

THE MINERAL COMPOSITION OF THE
COLLOIDAL CLAY FRACTION OF SOME ARIZONA SOILS

by

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A Thesis

submitted to the faculty of the

Department of Agricultural Chemistry and Soils

in partial fulfillment of
the requirements for the degree of

Master of Science

in the Graduate College

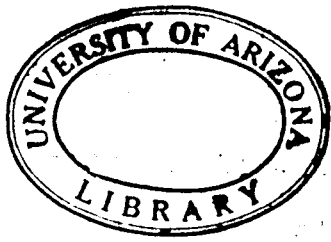
University of Arizona

1947

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May 16, 1947
Date



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ACKNOWLEDGMENTS

The author wishes to express his appreciation to his major Professor, Dr. T. F. Buehrer, for his help in planning and carrying out this research and in interpreting the results. Acknowledgments are also due to Dr. A. B. Caster for assistance in outlining methods for chemical analysis, to Professor H. V. Smith for furnishing some of the soil samples, and to J. E. Fletcher of the U.S. Soil Conservation Service and Dr. Ralph F. Grim of the Illinois Geological Survey for supplying standard clay mineral samples. Special appreciation is also extended to Miss Mary Lowenhaupt for help in preparing and reproducing the figures.

The author is indebted to the University of Arizona for the award of the Paul Steere Burgess fellowship and to the United States Government for assistance through the G. I. Bill of Rights.

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THE MINERAL COMPOSITION OF THE COLLOIDAL
CLAY FRACTION OF SOME ARIZONA SOILS

INTRODUCTION

As late as 1930 it was believed that the colloidal fraction of soils was composed largely of uncombined oxides or hydroxides of silicon, iron and aluminum (26)*, and although in 1927 C. S. Ross (44) of the U. S. Geological Survey pointed out that mineralogical and petrographical studies showed clays from soils to be well-defined minerals of definite crystal structure, the general belief that they were amorphous continued for several years. The nature of the base exchange reaction was not well understood, nor had the influence of the nature of the clay on this phenomenon and on the physical properties, fertility and tilth of the soil been determined.

Since that time much research has been done to determine the nature of the soil colloids. X-ray analyses, electron-micrographs and other studies have presented conclusive evidence that the clay fraction of soils is composed of crystalline minerals of plate-like structure (9). In fact, it is now definitely known that the clay minerals

* Numbers in parentheses refer to publications in the Bibliography, page 49.

found in soils are of three major types: (a) the Kaolinite group, which exhibits low base exchange capacity and shows but little adsorptive power for water and no swelling; (b) the Montmorillonite group, which has high base exchange capacity, exhibits high water adsorptive power and swelling; and (c) the Illite group which has about one-third the base exchange capacity of Montmorillonite, exhibits only slight swelling and is characterized chiefly by its content of non-exchangeable potassium.

The fact that the physical and chemical properties of these clay minerals, either in mixtures or separately, influence to a marked degree the structure, fertility and tilth of a soil emphasizes the importance of clay mineral studies. In Arizona where soil permeability is of prime importance in irrigation agriculture, and where the reclamation of desert land continues to be a major problem, clay mineral studies may have special practical significance. It is therefore desirable that the nature of the clay minerals present in Arizona soils and their influence on these soil properties should be investigated.

The first objective of this research was to determine qualitatively and quantitatively, as far as possible, the clay minerals in a group of Arizona soils. This was done by differential thermal, hydrothermal and chemical analyses.

The second objective was to correlate these data with field observations to discover any relationship that might exist between the nature of the clay fraction and the behavior of the soil in the field.

GENERAL REVIEW OF LITERATURE

One of the earliest methods used to differentiate between the various types of clay was the differential thermal method. This technique was devised and used by Le Chatelier in 1887 (30). Since that time some modifications and improvements have been made, but essentially Le Chatelier's method is still used today. The theory of the analysis is as follows:

One junction of a differential thermocouple circuit is embedded in powdered alumina inside a hole drilled in a sample block made of nickel or some other metal capable of withstanding high temperatures. The other junction of the circuit is embedded in a clay sample inside a similar hole in the sample block. As the block is heated from room temperature to about 1000° C., certain characteristic exothermic and/or endothermic changes take place in the clay. These changes are seen as differences in temperature between the inert material, alumina, and the clay. If the heating is done at a constant rate, the differential

temperature curve is quite reproducible. Further, when such a curve is compared with similar curves obtained from known clay samples, it will indicate the mineralogical composition of the unknown.

Little attention was paid to Le Chatelier's work until 1924 when Kurnakov and Urasov (29) made some additional thermal studies. Most of this early work, however, was concerned with clay as a ceramic material. It was not until after the work of Ross and other workers in the U.S. Geological Survey on the crystallinity of clay minerals that soil investigators undertook the study of clay minerals.

In 1933 Orceel and Caillere (39) applied Le Chatelier's differential thermal method to a number of clays and clay mixtures. They concluded that the method was sensitive to as little as three per cent of kaolinite. Sensitivity to montmorillonite, however, was only about twenty per cent.

Two years later Kelley (22) reported the results of X-ray analyses of clay minerals and soil colloids and suggested that the base exchange capacity of a soil depends on the mineral of the clay. In this same year Kelley, Jenny and Brown (21) published a study of the dehydration characteristics of clay and soil colloids. They suggested that dehydration curves up to a temperature of 800° C. could be used for clay mineral identification.

In 1939 Norton (37) made a critical study of the

differential thermal method for clay mineral identification. He suggested several improvements in apparatus and concluded that the method was particularly valuable in identifying clays that were too finely divided for petrographic methods or when they occurred in mixtures which made X-ray identification difficult. At this same time Kelley, Woodford, Dore and Brown (23) made some quantitative soil profile studies of Cecil and Susquehanna soils using X-ray and thermal dehydration analyses. Alexander and Nelson (3) published analyses on fifteen soils from various sections of the United States in which they identified and estimated amounts of kaolinite, montmorillonite and illite. The per cent of kaolinite was estimated from thermal analyses, the per cent of montmorillonite was determined from X-ray pattern densities with the per cent of illite being calculated from chemical analyses as well as from X-ray data.

Using Norton's improved thermal analysis method, Russell and Haddock in 1940 (47) published a semiquantitative study of some Iowa soils in which they used per cent K_2O as a basis for calculating illite. In 1941 Kelley, Dore and Page (25) completed their research on the clay minerals associated with alkali soils of the western United States. From X-ray analyses, dehydration curves and chemical data, they concluded that the effect of the

accumulation of sodium salts on the structure of the clay minerals was slight. Further, they found that solonchic soils contained no minerals that were specific to that particular soil type.

In 1942 a study of the differential method as a quantitative measure of clay mineral content was made by Schafer and Russell (49). Thermal curves for clay minerals and clay mineral mixtures showed that the areas of the endothermic peaks for dilutions of minerals were proportional to the area for pure minerals. The same year, however, Kelley and Page (27) published a paper showing that the differential thermal method, although sufficient for the determination of some minerals, was not entirely satisfactory for determining others. This conclusion was supported by work done by Speil in 1944 (57). He concluded that in some cases the method would give quantitative results to plus or minus 5 per cent. In the case of montmorillonite, however, the endothermic dips for various samples were found to differ both in area and in position making uncertain the determination of this particular mineral. In an investigation to determine the cause for such variations, Page (41) concluded that it must be due to substitution of elements within the crystal lattices.

One of the most comprehensive studies of the differential thermal analysis method and its application to

clays was published in 1945 by Speil, Berkelhamer, Pask and Davies (58). This paper gives a detailed description of techniques and apparatus and includes many standard curves and data for quantitative analyses. Much of the data and many of the curves are, however, the same as those published by Speil in 1944 (57).

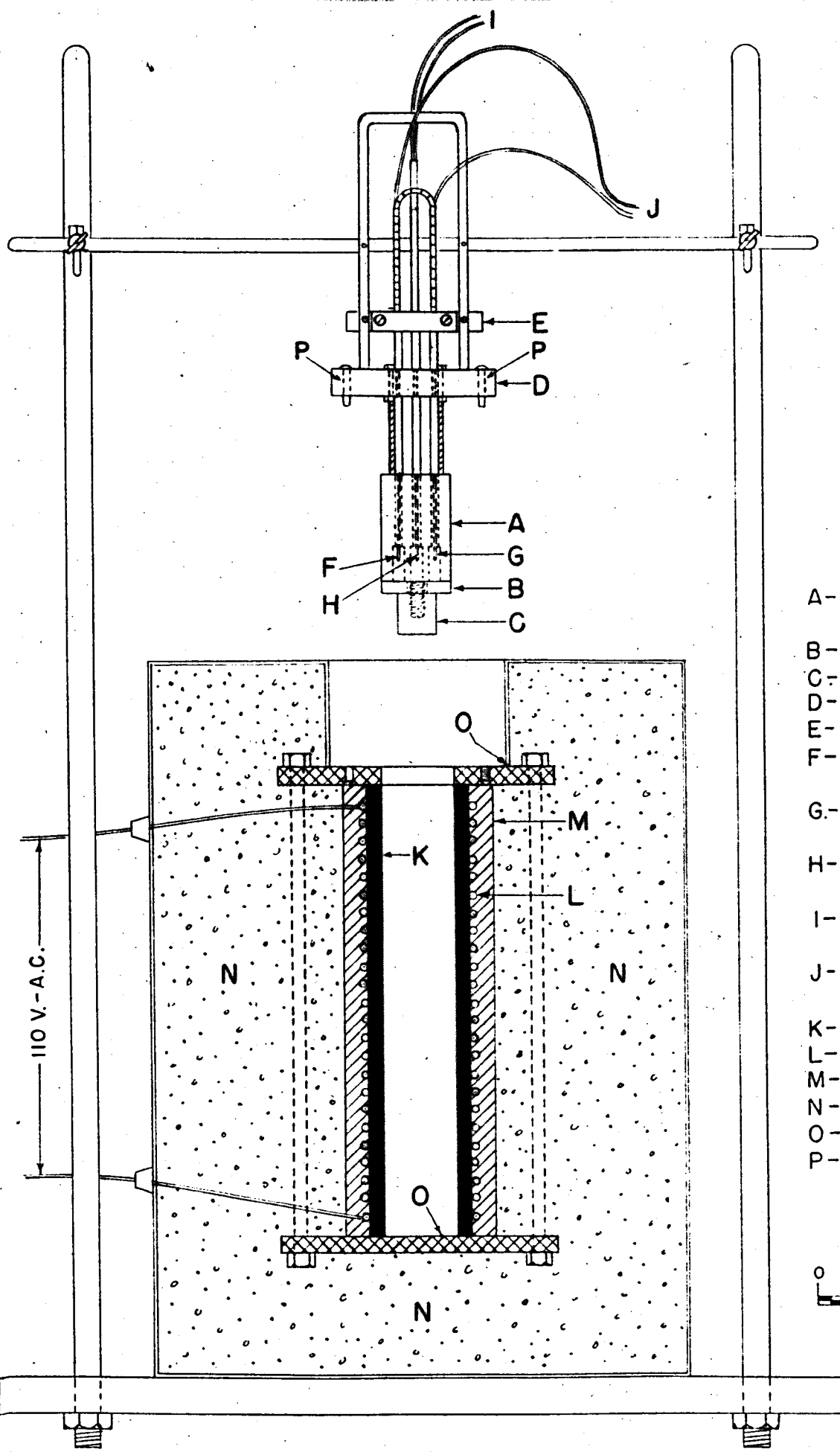
EXPERIMENTAL METHODS

Apparatus and Technique for Differential Thermal Analysis

In the present investigation the sample block consisted of a nickel cylinder $1\frac{1}{4}$ inches in diameter and $2\frac{1}{2}$ inches long. Three holes, $1/4$ inch by $5/8$ inch, were drilled in one end of the block, care being taken to place them equidistant from the outside periphery of the cylinder. Beyond the $5/8$ inch depth the diameter of these holes was reduced to a size that would just accommodate small porcelain insulators and continued through the entire length of the block. Three chromel-alumel thermocouple junctions were mounted through the porcelain insulators so that the junctions were centered in the $1/4$ inch holes. One of the three thermocouples in the block was connected through an ice junction to a Hoskins pyrometer to give the temperature of the block. The

other two junctions constituted part of the differential thermocouple circuit and were connected to a galvanometer. The sample block, as shown in Figure 1, was mounted by means of bolts to a Marinite Board furnace cover, and the latter to a frame for convenience in handling. To load the block for a determination, it was inverted and finely ground and ignited alumina was packed around the block temperature junction and one of the differential junctions. The clay sample to be analyzed was packed into the third hole. Care was taken during loading to obtain uniform compaction and to insure that the thermocouples remained centered. After loading, the powdered material was held in place by a nickel cap fastened to the bottom of the block by a nickel steel stud and nut.

The element of the furnace used for heating the sample block consisted of a silica tube wound with nichrome wire. This core was mounted rigidly in a metal container and insulated on all sides with approximately three inches of silocel. The furnace temperature was regulated by means of rheostats. This regulation was done manually as was the recording of both the furnace temperature and galvanometer deflections. After the initial runs were made, the approximate current requirement for the desired heating rate was known and very nice temperature regulation was possible. A heating rate of ten degrees per minute and a sample size of 0.3500 gram was made standard in all



- A- CYLINDRICAL NICKEL BLOCK.
- B- NICKEL COVER.
- C- INCONEL STUD AND NUT.
- D- MARINITE CAP.
- E- BAKELITE CLAMP.
- F- JUNCTION FOR SOIL COLLOID.
- G- REFERENCE JUNCTION OF DIFFERENTIAL COUPLE.
- H- JUNCTION FOR FURNACE TEMPERATURE.
- I- LEADS TO ICE JUNCTION AND PYROMETER.
- J- LEADS TO GALVANOMETER.
- K- SILICA FURNACE TUBE.
- L- HEATING ELEMENT.
- M- ALUNDUM CEMENT.
- N- SILOCEL INSULATION.
- O- TRANSITE CAPS.
- P- CENTERING PINS.

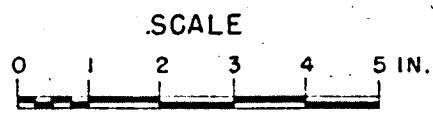


Fig. 1. Apparatus for differential thermal analysis.

of the thermal analyses.

During the early part of the research considerable difficulty was experienced because of the short life of the thermocouples. The sample junction would burn out after only a few runs. This problem was solved, however, when care was taken to get a good clean weld without weakening the wires at the junction. This was done by carefully twisting together, as uniformly as possible, the polished ends of the two thermocouple wires. Then, using a reducing flame and Calgonite flux, the twisted junction was superficially welded. This gave a smooth even weld along the surface of contact of the twist, but did not melt the body of the wire. This technique had the added advantage of simplifying the job of making two nearly identical junctions for the differential circuit. It also made possible the re-welding of junctions, in the event they burned out, with the wires still in the block.

Several test runs were made with alumina surrounding both of the differential junctions. In these tests the galvanometer deviation from the zero line was only about one half of a division and was usually nearly constant throughout the temperature range. (See Figure 2).

GALVANOMETER DEFLECTIONS

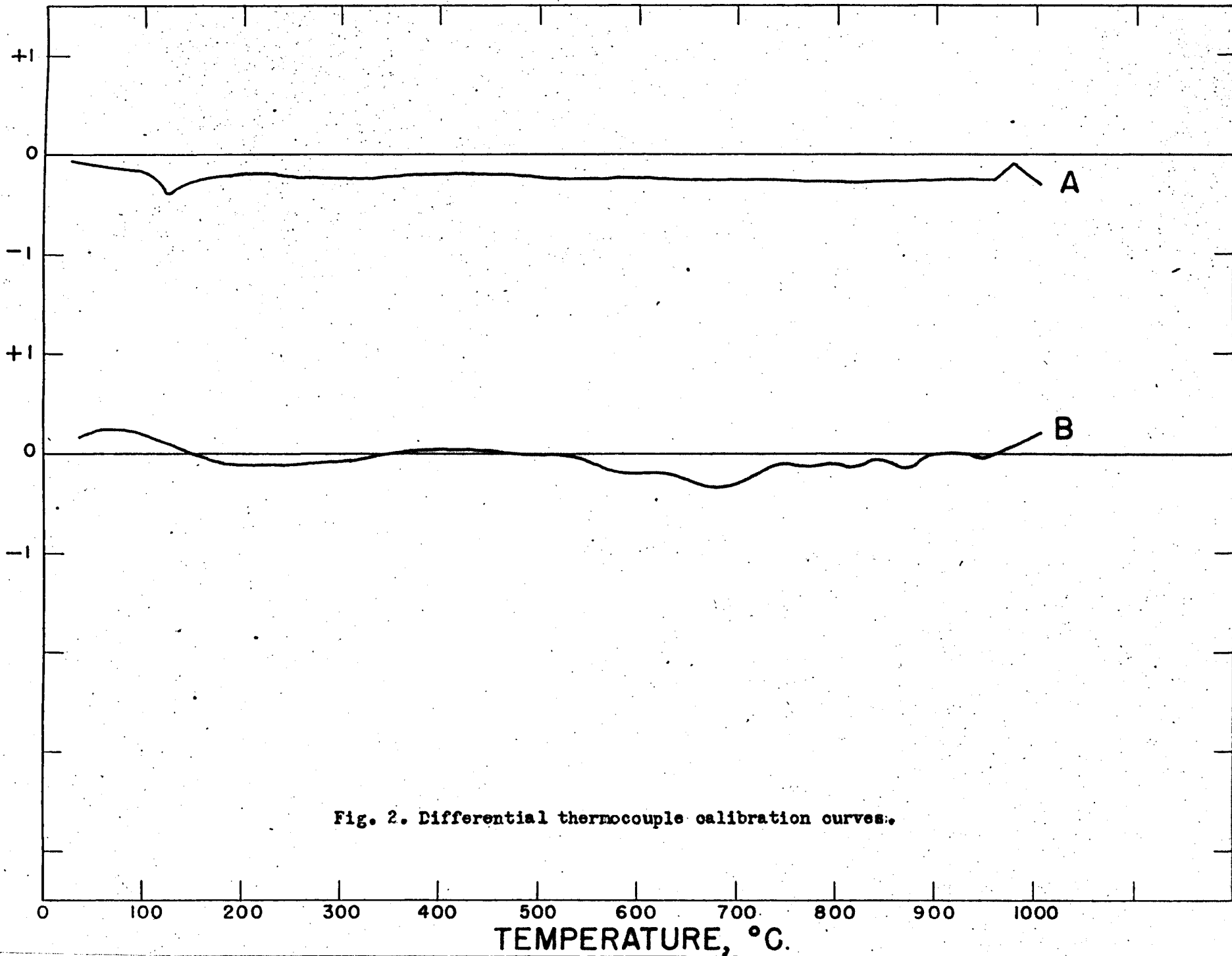


Fig. 2. Differential thermocouple calibration curves.

Calibration of Pyrometer

Calibration of the pyrometer was done by checking against fixed temperature points. The fixed points used were the boiling point temperature of water and the freezing point temperatures of different pure metals. The freezing points of the metals were measured as the halting points on the cooling curves of the molten metals. The metals used had been obtained from the U.S. Bureau of Standards and had freezing points as follows:

Tin	- - - -	231.9 ^o	C.
Lead	- - - -	327.4 ^o	C.
Zinc	- - - -	419.4 ^o	C.
Aluminum	- - - -	660.2 ^o	C.

Silver was purified by electrolytic deposition and had a freezing point of 960.5^o C.

The final calibration was made with a differential thermocouple circuit, one junction of which was maintained at 0^o C. by means of cracked ice and distilled water in a vacuum bottle. The other junction, which was used for the high temperature measurements, was enclosed in a carbon sheath, then immersed in the molten metal. A 725 watt Hoskins furnace was used for the calibration, the metals being melted in a graphite crucible. The desired cooling rate of six to eight degrees per minute was obtained by varying the amount of insulation (glass wool) around the outside of the furnace and, at the higher temperatures, by sending a small current through the furnace heating element.

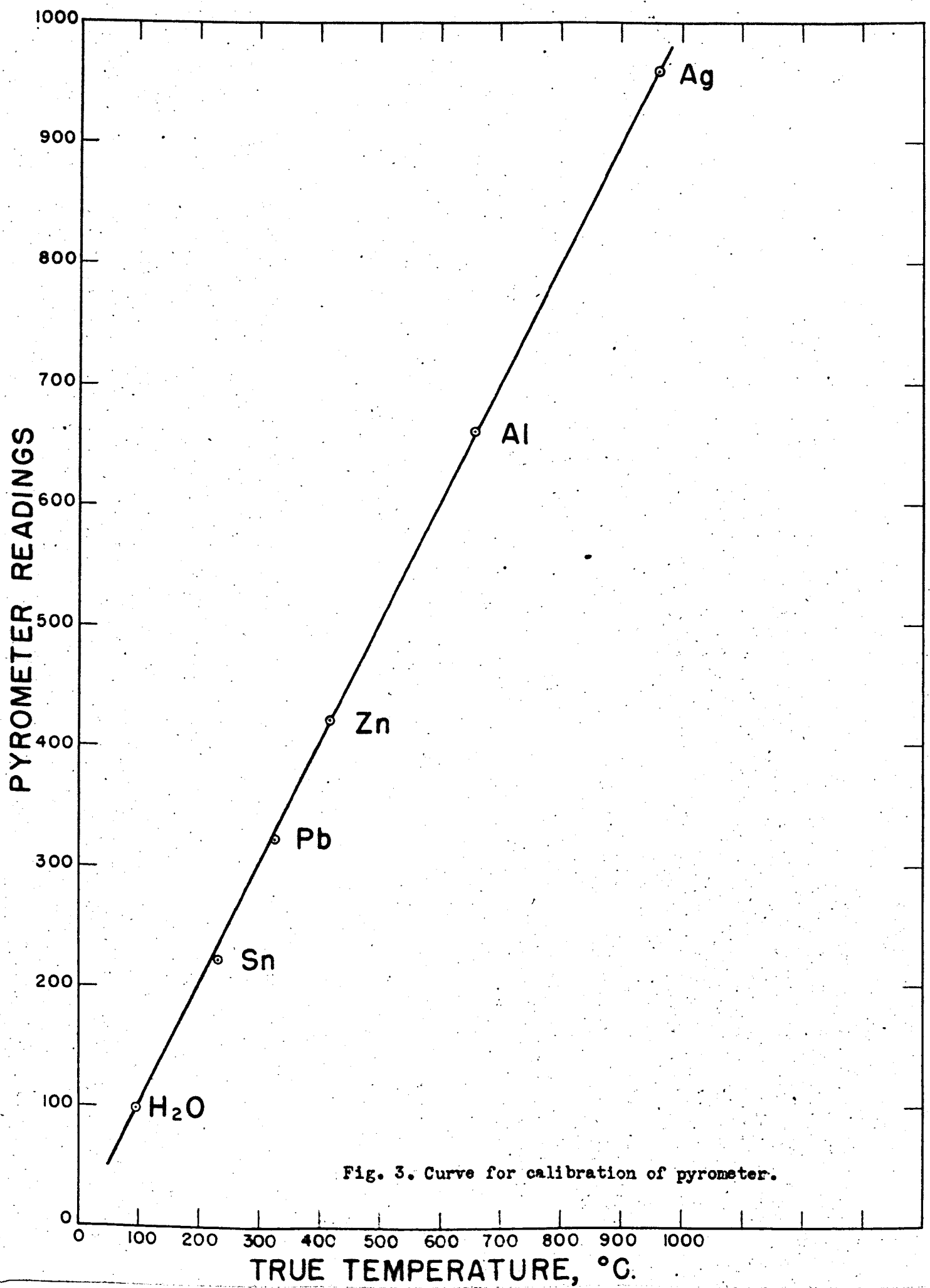


Fig. 3. Curve for calibration of pyrometer.

The pyrometer screw adjustment was turned until it gave a 0° reading when both thermocouple junctions were placed in the cracked ice and water. Since the pyrometer was essentially a milliammeter, the resistance of the thermocouple circuit had to be adjusted. This was done by varying the length of the lead wires to the pyrometer so that the correct reading of 960° was given at the freezing point of silver. The resistance was then set at this value. Results of calibration against other fixed points are given in Figure 3.

Calibration of the Galvanometer

The sensitivity of the galvanometer was determined by the potential divider method. A circuit was set up as shown in Figure 4 so that a small current was sent through the galvanometer. By observing the magnitude of the galvanometer deflection caused by this current, the sensitivity (amps per division deflection) was calculated. The difference of potential between a and b can be expressed:

$$V_{ab} = P I$$

also,

$$V_{ab} = i(R+G)$$

therefore,

$$P I = i(R+G) \quad (1)$$

The current through Q is (I+i). The drop of potential from a to c then is the voltage drop from a to b plus the drop from b to c. Therefore:

$$V = Q(I+i) + P I \quad (2)$$

Eliminating I between equation (1) and (2) and solving for i:

$$i = \frac{P V}{(P+Q) \times (R+G) + PQ} .$$

The sensitivity, F, or amps per division of deflection would be:

$$F = \frac{P V}{(P+Q) \times (R+G) + PQ} \times \frac{1}{d}$$

The resistances used and the observed values for the different factors were as follows:

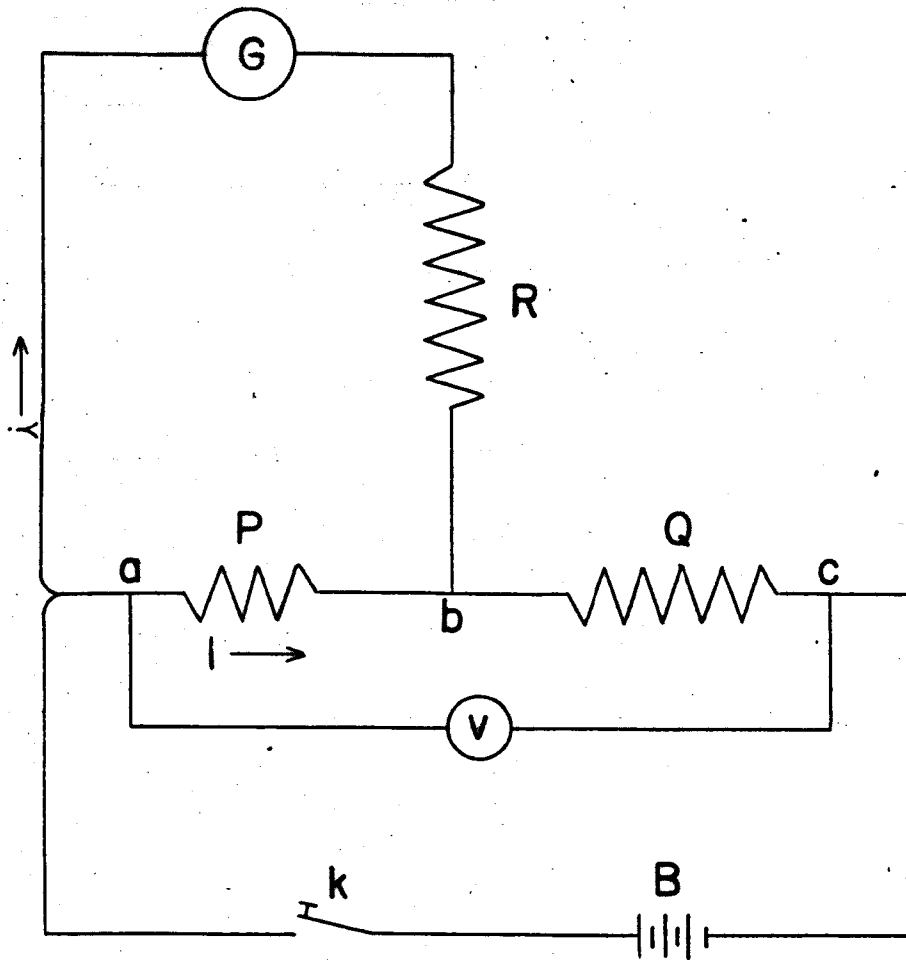
P	=	.8 ohms
V	=	1.6 volts
Q	=	49. ohms
R	=	200,000 ohms
G	=	3,800 ohms
d	=	10.5 divisions

Substituting these values in the equation:

$$F = \frac{.8 \times 1.6}{49.8 \times 203,800 + .8 \times 49} \times \frac{1}{10.5}$$

$$F = 1.154 \times 10^{-8} \text{ amps per scale division.}$$

From published values of EMF developed by chromel-alumel thermocouples, it is seen that the average EMF



LEGEND:

G- GALVANOMETER

V- VOLTMETER

R- }
 P- } RESISTANCES
 Q- }

K- KEY

B- BATTERY

Fig. 4. Circuit for calibration of galvanometer.

change caused by 1° C. is .041 mv. Using the above mentioned galvanometer and assuming that the resistance of the differential circuit to be that of the galvanometer (3,800 ohms), the value of one galvanometer division in degrees centigrade can be calculated:

If I is the flow of current caused by one degree temperature difference, then:

$$I = \frac{E}{R} = \frac{.000041}{3800} = 1.079 \times 10^{-8} \text{ amps.}$$

The temperature equivalent of each galvanometer division would then be:

$$\begin{aligned} 1 \text{ division} &= \frac{1.154 \times 10^{-8}}{1.079 \times 10^{-8}} \\ &= 1.069^{\circ} \text{ C.} \end{aligned}$$

Apparatus and Technique for Hydrothermal Analysis *

To obtain dehydration curves of the soil colloids, it was found necessary to devise a balance that would give direct and continuous reading of the weight loss of the clay samples as they were heated up to 1000° C. This was done by modifying an analytical balance as shown in Figure 5.

* In this paper the terms hydrothermal and thermal dehydration are used synonymously.

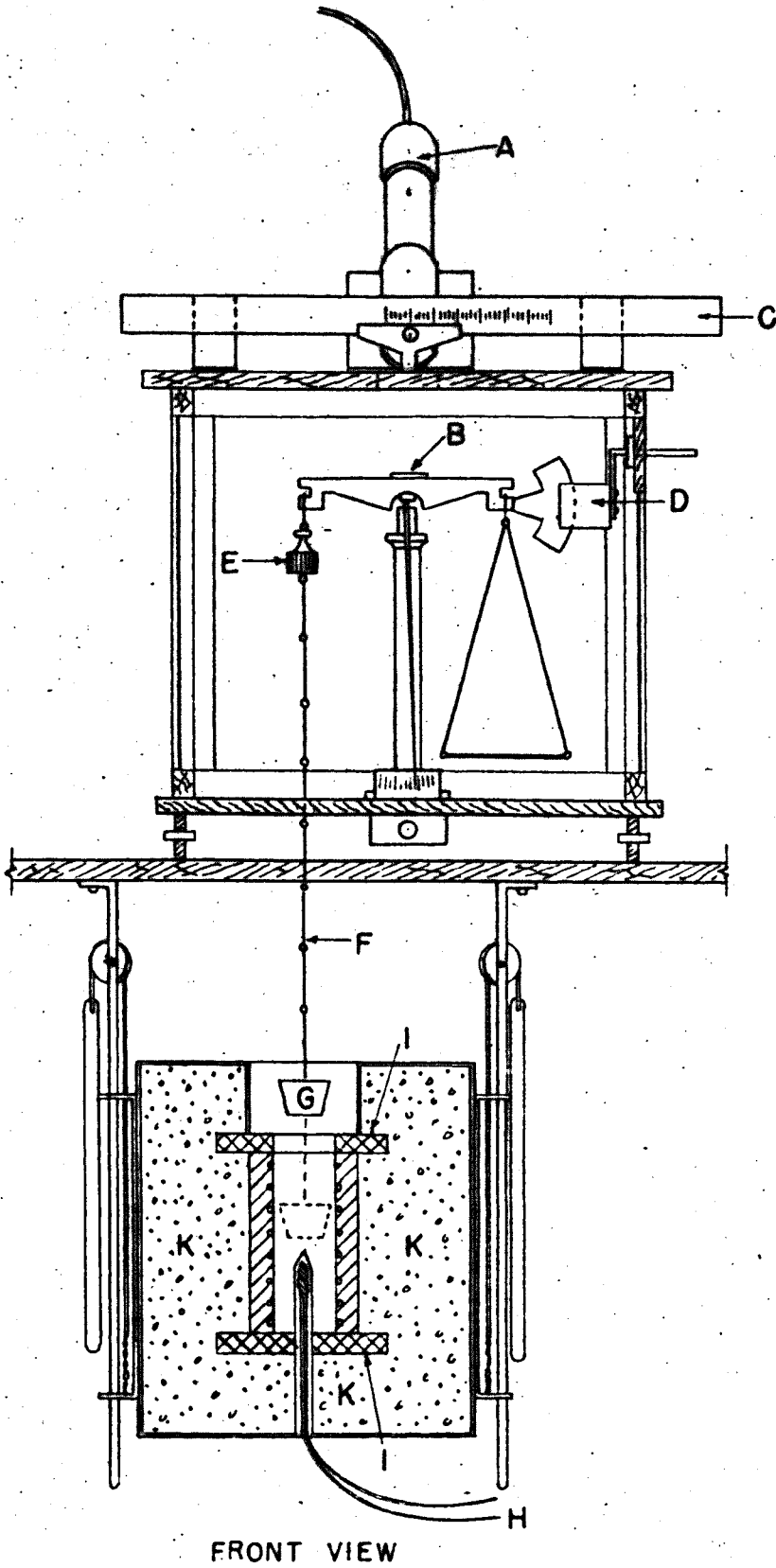
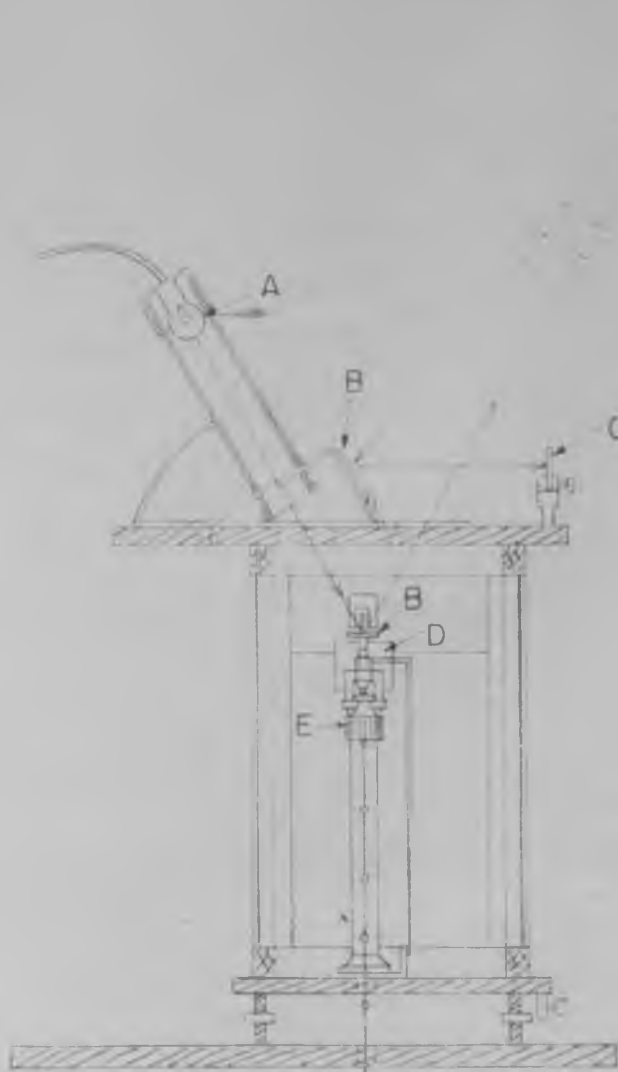
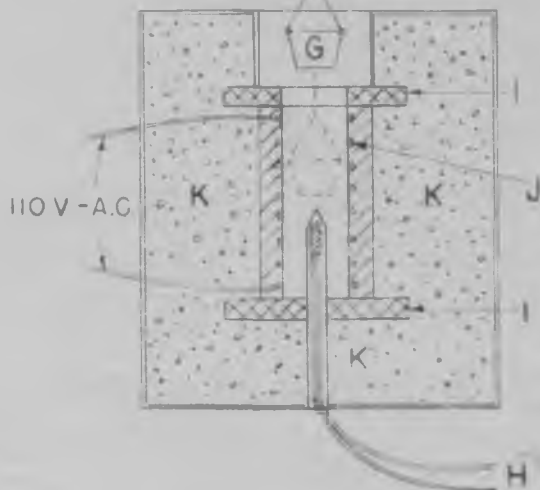


Fig. 5. Balance and furnace for hydrothermal analysis.(Front view).



- A - LINEAR FILAMENT LAMP.
- B - MIRRORS.
- C - SCALE.
- D - MAGNETIC DAMPER.
- E - COUNTER WEIGHT.
- F - PLATINUM CHAIN.
- G - PLATINUM CUP.
- H - THERMOCOUPLE LEADS.
- I - FIRE BRICK.
- J - HEATING ELEMENT.
- K - SILOGEL INSULATION.



SIDE VIEW

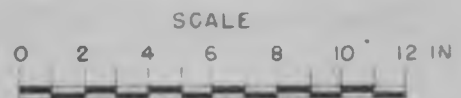


Fig. 5. Balance and furnace for hydrothermal analysis. (Side view).

A small mirror one centimeter wide and three centimeters long was mounted on top of the balance beam with Lucite cement. A light source consisting of a single straight-filament bulb in a tube provided with a focusing lens was mounted on top and to the rear of the balance case. A beam of light was focused from the light source upon the reflecting mirror on the balance beam and thence reflected to a second mirror mounted on the ceiling about two and a half meters away. From the second mirror the light was returned to a third mirror on top of the balance case and thence to a fifty-centimeter ground-glass scale. When the system was properly adjusted and focused, the image of the filament appeared as a straight vertical line on the scale.

The sensitivity of the balance was adjusted by adjusting the screw and collar on the balance pointer until a change of one milligram on the balance pan would give one centimeter change in reading on the scale. This 1:1 correspondence between weight in milligrams and scale distance in centimeters remained the same over the entire length of the scale with an accuracy of plus or minus two-tenths of a milligram, since the maximum angle change on the beam from a reading of zero to fifty was only three degrees. The balance was equipped with a strong magnetic damper so that the oscillations of the line on the scale would be kept at a minimum.

One of the balance pans was replaced by a counter weight and a platinum chain attached to it to serve as a suspension. This chain extended through a small hole in the bottom of the balance case and supported a platinum pan inside a tube furnace below the balance table. The furnace was well enough insulated so that a clay sample could be placed in the pan and heated to 1000° C. without changing the temperature inside the balance case more than one or two degrees. The furnace cap was made of transite with a stainless steel sheet on the under side of it to prevent any material from chipping off and falling into the sample pan.

As was the case in the differential thermal analyses, the furnace temperature regulation as well as the recording of temperature and weight loss readings was done manually. The heating rate was held constant at ten degrees C. per minute and a uniform sample size of 0.3500 gram used in all determinations.

The calibration of the pyrometer and thermocouple circuit was the same as already described. However the problem of actually measuring the temperature of the sample was difficult. It was evident that there would be some lag between the pyrometer reading and the furnace temperature and hence between the temperatures of sample and furnace. To overcome this as much as possible the thermocouple

sheath was made of a silica tube, the tip of which had been drawn down to a very small diameter and to a very thin wall. Moreover, this sheath was located so that the thermocouple junction was never more than a half inch from the bottom of the sample pan. The sample itself was distributed in a thin layer over the bottom of the pan, and since the pan had a diameter of one and one-fourth inches, the depth of the sample was less than one-sixteenth of an inch.

Several preliminary runs were made with an empty sample pan to check the heating rate and functioning of the balance. In all of these test runs there was a characteristic deviation in the weight of the pan from its initial value. The curve showing this effect is presented in Figure 6. There was always a rapid gain in weight as the furnace began to heat. This increase reached a maximum of approximately three and one-half milligrams at a temperature of 180° C. and then gradually decreased to the initial scale reading at approximately 775°. The curve obtained was very reproducible, and even with clay samples there was initially an apparent gain in weight or a slow initial loss in weight. All of the data subsequently obtained were, therefore corrected by means of the curve for the empty pan readings.

During these determinations and while the clays were

WEIGHT LOSS, MILLIGRAMS

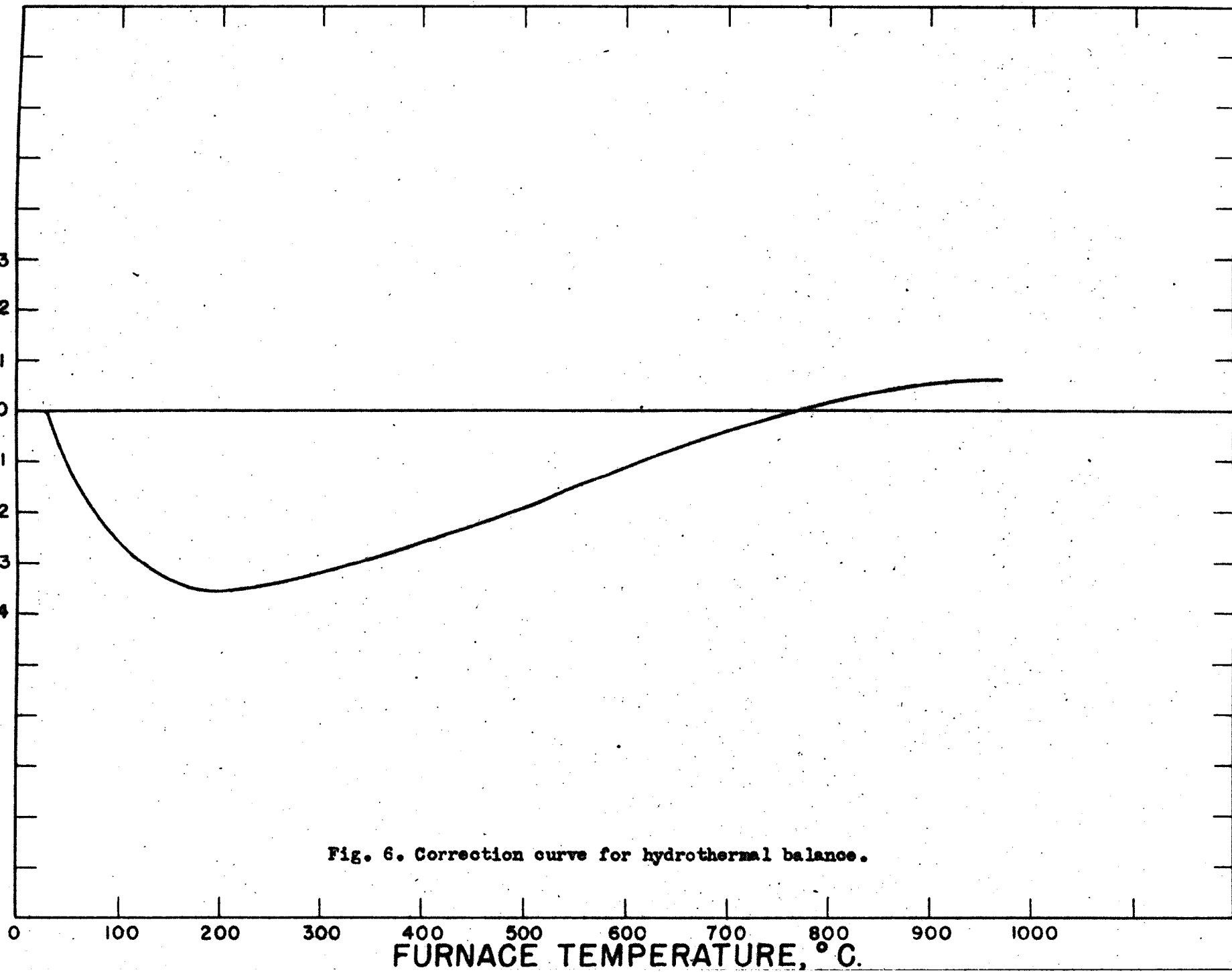


Fig. 6. Correction curve for hydrothermal balance.

decomposing in the pan, there was some oscillation of the line on the scale. These variations, however, were seldom greater than one centimeter and usually were much smaller. They were regular enough to allow reading of maximum and minimum positions from which fractions of milligrams could be closely estimated.

Separation and Purification of Colloids

The clay fraction with an effective diameter of less than 2μ was separated from the sample soils and standard minerals by dispersion and sedimentation. The clay thus separated was further prepared for analysis by removing organic matter and carbonates, saturating with calcium and washing free from soluble salts.

Previous investigators have reported removal of organic matter by the use of hydrogen peroxide. On preliminary tests, however, organic matter extracted from soil samples with sodium hydroxide was oxidized only partially by heating with thirty per cent H_2O_2 . Similar extracts were completely oxidized when heated with a small amount of liquid bromine. Further investigation showed that the bromine oxidation was slow and incomplete in neutral or acid solution but that it proceeded rapidly to completion in an alkaline solution. Sodium hyprobromite was

therefore chosen as the oxidizing agent. When the suspensions were made up to a concentration of approximately 0.3-Normal NaBrO, buffered to pH 9 - 10 and heated to boiling, oxidation was complete in only a few minutes.

The absence of color in the sodium hydroxide extract of the clay suspension was used as a qualitative test for completion of oxidation. The procedure for the test was to centrifuge a small amount of the suspension in a tube, decant the liquid, and mix the remaining clay thoroughly with approximately 10 cc. of 6-Normal sodium hydroxide. On centrifuging again, the clay was separated from the extract. Tests were made on some processed samples, care being taken to use about the same size samples and in general the extract color agreed qualitatively with the per cent of carbon obtained by combustion analysis of the purified colloid. On samples which gave no noticeable color to the extract the per cent of carbon was of the order of one-tenth of a per cent or less.

Saturation of the colloids with calcium and washing to remove soluble salts was done for the most part by the centrifuge technique. Calcium acetate, 2-Normal, was the reagent used. It was recognized that the relative amounts of saturating solution and clay sample would determine to a certain extent the effectiveness of each centrifugation. Therefore an effort was made in all

treatments to control the sample size so that after centrifuging it occupied only about one-sixth of the total volume of the centrifuge tube. Care was taken with each saturation or washing to stir the clay thoroughly into suspension. This was done by the use of a large policeman. Further, the centrifuge tubes were placed in boiling water for a few minutes after being mixed with the saturating solution in order to make the exchange reaction go more rapidly and more nearly to completion for each treatment. Heating the suspensions also resulted in more thorough mixing.

Some of the colloids were saturated and partly washed by sedimentation. The same general procedure and the same solution strengths were used, but instead of centrifugation, the colloid was allowed to settle out by gravity. This technique had the advantage of requiring less work in processing the colloid and simplified mixing the colloid with the saturating solution. It required large volumes of saturating solutions, however.

During the washing of several colloids by sedimentation, the dilution ratios were recorded. It was observed that the clays which had been saturated with calcium showed a tendency to disperse by the time the concentration of the calcium had been reduced by washing

with distilled water to about 0.008-Normal, and at concentrations of about 0.004-Normal the colloid was partially dispersed. The final washings were accomplished by centrifuging with methyl alcohol.

The following is a general outline of the procedure used in separating and preparing the clay samples:

1. Fifty grams of soil was put into a Hamilton Beach stirrer cup with 500 cc. of water and 5 cc. of normal NaOH and stirred vigorously for ten minutes.
2. After stirring, the suspension was screened through a 200-mesh sieve and put into a Bouyoucos cylinder. Water was added to make up to the mark and mixed well. The cylinder was then set aside for sedimentation. (If the sample yielded an excessive amount of clay as was the case with the standard minerals, the suspension was divided between two or three cylinders for sedimentation.)
3. After the suspension had settled for 24 hours, the suspended material was syphoned off to within two inches of the sediment layer or to a depth of 30 centimeters.
4. The suspension collected was coagulated by adding approximately 50 cc. of 2-Normal calcium acetate. After the suspension had settled, the clear supernatant liquid was syphoned off and the thick suspension transferred to a large beaker.
5. Sufficient sodium hypobromite solution was added to the suspension to make it approximately 0.3-Normal in that reagent. The suspension was adjusted to a pH between 9 and 10 and a small amount of sodium bicarbonate added to act as a buffer. The suspension was then heated with stirring until oxidation of organic matter was complete.

6. After oxidation, 0.5-Normal HCl was added to the suspension to remove all carbonates. The acidity of the suspension was not allowed to exceed a value of pH₂.
7. The suspension was centrifuged and the clear solution poured off. The clay was stirred with 2-Normal calcium acetate solution and heated by putting the centrifuge tubes in a beaker of boiling water for a few minutes. The suspension was centrifuged, the saturating solution poured off and the treatment repeated until four such treatments had been completed.
8. The excess calcium acetate was removed by washing and centrifuging twice with distilled water and then with 60% methyl alcohol until there was no test for calcium in the supernatant liquid after centrifuging. This usually required three washings with alcohol.
9. The sample was air-dried and then ground, either with a mortar and pestle or in a ball mill, until it would pass through a 100-mesh sieve.
10. Samples for differential thermal and hydrothermal analysis were humidified for not less than 48 hours over 50% sulfuric acid, which gives a relative humidity of about 37%.

Chemical Analysis of Soil Colloids

The chemical analyses made on the purified colloids were the base exchange capacity and the percentage of non-exchangeable potassium. The latter was used as a basis for determining the amount of illite in the clay samples while the base exchange capacity provided a method of

correlating the chemical and thermal analyses.

The base exchange capacity was determined by saturating the colloid with ammonium ion, washing out the excess and measuring the amount retained by distilling it into saturated boric acid solution and titrating back with standard acid. Approximately one gram of the purified colloid was put into each of two tared centrifuge tubes. The samples were dried at least two hours at 105° C., cooled in a desiccator and weighed. Obtaining the correct weight of sample was simplified by the use of screw capped centrifuge tubes which prevented the dry samples from absorbing moisture from the air during weighing. The clay samples were mixed well with 2-Normal ammonium acetate solution, heated for a few minutes in boiling water and centrifuged until clear. The supernatant liquid was poured off and the treatment repeated three times. The samples were then very carefully washed by centrifugation, twice with distilled water, once with sixty per cent methanol and once with absolute methanol. During each saturation and washing, extreme care was taken to prevent any loss of sample.

After washing, the samples were transferred to clean Kjeldahl flasks with approximately 300 cc. of water. A few unglazed porcelain boiling chips were added to the

suspension and the flask placed on the distilling rack. After an Erlenmeyer flask containing 50 cc. of saturated boric acid solution and a few drops of modified methyl red indicator had been placed under the receiving tube, 30 cc. of 30 per cent sodium hydroxide was poured into the distilling flask. This base was added quickly to avoid any loss of ammonia. The mixture was boiled until the receiving flask contained approximately 250 cc. of solution. The distillate was then titrated with 0.1054-Normal hydrochloric acid which had been standardized by titrating the distillate obtained when a weighed amount of pure ammonium sulfate was distilled over in the same manner. As is customary, the results were calculated to milliequivalents per 100 grams of sample.

To determine potassium the clay samples had to be dissolved. This was accomplished by using a modification of the hydrofluoric acid treatment described in Scott's Standard Methods of Chemical Analysis (50).

Samples of approximately one-half gram were put into tared platinum crucibles. These crucibles were placed in tared weighing bottles and dried at 105° C. for at least two hours, cooled in a desiccator and weighed. After the dried sample had been weighed, the samples were ignited over Meeker burners for about twenty minutes to break down the crystal structure of the clays. The ignited samples were then transferred to platinum dishes and

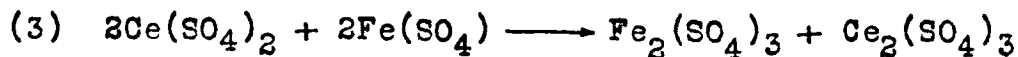
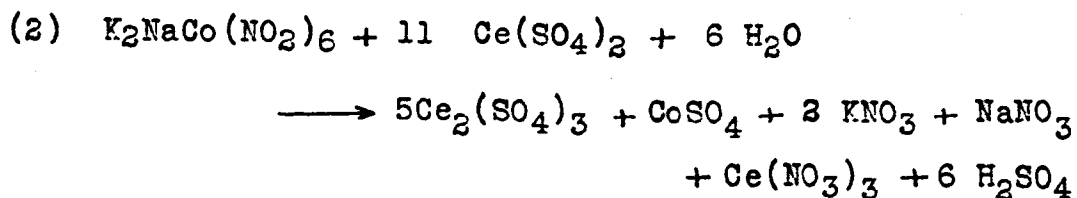
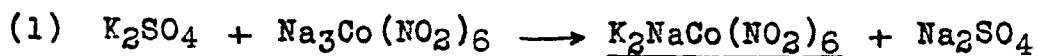
moistened with a drop or two of water. They were then covered with approximately 10 cc. of concentrated hydrofluoric acid and evaporated to dryness on a sand bath. When evaporation was complete, the residue was treated with another 10 cc. of concentrated hydrofluoric acid plus one-half cc. of concentrated sulfuric acid and again taken to dryness. After the second treatment, the residue was transferred to a 50 cc. beaker using 10 cc. of water.

The potassium in the residue was determined by the cobaltinitrite method. Five cc. of sodium cobaltinitrite reagent* was added to the residue in the 50 cc. beaker and allowed to stand at least one hour for complete precipitation of the potassium. The contents of the beaker were then filtered through an unglazed porcelain gooch crucible, after which the potassium cobaltinitrite precipitate was washed three times with 5 per cent acetic acid. Not more than 2 cc. of acid was used for each washing and with each portion the beaker was rinsed well

* The sodium cobaltinitrite reagent is prepared as follows:
(a) Dissolve 113 grams of cobaltous acetate in 300 cc. of hot water and 100 cc. of glacial acetic acid. (b) Dissolve 200 grams of sodium nitrite in 400 cc. of hot water. When the two solutions are cold, mix equal parts of (a) and (b) and bubble air through the mixture until red fumes are no longer evolved. If the reagent is cloudy, it should be filtered. It must be kept free from ammonia fumes and stored in a cool place.

using a policeman to insure complete transfer of the precipitate. After washing, the filter crucible was put into a 400 cc. beaker with 150 cc. of distilled water, 25 cc. of 0.0500-Normal ceric sulfate and 10 cc. of 18-Normal sulfuric acid. (Sometimes the amount of ceric sulfate was varied, depending on the quantity of precipitate in the crucible.) The beaker was then covered with a watch glass and heated slowly to boiling, after which it was set aside to cool. When cool, the excess ceric sulfate was titrated with 0.0513-Normal ferrous sulfate, using the ortho-phenanthroline-ferrous-complex as indicator.

The reactions for the determination can be written as follows:



In order to test the technique in this determination, the potassium was determined on a National Bureau of Standards clay sample. The average four determinations was 3.25 per cent K₂O, which is a little higher but compares favorably with the Bureau of Standards value of 3.17 per cent.

DESCRIPTION OF CLAY MINERALS AND SOIL SAMPLES ANALYZED

The standard minerals and soil samples analyzed were as follows:

1. Montmorillonite Standard. A sample of bentonite from the vicinity of Kanab, Utah. Supplied by J. F. Fletcher.
2. Montmorillonite from Yavapai County, Arizona
3. Bentonite from Otay, California.
4. Kaolinite from Spruce Pine, Mitchell County, North Carolina.
5. Halloysite (var. Indianaite) from near Bedford, Indiana. Supplied by Ward's Natural Science Establishment, Inc., Rochester, New York.
6. Illite from Pennsylvanian underclay near Fithian, Vermillion Co., Illinois. Supplied by F. F. Grim, Illinois State Geological Survey, Urbana, Illinois.
7. Pima clay from Tucson City Farm on Casa Grande Highway No. 89.
8. Gila sandy loam from University of Arizona Farm on North Campbell Avenue, Tucson.
9. Casa Grande loam from gypsum-experiment plot near Casa Grande. Supplied by W. T. McGeorge.
10. Sunrise clay from Refsnes Ranch south of Tempe. NW $\frac{1}{4}$ of NW $\frac{1}{4}$ of Section 27, T. 1N, R. 4E. Typical "slick spot". Very alkaline, clay hardpan 4 inches thick at depth of 3 $\frac{1}{2}$ feet.
11. Yuma clay loam from Henderson Ranch, Yuma. Section 25, T. 10S, R. 25W. Collected by E. S. Turville, February 15, 1946.
12. Palos Verdes sandy loam from north of Rancho Palos Verdes 8 mi. north of Tucson.

13. Gothard series. Gray-tipped pillared columns of 2 - 6 inch solonetz layer near East $\frac{1}{4}$ corner of Section 19, T. 13S, R. 25E. Sampled by H. V. Smith.
14. Ramona series. Subsoil from Field No. 69-2, Sulphur Springs Valley. Sampled by H. V. Smith.
15. Safford soil from farm of William Crum, 6 miles south of Safford, Arizona. NW corner of NW $\frac{1}{4}$ of NW $\frac{1}{4}$ of Section 6, T. 8S, R. 26E. Sandy soil, dispersed, surface packs hard with water.
16. Tubac series. Sample from surface of solonetz profile, taken near corner of Broadway and Wilmot Road, 6 miles east of Tucson.
17. Tubac series. Sample from pillared columnar B horizon, same location as No. 16.
18. McNeal series from two miles north of McNeal, Arizona. 0.07 mile east and 0.7 mile north of S $\frac{1}{4}$ corner. Section 2, T. 21S, R. 26E. Collected by H. V. Smith, May 24, 1946. Depth 0-4 inches.
19. McNeal series from same location as No. 18. Depth 4-12 inches.
20. McNeal series from same location as No. 18. Depth 12-28 inches.
21. McNeal series from same location as No. 18. Depth 28-48 inches.
22. Cameron clay. A bentonite clay from near Cameron, Arizona. Supplied by J. E. Fletcher.
23. Playa. Surface material (0-2 inches) from playas between Benson and Willcox, Arizona. Supplied by H. V. Smith.
24. Cecil series from Statesville, N.C. Colloid from B2 horizon, 32-60 inches. Supplied by Bureau of Agricultural Chemistry and Engineering, U.S.D.A., Washington, D. C.
25. Putnam series from University of Missouri farm, Columbia, Missouri. Colloid from heavy Putnam clay. Supplied by Dr. C. E. Marshall, Department of Soils, Missouri Agricultural Experiment Station.

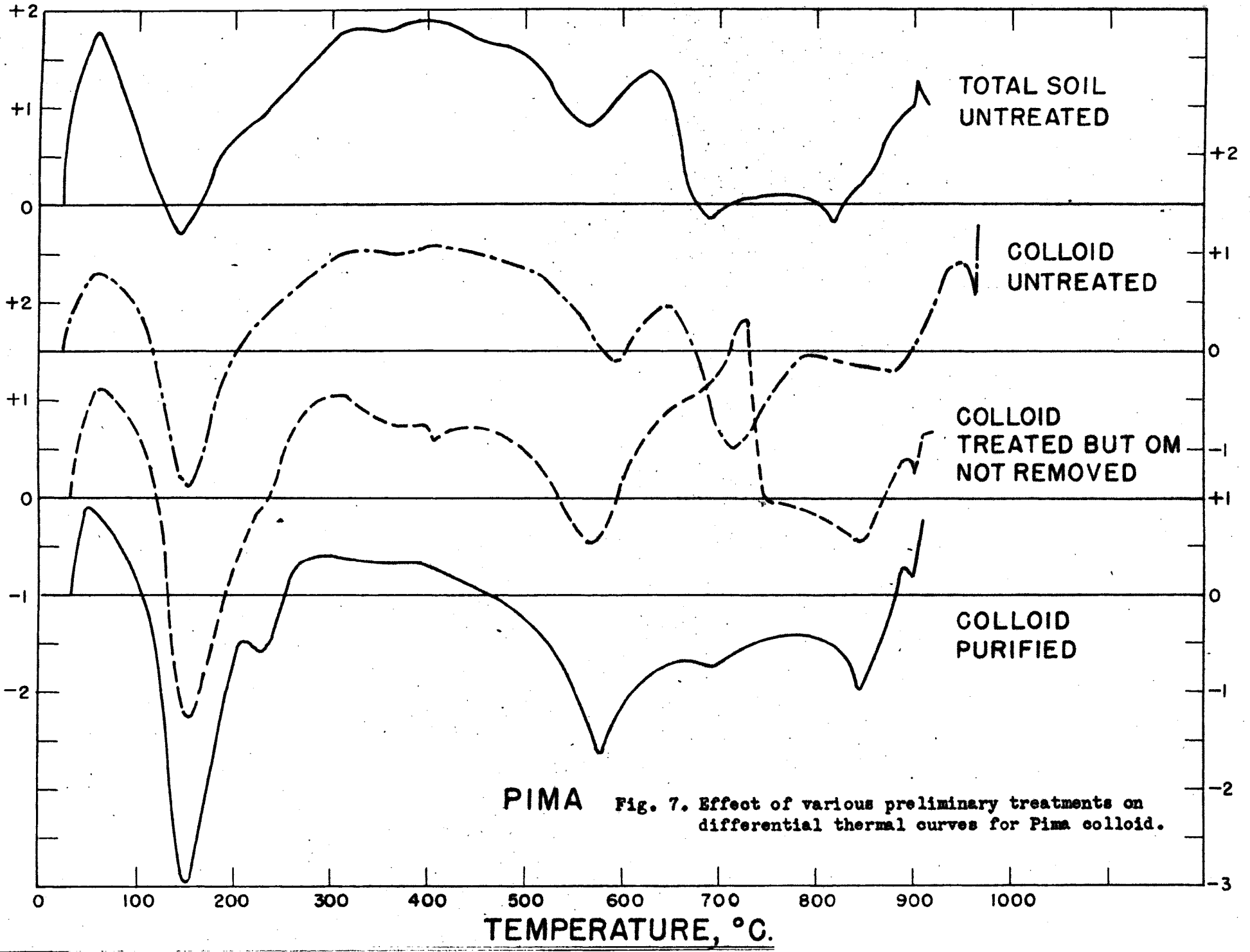
EXPERIMENTAL RESULTS AND DISCUSSION

Effects of Colloid Purification and Treatment

In order to determine the value of the various steps in preparation of the soil colloid for differential thermal analysis, a short study was made on Pima clay. Part of the results of this study are given in Figure 7. The curves represent four steps in the purification process: (1) The whole soil untreated; (2) The soil colloid separated by using only distilled water and hence contained all the soluble salts of the soil as well as carbonates and organic matter; (3) The colloid from which carbonates and soluble salts had been removed but still contained organic matter; and (4) The purified sample from which organic matter, carbonates and soluble salts had been removed and which had been saturated with calcium.

The value of the processing in making the endothermic reactions of the clay more pronounced is immediately seen from the curves. The curve for the whole soil scarcely goes below the zero line. The colloid curve shows some improvement but an endothermic reaction is registered at about 700° C. which does not remain through processing. This could be due to volatilization of some salt or reaction between soluble materials later washed out. The colloid containing organic matter, but otherwise purified, gives a marked exothermic reaction which was masked in

GALVANOMETER DEFLECTIONS



PIMA Fig. 7. Effect of various preliminary treatments on differential thermal curves for Pima colloid.

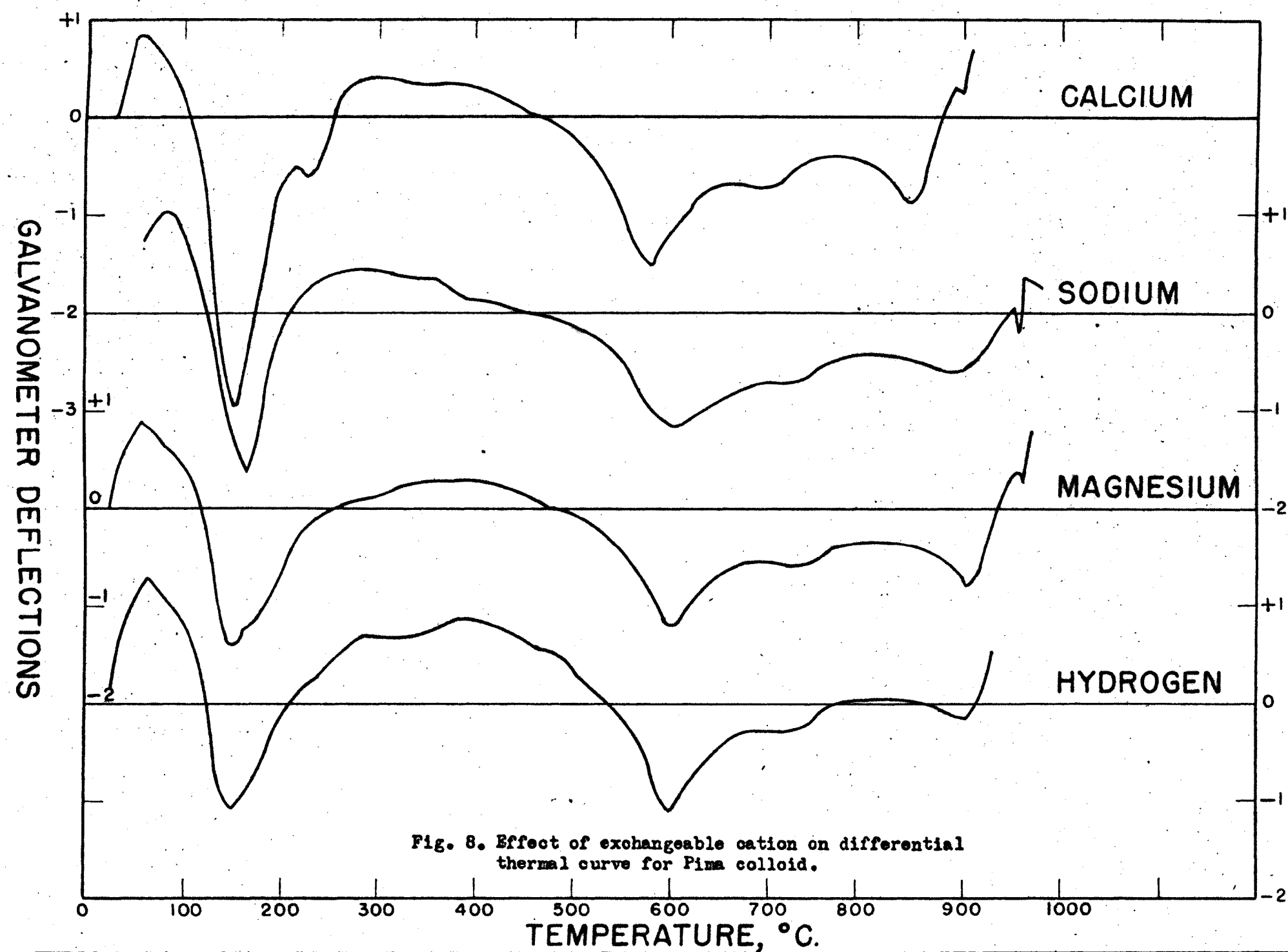


Fig. 8. Effect of exchangeable cation on differential thermal curve for Pima colloid.

the preceding curves. This reaction is evidently due to the organic matter and might represent oxidation of the carbon by iron oxides in the soil colloid. The curve for the purified colloid gives fairly sharp endothermic peaks and returns to within about one-half division of the zero line.

Effect of Saturation of the Colloid
with Various Cations

In addition to the effect of purification treatments, the effects of saturation with various cations was studied. Figure 8 shows curves for purified Pima clay which had been saturated with calcium, sodium, magnesium and hydrogen. The curves show that calcium-saturated clay gives the largest endothermic peaks and therefore seems to be preferable for differential thermal analysis. This is not entirely in agreement with the work published by Schafer and Russell (49) who reported only slight cation affects between calcium- and hydrogen-saturated clays. It is significant that the magnesium- and sodium-saturated samples give thermal curves that are very nearly identical.

In all of the curves obtained, there appears a marked upward rise from starting temperature to about 75° C. Ordinarily such a sharp rise would indicate that an exothermic reaction was taking place. This, however, is a doubtful

possibility. Perhaps the best explanation would be that at the start the heat conductivity of the clay sample is higher than that of alumina, the reference material. When packed into the block, the clay was completely humidified and was tamped tightly around the thermocouple. The alumina, on the other hand, was completely dry. The problem of variation in heat conductivity between the various clay samples and the reference material, as well as shrinkage of the clay on decomposition, must be recognized as a weakness of the differential thermal method. The latter affects primarily the contact of sample material with the thermocouple.

Other investigators have obtained good results with little pronounced effect of such heat conductivity differences by the use of unhumidified samples. In fact, the technique described by Speil, Berkelhamer, Pask and Davies (58) specifies that the sample be placed in a desiccator over anhydrous magnesium perchlorate for twenty-four hours before analysis.

In this study, samples were humidified at 37 per cent relative humidity so that they would be completely hydrated and therefore show maximum differential readings. This result was not attained, probably because of conductivity differences which placed the curve above the zero line at low temperatures when conductivity was high, and somewhat below the zero line at high temperatures after the colloid was dehydrated.

It is interesting to notice that this initial rise of the differential curve is shown by many of the curves published by Russell and Haddock (47), who also analyzed humidified samples.

Analysis of Standard Minerals

The differential thermal curves obtained for the standard clay minerals are given in Figures 9, 10 and 11. In general, they are in close agreement with published curves as to temperature of endothermic peaks. Although work by Page (41), Speil (57) and others indicate that montmorillonites are generally quite variable, the montmorillonite curves here obtained are almost exact duplicates of each other although coming from different localities. Published curves for halloysite and kaolinite are usually less variable than those for montmorillonite. The endothermic peaks of kaolinite and halloysite agree within a few degrees of those in the work published by Speil (57). The curve obtained for illite in this study seems to be superior to many published curves by reason of sharper deflections at the characteristic reaction temperatures.

The hydrothermal curves for the standard minerals (Fig. 12 and 13) agree nicely with the general pattern of the original dehydration curves published by Kelly, Jenny

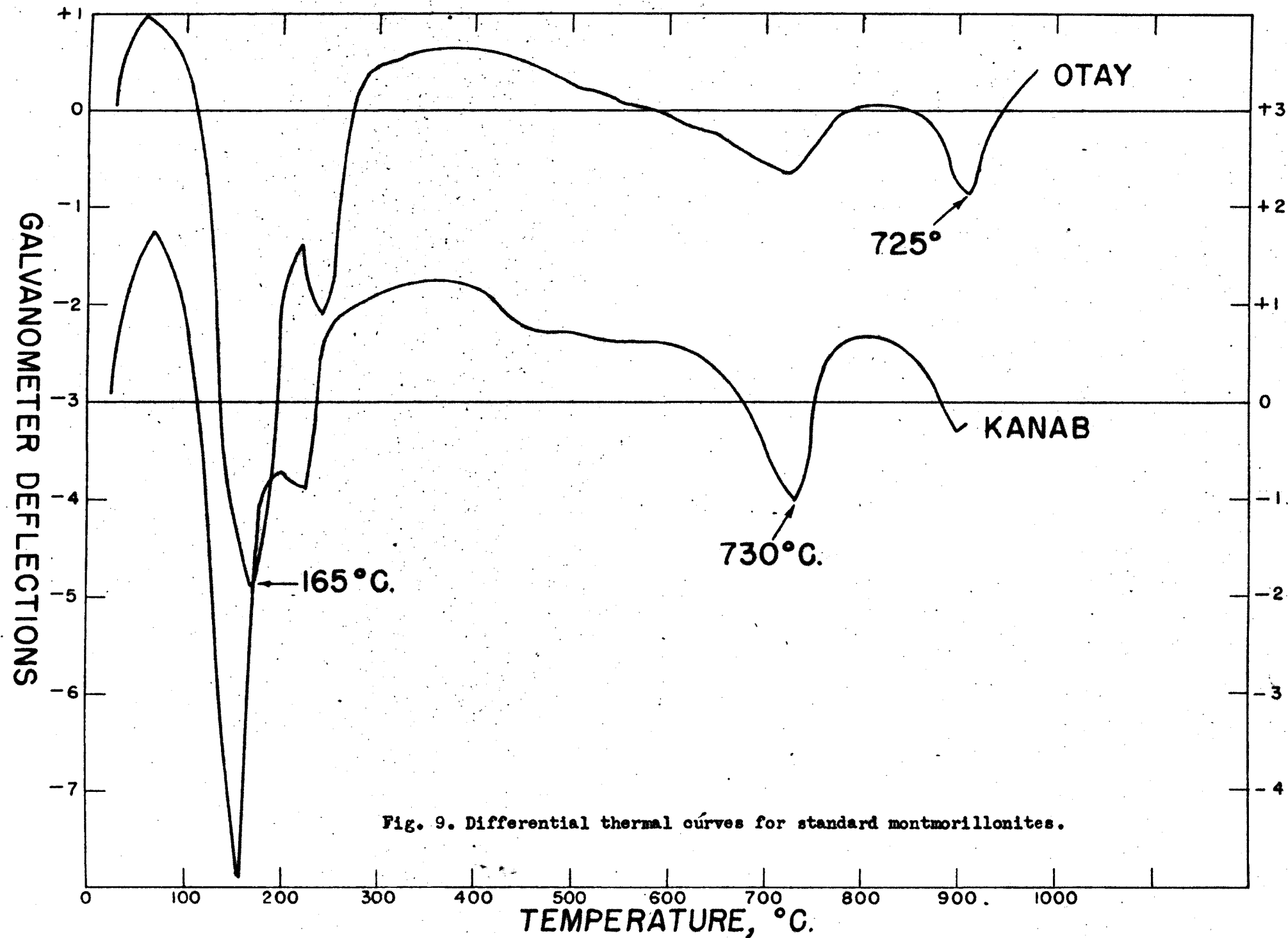


Fig. 9. Differential thermal curves for standard montmorillonites.

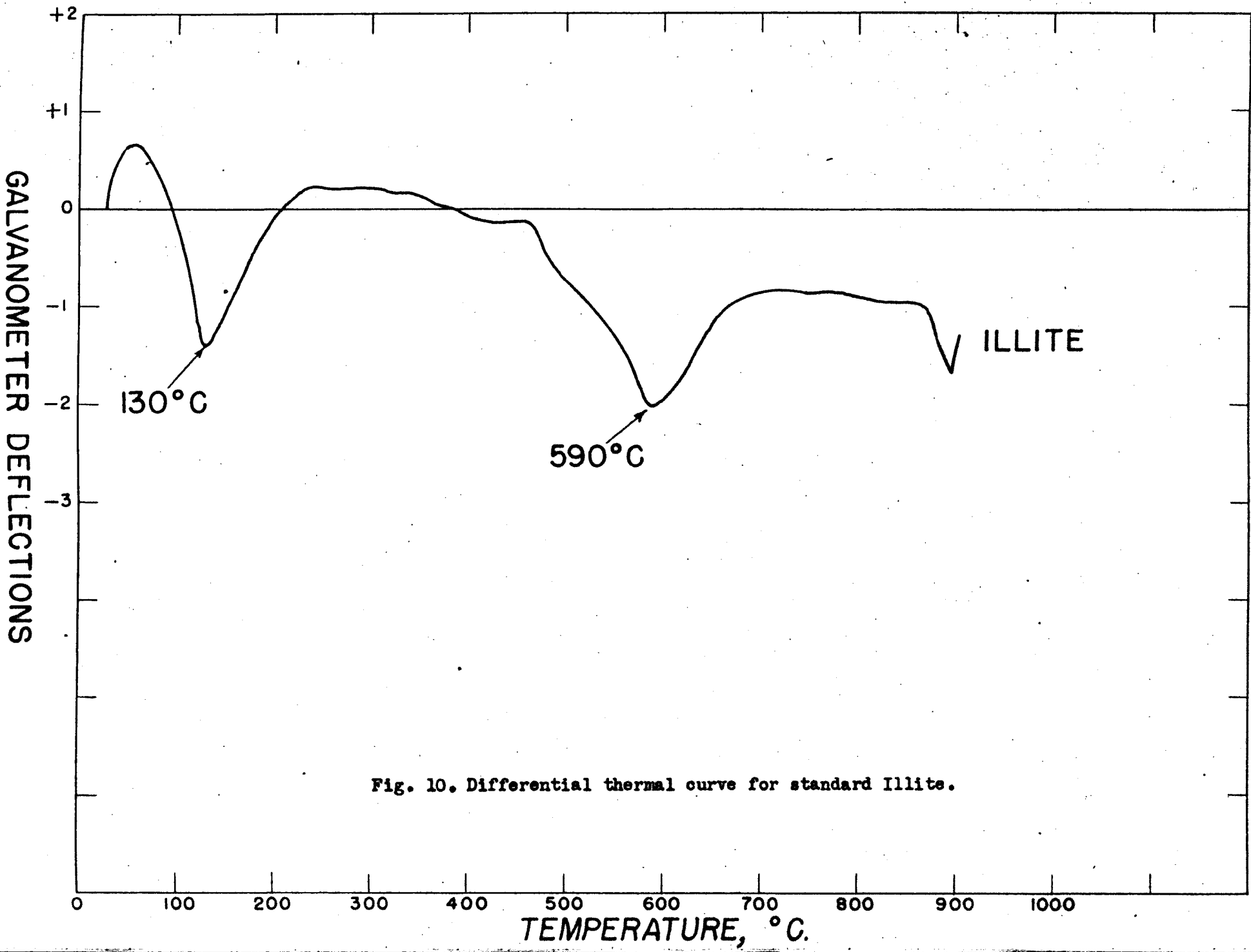


Fig. 10. Differential thermal curve for standard Illite.

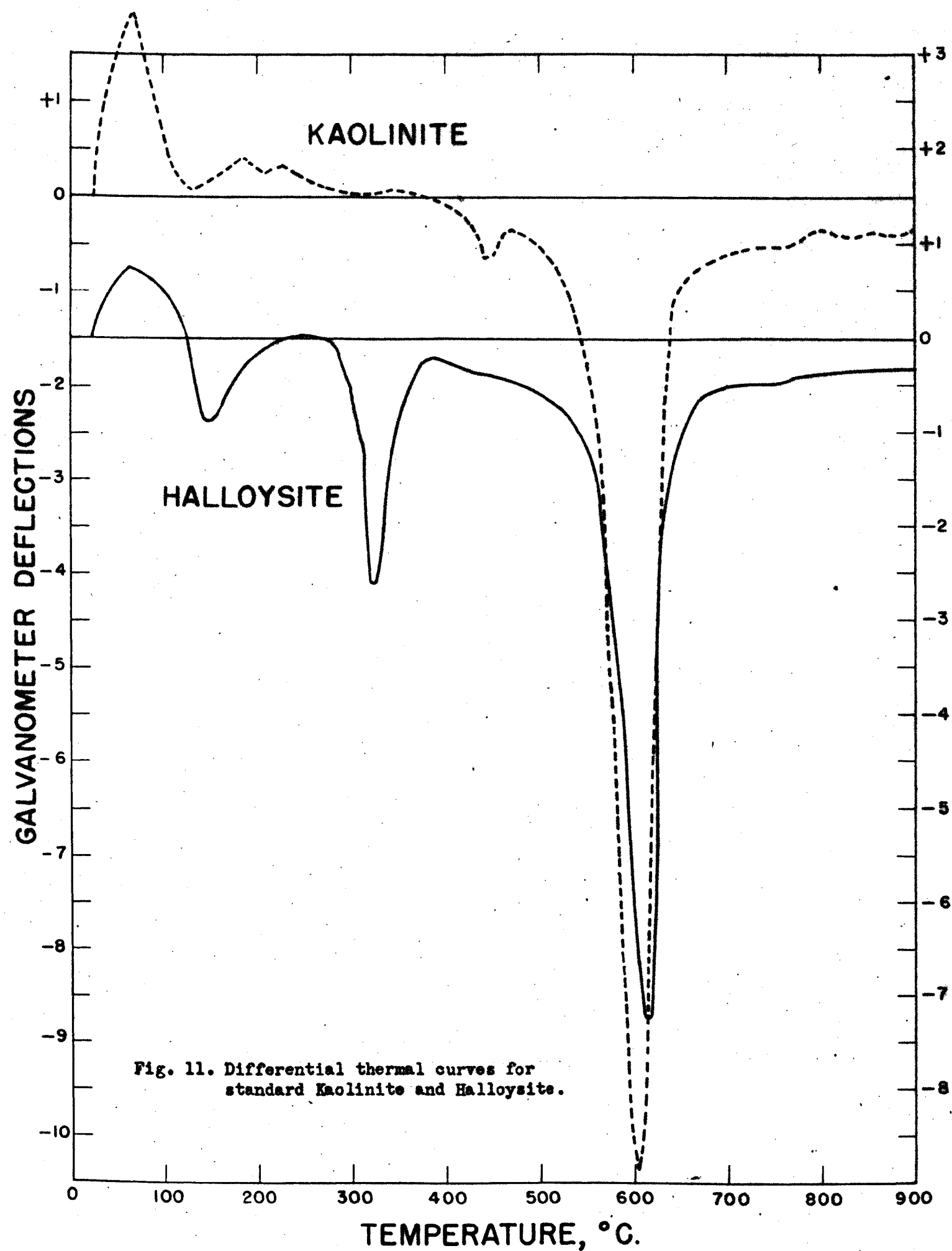


Fig. 11. Differential thermal curves for standard Kaolinite and Halloysite.

and Brown (21). The temperatures at which the water loss occurs for the various minerals reported in the two studies are not identical, however. The initial weight loss shown on montmorillonite curves agrees within a few degrees, but the kaolinite decomposition temperature as well as the high temperature dehydration of montmorillonite shows a lag from 50 to 100° C. Perhaps a heating rate of less than 10° per minute would have given more closely comparable curves. However, with a heating rate of 10 degrees per minute, the temperatures at which a leveling off begins on the dehydration curves corresponds very closely to the temperatures of the endothermic minima on the differential curves.

The chemical analysis data for the standard minerals are given in Table I. The results obtained for the montmorillonites show the typical high base exchange capacity with little or no potassium content. The other values are in good agreement with data published by Grim (9). Since illite is the only potash-bearing clay mineral, the percentage of K_2O is often used for calculation of the amount of this mineral present. There is some variation in published analyses of the illites, but the K_2O content is usually in the vicinity of 5 or 6 per cent. Ross has published data (46) on four different illite samples in which per cent K_2O varied from 5.4% to 6.5% and averaged 6.02%. With this

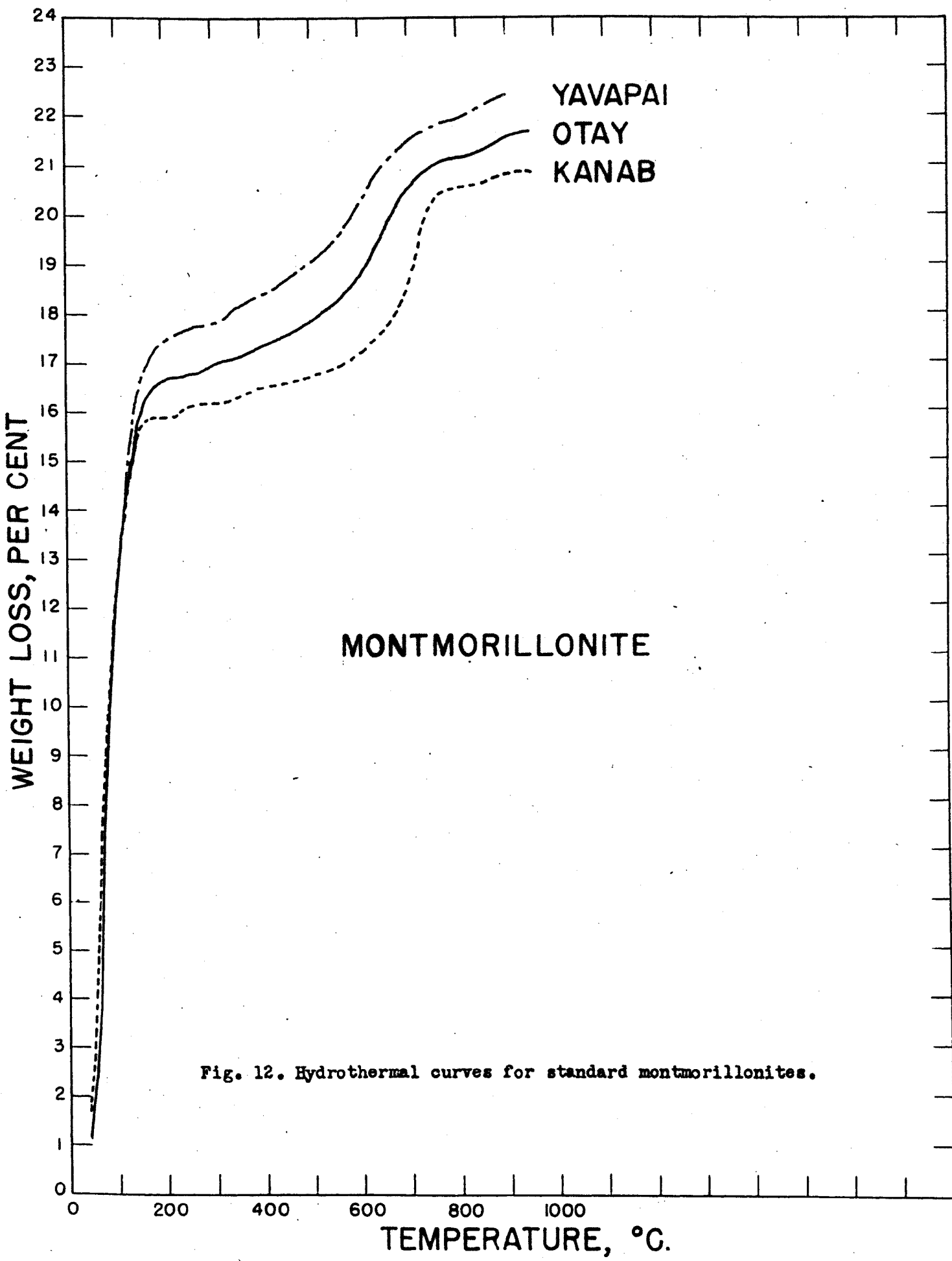


Fig. 12. Hydrothermal curves for standard montmorillonites.

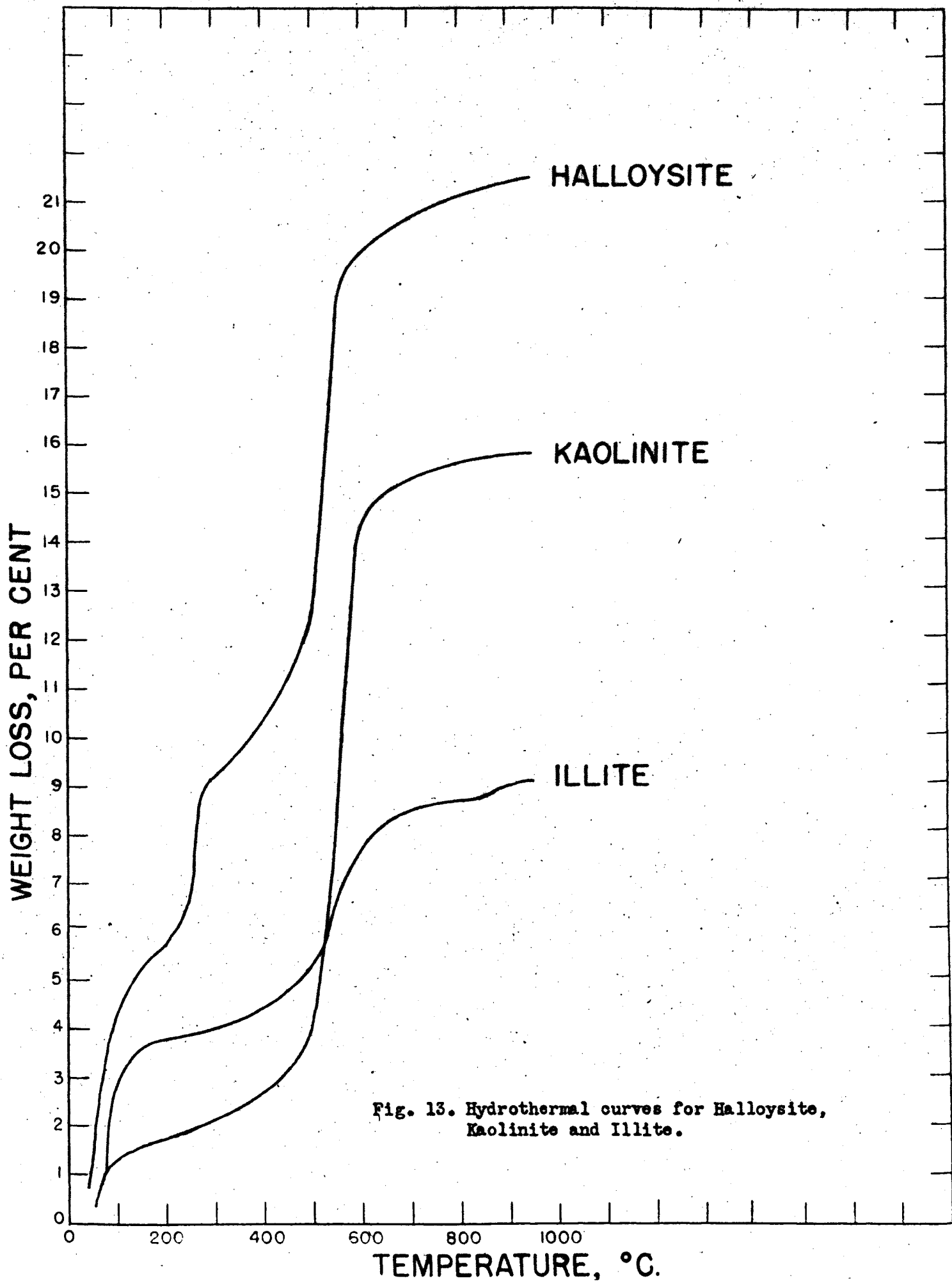


Fig. 13. Hydrothermal curves for Halloysite, Kaolinite and Illite.

in view it appears that 6.0% would be the most suitable figure for use in calculating per cent illite.

TABLE I
RESULTS OF CHEMICAL ANALYSES
OF STANDARD MINERALS

<u>Sample No.</u>	<u>Name</u>	<u>K₂O %</u>	<u>Base Exchange Capacity me/100</u>
1.	Kanab	0.03	115.3
2.	Yavapai	0	124.7
3.	Otay	0.14	129.8
4.	Kaolinite	.12	7.2
5.	Halloysite	0	19.3
6.	Illite	6.3	33.7

Analysis of Soil Colloids

The differential thermal and hydrothermal curves for soil colloids (Figures 14 to 21) show that the clays of Arizona soils are chiefly montmorillonite and illite. It is doubtful that the soils contain any kaolinite. The endothermic peak that occurs at 575° to 610° C. is most likely due to illite since chemical analyses of all the soil colloids show a fair per cent of K₂O. (See Table II).

The profile study of the McNeal soil (Figures 18, 19, and 20) shows a gradual increase of montmorillonite in

the colloid with depth. This is also shown by the hydro-thermal curves for Tubac subsoil and surface colloids, although it is not particularly evident from differential thermal analysis. Chemical analysis for the two profile studies shows decreasing K₂O and increasing base exchange capacity with depth which agrees in general with the thermal analyses. In a study of Cecil and Susquehanna profiles, Kelley, Woodford, Dore and Brown (23) also found montmorillonite predominating in the lower horizons of Susquehanna.

TABLE II

RESULTS OF CHEMICAL ANALYSES OF SOIL COLLOIDS

<u>Sample No.</u>	<u>Name</u>	<u>K₂O %</u>	<u>Base Exchange Capacity me/100</u>
7.	Pima	2.84	70.65
8.	Gila	4.00	58.2
9.	Casa Grande	3.90	56.50
10.	Sunrise	3.04	63.74
11.	Yuma	3.31	51.75
12.	Palos Verdes	3.10	50.20
13.	Gothard	2.59	68.7
14.	Ramona	2.79	48.41
15.	Safford	2.88	77.27
16.	Tubac Surface	3.82	50.15
17.	Tubac Subsoil	3.74	51.51
18.	McNeal 0-4"	4.26	48.50
19.	McNeal 4-12"	3.73	54.66
20.	McNeal 12-28"	3.42	58.4
21.	McNeal 28-48"	3.01	70.65
22.	Cameron	2.78	81.60
23.	Playa	4.49	70.50
24.	Cecil	.37	15.78
25.	Putnam	1.55	80.35

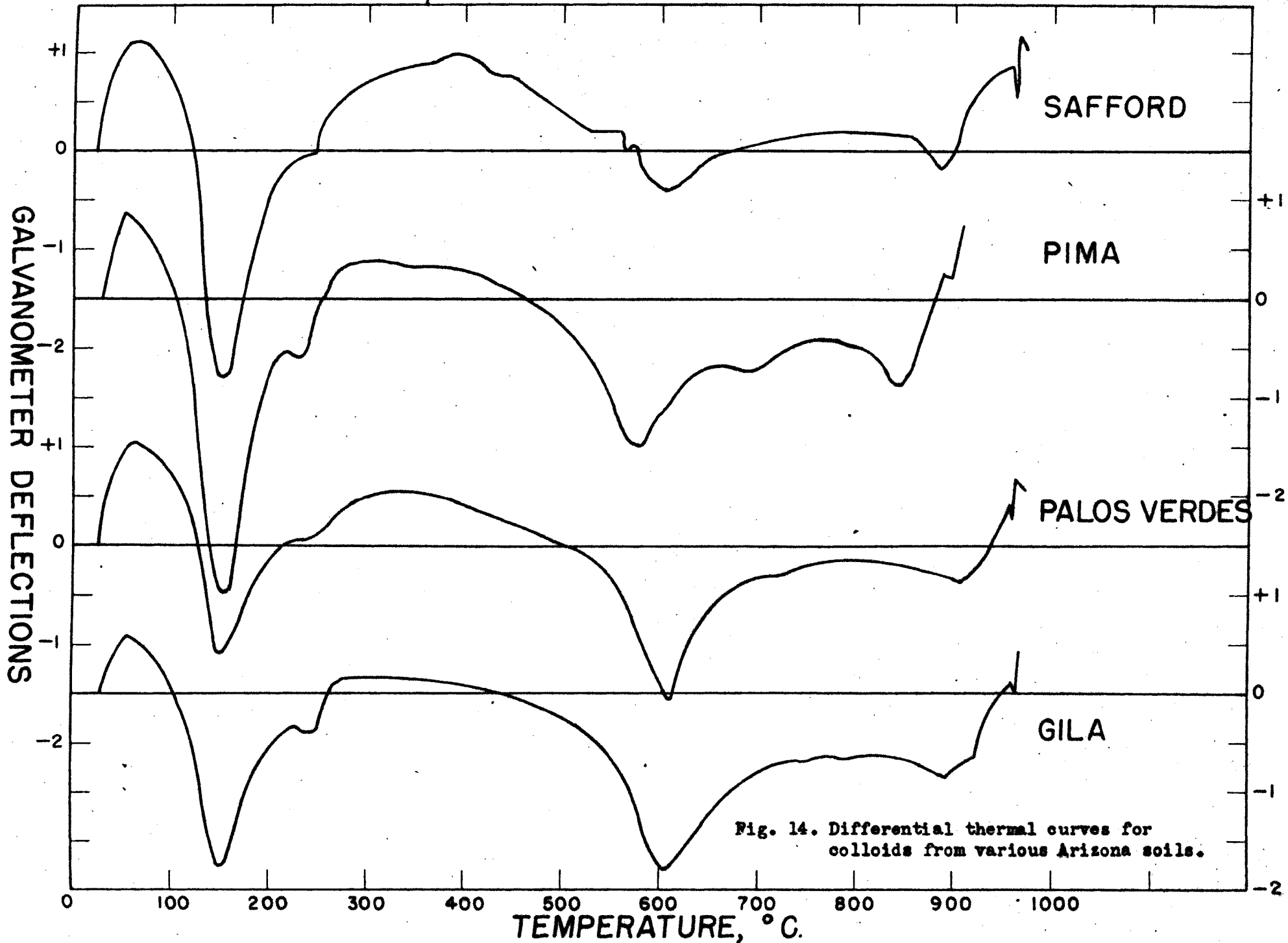


Fig. 14. Differential thermal curves for colloids from various Arizona soils.

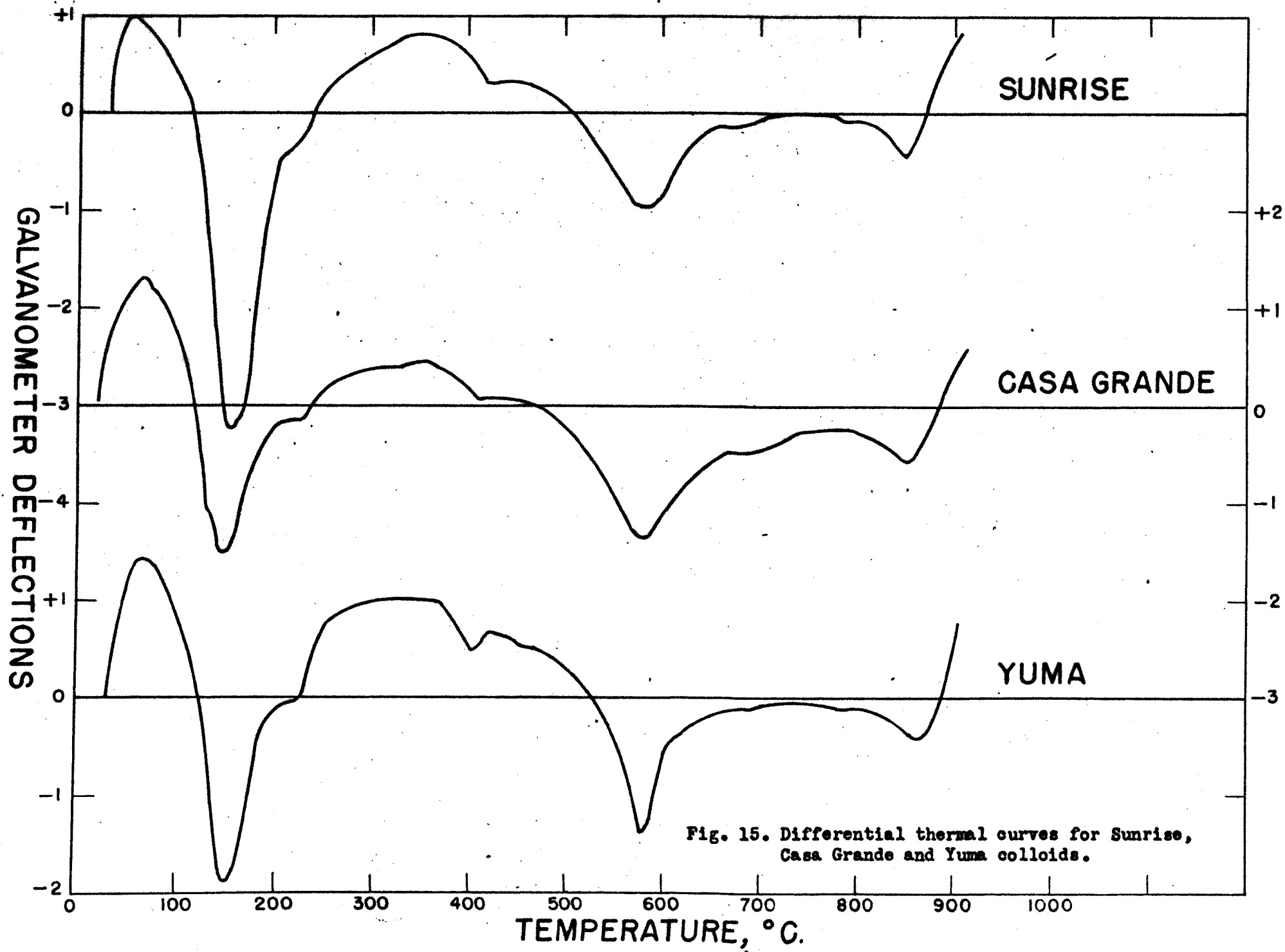


Fig. 15. Differential thermal curves for Sunrise, Casa Grande and Yuma colloids.

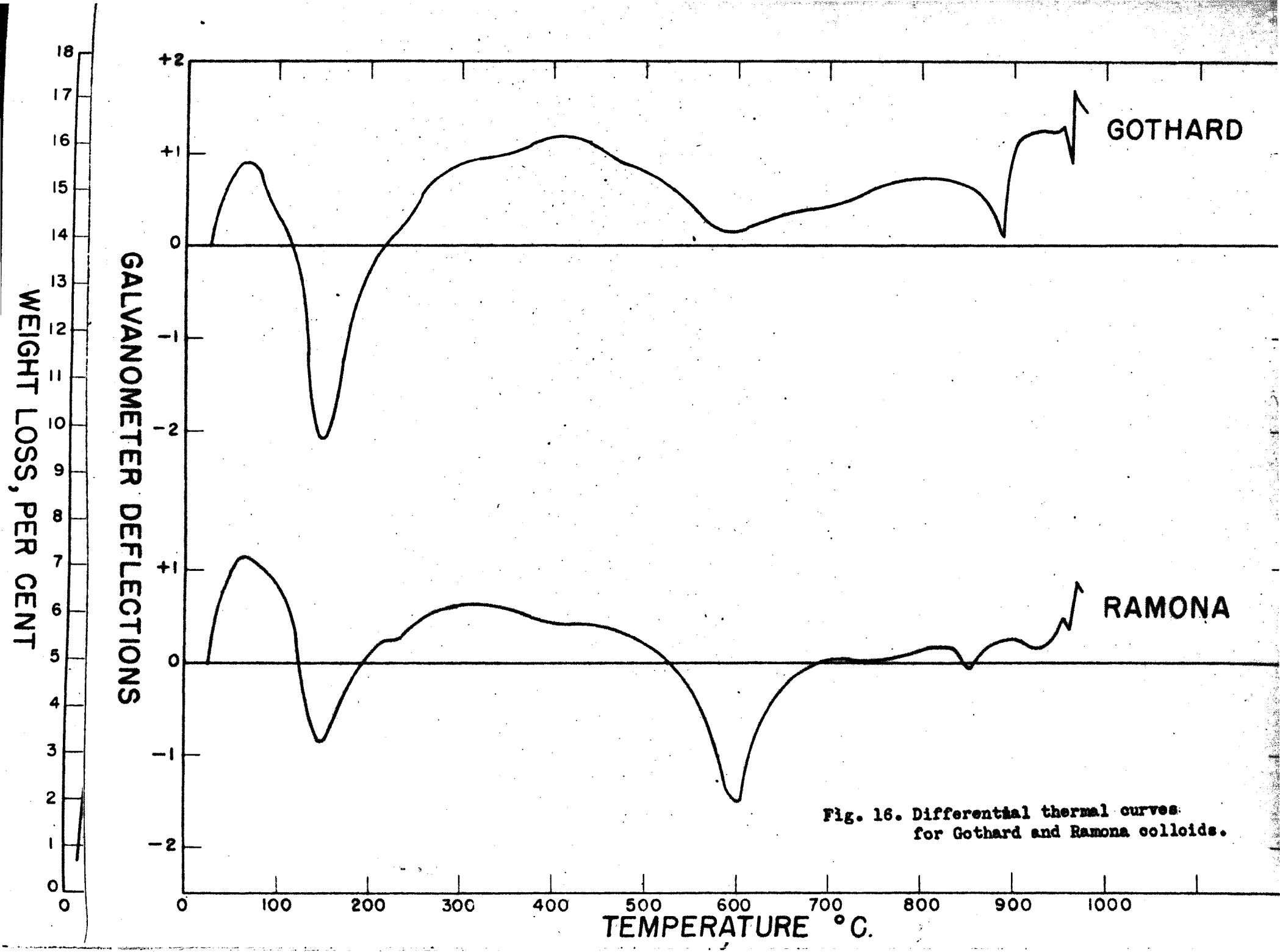


Fig. 16. Differential thermal curves for Gothard and Ramona colloids.

WEIGHT LOSS, PER CENT

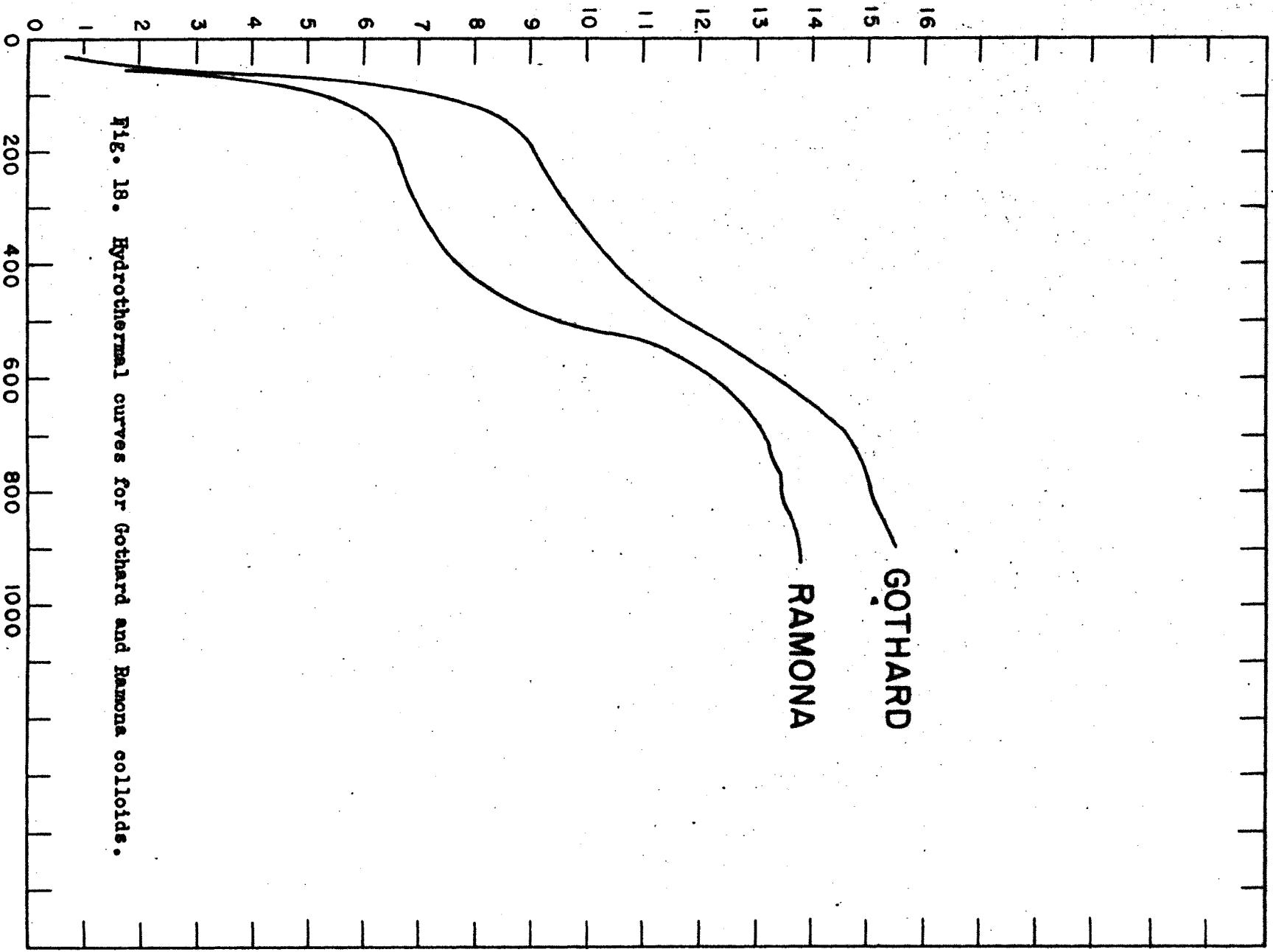
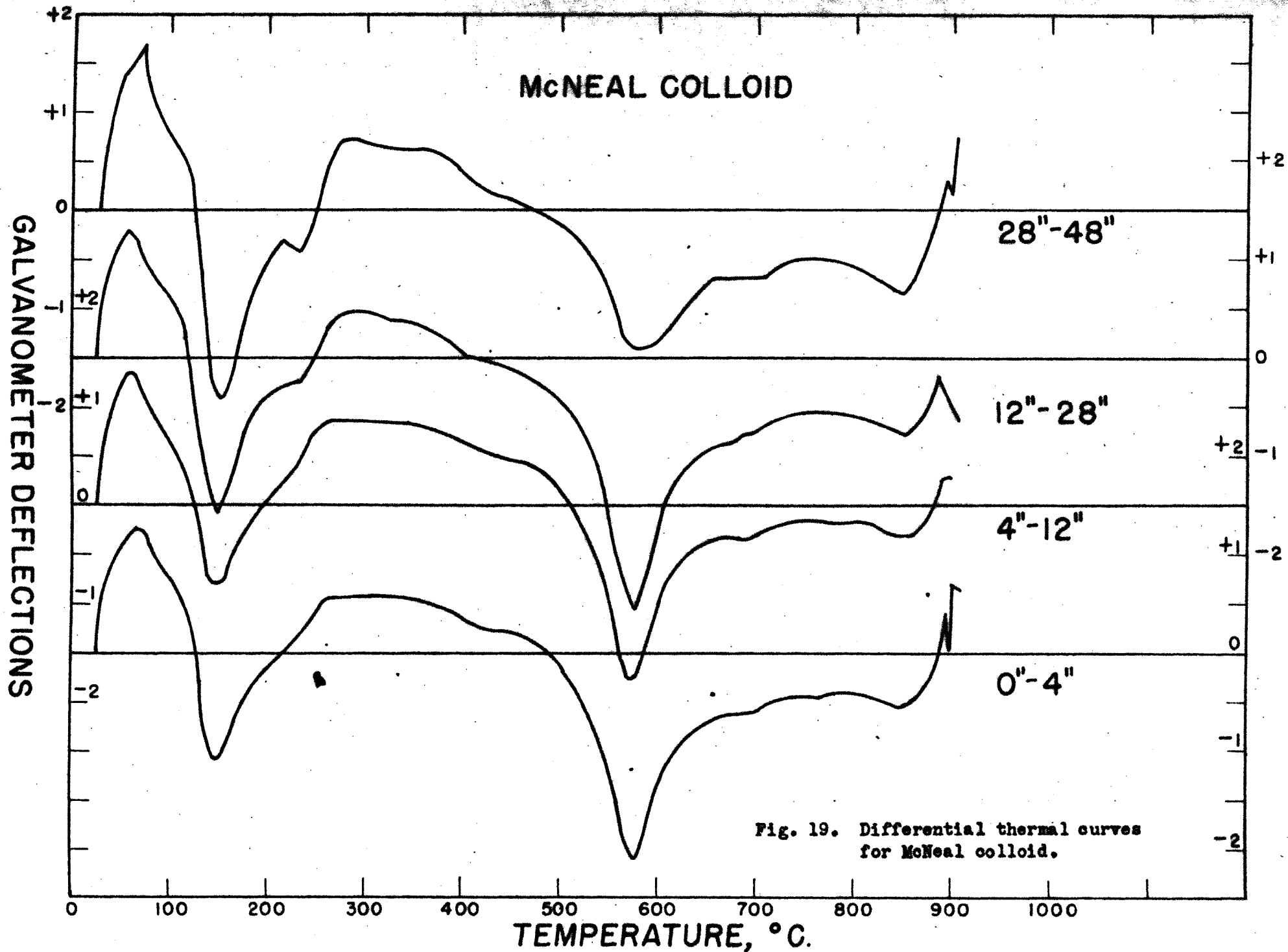
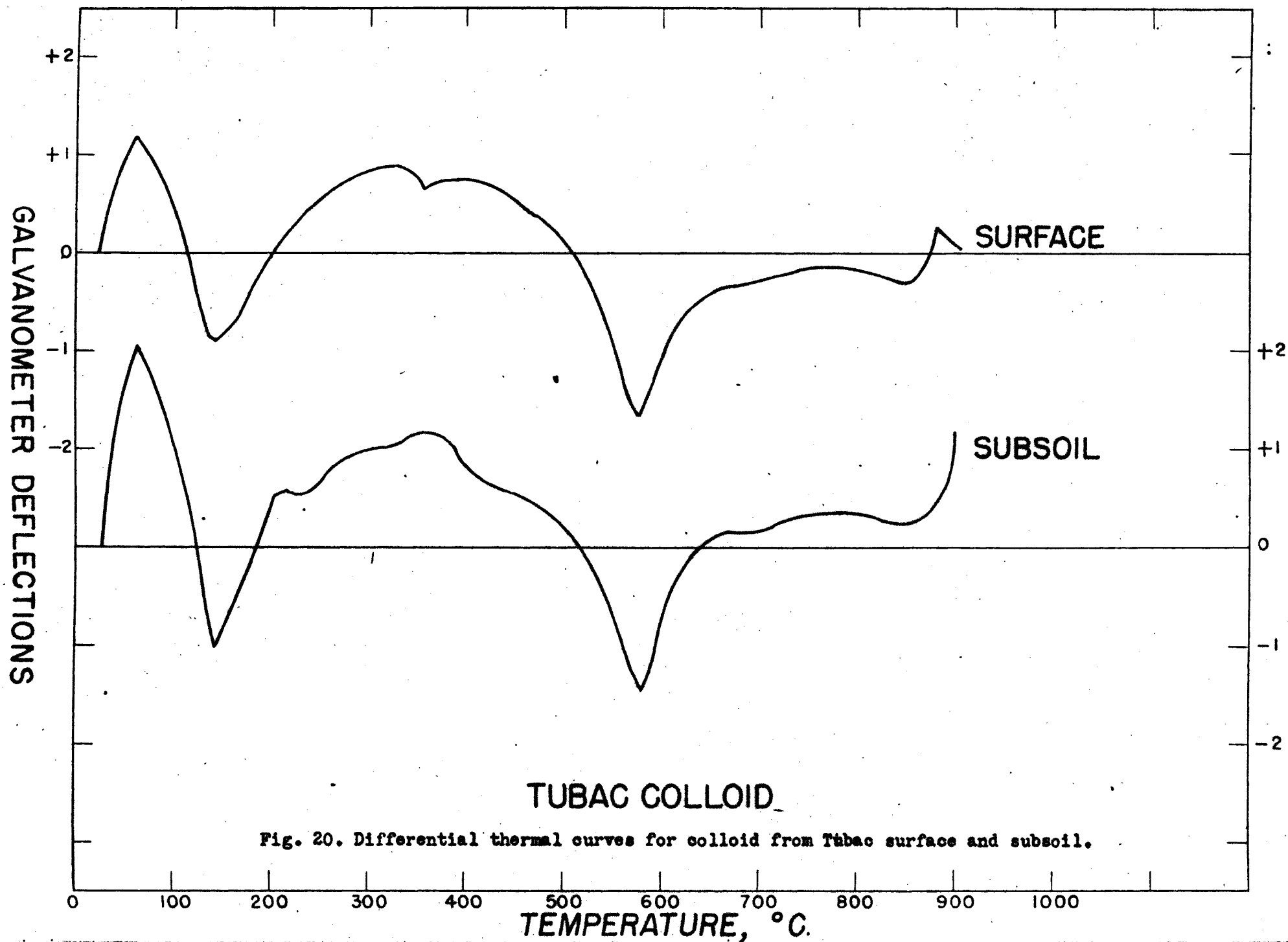


FIG. 18. Hydrothermal curves for Göthard and Ramona colloids.

TEMPERATURE, °C.



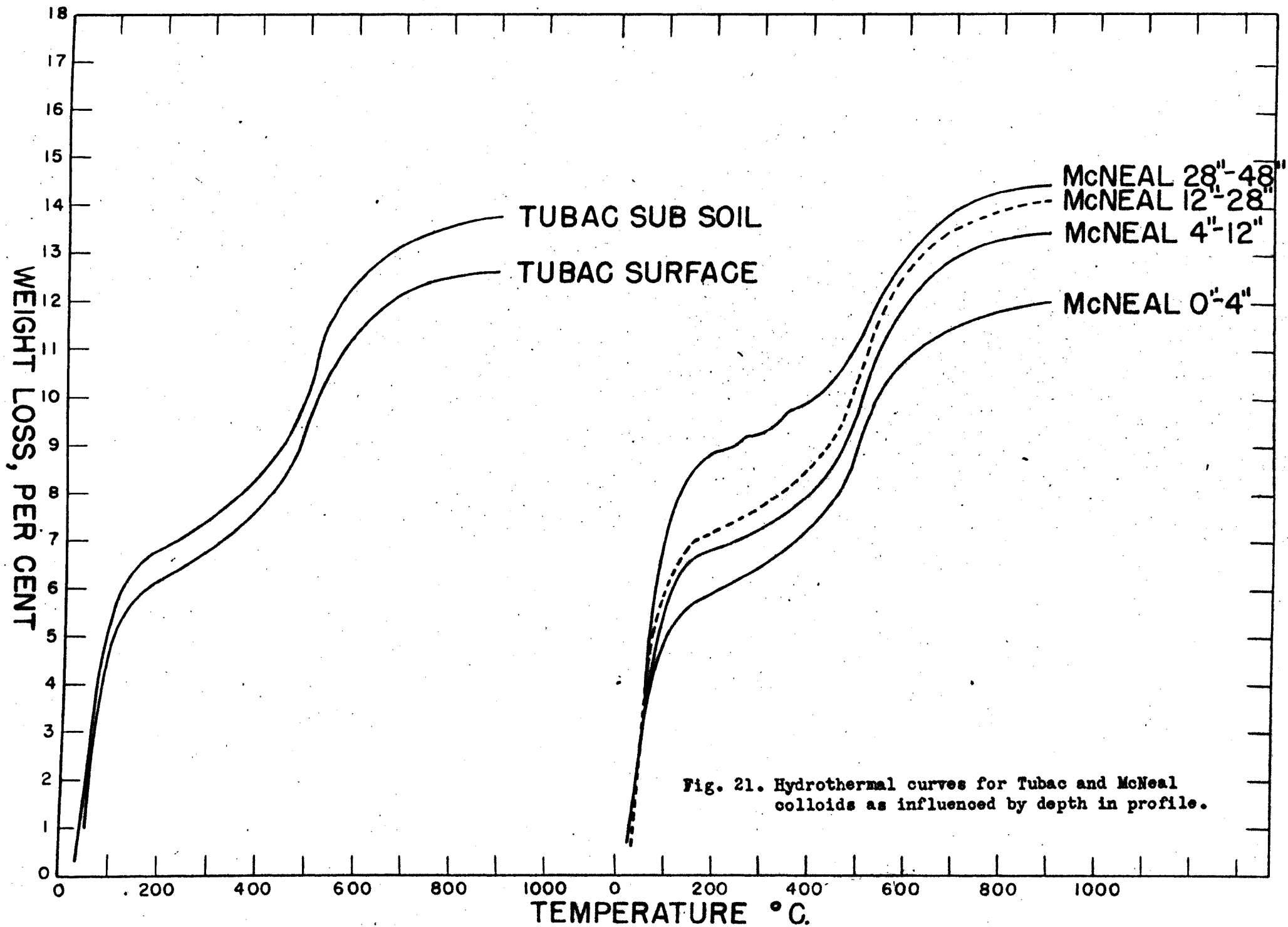


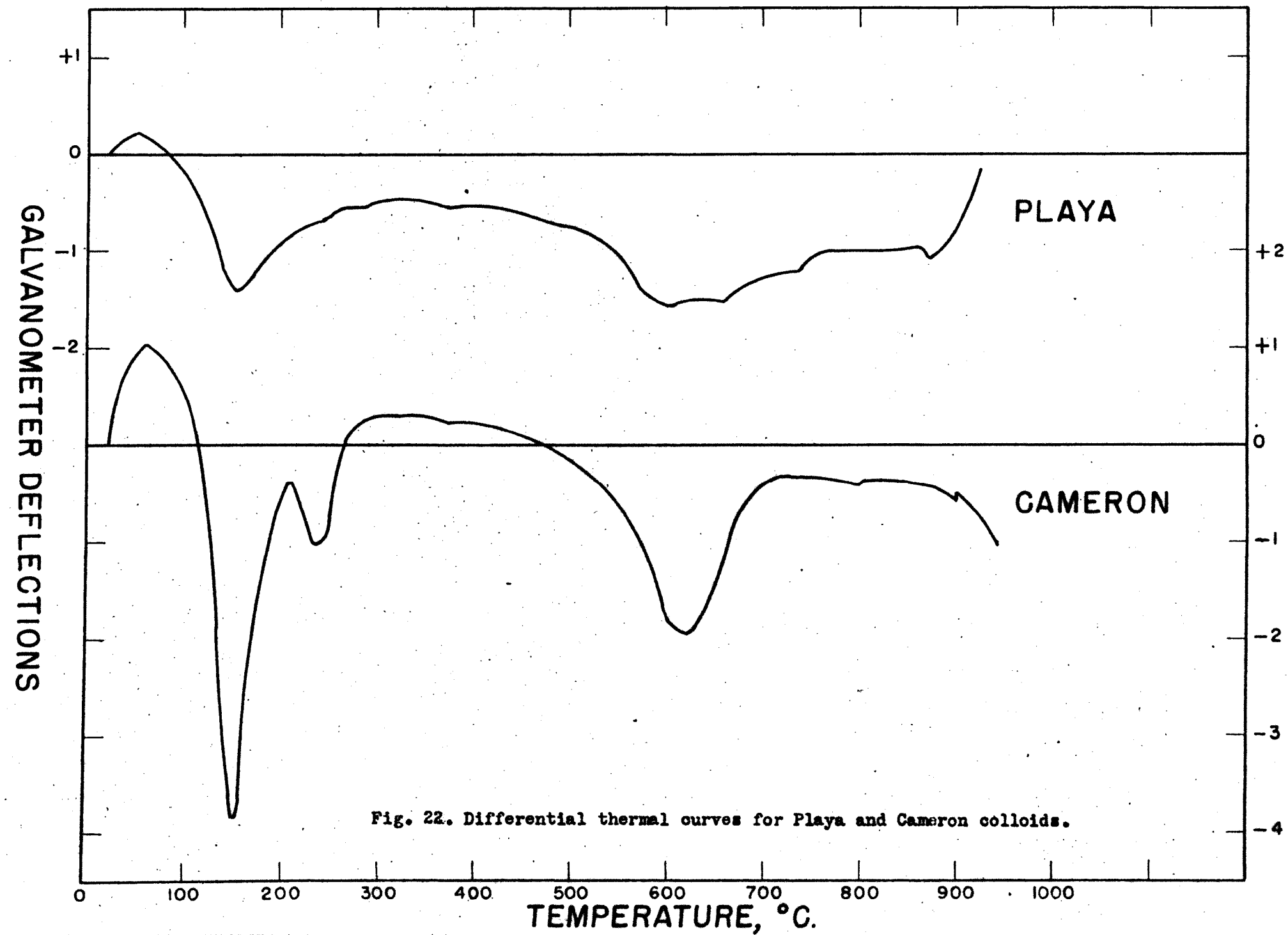
The Playa and Cameron samples shown in Figures 23 and 24 are not important as agricultural soil samples but give interesting dehydration curves. The Playa sample shows a continuous and nearly uniform rate of weight loss from 100° to 700° C. while the Cameron sample shows very narrow decomposition temperature ranges. The Playa dehydration curve resembles to some extent curves published by Kelley, Jenny and Brown (21) of minerals which had been very finely ground. Since the Playa is the surface material of a dried lake bed, it is comparable to the ground materials for which Kelley, Jenny and Brown obtained similar curves. In other words, grinding has the effect of breaking down the particles (clay mineral lattices) to such an extent that the mineral constituents decompose continuously over the entire temperature range.

Analyses were made on Putnam and Cecil colloids so that the results could be compared to results previously published by other investigators. The dehydration curves obtained are closely related to those published by Kelley and his co-workers (21) except for the temperature lag that has been described.

Quantitative Calculation of Clay Mineral Composition of Soil Colloids

Many investigations, including those of Norton(37), Russell and Haddock (47), Schafer and Russell (49), and Speil (57), have shown quantitative or semiquantitative calculations of minerals present in soil colloids. The data in Tables III, IV and V are calculations of per cent





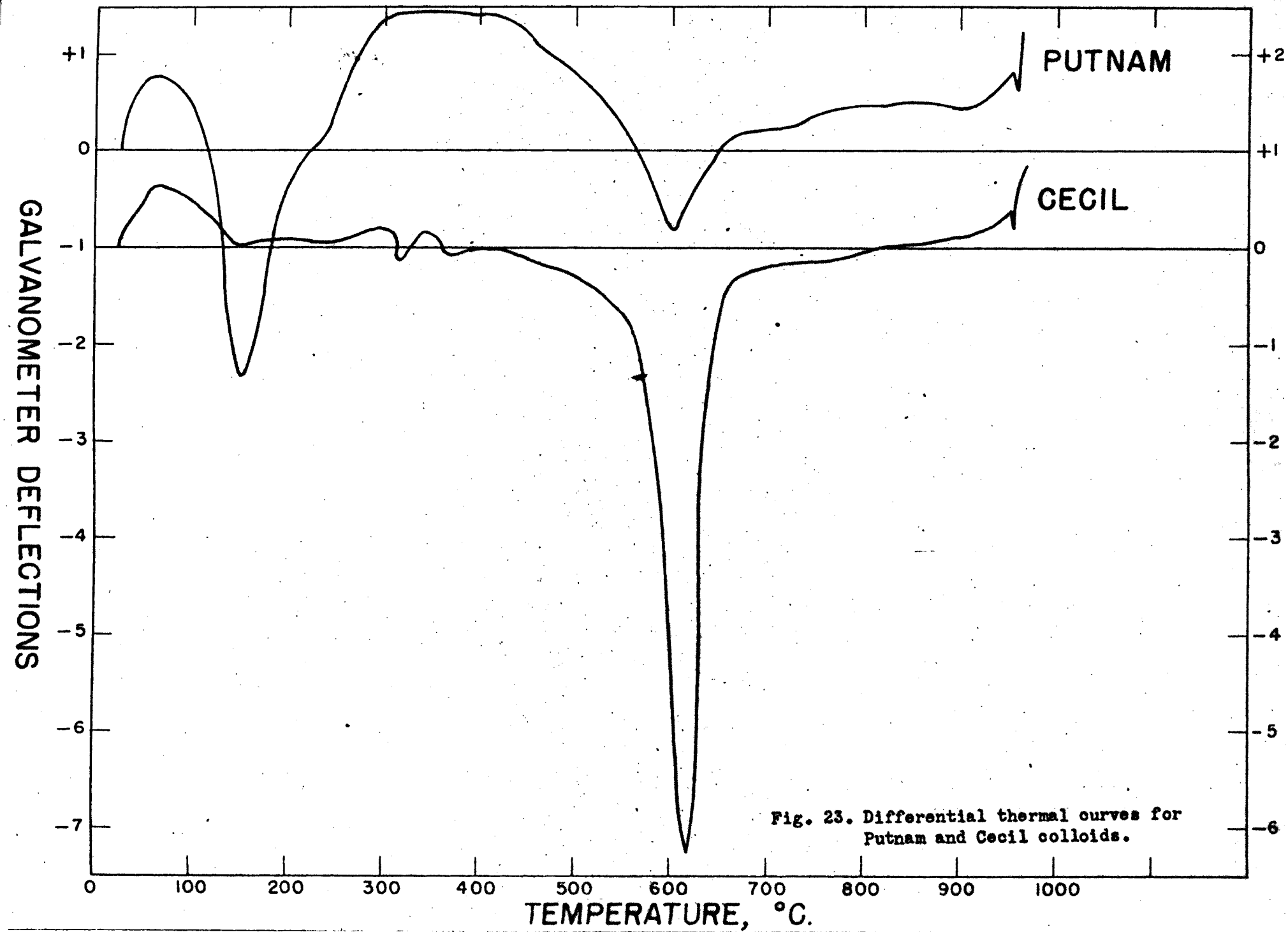


Fig. 23. Differential thermal curves for Putnam and Cecil colloids.

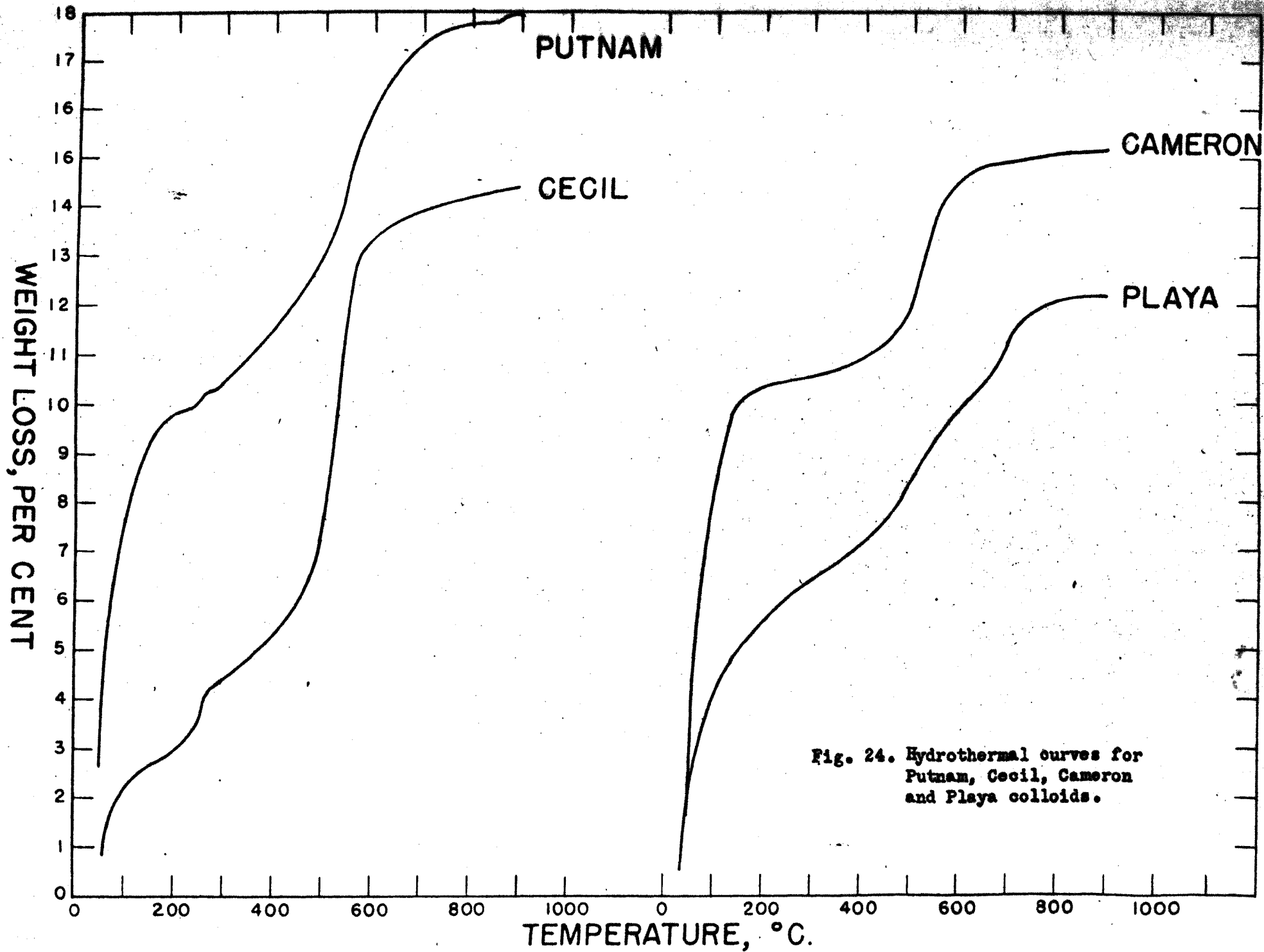


Fig. 24. Hydrothermal curves for Putnam, Cecil, Cameron and Playa colloids.

of the clay minerals from the soil colloids analyzed in this study.

The assumptions made as a basis for the calculations were: (1) that the illite and montmorillonite in the samples were responsible for both the base exchange capacity and the loss on ignition; (2) that illite contains 6 per cent K_2O and can be calculated from chemical analysis; and (3) that the area of the 150° endothermic peak is proportional to the per cent of montmorillonite.

The areas for both the Kanab and Otay montmorillonite were measured by planimeter. When the measurement of the curve was made below the zero line, it was found that Kanab gave a value of 1.35 square inches, whereas Otay gave a value of 2.44 square inches. When a straight line was drawn tangent to points on the curve on each side of the dip, the area enclosed measured 3.02 square inches for Kanab and 3.42 for Otay. The ratio between the area measured under the tangent line for the two standards was exactly the same as the ratio of their respective base exchange capacities. This ratio was not exactly the same as the ratio of the water-loss values from the two standards, but the agreement was quite close.

Table III gives the data calculated from the areas under the zero line, with Kanab being used as standard. Table IV lists similar calculations using the areas as

measured under a line drawn tangent to the curves. Calculation in Table IV, like Table III is also based on Kanab as standard. It is evident from both tables that the areas of the differential thermal dips obtained in this study are only roughly proportional to the per cent of montmorillonite. Variations up to 30 or 40 per cent are found in both methods of calculation. These results agree with the conclusion made in 1933 by Orceel (39) that the differential thermal method was sensitive only to about 20 per cent in analysis of montmorillonites. Speil has also concluded that the 150° endothermic reaction of montmorillonite was not dependable enough for quantitative determinations. It is interesting, nevertheless, to notice that whenever the computed per cent of montmorillonite and illite was near 100, the computed water loss was in close agreement with the observed value.

In an attempt to get better agreement with calculated and observed values, a correction of the area of the 150° dip was made by subtracting the area which would be given at that temperature by the per cent of illite found by chemical analysis. This correction seemed to be valid for samples of high base exchange capacity but did not improve the overall picture.

Calculation of per cent of montmorillonite was made from hydrothermal analyses also. It was assumed that

the total loss on ignition of a soil colloid would be due either to moisture lost by montmorillonite or illite. The per cent loss from the illite was computed by multiplying the total loss of the standard illite by the calculated per cent of illite in the sample. The difference between this value and the total loss was assumed to be due to the montmorillonite in the sample. The per cent montmorillonite was determined by dividing the computed montmorillonite loss by the loss given by the pure mineral. The results of these calculations are given in Table V. In general, the computed values for base exchange capacity are in closer agreement with the observed values than when calculations were made from differential thermal measurements. Further, the total per cent of the montmorillonite and illite accounted for seems to be a more reasonable value.

Correlation of Soil Problems and Clay Mineral Analysis

Three of the soils analyzed have exceptionally poor permeability. These are the Sunrise, Safford and Gothard. It is interesting to note that these three soils are among the highest in base exchange capacity and per cent of water loss on hydrothermal curves. This indicates high montmorillonite content.

TABLE III

MINERAL COMPOSITION OF COLLOID CALCULATED FROM PER CENT K₂O AND AREA OF 150° THERMAL DIP

Colloid		Montmorillonite		Illite	Total Minerals	B.E.C.		Water Loss	
No.	Name	Area for 150° Dip	Per Cent Calculated	Per Cent Calc. from K ₂ O	Present, Per Cent	me/100 mgs. Calc.	Obs.	Per Cent Calc.	Obs.
7	Pima	115	85	44	129	113	70.6	21.8	15.0
8	Gila	72	53	67	120	83	58.2	17.1	12.6
9	Casa Grande	49	36	65	101	62	56.5	13.4	13.7
10	Sunrise	108	80	51	131	110	63.7	21.3	15.3
11	Yuma	47	35	55	90	58	52.2	12.3	11.0
12	Palos Verdes	28	21	52	73	41	50.4	9.1	13.5
13	Gothard	60	44	43	87	65	68.7	13.2	15.5
14	Ramona	19	14	46	60	31	48.4	7.1	13.8
15	Safford	76	56	44	100	79	71.3	15.7	15.4
16	Tubac Surface	27	20	64	84	44	50.2	10.0	13.8
17	Tubac Subsoil	19	14	62	76	36	51.5	8.5	12.7
18	McNeal 0-4"	30	22	71	93	48	48.5	11.1	12.0
19	McNeal 4-12"	18	13	62	75	35	54.7	8.3	13.5
20	McNeal 12-28"	52	38	57	95	63	58.4	13.1	14.2
21	McNeal 28-48"	65	48	50	98	71	70.6	14.5	14.5
22	Cameron	127	94	43	137	122	81.6	23.5	15.3
23	Playa	95	70	75	145	105	70.5	21.4	12.2
25	Putnam	74	55	26	81	72	80.3	13.9	17.9

TABLE IV

MINERAL COMPOSITION OF COLLOID CALCULATED FROM PER CENT K_2O AND AREA OF 150° DIP
MEASURED UNDER A LINE TANGENT TO THE THERMAL CURVE

Colloid		Montmorillonite		Illite	Total	B.E.C.		Water Loss	
No.	Name	Area for 150° Dip	Per Cent Calculated	Per Cent Calc. from K_2O	Minerals Present, Per Cent	me/100 mgs. Calc.	Obs.	Per cent Calc.	Obs.
7	Pima	190	63.0	44	107.0	90.4	70.6	17.8	15.0
8	Gila	122	40.4	67	107.4	61.5	50.2	12.5	12.6
9	Casa Grande	154	51.0	65	116.0	72.6	56.5	14.6	13.7
10	Sunrise	215	71.2	51	122.2	96.8	63.7	18.9	15.3
11	Yuma	163	54.0	55	109.0	83.0	52.2	17.2	11.0
12	Palos Verdes	115	38.1	52	90.1	60.8	50.4	12.7	13.5
13	Gothard	171	56.6	43	99.6	87.0	68.7	17.9	15.5
14	Ramona	100	33.1	46	79.6	56.0	48.4	11.9	13.8
15	Safford	196	64.9	44	108.9	89.6	71.3	17.8	15.4
16	Tubac Surface	126	41.7	64	105.7	68.9	50.2	14.5	13.8
17	Tubac Subsoil	183	60.6	62	112.6	89.6	51.5	18.3	12.7
18	McNeal 0-4"	117	38.7	71	109.7	67.5	48.5	14.6	12.0
19	McNeal 4-12"	123	40.7	62	102.7	66.8	54.7	14.1	13.5
20	McNeal 12-28"	146	48.3	57	105.3	74.5	58.4	15.3	14.2
21	McNeal 28-48"	187	61.9	50	111.9	87.2	70.6	17.4	14.5
22	Cameron	213	70.5	43	113.5	106.0	81.6	21.5	15.3
23	Playa	91	30.1	75	105.1	48.6	70.5	10.2	12.2
25	Putnam	176	58.3	26	84.3	76.0	80.3	14.8	18.0

TABLE V

MINERAL COMPOSITION OF COLLOID CALCULATED FROM PER CENT K_2O AND TOTAL WATER LOSS

Colloid		Illite			Montmorillonite		Total	B.E.C.	
No.	Name	Per Cent Calc. from K_2O	Calc. H_2O Loss, %	Total Obs. H_2O Loss, %	Calc. H_2O Loss, %	Calc. Amt. Present, %	Minerals Present, %	me/100 gms. Calc.	Obs.
7	Pima	44	4.0	15.0	11.0	52.6	96.6	75.5	70.6
8	Gila	67	6.1	12.6	6.5	31.1	98.1	57.7	58.2
9	Casa Grande	65	5.9	13.7	7.8	37.3	102.3	63.9	56.5
10	Sunrise	51	4.6	15.3	10.7	51.2	102.2	76.8	63.7
11	Yuma	55	5.0	11.0	6.0	28.7	83.7	51.0	52.2
12	Palos Verdes	52	4.7	13.5	8.8	42.1	94.1	65.5	50.4
13	Gothard	43	3.9	15.5	11.6	55.5	98.5	77.8	68.7
14	Ramona	46	4.2	13.8	9.6	45.9	92.4	67.8	48.4
15	Safford	44	4.0	15.4	11.4	54.6	98.6	77.8	71.3
16	Tubac Surface	64	5.8	13.8	8.0	38.3	102.3	65.0	50.2
17	Tubac Subsoil	62	5.6	12.7	7.1	34.0	96.0	59.1	51.5
18	McNeal 0-4"	71	6.5	12.0	5.5	26.3	97.3	53.2	48.5
19	McNeal 4-12"	62	5.6	13.5	7.9	37.8	99.8	63.5	54.7
20	McNeal 12-28"	57	5.2	14.2	9.0	43.0	100.0	68.4	58.4
21	McNeal 28-48"	50	4.5	14.5	10.0	47.9	97.9	71.0	70.6
22	Cameron	43	3.9	15.3	11.4	54.5	97.5	76.6	81.6
23	Playa	75	6.8	12.2	5.4	25.8	100.8	54.7	70.5
25	Putnam	26	2.4	17.9	15.5	74.2	100.2	94.2	80.3

Safford soil seems to be closely related to Pima in clay mineral composition. Pima is usually a heavy soil often having poor permeability. In other cases, however, it shows good structure and presents no particular problem. The principal difference between these two soils seems to be in their organic matter content.

The Casa Grande soil is one of the few soils in the State which has responded favorably to gypsum treatment. Analysis shows that this soil is predominantly illite. This would indicate that when poor soil permeability is due to cation effects rather than the swelling properties of the soil colloid, gypsum should give a favorable response.

In general, those soils which show illite to be the major clay mineral constituent of the soil colloid seem to have better permeability than those which are primarily montmorillonitic.

Sedletskaa (51) has made extensive studies of the genesis and occurrence of the various clay mineral types. His investigations indicate that the colloids from chernozem and the solonetzic soils are dominantly montmorillonite. In general, chernozems are soils of good structure and permeability while the solonetzic soils have poor structure and permeability, notwithstanding similarity of the clay mineral constituent. It appears, therefore, that the problems of structure associated with the high montmorillonite content

in alkaline soils in arid regions is not due entirely to the properties of the clay mineral but in part to alkalinity and low organic matter content.

S U M M A R Y

1. A study has been made of a number of Arizona soils to determine qualitatively and quantitatively as far as possible, the mineral composition of the colloidal clay fraction.

2. The colloid was separated by sedimentation and purified by removing organic matter, soluble salts and carbonates and saturating with calcium.

3. The minerals in the colloid fraction were determined by a combination of differential thermal, hydrothermal and chemical analysis.

4. A new type of differential apparatus was designed and constructed for this study. For the hydrothermal analysis, an analytical balance was modified to give direct and continuous readings.

5. The percentage of montmorillonite was calculated from the area of the 150° C. differential thermal dip and also from the total water loss of the colloid. The percentage of illite was calculated from the K₂O content as

determined by ultimate analysis.

6. The montmorillonite content of the colloids as determined by the differential thermal method was not regarded as being as definite as that obtained by calculation from total water loss which was given by the hydrothermal curves. It was found to range between 26 and 55 per cent, averaging 46 per cent. The illite was found to range between 46 and 75 per cent, averaging 55 per cent.

7. Correlation between physical properties such as structure and permeability indicated that soils of poor structure were dominantly montmorillonitic. Moreover, one soil known to respond to gypsum treatment was dominantly illitic, to the extent of 65 per cent.

8. Mineral studies on colloids from various horizons in the profiles of Tubac and McNeal series indicated that the amount of montmorillonite increases with increasing depth.

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