DIFFERENTIAL THERMAL ANALYSIS OF NATURAL HYDROUS FERRIC OXIDES

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ABSTRACT

Differential thermal analysis and *x*-ray diffraction have been applied to nearly 100 specimens of hydrous ferric oxide aggregates.

The thermal curves of goethite and lepidocrocite are sufficiently different to permit semi-quantitative estimation of these minerals in natural mixtures. The common occurrence of lepidocrocite in most aggregates of natural hydrous ferric oxides (limonite) is surprising.

Thermal curves of artificial mixtures of these minerals are given and are used to interpret the natural mixtures. Synthetic hydrous ferric oxide of two types was prepared and the thermal curves discussed.

INTRODUCTION

Since the hydrous iron oxides are of considerable significance in geology, it is of interest to define the thermal curves for these minerals and the mineral aggregates in which they occur. Blanchard (1944) has studied the mineralogical composition of certain limonite specimens but made no thermal study. Systematic variations in the concentration of one of these minerals may be of considerable use in analyzing the nature of depositional sequence and areal extent. Such data may also be important in the study of the weathered part of hydrothermal deposits. Locke (1926) has shown that it is possible to identify certain types of mineralization by color differences and textures of "gossans" or "iron caps." A quantitative analysis of the mineral composition of such occurrences should yield information useful in scientific prospecting. Finally, the geochemistry of iron can be more fully appreciated if the substitution relationships in these common supergene minerals are determined.

This investigation was undertaken with the primary purpose of establishing the type differential thermal curves for goethite and lepidocrocite. A large number of representative specimens containing these minerals were analyzed. The effects of purity and grain-size on the thermal curves were studied by means of artificial mixtures of these hydrous iron oxide minerals with foreign constituents common to natural mixtures.

Precipitates of hydrous ferric oxide were prepared in the laboratory under various conditions and examined by thermal and *x*-ray technique.

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Mineral specimens were obtained from the mineral collection of the Department of Geology, Columbia University.

EQUIPMENT AND PROCEDURE

The experimental procedures used in this investigation included differential thermal analysis, *x*-ray diffraction, and optical examination.

The differential thermal analysis equipment and technique used is described by Kerr and Kulp (1948, 1949).

The theory of differential thermal analysis has been treated in several papers (Speil et al. 1945), (Kerr and Kulp 1948). A dual-terminal thermal couple is used, one terminal inserted in a thermally inert material, the other in the mineral to be tested. The rate of heating is maintained constant. Results are shown by plotting temperature-difference of the dual couple against temperature. Reactions involving heat change are indicated by characteristic deviations from a straight base line. The nature of the heat changes determines the direction and amplitude of the deviation. Loss of adsorbed or lattice water, decomposition, or changes in structure all may produce peaks.

All specimens were prepared for thermal analysis by grinding to 180–200 mesh to minimize variations due to particle size.

Debye powder patterns of the samples were taken with iron radiation. In general, the component of mixtures of iron oxide minerals could not be detected by *x*-ray technique unless their concentration was greater than 10%.

Artificial mixtures were prepared from ground samples of the pure components. The components were weighed with an analytical chemical balance and thoroughly mixed prior to (thermal) testing.

THE HYDROUS FERRIC OXIDES

1. *Hydrous Ferric Oxide Minerals*

Descriptions of the naturally occurring hydrous iron oxides have resulted in a sizeable list of mineral names. The members of the group have included turgite, goethite, lepidocrocite, hydrogoethite, limonite, xanthosiderite, hydrohematite, ehrenwerthite, kaliophite, hypoxanthite, melanosiderite, avasite, esmeraldaite and limnite.

Dehydration and *x*-ray studies of both natural and synthesized material have shown most of the former "minerals" to be invalid. Posnjak and Merwin (1919) have shown that no series of iron oxide hydrates exists, and their results have been substantiated by other investigators.

Only goethite ($HFeO_2$) and lepidocrocite $FeO(OH)$ have been accepted as minerals of the hydrous iron oxides in the 7th Edition of Dana's *System of Mineralogy*. Considerable information is available on the physical and chemical properties of these minerals, but a detailed thermal structural study has not been published.

2. *Chemistry of Hydrous Ferric Oxides*

Thermal curves of individual specimens labelled goethite or lepidocrocite have been published by Grim and Rowland (1942) and by Speil et. al (1945).

The hydrous iron oxide occurrences found as gossans are the result of the weathering of sulfide ore bodies. These characteristically have moderate to high iron content but negligible aluminum. Therefore, aluminum ions would not be present in any abundance during the formation of the hydrous iron oxide mineral and would not be observed as a substitution product.

The hydrous basic iron oxides, which are colloidally transported, are later precipitated as goethite or lepidocrocite. Aluminum is usually transported as colloidal clay particles (kaolinite, montmorillonite, or illite). These colloids have sufficiently different properties from the hydrous iron oxide colloids that they tend to be separated in precipitation. Moreover, free aluminum ions are not present for reaction during sedimentation and diagenesis.

The result is that the geochemical conditions generally separate iron and aluminum in weathering processes even though from a structural point of view substitution seems feasible.

Hydrous ferric oxide may be easily prepared by adding a soluble base, such as ammonium hydroxide, to a solution containing ferric ions. The precipitate formed will be of extremely small particle size. This can be attributed to the very low solubility of ferric oxide which produces a high degree of supersaturation preceding precipitation. A large quantity of water is entrained in these particles.

The *x*-ray diffraction patterns of such precipitates fail to indicate crystallinity.

However, if this "amorphous" material is aged under water for a sufficiently long time, crystallinity will appear accompanying the process of dehydration. This emphasizes the instability of form of hydrous ferric oxide gel and its general absence in nature.

Weiser and Milligan (1934, 1935) aged precipitates prepared by adding ammonium hydroxide to ferric chloride solution and examined the resulting material by *x*-ray diffraction methods. At room temperature, lines began to appear only after five months, and in order to obtain good patterns, aging for one year was found necessary. At 100° C., the transformation was visible after only one hour, and the lines were sharp after seventeen hours. The color changed from brown to red and, in every case, the final product was alpha-Fe_2O_3. This led Weiser and Milligan to conclude that the brown gel was nothing more than particles of alpha-Fe_2O_3 of a size below *x*-ray detection, containing absorbed water.

The polymorphs of the monohydrate of iron are:

1. Alpha-$Fe_2O_3 \cdot H_2O$ (goethite), gives alpha-Fe_2O_3 (hematite) on dehydration.
2. Beta-$Fe_2O_3 \cdot H_2O$ (not known in nature) also gives alpha-Fe_2O_3 on dehydration.
3. Gamma-$Fe_2O_3 \cdot H_2O$ (lepidocrocite), gives gamma-Fe_2O_3 (ferromagnetic) on dehydration.

Alpha-$Fe_2O_3 \cdot H_2O$ may be formed by the aging of the brown gel formed by the oxidation of ferrous compounds or slow hydrolysis of most ferric salts. A more hydrous form of alpha-$Fe_2O_3 \cdot H_2O$ may be formed by the oxidation of ferrous bicarbonate solution with peroxide, oxygen, or air at room temperature. This hydrous material will lose its absorbed water if heated in a stream of dry air at 100° C. for 48 hours, changing to the same composition as alpha-$Fe_2O_3 \cdot H_2O$.

The simplest method for preparing alpha-$Fe_2O_3 \cdot H_2O$ is by the slow hydrolysis of certain iron salts, such as ferric acetate, nitrate, bromide, and oxalate.

Gamma-$Fe_2O_3 \cdot H_2O$ is synthesized by the oxidation of freshly prepared hydrous Fe_3O_4, hydrous $2Fe_2O_3 \cdot 3FeO$, Fe_2S_3, and FeS, and ferrous chloride, the latter in the presence of pyridine or sodium azide in a solution with a pH of 2.0 to 6.5.

It is of interest to note that direct neutralization of ferric iron solutions results in hydrous ferric oxide which upon aging transforms to hematite rather than either to goethite or to lepidocrocite.

The color of hydrous and anhydrous oxides of iron is of interest. The red and the yellow hydrates have been found in nature side by side. It was once thought that the yellow type was the more unstable form and, upon dehydration produced the red monohydrate. Posnjak and Merwin (1919) believed both monohydrates to be stable at any possible normal surface temperature of the earth. The color differences appear to be largely determined by particle size.

EXPERIMENTAL RESULTS

Goethite

Figure 1 shows the differential thermal curves of some of the purest goethite specimens tested. The curve for pure goethite is apparently characterized by a single endothermic peak between 385 and 405° C. This endothermic reaction is due to the decomposition of the goethite lattice. All of the specimens are characterized by coarse crystallinity. The observed habits of these specimens included: fibrous, with fibers in concentric radial growth; fibrous, forming bands with the fibers arranged normal to the band; platy, with a tendency toward radial growth. The dense massive or light porous variety are not represented in this group.

The more brightly colored fibrous specimens have the lower peak temperatures. This is probably to be related to the smaller crystallite size. The average peak temperature for these high purity goethite specimens is 395° C. Since the experimental error in the determination of this temperature from one run to the next is of the order of 5° C., the range of peak temperatures for these specimens is probably 390–400° C.

Since goethite gave no reaction between 500 and 1000° C., most of the later thermal curves were not continued above 600° C.

To study the effect of particle size on the thermal curve of a single specimen, a series of samples were thermally analyzed.

The results are shown in Table 1. All six samples gave thermal curves with very similar shapes except the powdered material which started decomposing at about 300° C. instead of 340° C. (See Figure 1.)

TABLE 1. PARTICLE SIZE STUDY—CORNWALL, ENGLAND

Particle Size	Peak Temperature
Coarser than 50 mesh	405° C
50–80 mesh	405
80–100 mesh	400
100–120 mesh	400
120–200 mesh	395
Powdered	390

50–80 mesh goethite was intimately mixed with similarly ground hematite in various proportions. The hematite acted as an inert impurity, since it undergoes no decomposition or phase change in the temperature interval used. The calibration curve obtained by plotting height of reaction peak against concentration of goethite can be used to estimate the percentage of coarsely crystalline goethite in natural mixtures. Since hematite is a common constituent, the mixture was suitable. To a first approximation, other thermally inert constituents in a natural mixture would affect the goethite curve similarly.

Figure 2 shows the effect of the hematite on the goethite curve. Hematite, alone produces no distinctive thermal peaks as seen in the last curve. The peak temperature of the goethite was reduced from 405° C. to 375° C. when diluted with 90% hematite. The amplitude of the reaction decreased with the depression of the peak temperatures.

It is doubtful that this factor influenced the peak temperature of the goethite curves shown in Fig. 1, since the impurities were less than 5% of the volume of the material tested.

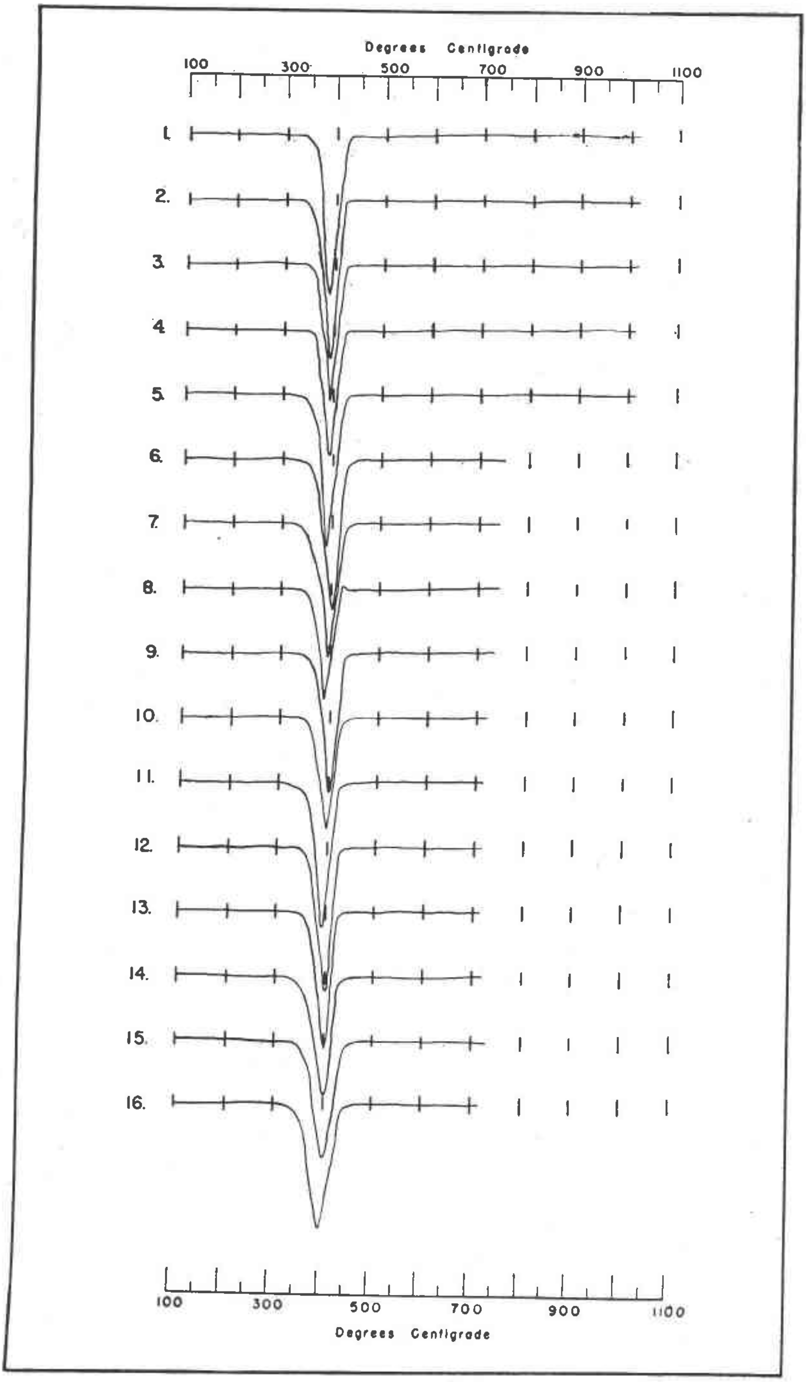

FIG. 1. For legend see top p. 29.

FIG. 1. Goethite specimens.*

Curve No.	Museum Label	Locality
1–1	442-2 Limonite and hematite	Lake Superior
1–2	32-2 Limonite	Lake Superior
1–3	185-5 Limonite (Fibrous)	Lake Superior
1–4	185-6 Limonite (Fibrous)	Lake Superior
1–5	160-1 Goethite	Superior Mine, Mich.
1–6	160-5 Goethite	Ironwood, Mich.
1–7	33-5 Goethite	Negaumee, Mich.
1–8	430-1 Goethite	Needle Ironstone, Jackson Mine, Mich.
1–9	162-1 Goethite	Cornwall, England
1–10	162-2 Goethite	Restormed Mine, Cornwall, England
1–11	169-5 Limonite	Schwartzenburg, Saxony
1–12	430-3 Goethite	Friedrichsrode, Thuringia
1–13	430-2 Goethite	Brazil
1–14	430-4 Goethite	Pikes Peak
1–15	430-5 Goethite	Pikes Peak
1–16	430-6 Goethite	Tavistock, Devonshire

* All specimens were *x*-rayed and showed only goethite lines.

Lepidocrocite

Figure 3 shows the thermal curves of specimens which were largely lepidocrocite. These curves have a number of interesting features. In general, lepidocrocite yields a thermal curve which has an endothermic reaction which begins between 250 and 300° C., culminates in a peak at 350° C. and is followed by a variable exothermic peak. There is no further reaction to 1000° C.

Pure lepidocrocite is represented by curves (Fig. 3) 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13. In these specimens it is noted that the initial break ranges from about 260° C. to 300° C. It is believed that this variation is a function of particle size. The peak temperature does not appear to be as sensitive to this factor as the temperature of the initial break. The width of the peak appears to be related to the particle (or better, crystallite) size distribution. The most uniform specimen was 3-4 (Ore Hill) which produced one of the sharpest peaks. The variations in the shape and temperature of the exothermic peak are numerous. It seems probable that if the removal of H_2O after the decomposition were sluggish, the presence of a small amount of water vapor would catalyze the transition from gamma-Fe_2O_3 to alpha-Fe_2O_3 (hematite).

The contrast of the goethite and lepidocrocite thermal curves is readily explained in terms of their structures (Bragg 1937). While they both have the same chemical composition ($Fe_2O_3 \cdot H_2O$), they differ structurally in the nature of the bonding of the hydrogen atom. In goethite the hydrogen atoms act as cations between oxygen atoms in two-fold coordination.

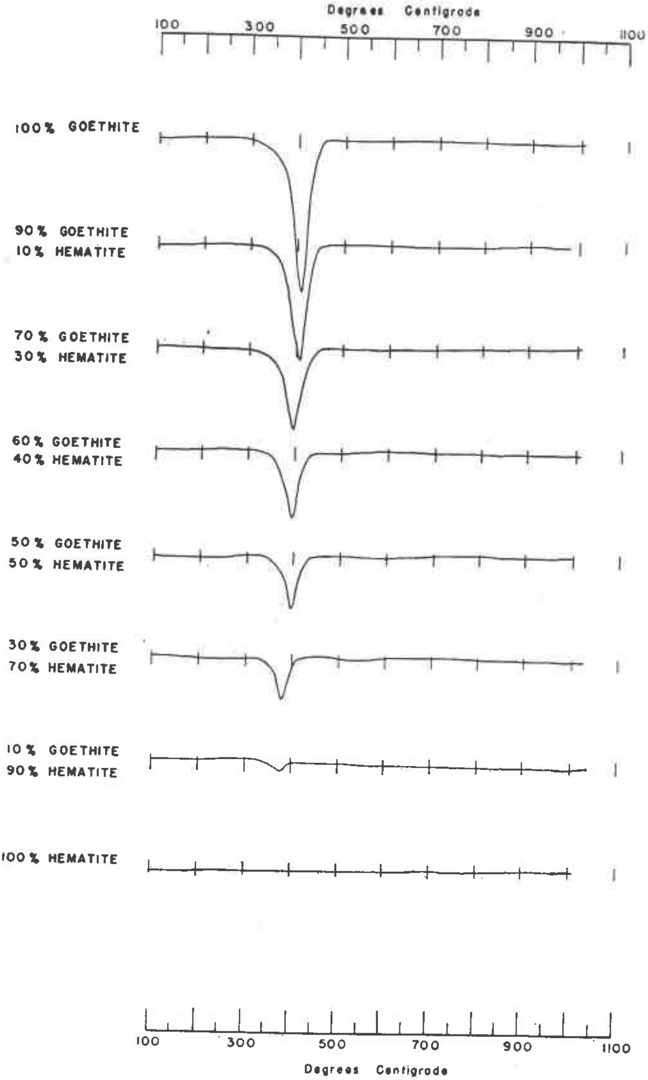

FIG. 2. Goethite-hematite artificial mixtures (50–80 mesh).

Lepidocrocite has the hydrogen atom in a discrete OH group. As might be expected, the former situation is more stable, hence the decomposition of lepidocrocite occurs at a lower temperature than goethite. While lepidocrocite decomposes to yield gamma-Fe_2O_3, goethite decomposing at a higher temperature gives alpha-Fe_2O_3 directly. The exothermic reaction in the lepidocrocite curve is due to the phase transformation of gamma-Fe_2O_3 to alpha-Fe_2O_3. This is also consistent with the observed facts that the goethite is harder and tends to be better crystallized than lepidocrocite. It is also noteworthy that the aluminum analogs, diaspore and boehmite show the same difference in decomposition temperature.

The differential thermal curve peak occurs, of course, at a temperature considerably higher than the equilibrium dehydration temperature. Gruner (1931) believes the equilibrium decomposition temperature to be between 140° C. and 200° C. for goethite. Tunell and Posnjak (1931) state that the decomposition temperature lies between 100° C. and 140°C. In either case, the rate must be very slow until about 350° C. at which temperature the reaction is detectable on the differential thermal curve.

These minerals apparently do not absorb much water since even the limonite mixture curves (Figs. 6, 7, 8) do not show the effect which such water would cause.

The grain size, purity, and physical structure are also important in determining the temperature of decomposition.

Generally speaking, a decrease in grain size tends to lower the peak temperature, but does not affect the area under the curve.

Impurities may also be expected to produce a downward shift in the temperature of the peak with an accompanying decrease in amplitude (Speil, et al. 1945).

The high purity specimens 3-2 and 3-3 show the highest peak temperatures. These were the coarsest specimens analyzed. Specimens 3-14 and 3-15 contain considerable inert impurity. 3-14 also contains some goethite, 3-1 is a mixture of goethite and lepidocrocite. In general, pure lepidocrocite shows an endothermic peak at 350° C. The shape of the low temperature side of the endothermic peak may also be used to detect the presence of a mixture. In the case of 3-1, the goethite present is a minor constituent and has very small particle size.

Known mixtures of lepidocrocite and goethite were prepared and analyzed thermally. The particle size was 100–120 mesh. Figure 4 shows the results of this analysis. It can be seen that a double peak exists in every percentage mixture, from 80% goethite and 20% lepidocrocite to 20% goethite and 80% lepidocrocite. The peak temperature of goethite is lowered from 400° C. to 384° C., while lepidocrocite was reduced from 357° C. down to 348° C.

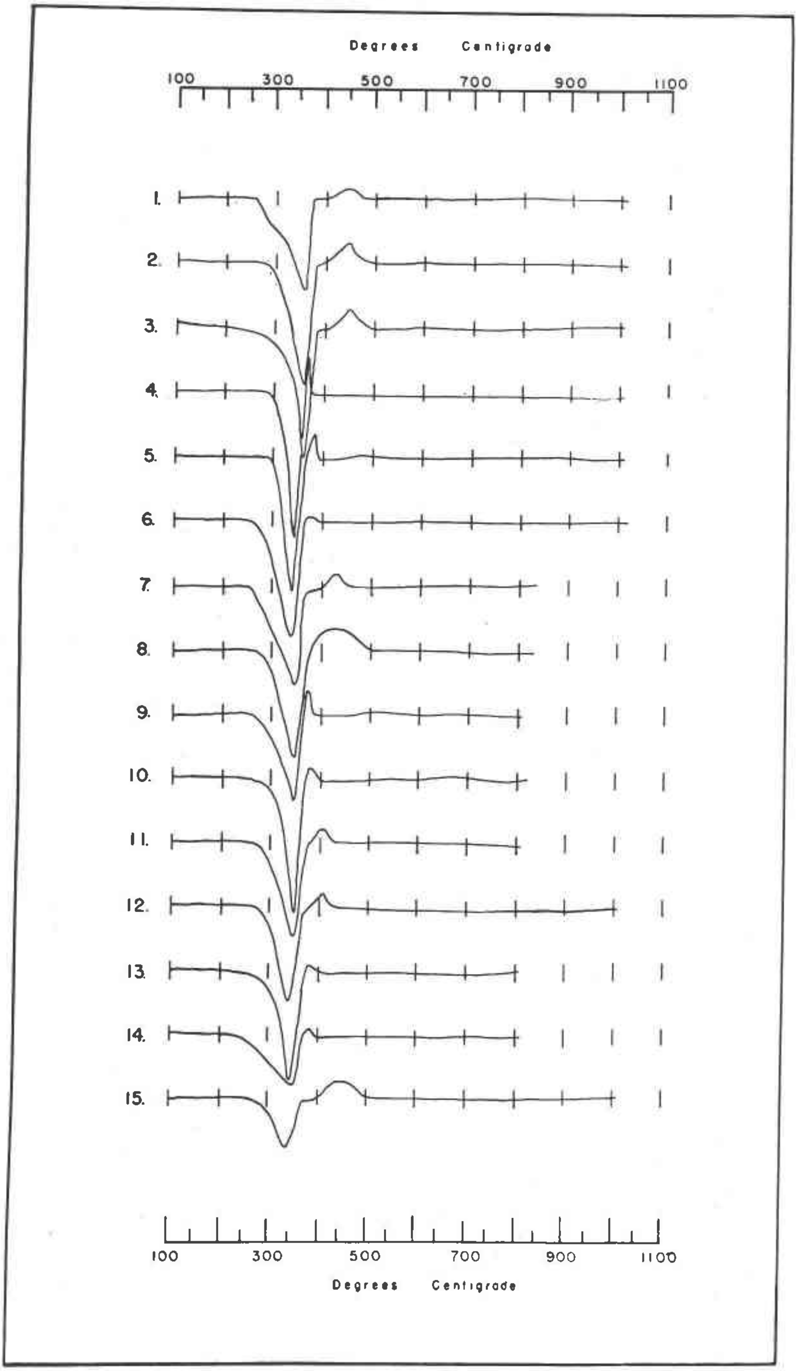

FIG. 3. For legend see top p. 33.

FIG. 3. Lepidocrocite specimens.

Curve No.	Museum Label	Locality	*X*-Ray Identification
3-1	34-2 Lepidocrocite	Easton, Pa.	Lepidocrocite, Goethite
3-2	431-3 Lepidocrocite	Easton, Pa.	Lepidocrocite
3-3	507-3 Lepidocrocite	Northampton, Pa.	—
3-4	452-1 Limonite	Ore Hill, Salisbury	Lepidocrocite
3-5	452-2 Limonite	Roxbury, Conn.	—
3-6	442-1 Limonite	Rimon Valley, Duchess County, N. Y.	—
3-7	34-4 Lepidocrocite	Richmond, Mass.	Lepidocrocite
3-8	185-3 Limonite	Gaston County, N. C.	Lepidocrocite
3-9	163-1 Limonite	Michigan	Lepidocrocite
3-10	169-1 Limonite	Camaria, Jahsio, Mexico	—
3-11	169-2 Limonite	Englenho, Velho, Brazil	Lepidocrocite
3-12	184-2 Limonite	Steiberg, Sweden	Lepidocrocite
3-13	185-1 Limonite	Schwartzenberg, Saxony	Lepidocrocite
3-14	32-1 Limonite	Sasa, Saxony	Lepidocrocite, Hematite
3-15	34-1 Xanthosiderite	Huttenholz, Thuringia	—

To show the effect of inert constituents on mixtures of lepidocrocite and goethite, artificial mixtures of lepidocrocite, goethite, and hematite, in various proportions were prepared and analyzed thermally. Figure 5 shows these results. The peak of the goethite is lowered from 400° C. to 394° C., and the lepidocrocite from 357° C. to 350° C. It is of interest that hematite alone lowered the peak of goethite more than a mixture of hematite and lepidocrocite. It is also important to note the relative amplitudes of the goethite and lepidocrocite peaks. These thermal curves (Figs. 4 and 5) may be used to estimate the concentration of goethite and lepidocrocite from thermal curves of natural mixtures. Caution must be exercised to take into account particle size effects.

Natural Aggregates

Figures 6, 7, and 8 give the thermal curves of natural aggregates of hydrous ferric oxide. In each case the museum label name has been included so that the correlation of the actual mineral composition with common hand specimen identification may be appreciated.

Figure 6 shows curves of specimens which are composed of both goethite and lepidocrocite, with or without additional inert impurities. Comparison of these curves with Figs. 4 and 5 will permit estimation of the composition. They range from dominantly goethite (6-15) to dominantly lepidocrocite (6-13). These specimens (mostly labelled "limonite") were not selected for lepidocrocite content. They show rather strikingly the importance of lepidocrocite in these natural aggregates.

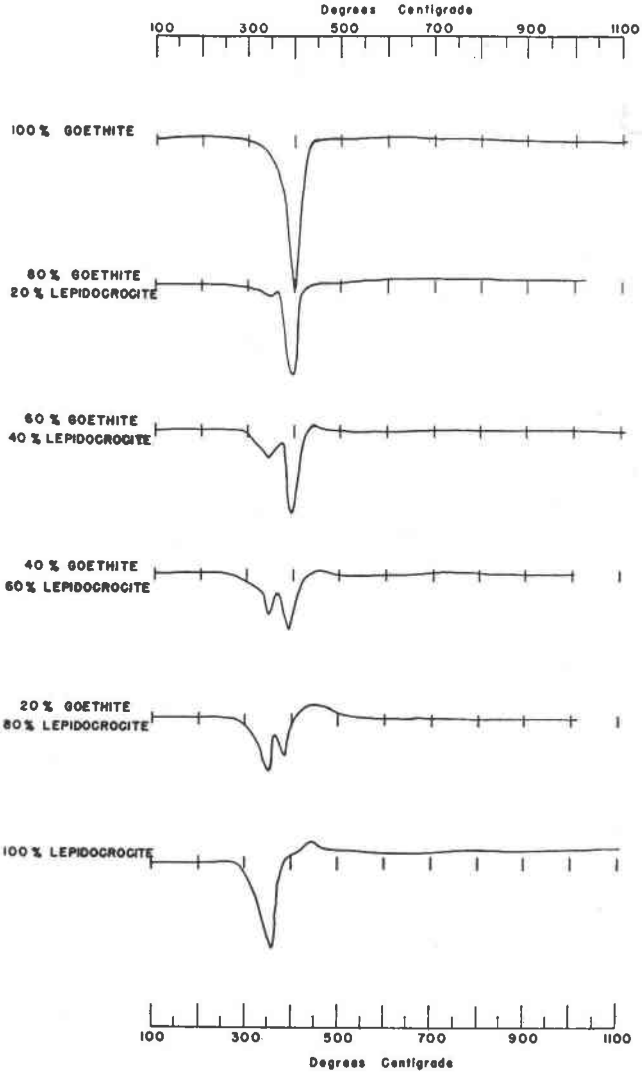

FIG. 4. Goethite, lepidocrocite, artificial mixtures (50–80 mesh).

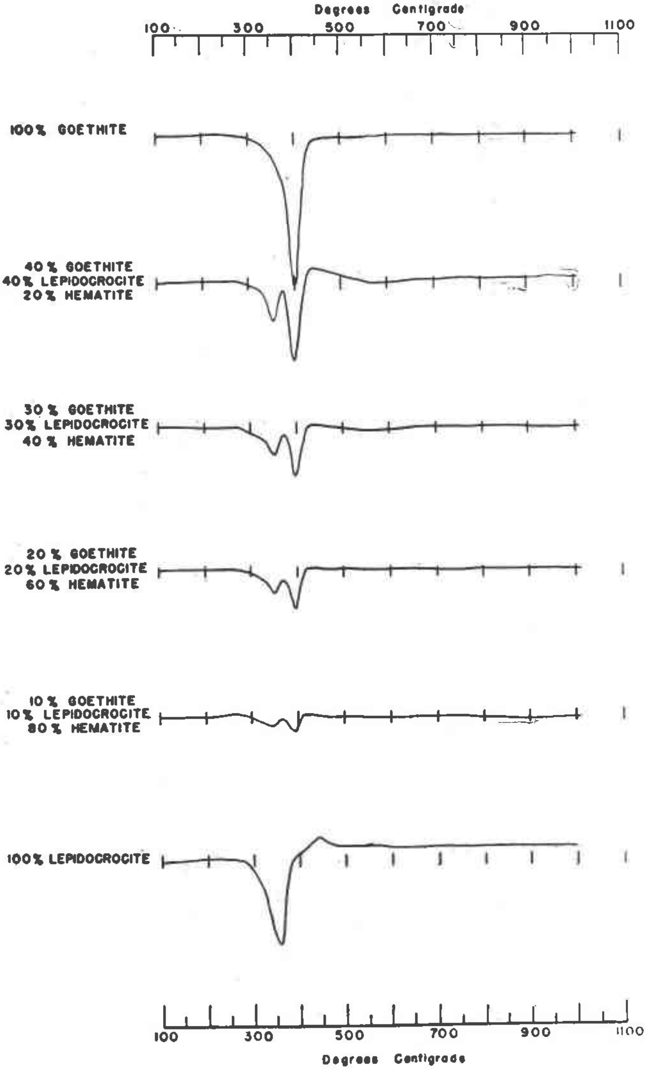

FIG. 5. Goethite, lepidocrocite, hematite artificial mixtures (50–80 mesh).

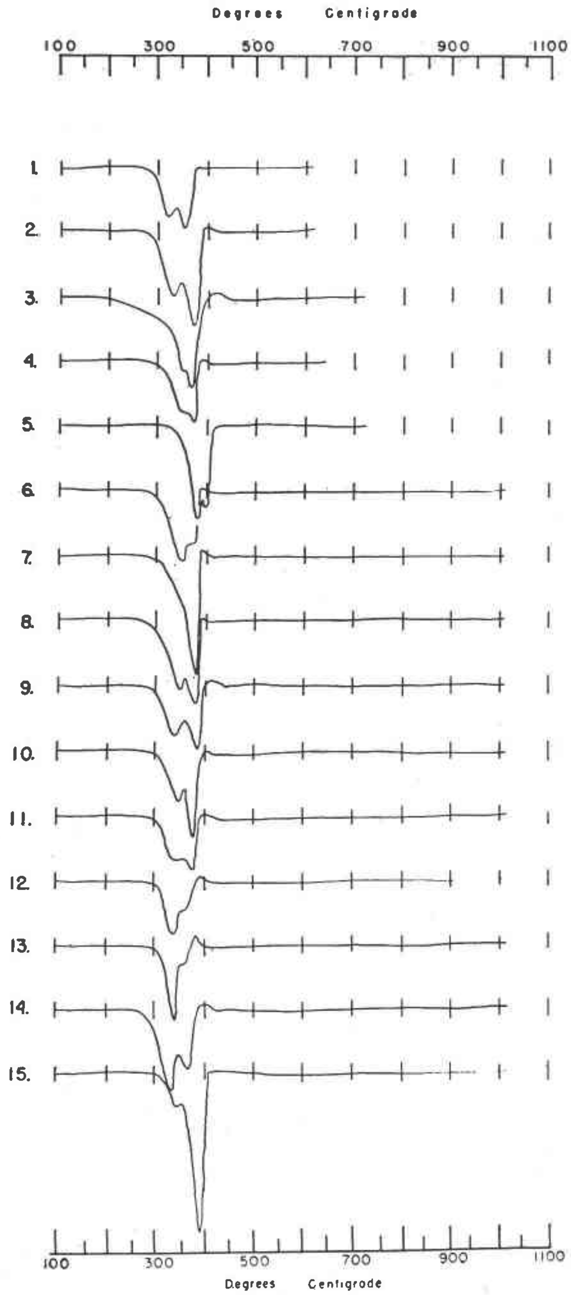

Fig. 6. For legend see top p. 37.

FIG. 6. Natural hydrous ferric oxide aggregates (mostly goethite and lepidocrocite).

Curve No.	Museum Label	Locality	*X*-Ray Identification
6-1	160-2 Goethite	Siegen, Prussia	Lepidocrocite, Goethite, Hematite
6-2	182-3 Limonite	Siegen, Prussia	Lepid., Goethite
6-3	431-5 Goethite	Herdorf, Siegen	Lepid., Goethite
6-4	162-6 Limonite	Gaston County, N. C.	Lepid., Goethite, Hematite
6-5	162-5 Limonite	Antonio Perciea, Brazil	Goethite
6-6	33-2 Goethite	Roxbury, Conn.	—
6-7	33-1 Goethite	Lake Superior	—
6-8	36-2 Limonite	Easton, Pa.	Lepid., Goethite
6-9	34-5 Limonite	Northampton, Pa.	Lepid., Goethite, Hematite
6-10	32-3 Limonite	Woodstock, Ala.	—
6-11	32-5 Limonite after Pyrite	Brunleya, Va.	Lepid., Goethite, Hematite
6-12	185-2 Limonite	Wilson, Wis.	—
6-13	184-1 Limonite	Salisbury, Conn.	—
6-14	182-6 Limonite	Salisbury, Conn.	Lepid., Goethite
6-15	184-3 Limonite	Llano County, Texas	Goethite, Lepid.

Figures 7 and 8 show the curves of some additional specimens labelled "limonite" and "goethite," as well as those labelled "lepidocrocite" and "turgite." In general, most of these specimens proved to be high in hematite. (7-7) apparently contains a small percentage (15%) of kaolinite in addition to 30–40% each of lepidocrocite and goethite. (7-13) is a typical lepidocrocite curve. (8-8) is the curve of a high purity goethite. The common occurrence of lepidocrocite is again noteworthy. (8-13) is a specimen consisting of hematite and quartz.

Substitution

An examination of the thermal curves of Figs. 1 and 3 does not reveal evidence of substitution. This is consistent with the facts derived from *x*-ray diffraction and semi-quantitative analysis. No shifts of the high angle lines indicative of cation substitution were observed. Semi-quantitative chemical analysis of a large number of these specimens showed no important contributors from such common ions as aluminum, magnesium, manganese or titanium. These might be expected on the basis of the crystal structure if substitution does occur. The ionic radius of aluminum ion is near that of ferric ion and both form common minerals. The structures of goethite and diaspore are the same as are the structures of lepidocrocite and boehmite. One must conclude that the absence of

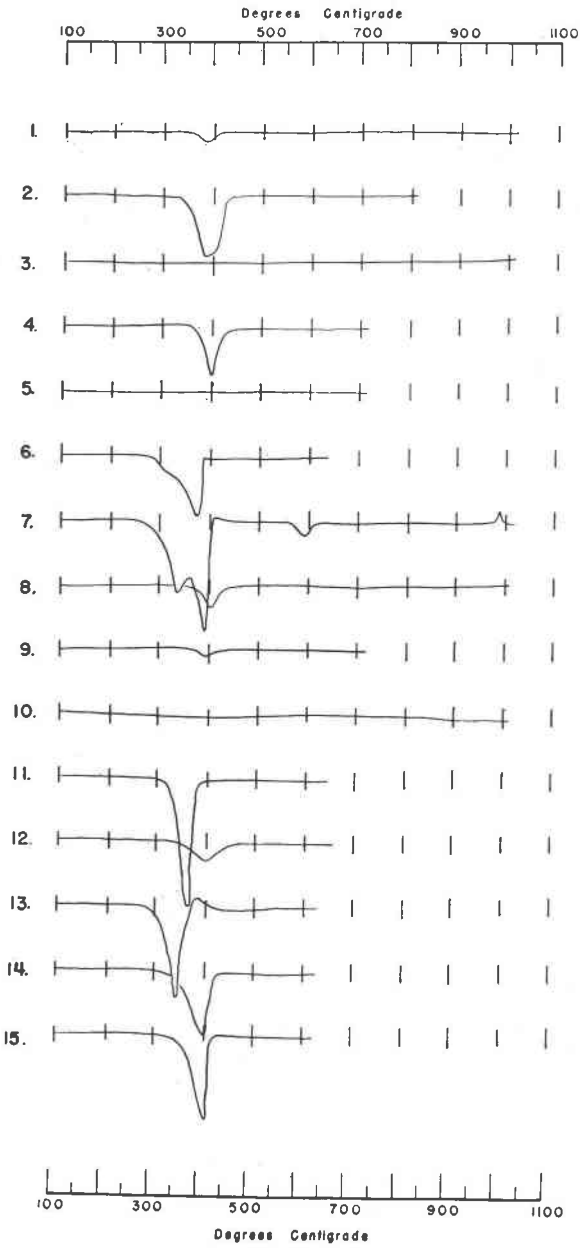

FIG. 7. For legend see top p. 39.

Fig. 7. Natural hydrous ferric oxide aggregates.

7-1	34-3 Lepidocrocite	Rossbach, Siegen	Goethite, Hematite
7-2	36-5 Goethite	Přizbram, Bohemia	—
7-3	36-3 Turgite	Woodstock, Ala.	Hematite
7-4	431-1 Goethite	Jackson Mine, Mich.	Goethite, Hematite
7-5	431-2 Goethite	Marquette, Mich.	—
7-6	160-6 Goethite	Marquette, Mich.	—
7-7	507-2 Lepidocrocite	Siegen	Lepid., Goethite, Kaolinite
7-8	507-5 Goethite	Rossbach, Siegen	—
7-9	507-6 Goethite	Přizbram, Bohemia	—
7-10	452-3 Turgite	Lehigh County, Pa.	Hematite
7-11	452-4 Turgite	Shelby County, Ala.	Goethite
7-12	452-5 Turgite & Limonite	Lancaster County, Pa.	—
7-13	161-1 Goethite	California	Lepidocrocite
7-14	161-2 Goethite	Pikes Peak	Goethite, Hematite
7-15	161-5 Goethite	Gotha, Germany	

substitution of ferric ion by aluminum is due to the geochemical separation of these ions in the process of weathering and deposition.

In the case of ordinary rock weathering the aluminum is generally locked up in the clay minerals. In gossans the iron is released from sulfide minerals essentially in the absence of free aluminum ions. Thus the chemical environment is not favorable to the formation of substituted goethite or lepidocrocite. The absence of evidence for substitution in these numerous natural aggregates is consistent with this concept.

Prepared Hydrous Ferric Oxides

An interesting set of thermal curves was obtained from the precipitation of ferric iron as the hydrous oxide under different laboratory conditions. The results of these experiments are shown on Fig. 9.

The first determination (1) was made on the iron precipitated by adding saturated $FeCl_3$ solution dropwise to a concentrated NH_4OH solution. The dense precipitate which was formed was filtered, washed once with dilute NH_4OH and allowed to dry at room temperature. Formation therefore took place under the conditions of rapid precipitation at a pH of 10 and a temperature of 25° C. The dried precipitate was analyzed thermally.

Its first endothermic reaction occurs slightly under 200° C., and is probably caused by the release of water adsorbed on the colloidal material. The major asymmetric exothermic peak at 490° C. is due to the recrystallization of the amorphous Fe_2O_3 to alpha-Fe_2O_3 (hematite). This was proved by x-ray patterns taken at 450° C. and 550° C. The slight dip prior to the major exothermic peak is attributed to the sublimation

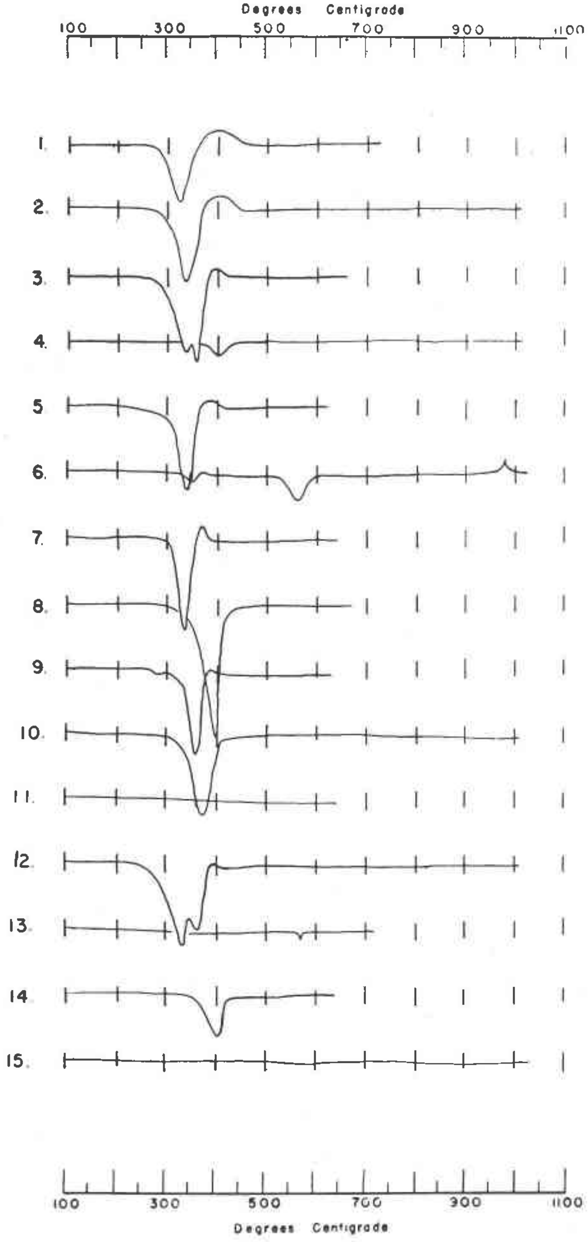

FIG. 8. For legend see top p. 41.

FIG. 8. Natural hydrous ferric oxide aggregates.

Curve No.	Museum Label	Locality	*X*-Ray Identification
8-1	183-5 Limonite	Terra do Curral, Brazil	Lepid, Hematite
8-2	183-6 Limonite	Pico de Italina, Brazil	—
8-3	431-6 Lepidocrocite	Herdorf, Siegen	Lepid., Goethite
8-4	186-1 Limonite	L'Ause, Lake Superior	—
8-5	442–3 Limonite	Osmond Mine, Kings Mtn., N. C.	Lepidocrocite
8-6	442-4 Limonite	Easton, Pa.	Goethite, Hematite, Kaolinite
8-7	442-5 Limonite	New York	Lepidocrocite
8-8	442-6 Limonite	Roxbury, Conn.	Goethite
8-9	182-1 Limonite	Salzburg, Austria	—
8-10	182-2 Limonite	Brazil (yellow)	—
8-11	182-4 Limonite	Brazil (brown)	Hematite
8-12	182-5 Limonite	Lenox, Mass.	Lepid., Goethite
8-13	33-3 Goethite	Přizbram, Boehmia	Hematite, quartz
8-14	33-4 Goethite	Pikes Peak	—
8-15	507-1 Turgite	Lake Superior	—

of NH_4OH. Thus, as might be expected, this method of preparation simply yielded colloidal $Fe_2O_3 \cdot xH_2O$ which dehydrates to hematite.

Curve 2 shows the thermal record of material prepared by adding concentrated NH_4OH dropwise to a saturated solution of $FeCl_3$. At the end of the precipitation the solution was faintly acid to litmus. The rapid precipitation took place at a pH of 5 and a temperature of 25° C. The color of the precipitate was a much lighter brown than that of the material obtained by the former method at a pH of 10. The precipitate was washed thoroughly with water.

The first large endothermic reaction at 178° C. is almost identical to that of Curve 1, but of slightly smaller amplitude. The exothermic peak at 278° C. is to be attributed to the recrystallization of amorphous Fe_2O_3 to hematite. This reaction is apparently catalyzed by the presence of hydrogen ions. A small endothermic kick is found at 400° C. which is due to a trace of NH_4OH not removed in the washing.

These experiments strongly suggest that in nature hematite is generally formed by the autodehydration of the hydrous ferric oxide gel which is a result of direct neutralization of a ferric ion solution. Goethite and lepidocrocite are not formed under these conditions but rather by the slow oxidation of certain ferrous compounds and the slow hydrolysis of ferric salts (goethite) or oxidation of iron sulfides and hydrous Fe_3O_4 gels (lepidocrocite).

The remaining curves represent mixtures of prepared hydrous ferric oxides precipitated in the presence of kaolinite. The reduced peaks of the

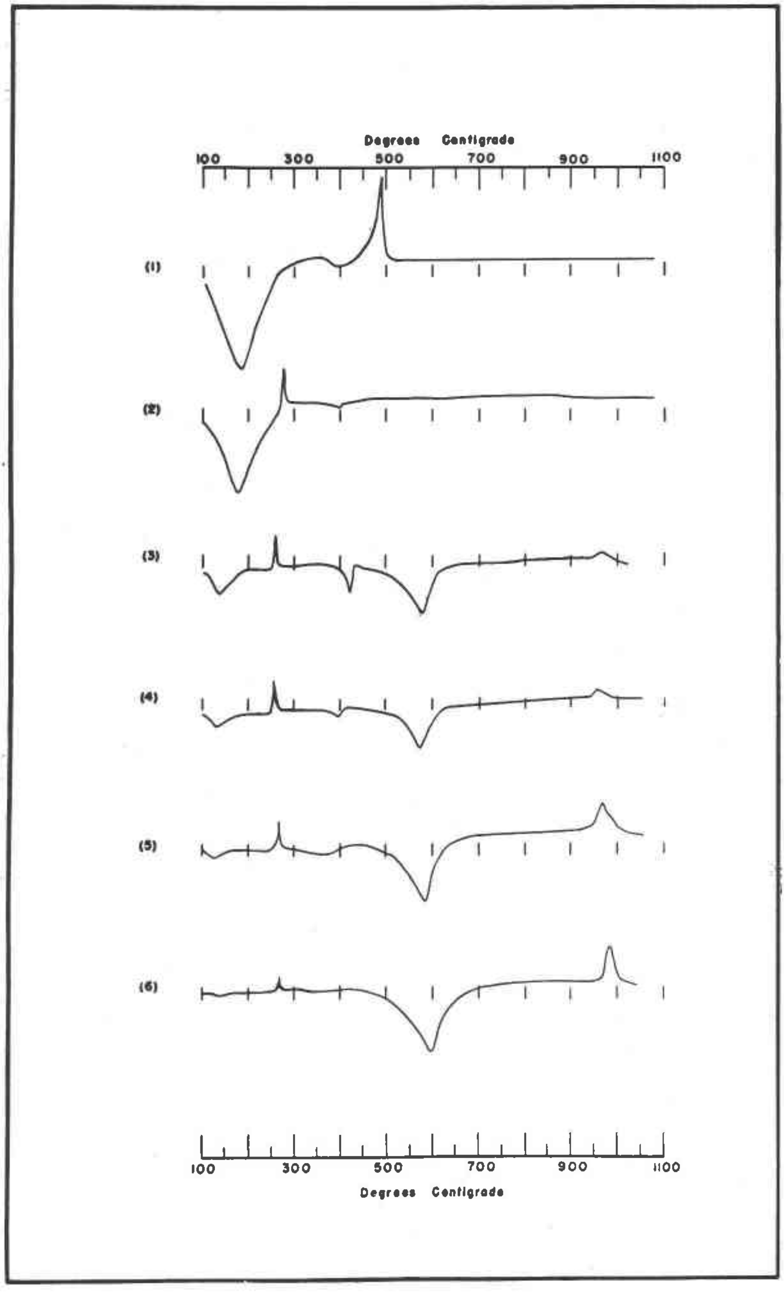

FIG. 9. For legend see top p. 43.

FIG. 9. Prepared hydrous ferric oxides.

Curve No.	Conditions
9-1	Precipitation at pH10; 25° C, thorough washing with dil. NH_4OH
9-2	Precipitation at pH5; 25° C, thorough washing with H_2O
9-3	Precipitation at pH5; 25° C, 40 gms. $FeCl_3$, 40 gms. kaolinite
9-4	Precipitation at pH5; 25° C, 25 gms. $FeCl_3$, 40 gms. kaolinite
9-5	Precipitation at pH5; 25° C, 15 gms. $FeCl_3$, 40 gms. kaolinite
9-6	Precipitation at pH5; 25° C., 5 gms. $FeCl_3$, 40 gms. kaolinite

kaolin may be seen at 579° C. and 952° C. The hydrous ferric oxides were prepared by adding NH_4OH dropwise to a solution containing $FeCl_3$ and kaolinite. The solution was acid to litmus during the precipitation. The precipitate was filtered, washed with water, and dried at room temperature for 3 days. In these experiments, the washing was not as thorough as in the case of curve (2). Note the decrease in the NH_4OH peak with the hydrous ferric oxide concentration.

This type of experiment could be profitably carried out with synthetic goethite and lepidocrocite. It would appear that considerable information of the geochemical condition which determine the relative concentration of these minerals could be ascertained in this way. The products of both the oxide formed in the acid and basic solutions gave alpha-Fe_2O_3 lines. Thus it appears that under these conditions colloidal hydrous iron oxide formed directly which goes over to hematite on dehydration.

CONCLUSIONS

The typical differential thermal curve of goethite seems characterized by a single endothermic reaction. For a heating rate of 12° C. per minute the peak on the thermal curve appears at 395° C. ± 10° C. depending somewhat on the crystallite size.

The typical lepidocrocite thermal curve also has a single endothermic reaction which seems to have a peak temperature close to 350° C. This is followed by an exothermic peak, due to the phase change of gamma to alpha-Fe_2O_3.

It is possible, then, to distinguish between goethite and lepidocrocite on the basis of their thermal curves.

Analysis of a large number of natural hydrous ferric oxide aggregates shows the presence of both lepidocrocite and goethite. Lepidocrocite appears to be much more common than is generally appreciated.

It is possible to estimate the percentage composition of the hydrous iron oxide minerals in these natural mixtures.

Inert impurities are effective in lowering the peak temperature of these minerals and frequently cause a broadening of the peaks, and a decrease of the amplitude.

Differences in particle size affect the peak temperatures. It was found that the smaller particle sizes produced lower peak temperatures. The difference in the temperature of the peaks may be as much as 25° C. when coarsely crystalline goethite is ground to pass 300 mesh.

Substitution of iron by other common cations was not detected in this study. This is related to the geochemical environment in which they are formed.

Artificially prepared hydrous ferric oxides gave thermal curves which depended on the pH of the solution in which they were formed. The presence of hydrogen ion catalyzes the recrystallization to hematite.

Differential thermal analysis appears applicable to a systematic study of gossans, since both goethite and lepidocrocite may be estimated semi-quantitatively. Systematic variations in the hydrous iron oxide mineral with position of an ore body or with type of ore mineral present might be expected. Such variations would certainly reflect changing geochemical conditions.

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