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ART. XX.—*The Hydrated Ferric Oxides*,¹ by EUGEN
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Introduction.

Our knowledge of the hydrated oxides of iron, notwithstanding the extended number of publications on this subject, is still very meager. Of the large number of supposed hydrated oxides to which at one time or another definite compositions have been assigned, the text-books usually describe the following series as minerals:

Turgite	$\text{Fe}_2\text{O}_3 \cdot \frac{1}{2} \text{H}_2\text{O}$
Goethite and lepidocrocite	$\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$
Hydrogoethite	$\text{Fe}_2\text{O}_3 \cdot \frac{4}{3} \text{H}_2\text{O}$
Limonite	$\text{Fe}_2\text{O}_3 \cdot \frac{3}{2} \text{H}_2\text{O}$
Xanthosiderite	$\text{Fe}_2\text{O}_3 \cdot 2 \text{H}_2\text{O}$
Limnite	$\text{Fe}_2\text{O}_3 \cdot 3 \text{H}_2\text{O}$

Of these goethite alone has been well defined physically and chemically. Descriptions of lepidocrocite (rubin-glimmer) leave a doubt as to its identity with goethite,

¹ This work was begun in connection with the secondary enrichment investigation pursued by this Laboratory in 1913-1915 in co-operation with Professor L. C. Graton and his colleagues.

although Lacroix² makes a definite optical distinction. Hydrogoethite has been supposed to contain more water than goethite but in its optical properties is said to be similar to lepidocrocite. The other names in the list have been given because of certain indefinite physical differences associated with plausible but not well established chemical formulas.

Below we have attempted to bring together the significant results of synthetic chemical work already done on the hydrated ferric oxides.

Work previously done.

Early investigations were brought to a conclusion by Tomasi³ who summarized the synthetic researches of his predecessors and his own by classifying the hydrated ferric oxides in accordance with their color in two series, differing in their properties: the red and the yellow hydrates. For each series a number of definite hydrates and their methods of preparation were described. Generally, according to Tomasi, the red hydrates were formed by precipitation of ferric salts with alkalies, while the yellow hydrates were produced by oxidation of ferrous oxide or carbonate.

More recently, van Bemmelen⁴ investigated such synthetic hydrated ferric oxides in respect to their water content. He came to the conclusion that the reddish-brown substance is a colloid and not a hydrate (or hydrates) as previously described. This substance he says "may undergo various changes and therefore has no definite composition but always comes to an equilibrium depending upon the surrounding vapor tension." The yellow substance is also a colloid. However, "it is not a variety of the brownish-red substance, since it is from the time of its formation in a denser and more stable, though variable condition." He found that between 50° and 200° the yellow colloid retains its water much more tenaciously than the brownish-red, but above 200° both colloids attain the same composition and become identical.⁵

² *Minéralogie de la France*, 3, 360.

³ *Ricerche sulle formule de costituzione dei composti ferrici*, Florence, 1879; *Ber. deutsch. chem. Ges.*, 12, 1929, 2334, 1879.

⁴ Van Bemmelen's collected papers, published under the title, "Die Absorption," pp. 70-77.

⁵ In a later paper (*Zs. anorg. Chem.*, 20, 185, 1899; *Die Absorption*, p. 370), which deals with the hydration and dehydration of the reddish-brown

In another paper⁶ van Bemmelen tried to verify statements found in the literature dealing with the preparation of crystallized ferric hydrates. He proved all of them to be erroneous, though he claimed to have prepared a crystallized ferric oxide monohydrate. It was formed when hexagonal plates of sodium ferrite were leached with water at 15°. His belief that a true hydrate was formed is based on the fact that this substitution did neither destroy the form nor the transparency of these crystals and that they were not hygroscopic. However, he found that they begin to decompose and lose their water below 100°, while the known natural hydrated ferric oxides are apparently perfectly stable at that temperature. Retention of transparency in cases of pseudomorphism are well known and it seems quite evident, therefore, that his crystals were not crystals of a definite hydrate but were pseudomorphs.

In view of the insufficiency of previously used methods to produce the hydrates of ferric oxide, O. Ruff⁷ determined to employ high pressure for that purpose. This, according to him, gave the desired results for "the red colloid immersed in water changed in the course of a few days under pressure, and a temperature of 30-42.5°, into the yellow hydrate $2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ corresponding to limonite; above 42.5° and up to 62.5° into the yellowish-red hydrate $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ corresponding to goethite, and above 62.5° into the brick-red hydrate $\text{Fe}_2\text{O}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ corresponding to turgite. The upper temperature limit of stability for the latter was not discovered." These products according to Ruff were so fine-grained that even under a magnification of 600 times, crystallinity could not be rec-

substance, van Bemmelen apparently changed his opinion, as he describes the yellow colloid belonging to the same class as the reddish-brown: "das gelbe, wasserhaltige Eisenoxyd . . . bindet das Wasser etwas staerker als das braunrote gel . . . muss jedoch diesen zugezaehlt werden." Only in the first-mentioned paper did van Bemmelen investigate the yellow substance and even then most of his attention is given to the reddish-brown substance. This statement is, therefore, based not on new facts but rather, we think, on his conception of colloids defined by him as follows: "Ich betrachte die kolloiden Verbindungen der Elemente, Oxyde, Sulfide, Salze u. s. w. mit Wasser nicht als chemisch bestimmte Individuen, sondern als unbestimmte Verbindungen in einem besonderen Aggregatzustand." (Die Absorption, p. 38.) This definition of colloids does not agree with our present knowledge; however, the fact stands, and is of interest, that van Bemmelen found certain differences in the properties of the brownish-red and yellow hydrated ferric oxides, although he was unwilling to give them sufficient consideration.

⁶ Die Absorption, p. 145; Journ. f. prakt. Ch. N. F. 46, 497, 1892.

⁷ Ber. deutsch. chem. Ges., 34, 3417, 1901.

ognized. The compositions of these products, however, agreed remarkably well with the formulas given for hydrates of ferric oxide, and the density determined upon this material was almost exactly as given in text-books for the corresponding minerals. The yellow colloid did not change under the pressure applied by Ruff in the temperature interval of 40-70° and he therefore assumes that it is "not a colloid but a true hydrate" which he suspects is xanthosiderite. But specimens of the two hydrated mineral ferric oxides, investigated under similar conditions,—"limonite" at a temperature of 70-75° and turgite at 40-50°,—did not show any change whatsoever (turgite and "limonite," respectively, should be formed if the two foregoing stability relations were true). This, however, did not deter Ruff from assuming that the problems of composition and the stability relations of the hydrated ferric oxides were thus satisfactorily solved, and he discusses on that basis the formation of natural deposits.⁸

Another investigation was undertaken by H. W. Fischer.⁹ By hydrolyzing ferric chloride solutions he came to the conclusion that at least three entirely different substances exist among the colloidal hydrated ferric oxides: the yellow, reddish-black and van Bemmelen's reddish-brown colloids.¹⁰ Now Fischer found that limonite has a characteristic dehydration curve; water is lost rapidly below 100°, then sparingly, although continuously, up to about 165°; above that temperature the loss is very large and is accompanied by a change in color from yellow to red. Just before the substance is heated above 165° it has approximately 1 mol. of water. This behavior of limonite corresponds, according to Fischer, to that of a colloidal hydrate,¹¹ and as the synthetic yellow colloid shows a similar dehydration curve he concludes that they are identical. The reddish-black colloid he thinks is identical with hematite and the reddish-brown colloid he believes (no experiments made) is identical

⁸ As a result of the present investigation the "data" presented by Ruff concerning the compositions and densities of the hydrated ferric oxides can only be considered accidental.

⁹ Zs. anorg. Chem., 66, 37, 1910.

¹⁰ Fischer defines colloids as "chemical individuals whose total energy depends besides the variables of state (Zustandsvariablen) on an additive quantity K, which may be interpreted as a function of time."

¹¹ Hintze, in his "Handbuch der Mineralogie," vol. 1 (2), p. 2008, draws the conclusion that limonite is the colloidal form of goethite.

with the substance of the composition $2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ prepared under pressure by Ruff,¹² which however he thinks is unstable and therefore does not occur as a mineral. Among the minerals he doubts the existence of xanthosiderite and believes turgite to be a dehydrated limonite.

As seen from this short review little definite knowledge exists in respect to any of the hydrated ferric oxides except goethite, and many contradictory conclusions have been drawn. Chemically as well as mineralogically the problem presents many difficulties and up to the present apparently no systematic investigation had been undertaken involving the *correlation of different properties*. In view of the abundance of hydrated ferric oxides in nature and the widespread interest in the processes of formation of ore bodies, more definite information about the nature and properties of the hydrated ferric oxides was thought desirable.

The plan of this investigation was, on the one hand, to examine chemically and microscopically a large number of hydrated iron oxides and to determine their physical properties; on the other, to synthesize them, if possible, by the study of a chemical system in which they were likely to occur. As such the system $\text{Fe}_2\text{O}_3\text{-SO}_3\text{-H}_2\text{O}$ was chosen. The results of the study of this system were, however, disappointing, as only "amorphous" and no crystallized hydrated ferric oxide was formed. Similarly various single experiments aiming at the formation of crystallized hydrated ferric oxides were unsuccessful. This led us to resort to thermal methods which, combined with the chemical examinations and the measured physical properties of the hydrated ferric oxides, yielded some of the desired information.

Analyses.

A large number of analyses of hydrated ferric oxides is found in the chemical and mineralogical literatures. However, most of them, except those of crystallized goethite, were made on materials not sufficiently defined physically, and accordingly show unaccountable variations to such an extent that from them no definite conclusions as to the hydrated form which they represent could safely be drawn. Most analyses are also comparatively old and for that reason probably unsatisfactory in respect

¹² Loc. cit.

TABLE I.
Analyses of Crystalline Hydrated Ferric Oxides.

No.	Locality.	Fe ₂ O ₃	FeO ^a	Al ₂ O ₃	Mn ₂ O ₃	CaO	MgO	SiO ₂	CO ₂	H ₂ O	Total.	$\frac{H_2O}{Fe_2O_3}$	Name of mineral as received.
1	Germany	97·83	-----	-----	-----	-----	-----	0·73	-----	1·30	99·86	0·12	Hematite
2	New York (No. 18330) ^b	93·68	0·49	-----	trace	-----	-----	0·68	0·30	4·12	99·27	0·39	Turgite
3	Missouri (No. 65269)	92·64	0·70	-----	0·10	-----	-----	0·90	0·43	4·68	99·45	0·44	Turgite
4	Rockingham Co., Va. (No. 17968).	-----	-----	-----	-----	-----	-----	-----	-----	5·39	-----	-----	Turgite
5	El Paso County, Colo.	89·65	-----	-----	-----	-----	-----	0·36	none	10·19	100·11	1·01	Goethite
6	Cornwall, England	89·03	-----	-----	-----	-----	-----	0·70	-----	10·22	99·95	1·02	Goethite
7	Harz, Germany (No. 84270)	86·39	-----	-----	-----	-----	-----	3·05	none	9·92	99·46	1·02	Xanthosiderite
8	Diamond Hill, Rhode Island (No. 17879)	88·24	-----	-----	-----	-----	-----	1·07	none	10·54	99·85	1·06	Limonite
9	Brazil (No. 80862)	87·19	0·34	-----	-----	-----	-----	1·17	0·21	10·95	99·86	1·09	Goethite
10	Michigan	86·55	-----	-----	-----	-----	-----	2·42	-----	10·80	99·77	1·10	Goethite
11	Easton, Pa. Easton, Pa. (No. 81909)	85·80	1·47	-----	trace	-----	-----	0·91	0·90	11·02	100·10	1·14	Goethite (Lepidocrocite)
12	Salisbury, Conn. (No. 17302)	82·67	1·82	0·24	1·24	none	0·12	0·92	1·09	11·68	99·78	1·25	Goethite
13	(No. 13973a)	82·12	1·73	0·27	1·27	trace	0·16	1·58	1·06	11·78	99·97	1·27	Limonite
14	Urals, Russia (No. 40352)	83·47	0·89	0·30	0·36	trace	-----	2·75	0·55	12·20	100·52	1·30	Limonite
15	Specimen A	80·67	2·09	0·18	0·89	0·08	0·09	1·82	1·28	12·00	99·10	1·32	Limonite
16	Pennsylvania	82·44	1·44	-----	0·19	-----	-----	3·18	0·70	12·47	100·12	1·34	Limonite
17	(No. 46746)	81·15	1·50	0·10	0·55	0·06	0·40	2·26	0·92	12·80	99·74	1·40	Limonite
18		80·13	0·29	0·29	-----	-----	0·12	4·92	0·18	13·85	99·78	1·53	Limonite

^a The amount of ferrous oxide was calculated from the determined amount of carbon dioxide on the assumption that the latter was derived from ferrous carbonate.

^b The National Museum's number of specimen.

to water determination. Water was usually determined by ignition loss and may, therefore, have included other volatile compounds. As the proposed hydrated ferric oxides differ only slightly in their water content an exact estimation of water is essential.

The analyses in Table I were made on carefully selected material¹³ examined microscopically in respect to its homogeneity. The iron was determined by titration with permanganate, manganese was determined colorimetrically. In cases where aluminum, calcium, etc., were to be determined, the iron was first removed by electrolysis. The water determinations were made according to Penfield's method,¹⁴ for some of the hydrated ferric oxides contained considerable amounts of carbonate which increase the value for water if the latter is determined by the ignition loss. In what form the carbonate is present could not directly be ascertained, for microscopically the analyzed hydrated ferric oxides appeared practically homogeneous. According to the analyses the carbonate might either be present as ferrous or as manganese carbonate. However, the corresponding amounts of manganese and carbon dioxide directly determined do not show any regularity whatever, though small amounts of ferrous iron could be detected (in No. 11 about 0.5%). It seems, therefore, that the carbonate present must be siderite, while manganese is present in a peroxidized condition which when the mineral dissolves oxidizes the ferrous iron and thus renders the direct determination of the latter impossible. Manganese is probably present as manganite ($Mn_2O_3 \cdot H_2O$) which is isomorphous with goethite.

That carbon dioxide was probably derived from ferrous carbonate finds some confirmation in the following observation. The ignition loss determined in some of the hydrated ferric oxides gave a certain excess compared with the amount of water found by the direct method. Assuming this to be due to the presence of ferrous carbonate, which reacts on ignition thus: $2FeCO_3 + O = Fe_2O_3 + 2CO_2$, the amount of carbon dioxide corresponding to

¹³ We wish to express our thanks to Dr. G. P. Merrill of the National Museum for the privilege of selecting these specimens; and to Dr. E. T. Wherry, formerly of the National Museum, for help in making the selections, and for specimens from his own collections; also to Professor R. J. Holden of the Virginia Polytechnic Institute for about 20 fine specimens.

¹⁴ See W. F. Hillebrand, *Analyses of silicate and carbonate rocks.*

this difference can be calculated. Table II shows the agreement of carbon dioxide calculated in this way with the amount directly determined.

TABLE II.

No.a	% ignition loss	% H ₂ O	Difference ^b	% CO ₂ calculated	% CO ₂ determined
13	12.71	11.78	0.93	1.13	1.06
15	12.99	12.00	0.99	1.21	1.28
16	13.08	12.47	0.61	0.74	0.70
17	13.60	12.80	0.80	0.98	0.92

^a The numbers refer to Table I.

^b This shows that the determination of water by the ignition loss, even on apparently homogeneous material, may easily be as much as 8% too high.

Some "amorphous" hydrated ferric oxides were also analyzed. The term "amorphous" is used here not to distinguish a special form of hydrated ferric oxide but only to indicate that the separate particles of the substance were of such fineness that their aggregates were essentially isotropic. They are primarily of interest in showing what influence the structure may have on the composition of the mineral. The results are given in Table III.

TABLE III.

Analyses of "amorphous" hydrated ferric oxide. ^a									H ₂ O
No.	Locality	Fe ₂ O ₃	FeO	CuO	SO ₃	SiO ₂	H ₂ O	Total	Fe ₂ O ₃
19	Cananea, N. M.,	83.34	...	1.23	1.34	1.73	13.26	100.90 ^b	1.41
20	Shasta Co., Cal.,	81.03	0.64	0.46	1.27	1.20	14.97	100.50 ^c	1.64
21	Shasta Co., Cal.,	76.29	0.25	0.15	0.35	5.67	17.41	100.12	2.02
22	Bisbee, Ariz.,	76.18	0.19	1.22	2.90	1.59	17.83	100.11	2.08
23	Shasta Co., Cal.,	74.95	0.25	0.50	1.67	1.50	17.76	100.67 ^d	2.10
24	Synthetic,	84.72	1.82	...	13.91	100.45	

^a Except No. 24 they are gossan ores received from Prof. L. C. Graton in connection with the investigation of the secondary enrichment of copper sulphide ores.

^b With trace Mn₂O₃. ^c Includes 0.93 MgO, trace Mn₂O₃. ^d Includes 4.04 Al₂O₃.

Discussion of Analytical Results.

In the last column of Table I is given the name under which the mineral was received. It is seen that with the sole exception of Nos. 5 and 6, which were definite crystals of goethite, the compositions of the hydrated ferric oxides differ considerably from their supposed formulas.

Thus a hematite (fibrous) is found to have as much as 1.3% water; two turgites considerably less water than is called for by the formula, while on the other hand goethites may have too much water. "Limonites" in most cases were found to be too low in water for the type of hydrate they supposedly represent, as was also the only specimen of xanthosiderite which we were able to obtain.¹⁵

The ratio of water to ferric oxide for the various hydrated ferric oxides is given in Tables I and III. The values of this ratio lie between 0.1 and 2.1 and embrace, therefore, with one exception— $\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ —all the supposed hydrated ferric oxides usually described as minerals, and mentioned in the beginning of this paper. However, this ratio shows practically a continuous variation instead of sudden changes as should be expected for a series of hydrates. It was rather surprising to find that the limited number of specimens which we analyzed presented such a gradation, as the selection of specimens for the analyses in Table I was made entirely on the basis of optical homogeneity and optical differences.

It may further be stated in respect to these analyses, that probably not all of the water determined in these substances belongs to the hydrated ferric oxide, but that some of it belongs to the "impurities," chief among which is silica. Usually the water content is higher the larger the amount of such impurities (see Tables I and III). The ratios of water to ferric oxide given in Tables I and II are, therefore, somewhat too high to be representative because the total amount of water was taken. It is noteworthy that even after this fact has been taken into account, the respective ratios of most "limonites" and turgites are not sufficiently high for the hydrates they supposedly represent. It seems, therefore, that on the basis of analytical data there is little foundation for the series of hydrates of ferric oxide, which is commonly assumed.

Optical and Crystallographic Study, with Synoptic Descriptions.

In order that the terms used in the latter part of the paper may have as definite a significance as can be given before those parts of the paper have been read, short descriptions including microscopical characteristics will be given at once.

¹⁵ Fischer, loc. cit., makes similar statements in respect to the last two minerals.

Goethite.¹⁶— $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$; orthorhombic with $a:b:c$ = about 0.90-0.92: 1: 0.600-0.605;¹⁷ density 4.28 ± 0.01 ; prismatic, bladed, fibrous;¹⁸ elongation parallel to c ; cleavage perfect b , good a ; refractive indices¹⁹ are $a = 2.26$, $\beta = 2.394$, $\gamma = 2.400$; fine powder is dull orange-yellow (16" i to 16' i Ridgway); thicker grains show slight pleochroism in orange-yellow browns (16 l), thinner grains are not perceptibly pleochroic and are clear yellow; for red $a = b$, $\beta = a$, $\gamma = c$, and for blue $a = b$, $\beta = c$, $\gamma = a$; $\beta = \gamma$ at 610-620 $\mu\mu$. Grains lying on the best cleavage face show a very characteristic green interference color, while colors of grains slightly tilted from this position pass through red and green without extinguishing. In white light the absorption formula is $a > c > b$.

The foregoing description applies to well-crystallized goethite, the following to *fibrous goethite*.

Aggregates of thin blades and fibers, subparallel with respect to the axis c , vary considerably physically and chemically. They usually appear microscopically homogeneous but their refractive indices are low; they contain water, silica, etc., as impurities, and they show confused interference figures, or are uniaxial at shorter wavelengths than is goethite owing to lack of parallel orientation with respect to a and b . The optical properties of these aggregates are best explained by the following considerations.

If very fine (diameter 0.5 μ or less) fibers or blades of goethite—elongation c —could be packed without pore space and with random orientation with respect to a and b , then slivers of the apparently parallel-fibrous aggregates would have a maximum refractive index parallel to the elongation equal to 2.40, and a minimum²⁰ throughout the plane perpendicular to the elongation equal to 2.33. Absorption would be slightly greater in the direction of the elongation.²¹

¹⁶ More complete descriptions appear near the end of the paper.

¹⁷ Crystallographic irregularities limit the accuracy. See p. 342, also G. Cesàro and A. Abraham, *Bull. Acad. R. Belg.*, 1903, 178.

¹⁸ See next section.

¹⁹ Dr. E. S. Larsen, of the U. S. Geol. Survey, has found $\alpha_{Li} = 2.21$, β_{Li} and $\gamma_{Li} = 2.33-2.35$ (unpublished).

²⁰ That is the maximum would equal γ of goethite and the minimum $\frac{a + \gamma}{2}$ approximately, and the aggregates would be essentially uniaxial positive with $\omega = 2.33$ and $\epsilon = 2.40$.

²¹ The diffusion of light at boundaries between differently refracting surfaces may affect the apparent pleochroism of fibrous substances. Grains should be observed in a medium having a refractive index midway between the refractive indices of the differently absorbed rays.

If instead of the random orientation there is a tendency toward parallelism, then there will be, for any bundle of fibers considered as a unit, three principal refractive indices: $\gamma = 2.40$, β variable between 2.40 and 2.33, and α variable between 2.26 and 2.33. For example $\gamma = 2.40$, $\beta = 2.35$, $\alpha = 2.31$; or $\gamma = 2.40$, $\beta = 2.34$, $\alpha = 2.32$.

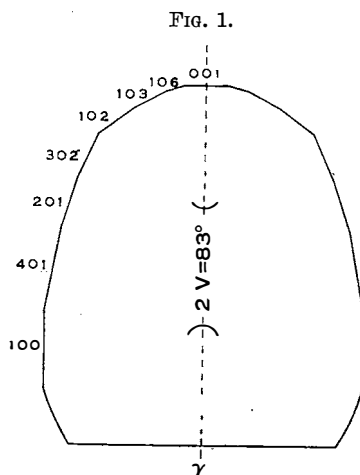
The presence of variable amounts of impurities in, and the physical behavior of, all our analyzed samples of bladed or fibrous goethite indicate that the fibers are not so tightly packed as just supposed but that the impurities (excess of water, silica, etc.) are in thin films among the fibers. By calculating as nearly as possible the volumes of the various impurities and assuming the additive relation for refractive index, the calculated mean refractive indices for several analyzed specimens have been found. Comparison of them with the observed values is found in Table IV. Most of these specimens were called limonite by the collectors.

TABLE IV.

No.	Mean refractive index calculated from analyses	Mean refractive index measured
9	2.28 ₆	2.30
10	2.27 ₂	2.28
13	2.22 ₅	2.21
14	2.22 ₂	2.19
15	2.20 ₂	2.19
16	2.17 ₈	2.17
17	2.16 ₈	2.17
18	2.11 ₇	2.12

Limonite.—When $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ is precipitated and hardened under natural conditions which do not permit definite crystallization, a porous mass is formed containing considerable excess of water, besides other impurities. So indefinite is the material that it cannot be characterized very satisfactorily. Its color in fine powder is scarcely distinguishable from that of fibrous goethite. Although often occurring in compact layered or botryoidal forms it does not possess decided fibrous fracture. The earthy varieties consist of minute loosely agglomerated spheroidal grains. Air-dried material possesses some pores of such size that, although microscopically invisible, they readily fill with such liquids as are used to immerse the grains for microscopic study. Thus, refractive-index determinations cannot be definitely interpreted; air-dried material does have observed apparent

refractive indices within the rather narrow limits of about 2.00 to 2.10 when saturated with a liquid of corresponding refractive index. Such material, which has often been called limonite, will be referred to as limonite here.²² Double refraction is common in such material, usually it is indefinite and not strong, but occasionally it reaches 0.04 and is almost as definite as in fibrous goethites. For example, in the cylindrical crusts around stalactites and in the spheroidal grains the ray vibrating along the radius is most strongly refracted as in fibrous goethite. In rare



cases a decided tendency for minute fragments to be splintery makes this material look somewhat like fibrous goethite.

Lepidocrocite.—Optical studies of the reddish, scaly crystals called rubinglimmer and lepidocrocite, led Lacroix to propose that they be classed together as lepidocrocite and separated from goethite, with which they had formerly been identified.²³ Crystals supposed to contain more water than goethite and which from later²⁴ descriptions were seen to be optically similar to lepidocrocite, were called hydro-goethite by Zemjatschensky.²⁵ Crystallographic measurements, mostly with the micro-

²² See A Review of the Amorphous Minerals, A. F. Rogers, J. Geol. 25, 528.

²³ Minér. d. France, III, 360.

²⁴ J. Samojloff, Zs. Kryst. 34, 701 and 35, 272, abs.

²⁵ Zs. Kryst, 20, 185 abs.

scope, were made by Cesàro and Abraham.²⁶ They used a different optical orientation from that of either Samojloff or Lacroix and classed their crystals as a special type of goethite.

Our determinations of refractive index and density have confirmed the idea that these crystals are entirely distinct from goethite; on the other hand their composition is like goethite.

By adopting the name and optical orientation proposed by Lacroix, and by combining our own crystallographic data with those of Cesàro and Abraham, we can write a fairly complete synoptical description of the mineral. For more details see fig. 1 and the description of specimens, p. 345.

Lepidocrocite, $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$, orthorhombic, $a:b:c = 0.43:1:0.64$. Density $4.09 \pm .04$. Habit, single thin scales $\{010\}$, slightly elongated c , or in scaly to compact bladed aggregates. Cleavage, $\{010\}$ perfect, $\{001\}$ less perfect, $100\}$ good. Streak dullish orange. Color of fine powder 13' i (Ridgway). Refractive indices: $a = 1.94$, $\beta = 2.20$, $\gamma = 2.51$, $a = b$, $\beta = a$, $\gamma = c$. Therefore $-2V = 83^\circ$, axial dispersion very slight. Pleochroism: in thicker grains a is clear yellow, β dark red-orange, γ darker orange-red; in thinner grains a is nearly colorless (yellowish), β and γ orange to yellow according to thickness.

Turgite.²⁷—The fibrous red oxide of iron containing variable amounts of water cannot be definitely characterized. Some specimens have primary structure, others are pseudomorphic. The primary structure is divergent-fibrous. Detached splinters have parallel extinction, negative elongation and negative (apparently uniaxial) optical character. The refractive indices thus far observed²⁸ range between a (or ϵ) = 2.3 to 2.6, β and γ (or ω) = 2.5 to 2.7. The color in fine powder is distinctly lighter and more inclined toward orange than hematite. The corresponding density is about 4.7, and the water content about 4 to 6 per cent.

Pseudomorphic turgite appears to result from the partial dehydration of fibrous goethite and primary turgite, and from the oxidation and slight hydration of magnetite

²⁶ Bull. Acad. Belg., 1903, 178.

²⁷ See p. 347.

²⁸ These include unpublished values kindly furnished by Dr. E. S. Larsen of the U. S. Geological Survey. Mixtures containing sulphur, iodine, arsenic, selenium and tellurium are suitable for making such measurements.

into martite.²⁹ Properties thus far observed indicate that pseudomorphic turgite is intermediate between hematite and primary turgite. The character of the filling of the space from which water has escaped affects the properties.³⁰

These observations together with studies of density and thermal properties (p. 337) indicate that turgite is probably a solid solution of goethite and hematite, often containing considerable but minor amounts of capillary and adsorbed water.

Thermal Study.

The identification of hydrates is usually accomplished by the study of the relation between their vapor pressure and composition under definite conditions. The vapor pressure can either be measured directly with a gauge or according to a method suggested by van Bemmelen by placing the substance in a series of known water vapor pressures. These methods require prompt reversibility, so that equilibrium can be reached from both sides. However, as in many other cases,³¹ this is impossible to do with the hydrated ferric oxides, because ferric oxide under ordinary conditions cannot be hydrated. The question whether such irreversibility is simply due to the extreme slowness of the rate of reaction, or whether dehydration causes a more stable molecular rearrangement, is still an open one.³²

For irreversibly hydrated substances Le Chatelier³³ suggested a method which is based on the fact that in general the velocity of such reactions increases according to an exponential function of the temperature. It consists in measuring the temperature at definite intervals while the substance in question is heated at a fairly uniform rate. In this way temperature-time curves are obtained which show a heat effect similar to those of melting or inversion temperature-time curves.

²⁹ Some martites studied contained 0.6 to 0.9% of water, and had decidedly lower indices of refraction than hematite. See *Trans. Am. Inst. Mining Engineers*, 58, 431, 1917.

³⁰ See p. 347.

³¹ Johnston, *Zs. phys. Chem.* 62, 330, 1908.

³² The difference in the behavior of irreversibly and reversibly hydrated substances is often explained by assuming that the former contain constitutional water while the latter contain water of crystallization. This, however, does not explain anything, as the two words have no exact physical meaning.

³³ *Zs. phys. Chem.* 1, 396, 1887.

According to Le Chatelier³⁴ the rate of heating influences the decomposition temperature but little. This, however, is true only for the comparatively rapid heating such as is used in making temperature-time curves. Only under such conditions are reproducible results obtained. These, however, give much higher temperatures for the decomposition than those obtained by heating the substance to constant weight at definite temperatures, as will be stated later. Such higher decomposition temperatures are probably caused by such factors as rate of reaction and physical character of substance, including the size of grains.

While, for that reason, the decomposition temperature found by this method could not be relied upon for the definite identification of hydrates, the curves obtained are quite valuable for a first orientation and quick information as to the way water is held. Water which enters into composition of such substances in a definite ratio, is readily distinguished by these curves from dissolved or adsorbed water. The former gives a curve with sharp heat effects due to rapid decomposition, while the latter, passing off gradually, produces fairly smooth curves.

The results for a number of decomposition curves are given in fig. 2. The substance was heated by means of an electric resistance furnace. The curves were taken by Roberts-Austen's differential device³⁵ against copper oxide as a neutral body and the temperature was measured with a platinum-rhodium thermoelement. The numbers of the curves refer to analyses in Tables I and III.

Except turgite, all the specimens of hydrated ferric oxide which have been investigated gave a strong heat effect. This was due to the decomposition of the substance, and no heat effect was produced on reheating. Some of these substances also show a slight heat effect just above 100°. This effect gradually increases with the total amount of water held by the hydrated ferric oxides and is undoubtedly due to adsorbed water, the greater part of which would come off at about this temperature. The temperature at which decomposition takes place can be reproduced for each sample very closely. However, as seen from the curves in fig. 2, there is a continuous gradation in the decomposition temperatures of the

³⁴ Loc. cit.

³⁵ See G. K. Burgess, Bull. Bureau of Standards, 5, p. 210, 1908; W. P. White, this Jour. 18, 453, 1909.

hydrated ferric oxides (except turgite). Crystalline goethite (No. 5) shows the highest decomposition temperature, while the "amorphous" hydrated ferric oxide (No. 22) decomposes at the lowest temperature. No definite identification of hydrated ferric oxides is therefore possible on the basis of these curves.

As has been stated, the curves for turgite differed greatly from those of the other substances. A slight heat effect is shown at about 110° , which, however, is not sharp and the curve falls off gradually; no other heat effect was observed between this temperature and 600° . The shape of the curve plainly signifies that the water in turgite is held in a different way from that in the other hydrated ferric oxides.

It has been previously mentioned that Fischer³⁶ attempted the identification of "limonites" by determining their decomposition temperature by slow dehydration at fixed temperatures. The choosing of the decomposition temperature for purposes of identification is rather unfortunate as this temperature may be influenced by the physical character of the substance. The rate of reaction also has to be considered. The longer the substance is kept at each temperature, the more, in all probability, would the influence of the rate of reaction be reduced. However, the irreversibility of the reaction leaves no definite criterion and the exact decomposition temperature must remain uncertain.

Fischer found that only above about 160° did "limonite" decompose (the decomposition curve however was not completed), although an appreciable amount of water was lost at lower temperatures. Just before decomposition his samples contained between 8.5 and 10.8% water which is much less than required by the formula usually assigned to "limonite." However, no definite conclusion could be drawn from these data as the substance was not sufficiently defined (only the amount of water determined by ignition loss is given).

In view of the sharpness of the curves obtained with Le Chatelier's method it was thought that slow dehydration at fixed temperatures might be made to yield valuable results. In principle both are identical; however, as the amount of water lost by the substance at each successive step is determined by the latter method, the resulting

³⁶ Loc. cit.

curve (extended considerably beyond the decomposition temperature) together with exact analytical data, should give definite information about the nature of the substance in question.

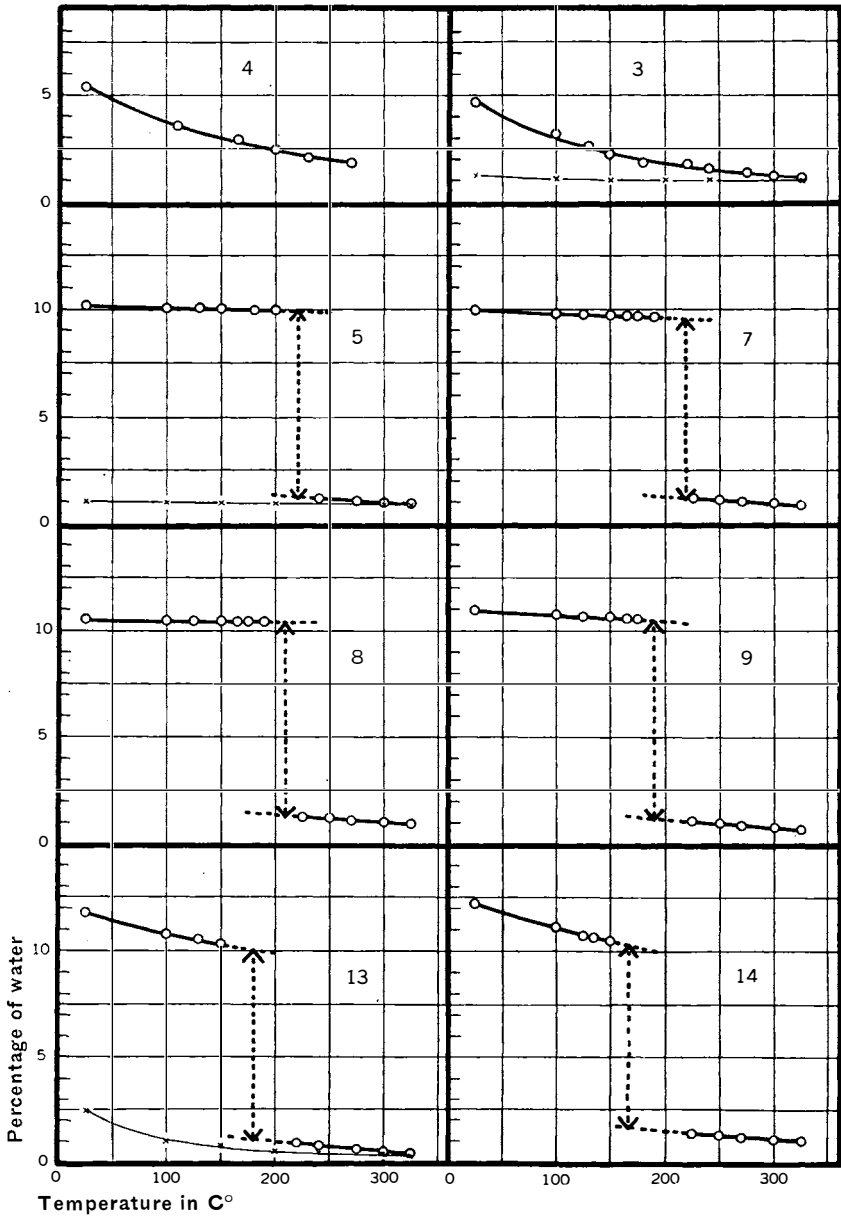
The hydration experiments were carried out at as slow a rate as practicable and the heating at all the temperatures required over four months. The substance was ground, placed in a small weighing glass and heated in an electric furnace which was kept constant within $\pm 5^\circ$. A slow stream of air, dried over sulphuric acid, was passed through the furnace. For weighing, the substance was quickly placed in a desiccator over sulphuric acid and, when sufficiently cooled, was covered and weighed. Before putting it back in the furnace the substance was slightly shaken up. At least twenty-four hours elapsed between successive weighings and the substance was treated at a different temperature only if no change occurred after two more days heating.

Most of the time required by the dehydration experiments was consumed for the decomposition of the substance. Before decomposition begins and after it is practically completed, the substance comes very rapidly to constancy under the conditions of experiment. Decomposition proceeds, however, at an exceedingly slow rate at the temperature at which it is first discovered and it was necessary to raise the temperature considerably to dehydrate the substance within a reasonable period.

The results of the dehydration experiments are given in figs. 3 and 4. With the exception of turgite, all the hydrated ferric oxides examined show similar dehydration curves which consist of three distinct parts. The decomposition of the substance takes place in the middle portion of the curve and is accompanied by the color change from yellow to red. It should probably take place at a single temperature, but owing to the practical irreversibility of the reaction and its slowness this temperature can not be fixed and decomposition therefore is determined within the temperature interval between the point at which continuous loss was first observed and the somewhat higher temperature at which for practical reasons the dehydration was carried out.³⁷

³⁷ In the drawings this interval is indicated by the broken line. The line connecting the upper and lower portion of the curves is drawn at the point at which continuous loss of water was observed, which however does not represent the exact decomposition temperature.

FIG. 3.



Temperature in C°

FIG. 3. Dehydration to constant weight at fixed temperatures. Numbers refer to analyses in Table I: 3 and 4—turgite; 5 and 8—bladed goethite; 7, 9, 13 and 14—fibrous (crystallized) goethite.

FIG. 4.

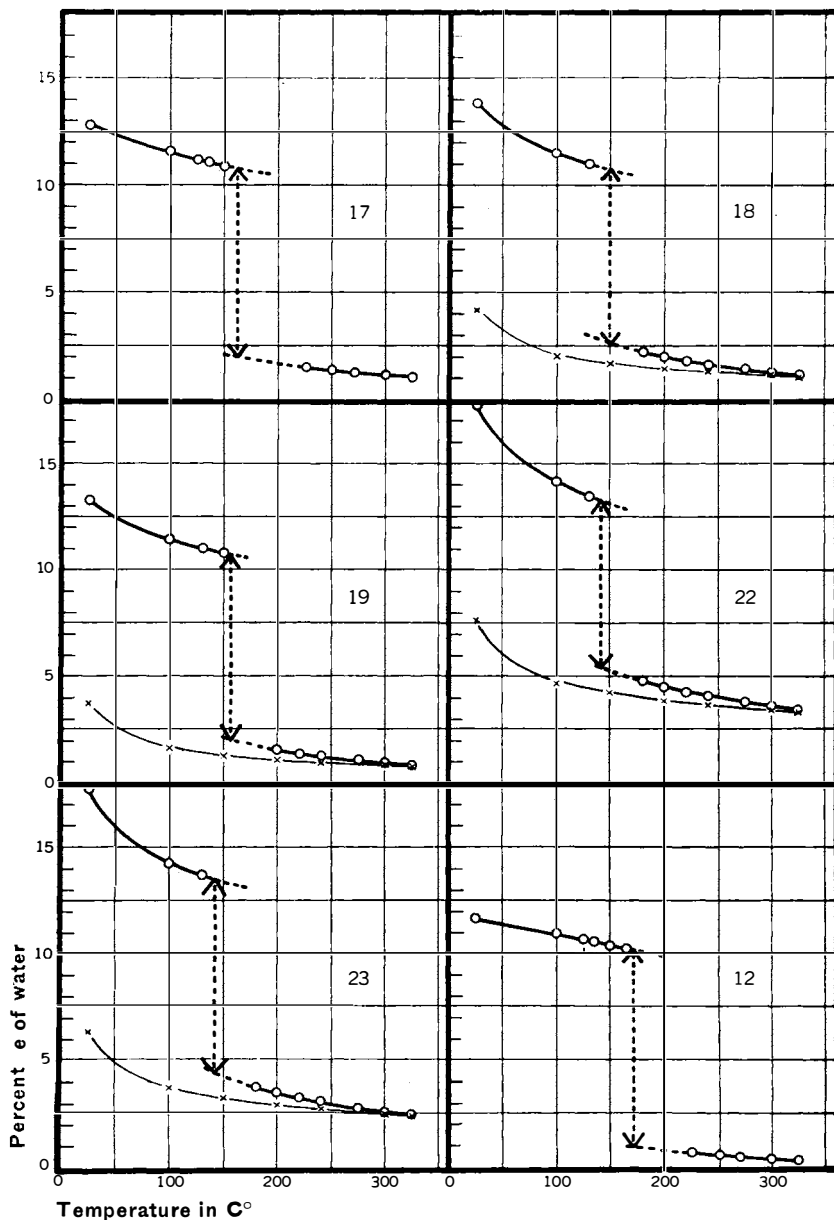


FIG. 4. Dehydration to constant weight at fixed temperatures. Numbers refer to analyses in Tables I and III: 17 and 18—fibrous (crystallized) goethite; 19, 22 and 23—limonite ("amorphous"); 12—lepidocrocite.

The temperatures of the dehydration intervals are considerably lower than the corresponding decomposition temperatures obtained by the rapid heating. This difference is probably caused by the slowness of the rate of reaction. In a comparative determination of the decomposition temperatures of several specimens, other factors, such as physical structure, size of grains, etc., will also prove of considerable influence, and it seems certain, therefore, that for purposes of identification the determination of decomposition temperatures is wholly unreliable.

As is seen from the figures, the dehydration curves consist of three distinct parts. The middle portion is formed by loss of water due to decomposition of the substance. The upper and lower portions of the curves show the losses in water not combined in a definite ratio. This is in all probability adsorbed and capillary water and the amount held will depend largely on the structure of the material. Comparison of curves for coarsely crystallized material with those for the more fibrous specimens strongly supports this view. It is also confirmed by rehydration experiments.

The results of rehydration are indicated by thin lines in a number of curves given. These experiments were carried out as follows: after the first dehydration up to the highest temperature the substance was left to come to constancy in the room;³⁸ then it was dehydrated in the same manner as before. The amount of water taken up in the room by the different samples was roughly equal to the amount lost in the first portion of the curves. Apparently dehydration did not appreciably change their original gross structure: thus the formerly crystallized goethite took up very little, while the originally fibrous and especially the "amorphous" samples took up correspondingly larger amounts.

The second dehydration gave perfectly smooth curves, which in the beginning approximately parallel the first portions of the corresponding original dehydration curves and later are practically identical with the third portion. The slight deviation is probably accounted for by shrinkage.³⁹ These experiments strongly suggest that a single cause must be responsible for the character of the first

³⁸ The humidity of the air was taken into account and the data refer to a relative humidity of approximately 40.

³⁹ Silica probably originally holds some of the water, which after heating is not so readily taken up again.

and third branches of the original dehydration curves. Judging from the smoothness of the curves, the quick adjustment, and the reversibility of the water contents, it is probable that it is due largely to adsorption. That adsorption of moisture to a considerable extent would take place could readily be foreseen from the fibrous (crystalline) and aggregated structure of most hydrated ferric oxides.

The part of the dehydration curve which gives information about the chemical nature of the substances in question, and is therefore of greater interest, is the middle portion. It is formed by the decomposition of the substance, and the amount of water lost in this portion serves for the chemical identification of the substance. These amounts may be approximately estimated⁴⁰ in the graphic way from the plots of the dehydration curves as follows: a parallel to the ordinate is drawn from the point at which decomposition begins and the lower branch of the dehydration curve is continued in the direction indicated by its curvature to the intersection with that line. The distance between the upper point and the intersection below indicates approximately the percentage of chemically combined water. Comparison on a mol basis of this amount of water with the amount of ferric oxide determined will indicate the chemical nature of the compound.

TABLE V.

No. of analysis in Tables I and III	% Fe ₂ O ₃	Graphical estimation of % of combined H ₂ O	Mol. ratio Fe ₂ O ₃ : H ₂ O	Name of mineral as received
5	89.65	9.1	1 : 0.90	Goethite
7	86.39	8.2	1 : 0.84	Xanthosiderite
8	88.24	9.0	1 : 0.91	Limonite
9	87.19	9.4	1 : 0.96	Goethite
12	82.67	9.4	1 : 1.01	Lepidocrocite
13	82.12	9.0	1 : 0.97	Limonite
14	83.47	8.8	1 : 0.94	Limonite
15	80.67	8.8	1 : 0.97	Limonite
17	81.15	8.9	1 : 0.97	Limonite
18	80.13	8.2	1 : 0.91	Limonite
19	83.34	8.8	1 : 0.94	"Amorphous" hydrated fer- ric oxides (gossan ores)
22	76.18	8.0	1 : 0.93	
23	74.95	9.0	1 : 1.06	

⁴⁰ These estimates may not represent the exact amount of water lost by the substance on decomposition. Decomposition somewhat changes the physical structure and thus through ab- or adsorption may influence the position of the lower branch of the curve. However, this probably would not cause a large enough error to change the results.

As seen from Table V this ratio in all cases is practically one. The fact that in most cases a slightly smaller value was obtained is probably caused by adsorption, due to the increase in surface on decomposition.

Slow dehydration of turgite confirmed the earlier conclusion, derived from the rapid curves, that this substance differs essentially from the other hydrated ferric oxides. The curves are given in fig. 3 (No. 4 and 3). They are smooth and show that water is given off gradually with every increase in temperature. No sudden decomposition takes place anywhere and it would seem that turgite, unlike the other hydrated ferric oxides, is not a definitely hydrated compound. The water this substance contains must either be adsorbed or in solid solution, or both. Some indication as to the way in which the water is held may be found in a rehydration experiment. But little water was taken up by the dehydrated substance on standing in the room for over two weeks, and on the subsequent dehydration up to the highest temperature it had the same composition as formerly. This could not very well be the behavior of adsorbed water, for reversibility in water content is characteristic in such cases provided no change of gross structure takes place (see p. 331). It appears, therefore, more likely that the water in turgite is largely held in solid solution. Support of this view was found later in some other observations (see density and microscopical descriptions).⁴¹

Considering the evidence presented by the dehydration experiments, we come to the conclusion that no series of hydrates of ferric oxide exists. According to the evidence presented the only definite compound actually in existence is ferric oxide monohydrate. Goethite has long been recognized as such a compound and the present study definitely established lepidocrocite as another substance of the same composition. As previously mentioned, Hintze⁴² concluded on the basis of Fischer's work that "limonite" is the "colloidal form of goethite." In view of the facts brought forward in the present paper such a conclusion seems rather hasty and, using the same terminology, it seems that "limonite" could just as well be the colloidal form of lepidocrocite. However, as the term colloidal does not imply anything about the modification of the substance (it can properly be used only to

⁴¹ Support of this view may also be found in the dehydration of the specimen from Germany (Table I, No. 1). This substance contained 1.3% water but lost less than 0.2% on heating to 300°.

⁴² *Handbuch der Mineralogie*, I (2), p. 2008.

describe properties caused by some general physical condition) it is still possible that "limonite" could also be a distinct polymorphic form of ferric oxide monohydrate. To decide this question some further study was necessary (density, optical properties, etc.).

Densities of the Monohydrates of Ferric Oxide.

Information about the number of polymorphic monohydrates of ferric oxide in existence was sought by means of density determinations. Available data for the supposed hydrates show considerable but irregular differences. Thus Dana gives in his "System of Mineralogy" the density of goethite (and lepidocrocite) as 4.0-4.4 and the density of limonite as 3.6-4.0. The density of hydrogoethite is given by Zemjatschensky and Samojloff as 3.5-3.7.

In view of the fibrous character of many of our specimens great care had to be taken, in determining this constant accurately, to drive out all the air. The substance to be examined passed a 100 mesh and was held by a 200 mesh (per linear inch) sieve. The pycnometer described by J. Johnston and L. H. Adams⁴³ for specific gravity determination was used and the air carefully boiled out under reduced pressure. Repeated determinations were in good agreement differing only in the third decimal. Comparative density determinations in xylol to determine whether complete filling of pores took place in our experiments were also attempted. However, only in cases where little excess water was present were these determinations successful and the values then obtained were identical with those in water. Where more water was present some was easily liberated in boiling out the air and small drops of it were observed in the xylol. The values for the specific gravity were accordingly considerably lower than in water and the latter probably essentially correct.

The specific gravities given in Table VI show the wide variation usually found in these substances. However, we know from the analyses that they contain a considerable amount of impurities and the result is therefore not surprising. Comparison of these data is possible only after the proper corrections are made for these impurities.

⁴³ J. Am. Chem. Soc. 34, 563 (1912).

TABLE VI.

No.	Specific gravity		Name of mineral as received
	in water	$\frac{\text{mineral } 25^\circ}{\text{water } 25^\circ}$ in xylol	
5	4.263	4.266	Goethite
6	4.250	Goethite
8	4.172	Limonite
9	4.107	(4.093)	Goethite
10	4.091	(4.087)	Goethite
13	3.970	Limonite
14	3.895	Limonite
15	3.951	(3.878)	Limonite
17	3.822	Limonite
11	3.854	Lepidocrocite
12	3.841	Lepidocrocite

The corrections of the specific gravity determinations were made on the basis of the analyses and in accordance with the evidence presented by the dehydration experiments that the specimens were monohydrates of ferric oxide. The analyses, as will be remembered, indicated as chief impurities silica (amorphous except in No. 5 and No. 6) and probably ferrous carbonate and manganite. For water in excess of the amount required to form the monohydrate with the ferric oxide a correction was made on the assumption that the water was free. The value taken for the specific gravity of amorphous silica was 2.3; for quartz 2.65; for ferrous carbonate 3.88, and for manganite 4.4. The approximate composition of the minerals and the specific gravities of the monohydrates of ferric oxide corrected on that basis are given in Table VII.

TABLE VII.

No.	—Approximate composition of mineral—					Sp. gr. at 25° for Fe ₂ O ₃ .	Name as labeled
	% Fe ₂ O ₃ .	% FeCO ₃	% Mn ₂ O ₃ .	% SiO ₂	% H ₂ O		
5	99.65	0.36	0.10	4.29	Goethite
6	99.08	0.70	0.17	4.29	Goethite
8	98.15	1.07	0.63	4.30	Limonite
9	97.44	1.17	1.08	4.28	Goethite
10	96.28	2.42	1.07	4.32	Goethite
13	91.38	2.79	1.42	1.58	2.37	4.34	Limonite
14	92.88	1.44	0.40	2.75	2.75	4.36	Limonite
15	89.76	3.37	0.99	1.82	2.81	4.35	Limonite
17	90.25	2.42	0.61	2.26	3.60	4.34	Limonite
11	95.44	2.37	...	0.91	1.38	4.07	Lepidocrocite
12	91.96	2.91	1.38	0.92	2.25	4.12	Lepidocrocite

As seen in the table (Table VII), lepidocrocite has a considerably lower specific gravity than goethite. The value 4.07 derived from No. 11 is probably the better value of the two given, since the substance was purer. The wide variation and difference of the observed specific gravities of goethite and the "limonites" have practically disappeared, but the corrected values of the "limonites" are now slightly higher than the value for goethite. However, it would not be safe to place much reliance on that difference as the corrections applied to most "limonites" are very large (about six times that difference). The assumed mineral compositions are also somewhat uncertain and the correction may therefore not be exact. It would be preferable for that reason to consider that the observed difference in the corrected values of goethite and "limonites" is caused by such errors and, as long as there is no other evidence in favor of their polymorphy, to assume that they are identical. The optical study furnishes much in favor of that assumption (see Table IV).

Specific Gravity of Turgite.—It will be remembered that the dehydration experiments indicated that turgite, on account of the gradual loss of water on heating, could not be a definite chemical compound. Analysis and optical observation showed the variability of this substance and thus supported this conclusion. These facts led to the view that the water in turgite must either be adsorbed or dissolved. Rehydration experiments, however, indicated that this water in all probability was mostly not adsorbed, and this finds further support in specific gravity determinations of turgite. These are given in Table VIII. The values corrected for the small amounts of silica and ferrous carbonate are also given, as well as the corresponding specific volumes.

TABLE VIII.

No. (Tab. I)	% H ₂ O	Sp. gr.		Sp. gr. cor- rected for SiO ₂ and FeCO ₃	Sp. volume	% hem- atite	% goeth- ite
		mineral 25° water	25°				
1	1.30	4.978		5.050	0.198	87	13
2	4.12	4.607		4.648	0.215	59	41
3	4.68	4.670		4.730	0.211	53	47

If the water is adsorbed the specific volume of turgite should be very nearly the sum of the specific volumes of

its components, *i. e.*, ferric oxide and water. In fig. 5 the broken line connects the specific volume of hematite (specific gravity 5.2) and water, and it is seen that this line greatly deviates from the points experimentally found. The solid line in the same figure, which connects the specific volumes of hematite and goethite, however, approaches these points very closely.⁴⁴ This tends to indicate that turgite is essentially a solid solution of ferric oxide (hematite) and ferric oxide monohydrate (goethite). All other evidence at hand is in favor of this assumption.

FIG. 5.

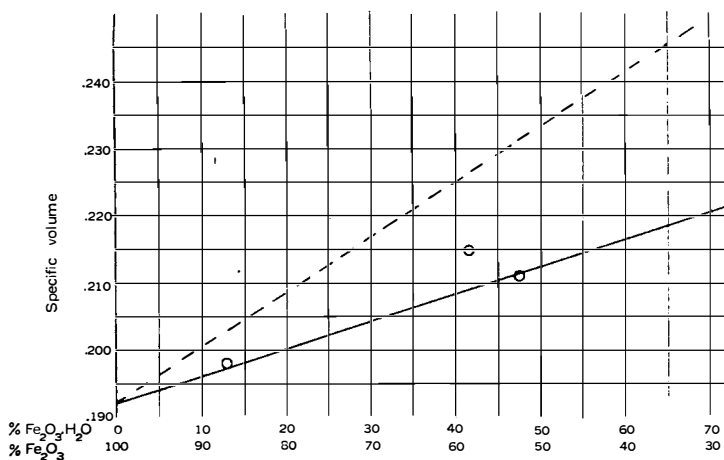


FIG. 5. Specific volumes of turgites. The solid line connects the specific volumes of goethite and hematite, while the broken one connects those of hematite and water.

Some Observations Concerning the Relative Stability of the Hydrated Ferric Oxides.

The questions that arise as a result of the present investigation concern the stability relation of the two forms of ferric oxide monohydrate, and the conditions of their formation, as well as of the solid solution. While

⁴⁴ The specific volume of No. 2 is somewhat higher and lies closer to the line connecting the specific volume of hematite and lepidocrocite. In view of the small number of turgite specimens at our disposal, the significance of this could not be ascertained, but it is evident that if, besides the water of solid solution some water in turgite is adsorbed, its specific volume would have a higher value. However, it is experimentally impossible at present to determine in this case the amount of adsorbed water.

no satisfactory answer can as yet be given, the discussion and recording of some observations in this connection may be useful in calling attention to the problems involved.

No thermal or optical indications of a transformation of either lepidocrocite or goethite could be observed on heating them between room temperature and the temperature at which they decompose. The transformation may take place at a different temperature or be very slow and it is not certain whether their relation is enantiotropic or monotropic. The microscopic study of some of our specimens (see p. 346) revealed that it is not uncommon to find lepidocrocite and goethite together, with either as the earlier mineral. It would seem that the conditions of their formation could not have been very different. However, as no crystals of goethite and lepidocrocite have so far been artificially prepared and their solubilities are not known, there is nothing to indicate their stability relation. It is probable that field observations will aid materially in the solution of this problem.

Not only are goethite and lepidocrocite found together, but turgite (the solid solution) may similarly appear with either of them. Pelikan⁴⁵ observed on some Brazilian specimens the formation of turgite on fibrous goethite⁴⁶ and from microscopic observations of their structure he concluded that the turgite could not have been derived by the dehydration of the goethite, but must have been deposited there directly.

Our observations (see description of specimens—lepidocrocite, Siegen, and R. C. 1489) lead us to the same conclusion, i. e., that turgite is not necessarily a dehydration product of goethite or lepidocrocite.

Red and yellow ferric oxides often occur in nature together, and the assumption is frequently advanced that the red ferric oxides are derived from the yellow ones. It has been supposed that in nature gradual dehydration of higher hydrates to some more stable ones or to anhydrous ferric oxide takes place under the influence of salt solutions or by atmospheric weathering.⁴⁷ This theory appeared plausible as long as a series of hydrates was supposed to exist, as it is obviously impossible for several

⁴⁵ Tsch. Mitth., 14, 1.

⁴⁶ Pelikan describes it as limonite.

⁴⁷ Stremme, Zs. prakt. Geol. 18, 18, 1910; Cornu, Zs. Chem. und Ind. d. Kolloide, 4, 285, 1909.

hydrates to be truly stable under any given set of conditions. The evidence presented in this paper as to the existence of only ferric oxide monohydrate and a solid solution of this substance and ferric oxide, however, dispenses of the assumed series of ferric oxide hydrates. The dehydration experiments further indicate that ferric oxide monohydrate is probably stable at any temperature which the earth's surface may normally reach and it is therefore unlikely that in nature the red ferric oxide is derived by the *direct* dehydration of the yellow. It is probable that both red and yellow substances may be formed at ordinary temperatures by somewhat different chemical reactions; both are relatively stable under the conditions usually met with near the earth's surface. No definite statement concerning their stability relation can be made at present and further studies are required for the solution of this problem.⁴⁸

Synthetic and Natural Hydrated Ferric Oxides.

As was previously mentioned, statements concerning the formation of definite crystallized hydrates were reinvestigated by van Bemmelen⁴⁹ and proved by him to be erroneous. The supposed crystals prepared by himself were undoubtedly pseudomorphs after sodium-ferrite and it seems certain that up to the present no synthesis of definitely crystallized hydrated ferric oxide has been suc-

⁴⁸ As mentioned in the beginning of this paper, attempts were made to form crystallized hydrated ferric oxides. Various reactions were tried but only "amorphous" red and yellow substances were obtained; finally the system $\text{Fe}_2\text{O}_3\text{-SO}_3\text{-H}_2\text{O}$ was systematically studied. A paper dealing with this system will soon be published. While this study did not yield all the information that was desired it may be of interest here to mention a few of the results obtained. Yellow hydrated ferric oxide, resembling in its optical and thermal behavior (see fig. 1, No. 24) the natural "amorphous" hydrated ferric oxide, was formed below approximately 120° , while only above that temperature were red hydrated ferric oxide, resembling turgite, and hematite formed. The temperature given may not be exact, as it was not possible on account of slow reaction to establish equilibrium from both sides; however, it seems certain that at lower temperatures only the yellow substance is stable under such conditions. Most of the hydrated ferric oxides thus formed contained considerable amounts of sulphate, which varied with the concentration of the solution and temperature and was proven to be adsorbed and not due to presence of ferric sulphates. The strong adsorptive power of the hydrated ferric oxides—(Biltz, Ber. 37, 3138, 1904 has shown that an adsorption phenomenon is responsible for its use, proposed by Bunsen, as an antidote for arsenic poisoning)—is probably one of the chief causes impeding the formation of crystallized products: the surfaces of the newly-formed nuclei becoming saturated due to adsorption. Another cause is the extremely small solubility of hydrated ferric oxide in pure water.

⁴⁹ Loc. cit.

cessful. The conditions of formation of hydrated ferric oxides are, therefore, not known and the numerous attempts to synthesize them produced apparently only substances of an indefinite composition, which gave rise to the idea of the existence of a large number of hydrated compounds. In regard to these synthetic products one fact, however, stands out more definitely, and that is that they were either red or yellow. Van Bemmelen⁵⁰ investigated the behavior of these hydrated ferric oxides and found their composition to vary considerably with the surrounding conditions. According to prevalent ideas he called the red and the yellow substances colloids and believed that as such they were not definite compounds and therefore could not essentially differ from one another. Our present knowledge, however, shows that colloids are not particular chemical substances or a distinct form of the substance, as was previously thought, but that any substance under certain conditions can be made to have properties characteristic of colloids; the term colloid, therefore, does not characterize the substance as such, but only indicates properties which are due to a certain condition of the substance. It is of interest now that van Bemmelen noticed a certain difference in the behavior of the red and yellow substances. He found that between 50° and 200° the latter held its water much more tenaciously than the former and that only above about 200° the two did become identical in their composition and behavior. Colloidal properties probably can not be responsible for this difference and in view of the marked difference in color it is more likely that the chemical nature of these two substances is different, although both of them may possess similar colloidal properties due to their physical condition. Fischer⁵¹ tried to verify this assumption and found that on dehydration the yellow synthetic substance behaves similarly to the natural "limonites" and at about 200° changes its color and becomes red. We were able to confirm the observation that the yellow synthetic substance behaves like a hydrated compound; in fig. 1 (No. 24) the dehydration curve of a yellow hydrated ferric oxide (formed by the hydrolysis of a dilute solution of ferric sulphate) is given and its similarity with the monohydrates of ferric oxide is readily seen. The optical properties of such

⁵⁰ Loc. cit.

⁵¹ Loc. cit.

preparations are similar to the natural "amorphous" hydrated ferric oxides, which were found to be from a chemical standpoint essentially a monohydrate of ferric oxide, and in all probability the two are identical. The synthetic yellow preparations present then the same possibilities in respect to their nature as those discussed in connection with the natural "amorphous" hydrated ferric oxides, *i. e.*, they ultimately may be found to be either goethite or lepidocrocite or isotropic ferric oxide monohydrate.

As to the synthetic red substance van Bemmelen⁵² proved by careful dehydration experiments that it was not a hydrate of ferric oxide, and concluded that the water it held was adsorbed. The latter may be true but it is also possible that these red substances are partly a solid solution of ferric oxide and ferric oxide monohydrate, analogous to turgite.⁵³ Due to the extreme fineness of such preparations they undoubtedly adsorb a considerable amount of water; some of the water, however, may be accounted for by the solid solution mentioned. To determine whether water is held only in one or both the ways just indicated is very difficult, owing to the character of the material, and is certainly impossible by dehydration experiments alone. Both possibilities must therefore be considered.

Since only "amorphous" substances have been prepared artificially no strict comparison of these preparations with the natural crystallized hydrated ferric oxides can be made. However, as the result of the present investigation, a certain analogy in their chemical composition can readily be seen: in both cases ferric oxide monohydrate is probably the only definite compound and it is likely that in both cases solid solutions of this compound and ferric oxide exist.

Description of Specimens.

GOETHITE.

Goethite, Negaunee, Michigan. (N. M. 84970).—The ends of two prismatic crystals were measured goniomet-

⁵² *Zs. anorg. Chem.*, 20, 185, 1899.

⁵³ Recently H. W. Foote and B. Saxton (*J. Amer. Chem. Soc.*, 38, 588, 1916; 39, 1103, 1917) attempted to determine the condition in which water exists in precipitated hydrated ferric oxide by observing volume changes on freezing such preparations. They came to the conclusion that it must be essentially a case of solid solutions.

rically. One, from excellent faces e , d , m , gave the ratios $a:b:c = 0.928:1:0.604$; the second, although giving good signal from faces p , e , d , m , b , gave less satisfactory axial ratios ($a:b:c = 0.931:1:0.605$) because two of the pyramid faces were rotated toward a 40' from their true position over m . Near the base of each crystal was a compact group of small crystals in sub-parallel positions. Uniaxial at 610 to 615 $\mu\mu$, at longer wave-lengths the optic plane is parallel to the elongation. $\alpha(\text{Na}) = 2.260 \pm 0.005$, $\beta(\text{Na}) = 2.393 \pm 0.005$, $\gamma(\text{Na}) = 2.398 \pm 0.005$. Absorption increases abruptly near 550 $\mu\mu$ as short wave-lengths are approached.

Goethite, Cornwall, England.⁵⁴—Coarse blades which have $\beta(\text{Na}) = 2.39_4$ and $\gamma(\text{Na}) = 2.40_0$. Uniaxial near 610 $\mu\mu$. Dispersion of $\gamma(\text{Na}) - \gamma(\text{Li}) = 0.60$.

Goethite, Florissant, Colorado.⁵⁴ (N. M. 84940). Uniaxial at 616 to 620 $\mu\mu$.

Goethite, Příbram, Bohemia, variety Sammetblende.—Slender separate filaments like the nap of velvet. The filaments, although only a few μ in diameter, are clearly made up of small, nearly parallel, fibers or blades elongated $\perp a$. Some filaments show the interference colors characteristic of goethite but interference figures (which were not very satisfactory) indicated the optic plane parallel to the elongation, and a slowly decreasing optic angle (toward blue). At 600 $\mu\mu$ $2E = \text{about } 80^\circ$.

$\gamma(\text{Na}) = 2.36_0$, $\beta(\text{Na}) = 2.35_0$, $\alpha(\text{Na}) = 2.23_5$. Dispersion $\alpha(\text{Na}) - \alpha(\text{Li}) = 0.040$.

Goethite, labelled limonite, Diamond Hill, Rhode Island.⁵⁵ (N. M. 17879.) The specimen consists of radial-fibrous aggregates which break radially with glistening surfaces. A bladed to fibrous structure is revealed by the microscope, and interference colors like goethite appear in some grains. These grains are uniaxial at 575 to 590 $\mu\mu$, and have $2E$ at 675 $\mu\mu$ and at 546 $\mu\mu$ 90° to 120° , or $2V = 35^\circ$ to 40° . For these grains $a = 2.24$ and both β and $\gamma = 2.37$; a is less absorbed. Dispersion $\gamma(\text{Na}) - \gamma(\text{Li}) = 0.053$.

Goethite, Brazil.⁵⁵ (N. M. 80862.) Botryoidal and stalactitic masses break radially with semi-lustrous surfaces. Relatively few grains in a crushed sample resemble goethite. These are nearly uniaxial at 575 $\mu\mu$, and have variable refractive indices: a , about 2.23, β

⁵⁴ Analyzed, see Table I.

⁵⁵ Analyzed (Table I).

about 2.32, γ about 2.35. Material which is more fibrous has α about 2.21 and β and γ about 2.31.

Goethite (labelled xanthosiderite), Neudorf, Germany.⁵⁵ (N. M. 84270.) Radial-fibrous, decidedly yellowish, interbanded with quartz. Microscopic fragments very cloudy with very minute inclusions or pores—which accounts for yellow color. γ near 2.37, β near 2.33, α near 2.27, all variable.

Goethite (labelled xanthosiderite), Ironwood, Michigan.⁵⁶ (Holden—K.)—Long fibers, yellow, translucent in microscopic grains, becomes slowly saturated with immersion liquids and thus becomes transparent. Its yellow color in mass is evidently due to invisible pores. γ varies around 2.33 and α around 2.25, as measured on material saturated with these immersion liquids.

Fibrous goethite.—A number of specimens marked “limonite” have the following characteristics in common: in the mass dark yellow-brown; breaking in radial splinters, which are transparent microscopically, and behave much like an optically positive mineral with prismatic cleavage. In some specimens lack of strict coincidence of the prismatic axis of small groups of fibers caused slight variation in the measured refractive indices. Other larger variations such as would result from structures, described on p. 320, or from lack of chemical homogeneity amounted usually to less than $\pm .02$. Table IX shows other optical properties of these specimens. The values given represent as nearly as could be determined the bulk of the material, taking account of observed variations. Absorption of light in the two principal directions was almost identical when determined in a liquid of intermediate refractive index; perceptible differences showed $\gamma > \alpha$.

TABLE IX.

Designation	γ	α	Remarks
*Chatfield, Conn., N.M. 17302	2.26	2.18	Very homogeneous.
N.M. 13972 _a	2.24	2.16	Variable indices
*Polevskoi, Urals. N.M. 40352	2.24	2.16	
*N.M. Specimen A.	2.23	2.14	
*Moselem, Pa., from E. T. Wherry	2.22	2.14	} γ distinctly more absorbed
*N.M. 46746	2.17	2.09	
N.M. 14116	2.23	2.14	
N.M. 83867	2.21	2.13	
From a geode, E. T. Wherry	2.20	2.13	

* Analyzed, see Table I.

⁵⁶The sample analyzed (Table I) labelled “goethite Mich.” was similar optically.

Pseudomorph after pyrite, Louisa County, Virginia (from Prof. Holden).—Felted fibers of goethite having γ near 2.27, and α near 2.20. Small amounts of felted grains of turgite are scattered irregularly through the brown ore.

Fibrous goethite on and under lepidocrocite, Rossbach, Germany.—Small hemispherical radial-fibrous aggregates on lepidocrocite scales, $\gamma = 2.26 - 2.28$, $\alpha = 2.18 - 2.20$. The scales grew upon fibrous goethite having γ and $\beta = 2.32 - 2.29$, $\alpha = 2.18 - 2.19$.

Fibrous goethite under lepidocrocite, Müsen, Germany.—Two structures are apparent: (1) the fibrous form cigar-shaped bundles; (2) these bundles are arranged in sub-parallel to radiating groups which do not extinguish well; γ about 2.28, $\alpha = 2.16 - 2.18$.

Fibrous goethite, R. C. 1489. Iron Mountain Mine, California. (From Prof. Graton).—Fibrous, yellowish layers in the walls of a vug containing residual sulphides. This is remarkable because microscopic splinters have (1) what appears to be very different absorption for light in the two principal directions and the character of the absorption is the reverse of that in all other specimens observed, that is, is greatest across the fibers; (2) great porosity; (3) when pores are filled with liquid having n about 2.0, apparent homogeneity when seen in light vibrating parallel to the length of the fibers and non-homogeneity across the fibers. In the latter position the structure appears fibrous, with the diameter of the fibers about 1μ . All three characteristics would appear in structures somewhat coarser than those described under goethite above. The anomalous absorption would then be explained by the lateral diffusion of light at the comparatively large surfaces between differently oriented goethite fibers. The apparent refractive indices of this material are decidedly lower than for any other fibrous goethite examined; $\gamma = 2.11$, α (which could not be determined accurately) is about 2.05.

LIMONITE.⁵⁷

1206 Cananea, New Mexico.⁵⁸—Transported ore in vug, outside hard. The earthy ore within and the hard crust

⁵⁷ See general description, p. 321. The first five of these specimens were collected by Prof. L. C. Graton, 1914, and the occurrences are given as described by him.

⁵⁸ Analyzed, Table III.

both made up of minute doubly refracting splinters with n about 2.08.

R. C. 701, Shasta County, California,⁵⁹ Analysis No. 20.—Gossan above ore body. Concentric but not readily separable layers of different n , double refraction about 0.03 in some parts, n about 2.09 (varies between 2.13 and 2.06).

R. C. 501, Mammoth Mine, Shasta County, California,⁵⁹ Analysis No. 21.—Gossan surrounding pyrite. Hardened clot-like masses with only traces of double refraction, $n = 2.00$ to 2.06. Cracks are coated with a thin film of *red material* showing no double refraction and having $n = 2.2$ to 2.3. Out of specimens from about 25 different occurrences of brown ores this is the only one having red material that did *not resemble turgite*.

1255, Holbrook Mine, Bisbee, Arizona,⁵⁹ from the 100-foot level.—Irregular ropy to platy open structure with glazed surfaces resembling the stalactitic limonite of Specimen D (see below). Layered structure conspicuous under the microscope, double refraction very marked (max. 0.04), $n = 1.99$ to 2.07. Alternating with the brown ore layers are interrupted layers of *turgite* amounting to 5 to 10% of the bulk of the material.

R. C. 683, Shasta County, California,⁵⁹ Analysis No. 23.—A botryoidal mass from a mine dump, separable layers having strong double refraction and n varying between about 2.01 and 2.06.

Oriskany Mines, Specimen D.⁶⁰—Stalactitic limonite from Botetourt County, Virginia. A porous lace-work of small stem-like filaments, irregularly double refracting, contains spherules of *turgite* in interrupted layers, n mostly < 2.06.

V 412, Wythe County, Virginia.⁶⁰—Residual ore from weathering of Shenandoah limestone; contains several per cent of red spherulitic granules mostly less than 5μ in diameter, having refractive index 2.4 and strong double refraction like *turgite*.

LEPIDOCROCITE.

N. M. 81909, Easton, Pennsylvania.—Micaceous, orange red, on fibrous goethite;

$$\gamma(\text{Na}) = 2.515; \gamma(\text{Li}) = 2.425; \beta(\text{Na}) = 2.20; \alpha(\text{Na}) = 1.935.$$

⁵⁹ Analyzed, Table III.

⁶⁰ From a series of selected specimens presented to us by Professor R. J. Holden, Virginia Polytechnic Institute.

A second analyzed specimen from the same locality consisted of scales set edgewise and closely aggregated, on fibrous goethite.

Roszbach, Germany.—Scattered erect red scales attached on base to fibrous goethite, or in loose rosettes. The bounding edges correspond to forms $\{102\}$, $\{001\}$, $\{100\}$, but the outlines are usually considerably rounded. Fig. 1.

Müsen, Germany.— $\gamma(\text{Na})$ slightly >2.50 . Like Roszbach but $\{103\}$ is a prominent bounding form or edge. $\beta(\text{Na}) =$ or <2.20 . Absorption for γ increases rapidly from 570 to $530\mu\mu$ and beyond, and from 640 to beyond $750\mu\mu$; for β absorption is nearly constant between 750 and $560\mu\mu$ and this increases rapidly to $520\mu\mu$ and beyond; for α no appreciable absorption except in blue and violet.

Siegen, Germany.—Compact aggregates of scales upon and under turgite. γ near 2.51.

N. M. 14118, near Lake Superior, Michigan.—Called goethite; closely aggregated erect scales in a layer on fibrous goethite. $\gamma(\text{Na}) = 2.51_5$, $\alpha(\text{Na}) = 1.941$, $\alpha(\text{Li}) = 1.92_2$. Scales of such thickness that $\beta = 8k$ (Ridgway's colors) have $\gamma = 7n - 9n$; also $\beta = 15i$ and $\gamma = 14k$; also $\beta = 23h$ and $\gamma = 23h$ to i .

R. C. 1489, Iron Mountain Mine, California.—Bladed to fibrous lepidocrocite lining a vug containing residual sulphides, on fibrous goethite and turgite; $\alpha = 1.92$.

TURGITE.⁶¹

Turgite, New York,⁶² No. 18330.— $\alpha(\text{Na}) = 2.58$, $\beta(\text{Li})$ and $\gamma(\text{Li}) = 2.55$; elongation of splinters negative, $\alpha(\text{Li}) = 2.46$.

No. 65269,⁶²—Refractive indices variable but about $\alpha(\text{Na}) = 2.56$, $\beta(\text{Li})$ and $\gamma(\text{Li})$ about 2.52; elongation negative. $\alpha(\text{Li}) = 2.43$.

Legal Tendre Hill, New Mexico. No. 48228.—Breaks irregularly and contains cavities (large and small); extinguishes very obliquely; refractive indices like No. 18330. Probably pseudomorphic after some fibrous mineral having oblique extinction.

Rockingham County, Virginia.⁶² No. 17968.— $\alpha(\text{Na}) = 2.46$, $\alpha(\text{Li}) = 2.38$, elongation negative.

Germany,⁶² "Hematite."—Fibrous, elongation *posi-*

⁶¹ See p. 323.

⁶² Analyzed, Table I.

tive, extinction parallel, contains many thin quartz veins; fibers cloudy and only translucent to feebly transparent; refractive indices variable, but the lowest is about 2.70 (Li). This is like a partly dehydrated fibrous goethite. (Are the quartz veins in shrinking cracks caused by dehydration?)

Cumberland, England.⁶³—Like the specimen from Germany, but is covered with and contains many minute veinlets filled with specular hematite.

Recapitulation.

The work of the foregoing pages proves rather conclusively that no *series* of hydrates of ferric oxide exists among the natural minerals. The only existing hydrate is ferric oxide monohydrate. This substance occurs in nature in two polymorphic forms—goethite and lepidocrocite, and in an “amorphous” condition—limonite. The two crystallized forms are contrasted as follows:

Goethite.—Orthorhombic, $a:b:c = 0.91 : 1 : 0.602$; density (grams per cc.) 4.28 ± 0.01 ; $\alpha = 2.26$, $\beta = 2.394$, $\gamma = 2.400$; streak, dull orange-yellow; pleochroism faint.

When crystallized in dense aggregates of thin blades and fibers enclosing much adsorbed and capillary water it has commonly been called limonite; however, sufficient proof is now given to show that such crystallized material is really goethite.

Lepidocrocite.—Orthorhombic, $a:b:c = 0.43 : 1 : 0.64$; density (grams per cc.) 4.09 ± 0.04 ; $\alpha = 1.94$, $\beta = 2.20$, $\gamma = 2.51$; streak, dull orange; pleochroism very strong.

The name *limonite* is retained for material which appears to be essentially isotropic ferric oxide monohydrate with adsorbed and capillary water. However, this substance should not be considered a distinct form of ferric oxide monohydrate, as the real nature of such “amorphous” substances is still uncertain.

The fibrous mineral *turgite* is variable in composition and considerable evidence is given that it probably represents solid solutions of goethite with hematite together with enclosed and adsorbed water.

The genetic conditions of the hydrated ferric oxides, and the stability relation of the two monohydrates, are unknown.

⁶³No. 1027 of R. B. Sosman and J. C. Hostetter in Trans. Am. Inst. Mining Engineers, 58, 427, 1917.

No definitely crystallized synthetic hydrated ferric oxide has up to the present been prepared. However, it seems certain that only two distinct types of "amorphous" hydrated ferric oxide exist: one yellow and the other reddish-brown. The yellow is apparently essentially ferric oxide monohydrate, while the reddish-brown substance may hold its water in either a dissolved or an adsorbed condition (or both). Thus the synthetic and the natural hydrated ferric oxides exhibit, chemically, great similarity.

Geophysical Laboratory, Carnegie Institution of Washington,
Washington, D. C., January, 1919.