Thermal Processes of Titanomaghemite in Volcanic Rocks

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Detailed thermomagnetic, reflection microscopic and electron-probe microanalyzer studies of 27 selected, mostly andesitic rocks have indicated that partly maghemitized titanomagnetite decomposes at temperatures ranging from 200° to 600°C to ilmenite, ilmeno-hematite, and titanomagnetite forming intergrowths of exsolution lamellae. The unmixed phases are then homogenized to titanomagnetite at temperatures between 500° and 800°C.

Difference in thermomagnetic curves in a cycle of heating and cooling between room temperature and 600°C is mostly owing to whether or not the mixing temperature is higher than 600°C. If the mixing proceeds in the thermomagnetic cycle, the Curie temperature observed in a cooling cycle is much lower than the initial value, since titanium content in titanomagnetite increases with mixing of ilmenite and ilmeno-hematite caused by heating.

Size dependence of the mixing rate has also been revealed by thermal experiment with pulverized and separated specimens.

1. Introduction

Degree of low-temperature oxidation of titanomagnetite in a majority of volcanic rocks formed on land is usually low and heterogeneous (AKIMOTO and KUSHIRO, 1960; SASAJIMA, 1961; KATSURA and KUSHIRO, 1961; SASAJIMA and MAENAKA, 1973; Momose, unpublished). Oxidized titanomagnetite (titanomaghemite) occurs only along rims and cracks of its parent phase. Titanomaghemite is stable at room temperature but unstable at high temperatures and decomposes so that its magnetic properties are irreversible with a cycle of heating and cooling.

Two different processes of thermal decomposition have been proposed; (1) titanomaghemite decomposes into a pair of titanomagnetite and ilmeno-hematite with equal Ti–Fe ratio (OZIMA and LARSON, 1967), (2) it decomposes into intergrowth of magnetite and ilmenite with minor components of other Fe–Ti oxides (READMAN and O'REILLY, 1970; OZIMA and LARSON, 1970).

The author investigated the processes of thermal decomposition of ferromagnetic minerals and associated changes in magnetic properties of a number of rocks. Although environmental condition of heating was kept constant throughout the present study, various types of thermomagnetic behavior were observed. Origin of the variety of thermal behavior was thus carefully examined with well-controlled samples by magnetic, micro-

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scopic and electron-probe microanalyzer techniques.

2. Thermomagnetic Analyses

2.1 Samples

One hundred and eighty-four rock samples were collected at 63 sites in 6 regions; Hakone volcanic area, Shidara Basin in Aichi Prefecture, Warabidaira in Yamanashi Prefecture, Kume-shima of the Ryukyu Islands, Enrei area in Nagano Prefecture, and Iwaine district in Toyama Prefecture.

Among these rocks, 27 samples consisting of 17 andesites, 6 dolerites, 3 basalts, and a dacite (Table 1) were selected under ore microscope. Each selected rock contains partially maghemitized titanomagnetite, but no deuteric intergrowths were found under reflection microscope with the highest magnification.

Table 1. Samples and thermomagnetic results.

Specimen code	Rocks*	Locality longitude	latitude	J_s - T type	J_2/J_1	Initial T_c (°C)	Reduced T_c (°C)
HK13	A.	139° 8.6'E	35°12.5'N		0.83	565	470
HK39	A.	139° 3.2'	35°11.9'		0.84	545	
KS01	A.	Kume island (Okinawa)			0.92	560	465
WB31	d.	138°29.8'	35°27.0'	A-I	0.90	520	430
WB32	d.				0.93	520	
WB33	d.				0.97	520	
WB34	d.				0.91	515	430
WB36	d.				0.96	540	
IW31	A.	137°13.5'	36°32.0'	B-I	0.99	550	395
HK05	A.	139° 6.0'	35°13.2'		1.33	540	
HK12	A.	139° 7.0'	35°11.9'		1.38	540	
HK28	A.	139° 8.4'	35°11.0'		1.25	560	
HK52	A.	139° 6.1'	35° 0.4'	C-I	1.29	520	330
HK58	A.	139° 5.4'	35°13.2'		1.14	550	
IW11	B.	137°12.9'	36°32.5'		1.30	510	360
IW23	B.	137°13.4'	36°32.3'		1.32	525	345
WB35	d.	138°29.8'	35°27.0'		1.06	540	325
HK47	A.	139° 1.9'	35°12.3'		0.93	525	480
HK49	A.	139° 2.8'	35°12.5'	A-II	0.92	510	480
HK62	A.	139° 5.9'	35° 6.9'		0.90	540	420
HK20	A.	139° 6.4'	35° 9.2'		1.00	500	365
HK45	A.	139° 2.8'	35°14.2'	B-II	0.95	465	
HK59	D.	139° 6.6'	35° 8.9'		1.00	500	390
HK10	A.	139° 8.7'	35°12.8'		1.02	505	320
HK34	A.	139° 5.7'	35° 9.9'	C-II	1.02	520	
HK64	B.	139° 2.8'	35° 9.9'		1.12	475	400
EN01	A.	138° 2.1'	36° 5.3'		1.06	500	380

*Rocks: A., andesite; B., basalt; D., dacite; d., dolerite.

2.2 Thermomagnetic curves

Change of saturation magnetization, J_s ($H = 2.4 \times 10^5$ A/m), with temperature T were measured between room temperature and 600°C by means of a quartz-spring thermomagnetic balance in vacuum of $0.5\text{--}0.01$ Pa. Rate of heating and cooling is 300°C/hr .

Various types of thermomagnetic curves thus obtained were classified into types I and II as well as types A, B, and C (Fig. 1) according to the following criteria:

1) In type I, the Curie temperature T_C determined from initial heating curve (hereafter called "initial T_C ") is nearly coincident with T_C determined from thermomagnetic

Fig. 1. Six typical J_s - T curves of titanomaghemite-bearing rocks. Solid and dotted curves denote heating and cooling, respectively. See text reading experimental conditions.

curve cooled from the maximum temperature of 600°C (called “cooling T_C ”). The cooling T_C is apparently lower than its initial T_C in type II.

2) J_2 , saturation magnetization at room temperature after a heating-cooling cycle, is smaller than J_1 , saturation magnetization at room temperature before heating, in type A. J_2 is equal to J_1 in type B and is larger than J_1 in type C.

Six different types are distinguishable by combination of these twofold classifications. Type B-I curve is reversible in a cycle of heating and cooling.

1.3 Heat-treatment at higher temperatures ($680^{\circ}\text{--}950^{\circ}\text{C}$)

Twenty-seven selected samples were heated at $680^{\circ}\text{--}950^{\circ}\text{C}$ in vacuum of $0.5\text{--}0.01$ Pa. Thermomagnetic analysis was repeated after the samples were cooled to room temperature. The Curie temperature T_C of such heat-treated samples is substantially lower than the initial T_C of the original samples. T_C of heat-treated samples is called “reduced Curie temperature” and listed in Table 1 together with the initial T_C of the original samples.

Figure 2 shows relation between J_2/J_1 and reduced T_C with type I samples (solid marks) and type II (hollow marks). It is noteworthy that J_2/J_1 values are roughly inversely proportional to the reduced T_C , while J_2/J_1 of type I is generally larger than that of type II. Significance of this tendency will be discussed later.

Fig. 2. Correlation between reduced T_C and J_2/J_1 ratio. Value of J_2/J_1 ratio is determined from J_s - T curve of the initial sample. The J_2/J_1 ratios of type I (solid marks) and type II (hollow marks) range $0.83\text{--}1.32$ and $0.90\text{--}1.12$, respectively.

3. Microscopic Observations of Thermal Processes

3.1 *Experimental procedure*

A pair of the original (unheated) and heated samples were mounted in raisin and polished to be examined under a reflection microscope and by an electron-probe microanalyzer (EPMA). Due to restriction of magnification only phenocryst-size opaque minerals were investigated by this method. The original samples contain partially maghemitized titanomagnetite. Figure 3 shows an example of highly maghemitized grains. Titanomaghemite (bright) occurs only partly, in several volume percent of titanomagnetite (dark). Ti content of titanomaghemite is slightly higher than that of titanomagnetite, indicating that oxidation proceeds by bleaching of Fe ions.

Fig. 3. Initial state; unheated KS01. (a), Partially maghemitized titanomagnetite. titanomagnetite (inside, gray) and titanomaghemite (marginal, white-gray) are seen. (b), Titanium profile on the marked line; 1, $\text{TiO}_2 = 11.6 \text{ wt}\%$, 2, $\text{TiO}_2 = 15.4 \text{ wt}\%$.

3.2 Unmixing stage

Photomicrograph of the same sample after heating at 250°C (Fig. 4) indicates that the oxidized titanomagnetite decomposes at such low temperatures. Lamellae of ilmenohematite are clearly seen in the margin of titanomagnetite grain.

If the same sample is heated at 390°C, ilmenohematite lamellae grow longer toward the inner part of titanomagnetite crystal (Fig. 5), while the core of titanomagnetite is apparently unchanged. After the sample is heated at above 390°C, trellis lamellae are formed all over the titanomagnetite grain (Fig. 6a). Each intergrowth consists of sandwiches of ilmenite and ilmenohematite (Fig. 6b).

A profile of Ti-content obtained by EPMA (Fig. 6c) indicates that unmixing in the right-hand side is stronger than in the left-hand side. Background level of Ti is lower in the right-hand side than in the left, implying that Ti-content in titanomagnetite (spinel-cubic phase) decreases as unmixing proceeds. After the sample is heated at 600°C, unmixing further proceeds and ilmenite lamellae increase by consuming lamellae of ilmenohematite (Fig. 7). After heating at 680°C, ilmenite is dominating (Fig. 8).

3.3 Mixing stage

Heating at higher temperatures causes mixing of ilmenite and ilmenohematite with titanomagnetite. In some samples, the mixing takes place at temperatures above 500°C, and in most samples at temperatures higher than 700°C. Mixing starts with disappearance of ilmenite lamellae (Fig. 9), and is followed by formation of Ti-rich titanomagnetite in the original titanomagnetite to cause coexistence of two phases of titanomagnetite (Fig. 10).

Fig. 4. Early stage of unmixing; KS01 heated at 250°C (0.5 Pa, 3 hr). Titanomagnetite (lower, gray) and unmixed products from titanomaghemite (marginal part) are seen. White trellis lamellae are ilmenohematite.

Fig. 5. Slightly advanced unmixing; KS01 heated at 390°C. Ilmenohematite lamellae (white) apparently invade into titanomagnetite part (gray).

Eventually these two phases are homogenized (mixed) to form nearly uniform titanomagnetite (Figs. 11 and 12).

3.4 Relevance of mineralogical changes to thermomagnetic behavior

Microscopic observation shows that temperatures at which unmixing and mixing proceed vary with samples and difference in types of thermomagnetic curves depends primarily upon such variations in the critical temperatures.

Opaque mineral in type I samples heated at 600°C are still very heterogeneous. The cooling T_C is therefore nearly equal to the initial T_C in type I. Mixing proceeds at temperatures much higher than 600°C.

On the contrary, opaque minerals in type II samples are homogeneous titanomagnetite after heating at 600°C. Such mixed titanomagnetite has higher Ti-content than unmixed stage of this titanomagnetite, and therefore, the cooling T_C of type II is lower than its initial T_C . At least, the difference (thermal behavior between type I and type II) seems to be neither due to Ti-content of titanomagnetite nor to maghemitization degree of the mineral. Because, these differences are observed among samples with various Ti-content (Fig. 2).

Distinction among samples of types A, B, and C seems to be correlatable to Ti-content of titanomagnetite, because results of the present thermomagnetic analyses indicate rough inverse correlation between J_2/J_1 and reduced T_C (Fig. 2). As T_C of mixed phase is roughly inversely proportional to Ti-content in titanomagnetite, type A sample is the richest in Ti and type C is the poorest in Ti.

Fig. 6. Middle stage of unmixing; KS01 heated at 390°C. (a), Whole-grain intergrowth. (b), Highly magnified photograph (dotted area in (a)). Titanomagnetite (gray), ilmenohematite (white) and ilmenite (dark) are seen. Ilmenite is sandwiched between ilmenohematite lamellae. (c), Titanium profile on the marked line; 3, TiO₂ = 38.6 wt%, 4, TiO₂ = 6.4 wt%.

Fig. 7. Middle to late stage of unmixing; KS01 heated at 600°C. Ilmenite lamellae (dark) grow, and ilmenohematite (white) decreases. The former has direct contact to titanomagnetite (gray).

Fig. 8. Late stage of unmixing; KS01 heated at 680°C (0.5 Pa, 1 hr). Ilmenite lamellae (dark) become dominant. Some spinel or rutil (unidentified, small black whiskers) is seen.

Fig. 9. Beginning of mixing; HK20 heated at 680°C (0.5 Pa, 3 hr). Ilmenite lamellae are mixed into titanium-rich titanomagnetite (dark patches and checkers). Remaining lamellae are ilmenohematite (white).

The above-mentioned thermal behaviors of titanomagnemite-bearing rocks from land are in remarkable contrast to those of submarine pillow basalts. Origin of the contrast is due to be larger grain size (discussed in the next section) and smaller degree of maghemitization in land rocks than in submarine pillow basalts.

4. Effect of Grain Sizes on the Thermomagnetic Behavior

The present investigation so far described is concerned with the whole rock fragments for thermomagnetic analyses and with phenocryst-size minerals for microscopic examination. However, the rocks contain fine grains of ferromagnetic minerals in groundmass. Role of fine-grained titanomagnetite is investigated here.

4.1 Sample preparation

Samples used in the thermomagnetic analyses described above are the *whole-rock* samples of about 1 mm in diameter which is pulverized and sieved from fragments of rocks. They are ground and washed in acetone to prevent oxidation to grains of about 0.5 mm in diameter. Ferromagnetic components are extracted by a hand magnet to obtain *phenocryst-size* samples. As described already, the phenocryst-size samples consist of partially maghemitized titanomagnetite.

Remaining fractions consist of various minerals, including fine-grained (less than several microns) ferromagnetic minerals, that are mostly maghemitized titanomagnetite

Fig. 10. Middle stage of mixing; KS01 heated at 800°C (0.01 Pa, 1 hr). (a), Titanomagnetite with two phases. (b), Titanium profile on the marked line; 5, $\text{TiO}_2 = 11.1 \text{ wt}\%$, 6, $\text{TiO}_2 = 12.0 \text{ wt}\%$.

(titanomaghemite). They are finely pulverized in acetone and ferromagnetic components are extracted to obtain *fine-A* samples. Besides, the phenocryst-size sample is pulverized to fine particle size to prepare *fine-B* samples (Fig. 13).

4.2 Thermomagnetic analyses

J_s - T curves of the whole-rock, phenocryst-size, *fine-A* and *fine-B* samples are represented in Fig. 14. Thermomagnetic behavior of the whole-rock is nearly identical to that of phenocryst-size samples, indicating that contribution of groundmass to the bulk saturation magnetization is negligibly small.

Thermomagnetic curves of *fine-A* and *fine-B* are similar to each other, but distinctly different from those of the whole-rock and phenocryst-size samples. As no chemical changes are expected in the grinding procedure from phenocryst-size to *fine-B* samples, different thermomagnetic behavior of *fine-B* samples compared to phenocryst-size samples may be caused by difference in grain size, i.e. as the grain size becomes smaller, rate of

Fig. 11

Fig. 12

mixing at 600°C decreases so substantially that the cooling T_C of fine samples is not reduced by formation of Ti-rich titanomagnetite owing to mixing. Unmixed samples often have higher saturation magnetization, as shown in thermomagnetic curves of submarine basalts.

5. Summary

(1) Titanomaghemite decomposes at temperatures ranging from 200° to 600°C to form intergrown exsolution lamellae of ilmeno-hematite, ilmenite in titanomagnetite.

(2) The unmixed intergrowth is homogenized to titanomagnetite at temperatures between 500° and 800°C.

Fig. 13. Sample preparation procedure.

Fig. 11. Middle to late stage of mixing; KS01 heated at 800°C (0.01 Pa, 1 hr). Most part of the grain is homogenized. Titanium-rich titanomagnetite remains along rims and cracks of the grain in a particular shape.

Fig. 12. Late stage of mixing; KS01 heated at 950°C (0.01 Pa, 1 hr). Almost completely homogeneous titanomagnetite containing small inclusions (see sketch).

Fig. 14. Thermomagnetic curve of each sample prepared from a rock sample (HK20). Solid circle and line denote heating, and open circle and dotted line cooling. Experimental conditions are the same as Fig. 1.

(3) Rate of mixing depends upon grain size of titanomagnetite. If the size is larger than one-tenth of millimeter, mixing usually proceeds at temperatures at or slightly lower than about 600°C in an experimental time interval. If the size of titanomagnetite is much smaller, mixing is observed only after it is heated at a temperature higher than 650°C (680° to 900°C), although the rate of mixing seems to depend also upon chemical and crystallographic conditions of titanomagnetite.

(4) Various thermomagnetic behaviors of natural rocks may be explained by combination of unmixing and mixing during heating.

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REFERENCES

- AKIMOTO, S. and I. KUSHIRO, Natural occurrence of titanomagemite and its relevance to the unstable magnetization of rocks, *J. Geomag. Geoelectr.*, **11**, 94–110, 1960.
- KATSURA, T. and I. KUSHIRO, Titanomagemite in igneous rocks, *Am. Mineral.*, **46**, 134–145, 1961.
- OZIMA, M. and E. LARSON, Study on irreversible change of magnetic properties of some ferromagnetic minerals, *J. Geomag. Geoelectr.*, **19**, 117–127, 1967.
- OZIMA, M. and E. E. LARSON, Low- and high-temperature oxidation of titanomagnetite in relation to irreversible changes in the magnetic properties of submarine basalts, *J. Geophys. Res.*, **75**, 1003–1017, 1970.
- READMAN, P. W. and W. O'REILLY, The synthesis and inversion of non-stoichiometric titanomagnetites, *Phys. Earth Planet. Inter.*, **4**, 121–128, 1970.
- SASAJIMA, S., γ -titanohematite in nature and the role they play in rock-magnetism, *J. Geomag. Geoelectr.*, **12**, 190–215, 1961.
- SASAJIMA, S. and K. MAENAKA, Paleomagnetic stratigraphy of Neogene Tertiary in Kume island, *Report of structural geology on G.D.P.*, **1**, 75–82, 1973 (in Japanese).