

HEMATITE-GOETHITE RELATIONS IN NEUTRAL AND ALKALINE SOLUTIONS UNDER PRESSURE

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ABSTRACT

A series of experiments on the stability of goethite ($\alpha\text{-FeO}\cdot\text{OH}$) shows that it decomposes to hematite ($\alpha\text{-Fe}_2\text{O}_3$) in neutral solutions above $125 \pm 15^\circ\text{C}$. and in alkaline solutions above $165 \pm 5^\circ\text{C}$. at a pressure near the vapour pressure of the solutions. Increase of pressure raises the decomposition temperature of goethite less than 5°C . per 1000 atmospheres, up to 2000 atmospheres. The possible use of the pressure insensitive pair, hematite-goethite, in geothermometry is discussed.

INTRODUCTION

A considerable amount of experimental work has been done on the stability relations of the ferric oxides at various temperatures, with especial reference to the occurrence of hematite ($\alpha\text{-Fe}_2\text{O}_3$), the less stable ferro-magnetic maghemite ($\gamma\text{-Fe}_2\text{O}_3$), and the polymorphic monohydrates, goethite ($\alpha\text{-Fe}_2\text{O}_3\cdot\text{H}_2\text{O}$ or $\alpha\text{-FeO}\cdot\text{OH}$) and lepidocrocite ($\gamma\text{-Fe}_2\text{O}_3\cdot\text{H}_2\text{O}$ or $\gamma\text{-FeO}\cdot\text{OH}$). Posnjak and Merwin (1919) showed in the first systematic study of ferric oxide and its hydrates that the monohydrate was the only one that can be considered to be a compound. Other hydrous varieties are turgite, which was shown to be hematite plus adsorbed water, and limonite, to be goethite with adsorbed water. Maghemite occurs as an oxidation product of magnetite, or as a product of dehydration of lepidocrocite. Maghemite is transformed at high temperatures into the much more stable hematite. No demonstration of the transformation of lepidocrocite into goethite appears to have been published. The synthesis of another monohydrate, *in vitro*, was described by Weiser and Milligan (1935) who called it $\beta\text{-Fe}_2\text{O}_3\cdot\text{H}_2\text{O}$ (or $\beta\text{-FeO}\cdot\text{OH}$). On boiling it is dehydrated into hematite. Thus the ultimate product of heating any one of the three polymorphic monohydrates is hematite. In the present study only hematite and goethite will be considered.

Posnjak and Merwin (1922) succeeded in synthesizing crystalline goethite in the system, $\text{Fe}_2\text{O}_3\text{-SO}_3\text{-H}_2\text{O}$. It resembled microscopically natural fibrous goethite and appeared "only below the temperature of 130°C . in individual or clustered yellow spherical grains less than 0.01 mm. in diameter." All of the preparations from which the monohydrate was obtained were in the furnace "for several weeks and had become compact and granular. The precipitate which formed when the tubes were first filled were flocculated and showed no evidence of crystallinity.

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TABLE 1. SUMMARY OF PREVIOUS WORK

Reference	Container	Reaction	Starting Materials	Nature of Medium
Posnjak & Merwin (1919)	Open weighing glasses	Decomposition	Natural bladed goethite	Dried air
			Natural fibrous goethite	Dried air
			Microcrystalline "limonite"	Dried air
Posnjak & Merwin (1922)	Sealed Jena tubes $\frac{1}{2}$ full	Decomposition	Ferric sulphate	Very dilute solutions
Tunell & Posnjak (1931)	—	Decomposition	Natural goethite	N/10 HCL solution
Böhm, J. (1925)	—	Boiling	Amorphous hydrated ferric oxide (brown gel)	H ₂ O or solutions of KCl or NH ₄ Cl
	Autoclave	Aging	Brown gel	2N KOH
Katsurai & Watanabe (1930)	Autoclave	Decomposition	Gelatinous Fe (OH) ₃	Very dilute HCl solu- tion
	Autoclave	Hydrolysis	FeCl ₃ solution	0.5 N 0.25 N 0.2 N 0.1 N
Hüttig & Garside (1929)	—	Decomposition	Natural Lepidocrocite	—
			Natural Goethite	—
Gruner (1931)	Sealed glass tubes	Decomposition	Natural Goethite	Distilled water
Williams & Thewlis (1931)	—	Decomposition	Artificial Lepidocrocite	—
Nicholas, Kraemer & Bailey (1932)	—	Hydrolysis	Ferric chloride	0.005 M 0.037 M
Weiser & Milligan (1935)	—	Aging	Fresh amorphous brown gel	Distilled water
		Rapid hydrolysis	Ferric salts	Water solution
		Slow hydrolysis	Ferric chloride	Water solution
		Slow hydrolysis	Other Ferric salts	Water solution
		Decomposition	FeO · OH	Dried air

pH of Medium	Temp. ° C.	Pressure	Length of Experiment	Products	Identification
—	210-220	—	A number of weeks	Hematite	X-ray
—	150-215	—	A number of weeks	Hematite	X-ray
—	145-155	—	A number of weeks	Hematite	X-ray
Acid	up to 130	Vapor pressures	8 to 10 weeks	Goethite	X-ray
Acid	About 100	—	"A few weeks"	Hematite	X-ray
Acid	About 100	—	—	Hematite	X-ray
Alkaline	150	—	Nearly 2 hours	Goethite	X-ray
Acid	150	—	1 hour	Hematite	X-ray
Acid	120	—	1 hour(?)	Hematite	X-ray
Acid	140 & 150	—	1 hour	Hematite	X-ray
Acid	160	—	1 hour(?)	Hematite	X-ray
Acid	180-185	—	1 hour(?)	Hematite	X-ray
—	240	10 mm.	—	Maghemite	Colour
—	275	10 mm.	—	Hematite	Colour
Neutral	200	Vapour pressures	Over 90 days	Hematite	X-ray
	250				
	275				
—	250-300	—	—	Maghemite	—
	500-600	—	—	Hematite	—
Acid	100	—	1 hour	Amorphous	X-ray
			24 hours	Hematite	X-ray
Acid	100	—	1 hour	Hydrous Fe ₂ O ₃ of unknown identity	
			8 hours	Hematite	X-ray
—	25	—	few weeks	Hematite	X-ray
	near b.p.	—	few hours	Hematite	X-ray
Acid	25	—	—	Hematite	X-ray
Acid	25	—	—	β-FeO · OH	X-ray
Acid	25	—	—	Goethite	X-ray
—	150-184	—	—	Hematite	X-ray

As heating progressed nuclei formed in the solution, not only within the limits of the tube occupied by the precipitate, but, especially at higher temperatures, above the original precipitate. The nuclei became centers of spherulites which, especially at higher temperatures, grew to determinable sizes or disappeared while larger ones grew."

At the boiling temperature of about 1/10 normal HCl solution, natural goethite was decomposed into hematite in a few weeks (Tunell and Posnjak, 1931). Tunell and Posnjak held that this conversion at practically 100° C. does not conflict with the higher transition temperature in the binary system, $\text{Fe}_2\text{O}_3\text{-H}_2\text{O}$, obtained as a limit in the system, $\text{Fe}_2\text{O}_3\text{-SO}_3\text{-H}_2\text{O}$, since the hematite and goethite fields may overlap more in the system, $\text{Fe}_2\text{O}_3\text{-HCl-H}_2\text{O}$, than in the system, $\text{Fe}_2\text{O}_3\text{-SO}_3\text{-H}_2\text{O}$ and further experimental work on the former system may show the transition temperature to be the same in both systems. Böhm (1925) obtained similar results in pure water or solutions of KCl or NH_4Cl .

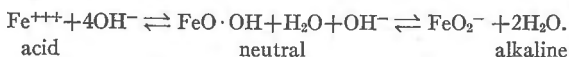
The reactions in the system, $\text{Fe}_2\text{O}_3\text{-H}_2\text{O}$ are extremely slow and are not promptly reversible. Ferric oxide under ordinary conditions apparently cannot be hydrated. Most of the time spent by Posnjak and Merwin (1919) in the dehydration experiments was used to decompose the substance undergoing test. "Decomposition proceeds 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." In experiments made in open weighing glasses with no regard for the pressures, they found that complete decomposition of well crystallized and optically amorphous goethite took place in several cases below 200° C. Dehydration data of Posnjak, Merwin, and other workers are summarized in Table 1.

About 50 experiments by Gruner (1931), some of them over periods of 90 days, in pure water showed that goethite is unstable at 200° C. In no case was complete dehydration obtained but 2.5 to 3% of water remained with the product.

The remainder of the experiments summarized in Table 1 were done over periods of the order of an hour and all but one were carried out either in pure water or acid solutions. The exception is that of Böhm (1925) who obtained goethite by heating amorphous hydrated ferric oxide in 2N KOH solution in an autoclave at 150° C. for nearly two hours. Katsurai and Watanabe (1930) also made autoclave runs and used FeCl_3 solutions of various strengths to obtain hematite (rouge) at as low as 120° C. by hydrolysis of 0.5N FeCl_3 . They made hematite from gelatinous ferric hydroxide in very dilute HCl solution by heating at 150° C. for one hour.

The qualitative effect of pH on the decomposition of iron oxide monohydrate is shown in Table 1. In acid solutions the decomposition tempera-

ture is near 100° C., and in alkaline solutions is above 150° C. The increase in the decomposition temperature in acid solutions up to approximately 130° C. in neutral solutions is summarized by Tunell and Posnjak (1931). The exact relations, however, are uncertain. In acid and neutral solutions, iron oxides are in equilibrium with the solutions containing ferric iron ions (Fe^{+++}), but in alkaline solutions, they can be considered to be in equilibrium with solutions containing ferrate ions (FeO_2^-), or some derivative of ferrate ions. The equilibrium would then be summarized as follows:



If the iron oxide monohydrate has a hydroxyl group in the unit cell, *i.e.*, its formula is $\text{FeO} \cdot \text{OH}$, it should be more stable in alkaline solutions. Bragg (1937) suggested on the basis of Ewing's work that the formula of goethite is HFeO_2 while that of lepidocrocite is $\text{FeO} \cdot \text{OH}$. If this is correct, then lepidocrocite should be more stable in alkaline solutions. However, Peacock recently (1942) gave the hydroxide form to both monohydrates: goethite, $\alpha\text{-FeO} \cdot \text{OH}$ and lepidocrocite $\gamma\text{-FeO} \cdot \text{OH}$. It would then appear that both forms of monohydrate are more stable in alkaline than in acidic solutions, but their relationship with each other is still unknown.

The effect of pressure as an independent variable of the hematite-goethite equilibrium has not yet been systematically studied. In two of the experiments listed in Table 1, by Hüttig and Garside (1929), the pressure was measured, but it was only 10 mm. in each case. In other cases the pressures were either vapor pressures or not reported at all. Gruner (1931) pointed out that the molecular volumes of hematite, water, and goethite are 30.38, 18.00, and 41.58, respectively and he suggested that the decomposition point of goethite would be raised by higher pressures.

It was concluded that further data on the decomposition temperature of goethite would be useful, especially at elevated pressures, and including alkaline as well as neutral water solutions in the system.

EXPERIMENTS

A summary of the experimental data and results is shown in Table 2. The first six experiments were made in a one-litre Cook autoclave. In all but one of these six runs, the pressure was the vapour pressure of the closed $\text{Fe}_2\text{O}_3\text{-H}_2\text{O}$ system at the temperature of experiment. In the other autoclave run, nitrogen gas supplied the pressure. Heating was by means of a gas burner and the temperatures were measured with a mercury thermometer. The remaining thirty-one runs were carried out in a pres-

TABLE 2A

Exp. No. (Series Fe)	Bomb Charge					Equilibrium Temperature °C	Calculated Pressure Atm.	Time of Heating
	Iron Oxide Solid			Aqueous Liquid Medium				
	Form	Weight grams	H ₂ O in Iron Oxide %	Composition	Degree of Filling %			
1	Hematite	10.0	—	H ₂ O	80	108 ± 1	1.3	5 hours
2	Goethite	10.0	—	H ₂ O	80	141 ± 1	3.6	24 hours
3	Goethite	10.0	—	H ₂ O	80	140 ± 1	25.0	10 hours
4	Goethite	10.0	—	H ₂ O	80	170 ± 1	7.8	18 hours
5	Goethite	10.0	—	H ₂ O	80	200 ± 1	15.3	18 hours
6	Goethite	10.0	—	H ₂ O	80	227 ± 3	27.6	24 hours
7	Hematite	6.0	12.20	H ₂ O	67	435 ± 1	1500	44 hours
8	Hematite	6.0	12.20	H ₂ O	67	300 ± 1	80	40 hours
9	Goethite	6.0	12.60	H ₂ O	67	215 ± 10	20	36 hours
10	Goethite	6.0	12.60	H ₂ O	83	300 ± 1	1080	3 days
11	Goethite	6.0	12.60	H ₂ O	88	255 ± 1	1130	4 days
12	Goethite	6.0	12.60	H ₂ O	93	205 ± 1	1250	7 days
13	Goethite	6.0	12.60	H ₂ O	91	230 ± 1	1700	7 days
14	Goethite	6.0	12.60	0.1M NaOH	93	227 ± 4	1600	3 days
15	Goethite	6.0	12.60	"	93	210 ± 1	1300	2 days
16	Goethite	6.0	12.60	"	96	270 ± 1	2320	10 hours
17	Goethite	6.0	12.60	"	96	192 ± 1	1400	3 days
18	Goethite	6.0	12.60	"	93	205 ± 1	1200	2½ days
19	Goethite	6.0	12.60	"	93	196 ± 3	1200	2 days
20	Goethite	6.0	12.60	"	91	194 ± 2	600	3 days
21	Hematite from Exp. 13	2.0	1.08	"	91	192 ± 1	600	2 days
22	Goethite	2.0	12.60	"	91	200 ± 2	650	4 days
23	Goethite	2.0	12.60	"	88	195 ± 2	250	5 days
24	Goethite	2.0	12.60	"	91	173 ± 3	250	5 days
25	Goethite	2.0	12.60	"	92	164 ± 2	50	5 days
26	Goethite	2.0	12.60	"	90	171 ± 1	90	7 days
27	Goethite	2.0	12.60	"	98	192 ± 1	1900	6 days
28	Goethite	2.0	12.60	"	99	181 ± 1	2000	6 days
29	Goethite	2.0	12.60	"	100	160 ± 3	1860	5 days
30	Goethite	2.0	12.60	"	100	142 ± 1	1600	7 days
31	Hematite	2.0	11.92	"	100	142 ± 1	1600	6 days
32	Hematite	2.0	11.92	"	99	150 ± 1	1700	7 days
33	Hematite	2.0	11.92	"	95	145 ± 1	500	7 days
34	Goethite	2.0	12.20	"	94	150 ± 1	500	7 days
35	Goethite	2.0	12.20	"	93	159 ± 1	500	6 days
36	Goethite	2.0	12.20	"	93	165 ± 1	500	8 days
37	Hematite	6.0	11.92	"	100	167 ± 1	2000	5 days

TABLE 2B

Exp. No.	Bomb Products			Remarks
	Iron Oxide Solid		H ₂ O in Iron Oxide %	
	Form	Method of Determination		
1	Goethite	X-ray	—	Orange coloured fine-grained solid and solution.
2	Hematite	X-ray	—	Bright red solid.
3	Hematite	colour	—	Bright red solid, hard to filter.
4	Hematite	colour	—	
5	Hematite	colour	—	Bright red solution. Very finely divided solid.
6	Hematite	colour	—	
7	Hematite	colour	0.00	Solution was red. Bright red precipitate.
8	Hematite	colour	1.15	
9	Hematite	colour	6.37	
10	Hematite	colour	1.27	Bright red solid.
11	Hematite and Goethite	colour	0.06	Bright red mass with yellow specks of goethite.
12	Hematite and Goethite	colour	8.09	Yellow solid with red particles of hematite.
13	Hematite	colour	1.08	Temp. rose from 230° to 263° in last 12 hours.
14	Hematite	colour	3.68	Solid is dark red exactly as in natural hematite. Clear solution.
15	Hematite	colour	0.49	Dark red present. Clear solution.
16	Hematite	colour	1.73	
17	Hematite and Goethite	colour	9.80	Yellow product with red specks of hematite.
18	Hematite	tabular crystals	0.41	Mass of red crystalline hematite. Clear solution.
19	Hematite and Goethite	colour	8.36	Yellow solid with very minute red hematite specks.
20	Hematite and Goethite	colour	7.00	Brown mass. Clear solution.
21	Hematite	colour	1.35	Dark red product.
22	Hematite	colour, crystals	2.50	Red crystalline mass. Clear solution.
23	Hematite	colour	0.50	
24	Hematite and Goethite	colour	4.86	Brownish-red product mostly hematite. Few flecks of goethite in bottom.
25	Goethite	colour	11.77	Yellow, same colour as starting solid.
26	Hematite and Goethite	colour	6.12	Pale yellow solution. Top of solids is red but mass is otherwise yellow-brown.
27	Hematite	colour	0.82	Clear solution. Reddish brown mass with yellow lumps.
28	Hematite and Goethite	colour	4.68	Reddish solution. Lumps of original charge coated with red hematite.
29	Hematite and Goethite	colour	—	Red solution. Very fine orange-red residue.
30	Goethite	colour	10.60	Clear solution. Residue all yellow from top to bottom.
31	Hematite and Goethite	colour	8.00	Clear solution. Film of hematite on top of yellow mass. Upper sides of pot and lid show yellow particles.
32	Hematite and Goethite	colour	11.05	Clear solution. Reddish brown mass.
33	Hematite and Goethite	colour	—	Clear solution. Layer of yellow patches on top of brown mass.
34	Goethite	colour	11.50	Solution clear. Product all yellow.
35	Goethite	colour	12.30	Clear solution. Product all yellow.
36	Goethite	colour	11.02	Green solution. Yellowish-brown mass.
37	Hematite	colour, crystals	0.25	Clear solution.

sure bomb which has been described previously (Smith, 1947). The heating was by means of an electrical resistance jacket furnace. The temperatures were measured with a chromel thermocouple and a potentiometer.

All of the experimental runs consisted of adding a weighed amount of prepared iron oxide material to a measured volume of the liquid in the autoclave or bomb, sealing the vessel, bringing the system up to the desired temperature, keeping the system at that temperature for a certain period of time, and finally cooling the sealed vessel back to room temperature.

In the bomb runs, the charge was contained in a graphite pot with lid to minimize the possible formation of magnetite by the action of the solutions on the bomb wall. The inner volume of the graphite pot with the lid on was 82.2 cc. The graphite pot was kept saturated with water between runs.

An indirect method was used to measure the pressure of the system at the maximum temperature of experiment. It was assumed that the liquid phase in the system had the thermal expansion properties of pure water and the pressures for the various degree of filling of the bomb and the experimental temperatures were read directly from a chart showing the relations between specific volume of water, temperature, and pressure, as compiled by Béland (1948).

The runs described in Table 2 can be grouped according to the iron oxide material added to the solution. A brown iron oxide gel was prepared by mixing 10 litres of distilled water, 540 grams of ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, Baker's analysed reagent) and 3 litres of 15N ammonium hydroxide, in that order. A yellow iron oxide gel was made from 225 grams of ferrous chloride (Baker's analysed reagent) in 5 litres of distilled water, to which were added 170 grams of ammonium carbonate in 4 litres distilled water to produce ferrous carbonate, which was then oxidized to the monohydrate by 600 cc. of 3% hydrogen peroxide. After standing overnight, each gel was washed until they gave negative tests with silver nitrate. X-ray powder photographs of them showed the brown gel to be pure hematite and the yellow gel to be pure goethite. A portion of the brown and yellow gels, dried at 105°C ., gave red and yellowish brown streaks, respectively.

The runs described in Table 2 A and B can also be grouped according to the composition of the solution in contact with the iron oxide. The earlier experiments were carried out in pure water, the later ones in 0.1M NaOH solution. The recrystallization and conversion of the iron oxide material added to the charge was found to be very much more rapid in the alkaline solutions.

The brown iron oxide gel (hematite x -ray pattern), left to stand in

water at room temperature (20° – 27° C.) for 2 years, assumed a bright yellow color. It gave the goethite x -ray powder diffraction pattern.

DISCUSSION OF EXPERIMENTAL RESULTS

Our results are in accord with those of Posnjak and Merwin (1919) and of Böhm (1925), in that there is an increase in the decomposition temperature of goethite with increasing pH . By projecting back to negligible pressure on the $t-p$ plot, we believe that in pure water the decomposition temperature of goethite is $125^{\circ} \pm 15^{\circ}$ C., and in 0.1M NaOH

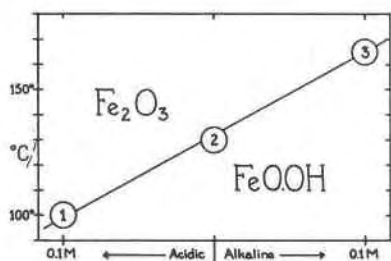


FIG. 1

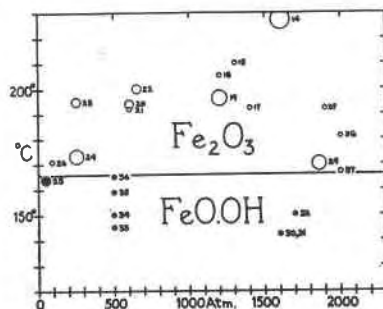


FIG. 2

FIG. 1. The decomposition temperature of goethite in contact with water solution at a pressure of 1–2 atmospheres, as a function of the acidity-alkalinity of the solution. Point 1 is from data of Tunell and Posnjak (1931), Point 2 is from data of Posnjak and Merwin (1922), and Point 3 was located by extrapolating to low pressure from our data.

FIG. 2. The stability field boundary, hematite-goethite, in 0.1 M NaOH solution, as a function of temperature and pressure. The filled circles mean that hematite was converted to goethite, or that goethite was not converted to hematite, and the open circles mean that goethite was converted to hematite, or that hematite was not converted to goethite. The other conditions are described in Table 2, to which the experiment numbers refer.

solution, the decomposition temperature is $165^{\circ} \pm 5^{\circ}$ C. Allowing for the fact that the decomposition point is difficult to locate near neutrality due to the great insolubility of iron oxide in water, the best data has been plotted in Fig. 1. This gives the approximate decomposition temperature of goethite at a low pressure as a function of acidity-alkalinity. Probably the limits of $\pm 0.1M$ free acid and alkali enclose most of the conditions in hydrothermal solutions, and therefore limit the range of the decomposition point at low pressures in nature.

The effect of pressures up to 2000 atmospheres on the decomposition temperature of goethite in neutral and alkaline solutions is of a small order. The decomposition temperature is raised less than 5° C. per 1000 atmospheres pressure in 0.1M NaOH solutions. The experimental points

and the phase boundary in the alkaline solution are shown in Fig. 2.

Since the decomposition temperature of goethite is virtually insensitive to pressures as high as those which would be found in the earth where temperatures near the decomposition point prevail, the goethite-hematite relation can be used in geological thermometry. Normal hydrothermal solutions stable with the rock forming minerals must be neutral to weakly alkaline, so that the decomposition temperature of goethite may be taken with some assurance to be $150^{\circ} \pm 20^{\circ}$ C. in hydrothermal solutions. If such solutions deposit ferric oxide above this temperature, it will be as hematite, and below, as goethite. The stable field of the rare mineral lepidocrocite, is not yet defined.

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