test apparatus employed was similar to the one described by Norton (*37*). Essentially the method consists of measuring the temperature difference between alpha alumina, which is inert and has no heat effects, and the test sample.   The voltage developed by the differential thermocouple was measured with a Leeds & Northrup type K potentiometer sensitive to 10^{-7} volt.   The differential temperature was plotted against the temperature of the furnace.   An effective positive difference indicated an exothermic reaction and a negative endothermic.

A 3/10-gram air-dried sample was used in making an analysis. For this size of sample and the experimental set-up each vertical division in the graphs subsequently presented is equivalent to a temperature difference of 1° C.   A heating rate of 5.5° C. per minute was used.   It is important that the heating rates be considered in comparing peak temperatures of various published curves because the endothermic and exothermic reactions are a function of temperature and time, that is, heat work, and their peaks will shift slightly with different heating rates.   Accurate quantitative work is possible by measuring areas outlined by the heat effects, but precautions should be taken to insure constancy of all test factors at all times if this is attempted.

ALUMINA EXTRACTIONS
BUREAU OF MINES METHOD
The samples to be tested were quartered, ground to minus 100-mesh, and dried overnight at 130° C.   Two ½-gram portions were calcined for 1 hour at the desired temperature.   Calcination temperatures of 600° and 800° C. were generally employed, although different temperatures were used on specific clay samples.

The calcined samples were extracted by boiling for one-half hour in 35 ml. of 20-percent solution of H_2SO_4 by weight.   After the boiling period the clay residue was filtered off and discarded.

One filtrate was used to determine the so-called "available" Al_2O_3, the other the "available" Fe_2O_3.   The "available" SiO_2 was determined for some of the samples.

PRESSURE DIGESTION

A test procedure for determining the effect of higher temperature and pressure on alumina extraction from uncalcined clay was devised.   It consisted of weighing two $\frac{1}{2}$-gram samples into test tubes, adding 35 ml. of 20-percent H_2SO_4 solution, and sealing the tubes with a flame.

The sealed tubes and some hot water were placed in a rotating pressure digester, which was electrically heated.   The digester rotated about a central axis, subjecting the clay-acid suspension to thorough mixing as well as to heat and pressure.   Approximately 1 hour was required for the steam temperature to reach 155° C. and a total pressure of 5.4 atmospheres or 79 pounds per square inch.   The pressure inside the tubes was slightly less, owing to the difference in vapor pressure of 20-percent H_2SO_4 solution and water.   The temperature was kept at this point for one-half hour; then the steam pressure was slowly released, and the tubes were removed.

The tips of the tubes were carefully broken off, and the suspension was washed out.   After the clay residue was filtered off, the filtrates were analyzed for Fe_2O_3 and Al_2O_3 and, in some cases, also for SiO_2.

RESULTS AND DISCUSSION

REFERENCE MINERALS

The chemical analyses for the reference minerals are listed in table 22, alumina-extraction results in table 23, and differential thermal analysis curves in figures 32 and 33.

The percentage available alumina value represents the acid-soluble or acid-extractable Al_2O_3 per 100 parts by weight of dried specimen.   The percentage alumina extraction is the actual percentage of the total alumina that was removed.   The former is the practical value, while the latter indicates the efficiency of the leaching process.

The acid-extractable Fe_2O_3 has been found in practically all instances to equal about 70 percent of the total Fe_2O_3 content.   Therefore, the Fe_2O_3 extractions have not been included in the reported data.   Filtrates tested for TiO_2 often contained roughly 10 percent of the total TiO_2 content, and the silica was found to range between 0.5 and 2 percent.   These determinations were discontinued in later work because of their lack of significance.

KAOLINITE GROUP

Samples *A*, *B*, *C*, *D*, *E*, *F*, and *G* are members of the kaolinite group.   On thermal analysis (figs. 32 and 33) all show an exothermic reaction with a sharp peak at 980° to 995° C., which is sufficient to identify them as belonging to this group.   The individual members can be distinguished by their characteristic endothermic peak: 685° C. for dickite, 580° for kaolinite, and 555° to
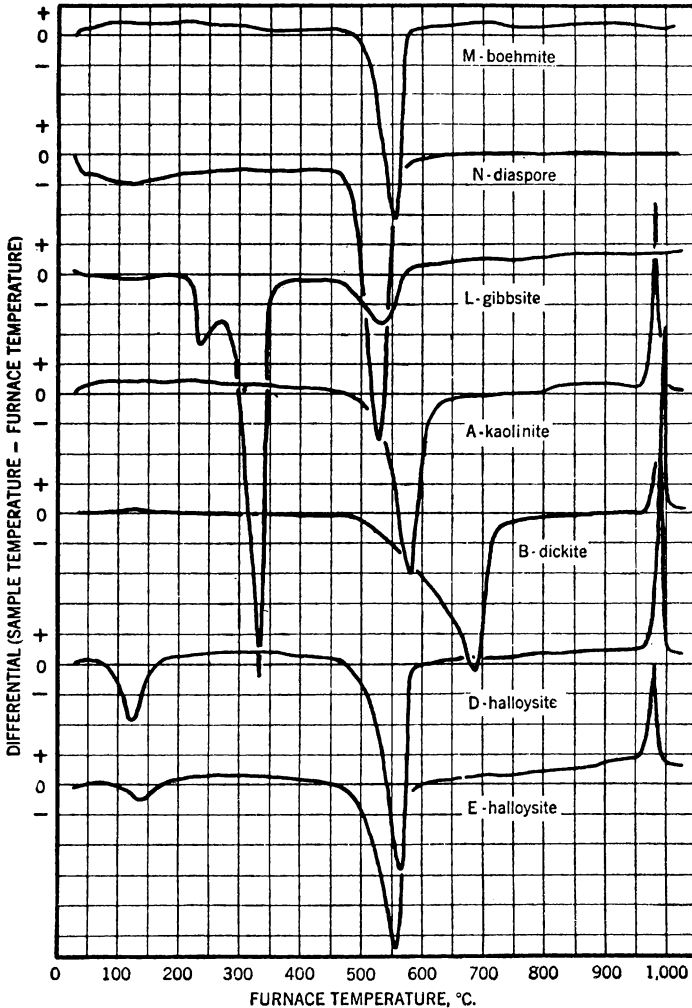
FIGURE 32.—Thermal analyses of reference minerals.

565° for halloysite. Since endellite inverts to halloysite with slight heating, its curve would be similar to that for halloysite. Nacrite, which was unavailable for this work, would have a peak above 685° C. as indicated by Norton (*37*) in his thermal analysis work and by Ross and Kerr (*43*) in their dehydration studies. Anauxite would be similar to kaolinite.

The endothermic reactions, with a peak at about 130° C., are caused by evaporation of mechanically held water, and their magnitude varies with the humidity of the atmosphere to which the clay had been exposed. For a given humidity, endellite should have the greatest reaction, followed by halloysite, kaolinite, anauxite, dickite, and nacrite. This series depends upon particle size, which in turn is a result of the crystal structure. Halloysite can

further be distinguished from the others by steep slope of the thermal analysis curve on its return to a minimum differential temperature just after the main endothermic reaction.

The thermal analysis curve of dickite (sample B) shows the presence of either diaspore or kaolinite because of the semblance of another reaction starting at 475° C. and blending into the characteristic peak. Sample G, obtained as an allophane, is actually halloysite, as indicated by the steep slope of the curve after the main endothermic reaction. The small peak at 300° C. indicates the presence of a small amount of gibbsite. A small quantity of allophane could account for the slightly higher Al_2O_3 content for dickite and the halloysites than the expected theoretical value.

The large endothermic reaction of the kaolinite-group minerals

FIGURE 33.—Thermal analyses of reference minerals.

TABLE 22.—*Chemical analyses of reference minerals, percent*

	A	B	C	D	E	F	G	H
Ignition loss	13.4	14.2	7.6	14.8	14.7	14.6	14.6	7.3
SiO₂	44.3	43.2	67.2	43.4	44.1	43.8	41.8	50.0
Al₂O₃	39.6	41.5	20.2	41.8	41.7	41.0	43.2	25.7
Fe₂O₃	1.3	.4	3.4	.6	.3	.6	.6	6.5
TiO₂	1.3	.0	1.0	.1	.0	.0	.0	.1
Total	99.9	99.3	99.4	100.7	100.8	100.0	100.2	89.6

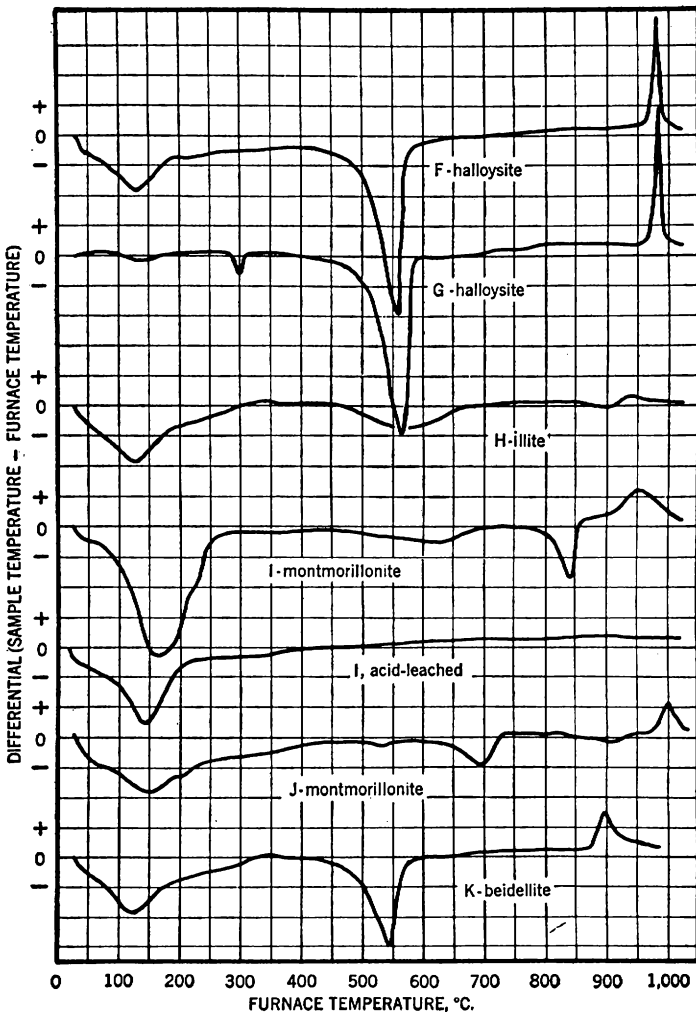|	I	J	K	L	M	N	O
Ignition loss	8.9	5.2	10.9	31.6	16.1	14.1	5.0
SiO₂	59.5	69.3	45.3	------	------	1.7	43.3
Al₂O₃	19.7	19.7	31.4	68.0	83.8	80.9	33.4
Fe₂O₃	3.9	.8	7.3	------	------	1.1	5.6
TiO₂	.5	.1	.5	------	------	3.0	Trace
Total	92.5	95.1	95.2	99.6	99.9	100.8	८7.3

A—Kaolinite, sold commercially as Pioneer washed china clay by Georgia Kaolin Co.
B—Dickite, Chihuahua, Mexico; through Sidney Speil, Bureau of Mines Electrotechnical Laboratory, Norris, Tenn.
C—Anauxite, separated from sandstone, Mokelumne River, Calif.; through Victor Allen, Geological Survey.
D—Halloysite, Dragon mine, Eureka, Utah; through Sidney Speil.
E—Halloysite, Indiana; through R. E. Esarey, State geologist.
F—Halloysite; through Kentucky State Geological Survey.
G—Halloysite, Bedford, Ind.; purchased as allophane.
H—Illite, Grundy County, Ill.; through R. E. Grim, Illinois State Geological Survey.
I—Montmorillonite, Yavapai County, Ariz.; purchased.
J—Montmorillonite, Texas; through Sidney Speil.
K—Beidellite, Namiquipa, Chihuahua, Mexico; through Sidney Speil.
L—Gibbsite, alpha alumina trihydrate; through G. H. Wagner of Aluminum Ore Co., East St. Louis, Ill.
M—Boehmite, alpha alumina monohydrate; through G. H. Wagner.
N—Diaspore, Missouri; through H. A. Buehler, State geologist.
O—Muscovite; from G. E. Goodspeed, Department of Geology, University of Washington, Seattle.

TABLE 23.—*Results of the extraction of alumina from reference minerals with sulfuric acid*

Mineral	Total Al₂O₃ content	Available alumina, percent			Extraction, percent		
		Clay dried, 130°C.	Calcined, 800°C.	Pressure digestion, 155°C.	Clay dried, 130°C.	Calcined, 800°C.	Pressure digestion, 155°C.
A—Kaolinite	39.6	1.2	39.6	27.6	3	100	70
B—Dickite	41.5	.0	26.0	2.2	0	63	5
C—Anauxite	20.2	1.8	19.1	U	9	95	U
D—Halloysite	41.8	26.3	41.9	40.8	63	100	98
E— Do.	41.7	21.0	40.0	U	50	96	U
F— Do.	41.0	36.7	U	U	90	U	U
G— Do.	43.2	33.6	43.2	43.1	78	100	100
H—Illite	25.7	2.9	13.3	22.4	11	52	87
I—Montmorillonite	19.7	17.1	5.6	16.7	87	28	85
J— Do.	19.7	6.4	3.7	18.4	33	19	93
K—Beidellite	31.4	20.6	28.3	31.3	66	90	100
L—Gibbsite	68.0	68.3	29.0	U	100	43	U
M—Boehmite	83.8	7.6	8.0	70.3	9	10	84
N—Diaspore	80.9	.0	2.4	2.2	0	3	3
O—Muscovite	33.4	5.5	9.6	U	17	29	U
P—Pyrophyllite	U	.0	.0	U	U	U	U
Q—Biotite	U	9.4	8.4	U	U	U	U
R—Orthoclase	U	U	.1	U	U	U	U

U—Undetermined.

represents the break-down of the crystal structure, accompanied by evolution of the chemically combined water. Insley and Ewell (*27*) believe that an amorphous mixture of alumina and silica then results. The amorphous silica restrains the alumina from crystallizing to gamma-Al₂O₃ until a temperature is reached at which this restraint is overcome, and the Al₂O₃ crystallizes almost spon-

taneously with an evolution of heat to form the exothermic peak. Another theory presented in literature states that instead of an amorphous mixture an amorphous compound, referred to as metakaolin, is the result of the decomposition of the clay molecule.

Maximum alumina solubility for the kaolinite group is obtained in the range between the endothermic and exothermic reactions while an amorphous condition is present. The values approach 100 percent, except for dickite and probably nacrite. With the crystallization of gamma-Al_2O_3 the solubility drops to a few percent. At temperatures below the endothermic reaction only halloysite and endellite have appreciable solubility. Endellite will change irreversibly to halloysite on drying. In the field halloysite may contain varying amounts of endellite, depending upon the conditions to which the deposit was exposed. Endellite is more soluble, as indicated by sample E, which had 83-percent alumina extraction in an undried state and 50-percent when dried at 130° C. The higher solubility of halloysite and endellite can be attributed partly to their much finer particle size and lath-shaped crystals, resulting in a considerably increased surface that is exposed to the action of the dissolving solution.

ILLITE GROUP

The illite specimen (sample H) was the minus 1-micron fraction separated by sedimentation from an illite-bearing clay. The thermal analysis curve in figure 33 shows three endothermic reactions with peaks at 125°, 575°, and about 900° C. The last of these reactions is followed immediately by a small exothermic peak at about 935° C. The curve agrees with the one presented by Grim and Rowland (15). Their curves for other illite samples showed slight variations in positions of peaks, substantiating the fact that an isomorphous group was under consideration.

The first endothermic reaction is the result of the evaporation of mechanically held water. Most of the water of crystallization is driven off at the second peak, but the essential micaceous character is retained. The final break-down of the crystal structure is indicated by the third peak. This is followed immediately by the formation of a spinel (13) from the alumina, magnesia, and iron in the gibbsite sheet.

The alumina extraction was low — 52 percent at 800° C. and 11 percent for the dried clay. A general indication of the behavior of illite thus can be deduced, but it is expected that the specific results will vary for different members of the group.

MONTMORILLONITE GROUP

Samples I and J, members of the montmorillonite group, gave appreciably different results, as shown in table 23. In the thermal analysis, however, both samples have three endothermic reactions, followed by an exothermic, which are characteristic of the 2:1 lattice type of clay minerals. Sample I shows peaks at 175°, about 625°, and 840°, followed by an exothermic peak at about 950° C.; and sample J at about 150°, about 695°, and about 915°, followed by one at 1,000° C. Grim and Bradley also found

a variation in the curves of different samples of the group. The position of the peak for the second endothermic reaction is sufficient to distinguish members of the montmorillonite group from the illites. The peak is above 600° C. for the former and lower for the illites.

The first endothermic reaction represents the removal of mechanically held water, including the nH_2O held between the montmorillonite layers. The second reaction accompanies a partial break-down of the molecule, with elimination of most of the water of crystallization, and the complete break-down is indicated by the third peak. Crystallization of spinel accounts for the exothermic reaction.

Table 24 shows that on treatment of sample I with acid the percentage alumina extraction was highest for the uncalcined specimen and decreased with calcination temperature. At 800° C. the montmorillonites had the lowest solubility of all the clay minerals — 28 and 19 percent. Additional work is necessary to determine the specific relationship of the solubility to the composition.

TABLE 24.—*Results of extractions of alumina from montmorillonite*

Temperature, °C.	Time, hours	Ignition loss, percent	Available Al_2O_3, percent	Extraction, percent
Room_____	_____	_____	[1] 17.4	88
130_____	16	_____	17.1	87
300_____	1	0.5	11.8	60
400_____	1	U	7.4	38
600_____	1	6.9	5.1	26
775_____	[2] T.A.R.	U	6.0	31
800_____	1	7.0	5.6	28
875_____	½	8.2	.0	0

[1] Extraction calculation was based on total weight when dried at 130° C.
[2] Sample was heated in a furnace at thermal analysis rate of 5.5° C. per minute and removed when indicated temperature was reached.
U—Value not determined.

The montmorillonite structure of sample I was completely destroyed when an uncalcined portion was leached with sulfuric acid, since a thermal analysis of the residue (curve *I*, acid-leached) showed only one endothermic reaction at 145° C. This peak, plus an ignition loss of 9.2 percent, indicated that the residue consisted primarily of a hydrated silica gel with a mixture of other nonleached oxides.

BEIDELLITE

The values for the Al_2O_3 and SiO_2 content of beidellite (sample K) were intermediate between those for kaolinite and montmorillonite. Some K_2O in the chemical analysis would indicate that a small amount of illite was also present. The thermal analysis (fig. 33) was similar to those for the kaolinite group, but the main reactions occurred at lower temperatures. Endothermic peaks were present at 125° and 545° and an exothermic peak at 895° C. Grim and Bradley's curve for a sample from the same locality agreed. They also gave curves for a number of other beidellite samples.

Alumina extractions of beidellite at a number of calcination temperatures are listed in table 25. These results are also intermediate between those for kaolinite and montmorillonite. The increased solubility after the endothermic reaction is similar to the behavior of kaolinite. The lack of complete solubility at 600° and 800° C. can be due to a small amount of montmorillonite. An extraction value of 34 percent at 875° C. indicates that the exothermic reaction was not completed in the time allowed.

TABLE 25.—*Results of extractions of alumina from beidellite*

Temperature, °C.	Time, hours	Available Al_2O_3, percent	Extraction, percent
130	16	20.6	66
600	1	27.6	88
800	1	28.3	90
875	½	10.8	34

The authors suggest that an intergrowth or interstratification of layers of the kaolinite and montmorillonite groups in indefinite sequence is present. Such an intergrowth would be homogeneous and would have measurable optical properties. The thermal analysis curve would show the heat effects of both types of layers if present in sufficient quantities. Also, it would be expected that in such an intimate mixture the temperatures of the reactions would be influenced, resulting in a shift of the peaks. In this case the kaolinite layers predominated. For some beidellites the montmorillonite layers will be more numerous, and the thermal analysis will show the montmorillonite reactions more prominently. This is the case with beidellite from the type locality Beidell, Colo., whose curve was published by Grim. In intergrowths of this type the size of the kaolinite layers will be of the order of those for montmorillonite or intermediate, thus being a factor in increasing their solubility and accounting for some of the alumina extraction from the uncalcined sample.

It is thus suggested that the name beidellite be retained for a series of minerals formed by the intergrowth or interstratification of kaolinite and montmorillonite layers instead of by isomorphous substitution of Al^{+++} for Si^{++++} in the silica sheets of the montmorillonite structure. Determination of the extent of this intergrowth with the corresponding effect on the appearance of the thermal analysis curve requires additional investigation.

ALLOPHANES

No true allophane was obtained for this study. A curve for a sample from Hillsboro, Ohio (according to Sidney Speil, Electrotechnical Laboratory, Bureau of Mines, Norris, Tenn.), showed an initial endothermic reaction with a peak at about 75° C., which gradually approached the temperature of the reference sample and an exothermic reaction at about 950° C. This agrees with the weight-loss versus temperature data given by Ross and Kerr (*42*) and the curves for mixture of alumina and silica gels obtained by Insley and Ewell (*27*). Small amounts of allophane

mixed in with members of the kaolinite group would be impossible to detect with the thermal analysis method.   The alumina extraction would be expected to be complete.

ASSOCIATED NONCLAY MINERALS

The thermal analysis curve of synthetically prepared boehmite (sample M), shown in figure 32, is characterized by a single endothermic reaction with a peak at 555° C. as a result of the dissociation of the molecule accompanied by removal of most of the chemically combined water.   The highest alumina extraction (35 percent) was obtained just above this reaction, which was followed by a decrease to 10 percent with an increase of calcining temperature to 800° C., as indicated in table 26.   The high value was the result of the formation of amorphous alumina, and the subsequent decrease in solubility was accompanied by its gradual crystallization to insoluble gamma-Al_2O_3.   The last traces of water that are so difficult to remove may be responsible for the persistence of some of the amorphous alumina to higher temperatures. Jagitsch (28), on the other hand, believes that the gamma-Al_2O_3 when formed is composed of extremely fine particles and that with increase of temperature the particles coalesce to cause gradual decrease in surface area.   This may account for the corresponding decrease in solubility.

TABLE 26.—*Results of extractions of alumina from boehmite*

Temperature, °C.	Time, hours	Ignition loss, percent	Available Al_2O_3, percent	Extraction, percent
130	16		7.6	9
450	[1] T.A.R.	0.6	4.8	6
600	1	14.5	28.9	35
700	1	15.3	21.1	25
800	1	15.8	8.0	10

[1] Sample was heated in a furnace at thermal analysis rate of 5.5° C. per minute and removed when indicated temperature was reached.

Diaspore (sample N) had a sharp endothermic peak at 530° C. because of the evolution of the chemically combined water.   An alumina extraction of 5 percent at 600° C. was the highest value obtained.   The mineral specimen contained 1.7 percent SiO_2.   Instead of being part of another mineral as an admixture it is suggested that a small amount of SiO_2 may actually be present in the diaspore crystal structure.   This may be responsible for the lower solubility and the failures in attempts to produce synthetic diaspore or beta alumina amonhydrate.

Synthetic gibbsite (sample L) showed three endothermic reactions with peaks at 235°, 330°, and 530° C.   The second is the most prominent and is characteristic for identification of this mineral.   The first peak is probably a result of the decomposition of cliachite, since the impurities are too small in amount to account for the presence of other compounds.   The third reaction is due to the break-down of boehmite or diaspore.   Two possible explanations can be made for its presence:

(1) An actual mixture may have existed.   The sample con-

tained 68.0 percent Al_2O_3, but the theoretical content for gibbsite is 65.4 percent.   By calculation, 17.5 percent of boehmite or diaspore could be responsible for the increased alumina content, assuming that the amorphous cliachite was equal in composition to gibbsite.   The peak can be due to boehmite, as well as the diaspore, because in mixtures the tendency has been noted for some characteristic peaks to shift to lower temperatures.

(2) The peak may be part of a decomposition process. Schwiersch (45) has found that gibbsite first loses water to form boehmite, which continues to lose water to form gamma-Al_2O_3. In this case the amorphous cliachite would have to account for the excess Al_2O_3 in the analysis.   The ignition-loss data favor Schwiersch's theory; however, this question requires additional investigation.

Table 27 shows that the uncalcined sample had the highest alumina extraction; but with increase of temperature the solubility decreased, becoming appreciable above 600° C.   The discussion about sample M relative to solubility would also apply here.

A thermal analysis of muscovite (sample O) had no significant heat effects, although Grim found a very slight endothermic effect at about 800° C.   The alumina extraction was low for the uncalcined and calcined specimens — 17 and 29 percent.

Pyrophyllite (sample P) was found to be insoluble.   The available alumina content for biotite (sample Q) was 9.4 percent and after calcining at 800° C., 8.4 percent.   Orthoclase (sample R), calcined at 800° C., had an available alumina content of 0.1 percent.

TABLE 27.—*Results of extractions of alumina from gibbsite*

Temperature, °C.	Time, hours	Ignition loss, percent	Available Al_2O_3, percent	Extraction, percent
130	16		68.0	100
250	[1] T.A.R.	1.2	59.0	87
400	[1] T.A.R.	23.1	55.7	82
600	[1] T.A.R.	29.5	53.3	78
700	1	30.0	36.8	54
800	1	30.9	29.0	43

[1] Sample was heated in a furnace at thermal analysis rate of 5.5° C. per minute and removed when indicated temperature was reached.

CLAY SAMPLES FROM THE PACIFIC NORTHWEST

A number of local clays were selected for the purpose of analyzing their mineralogical content, and extraction results in the light of the knowledge gained from the examination of the standard minerals are listed in the preceding section; thus, each clay sample is presented as a case history.

The chemical analyses and extraction results are listed in tables 28 and 29 and the thermal analysis curves in figures 34 and 35.

CASTLE ROCK, WASH.

Sample CR–1 consisted principally of a member of the kaolinite group, as shown in figure 34, by the endothermic reaction with a peak at 575° C. and the exothermic reaction of 970°.   It is a
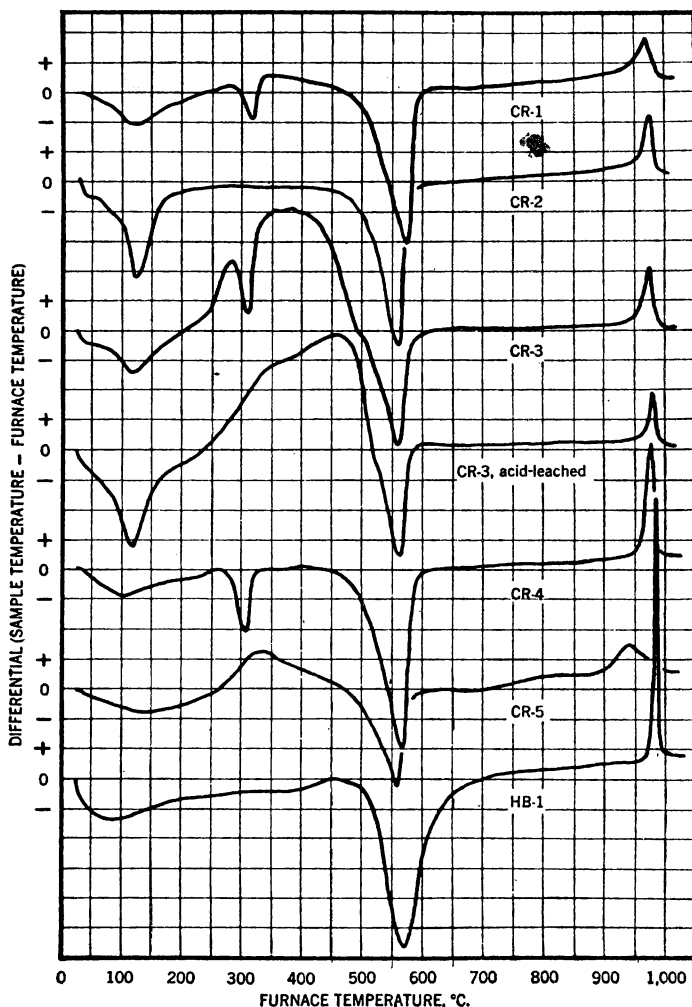
FIGURE 34.—Thermal analyses of selected Pacific Northwest clay samples.

kaolinite probably approaching halloysite in particle size, since the temperature of the endothermic peak and the slope of the line just after the peak are intermediate between the two. .A small amount of intergrowth of montmorillonite layers, similar in nature to the beidellites, is indicated by the exothermic peak, which is smaller and occurs at a slightly lower temperature than the one for the kaolinite-group minerals, and by the 3.3 percent of Fe_2O_3 in the chemical analysis. A small amount of gibbsite is indicated by the endothermic reaction at 320° C. The presence of a broad exothermic reaction between 250° and 450° C. is due to a small percentage of carbonaceous material. The gibbsite, kaolinite-halloysite, and montmorillonite intergrowth combines to give the uncalcined sample an extraction of 38 percent of alumina. A value of 89 percent instead of 100 for the sample calcined at 800°

C. is due to the loss in solubility by the gibbsite, and the montmorillonite layers.
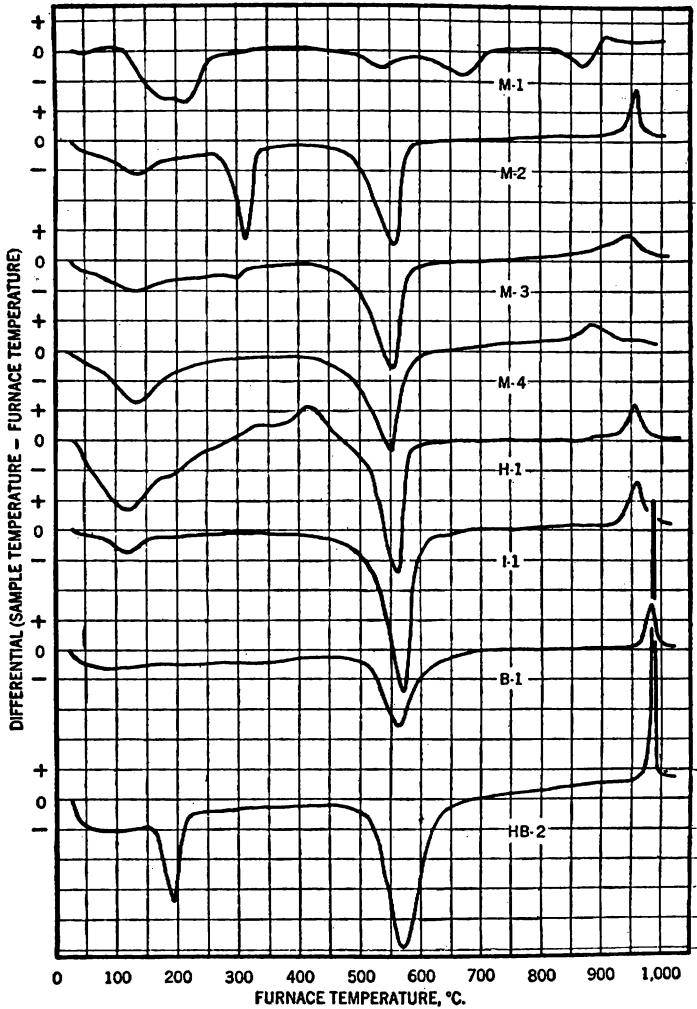
FIGURE 35.—Thermal analyses of selected Pacific Northwest clay samples.

TABLE 28.—*Chemical analyses of selected Pacific Northwest clay samples, percent*

	CR–1	CR–2	CR–3	CR–4	CR–5	HB–1	HB–2
Ignition loss_____	15.2	13.5	20.8	17.0	U	13.3	12.5
SiO₂_____	42.7	42.8	32.5	36.6	U	45.3	42.0
Al₂O₃_____	38.9	37.3	39.4	42.3	32.1	39.1	42.7
Fe₂O₃_____	3.3	3.2	4.1	.9	5.0	.9	1.4
TiO₂_____	2.0	2.9	2.1	2.5	U	2.4	2.3
MgO_____	U	U	U	U	U	U	U
CaO_____	U	U	U	U	U	U	U
Total_____	102.1	99.7	98.9	99.3	U	101.0	100.9

TABLE 28—Contd.

	M–1	M–2	M–3	M–4	H–1	I–1	B–1
Ignition loss	7.6	16.5	11.8	10.4	12.0	11.3	5.8
SiO_2	56.5	36.6	46.1	49.1	52.5	52.4	77.1
Al_2O_3	22.5	38.2	30.1	26.9	27.0	30.6	16.0
Fe_2O_3	6.0	5.6	9.6	9.5	4.8	3.0	.3
TiO_2	1.0	2.2	1.6	2.5	1.3	1.9	.5
MgO	4.0	.1	U	U	U	U	U
CaO	.9	.4	U	U	U	U	U
Total	98.5	99.6	99.2	98.4	97.6	99.2	99.7

U—Undetermined.   H—Harris deposit, Wash.
CR—Castle Rock, Wash.   I—Ione formation, Calif.
HB—Hobart Butte deposit, Oreg.   B—Bend, Oreg.
M—Molalla deposit, Wash.

Sample CR–2 has a thermal analysis curve that matches halloysite: The endothermic peak is at 560° C., the slope of the return temperature line is steep, and the characteristic endothermic peak at 130° C. is present. The percentage extractable alumina values were also similar to those for halloysite. The Fe_2O_3 in this case is more likely to be in the form of a mineral admixture than a montmorillonite intergrowth.

Sample CR–3 is similar to CR–1 but has a much higher carbonaceous-material content, as shown by the large exothermic reaction between 250° and 490° C. Gibbsite is responsible for the higher alumina: silica ratio. The carbonaceous material did not seem to have a deleterious effect on the solubility of the alumina. Gibbsite is dissolved upon leaching with the H_2SO_4 solution, as indicated by the absence of the endothermic peak at 310° C. in the thermal analysis (curve CR–3, acid-leached) of the residue.

Sample CR–4 is similar to CR–1 and CR–3 in that it consists of kaolinite-halloysite and gibbsite, but it is free of carbonaceous material. The larger exothermic peak at 975° C. indicates a smaller amount of montmorillonite intergrowth, if any, which agrees with the 0.9 percent Fe_2O_3 content of the sample. An alumina extraction from the calcined sample of 92 percent instead of 100 is due to loss of solubility of the gibbsite.

Sample CR–5, with an endothermic peak at 560° C. and a small exothermic at 940°, still consists primarily of kaolinite-type layers, but the shift in the latter peak indicates the presence of a sufficient amount of montmorillonite intergrowth for the sample to be approaching beidellite in nature. The extractable alumina values obtained are thus accounted for.

HOBART BUTTE, OREG.

The thermal analysis of sample HB–1 in figure 34 indicates it to be primarily a kaolinite because of the endothermic peak at 570° C. and the sharp exothermic peak at 980°. A tendency for some dickite to be present is shown by the slowness of the curve to reach zero differential just beyond the endothermic point. The extractable alumina content of 87 percent instead of 100 could be explained by the presence of the dickite or by the physical properties of this sample, which was hard and flintlike.

TABLE 29.—*Results of extraction of alumina from selected Pacific Northwest clay samples with sulfuric acid*

Sample	Mineral composition		Total Al₂O₃ content	Available alumina			Extraction, percent		
	Principal	Minor		Clay dried, 130° C.	Calcined, 800° C.	Pressure digestion, 155° C.	Clay dried, 130° C.	Calcined, 800° C.	Pressure digestion, 155° C.
CR–1	Kaolinite-mont.[1]	Gibbsite	38.9	14.7	34.6	38.5	38	89	99
CR–2	Halloysite		37.3	18.7	36.9	U	50	99	U
CR–3	Kaolinite-mont.[1]	Gibbsite	39.4	15.1	36.7	38.9	38	93	99
CR–4	Kaolinite	do	42.3	U	39.1	U	U	92	U
CR–5	Beidellitelike		32.1	5.2	23.1	29.6	16	72	92
HB–1	Kaolinite	Dickite(?)	39.1	2.2	34.0	U	6	87	U
HB–2	do	Dickite(?), scorodite	42.7	5.5	35.9	U	13	84	U
M–1	Montmorillonite	Illite	22.5	13.8	5.0	22.4	61	22	100
M–2	Kaolinite-mont.[1]	Gibbsite	38.2	22.0	33.3	38.2	58	87	100
M–3	Beidellitelike		30.1	8.5	25.3	30.1	28	84	100
M–4	do		26.9	U	22.3	U	U	83	U
H–1	Kaolinite-mont.[1]		27.0	3.7	24.5	U	14	91	U
I–1	do	Anauxite(?)	30.6	2.2	27.5	U	7	90	U
B–1	Kaolinite	Quartz, dickite	16.0	1.0	14.2	U	6	89	U

U—Undetermined.

[1] This notation indicates a small amount of montmorillonite intergrowth.

Sample HB–2 was similar to HB–1 but had an additional endothermic peak at 195° C. (fig. 35) that may be due to scorodite, a compound containing aluminum, iron, and arsenic. This mineral was discovered by Denning (7) in a sample from Hobart Butte whose description corresponded to sample HB–2. Scorodite would be responsible for the higher alumina content and probably also for the higher alumina extraction from the dried sample, as seen in table 29.

MOLALLA, OREG.

Sample M–1 consists primarily of montmorillonite, as indicated in figure 35 by the three endothermic reactions with peaks at 175° to 215°, 675°, and 870°, followed by the slight exothermic reaction at 905° C. The endothermic peak at 530° C. is caused by a small amount of kaolinite-type material or illite that is present either as an intergrowth or a mechanical mixture. Of the two, illite—the only one containing K_2O—is the more likely, since K_2O probably makes up the unaccounted difference of 1.5 percent in the chemical analysis in table 25. A 22-percent extraction for the calcined sample also points to this deduction, since it is expected that a kaolinite mineral would have raised this value.

Sample M–2 is essentially a kaolinite-halloysite with a considerable amount of gibbsite as an admixture, as shown by the peak at 310° C. The shift in the exothermic peak and lack of MgO in the chemical analysis indicate the presence of an intergrowth of montmorillonite layers approaching nontronite in composition. The extractable alumina values are commensurate with the mineral analysis: 58 percent for the uncalcined sample due to gibbsite, halloysite, and intergrowth and 87 percent for the calcined sample due to decrease of solubility of gibbsite and intergrowth.

Sample M–3 approaches beidellite in composition. The small, broad exothermic reaction at 940° C. is the result of an intergrowth of montmorillonite which is substantiated by the presence of 9.6 percent of Fe_2O_3 in the chemical analysis. The lower solubility of the uncalcined sample in comparison with M–2 is explained by the absence of gibbsite. Montmorillonite accounts for the lack of complete solubility of the calcined sample.

Sample M–4 is similar to the curve for beidellite (sample K). The exothermic reaction is small, with a peak at 885° C. The extractions and chemical analysis agree with the determined mineral composition.

HARRIS, WASH.

Sample H–1 is primarily a kaolinite, but an intergrowth is indicated by the shift of the exothermic peak. The intergrowth may be montmorillonite or illite, depending upon the presence of K_2O in the unaccounted-for portion of the chemical analysis. Some carbonaceous material is present. The extractable alumina values correspond with the mineral analysis.

IONE FORMATION, CALIF.

Sample I–1 had a thermal analysis curve that corresponded to one for kaolinite in appearance, except for the slight shift in the

exothermic peak, which was probably due to an intergrowth of a small amount of montmorillonite. The sample is believed to contain anauxite. If this is the case, the curves for kaolinite and anauxite coincide as to critical temperatures, just as the optical properties were found to be identical by Ross and Kerr (*43*). The alumina extraction of 90 percent for the calcined sample is thought to be due to the montmorillonite rather than the presence of excess silica in the form of anauxite.

<div align="center">BEND, OREG.</div>

The thermal analysis curve of sample B–1 in figure 35 is similar to that for HB–1, except for the considerably smaller magnitude of the peaks. The heat effects are reduced because of dilution of the clay mineral by free quartz, which was identified by petrographic examination and is substantiated by the high silica content in the chemical analysis. Again, indication of some dickite is probably responsible for the 89-percent extraction of alumina from the calcined sample. The interesting fact with regard to this sample and HB–1 is their similarity in the thermal analyses and likewise the percentage extraction of alumina values.

EFFECT OF SOME VARIABLES ON EXTRACTION OF ALUMINA

EFFECT OF DIGESTION UNDER PRESSURE

A number of reference minerals and Pacific Northwest clay samples after drying at 130° C. were digested with the 20-percent H_2SO_4 solution in a rotating pressure digester at 155° C. The alumina-extraction results are listed in tables 23 and 29 in conjunction with other data. The extractable silica values again are not included, since they were found to be practically constant. It was found, however, that the values were slightly higher than those after atmospheric leaching, in a few cases reaching 3 percent. The solubility of Fe_2O_3 in all cases exceeded 70 percent.

Dickite and diaspore gave poor results. Kaolinite improved considerably but reached only 70-percent alumina extraction. Illite, montmorillonite, and boehmite were very good. All the other samples approached complete solubility of alumina. It is felt that additional experimentation would indicate pressure-digestion conditions under which the kaolinite would become more completely soluble, and in turn improve the values for the others. The low extractions for dickite and diaspore, however, were not considered disturbing, as they rarely occur in large qantities in clay deposits. This method is of interest, since it would eliminate the calcination step which requires large quantities of fuel and perhaps also eliminate the fine grinding because the agitation under pressure probably would tend to disperse the clay.

EFFECT OF QUARTZ ADMIXTURE ON EXTRACTION

A sample of quartz that was ground through 400-mesh by an industrial concern was separated into a number of fractions by means of sedimentation. The finest fraction consisted of minus ½-micron particles and the coarsest of 10- to 20-micron particles.

The different fractions were thoroughly mixed according to
A. S. T. M. specifications with 50 percent of kaolinite, and then
percentage extractions of alumina were determined on the sam-
ples calcined at 800° C. No deleterious effect of the quartz was
apparent. On the basis of these data and a study of the results
presented in the report, the authors believe that free quartz func-
tions only as a diluent.

However, the question of the effect of quartz probably requires
some additional work, since Tilley, Millar, and Ralston (48) have
found in their experiments that the presence of quartz did lower
the percentage extraction of alumina from a California clay.

SUMMARY

A correlation has been found between the mineralogical compo-
sition of a clay, as determined by a thermal analysis method, and
the alumina that may be extracted from it with dilute sulfuric
acid after calcining for 1 hour at 800° C.

The kaolinite group of clay minerals is the most important, as it
contains about 39 percent Al_2O_3. The alumina of kaolinite, hal-
loysite, and anauxite is virtually completely soluble, while that of
dickite is not.

Two other commonly occurring groups of clay minerals are illite
and montmorillonite. These, however, are not of interest as
sources of alumina, since their total Al_2O_3 content and percentage
of extractable alumina are low. Illite has about 25 percent Al_2O_3,
about half of which is soluble; montmorillonite has about 20 per-
cent Al_2O_3, but only 20 to 30 percent is soluble.

Deposits of pure kaolinite-group minerals are not frequent and
extensive, because small quantities of other clay minerals, such as
members of the illite or montmorillonite groups, generally are
present as admixtures or intergrowths. The presence of these
minerals will naturally lower the total Al_2O_3 content of a kaolinite
clay and the percentage extraction. If the intergrowth exceeds
a certain amount, the authors believe that the resulting mineral is
beidellite.

Gibbsite, which has been found frequently in the samples tested,
raises the total Al_2O_3 content but lowers the percentage extraction,
since its solubility was found to drop to 43 percent after calcina-
tion at 800° C. Boehmite and diaspore, when present, lower the
amount of soluble alumina still further.

Extractions of alumina from uncalcined samples are unsatisfac-
tory. Of the kaolinite group, halloysite is the most soluble; four
samples showed that 50, 63, 78, and 90 percent of the alumina was
extractable. Two montmorillonite samples gave values of 87 and
33 percent and beidellite 66 percent, but the other clay minerals
were low. Gibbsite, on the other hand, is completely soluble.

A number of other calcination temperatures were also employed.
It was found that the kaolinite-group and beidellite minerals have
maximum solubility when calcined at temperatures between their
strongest endothermic and exothermic reactions, illites at temper-

atures between their second and third endothermic reactions, and montmorillonites in an uncalcined condition.

Pressure digestion without calcination offers possibilities, since all samples showed good extraction of alumina and low extraction of silica. Therefore, it appears desirable to examine other technical factors in connection with this method.

Thus, with a knowledge of the mineral composition of a clay and also the behavior of the different clay and nonclay minerals, the percentage of extractable alumina with dilute sulfuric acid for a given calcination temperature can be predicted.

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