

Studies on the Hydrated Iron Oxides. IV : Iron Oxide Minerals Altered from Magnetite by Weathering

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Iron Oxide Minerals Altered from Magnetite by Weathering*

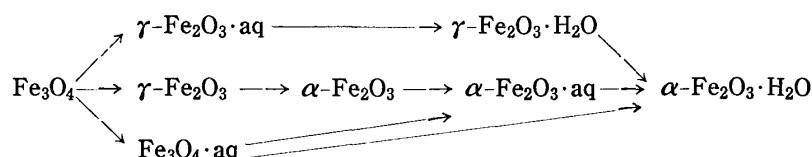
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Synopsis

The alteration process of natural oxidation of magnetite from the capping of magnetite deposits at Takanokura Mine, Fukushima Prefecture may be induced as follows :



The natural oxidation of magnetite from all other deposits in Japan may be taken to have followed some part of the above formula. In this report, the mineralogical properties of some minerals altered from magnetite, namely, hydrous magnetite, maghemite and goethite, are also described.

I. Introduction

Many works⁽¹⁾⁽²⁾ have been reported on the natural oxidation of magnetite. In most cases, however these reports contain only fragmentary informations on the subject and are not adequate enough to reveal the general alteration processes of magnetite. Besides, there are as yet many points to be elucidated on the minerals formed by alteration of magnetite.

The present author have been observing the natural oxidation of magnetite at the outcrops of deposits in many parts of Japan and studying the process of oxidation of magnetite and the mineralogical properties of its oxidation products.⁽³⁾ In this paper, the author will present the results of such studies made on ores from Takanokura Mine as the representative samples.

II. Intergrowth between magnetite and its alteration products

Takanokura Mine is located in the Abukuma Mountains about 13 km west of Haranomachi Station on the Jōban Line, Japanese National Railway. The contact metasomatic magnetite deposits of this mine have developed in a lenticular form at the contact zone of palaeozoic limestone and schistosed biotite-granite.

* The 103rd Report of the Research Institute of Mineral Dressing and Metallurgy.

(1) J. W. Gruner, *Econ. Geol.*, **21** (1926), 375.

(2) H. G. Backmann, *N. Jb. Miner., Mh.*, H. **6** (1954), 131.

(3) M. Nambu, *Bull. Res. Inst. Min. Dress. Met.*, **11** (1955), 35.

The main ore mineral consists of magnetite, besprinkled with small quantities of pyrrhotite, pyrite and chalcopyrite. The skarn mineral mainly consists of garnet, accompanying more or less diopside, epidote, green hornblende, calcite and quartz.

The deposits show marked limonitization at the outcrops, and frequently intermediate products between magnetite and limonite, including maghemite, hydrous maghemite, hematite, hydrous hematite, lepidocrocite and goethite, have been formed.

Maghemite is found developed around magnetite and along its cracks, as shown in Fig. 1-A. Under ore microscope, it is seen in a blue-grayish tint and can be

readily distinguished from hematite and magnetite.

Hematite is developed around magnetite and on its crystal faces (100), (110), (111), and (211). Microscopically, most of it is found to have been produced by direct oxidation of magnetite, but a part of it is found to have been formed by alteration of maghemite changed from magnetite, as shown in Fig. 1-A.

Hydrous hematite is frequently found to have developed covering hematite in thin films, as shown in Fig. 1-B. Its polished surface is found to be disjointed. The properties of this mineral have been reported previously,⁽⁴⁾ and the author will not repeat the description here.

Maghemite is usually altered into lepidocrocite through filmy

intermediate products (1-C), which are too small for examination of their physical and chemical properties in detail, but since they show a very close resemblance to maghemite under microscope, we may well assume them to represent intermediate products of hydrous maghemite.

In some rare cases, a part of magnetite alters into hydrous hematite or goethite. (Fig. 1-D) Hydrous magnetite has already been studied thoroughly by K. Starke,⁽⁵⁾ who says that a part of the oxygen in magnetite is substituted by OH and a part of F^{++} located at 16C is vacant, thus forming this hydrous type.

The final oxidation product of magnetite is goethite or hydrous goethite which is found at the margin or in the cracks of the one.

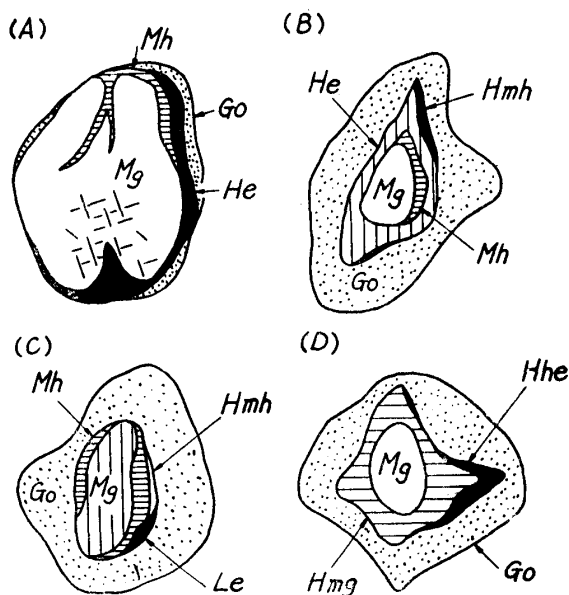


Fig. 1. Microscopic sketch of polished section of limonitized magnetite, $\times 200$.

- Mg : Magnetite
- Hmg : Hydrous magnetite
- Mh : Maghemite
- Hmh : Hydrous maghemite
- He : Hematite
- Hhe : Hydrous hematite
- Go : Goethite
- Le : Lepidocrocite

(4) M. Nambu, Sci. Rep. RITU, A-9 (1957), 534.

(5) K. Starke, Z. Phys. Chem., 42B (1939), 159.

III. Mineralogical properties of magnetite, hydrous magnetite, maghemite and goethite

1. Chemical composition

The results of chemical analysis of these minerals are shown in Table 1. The other intermediate products, besides being too small in quantity, contained too much impurities for analysis.

Table 1. Chemical analyses of magnetite, hydromagnetite, maghemite and goethite.

	Magnetite	Hydromagnetite	Maghemite	Goethite
	Wt.%	Wt.%	Wt.%	Wt.%
Fe ₂ O ₃	68.95	73.81	92.06	82.95
FeO	30.82	21.20	3.12	tr
SiO ₂	0.03	0.15	1.22	2.16
TiO ₂	tr	—	—	tr
Al ₂ O ₃	0.19	0.50	0.31	0.57
MnO	tr	0.02	—	tr
MgO	tr	0.05	—	tr
CaO	0.02	0.10	—	0.39
S	tr	—	—	0.08
P	tr	—	—	tr
H ₂ O(+)	0.01	4.01	0.38	10.98
H ₂ O(-)	0.03	0.62	2.08	2.30
Total	100.05	100.46	99.75	99.75

The composition of magnetite was approximately in agreement with the theoretical composition. Hydrous magnetite was found to contain ca. 9 per cent less ferrous oxide but 5 per cent more ferric oxide than magnetite, and about 4 per cent of H₂O(+). These results clearly reflect the origin of hydrous magnetite. In maghemite, ferrous oxide occupies only 3.12 per cent, the majority consisting of ferric oxide. This is a compound closely approaching the end member γ -Fe₂O₃ of the Fe₃O₄- γ -Fe₂O₃ system.

2. X-ray powder data

The data of X-ray powder patterns of maghemite and goethite are given in Tables 2 and 3 respectively. The three kinds of patterns shown in Table 2 are all

Table 2. X-ray powder patterns of magnetite, hydromagnetite and maghemite.

(hkl)	Magnetite		Hydromagnetite		Maghemite	
	d(Å)	I	d(Å)	I	d(Å)	I
220	3.00	w	3.01	vw	2.99	vw
003	2.79	vw	2.80	vw(b)	2.77	vw
311	2.54	vs	2.56	vs	2.53	vs
400	2.10	m	2.11	w	2.09	w
422	1.75	vw(b)	—	—	1.75	vw(b)
511, 333	1.62	m	1.63	w	1.62	w
440	1.49	s	1.51	s	1.48	vs
145	1.28	vw	1.29	vw(d)	1.27	vw
335	1.26	w	1.26	w	1.25	w
137, 355	1.09	m	1.10	m	1.08	m
800	1.05	w	1.05	vw	1.04	w

Table 3. X-ray powder patterns of goethite.

(hkl)	d(Å)	I
110	4.22	vs
—	3.89	w(b)
130	2.71	m
111	2.47	vs
121	2.25	vw
140	2.19	vw
230	1.91	vw
141	1.80	vw
240	1.71	s
160	1.55	m
—	1.50	w
080	1.44	w
132	1.31	w
302	1.12	w

of inversed spinel type, but they show some difference in their interplanar spacings. There have been a few studies⁽⁶⁾ on the diminution of the lattice constant with the increase of vacancies of Fe^{++} during the change of magnetite into $\gamma\text{-Fe}_2\text{O}_3$, and the specimens in this study show the same tendency. The lattice constant of hydrous magnetite, however, is larger than that of magnetite. This seems to suggest the distribution of $\text{H}_2\text{O}(+)$ in the former and further study is required on the subject.

3. Differential thermal analysis curve

The differential thermal analysis curves of the four minerals above are shown in Fig. 2. As specimens, 0.5 gm each of mineral powder of -200 mesh was used, and the temperature was raised always at the rate of $10^\circ\text{C}/\text{min}$. The curve of

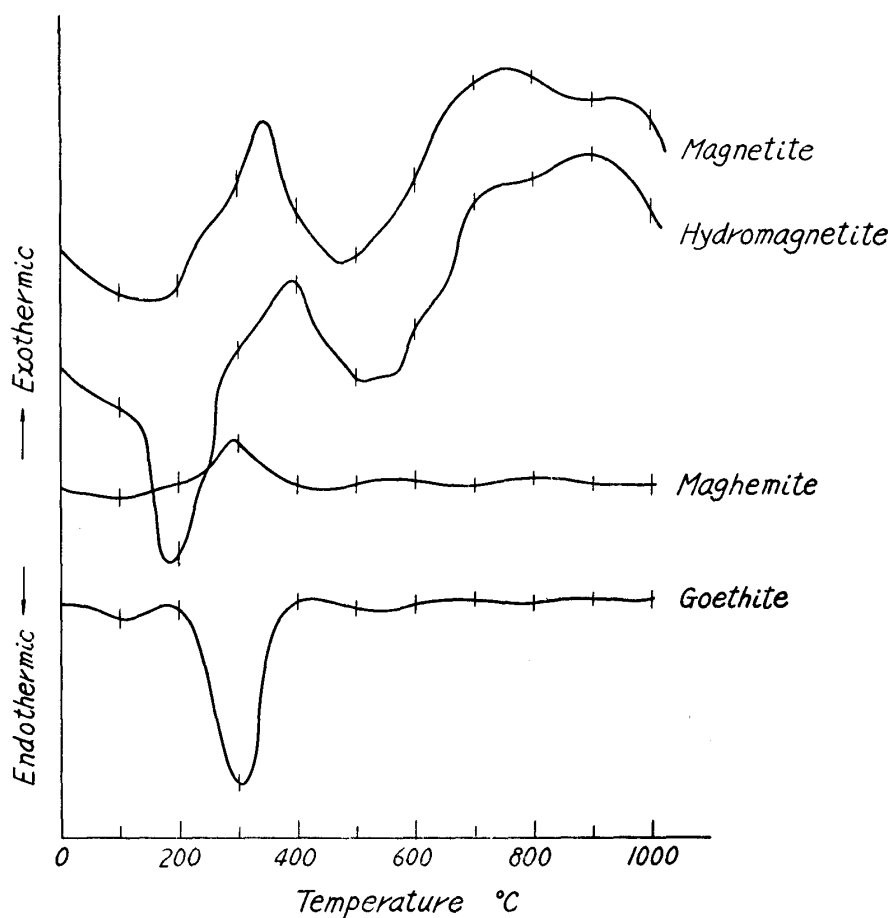


Fig. 2. Differential thermal analysis curves of magnetite, hydromagnetite, maghemite and goethite.

(6) G. Hägg, *Z. Phys. Chem.*, **29B** (1935), 95.

magnetite had a steep exothermic peak at 340°C and a plateau-like exothermic peak above 600°C. According to E. R. Schmidt and F. H. S. Vermass⁽⁷⁾, these peaks are caused by oxidation of the surface and the internal parts of the mineral respectively, but some authors⁽⁸⁾⁽⁹⁾ attribute the peak formation to other causes and we look forward to further researches to settle the question.

The curve of hydrous magnetite is little different from that of magnetite in form, except that there is a large endothermic peak at 190°C in the former, differentiating it from the latter.

The curve of maghemite has one exothermic peak at 290°C. This is due to the transition of γ -Fe₂O₃ into Fe₂O₃, which is a feature differentiating this mineral from the others.

The endothermic peaks at 105°C and 350°C in the curve of goethite are due to the dehydration of adsorbed water and combined water respectively.

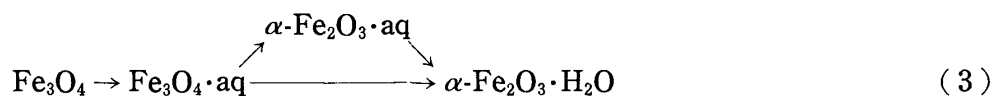
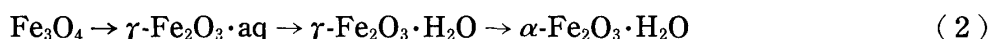
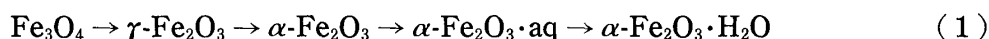
IV. Natural oxidation process of magnetite

The magnetite from Takanokura Mine commonly changes into hematite and thence into goethite by natural oxidation. During this process, sometimes maghemite is produced between magnetite and hematite and hydrous hematite between hematite and goethite. In some cases, a part of magnetite becomes hydrous magnetite and then goethite.

As far as the author could ascertain, the alteration process of magnetite at any outcrop of deposits in Japan can be explained as reflecting a part of the above processes shown by the specimens from Takanokura Mine.

Summary

1. The alteration processes by weathering of magnetite from Takanokura Mine comprise the three following types:



The process (1) was overwhelmingly predominant, the processes (2) and (3) being found only on rare occasions.

2. The oxidation process of magnetite in any known outcrop of deposit in Japan can be interpreted as representing some part of one of the above processes.

3. The chemical composition, the X-ray powder patterns and the differential thermal analysis curves of magnetite, hydrous magnetite, maghemite and goethite from Takanokura Mine have been explained.

(7) E. R. Schmidt and F. H. S. Vermass, *Am. Miner.*, **40** (1955), 422.

(8) M. A. Gheith, *Am. J. Sci.*, **250** (1952), 677.

(9) H. Lepp, *Am. Miner.*, **42** (1957), 679.

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