THE MINERALOGY OF A DRILL CORE OF ARKANSAS BAUXITE

By

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Submitted in Partial Fulfillment of the
Requirements for the Degree of
DOCTOR OF SCIENCE
from the
Massachusetts Institute of Technology
1947

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August 22, 1947

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ACKNOWLEDGMENTS

The problem was suggested by Dr. R. R. Shrock, and the drill core was obtained through him from the Reynolds Mining Corporation of Little Rock, Arkansas.

The writer is particularly indebted to Dr. H. W. Fairbairn under whose guidance the laboratory investigation was made.

The uranium determinations were made by Miss Geraldine Sullivan.

To the many others who lightened the burden of daily details, particularly my wife and Dr. N. J. Grant of the Metallurgy Department, I express my sincere thanks.

I. INTRODUCTION

The Mineralogy of a Drill Core of Arkansas Bauxite

Much has been written concerning the chemical changes that take place during the weathering of different types of rocks to form the aluminous laterites better known as bauxites. The constituent minerals of the several kinds of laterites have been thoroughly investigated so their physical and chemical properties are now well known. On the other hand, the changes in mineralogy, accompanying the chemical changes are imperfectly known and have been the subject of controversy in recent literature.

The purpose of this thesis is to attempt to determine by as many different methods as possible the changes in the mineralogy of a drill core of an aluminous laterite from the bauxite deposit of Arkansas.

Laterite and bauxite deposits have been studied for many years but the significance of the mineralogy of these deposits has not be geologically applied to any great extent principally because of uncertainty in identification of the individual minerals.

Lapparent(35,36) describes bauxites under four headings:

1. Bauxites with boehmite.
2. Bauxites with gibbsite.
3. Bauxites with diaspore.
4. Bauxites with mixtures of these minerals.

Boehmite-containing bauxites are usually high in iron and silica and are closely associated with carbonaceous formations, lignites and coals. Lapparent ascribes the well developed boehmite crystals as due to the influence of the "humic waters" coming from overlying carbonaceous matter. In order that boehmite develop in humic waters it is necessary that the material undergoing alteration remain at ground water level (au niveau des eaux) for a considerable period of time. The iron is a sesquioxide. It is more generally anhydrous, but may be hydrous.

The gibbsitic bauxites develop from many types of rocks. If the only aluminum hydroxide mineral is gibbsite, Lapparent states that "since the epoch of their formation the bauxitic surface has tended to be elevated in relation to the ground water level". The iron in these deposits exists both as anhydrous and hydrous sesquioxides. If the bauxites are siliceous, the silica is fixed in the form of kaolinite.

Bauxites containing both boehmite and gibbsite are present in the region of Baux in France. Lapparent states that the boehmite developed by the decalcification of clays at ground water level. Subsequently the land was rejuvenated. The bauxite formed on further decalcification of the clay and now consists of form of gibbsite which fills the cracks of the boethmite pisolites and other openings. The gibbsite, then, developed while the land was above ground water level.

Diaspore-containing bauxites are widely distributed. The iron in them is largely in the ferrous form. When large amounts of silica are present in the diaspore recrystallizes usually forming either amesite or corundophyllite instead of kaolinite. The chlorites that are commonly associated with these deposits are the "elements of neoformation" caused by the recrystallization of aluminum, silica and iron minerals. Bauxites containing diaspore show evidence of subsidence. The development of diaspore instead of boehmite or gibbsite is due to the relatively high temperature of the geothermal zone in which the aluminum hydroxides crystallized.

Determining the mineralogical composition of a given bauxite deposit may therefore indicate the fluctuations of the ground water table and may aid in deciphering the geologic history of the formation in which the deposit lies.

According to Lapparent, as outlined in the foregoing abstract of several of his papers(35,36),

1. Boehmite-containing bauxites are formed <u>at</u> ground water level.
2. Gibbsite-containing bauxites are formed <u>above</u> ground water level.
3. Diaspore-containing bauxites are formed <u>below</u> ground water level.

II. THE PROBLEM OF MINERAL DETERMINATION

The principal mineral constituents of any laterite are hydrated aluminum and iron oxides and certain hydrated silicates. These minerals rarely occur as crystals of large enough size for positive determination by optical means. They occur as intergrowths of crystals of such small size that some difficulty is experienced even with x-ray techniques. Standard chemical methods yield information as to the relative abundance of the atoms of the minerals concerned; they do not indicate the abundance of the minerals themselves nor do they give a unique mineral identification.

In 1887, Le Chatelier pointed out that the application of heat to many minerals gave rise to significant endothermic and exothermic reactions. Although this thermal technique has been applied almost exclusively to the "clay" and associated minerals, any mineral that is hydrated or undergoes a physical or chemical change such as an inversion, loss of water, carbon dioxide, etc., can be investigated.

It is with this thermal method, along with a combination of other methods, that the problem of mineral identification in this laterite is attacked.

Description of the Drill Core

The material used was a three-inch drill core obtained from an aluminous laterite, mined as bauxite, located in the extreme southwest corner of the SW$\frac{1}{4}$ of the NE$\frac{1}{4}$, Section 13, in Saline County, Arkansas.

The core represents a cross-section of an undisturbed bauxite, the top of which is fifty eight feet below the surface of the present topography, down to and including a portion of the underlying, highly altered nepheline syenite. The drill core was divided into sections and numbered according to the interval (in feet) which each section represents. As shown in the adjacent sketch, the original core was thirty feet long. Representative portions from each sample interval were taken in the field, labelled as described, boxed and shipped. The total length of boxed core was nine feet. The chemical analysis of each section of the core is given in Table I.

Preparation of Samples for Analysis

Each portion of the core was sampled. The sample was ground in an agate mortar so that the particles would pass through a 65-mesh screen; it was then reduced in size by coning and quartering. One-half of the sample was further ground until it would pass a 150-mesh screen; both samples were then placed in labelled bottles. After coning and quartering to obtain the amount of material required, all of the material used for the different phases of the investigation on a particular portion of the core was taken from the same bottle. This precaution tended to eliminate sampling errors and to insure that the results of the different methods were comparable.

Thin and polished sections of each portion of the core were prepared and studied.

Samples from each portion of the core were prepared for analysis by:

A. By x-ray methods
   1. Photographically
   2. In a x-ray spectrometer

B. In a differential thermal analyzer

C. Spectrographically

D. Optically
   1. In thin section
   2. In polished section

E. By Staining Techniques

TABLE I. CHEMICAL ANALYSIS OF THE DRILL CORE

SAMPLE INTERVAL	SiO_2	Fe_2O_3	TiO_2	Al_2O_3	IGNITION LOSS
58-59	19.62	37.40	1.15	16.38	25.45
59-61	6.56	11.60	3.50	49.63	28.71
61-63	5.07	11.40	2.35	51.43	29.75
63-65	2.81	11.20	1.85	53.28	30.86
65-67	4.23	11.50	2.00	51.83	30.44
67-69	2.93	9.90	1.80	54.56	30.81
69-75	2.00	10.10	1.85	56.10	29.95
75-77	8.09	8.30	2.25	52.21	29.15
77-83	12.30	3.40	2.10	54.50	27.70
83-85	17.77	1.60	1.75	53.21	25.67
85-87	42.97	1.20	1.20	40.22	14.41
87 +	38.77	20.70	TRACE	28.72	13.81

ANALYSIS BY MR. THOMAS DAVIS, APRIL 8, 1947.

TABLE II. CALCULATED MINERAL COMPOSITION FROM CHEMICAL ANALYSIS

SAMPLE INTERVAL	KAOLINITE	GIBBSITE	TiO_2	SIDERITE	Fe_2O_3	QTZ.	TOTAL
58-59	11.0	16.23	1.15	54.20		16.0[1]	97.43
59-61	14.11	67.46	3.50	14.31[2]	1.74[2]		101.12
61-63	10.91	72.12	2.35	8.56[2]	4.13[2]		98.07
63-65	6.05	77.89	1.85	9.75[2]	4.48[2]		100.02
65-67	9.09	73.88	2.00	10.35[2]	1.67[2]		96.97
67-69	6.30	79.69	1.80	11.51[2]	1.98[2]		101.28
69-75	4.30	83.30	1.85	11.71[2]	2.02[2]		103.18
75-77	17.51	69.29	2.25	3.00[2]	6.23		98.28
77-83	26.45	67.15	2.10	TRACE	3.40		99.10
83-85	38.39	52.81	1.75	TRACE	1.60		99.55
85-87	92.38	5.43	1.20		1.20		100.21
87+	KAOLINIZED FELDSPAR		TRACE	30.0			

[1] FROM A MINERAL COUNT OF A THIN SECTION USING A HURLBUT COUNTER

[2] SIDERITE MEASURED USING HURLBUT COUNTER; THE AMOUNT OF IRON REQUIRED FOR SIDERITE WAS SUBTRACTED FROM THE TOTAL IRON AND THE DIFFERENCE CALCULATED TO IRON OXIDE.

TABLE III. MINERALS DETECTED BY THEIR X-RAY DIFFRACTION PATTERNS

SAMPLE INTERVAL	KAOLINITE	GIBBSITE	SIDERITE	QUARTZ
58-59		X	X	X
59-61	X	X	?	
61-63		X	X	
63-65	X	X	X	
65-67	X	X	X	
67-69	X	X		
69-75	X	X	X	
75-77	X	X		
77-83	X	X		
83-85	X	X		
85-87	X	X		
87+	X		X	

TABLE IV. MINERAL COMPOSITION AS INDICATED BY THE THERMAL CURVES

SAMPLE INTERVAL	KAOLINITE	GIBBSITE	SIDERITE
58-59		10	78
59-61	17	69	X
61-63		77	X
63-65		78	X
65-67		92	X
67-69		97	X
69-75		82	X
75-77	23	77	X
77-83	26	72	X
83-85	39	67	X
85-87	95		X
87+			42

X SIDERITE DETECTED BUT AMOUNT NOT ESTIMATED.

III. THE X-RAY DIFFRACTION INVESTIGATION

Samples were prepared from each interval of the core and analyzed in the six-target x-ray diffraction unit shown in Figure 1.

The results are listed in Table III.

The following technique was used to prepare specimens. A small amount of material (approximately 0.05 gram or less) is finely ground in a small agate mortar. In order to obtain sharp lines in an x-ray photograph, the particle size should not be finer than 500 Å nor larger than about 40 microns. For this reason, the powder must be ground thoroughly to reduce the size of the larger particles. The powder resulting from the grinding operation is carefully scraped from the mortar onto a glass plate and mixed into a small drop of glue or paste with the point of a needle. After the mixture has started to congeal, it is scraped off the plate with a razor blade and placed on the side of the hand. The mixture is then rolled with a finger until a long, very thin rod is formed. About a $\frac{1}{4}$-inch portion of the rod is selected, picked up with the point of a needle, and placed in a sample holder containing a small amount of glue. The specimen will remain erect in the holder if the glue is of the proper consistency.

The specimen is placed in the camera and the camera loaded with film. The specimen description is marked with a pencil on the end of the film before loading in the camera.

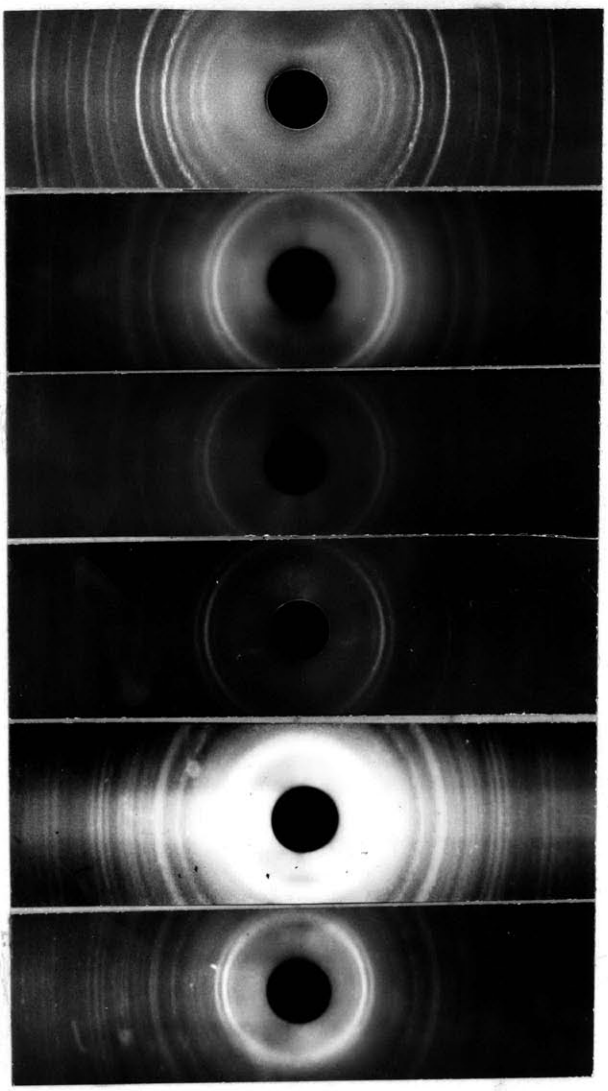
Considerable difficulty was experienced in obtaining satisfactory diffraction patterns. Some of the material was very fine grained and the resulting diffraction pattern often appeared as a series of diffuse lines. At times, the small iron content of the specimen caused scattering; this difficulty was obviated by the use of an iron target. Figure 2 illustrates the x-ray diffraction pattern produced by different portions of the core. The original films have a better resolution than is reproduced in the prints.

The identification of mixtures of fine-grained mineral aggregates by x-ray means is not simple. If the diffraction patterns are diffuse, errors in determining the d-values may be of such magnitude that the pattern be ascribed to any one of several minerals. This is particularly true when considering layer-lattice minerals of the 'clay family' and associated minerals. The d-values of an unknown mineral are checked against those obtained from known samples. The data given for a particular mineral in the Hanawalt Tables and in other publications vary considerably; for instance, at least five different sets of values are listed for gibbsite.

To reduce the errors of measurement to a minimum, three separate diffraction photographs, and in some cases five photographs, were obtained for each sample. The lines in each film were measured three times and the results, if they checked, were used to calculate the "d-values".

Of particular interest is the fact that one set of "d-values" for gibbsite would satisfy the unknown lines in one sample, whereas a different set would satisfy the unknown lines for another sample. This indicates that the gibbsite in the core was not of a uniform composition and structure, but 1) may contain different amounts of 'foreign atoms' in solid solution in the lattice, or 2) may contain a layer or sheet of different material between the gibbsite layers.

FIGURE 1. The Cold-Cathode X-Ray Tube Used For This Investigation.

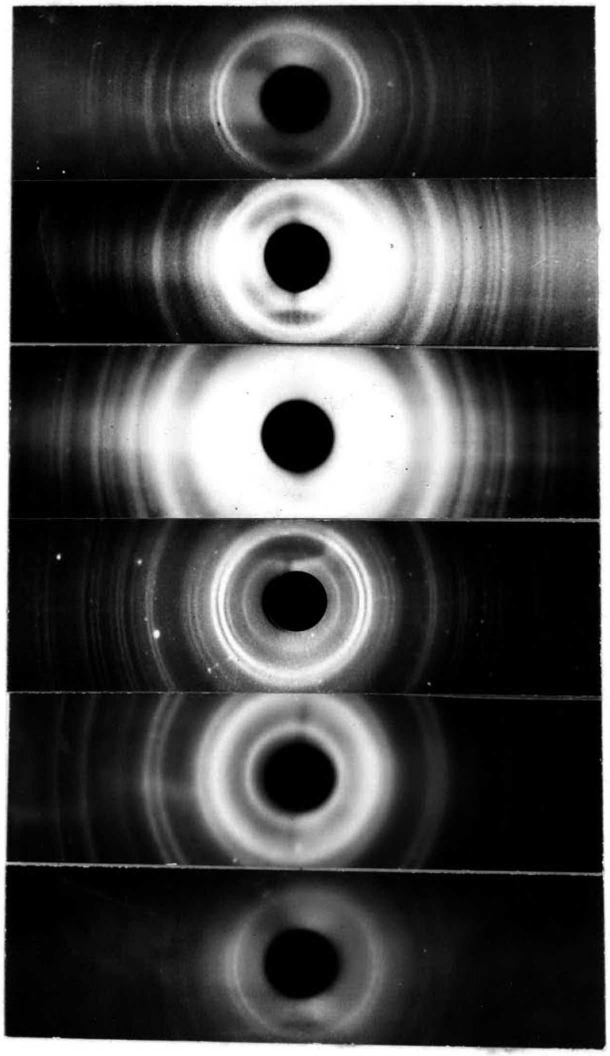


Sample Interval		Minerals Present
58	I	Gibbsite Siderite Quartz
59-61	I	Gibbsite Kaolinite Siderite (?)
61-63	I	Gibbsite Siderite
63-65	I	Gibbsite Kaolinite Siderite
65-67	II	Gibbsite Kaolinite Siderite
67-69	II	Gibbsite Kaolinite

I = Fe K_α radiation

II = Cu K_α radiation

FIGURE 2. The Small-Angle Portion of the X-Ray Films of the Individual Core Samples.



Sample Interval	Minerals Present
69-75 II	Gibbsite Kaolinite Siderite
75-77 II	Gibbsite Kaolinite
77-83 II	Gibbsite Kaolinite
83-85 II	Gibbsite Kaolinite
85-87 II	Gibbsite Kaolinite
87+ II	Kaolinite Siderite

I = Fe K_α radiation

II = Cu K_α radiation

FIGURE 2 (Cont'd.) The Small-Angle Portion of the X-Ray Films of the Core Samples.

Results from the X-Ray Spectrometer

Several samples were run in the Geiger-counter X-ray spectrometer in the laboratory of Dr. J. T. Norton of the Metallurgy Department. In the x-ray analysis of certain classes of substances this instrument gives quantitative results accurate to within five percent of the amount present if that amount is above a certain minimum. Although the sensitivity and resolving power are no greater than that of the photographic x-ray methods (the sensitivity is slightly less) the advantage of its use lies in the fact it produces curves, representing the lines of the diffraction pattern, directly on the graph. The areas under the curves indicate intensity of the reflection from a plane in the crystal, hence is comparable to a photometric graph of the lines from a film. The time and skill required to use this instrument is only a fraction of that necessary for the photographic methods.

However, because of the difficulty in preparing the samples for analysis, reproducible results were not always obtained. Inasmuch as the minerals in the samples that were analyzed were of the layer-lattice type, there was a strong tendency for them to assume a preferred orientation. In some investigations this may be a distinct advantage* but in this one, where difficulty was encountered in identifying the constituents of the sample when all the lines were present, it was a distinct disadvantage.

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* Clark, Grim and Bradley(18) have described an x-ray technique by which the tendency of the clay minerals to orient, with their cleavage faces parallel to a surface, can be used to advantage.

Several different methods of sample preparation were tried but none was completely satisfactory. For this reason, further research with this instrument as applied to the problem at hand was discontinued.

Summary of the X-Ray Investigation

X-ray techniques were used as preliminary methods to identify the minerals in the different portions in the core. Because of its slightly greater sensitivity, the photographic method was used rather than the x-ray spectrometer. Once the minerals or family of minerals of a sample are determined, the spectrometer can be used to advantage. It is very difficult, in fact often impossible, to identify different members of a "family" of clay minerals by x-ray means if a rotating powdered specimen is used. Because the basal spacing of the clay minerals is quite characteristic, oriented specimens facilitate the identification of minerals that give similar x-ray patterns. The tendency for the clay minerals to orient as a result of the treatment used in preparing samples for the x-ray spectrometer obviates the use of the special preparation techniques suggested by Clark, Grim and Bradley(18). The use of photographic methods for preliminary studies and the x-ray spectrometer for detailed quantitative studies would greatly simplify research on material containing different clays.

Because the characteristic lines of the hydrous iron oxide minerals are quite weak, these minerals cannot be detected by x-ray methods when they occur as minor constituents. For this reason these minerals, which are known to be present in the core by optical examination, were not detected by the x-ray techniques employed.

IV. DIFFERENTIAL THERMAL ANALYSIS

Apparatus and Operation

The apparatus used is illustrated in Figure 3. The furnace was patterned after the details published by the U. S. Bureau of Mines (10,49,56) and is the same as that used by Norton(43,44), Grim(28) and others(20,48). The rate of temperature rise was controlled by a motor-driven variable resistance. The heating rate was not strictly uniform. From room temperature up to 700° C it was almost constant - a rise of 14 degrees C per minute. From 700° the rate of heating slowly decreased until at 1000° C, it was 11.5 degrees per minute.

After most of the thermal work presented on the following pages was completed, the furnace was reqound to give it a faster and more uniform rate of heating. The new rate of heating was 16.2 degrees per minute. This faster rate is desirable because the inflections in the curves are much more abrupt and have a greater amplitude. The area under each curve, however, remains essentially the same. The exothermic peakfor kaolinite was 1.75 inches high when tested with the new rate of heating, compared with a 0.5 inch peak obtained using the slower heating rate. The curves for some pure siderites, shown in Figure 10, are excellent examples of how the faster rate gives both the endothermic and exothermic inflections a greater amplitude. As with the kaolinite curve, the areas under the siderite curves are almost exactly the same as for the curves obtained at the slower heating rate. It is probable that the slower rate of heating would not reveal the sharp exothermic reaction for magnesite but would only show a small "bump" that would have the same area as the sharp curve. A "bump" over a larger temperature range would hardly be noticed and would be very difficult to interpret.

The standard method of recording the differential thermal curve is to photograph the portion of a ray of light, reflected from a galvanometer, that passes through a slit on to photographic paper. In the new apparatus used in this investigation, the thermocouples from the sample block are connected to an electronic instrument originally designed by Beck(8) but rebuilt and altered by Micheal Frueh in the Geology Department at MIT. This electronic device amplifies the current caused by differential heating effects. The current is passed to a power unit which operates a recorder and traces a curve on a sheet of graph paper.

All samples tested were ground to pass through a 100-mesh screen. Within a limited range, the particle size did not affect the size or shape of the curves because the grain was usually an aggregate of finer particles. However, as was shown by Speil(56) the particle size of the individual minerals in the aggregate affect the shape and area of the curves.

The sample was packed into the sample hole with great care. If the position of the thermocouple bead is shifted the base line of the curve is affected, so care was taken not to disturb the thermocouple during the packing and removal of the sample. Three small tools,

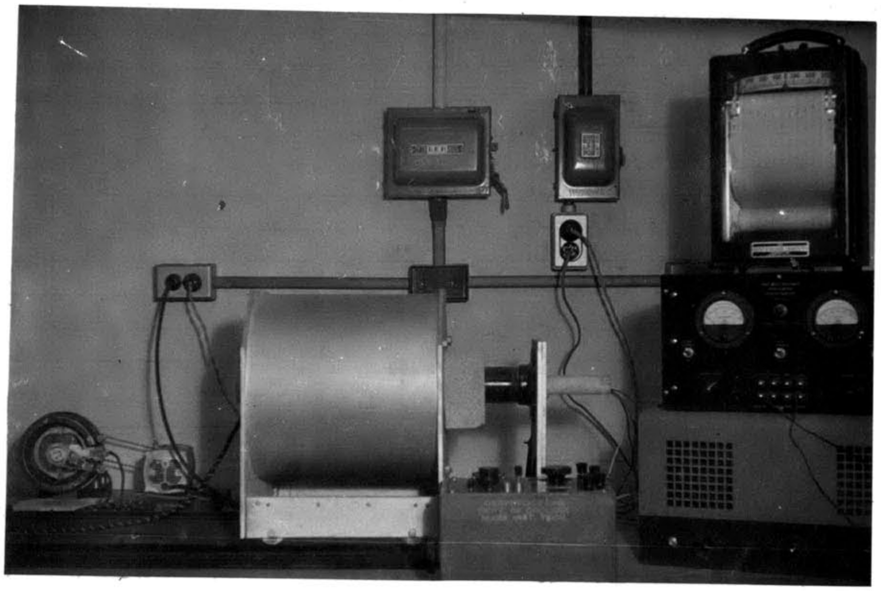

FIGURE 3. The Differential Thermal Apparatus.

shown in Figure 4 were designed for these operations. A portion of the weighted sample is dropped into the hole with tool B and tamped in place with tool A. Using tool A the sample is tamped under the thermocouple bead without disturbing it. When the hole is tamped to the level of the thermocouple bead the remainder of the hole is filled by introducing small increments that are tamped repeatedly with the other end of the tool. Tool C is used to loosen the sample after a run is made. The material is blown out of the hole by the use of a blowpipe. The sides of the hole are then scraped clean with the reverse end of tool C which has a chisel end and sharp sides.

Much of the early trouble with thermocouples was due to the lack of proper care in placing the sample in the hole and failure to clean the hole scrupulously after each run. An 'oxide' film or coating gradually forms in the sample hole and must be removed periodically by reaming.

After packing the sample in the hole, the block was moved to a mark on the block holder to insure an identical heating environment for each run. The furnace is rolled into position, a plug placed in the rear of the furnace and, after setting the rheostat at a predetermined position, the two switches are closed and the run is started.

The base line may not always be straight. Drift of the base line may be due to one of the following causes:

1. The thermocouple junctions (the bead) may not be centered in the sample hole. This causes one side of the bead to heat at a faster rate than the other.

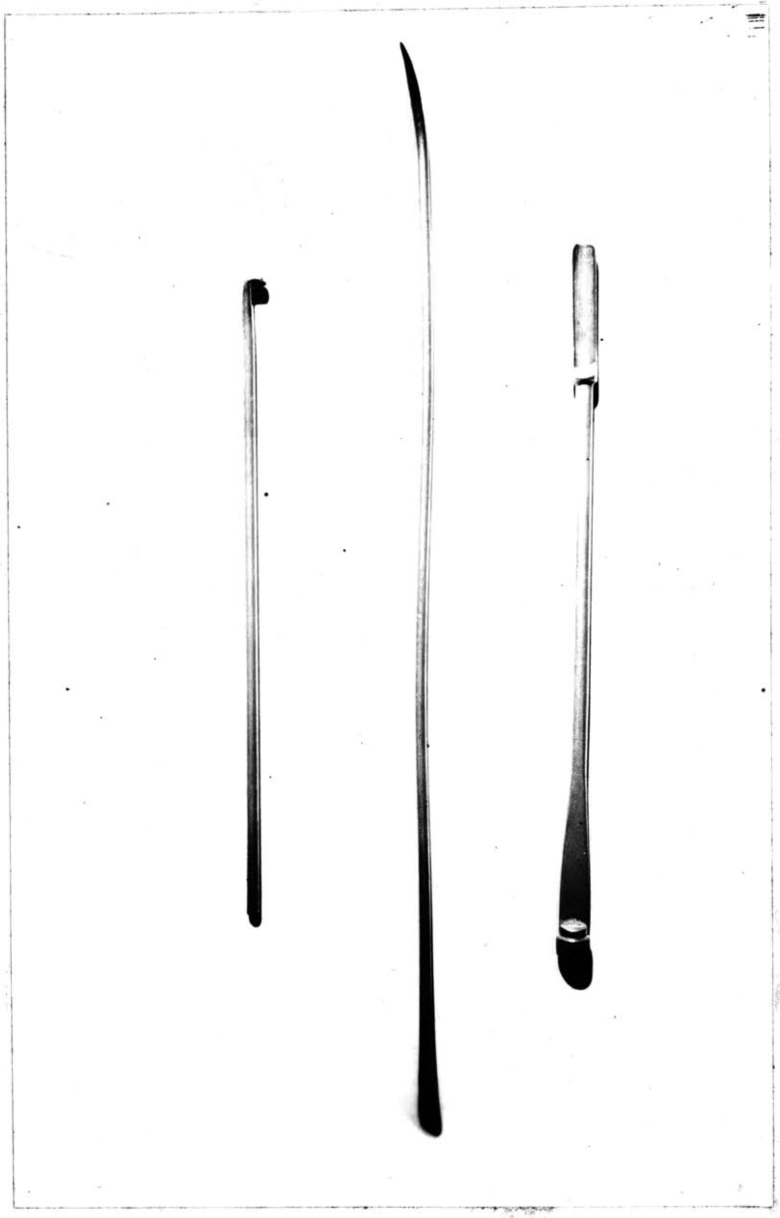

FIGURE 4. Tools Used in Loading, Tamping and Cleaning the Sample Hole. (See text for explanation of specific uses.)

2. If the bead of the thermocouple in the "standard" hole is of a different size than the thermocouple bead in the "sample" hole it will heat at a different rate than the sample thermocouple and the base line may deviate from a straight line.

3. The lengths of the thermocouple leads should be the same.

4. Differences in thermal conductivity of the standard and sample material at low temperatures may cause the base line to drift. This should not affect the base line above a temperature of about 150° C.

A potentiometer indicates the temperature of the block and 50- and 100-degree intervals are marked by hand on the curve traced by the recording instrument.

After the temperature has reached 1000° C the power is shut off, the furnace rolled back and the plug removed. The sample block is allowed to cool slowly, or more rapidly with an air blast.

The coordinates on which the thermal curves are plotted are temperature (abscissa) and temperature difference (ordinate). Because the area under the curves, not the height of the peak, is fundamental, no attempt was made to label the ordinates. Endothermic reactions (heat absorbing) cause the curves to go below the base line and reactions that evolve heat (exothermic reactions) cause the curve to go above the base line.

V. THERMAL ANALYSIS OF STANDARDS

In an attempt to determine quantitatively the major constituents in the core, mixtures were made of pure minerals and alumina. The dilution curves for gibbsite, kaolinite and siderite are shown respectively in Figures 6, 7 and 8. In order to compare the thermal curves obtained by other investigators with those produced by the instrument used, a series of minerals was tested. These curves are shown in Figures 9 and 10. The areas under the curves were measured with a planimeter and plotted against percentage composition. The curves obtained are shown in Figure 5.

The peak temperatures of the minerals run are listed in Table V.

The temperatures at which the peaks occur when tested in this instrument are all uniformly higher than those listed in the literature by approximately 5° C, with the exceptions described in detail below.

Kaolinite

The endothermic and exothermic peaks for kaolinite have been determined by several investigators. Norton(44) lists peak temperatures of 610° and 980° C respectively for the endothermic and exothermic peaks. The curves that are described later, run in Norton's apparatus, show a variation of 5 to 20° for the endothermic peak and as much as a 90° shift for the exothermic peak. Grim and Roland(28) list ranges of 550° to 600° and 950 to 1000° C respectively. Berkelhamer(10)

TABLE V

Peak Temperatures for Pure Minerals

Mineral	Endothermic Peak (°C)	Exothermic Peak (°C)
Kaolin	635	980
Gibbsite	360	
Siderite	560	620-800
Goethite	455	
"Limonite"	380	430-670
Calcite*	940	
Magnesite*	745	
Dolomite*	835 and 975	

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*These minerals were tested in the furnace after it was rewound. The new heating rate was more uniform and faster (16.2 °/min.)

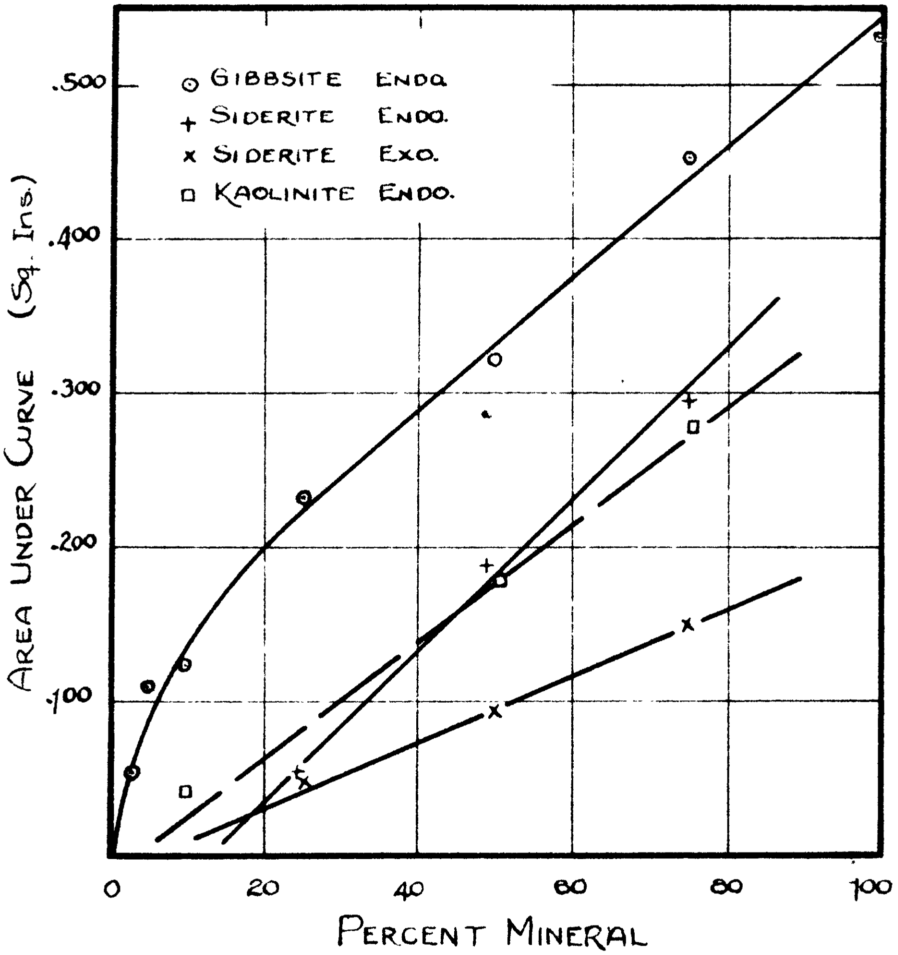


FIGURE 5. Curves Showing the Relationship Between the Percentage of a Mineral Present in a Specimen with the Area Under the Thermal Curve.

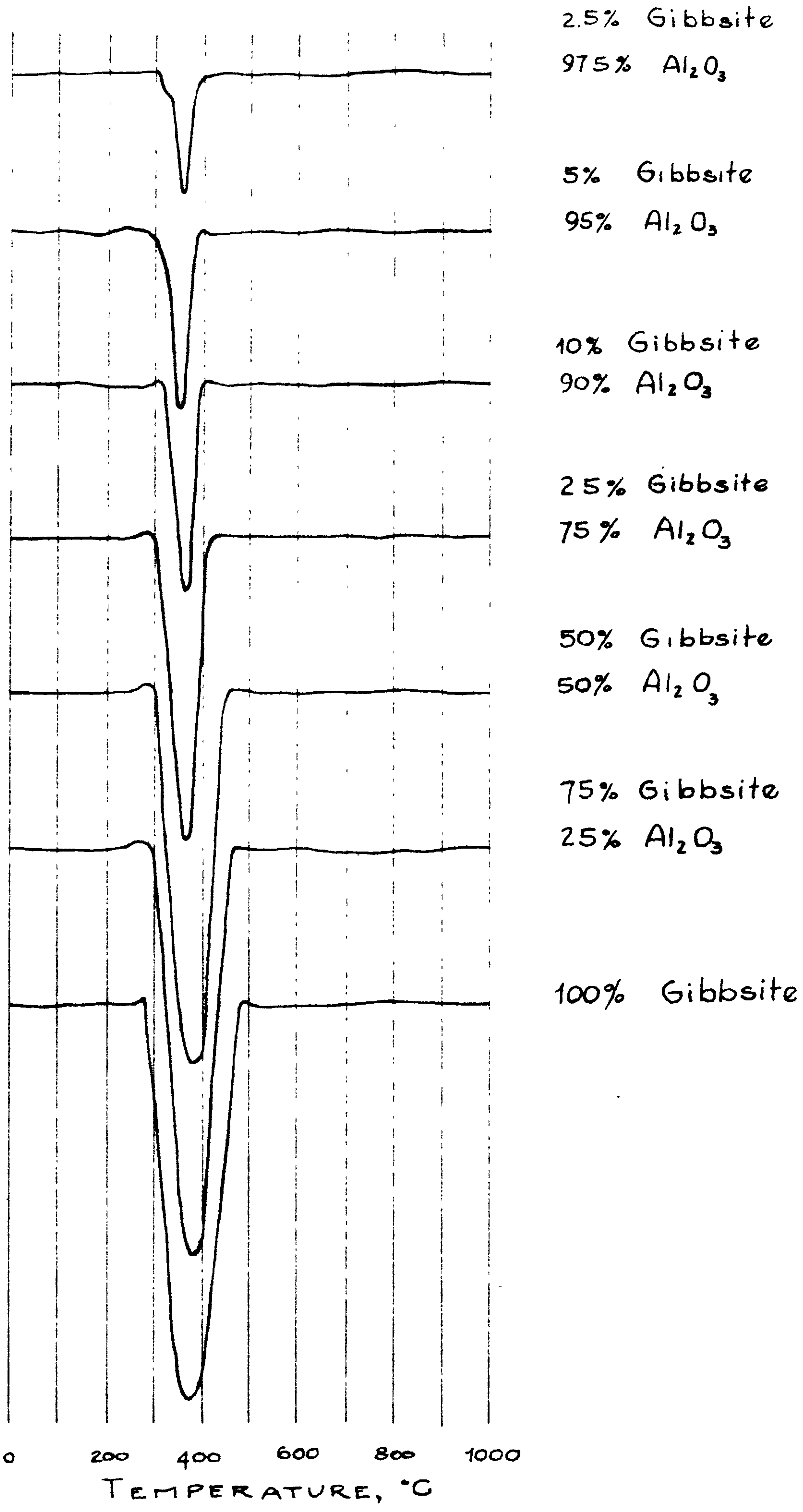


FIGURE 6. Dilution Curves for Gibbsite.

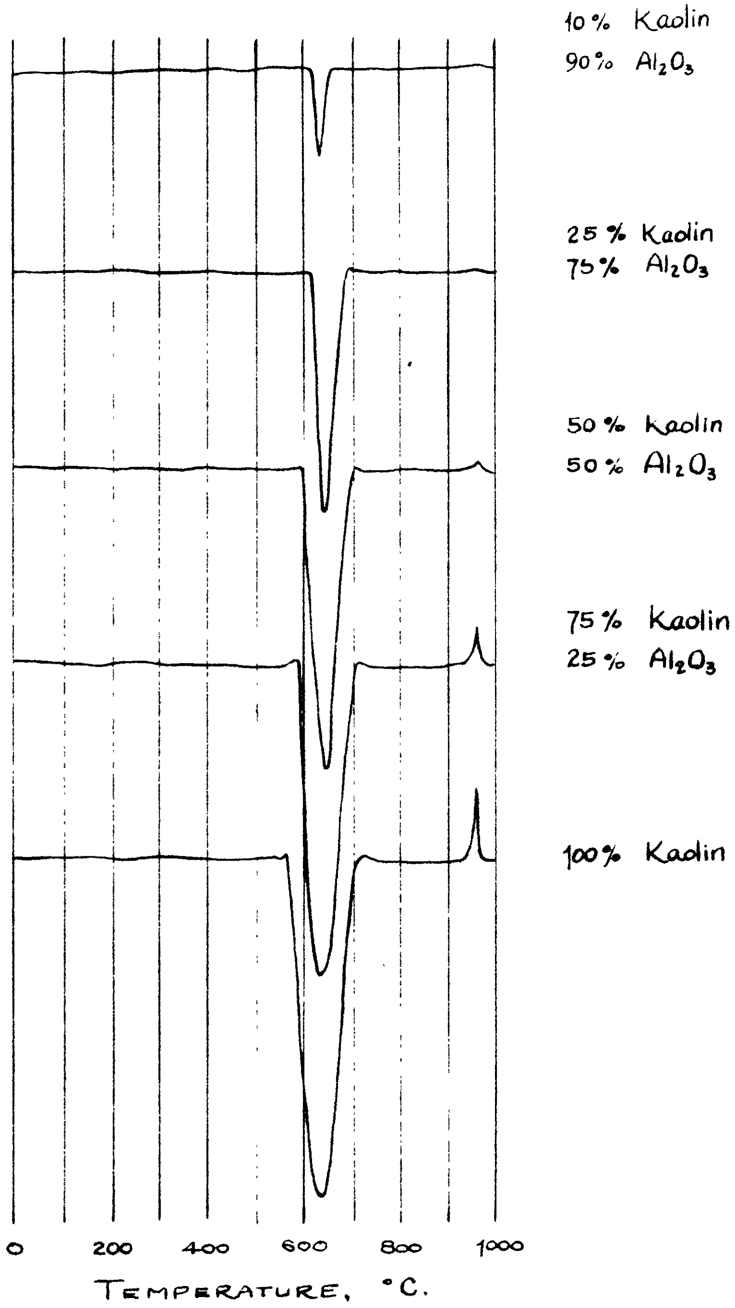


FIGURE 7. Dilution Curves for Kaolinite.

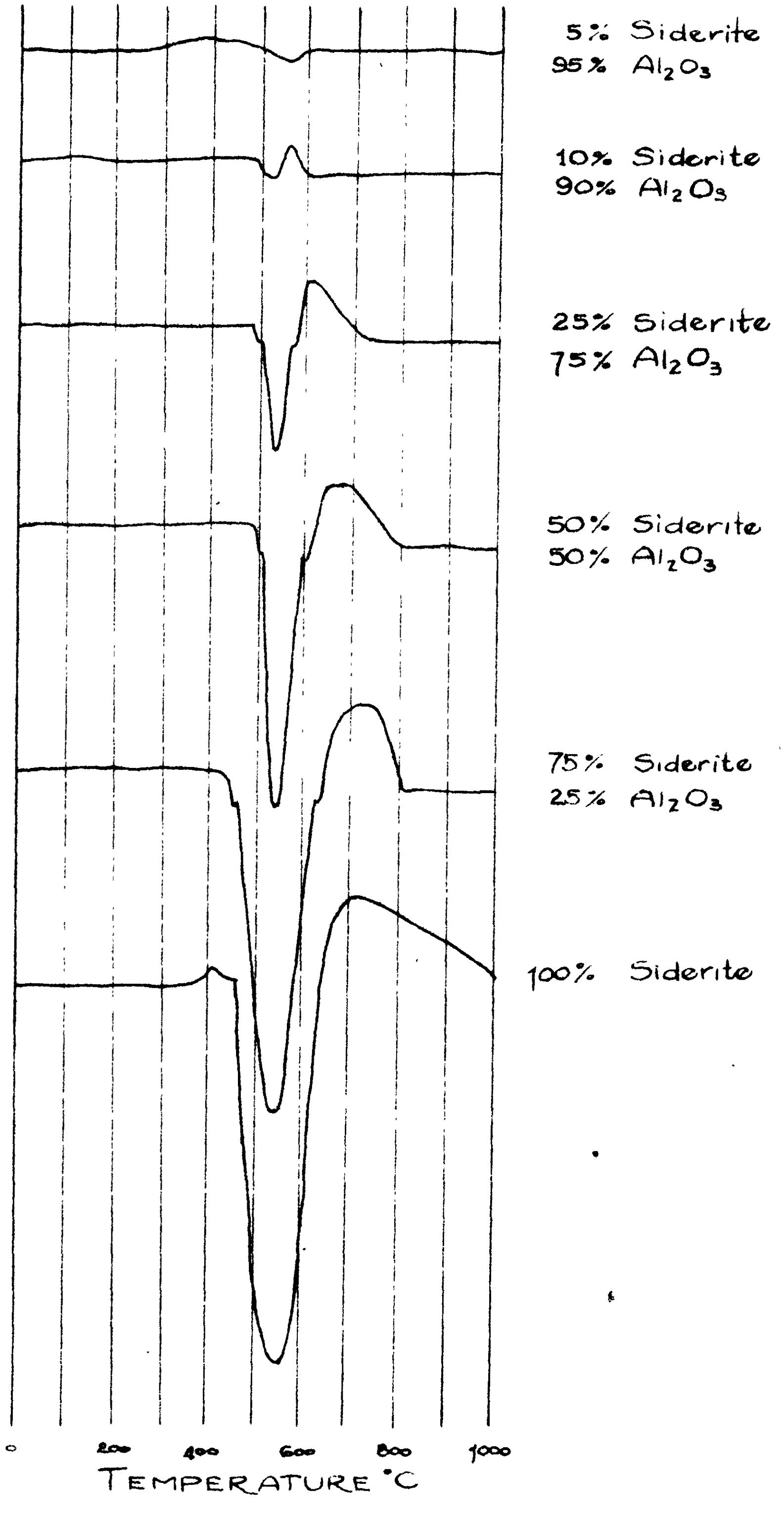


FIGURE 8. Dilution Curves for Siderite.

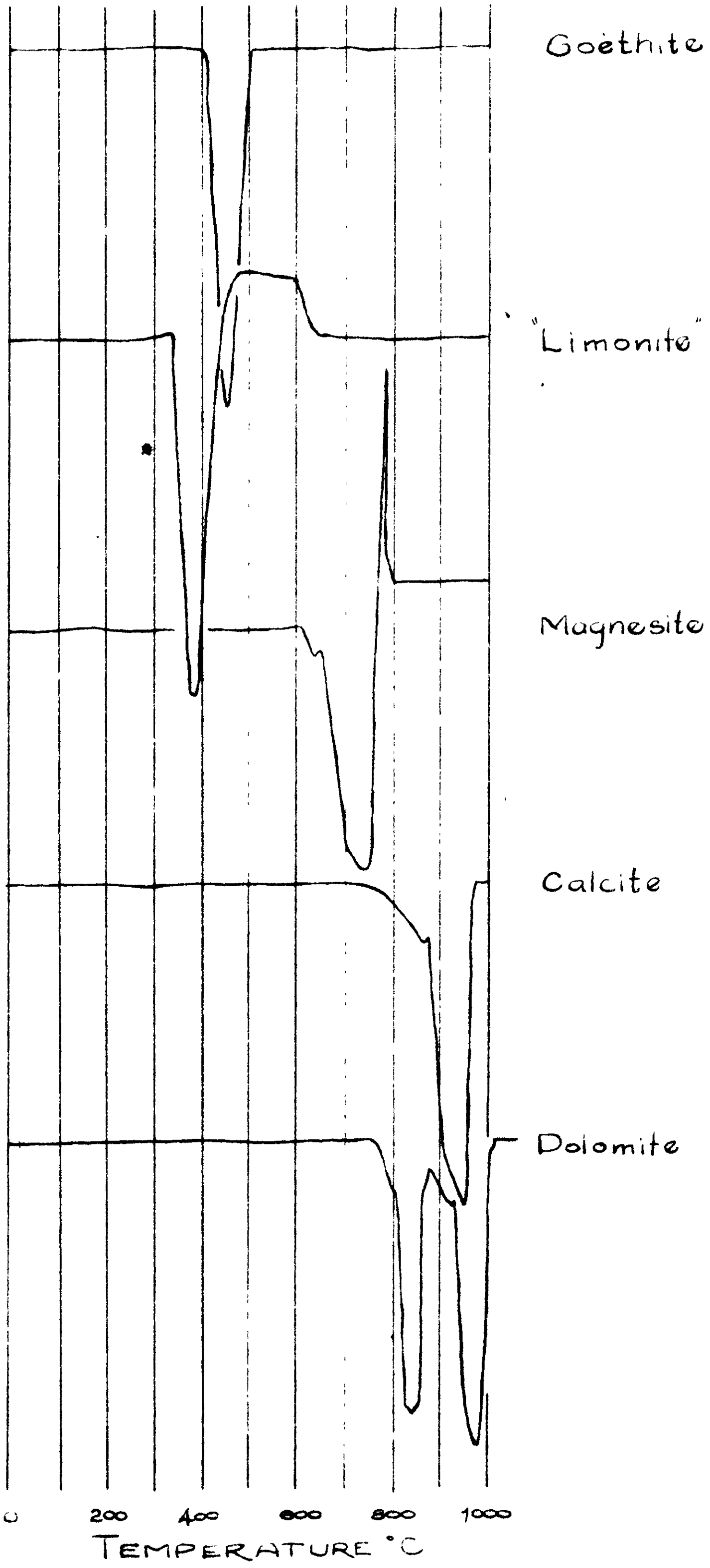


FIGURE 9. Thermal Curves for Some Common Minerals.

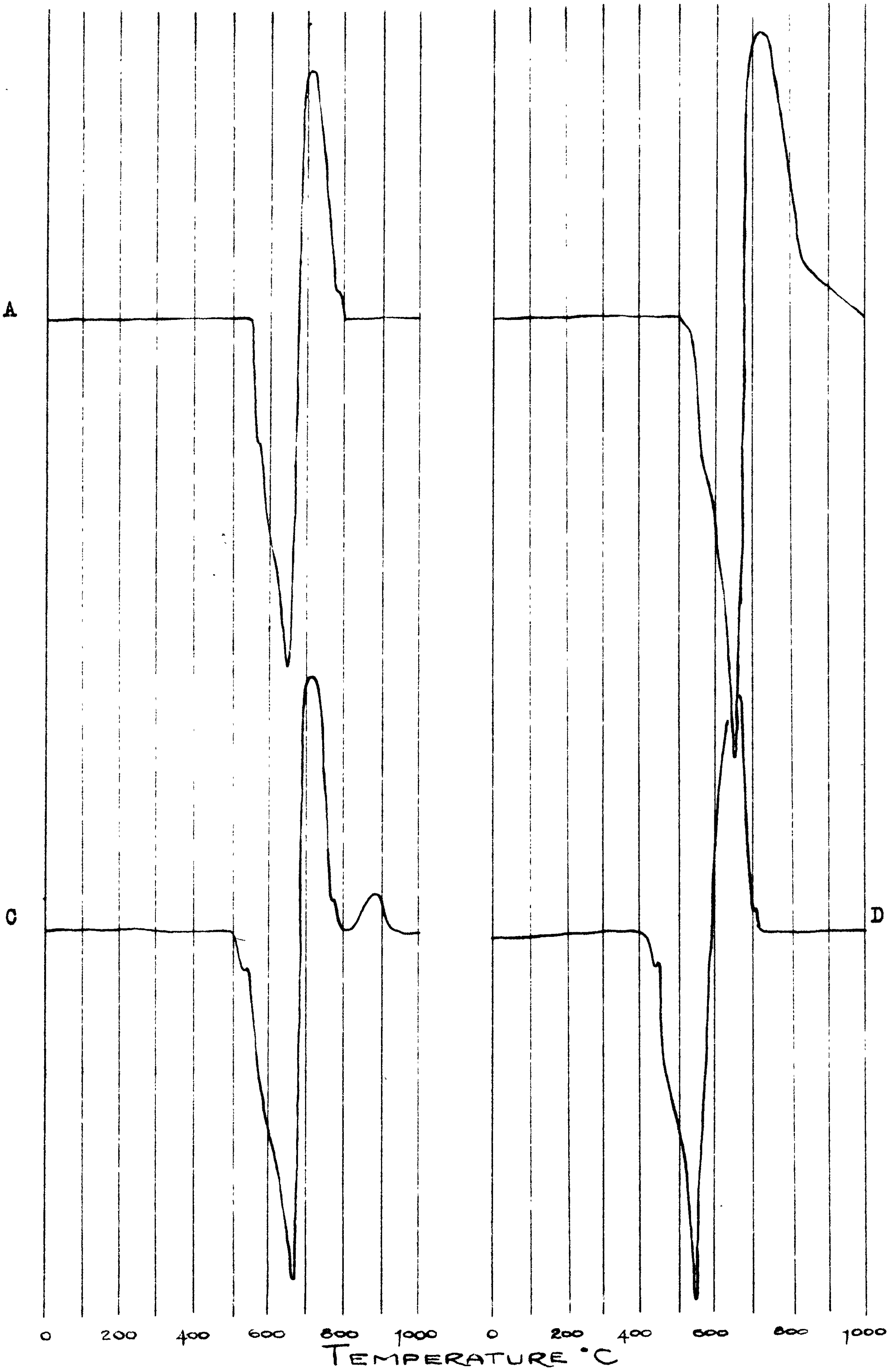


FIGURE 10. Thermal Curves for Various Siderites.

A. Roxbury Siderite
B. Botryoidal Siderite
C. Clear siderite from England
D. Siderite used as standard

found that the endothermic peak for six kaolins was reached at about 610° to 620° C while two others gave peak temperatures of about 595° C. Pask and Davis(49) list 580° C for the endothermic peak temperature.

The difference in the rate of heating may account for the shifts in peak temperatures listed by the different authors but does not account for the differences noted by Berkelhamer.

The Effects of Heat on Kaolinite

The decomposition of kaolinite, on heating, is considered(31) to be represented by the following reactions:

a. 550° C. $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O \longrightarrow Al_2O_3 \cdot 2SiO_2 + 2\ H_2O$

b. 850-1050° C. $Al_2O_3 \cdot 2SiO_2 \longrightarrow \gamma\text{-}Al_2O_3$ + mixture of SiO_2 and Al_2O_3

c. 900° C Upwards. $\gamma\text{-}Al_2O_3$ + mixture of SiO_2 and $Al_2O_3 \longrightarrow$
$3\ Al_2O_3\ \ 2\ SiO_2$

These reactions result in three peaks for kaolinite:

1. An endothermic reaction beginning at about 550° C, which results in a peak at about 600-650° C depending on the amount of material present. The peak is caused by the loss of water from the lattice and may be represented by equation a.

2. An exothermic peak beginning at 850-900° C and ending at 950-1050° C.

3. An exothermic peak starting at 1150° C and ending at 1250° C. (This peak is not shown on any of the curves in the figures.)

Eitel(22) has shown that kaolinite heated from zero to 500° C shows no change in its electron microscope picture or diffraction diagram. At 550° C diffuse halos appear in the x-ray diffraction diagrams. Up to 800° C these halos remain unchanged in position and sharpness but increase in intensity with increasing temperature. At about 900° C in an x-ray diagram all of the kaolinite lines have disappeared and the first lines of the mullite diagram are seen. Above 1100° C these lines predominate. Finally, according to Hyslop(31), typical lines of cristobalite appear.

If kaolinite is heated beyond 550° C(31) a compound, $Al_2O_3.2SiO_2$, is formed that breaks down to form the free oxides at 950° C, SiO_2 and αAl_2O_3. This compound, $Al_2O_3.2SiO_2$, probably should be considered as a homogenous amorphous complex in which the SiO_2 is stabilized. If the SiO_2 existed in the free state it would be soluble in hot alkaline soda solutions. Experiments by Hyslop(31) have shown that, in the compound formed when kaolinite is heated between 650 and 950° C, there is almost no silica soluble in alkaline solutions. The alumina could not be free because pure amorphous alumina would crystallize to form γ-Al_2O_3 at temperatures well below 850° C.

If kaolinite is heated beyond 850° C the compound $Al_2O_3.2SiO_2$ breaks down into γ-Al_2O_3 and a mixture of alumina and silica in which the silica is inactive. This may be due, as explained above, either to the formation of amorphous compounds or to the stabilizing effect of the Al_2O_3 in solid solution with the SiO_2.

On the continued heating beyond 900° C, the compound, $3\ Al_2O_3.2SiO_2$, mullite, starts to form. This reaction results in an exothermic peak occurring between 1150° and 1250° C (equation c).

Caillere, Henin and Terc(16) have found, however, that if kaolinite is heated just to the influction of the curve, between 900° - 1000° C, a mixture of corundum and tridymite results; and, if heated to higher temperatures mullite and tridymite are formed.

Although there is a contradiction as to whether tridymite (Caillere, etc.(16)) or cristobalite (Hyslop(31)) forms after the 950-1000° C reaction occurs, it may only be an apparent difficulty. As shown by Buerger(12), with an increase in temperature the tridymite or the cristobalite structure may prevail depending on the amount of impurity in the structure or, what amounts to the same thing, the number of cristobalite-structure voids occupied. If most of these voids are occupied, the high temperature form, cristobalite, cannot transform into the tridymite structure. Insley and Ewell(32) have shown that transient γ-Al_2O_3 may occur along with aluminum silicate (sillimanite or mullite), therefore under the special heating conditions used by Caillere, et al., the presence of corundum instead of the products listed in equation c is not necessarily contradictory.

Some of the factors influencing the position, shape and magnitude of the endothermic and exothermic curves are of interest. As Caillere, Henin and Terc(16) have shown, kaolinite that recrystallizes the best on heating through 950-1000° C, gives the largest exothermic peak; whereas kaolinite that is poorly recrystallized, as shown by x-ray examination, gives a small exothermic peak. The magnitude of the exothermic phenomena seems to be the consequence of a quasi-explosive course of the recrystallization process. Anything that affects the rate of recrystallization affects also the exothermic peak. Caillere, et al.,(16) found that the fixation of Al, H or NH_4 increased the magnitude of the exothermic peak while Ca, Mg, Na, K, Fe and alkaline earths decreased it. The exothermic reaction of some clays can be affected to such an extent(16) that, if the clay behaves as a H, or a NH_4 clay, the inflection of the thermal curve does not imply necessarily the existence of kaolinite.

Simultaneously flocculated silica and alumina gels give an inflection at the lower temperature listed above, 950° C(32), and, as can be seen in Figure 14, the position of the curve can be influenced by various impurities, causing the curve to be shifted between 970° and 1060° C.

In summary, some of the factors that influence the size and position of the exothermic reaction for kaolinite are:

1. The amount of kaolinite present in the sample,
2. The particle size(15)(56),
3. The crystallinity of the material,
4. The nature and amount of the fixed ions,
5. The nature in which the ions were fixed, and
6. The rate of heating of the sample.

As pointed out by Grim and Rowland(28), the position of the endothermic peak depends on the amount of material present in a given sample. According to them the important point on the thermal curve is the start of the inflection instead of the maximum or peak of the reaction. This is contrary to what was found in this investigation. As can be seen in Figures 7 and 8, the peak temperature is almost constant for mixtures of inert material and varying amounts of sample. Further work will have to be done to explain this discrepancy.

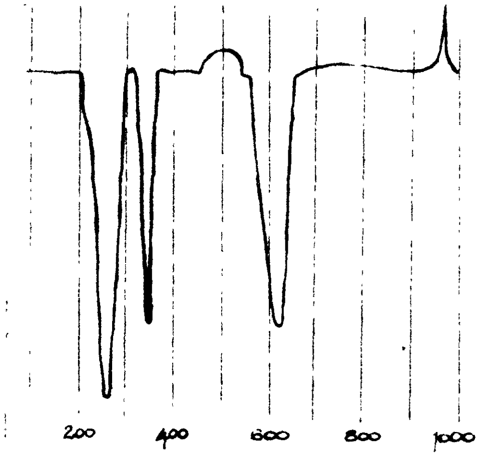
Page's study of montmorillonite(48) showed that the extent and nature of iron substitutions are reflected in the position and shape of certain of the inflections for that mineral. Although no one has noted such a correlation, in the literature surveyed by the writer, for the kaolin minerals, it should be sought.

Gibbsite

The gibbsite used for all determinations was obtained from the mineralogical collection of the Geology Department of the Massachusetts Institute of Technology. It is an aggregate of pale, greenish-white, crystalline aggregates free from most impurity except a very small amount of tan colored clay.

The only peak given was an endothermic peak at 360° C. This agrees very well with the peak temperatures listed by Norton(44), 360° C; Speil(56), 360° C; Berkelhamer(10), 365° C, and Pask and Davies(49), 330° C.

The shape of the curve is identical with all those listed above except that of Pask and Davies(47). Their curve shows an additional peak at 230° C. This small peak can be produced by leaching gibbsite with either HCl or ammonium tartrate. Compare the curve in Figure 14 from Sample 83-85, after leaching with ammonium tartrate.



The small peak is evidently due to the decomposition of part of the gibbsite to an amorphous aluminum hydrate. Further leaching will completely decompose a given gibbsite sample resulting in a large peak at 260° and no peak at 360° C. (The leaching treatment also seems to enhance the kaolinite exothermic peak.)

The effects of heat on aluminum hydroxide.

Four definite crystalline forms of aluminum hydroxides are known(37):

Mineral	Form of Al_2O_3 resulting from heating the mineral to 1000° C.
1. Diaspore $Al_2O_3 \cdot H_2O$	Hexagonal-rhombohedral α-Al_2O_3 (corundum)
2. Boehmite $Al_2O_3 \cdot H_2O$	Cubic γ-Al_2O_3
3. Bayerite $Al_2O_3 \cdot 3H_2O$	Cubic γ-Al_2O_3
4. Gibbsite $Al_2O_3 \cdot 3H_2O$	Cubic γ-Al_2O_3

The γ- alumina forms are listed in the order of their increasing stability.

As illustrated in Figure 11, boehmite is the first product of aging aluminum hydroxide gel precipitated from solutions of aluminum salts with alkali. Boehmite can also form by the slow thermal disintegration of gibbsite. Well crystallized boehmite is very stable and does not exhibit any signs of aging.

Bayerite is produced slowly from boehmite gel by aging under cold water; it is produced rapidly by aging in the presence of dilute alkali solutions. Shaking in dilute alkali (at 50-60° C) causes bayerite to transform into gibbsite.

If carbon dioxide is allowed to pass slowly into the aluminum hydroxide solutions at room temperature, so that days are required for complete precipitation, bayerite is developed. If the carbon dioxide is allowed to act very slowly at ordinary temperatures, as, for instance, by allowing the solutions to stand exposed to the air, gibbsite is obtained. (For complete details, see the work of Fricke, R.,Z". anorg. Chem., 175, p. 249, 1928, and his subsequent articles.

For information on the system alumina-water in equilibrium see (37)). If, however, carbon dioxide is added rapidly to aluminum hydroxides, an amorphous gel is obtained. If air is excluded, a slow precipitation of the aluminum hydroxides favors the development of gibbsite, whereas a rapid precipitation favors bayerite.

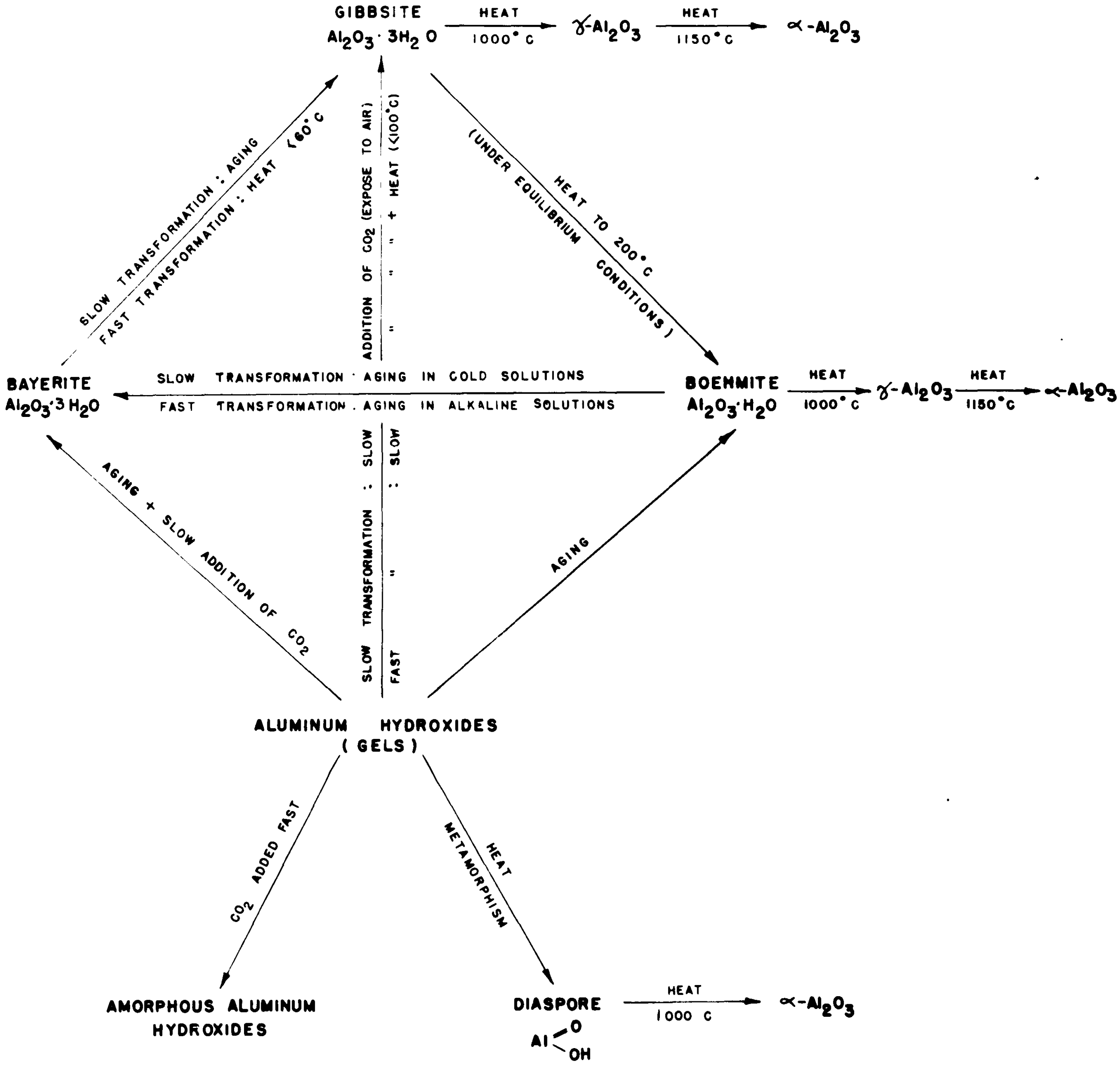
At 120° C bayerite decomposes, as does gibbsite at 165° C, to form boehmite. The decomposition of bayerite to boehmite is not shown in Figure 11. It is unstable and not found in nature.

In addition to the forms of aluminum hydroxide listed above, numerous others are described in the literature. Lehl(39) and Beevers and Ross(9) however, has shown that the β-, δ- and ζ-Al_2O_3 compounds are, in reality, identical to either the γ- or α- fom. The above conclusions are essentially an abstract of Lehl's(39) paper which should be consulted, along with his bibliography, for a complete discussion on this subject.

Crystal structure work, by Verwey(59) has shown that, in addition to γ-Al_2O_3, a γ'-Al_2O_3 exists. He calls γ'-Al_2O_3 an "amorphous state", which transforms, by careful heating, into the partially arranged γ-Al_2O_3 structure. All intermediate combinations of the γ- and γ'-form seem to exist. γ'-Al_2O_3, then, represents the first crystal structure that develops from aluminum hydroxide gel. Its diffuse and broadened x-ray diffraction lines indicate an imperfect and distorted lattice which gives a high degree if dispersion.

Staeche and Wetzel(57) found that the lattice constants of α-Al_2O_3 varied with the type of starting material (pure precipitated gels or natural minerals) and attributed the shift to the presence of foreign atoms in the lattice.

FIGURE 11. THE ORIGIN OF SOME ALUMINUM MINERALS



Hansen and Brownmiller(29) prepared mixtures of aluminum and iron hydroxides, heated them for one hour, and measured the shifts in the haemetite lines caused by varying amounts of corundum in solid solution. Their results were in approximate agreement with Forestier and Chandron(23) who report that α-Fe_2O_3 takes up a maximum of 12 percent Al_2O_3 in solid solution.

X-ray investigation of the material in the core revealed that there must be certain impurities in the gibbsite because different sets of d-values were obtained for gibbsite from different positions in the core. The cause of the shift in the d-values for the gibbsite in various portions of the core, for reasons set forth below, is believed due to varying proportions of iron as an impurity in the gibbsite lattice.

The crystal structure of gibbsite is shown in Figures 12 and 13, with the atoms in Figure 12 drawn to scale. The side elevation view is not strictly correct. Gibbsite is monoclinic with $\beta = 85^\circ 26'$, but is shown in the figure as 90°. The figure, in spite of its inaccuracy, was included to give a picture of the magnitude of the 'holes' in the gibbsite lattice.

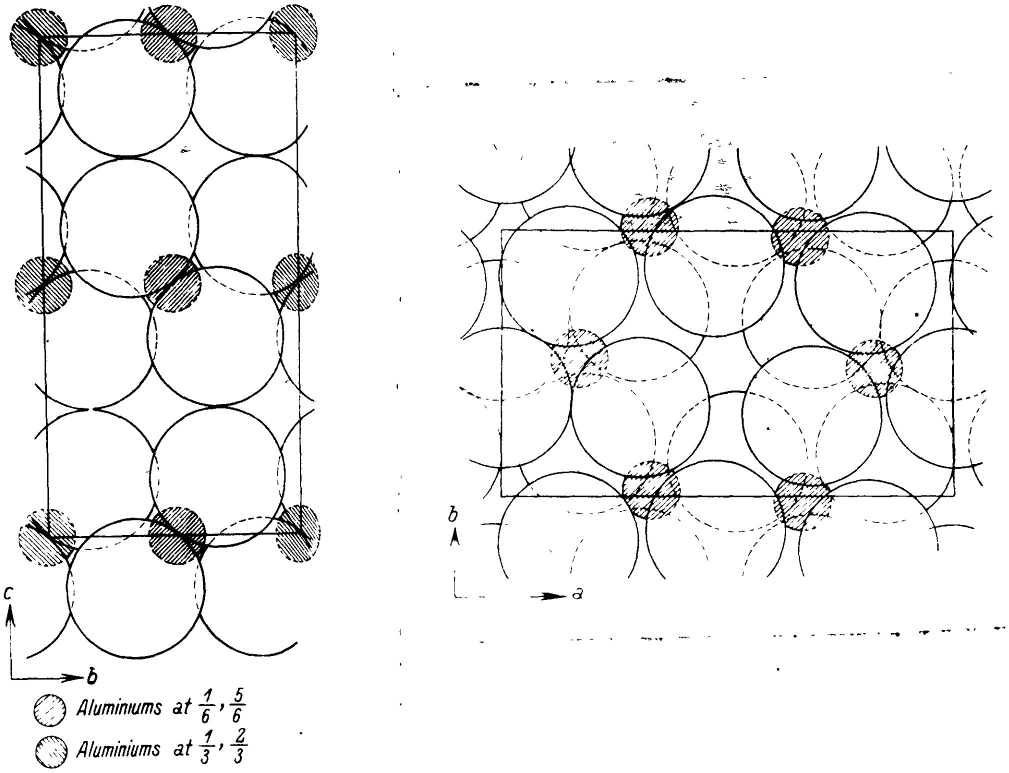
Figures 12 and 13 show that Al occupies only 2 out of 3 possible positions in the lattice. Impurities could either replace the Al in the lattice or fill one of the unoccupied voids. Other cations would then be adsorbed on the lattice to balance the charge.

Ferric iron could substitute for aluminum and the structure would remain electrically neutral. Magnesium can also replace aluminum, giving a negative charge to the layer which must be balanced by a univalent cation per atom of magnesium. Alternatively, as pointed out by Marshall(40), one can regard 3 Mg as taking the place of 2 Al to give a mixed brucite-hydrargillite structure. If titanium was in the trivalent state it could, and undoubtedly does, substitute for aluminum without affecting the electrical neutrality of the structure.

Although a spectrographic examination was made on the core samples none was made on any of the individual minerals from the core (except the titanium minerals) because none were separated in anything approaching a pure state. It is suggested, however, that a spectrographic examination of the aluminum hydroxide minerals would reveal the substitutions discussed above and probably(61,62) also, other cations that were adsorbed to stabilize the aluminum hydroxide gels from which the aluminum minerals were developed.

During differential thermal analysis, equilibrium conditions are not achieved for the decomposition of gibbsite to boehmite, as discussed earlier, so the gibbsite loses two molecules of water at about 350-360° C. The resulting 'boehmite' loses water gradually. Achenbach(1) found that small amounts of water remain up to 1000° C.

According to Staeche and Wetzel(57), who followed the decomposition of some aluminum hydroxides by x-ray techniques, the lines of γ-Al_2O_3 first appear at 450° C, become as strong as the boehmite lines at 500° C and, at 600° C, are the only remaining lines. At 900° C the first lines of α-Al_2O_3 appear and at 1150° C, the α-Al_2O_3 lines predominate.



Side Elevation **Plan View**

FIGURE 12. The Gibbsite Structure in Side Elevation and Plan View.

The relative sizes of the atoms are drawn to scale. (Taken from Megaw(42)).

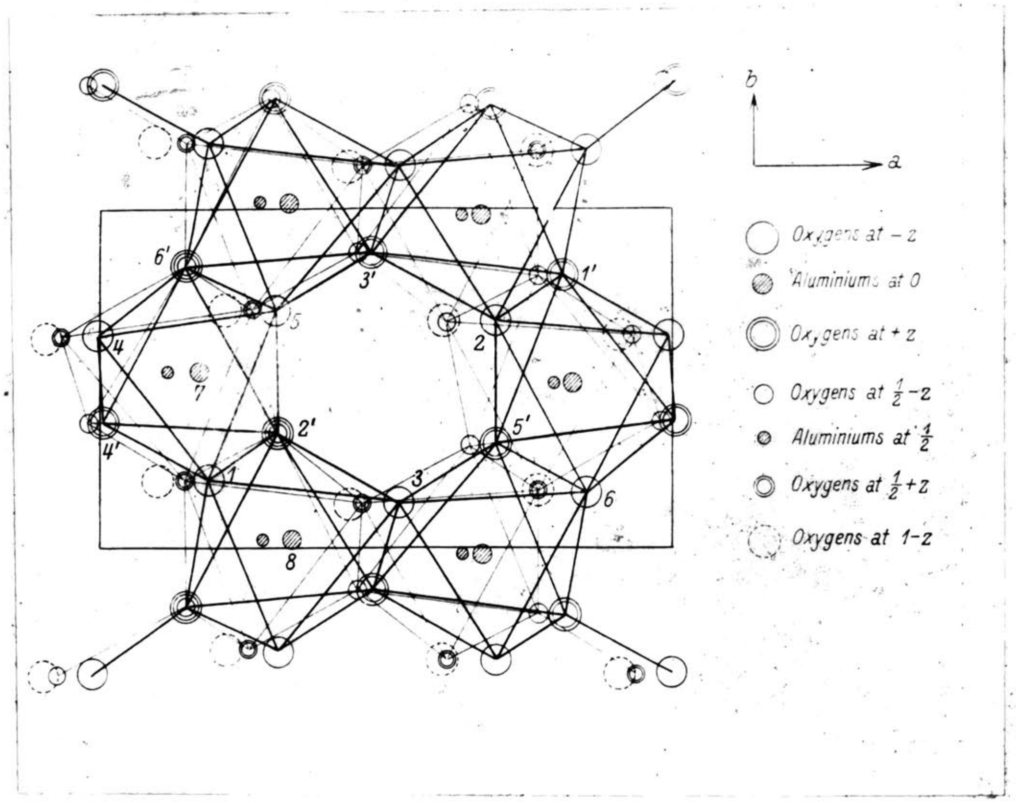


FIGURE 13. **Plan View of Gibbsite Showing Its Monoclinic and Pseudohexagonal Structure.**

The sides of the hexagons that are shared are shortened, thereby distorting the structure. (Taken from Megaw(42)).

Certain impurities, however, stabilize the γ-Al_2O_3 structure. The ζ-Al_2O_3 obtained by Barlett(7) by fusing alumina with 0.35 percent Li_2O is identical, according to Verwey(60), with γ-Al_2O_3. This indicates that the γ-Al_2O_3 is stabilized by the Li_2O because it remains in the γ-form up to 1600° C; only on fusion does this mixture transform to the α-form. Chemical work on β-Al_2O_3(9) has shown that the Al_2O_3 has been stabilized by Na_2O. Its formula should be $Na_2O \cdot 11Al_2O_3$ and not pure Al_2O_3. On the basis of the above explanations it is reasonable to expect that γ-Al_2O_3 in natural minerals will be stable at higher temperatures than those listed in the literature for pure gels. The work cited above seems to confirm the conclusion(57) that impurities were the cause of the shift of the α-Al_2O_3 lines derived from different materials.

Goethite and "Limonite"

The curve produced by a mineral specimen identified by its x-ray diffraction pattern as goethite gives an endothermic peak at 455° C.

Speil(56) lists 345° for this peak as does Berkelhamer(10). Norton(44) lists 425° C and Grim and Rowland(28) give 400° C.

At present no satisfactory answer can be given as to why there is such a large difference in the published peak temperatures for this mineral. It is highly probable, however, that Speil and Berkelhamer were working with 'limonite' instead of goethite.

Although the stable oxide of iron is α-Fe_2O_3, the γ-form also exists. γ-Fe_2O_3 (or ferromagnetic iron oxide) can be prepared by the oxidation of precipitated Fe_3O_4 at low temperatures or by careful dehydration of goethite (lepidocrocite; γ-$Fe_2O_3 . H_2O$) (55,59); it is not very stable and is transformed rapidly into the α-oxide above 250° C. The differences between the x-ray diagrams for γ-Fe_2O_3 and Fe_3O_4 are very slight but Verwey(59) reports that the (111) reflection for Fe_3O_4 is not present in the γ-Fe_2O_3 diagrams.

The diffraction pattern of goethite does not contain lines of sufficient intensity (30) to permit the ready identification of this mineral in mixtures in which it is a minor constituent. In the samples of the core no goethite was detected either by thermal or x-ray methods although it was identified by optical methods.

The endothermic peak for limonite at 380° C and the exothermic curve over a range from 430° to 670° C is not comparable with any in the published literature.

Norton(43) shows a double endothermic peak occurring over a range from 275-400° C with the largest peak at 375° C. His curve does not show any exothermic reaction. Berkelhamer(10) lists an endothermic peak at 375° C but evidently does not consider the portion of his curve above a base line from 400° to 550° C as an exothermic reaction although it generally compares in shape if not in magnitude to the one obtained on the MIT instrument.

Limonite is goethite(21) with adsorbed or capillary water and appears as hardened gel masses of a mixture of hydrous basic ferric oxide, $FeO(OH).nH_2O$. Because it is a mixture and not a definite chemical compound it is reasonable to assume that the materials tested by the different authors did not have the same chemical composition and, for this reason, different thermal curves were obtained.

Siderite

The siderite curve shows an endothermic peak at 545° C and an exothermic reaction occurring over a range of temperatures from 620° to 1000° C. The only curve for siderite showing an exothermic reaction is that of Spiel(56). He lists a strong endothermic peak at 590° C and an exothermic reaction at about 720° C. The siderite curve published by Burkelheimer shows a very strong endothermic reaction, the curve goes a considerable distance above the base line. He evidently does not consider this as an exothermic reaction for he makes no mention of it.

Although only one investigator lists an exothermic reaction for siderite such a reaction should be expected on the basis of the following data listed by Kelley and Anderson(33):

$$FeCO_3 \longrightarrow FeO + CO_2 \qquad \Delta H = 19{,}790 \text{ cal/mol.}$$

$$3FeO + O \longrightarrow Fe_3O_4 \qquad \Delta H = -73{,}000 \text{ cal/mol.}$$

$$2FeO + O \longrightarrow Fe_2O_3 \qquad \Delta H = -66{,}000 \text{ cal/mol.}$$

Thus Kelley finds that the dissociation of siderite to ferrous oxide and carbon dioxide is an endothermic reaction with a heat of formation of 19,790 calories per mol. From similar thermodynamic calculations he finds that the oxidation of ferrous oxide to either Fe_3O_4 or Fe_2O_3 is a strong exothermic reaction. He also calculates that the dissociation temperature comes at 459° C but mentions that it seems too low. The thermal curves show, however, that siderite starts to dissociate almost exactly at this temperature (see Figures 8 and 10).

The shape of the exothermic curve will depend on the amount of siderite originally present in a sample, the partical size and the nature of the material with which it is mixed, and the rate at which it is heated.

The rate of oxidation of the ferrous oxide would be inversely dependent on the partical size; the finer the partical size (after a certain critical size has been reached) the faster the reaction. For a given particle size, the length of time needed to completely oxidize the ferrous oxide to the ferric state depends on the amount of the siderite present in the sample.

When ferrous oxide is oxidized, it is not known with certainty whether it is converted completely to Fe_2O_3, to Fe_3O_4 or a mixture of the two. If the FeO in Fe_3O_4 were completely oxidized to Fe_2O_3, the exothermic peak found for limonite may be explained. After heating to 1000° C all the siderites were ferromagnetic indicating that all of the ferrous oxide was not oxidized to the ferric state(55).

It is interesting to note that Cuthbert and Rowland(20) show only an exothermic peak for a mixture of siderite and alumina. They used a mixture of 25 percent siderite and 75 percent alumina. The heats of formation listed above show that the exothermic reactions evolve about 2.5 times as much energy as the endothermic reaction. It is possible that, with continued dilution of the siderite, there will be a point where the endothermic reaction is very small as compared to the exothermic reaction. This is indicated, to a degree, by the curves in Figure 8. At a concentration of siderite of less than 25 percent siderite in alumina, the endothermic peak is suppressed until, at a concentration of 10 percent siderite, one cannot tell whether the endo- or exothermic peak is the larger. At a concentration of 25 percent siderite, however, a definite endothermic peak occurs in the mixtures prepared by the writer.

Calcite, Magnesite and Dolomite

The shape of the thermal curves for calcite and dolomite are the same as the ones published by Cuthbert and Rowland(20), but the peak temperatures are about 100° C higher. Beck(8) also obtained curves which had peaks at the same temperatures found in the present investigation. The rate of heating used by Beck was 14 degrees per minute, whereas Cuthbert and Rowland used a rate of 10 degrees per minute. The difference in rate of heating, however, cannot satisfactorily account for the large difference in peak temperatures obtained for these minerals because Grim and Rowland(28), using the same apparatus as did Cutbert and Rowland, obtained the same values for the peak temperatures for kaolinite as did the writer and Beck.

The curve for magnesite, however, is essentially the same as that found by Cuthbert and Rowland except that it has a sharp exothermic reaction. The other minor irregularities in the thermal curves obtained with the equipment used for this investigation indicate that the electronic method, for recording thermal changes in a specimen, is much more sensitive than the photographic method. As the galvanometer used in the photographic method always has a certain amount of inertia it does not register small reactions occurring over a short period of time. Also, as Grim and Rowland(28) point out, the galvanometer does not always return to the neutral point after a strong reaction and may cause an inflection in the curve that does not represent a reaction in the specimen.

The sharp exothermic reaction in magnesite is interpreted in a similar manner to that for the exothermic reaction for siderite. It is probably caused by the oxidation of a small amount of ferrous iron substituting for magnesium in the magnesite lattice. A spectrographic examination of the magnesite revealed that approximately 1 to 2 percent iron was included as an impurity.

After the magnesite exothermic reaction occurred, the curve did not return to the base line from which the endothermic reaction started. This was checked several times. The significance of this is not known. Also, the curves for small quantities of siderite ended up below the base line (See Figure 8). This phenomenon is not a characteristic of the apparatus because the curves of other minerals behave as expected; that is, the curve returns to base line after a reaction.

The sharp exothermic reaction for magnesite, if the explanation proposed is correct, could be of great use to anyone interested in the purity of certain minerals containing ferrous iron, either as a main constituent or as an impurity. As the amount of energy involved in the oxidation of iron from the ferrous to the ferric state is large, small quantities of ferrous iron occurring as an impurity in a material could be determined by the thermal method using an apparatus with an electronic recorder.

The curve for dolomite is of the same general form as that shown by Cuthbert and Rowland(20). The peaks of the curves are higher, but, as explained before, this is probably due to the relatively fast heating rate used by the writer. Here, again, the electronic method of recording seems to be the more sensitive of the two methods. Each curve, the one representing the decomposition of the dolomite until no magnesium carbonate remains, and the other, representing the decomposition of the remaining calcium carbonate, is distinctly separate.

VI. THERMAL ANALYSIS OF THE CORE

The thermal curves obtained for each portion of the core are shown in Figure 14. The actual size of the curves obtained on the U. S. Bureau of Mines - type apparatus are shown in Figure 15. These curves were reduced in size and traced along side of the curve obtained using the MIT differential thermal apparatus. The characteristic curve for gibbsite, with a peak temperature at 360° C, is easily distinguished. In the absence of siderite, the characteristic endothermic peak for kaolinite at about 610° C is also easily distinguished. However, where appreciable quantities of both siderite and kaolinite occur together it is very difficult to interpret the significance of the resulting peak.

The endothermic peak for kaolinite overlaps the exothermic peak of siderite. Mixtures of gibbsite, siderite and kaolinite were prepared to study the effect of the endothermic curve of kaolinite on the exothermic curve of siderite. The thermal curves obtained for these mixtures are illustrated in Figures 16 and 17.

In Figure 16 it can be seen that large amounts of siderite shift the gibbsite peak to the right a few degrees and change the symmetry of the curve. Small amounts of kaolinite 'punch a hole' in the exothermic curve of siderite. Increasing amounts of kaolinite, with smaller amounts of siderite almost completely mask the siderite reactions. In the curves in Figure 16 any estimate of the amount of siderite present would be purely guess work, and quite impossible in Figure 17.

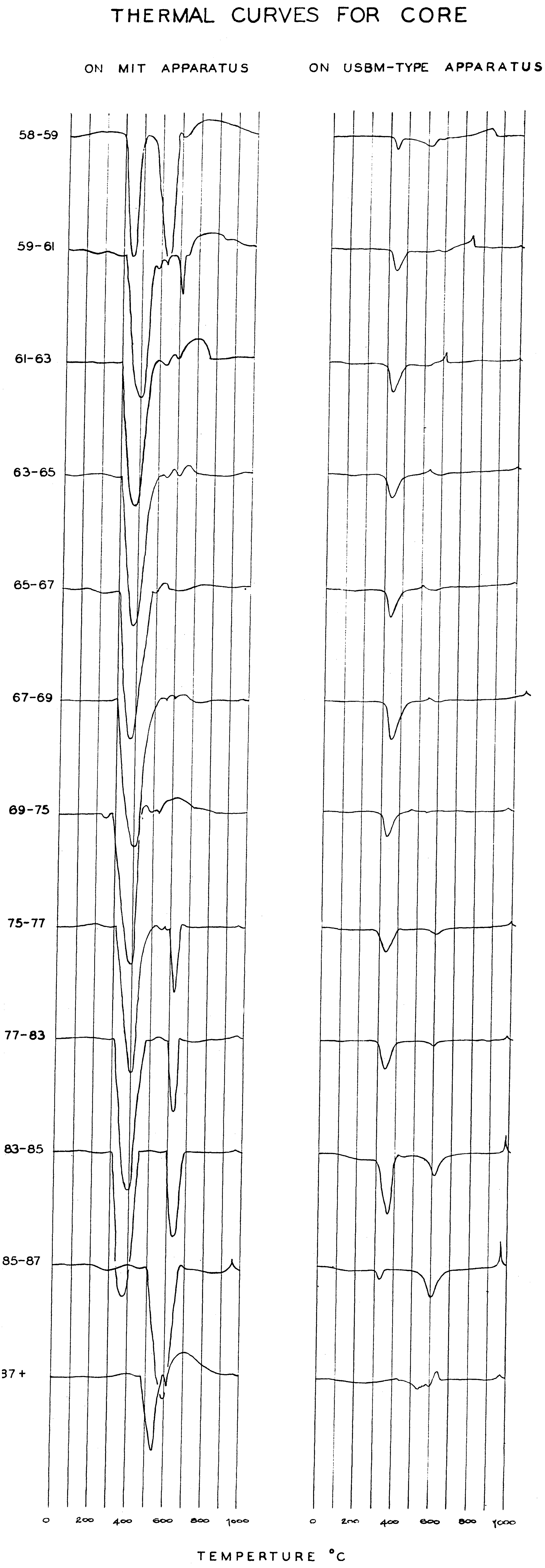


FIGURE 14. Thermal Curves for Each Portion of the Drill Core.

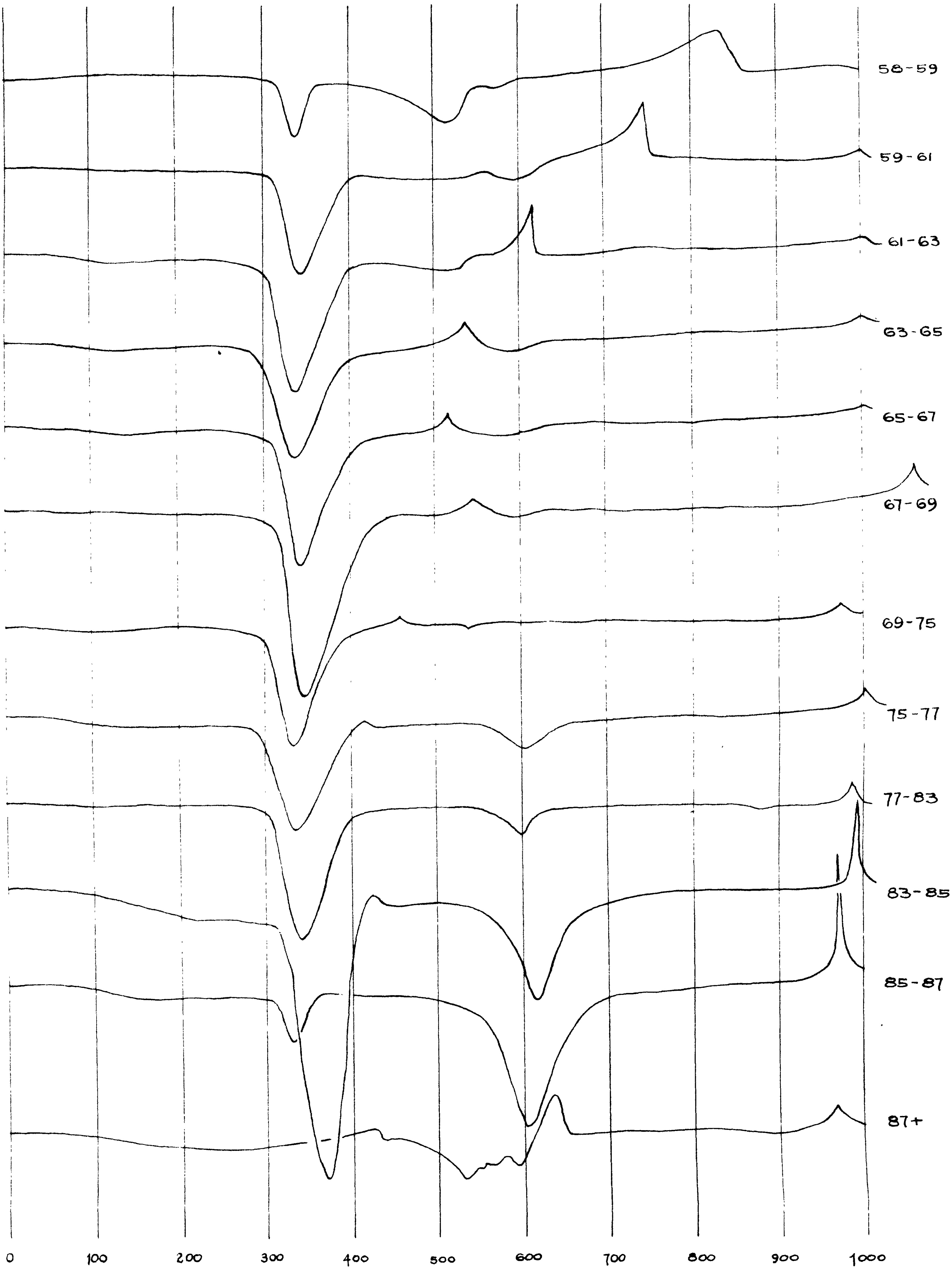


FIGURE 15. The Thermal Curves for Each Portion of the Core as Obtained from a USBM-type differential Thermal Apparatus.

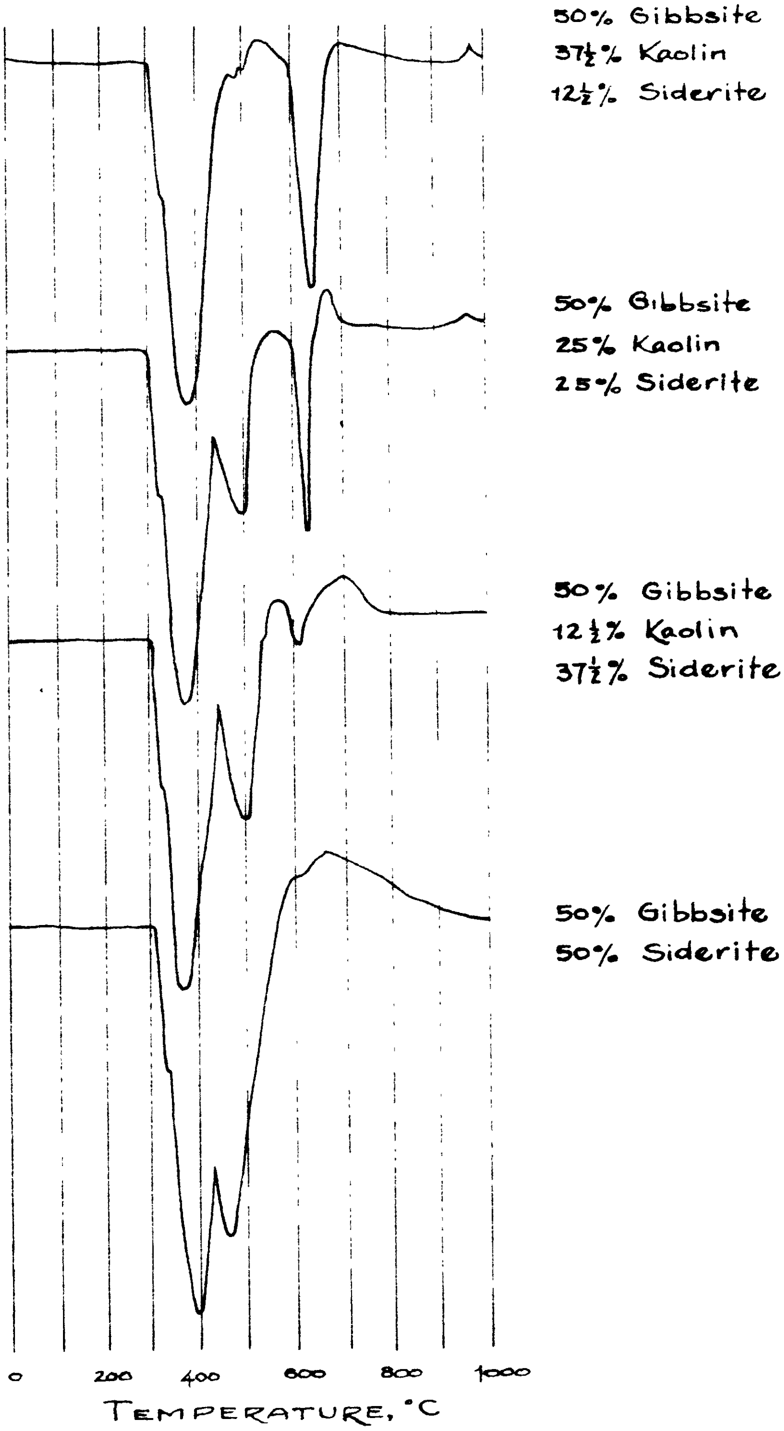


FIGURE16. The Effect of Siderite on the Curves of Gibbsite and Kaolin.

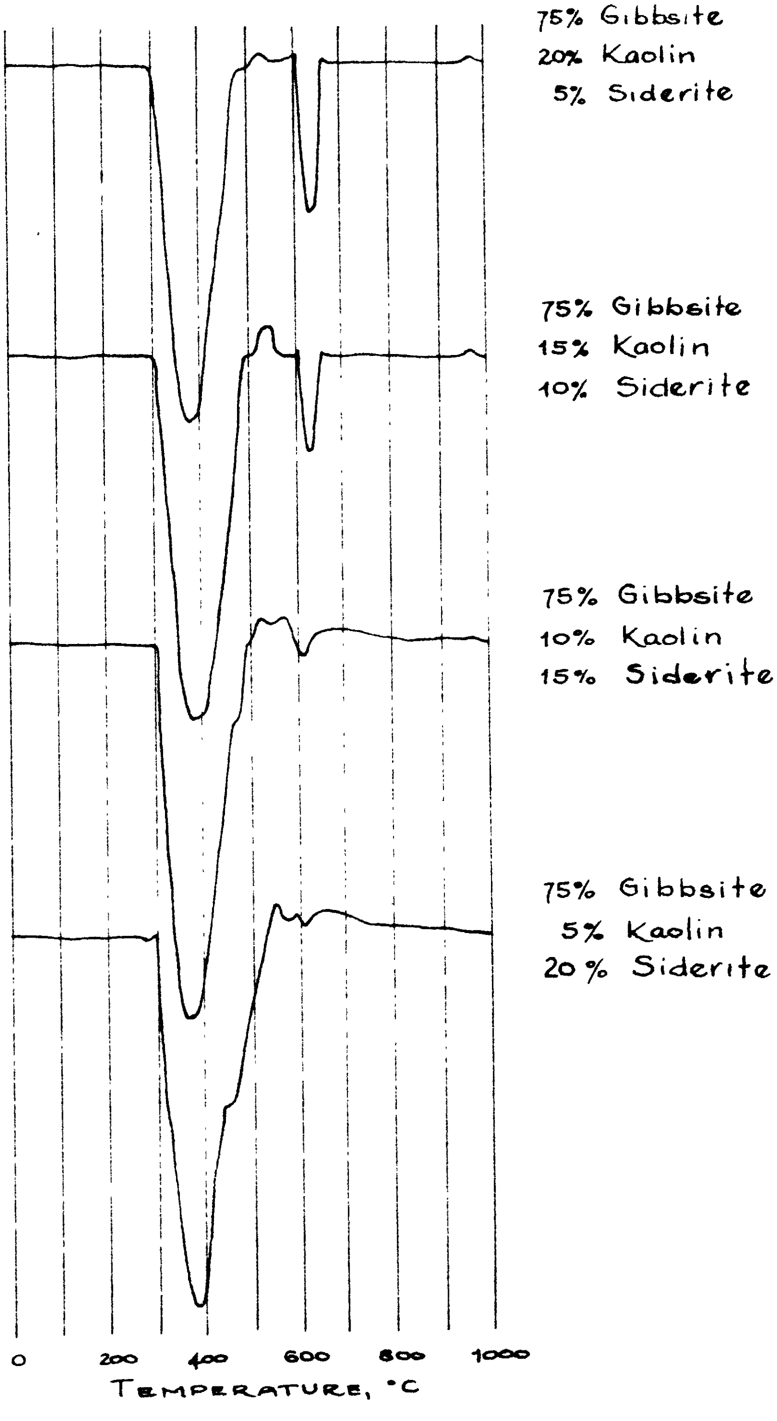


FIGURE 17. The Effect of Small Amounts of Siderite on the Curves of Gibbsite and Kaolin.

TABLE VI

Comparison of Mineral Quantities as Determined By The Thermal Methods and Calculation From Chemical Analysis

Method	Sample Interval											
	58-59			59-61			61-63			63-65		
	K	G	S	K	G	S	K	G	S	K	G	S
Calculation	11.0	16.2	54.2	14.1	67.5	14.3	10.9	72.1	8.6	6.1	78.0	9.8
Thermal	-	10	76	17	69	X	-	77	X	-	78	X
	65-67			67-69			69-75			75-77		
	K	G	S	K	G	S	K	G	S	K	G	S
Calculation	9.1	73.9	10.4	6.3	79.7	1.8	4.3	83.3	1.9	17.5	69.3	3.0
Thermal	-	92	X	-	97	X	-	82	X	23	77	X
	77-83			83-85			85-87			87		
	K	G	S	K	G	S	K	G	S	K	G	S
Calculation	26.5	67.2	Tr.	38.4	52.8	Tr.	92.4	5.4	-	-	-	30
Thermal	26	72	X	39	67	X	95	-	X	-	-	42

K = Kaolinite
G = Gibbsite
S = Siderite
X = Detected but amount not estimated.

The conflicting curves obtained when using smaller amounts of siderite and kaolinite are also very difficult to interpret. The third curve in Figure 17 closely approximates the mineral content of sample 63-65 as calculated from the chemical data. It closely matches the curve of the sample from the drill core shown in Figure 14.

Interpretation of the Thermal Curves of the Core Samples

For comparison the chemical data listed in Table I were calculated into mineral compositions on the assumption that all of the silica was combined to form kaolinite except where free quartz was observed in thin section. (Free quartz was observed only in sample 58-59.) The required amounts of alumina and water added to the silica formed kaolinite. The remaining alumina was recalculated to gibbsite by adding the required amount of water. The results are given in Table II.

The areas under the thermal curves were measured with a planimeter and the percentage of the different minerals so determined by the use of the curves in Figure 5 are tabulated in Table IV.

Table V indicates that even a small amount of siderite increases the area included under the gibbsite curve. In the absence of siderite the percentage of kaolinite can be estimated within an accuracy of a few percent. Even a small amount of kaolinite influences the exothermic curve of siderite to such a degree that no use can be made of it to calculate the percentages of siderite present. However, the relative amounts of siderite and kaolinite can be roughly estimated by comparing the "unknown" curve with the curves obtained by mixing the two minerals in various proportions as in Figures 17 and 18.

Summary of the Thermal Analysis

The thermal investigation indicated that the principal constituents of the core are gibbsite, kaolinite and siderite. The most serious limitation to the thermal method is caused by interference of the reactions that occur at almost the same temperatures. The kaolinite endothermic and the siderite exothermic reactions are a good example. If the peaks for the different reactions are close together, quantitative work cannot be done with any great degree of accuracy.

Although the hydrous iron oxide minerals give endothermic and some exothermic reactions, none of their characteristic peaks was observed in the curves for samples known (by optical examination) to contain these minerals. The thermal investigation did not reveal the presence of any quartz, probably because the small endothermic reaction was completely obscured by the exothermic reaction for siderite.

The sensitivity of the electronic method of recording is much greater than that of the photographic method. This great improvement should open new fields for research and for the practical application of thermal techniques.

VII. OPTICAL EXAMINATION OF THE CORE

The minerals determined by their optical properties in thin sections from each portion of the core are quartz, siderite, gibbsite, kaolinite and zircon.

Quartz grains were present only in the top section of the core (sample 58-59). Some of them are rounded and show evidence of secondary growth (see Figure 23). These grains were evidently washed into the bauxite deposit and were cemented by siderite.

The pisolites in sample 58-59 are almost always compound or are made up of material formed around ilmenite and titanite grains. In hand specimen, the rock is grey because of the ferrous carbonate. This is the only portion of the core that shows any evidence of compaction. There is a marked fissility normal to the axis of the core. This can be seen in Figure 22 which shows cracks traversing all of the grains.

A sharp demarcation occurs between sample interval 58-59 and 59-61. The latter sample is a very hard, dense rock with splotches and streaks of iron stain of different shades of red interspersed with some grey carbonate material.

The carbonate-bearing solutions have attacked the original red-stained pisolites that contain many vugs filled with recrystallized gibbsite. Where the carbonate solutions have come into contact with the ferric iron-stained pisolites, they have bleached them to a grey color. The siderite occurs as veinlets and as vug fillings (see Figures 18, 20, 21, 24 and 25.).

Although this portion of the core contains 68 percent gibbsite, only about 5 percent of the material in the section is crystalline gibbsite and can be identified optically. The remaining material is a semi-opaque mixture of gibbsite and kaolinite. This material is of colloidal origin as shown by many small pisolites and by the rythmic banding found along with other features common to the colloidal state.

The next portion of the core, sample 61-63, is much the same as the preceeding one except that it contains more crystalline material. The crystalline material is found almost exclusively inside the larger pisolites. The pisolites seem to act as coatings around the residual and early-formed minerals. This protective action isolates them from the dissolving action of later solutions. All of the pisolites are heavily stained with ferric iron and are almost black when observed in hand specimen (see Figure 18). The later solutions which bleached the rims and cracks of the pisolites must have been reducing.

The term "solutions" is used for the lack of a better term. This media had a high colloidal content and ions moved through it principally by diffusion instead of "flowing". The evidence for this statement can be seen in thin sections from almost any portion of the core.

Where these basic carbonate "solutions" came into contact with pisolites that are heavily stained with ferric iron, banded effects are commonly visible. This banding (Lisegang phenomena) is characteristic of the colloidal state and represents diffusion of ions through a gel or colloid (Figures 18 and 24). On crystallization, these colloids form small spherules, pisolites, etc., and leave a large pore space that is usually filled with siderite. Where these colloids penetrate and fill preexisting vugs or holes, crystalline material commonly develops (see Figure 24). If a small amount of silica accompanies the aluminous gels, kaolinite crystals start to grow (see Figure 28). The pisolites must have contained a relatively large amount of water because, as they dried, large radial and concentric cracks formed (see Figures 18 and 24).

Excepting the top sample, the core, down to sample 75-77, consists of variations of the texture and composition described above: sometimes predominantly hard, red, pisolitic matter and sometimes grey, opaque, almost structureless, amorphous-appearing matter, with all intermediates variations.

Sample 75-77 is separated from the upper portion of the core by its softer, white-to-cream appearance. Many pisolites in this zone have a light colored shell and a dark interior. Some of them are hollow, and in these, small red-black oolites are sometimes present. Thermal analysis indicates that these oolites are almost pure goethite. The outer shells, which can be peeled off like an onion skin, are almost pure gibbsite.

Thin sections of this sample show many kaolinite crystals in the reworked aluminous material. (See Figure 19 which illustrates the "contact" between sample 69-75 and 75-77 showing the bleached, reworked aluminous material in which the kaolinite crystals are growing.)

Thermal analysis of individual pisolites from this sample of the core clearly indicates that kaolinitic material is displacing the gibbsite from the centers of the pisolites. The iron may remain as small oolites or migrate with the displaced gibbsitic material.

The pisolites in the next two samples, 77-83 and 83-85, have centers showing varying degrees of kaolinization. The iron has been almost competely removed. By using a solution of one part malachite green in 200 parts water as a stain, the kaolinite content can easily be recognized in hand specimen. Kaolinite stains a blue-green color whereas the other minerals are not affected. (The stain must be painted on the specimen rapidly. If the specimen is soaked with the stain the whole mass turns a dull green color.)

In thin section, all of these pisolites in the two samples appear as ghosts of the red, ferric-iron stained pisolites previously described (see Figure 27).

Sample 85-87 consists almost entirely of a soft, massive, structureless kaolinitic material. This portion of the core represents the complete alteration of the pisolitic material. Although practically no gibbsite or ferric iron now remains in the sample, the proof that they once were there is found by noting the ghost or phantom outlines of pisolites exactly like the ones previously described. Large kaolinite crystals as much as one-eighth of an inch long have grown from the structureless ground mass (See Figure 28).

In sample 87+, which represents the kaolinized syenite, only kaolinized feldspars, remnants of biotite crystals, siderite, zircon, and a few grains of opaque material are recognizable.

Summary

In summary the following conclusions can be reached:

1. The oldest recognizable material in the core consists of fragments of gibbsitized feldspar. That these fragments were once feldspar is deduced from the fact that the gibbsite seems to be oriented. Different

portions of a fragment alternately extinguish when the microscope stage is rotated, in much the same manner as some feldspars.

2. The gibbsitized feldspar is surrounded and protected by an "armor" of ferric-iron stained, structureless, gibbsitic material in the form of pisolites. Although this material has an amorphous appearance, it is not amorphous, as stated by other authors(41) because x-ray patterns can be obtained from it.

3. The iron stained pisolites also contain zircon and ilmenite crystals (see zirconium discussion).

4. The pisolites represent many stages of reworking and concentration of the colloidal material. The evidence for this statement lies in the fact that the pisolites have a very complicated structure. There are often four or more sets of pisolites, one within the other. Each individual pisolite may also show many concentric shells that indicate successive stages of growth. Many of these "pisolites-within-pisolites" show cracks, bleached shells, and other evidences of having gone through both wet and dry stages before they were enveloped by later material.

5. On the basis of the above facts, it can be concluded that some of the aluminous material now found in this core was derived from original material and some was introduced from an outside source. The actual relative amounts of aluminous material so produced can not be determined.

6. During and after the reworking of the gibbsitic material, ferric iron colloids were introduced. That they were not present from the start is shown by the clear unstained gibbsitic material that replaced the original feldspars.

7. The next stage in the development of the bauxite, as now found, was the concimitant introduction of ferrous carbonate and siliceous colloids. These colloids and solutions again reworked the early formed aluminum minerals. The early ferric iron was reduced to the ferrous state and was leached from the pisolites or driven into their centers where it formed goethite oolites. These basic solutions also attacked the gibbsitic material and caused it to migrate. The titanium minerals and zircons, formerly protected by the pisolites, were attacked as described later.

8. The colloidal silica combined with some of the reworked aluminum colloids to form kaolinite. That the silica was not present in quantity at an earlier stage is shown by the fact that kaolinite crystals develop only in the later, structureless material and are never found in pisolites that developed at an early date.

Kaolinization and carbonatization then, are the last stages in the alteration of the aluminous mass and its underlying syenite.

The conclusions reached form the study of this drill core are in accordance with those reached by some authors who have studied the Arkansas bauxite and other aluminous laterites.

In an early paper, Mead(41) concluded that kaolinization was an intermediate step in the weathering of nepheline syenite to bauxite. Goldman and Tracey(24) question this conclusion.

The field fact that kaolinite exists between the bauxite and the nepheline syenite is not questioned by anyone. Mead evidently believes that gibbsite can develop without the intermediate formation of kaolinite for he clearly states (pages 41-42) that:

> "The pisolitic type of ore is made up largely of the amorphous form (of gibbsite) but this type of ore contains a considerable amount of the crystalline form in the shape of remnants of feldspars which have been competely altered to gibbsite. It would seem from this that the hydrous aluminum oxide develops first in the form of gibbsite and that when it undergoes change, as in the development of the pisolitic type of ore, it tends to take on the amorphous form". (Words within the brackets were added by A. F. F.)

He also must believe that gibbsite can develop from kaolinite because, later, page 44, Mead states that:

> "The texture of the kaolinized syenite has been essential to the alteration of the kaolin to bauxite."

On page 50 he also states:

> "It appears that normal weathering of the syenite to kaolin and allied minerals has simply continued one step further in breaking down these hydrous aluminum silicates to hydrous aluminum oxide."

Definite evidence was noted in this investigation that kaolinite developed later than bauxite; no evidence was found that would indicate that bauxite developed from kaolinite.

If these last statements by Mead are what Goldman and Tracey interpret as the "intermediate step", the question that they raise as to whether bauxite develops from kaolinite is a pertinent one.

Feldspars derived from many types of rocks have been reported to alter directly to gibbsite without the intermediate step of kaolinization (5,34,36,50 and 51). It has been further reported that kaolinite often develops later as a consequence of "resilication". Numerous workers in this field have also pointed out the remarkable stability of kaolinite under a wide range of field conditions. Laboratory work has shown the remarkable stability of kaolinite. Experimentally conducted work by Norton(45) showed that the minerals which he tested altered directly to a stable end-product without the formation of any intermediate steps. From the above work it seems quite certain that kaolinite does not decompose or alter to gibbsite under the conditions that normally produce bauxite deposits.

In a discussion with the author, Mead pointed out that the syenite in the area where the bauxite deposits occur alters on a regional scale to kaolin, and that as he described in his paper(41), the bauxite was only rarely found directly on the syenite. He also pointed out that the bauxite deposit is sometimes transected by kaolinite veins, as described by Goldman and Tracey(24), but that, quantitatively, these veins were rare. He mentioned that he could not believe that the major portion of the kaolinite could be due to "resilication" processes. As Mead's observations are based on a large amount of field experience covering an interval of many years, the field facts presented by him cannot be passed over lightly.

The conclusions reached here, based on one core, cannot carry much weight in any discussion of the origin of the bauxite deposit. The present investigation, however, shows that these bauxite deposits have a much more complex history than previously supposed. It presents, moreover, a combination of methods which, correlated with field work, should be able to resolve the conflicting opinions concerning the paragenetic relationships of gibbsite and kaolinite presented above.

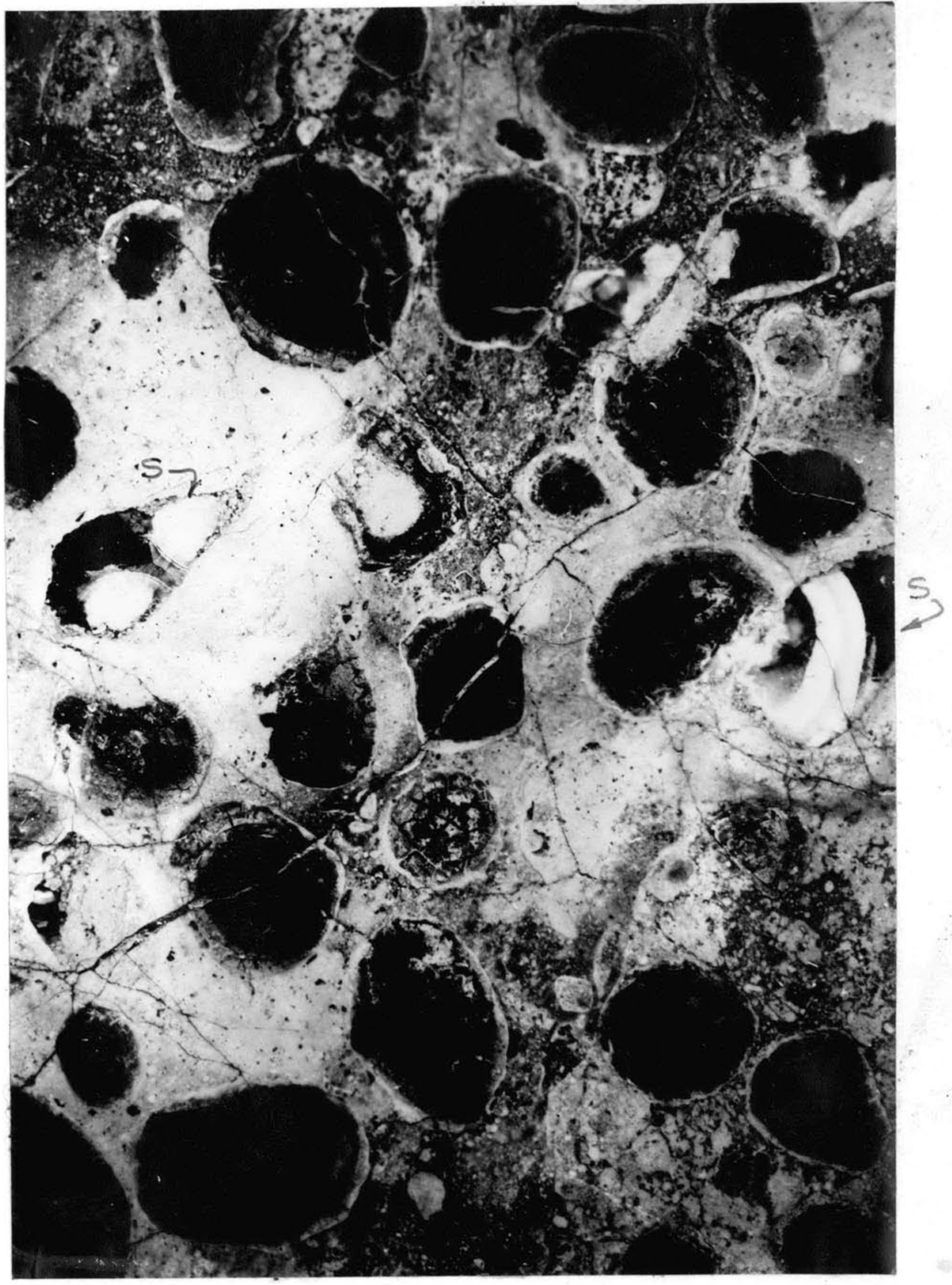
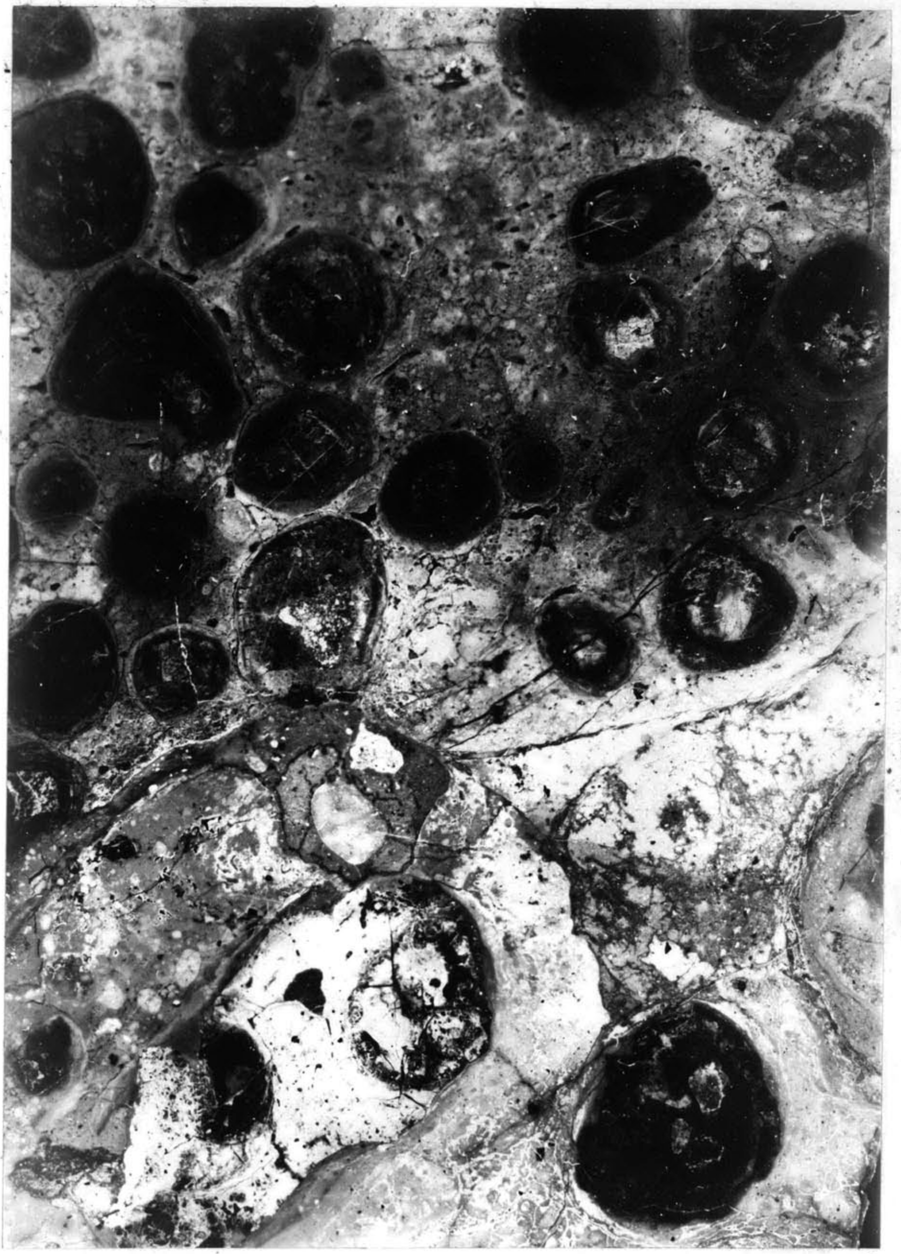


FIGURE 18. A Polished Section of Sample 69-75, Showing Black Pisolites Being Attacked by Carbonate Solutions.

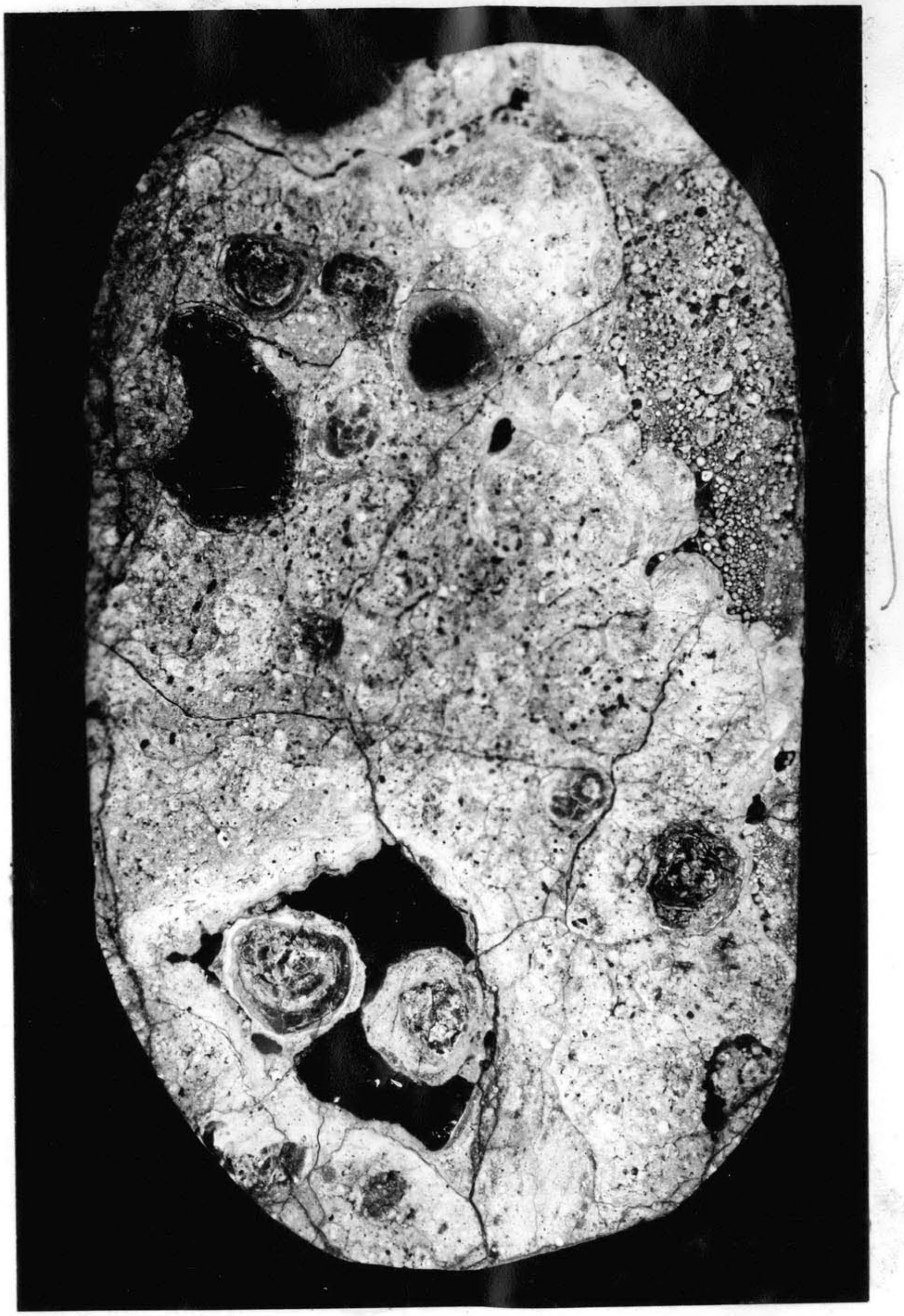
Note the bleached edges of the pisolites and the two vugs filled with banded siderite (marked S).



Magnification: 5X

FIGURE 19. A Polished Section Showing the Contact Between Sample 63-65 and 65-67.

The carbonate solutions have bleached and reworked much of the early iron-stained material. Only a few resistant pisolites remain in the bleached zone. Kaolinite crystals (as seen in thin section) are growing in the "amorphous-appearing" light-colored material. The mode of occurrence of the kaolinite clearly indicates that some silica was introduced with the carbonate solutions and that kaolinite was one of the last minerals to form in the core.



Magnification: 7X

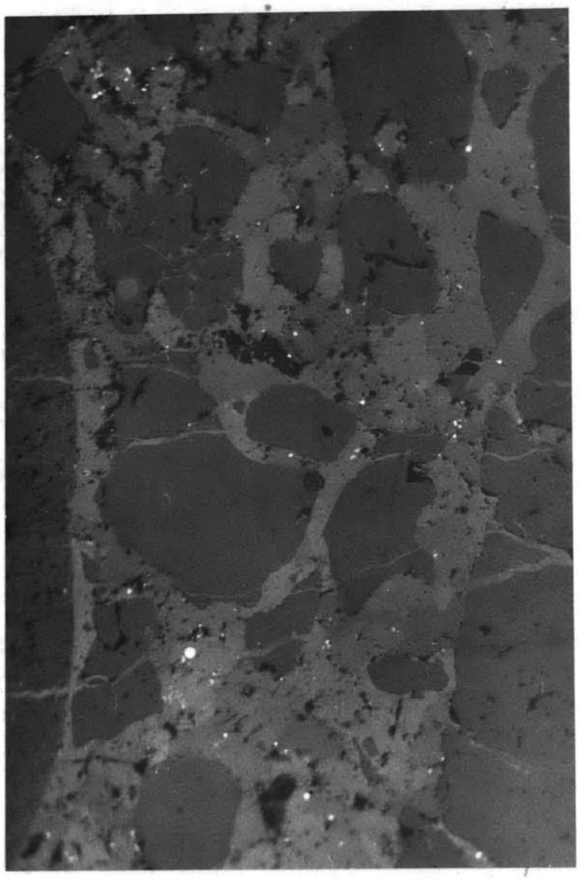
FIGURE 20. A Polished Section of Sample 67-69 Showing The Appearance of the Core after It Has Been Attacked by the Bleaching Carbonate Solutions.

The large black zones are holes filled with siderite. A few iron-stained pisolites remain. Note the light-colored zone around the hole containing the two pisolites. This zone contains late gibbsite that accompanied the carbonate solutions. The zone indicated by the bracket consists entirely of siderite surrounding small oolites of gibbsite that have separated from the siderite. This zone is also surrounded by a light-colored area of reworked gibbsite.

Magnification: 5X

FIGURE 21. Altered Pisolites as Seen in a Polished Specimen of Sample 61-63.

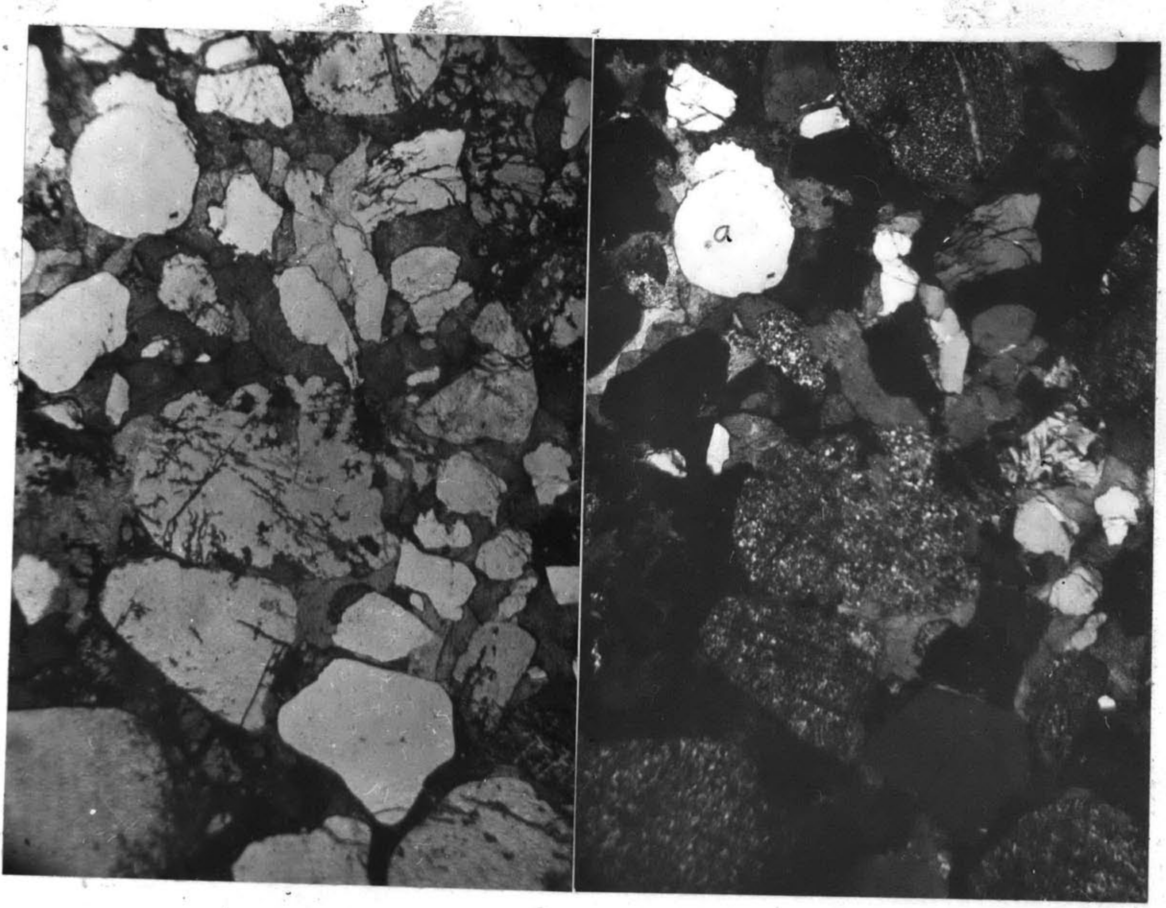
The black material marked S is siderite. The shades of grey indicate the intensity of the ferric iron stain driven in front of the altering solutions. Notice the compound pisolites. (Check table II for composition.)



Magnification: 48x

FIGURE 22. A Polished Section of Sample 58-59, Taken Parallel to the Axis of the Core, Showing Fissility as Indicated by the Light Grey Cracks Filled with Siderite Cross-cutting Quartz Grains (smooth grey particles) and Pisolites (pitted particles).

The white spots are small grains of pyrite that are seen only in this portion of the core.



Plain Light X-nicols

Magnification: 24X

FIGURE 23. A Thin Section Showing Pisolites and Quartz Grains.

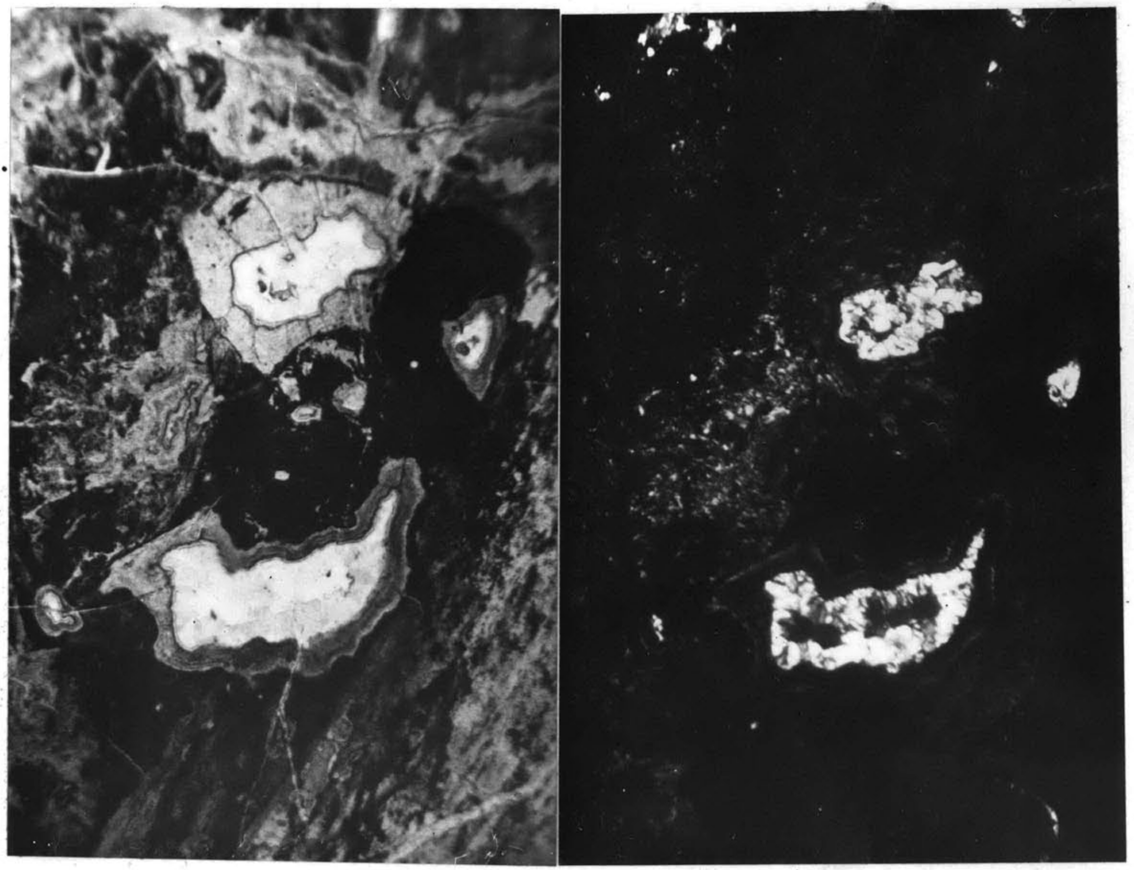
The smooth grey grains are quartz; the pitted (in plain light) and speckeled grains (x-nicols) are crystalline gibbsite. The remainder of the material is siderite and kaolinite. The kaolinite is in the pisolites but is fine grained and cannot be determined optically. Note the secondary growth of the well-rounded quartz grain (a); and the quartz grain going into the solution (b).

Plain Light

Magnification: 7X

FIGURE 24. Thin Section Showing Siderite-filled Vugs.

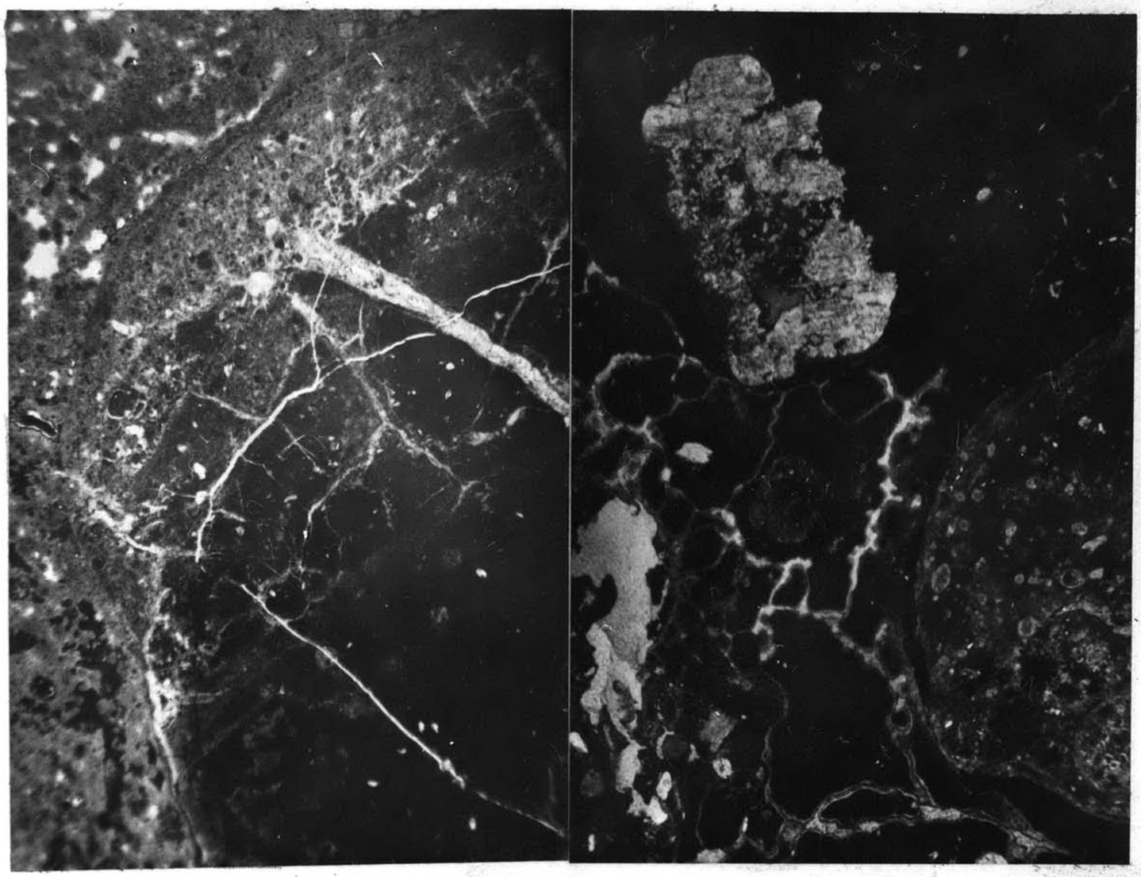
Carbonate-bearing solutions have deposited siderite in the vugs (notice the colliform banding) and have attacked the pisolites. Only relicts of some pisolites remain. Notice the shrinkage cracks that must have developed during the early history of the pisolites.


Plain Light X-nicols

Magnification: 12X

FIGURE 25. Crystalline Gibbsite Growing from "Amorphous-Appearing" Gibbsite Coating a Vug.

This gibbsite is material that accompanied the carbonate solutions and was deposited in vugs where it had time to develop well-formed crystals. This gibbsite has a different appearance from that found as relict pseudomorphs protected by the pisolites. (See the following figure.)



A. Plain Light

Magnification: 12X

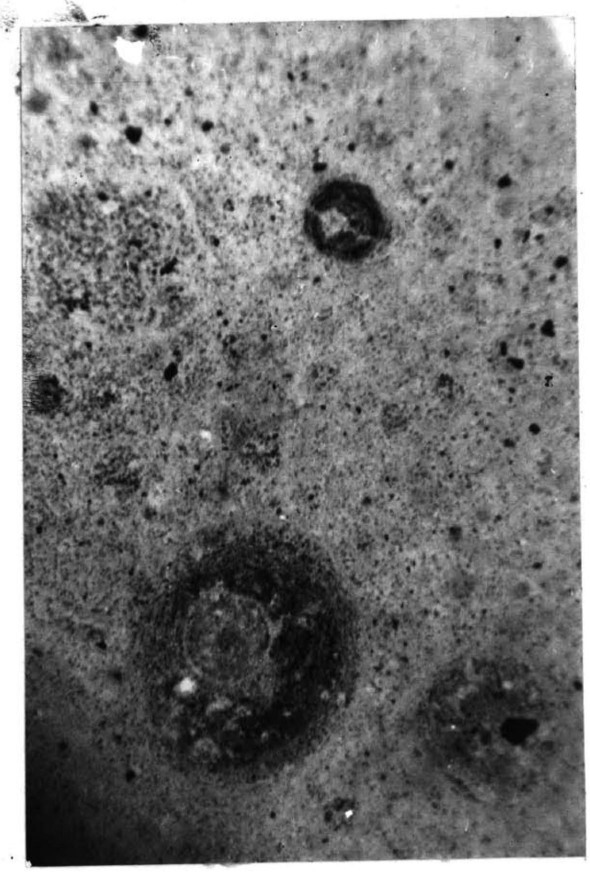
B. X-nicols

Magnification: 24X

FIGURE 26. Thin Sections Showing "Migrating" and "Insolated" Gibbsite.

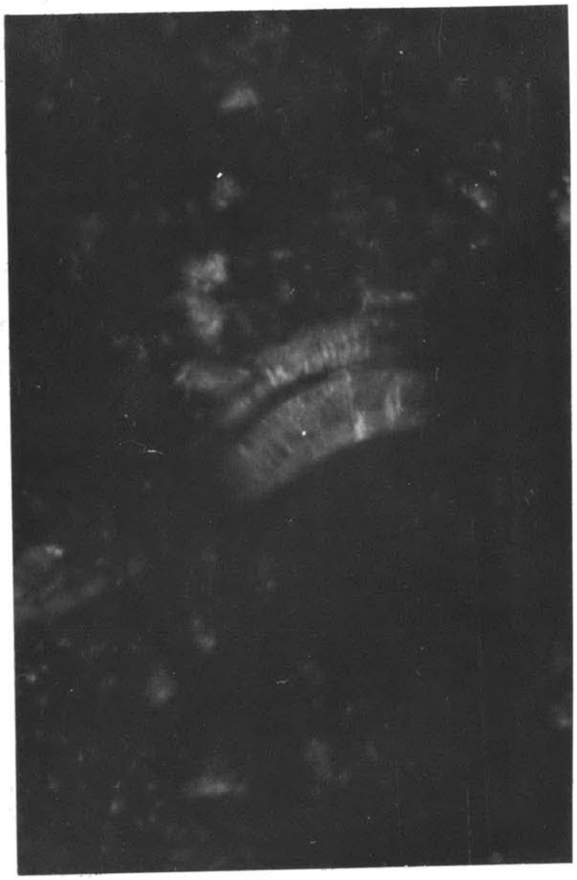
A: The mode of access of the later gibbsitic material is through veinlets that penetrate the pisolites. This photomicrograph shows an enlarged altered boundary of a heavily iron-stained pisolite. Coarse-grained gibbsite has developed from the "amorphous-appearing" gibbsite in the veinlet.

B: This central portion of a large pisolite shows fine-grained gibbsite pseudomorphous after feldspar. The small irregular veinlets and vugs contain siderite. Note the compound nature of the pisolite within the larger pisolite. The large pisolite "insolated" the gibbsite from later altering solutions.



Magnification: 12X

FIGURE 27. Relict Outlines of Pisolites Resulting from the Removal of the Ferric Iron from the Black Pisolites.



X-nicols

Magnification: 80X

FIGURE 28: Photomicrograph of a Kaolinite Crystal.

A kaolinite crystal growing from the semi-opaque matrix material of sample 85-87. The streaks normal to the axis of the crystal indicate basal cleavage. Kaolinite crystals can be recognized by this characteristic curved shape and their very low birefringence.

Kaolinite was found to develop in recognizable crystals only from the "amorphous-appearing" material accompanying the siderite-bearing solutions. Pisolites altered by these late solutions (in samples 83-85 and 85-87) contain large amounts of kaolinite whereas the early, iron-stained pisolites contain almost no kaolinite. These are the reasons why kaolinite is considered to be one of the last minerals to develop during the formation of this bauxite core.

VIII. SPECTROGRAPHIC EXAMINATION

To round out the investigation, a qualitative spectrochemical program was carried out.

The different portions of the core were prepared and examined in a Wadsworth-type grating spectrograph having a dispersion of 2.5 Å per mm. Using the method described by Ahrens(3), each sample of the core was dissolved in hydrofluoric acid and evaporated to dryness five times. The resulting powder, after grinding, was placed in spectrographically pure carbon electrodes and arced (using 220 volts, DC) according to the following schedule:

1. Arc for 30 seconds at 3 amps; move film down 3 mm.
2. Arc for 60 seconds at 3 amps; move film down 3 mm.
3. Arc for 60 seconds at 6 amps; move film down 3 mm.
4. Arc for 60 seconds at 6 amps.

Usually, the sample was completely volatilized in less than three minutes.

Using the above technique, selective volatilization was reduced to a minimum, although not completely eliminated. The background density due to cyanogen emission, in the first two steps, is practically zero; the cyanogen bands appear in step three and are strong during the last period of arcing. In this manner, many lines located in the cyanogen-band region could easily be determined.

The results of the examination are listed in Table VI.

Although many of the minor elements noted in the core are of interest, only those that occur in fairly large amounts will be discussed in detail (See following sections.).

TABLE VII

Results of the Spectrographic Examination of the Drill Core

Elements Present	Sample Interval 58-59	59-61	61-63	63-65	65-67	67-69	69-75	75-77	77-83	83-85	85-87	87	Fresh Syenite
Ag	2	-	-	-	-1	2	2	1	-	?	-	1	-
Ca	2	4	2	3	4	4	5	5	4	3	4	4	vs
Cb	2	3	3	5	3	4	3	5	5	4	3	2	2
Ce	?	-	-	-	-	-	-	-	-	-	-	1	1
Co	5	vs	vs	vs	vs	vs	vs	vs	vs	vs	vs	5	5
Cu	4	3	3	4	4	vs	5	4	5	4	vs	4	5
Ga	2	5	5	5	5	5	5	5	5	5	5	5	1
Gd	?	2	1	1	-1	?	?	-	?	?	-1	-	?
K	-	-	-	-	-	-	-	-	-	-	-	5	vs
La	-	1	1	1	?	?	?	1	1	1	1	-	-
Mg	1	-	-	-	-	3	5	3	-	-	-	1	5
Mn	vs	vs	vs	vs	vs	vs	vs	vs	vs	vs	vs	vs	vs
Mo	-	1	1	1	1	1	1	1	1	1	1	-	-
Na	-	-	-	-	-	-	-	-	-	-	-	5	vs
Nd	?	-	-	-	-	1	1	1	-	-	-	-	-
Ni	2	3	2	3	3	4	5	4	4	3	3	-	-
Pb	-	-	-	-	-	-	-	-	1	1	1	vs	?
Pr	1	1	1	1	1	1	1	1	1	1	1	-	?
Rb	-	1	1	1	1	-1	1	1	2	2	2	?	-
Re	1	-	-	-	-	1	-1	1	-	-	-	1	1
Sc	1	1	1	2	2	2	3	3	3	3	3	1	?
Sr	1	3	vs	vs	vs	vs	vs	vs	vs	vs	vs	vs	vs
U	1	1	1	1	1	1	2	2	3	2	2	-	?
V	1	3	4	4	3	2	3	4	3	2	2	-	-
Yb	-	2	2	2	-1	1	1	2	2	1	1	-	-
Yt	-	-	1	-1	1	1	1	1	1	-1	-	-	vs
Zn	-	-	-	-	-	-	-	-	-	-	-	5	vs
Zr	vs	vs	vs	vs	vs	vs	vs	vs	vs	vs	vs	vs	vs

1 = very weak
5 = strong
vs = very strong

IX. CHEMICAL PROBLEMS RELATED TO THE MINERALS IN THE CORE

The Mode of Occurrence of Titanium in the Core

A glance at Table I indicates that relatively large amounts of titanium are distributed more or less evenly throughout the core. This investigation indicates that, in this core, titanium occurs in at least four different forms:

1. In the mineral titanite,
2. In the mineral ilmenite,
3. In polymorphous forms of TiO_2, principally brookite, and
4. In substitutional solid solution in the aluminum minerals.

Titanite was observed in the fresh syenite and was collected from several horizons in the drill core. The examination of thin sections and the products from concentrating experiments reveal that the titanite is dissolved readily where it is not protected by a pisolitic coating. It occurs in the upper portions of the core only as inclusions in pisolites. The titanite concentrated from the core was highly corroded.

A black mineral is found throughout the core. In places the grains are quite large but the usual appearance resembles "pepper" sprinkled through a given specimen. The x-ray diagram for this mineral indicates ilmenite. It alters to a yellow, earthly-appearing substance commonly occurring as pseudomorphs after ilmenite. (See Figure 29.) Several concentrates of the yellow mineral were made and analyzed by x-ray methods.

One concentrate was prepared by rolling altered ilmenite grains between two thin-section glasses. Ilmenite rolls off the glass and the yellow material remains if the slide is first rubbed with a finger to put a very slight film of oil on it. This concentrate yielded a x-ray pattern identical with brookite.

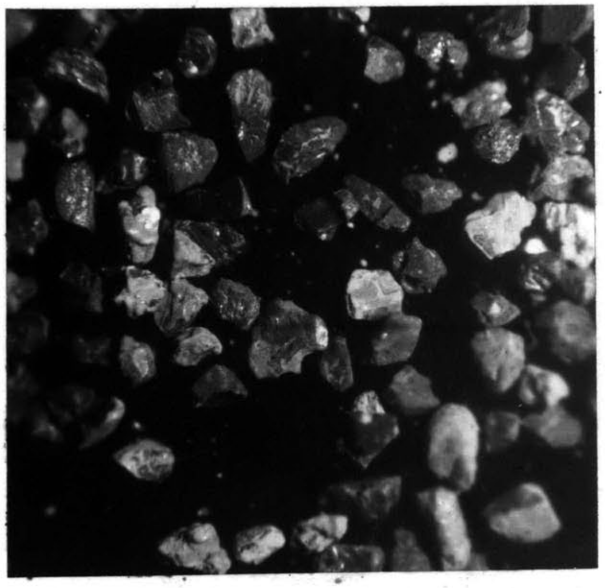
Another concentrate of yellow grains which appear to be pseudomorphs after some titanium mineral yielded a pattern indicating the presence of brookite, ilmenite and the probable presence of a small amount of anatase.

The x-ray diagram pattern of the third concentrate indicated the presence of brookite and ilmenite. A small amount of titanite was present as an impurity.

A spectrographic analysis of a carefully cleaned sample of the yellow material revealed the presence of the following elements:

Element	Estimated Percentage
Ti	Large
Fe	0.5-1.0
Zr	small (0.3)
Al	1.0-1.5
Ca	1.0-1.5
Si	Trace

The iron and the zirconium undoubtedly substitute for titanium in solid solution; the aluminum and particularly the calcium indicate that a small amount of titanite was included as an impurity in the sample.



Magnification: 10X

FIGURE 29. Ilmenite Grains Altering to Brookite.

All of the ilmenite grains have been corroded. Some of the ilmenite grains have a yellow coating; in others the alteration starts in cracks and irregularities in the crystals and alter most of the grain leaving small pieces of ilmenite surrounded by brookite.

This yellow material is evidently what many authors describe as xanthitane. At this point in the discussion some of the names applied to this yellow mineral, and their relation to other forms of TiO_2, are of interest. According to Dana(21):

1. Leucoxene, xanthotitane, xanthitane, and hydrotitanite are all identical with anatase.

2. Anatase, TiO_2, is polymorphous with brookite and rutile.

3. "Leucoxene" is a term loosely applied to dull, fine grained, yellowish to brown alteration products high in titanium. It is found as an alteration product of titanite, ilmentite, perovskite, titanium magnetite, or other titanium minerals. The material consists in most instances of rutile; also, less commonly, of anatase, or sphene (titanite).

The leucoxene of Coil(19), the xanthitane of Coghill(17), and others, is, then, one of the polymorphous forms of TiO_2. In this case, it occurs as brookite.

Two hydrates of titanium oxide, $TiO_2 \cdot H_2O$ and $TiO_2 \cdot 2H_2O$, have been described(38), but very little is known about their solubility. The unhydrated oxide does not dissolve appreciably in other acids or bases; the hydrated forms are somewhat soluble in both.

The alteration of ilmenite or titanite to brookite must obviously be a reconstructive transformation*. Because the transformation

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*A reconstructive transformation is one in which a crystal structure is destroyed and some or all of the resulting atoms recombine to form a different structure. It contrasts with displacive transformations which involve only a slight displacement of parts of the structure. If a certain critical temperature is passed, displacive transformations of the high-low type instantaneously occur (example: low-quartz to high-quartz).

took place in an aqueous medium, the individual atoms or atom groups involved in the transformation must have been hydrated at one time or another. Large, recrystallized particles (they are recrystallized because they yield a x-ray diagram) have only adsorbed water; smaller particles or atom groups (in the colloidal range of sizes) may behave as gels, whereas still smaller units form true hydroxides:

$TiO(OH)_2 \rightarrow TiO^{++} + 2OH^-$ (See Latimer(38))

If enough solution is present, the process of hydration can go to completion, that is, it could convert all of the unhydrated material into titanate ions; if only a limited amount of solution is present, it could act as a transporting medium through which the ions involved in the reconstructive transformation could travel. These ions could then order themselves and develop into one of the polymorphs of TiO_2.

If, then, titanium can travel in solution as a gel or as titanate ions, it is not necessary to resort to explanations such as compaction(6) to account for concentrations of titanium in clay and bauxite deposits.

The only stable oxidation state of titanium(38) is + 4 and this is the only state that is stable in solutions. Where it substitutes for aluminum in the aluminum minerals an extra cation must be adsorbed in order to maintain the electrical neutrality of the structure (see discussion under gibbsite.)

Zirconium

Although Bramlette(11) states that no zircons occur in the bauxites from the Bauxite, Arkansas area, zircons were reported by Mead(41) and were found throughout this drill core.

It is interesting to note that the only places in the core where zirconium is found in the form of zircon crystals is in the pisolites. Well formed zircon crystals are found in red, unleached pisolites containing gibbsitized feldspar remnants. In the pisolites that have been leached by later solutions the remaining zircons show corroded irregular outlines.

The chemistry of zirconium is quite similar to that of titanium. The only oxidation state of zirconium stable in water solutions is the +4. The dioxide is somewhat more basic than titanium dioxide and, when hydrated, dissolves fairly readily to form the zirconyl ion, ZrO^{++}

$$ZrO(OH)_2 \longrightarrow ZrO^{++}\ 2OH^-$$

The solubility of the oxide in alkaline solution is slight and the zirconates are much less stable than the titanates (see Latimer(38)).

Zirconium, then, is removed in solution more easily than titanium and does not form secondary zirconium minerals. The large percentage of the zirconium determined in the spectrographic examination must be adsorbed as zirconate ions on the aluminum hydroxide minerals.

Because the ionic potentials* of titanium (2.43^{+4}), zirconium (2.24^{+4}) and aluminum (2.45^{+3}) ore almost equal, the first two substitute for Al in the various aluminum minerals.

Zr was also found in a concentrate of yellow brookite, indicating that Zr^{+4} also substitutes for Ti^{+4} in some of the titanium minerals.

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* Ionic potential * $\frac{Z}{r}$ where Z = valence of the iron and r = the ionic radius.

Uranium

The spectrographic determination of uranium was not satisfactory. None of the lines measured was beyond question as to its exact wave length. The most sensitive uranium line (4241.67) was obscured by a heavy zirconium line (4241.687). Because doubt existed as to the presence of uranium in the core, two samples were run in a beta-counter in the geochemical laboratory at the Massachusetts Institute of Technology.

When compared with a standard containing 0.0004 grams of U_3O_8, sample 65-67 of the core showed an equivalent amount of 0.0002 grams of U_3O_8 or 13.1×10^{-12} gms/gm of radium equivalents. These results indicate an amount of uranium present in the sample approaching the threshold sensitivity of the spectrograph for this element.

A few remarks taken from Latimer concerning the chemistry of uranium not seen in geological literature on this subject have geochemical significance.

The oxides UO_2 and UO_3, as well as the intermediate oxide U_3O_8 and probably $UO_2 \cdot 2UO_3$ of $U(UO_4)_2$, are stable. Complex ions of the +3 and +4 states exist in solution. Hydrates of the trioxide, $UO_3 \cdot H_2O$ and $UO_3 \cdot 2H_2O$, are quite soluble in acids, forming the uranyl ion, UO_2^{++}(38). This ion is remarkably stable, and has the properties of a large, simple, doubly charged metallic ion. It forms compounds that are slightly soluble, such as $Na_4UO_2(CO_3)_3$, $UO_2(IO_3)_2$, etc.

The addition of alkalies to uranyl solutions precipitates alkali diuranates, for example, $K_2U_2O_7$. These compounds are only slightly soluble.

It is here suggested that the principle reason for the wide distribution of uranium throughout the sedimentary crust of the earth is due to its tendency to form large UO_2^{++} ions. The resulting large ionic radius is comparable with the radii of potassium, rubidium, cesium, and other large ions of low ionic potential. They concentrate only in the evaporates* if they are not first adsorbed by base exchange on the clays and other layer lattice minerals.

If this reasoning is correct, most of the uranium in shales, in slates, and in other sedimentary rocks should be in the form of adsorbed ions and not as discrete minerals. Whether or not this deduction is true is not known. Some support for this suggestion, however, may be implied from the work of Rothe(52). Tests of source rocks demonstrated that kaolin deposits showed very slight to no radioactivity. He reported, however, that clays found in a quarry of rhyolite had an exceptional activity. He also noticed a concentration of activity associated with wad deposits.

It is quite interesting to note that kaolinite, which has almost no base exchange capacity, also showed negligible radioactivity. Other clays, however, such as the montmorillonites which develop from volcanic ash and flows have a large base exchange capacity. While Rothe did not specifically state the type of clay associated with the Permian rhyolite that was so highly radioactive, it is almost certain that it was one of the montmorillonite clays. This leads to

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*Evaporates are saline deposits such as salts found in desert lake beds, etc.

the obvious conclusion: If the source rocks containing uranium are weathered to clays with a high base exchange capacity, these clays should show a high radioactivity.

A world wide association of carbonaceous material with vanadium and uranium materials has been observed. This close association must be due to some unique feature of the chemistry of carbon. The principal characteristic of the chemistry of carbon is its four tetrahedral electron pair bonds and the remarkable stability of these bonds with hydrogen, oxygen, nitrogen, sulfur, the halogens, and especially with other carbon atoms. All forms of so-called amorphous carbon are graphitic in character, from lamp-black and coke to charcoal. They are composed of portions of the graphite structure without, however, the regular 3-dimensional periodicity characteristic of crystalline graphite. On account of its structure, with its extensive internal surfaces and unsatisfied valencies, charcoal, and similar forms of carbon, possess the property of adsorbing ions to a remarkable extent and therefore also of catalysing reagents. The layer structure of graphitic material behaves in much the same manner as do certain of the layer-lattice clay minerals. Oxygen atoms may attach themselves to the graphite sheets and cause them to swell, forming the so-called graphitic oxides. Water may then be adsorbed until two layers of water molecules are between successive layers of graphite.

It is important to note that the unique UO_2^{++} ion consists of two oxygen atoms located at opposite sides of the uranium atom. It is quite possible that this UO_2^{++} ion is adsorbed between the graphite layers of carbonaceous material, forming a strong structure due to the stability of the UO_2^{++} ion holding the two layers together. In this manner uranium may be concentrated to a remarkable degree in carbonaceous materials.

A possible method of concentration of uranium in sedimentary deposits may be as follows:

Uranium ions are released, on weathering, from the granitic, rhyolitic, etc., rocks in which they occur in relatively large amount. These ions are then adsorbed, by base exchange phenomena, on layer lattice minerals such as certain clays. This may be considered the first step in the process of concentration of the uranium.

Either due to an increase in the thermal environment of the clays, aging of the material, or the introduction of chemically more active ions into the system, the uranium is displaced and again put into solution. Carbonaceous material, in the path of the displaced ions, would act as a filter and again concentrate, and this time fix, the uranium ions.

For the concentration of uranium according to the above suggestions it is probably important that an oxidizing environment prevail. Alkaline solutions cause the graphite layers to expand to such an extent that they may be converted into a colloidal suspension, leading to a final breakdown of the grahite structure. Colloids containing uranium would then be adsorbed again on clays and similar minerals*.

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*Could a process such as this account for the high radioactivity of certain carbonaceous shales or have something to do with the formation of oil by the polymerization of the highly active carbon into hydrocarbons by radioactive processes?

As most ceramists know, some carbonaceous material is associated with most clays. Nutting(44) has pointed out that part of this carbonaceous matter cannot be abstracted with the usual organic solvents and raised the question of the strong fixation of the carbon in the clays. One is tempted to propose a base exchange process to explain this fixation. It would be very interesting to determine whether or not there is any correlation between radioactivity and the amount of strongly fixed carbon in certain clays.

The above digression does not, however, account for the uranium in the bauxite core. The clay mineral in the core is kaolinite - a clay with very little base exchange capacity. The reducing conditions in the core caused by the carbonaceous material should disperse or leach the uranium from the core. When tested in a β-counter the carbonaceous material showed no radioactivity.

It is interesting to note that titanium, zirconium, and uranium form similar ions:

$$TiO(OH)_2 \longrightarrow TiO^{++} + 2OH$$

$$ZrO(OH)_2 \longrightarrow ZrO^{++} + 2OH$$

$$UO_2(OH)_2 \longrightarrow UO_2^{++} + 2OH$$

The writer believes that the uranium was introduced into the deposit in the form of one of the above ions and concentrated, along with the titanates and zirconates as adsorbed ions on the aluminum minerals, to give rise to the relatively high radioactivity found in the core. The radioactivity of some of the samples from the drill core is listed in Table VIII.

The β-radioactivity of 233 oil shales tested in the MIT Geochemical Laboratory averaged 9×10^{-12} gms/gm Ra equivalents.

TABLE VIII

The Radioactivity of Some of the Minerals in the Drill Core

	10^{-12} gms/gm Ra equivalents*
Samples from the drill core	
Ilmenite, and Brookite	8.1
Sample 85-87 (92% Kaolinite)	9.6
Sample 65-67 (74% Gibbsite)	13.1
Sample 58-59 (54% Siderite)	8.6

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*As determined in a β-counter using a synthetic, analyzed carnotite standard.

This figure may be used as a basis of comparison for the radioactivity of the minerals in the drill core. Almost all of the uranium is located in the sample containing a large amount of gibbsite, whereas the kaolinite specimen showed very little radioactivity. These results tend to confirm the previous discussion.

Although Tomkeieff(58) pointed out that a considerable amount of uranium is found in the titanates, Table VIII indicates that, at least in this syenite, the titanates contain very little uranium.

Using the reasoning presented above, the reducing nature of the siderite should tend to disperse instead of concentrate uranium. The small amounts of radioactivity measured from the siderite specimen seems to confirm this conclusion.

In an attempt to determine the source of the uranium found in the core, an unaltered sample of syenite was obtained from the same locality as the drill core. It was crushed, sized, and concentrates of its constituent minerals were made. The radioactivity of the syenite and some of its minerals is listed in Table IX.

β-counters register the total β emission from a sample. In order to determine the amount of the radioactivity of the feldspar fraction that was due to the isotope K^{40}, two grams of the concentrate were fuzed in vacuum and the radon, in equilibrium with the uranium series, was released. The radon was swept into an ionization chamber where an α count was made. The α activity was exceptionally high - too high to be counted in the type of apparatus used.

Dr. Patrick Hurley, who made the above determination, stated that the activity for this type of material was very high - higher than any similar material tested by him.

TABLE IX

The Radioactivity of the Syenite and Some of Its Minerals

	10^{-12} gms/gm Ra Equivalents*
Unaltered syenite	42.7
Feldspars and nepheline	33.8
Biotite	28.2
Ferromagnesian minerals	18.5
Titanite	9.1

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*As determined in a β-counter using a synthetic, analyzed carnotite standard.

This check indicates that the β-measurements in Table IX are undoubtedly due to elements in the uranium-thorium series and not due to the isotope K^{40}. The exceptional radioactivity possessed by the material tested merits further investigation.

Gallium

Because of the close similarity of the atomic radii of gallium (0.62A) and aluminum (0.57A), gallium is invariably found associated with aluminum rich sediments. Ahrens(2) found that clays poor in alumina, such as nontronite, did not contain any gallium. From this evidence it seems quite certain that gallium substitutes for aluminum in the gibbsite and kaolinite found in this core.

Calcium, Manganese, Cobalt, and Nickel

The relatively large amount of calcium is accounted for by assigning it to the mineral titanite which occurs in quantity in the core.

The large amounts of manganese can only be satisfactorily accounted for by assuming that it replaces ferric iron in the red pisolites or the iron gels in the zones rich in this material.

The ionic potentials of the triad, Fe^{+2} (1.56), Co^{+2}(1.56), Ni^{+2} (1.60) show very little variation. Because of this and their closely related chemical properties, they are commonly found together. In this deposit some of the divalent nickel and trivalent cobalt are believed to substitute for ferrous iron and should be found in the siderite. The spectrographic examination on hand picked siderite confirmed this conclusion.

Strontium and Copper

Although a small amount of strontium may be accounted for by assuming that it occurs in the titanite(53), this explanation does not account for the relatively large amounts found throughout the core.

Ions that can be adsorbed strongly are required to stabilize the hydroxides when they form gels(61,62). According to the Schulze-Hardy valence generalization, the ions with a larger charge are adsorbed much more tenaceously than ions with a lower charge. For this reason strontium and calcium are the stabilizing ions for the gels found in the core, whereas sodium and potassium are almost completely removed in solution.

No satisfactory explanation is offered to account for the occurrence of the copper throughout the core.

Others* have noticed the anomalous behavior of copper but have offered only tentative explanations for it.

Summary of the Spectrographic Examination

The investigation of the minor constituents in the drill core may furnish valuable clues concerning the genetic history of this bauxite deposit. The minor elements accompanying the different solutions and gels that altered the aluminum minerals should indicate their chemical character. As certain elements and ions are stable only in a certain environment, therefore the changes in the environment can be traced by the variations in the minor constituents that

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*Dr. L. H. Ahrens, in a personal discussion, mentioned that he has noticed the anomalous behavior of copper and pointed out that Goldschmidt, in one of his early papers (not listed in the bibliography), has discussed this problem.

are also stable under these same conditions. The source of the materials that are now represented by the bauxite may also be traced by examining the minor constituents of various rocks and comparing them to those now found in the bauxite. Work of this type, however, must be closely correlated with field work in order to achieve full significance.

The isolation and identification of brookite as the alteration product of ilmenite is a step toward the understanding of the poorly known role that titanium plays in laterites. Much more quantitative work must be done to determine the exact amounts of titanium occurring as titanate ions in the aluminum minerals and as titanium ions in titanite and ilmenite.

The main contribution of the spectrographic work on the core was to indicate the many geochemical problems presented by a deposit of this type. Study of these problems will undoubtedly greatly increase our knowledge concerning the mechanism of formation of laterites and other weathering products.

X. SUMMARY

Although much chemical work has been done on laterites and bauxites very little is known about the mechanism of their formation. Although the minerals comprising these deposits are relatively well known, their genetic relations are practically unknown except in a vague qualitative manner. In order to solve these problems a large amount of quantitative mineralogical work must be done. A major contribution of this thesis is the presentation of some methods of investigation by which these problems can be attacked. Application of some of these methods has demonstrated that the minerals of a bauxite deposit can be quantitatively determined only by a combination of techniques.

The minor elements in the core were revealed by spectrographic analysis.

The electronic-type thermal apparatus, in comparison with the photographic type commonly used, proved to have a relatively higher degree of sensitivity. This added sensitivity greatly extends the usefulness of the thermal techniques; quantitative results can be obtained from a thermal apparatus only when the reactions of different minerals in the sample do not conflict. Although not applied in this work, quantitative x-ray techniques may be used to determine the minerals when these conflicts occur.

The x-ray spectrometer promises to be a very useful tool to identify different minerals in some of the clay families, although some preliminary work must be done to determine how it can be used to the best advantage.

All of the minerals in the core were satisfactorily determined except the hydrated iron oxides. Neither thermal nor x-ray methods revealed these minerals quantitatively or qualitatively. Pre-heating before x-ray analysis, may possibly solve this problem.

The identification of brookite as the alteration product of ilmenite may clarify some of the confusion concerning this material. The suggestion that some of the titanium must be concentrated in the core in the form of titanates adsorbed and included with the aluminous-gel minerals leads to a line of reasoning that may also account for the concentration of zirconium and, of more interest, uranium.

The exceptionally high radioactivity displayed by the syenite appears anomalous. The high values listed in the tables should be checked and, if confirmed, may be of practical as well as scientific interest.

The writer was led to appreciate the significance of ionic potential as a very important controlling factor in the distribution of elements in the earth's crust. The geometry of the atoms and ions is just as important geochemically as their chemical properties. The ionic potential(14,15,25,26) dominates the interactions between the ions and water molecules. Ions with a low ionic potential (large ions with a small charge) tend to concentrate in the evaporates if they are not first adsorbed by the "hydrozates" (hydrated oxides). This idea and its consequences are of the utmost importance in attempting to deduce where a certain ion will be found in a given geologic environment.

By appreciating the geometry of the atoms and by using the principle of ionic potential, Goldschmidt(25,26) has worked out a classification of mineral deposits of surface origin that is not just descriptive. Perhaps from concepts such as these, the geologist will some day be able to predict where certain elements should be and then go out and find them.

Gibbsite was the only aluminum hydroxide mineral found in the core. If the ideas of Lapparent(35,36) are applied (see Introduction) this indicates that the bauxite was formed above the ground water table in a well drained environment. The absence of boehmite is significant in that it confirms the field observation(11,41) that the overlying carbonaceous material formed after, not during, the development of the bauxite.

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