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# On the Imperfection of Magnetite from Kamaishi Mine, Iwate Prefecture, Japan

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## Synopsis

Two kinds of magnetites, one dense lumps (magnetite I) and the other with conspicuous parting in the direction of  $\{111\}$  (magnetite II), are produced at Kamaishi Mine. Upon examinations of these two kinds of ores under a reflection microscope, by chemical analysis, by X-ray powder photography, by magnetic property tests and by thermal experiments, it has been established that the magnetite II above is fluctuating somewhat on the side of hematite, as follows.

## I. Introduction

It is well known that the problem of imperfections in minerals constitutes one of the most notable fields of mineralogy at present. In the series of studies on the iron oxide minerals, the authors have discovered the presence of fluctuated magnetite to the side of hematite, occurred from Kamaishi Mine, Iwate Prefecture, Northern Japan of which will be reported in the following.

## II. Magnetites from Kamaishi Mine and their paragenesis

Iron oxide ores from Kamaishi Mine include magnetites, hematites, maghemites and limonites. The magnetites can be again subdivided into the three following variations.

- 1) Lump magnetites: These are of irregular granular crystals of magnetite aggregated into dense masses, and represent the largest majority in quantity. They are found accompanying skarn minerals of early crystallization, such as diopsides, hedenbergites, andradites, grossularites and ludwigites.
- 2) Magnetite crystals: These are crystals of about 1 cm length found in the druses formed in the mass of the above lump magnetites. They consist mainly of single forms of  $d\{110\}$ , combinations of  $o\{111\}$  and  $d\{110\}$ .
- 3) Quasi-micaceous magnetites: These show a conspicuously developed parting in the direction of  $\{111\}$  of their crystals, have a silver-white lustre, and have the shape of aggregated scales, so that they give the appearance of micaceous hematites. They accompany minerals of later crystallization, such as epidotes, calcites, quartz and pyrites, in some cases forming banded intergrowth with epidotes.

The order of the crystallization of the above three types of magnetites is approximately 1)→2)→3), the last being conspicuous in being found penetrating

layers of 1) and 2). In the following comparative study of 1) and 3), 1) and 2) will be referred as magnetite I, and 3), with conspicuously developed parting as magnetite II, for brevity's sake.

### III. Magnetites I and II under a reflection microscope

Both appear gray in color, show isotropy, turn slightly darker upon contact with HCl (1:1), which condenses into a yellow liquid, but are proof against any other standard reagent, thus showing good conformance with the past descriptions of its characteristics. It is impossible to distinguish magnetites I and II by microscopic examination.

### IV. Chemical composition

Chemical analysis shows that the two types of magnetites are quite similar in composition, as shown in Table 1, and both belong indisputably to magnetite in this respect. The molecular ratio of FeO against  $\text{Fe}_2\text{O}_3$  stands at 1.06 with magnetite I and 1.03 with magnetite II, so that the latter is slightly richer in  $\text{Fe}_2\text{O}_3$ <sup>(1)</sup>.

Table 1. Chemical composition of magnetite I and II from Kamaishi Mine. (Analysed by S. Nagano)

	Magnetite I	Magnetite II
$\text{Fe}_2\text{O}_3$	65.06	66.03
FeO	31.11	30.48
$\text{Al}_2\text{O}_3$	0.65	0.64
MnO	0.55	0.57
CaO	0.86	0.86
MgO	0.46	0.54
$\text{TiO}_2$	none	none
$\text{SiO}_2$	1.21	0.86
S	tr	tr
P	tr	tr
-H <sub>2</sub> O	0.03	0.02
Total	99.93	99.98
FeO/ $\text{Fe}_2\text{O}_3$ mol ratio	1.06	1.03

### V. X-ray powder photography

Both the types of magnetites show the same Debye-Scherrer's lines, as shown in Photos. 1-1 and 1-2.

(1) In view of the nature of the discussion, the existence of impurities was not taken into consideration here. The samples are somewhat different in their  $\text{SiO}_2$  contents, but in other respects, they are much the same, so that even if the unequal distribution of Al, Mn, Mg, Ti and such impurities is taken into account, the above tendency will not be disturbed. From the results of a few other tests, we found that the ratio FeO/ $\text{Fe}_2\text{O}_3$  shows some latitude, in both the types, but in statistical summary, it was clear that magnetite II had a smaller ratio than magnetite I.

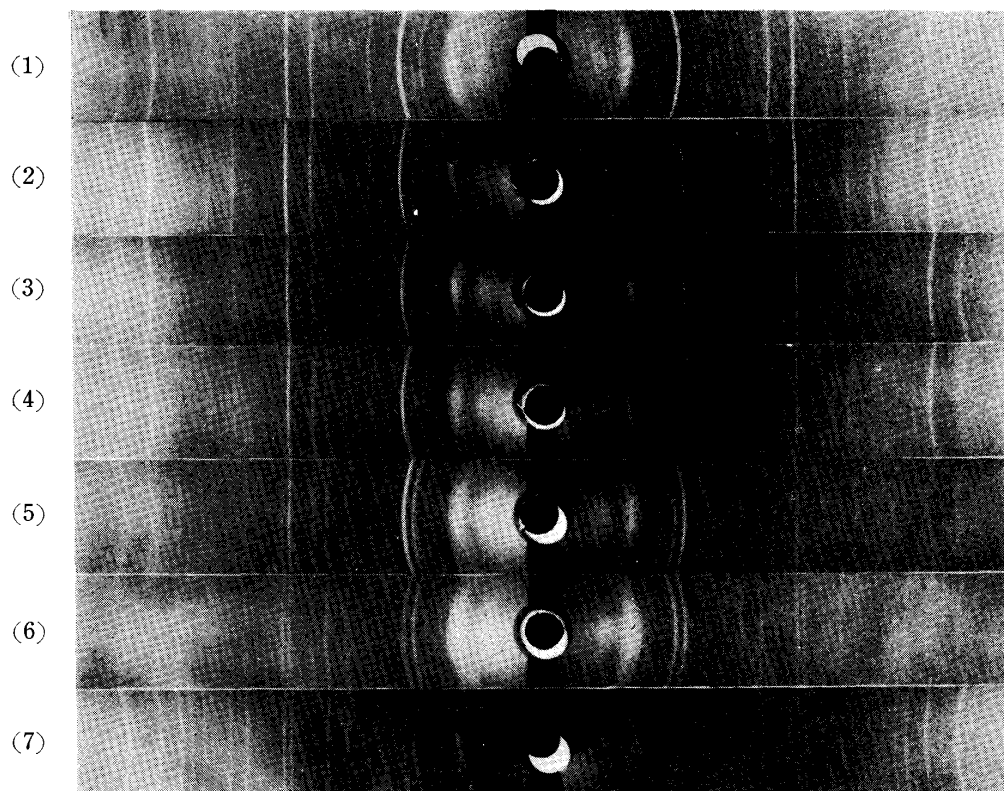


Photo. 1.

X-ray powder photographs of magnetite I and II

1. Magnetite I, room temp.
2. Magnetite II, room temp.
3. Magnetite I, 950°C, 1 hr.
4. Magnetite II, 950°C, 1 hr.
5. Magnetite I, 1,000°C, 1 hr.
6. Magnetite II, 1,000°C, 1 hr.
7. Hematite, Wakasennin Mine, room temp.

## VI. Magnetic property

The magnetic hysteresis curves for the two types of magnetites shown in Photo. 2 were taken by means of a hysteresis curve tracer<sup>(2)</sup> provided with a Braun tube and from these curves their respective coercive force ( $H_c$ ) and their magnetic saturation values ( $I_s$ ) were calculated, as shown in Table 2. This Table shows that magnetite I is similar to lump magnetite ores from Kuriki Mine, Iwate Prefecture, in magnetic properties, but magnetite II has larger

Table 2. Magnetic properties of magnetite I and II.

Variety	Locality	$H_c$ (Oersted)	$I_s$ (Gauss)
Magnetite I	Kuriki Mine, Iwate Pref.	28.5	441.3
Magnetite I	Kamaishi Mine, Iwate Pref.	28.5	441.3
Magnetite II	Kamaishi Mine, Iwate Pref.	38.1	352.5

(2) An instrument installed in Prof. Okamura's laboratory in Research Institute for Scientific Measurement, Tohoku University was used. We hereby express our thanks to the Prof.

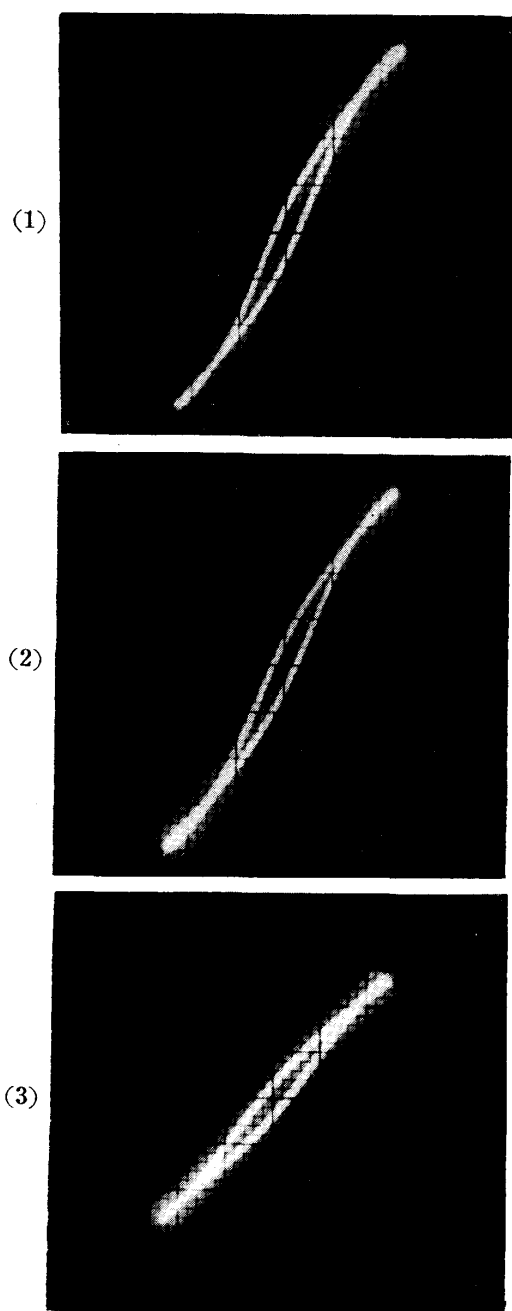


Photo. 2.

Hysteresis curve of magnetite I and II  
 (1) Magnetite I from Kamaishi Mine  
 (2) Magnetite I from Kuriki Mine  
 (3) Magnetite II from Kamaishi Mine

but at 950°C, they both suffer some oxidation and some lines revealing existence of hematite begin to appear. There is no change up to 970°C but at 1,000°C, all Debye-Scherrer's lines from magnetite II turn into hematite lines, while some magnetite lines remain visible in the X-ray powder photographs of magnetite I at this temperature.

(3) It is known that maghemite has stronger magnetic coercive force and lower saturation value than magnetite.

coercive force and smaller magnetic saturation value than magnetite I, showing a trend of fluctuation to the side of maghemite<sup>(3)</sup>.

### VII. Heating tests

Concentrate samples of both the types of magnetites were ground down to the size below 150 mesh and 0.2 g each of the samples was tested by heating to the temperature of 850~1,000°C under a current of nitrogen with low partial pressure of oxygen. As marketed nitrogen contains about 1~3 per cent of oxygen, it was purified with alkaline solution of pyrogallol, cuprous ammonium chloride solution, sulfuric acid, a copper net heated to 850°C and calcium chloride, to bring down the partial pressure of oxygen to around 0.2 per cent. The rate of flow was kept at 80 cc min., the temperature raised at the rate of 100°C 30 min and kept at the testing heat for one hour and the change of weight of the samples was determined after the furnace has cooled, while X-ray photographs were taken of the heated powder samples, as illustrated in Photo. 1 and Table 3. The said change of weight represents the difference of what has been lost by the escape of volatile components up to that temperature and what has been gained by the addition of oxygen by oxidation. Both the types of samples show little change up to 900°C and the Debye-Scherrer's lines observed are all due to magnetite alone,

Table 3. Changes of weight and Debye-Scherrer's lines of heated magnetite I and II at various temperatures.

Temperature (°C)	Magnetite I		Magnetite II	
	Change (wt%)	Debye-Scherrer's line	Change (wt%)	Debye-Scherrer's line
850	-0.60	magnetite	-0.63	magnetite
900	-0.73	"	-0.65	"
950	+0.03	magnetite+hematite	+0.63	magnetite+hematite
970	+0.20	"	+0.70	"
1,000	+1.65	"	+1.91	hematite

Table 4. Degree of oxidation of magnetite I and II at various temperatures.

Temperature (°C)	Magnetite I			Magnetite II		
	FeO (wt%)	Fe <sub>2</sub> O <sub>3</sub> (wt%)	FeO/Fe <sub>2</sub> O <sub>3</sub> mol ratio	FeO (wt%)	Fe <sub>2</sub> O <sub>3</sub> (wt%)	FeO/Fe <sub>2</sub> O <sub>3</sub> mol ratio
Room temp	30.82	67.71	1.01	27.66	64.67	0.95
850	29.89	69.36	0.96	25.72	67.43	0.85
900	29.45	69.97	0.94	26.08	68.49	0.85
950	24.14	75.11	0.70	14.44	78.77	0.41
970	22.13	77.17	0.64	12.28	81.07	0.34
1,000	12.10	89.33	0.31	3.17	90.11	0.08

Next, the heated samples were analysed for the contents of FeO and total Fe and the molecular ratio FeO/Fe<sub>2</sub>O<sub>3</sub> was calculated as shown in Table 4. These values plotted against the temperature resulted in Figure 1.

These Table and Figure show that magnetite II is oxidized into hematite in a smooth linear course above 900°C, but magnetite I is more difficult to oxidize up to 970°C, so that at 1,000°C, a part of it remains unchanged. That is to say, the type called magnetite II may be said to be deviated in its crystal structure to the side a little proner to oxidation<sup>(4)</sup>.

### VIII. Imperfection of magnetite II

In chemical composition, magnetite II is slightly richer in Fe<sub>2</sub>O<sub>3</sub> and tends to approach maghemite in its magnetic

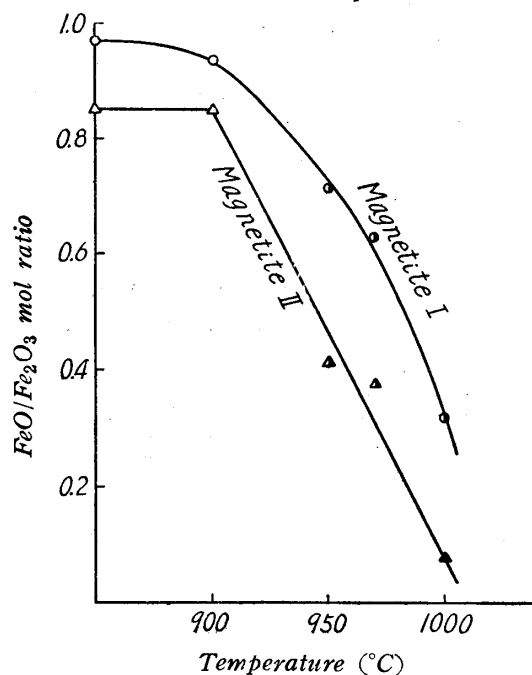


Fig. 1. Oxidation curve of magnetite I and II  
 ○△ : Magnetite,  
 ●▲ : Magnetite+Hematite,  
 ▲ : Hematite

(4) The proneness to oxidation show difference according to the size of grains, but in the case under consideration, the effect of grain size is negligibly small.

property. Thus it was revealed that magnetite is subject to a fluctuation in its properties, though may be in a very slight degree.

With due consideration to the above mentioned paragenesis of the two types of magnetites, it may be presumed that the conditions under which magnetite II crystallized together with epidotes, calcites, quartz and pyrites in the hydrothermal stage were more favorable to oxidation than those obtaining in the pneumatolytic stage when magnetite I crystallized in intergrowth with the earlier skarn minerals.

### Summary

- (1) Kamaishi Mine produces lump magnetite (magnetite I) as well as magnetite with conspicuous tendency for parting (magnetite II).
- (2) It is difficult to distinguish the two types of magnetites under a reflexion microscope.
- (3) Both the types show identical Debye-Scherrer's lines in their X-ray powder photographs.
- (4) They are quite similar in chemical composition, but magnetite II is slightly richer in  $\text{Fe}_2\text{O}_3$  content.
- (5) In magnetic properties, magnetite II is stronger in coercive force, but lower in magnetic saturation value.
- (6) Magnetite II is slightly more easily oxidized than magnetite I.
- (7) Magnetite I was crystallized in the pneumatolytic stage simultaneously with earlier skarn minerals, and magnetite II in the hypothermal stage together with epidotes, calcites, quartz and pyrites. The fluctuation observable in magnetite II seems to be due to the conditions of crystallization being more favorable to oxidation for magnetite II than for magnetite I.

In conclusion, we must mention with deep appreciation that Mr. Shiro Imai, Manager of Kamaishi Mine and Mr. Narundo Wada have been helpful to us in various matters concerning our study. Thanks are also due to Messrs. Kenzo Ito, Kazunori Gondo, Shozo Nagano and Tsuyoshi Endo for their cooperation with our experiments, and Mr. Masaaki Azumi for his assistance in our collection of materials. We are also grateful for the fact that a part of this study was made possible by the allocation of Scientific Research Fund by the Education Ministry.