Grain Size Effect on the Low-Temperature Oxidation of Titanomagnetite

Tadashi Nishitani* and Masaru Kono**

Geophysical Institute, University of Tokyo, Bunkyo-ku, Tokyo 113, Japan

Abstract. The low-temperature oxidation process in titanomagnetite has been investigated. Using samples with controlled grain sizes, it has been shown that there is a critical grain size in the oxidation behaviour of titanomagnetites; smaller grains undergo low-temperature oxidation, while larger ones separate to Fe-rich titanomagnetite and Ti-rich hemo-ilmenite (high-temperature oxidation). The difference between the results of similar experiments by Ozima and Sakamoto (1971) and by Readman and O'Reilly (1972) can be explained in terms of differences in particle sizes of titanomagnetites. Comparable results were obtained from natural subaerial and submarine basalts; when they are heated to temperatures between 150° C and 375° C, oxidation proceeds in submarine basalts, but it does not in subaerially erupted basalts and a high-temperature oxidation process occurs. This fact indicates that the grain size of the magnetic minerals is one of the most important controlling factors in low-temperature oxidation of titanomagnetites.

Key words: Rock magnetism – Low-temperature oxidation – Titanomagnetite – Grain size effects

Introduction

In igneous rocks, titanomagnetites

$$x\text{Fe}_2\text{TiO}_4 \cdot (1\text{-}x)\text{Fe}_3\text{O}_4$$
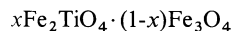
are often found to be the carriers of remanent magnetization and their magnetic properties have been extensively studied (e.g., Akimoto and Katsura 1959; Nagata 1961; Ozima and Sakamoto 1971; Readman and O'Reilly 1972). The magnetic properties of titanomagnetite, especially hysteresis properties, vary considerably due to grain size (Day et al. 1976, 1977). Levi and Merrill (1976) reported the grain size dependence of the intensity of anhysteretic remanent magnetization (ARM) and thermoremanent magnetization (TRM) in magnetite. The grain size of titanomagnetite may also affect the process of low-temperature oxidation. However, such effects have not been studied in detail in previous experiments.

The phenomenon of low-temperature oxidation was first investigated by Akimoto et al. (1957) and by Akimoto and Katsura (1959). They heated titanomagnetites in air at temperatures of 400°–500° C and studied magnetic properties of titanomagnetites and their changes with oxidation. However, it was later pointed out that they did not produce pure titanomaghemite as their samples contained high-temperature oxidation products (Ozima and Larson 1970). Sakamoto et al. (1968) demonstrated that titanomaghemites might be obtained if titanomagnetites were first ground in water and then heated in air at temperatures below 300° C. Readman and O'Reilly (1970) prepared samples by ball-milling sintered titanomagnetites in a water slurry for 100 h and obtained cation deficient titanomagnetites (titanomaghemites) by heating in air at temperatures between 200° and 300° C. As a result of the above experiments, it is generally thought that the experimental results can be trusted only if the samples are prepared by ball-milling or wet-grinding titanomagnetites.

Ozima and Sakamoto (1971) and Readman and O'Reilly (1972) carried out systematic studies of low-temperature oxidation. However, their results were not consistent with each other. Ozima and Sakamoto (1971) performed oxidation experiments on wet-ground titanomagnetites of high ulvospinel ratios ($x = 0.7$, 0.9 and 1.0) and reported parameters such as lattice constants and Curie temperatures. Readman and O'Reilly (1972) used ball-milled samples with four compositions ($x = 0.0$, 0.4, 0.7 and 1.0). The above two authors defined an oxidation parameter z, and in this study this parameter is also used. The definition of z is

$$\text{Fe}^{2+} + \frac{z}{2}\text{O} \rightarrow z\text{Fe}^{3+} + (1\text{-}z)\text{Fe}^{2+} + \frac{z}{2}\text{O}^{2-} \quad (0 \leqq z \leqq 1)$$
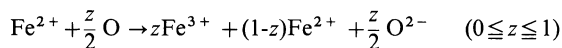
$z = 0.0$ stands for stoichiometric titanomagnetite and $z = 1.0$ for fully oxidized state. As for the oxidation state reached under laboratory conditions, Ozima and Sakamoto (1971) concluded that $z \sim 0.3$ was the maximum after which the separation of titanomagnetites proceeded, while Readman and O'Reilly (1972) reported that titanomagnetites could be completely oxidized. These differences are clearly shown for $x = 0.7$ titanomagnetite in Figure 1. In the results of Nishitani (1979), there is no hemo-ilmenite phase visible on the X-ray measurements. More recently, Keefer and Shive (1981) made Curie temperature and lattice parameter measurements on synthetitc titanomaghemite samples. Their results are not very different from those of Ozima and Sakamoto (1971).

It appears necessary to re-examine the low-temperature oxidation scheme with special reference to the effect of grain size of the titanomagnetites. In the present work, the oxidation states were determined using the results of the detailed study of titanomaghemites by Nishitani (1979). Titanomagnetite samples with

* *Present address.* Institute of Mining Geology, Mining College, Akita University, Akita 010, Japan
** *Present address:* Department of Applied Physics, Tokyo Institute of Technology, Megro-ku, Tokyo 152, Japan
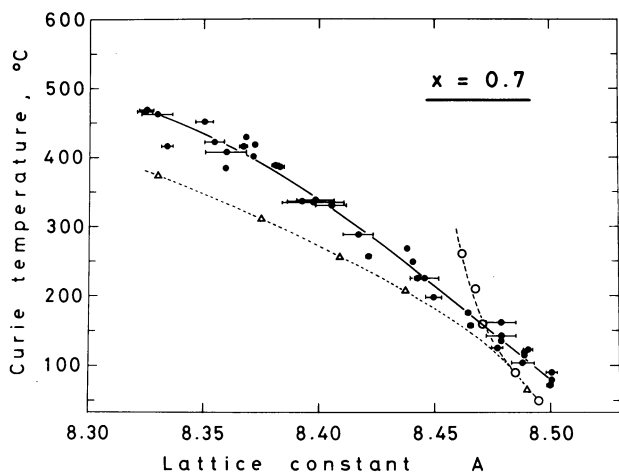
Fig. 1. Relation between lattice constant and Curie temperature for $x = 0.7$ titanomagnetite. *Solid circles* represent experimental points for $x = 0.7$ (ball-milled) titanomagnetite by Nishitani (1979). Error bars indicate standard deviations of lattice constants. Results of Ozima and Sakamoto (1971) are shown by *open circles* and those of Readman and O'Reilly (1972) by *open triangles*
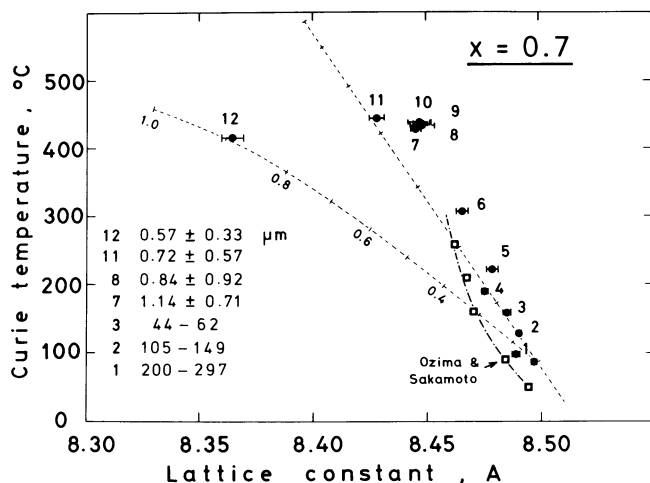

Fig. 2. Relationship between lattice constant and Curie temperature when different sizes of titanomagnetites ($x = 0.7$) are heated for 300 minutes at 300° C. The results of Ozima and Sakamoto (1971) for $x = 0.7$ are represented by *open squares*. Grain sizes are listed on the Figure

particle sizes ranging from 0.57 ± 0.33 μm–300 μm were prepared and were oxidized at low temperatures.

Sample Preparation

To produce titanomagnetite of the desired composition, pure TiO_2 and Fe_2O_3 were mixed in the stoichiometric proportion and well ground in an agate mortar for several hours. The mixtures were then sintered in air at 1,200° C for an hour. After that they were well ground and sintered again. Sintered materials were then crushed to about 2 mm and kept at 1,200° C in a furnace with controlled oxygen fugacity (P_{O_2}) for several hours. They were quenched to about 0° C and the lattice constant was determined using an X-ray diffractometer to ascertain that a single phase titanomagnetite was formed. These heatings were repeated until the specimen homogeneity was sufficient that the two peaks of $FeK\alpha_1$ and $FeK\alpha_2$ in (511) and (400) reflections could be seen clearly. Details of the method of synthesis are described in Nishitani (1979).

Titanomagnetite samples ($x = 0.7$) which cover the particle size from 0.57 ± 0.33 μm–300 μm were prepared. The following size fraction of titanomagnetite were obtained using sieves; 200–249 μm (sample No. 1), 105–149 (No. 2), 44–62 (No. 3). Samples with particle sizes less than 44 μm were obtained using an agate mortar or a ball-mill. Ball-milling was done in an ethyl alcohol. Titanomagnetites were ground in an agate mortar for about two hours, mixed with acetone and stirred well. After about 40 seconds the top layer of acetone was skimmed and this procedure was repeated several times. Acetone was added to the mixture and again stirred well. After about 15 seconds

the top of the acetone was again skimmed. In this way, different time intervals classified titanomagnetite samples into different size ranges.

Precipitated parts were also availbale in this experiment. Samples classified into the size ranges were numbered No. 4 to No. 10. The same procedure was used on a ball-milled titanomagnetite and samples No. 11 and 12 were obtained. As the size of the titanomagnetite becomes small the sample number increases (No. 1–No. 12). Particles sizes less than 44 μm were determined from photographs taken by an electron microscope at magnifications of 5000–20000. The particle sizes of such samples are summarized in Table 1.

Other titanomagnetite samples ($x = 0.5$ and 0.3) were synthesized and divided into two fractions: one was ball-milled and the other was ground in an agate mortar. Though their grain sizes were not measured directly, they are probably similar in size to $x = 0.7$ titanomagnetites.

Grain Size Effect on Oxidation Behaviour

Samples of $x = 0.7$ titanomagnetite were heated in air and kept at a temperature of 300° C for 300 minutes. The relation between the lattice constants and the Curie temperatures of the heated samples are shown in Figure 2. The broken lines show the trends for composition changes in stoichiometric titanomagnetite (right) and for oxidation of $x = 0.7$ titanomagnetite obtained by Nishitani (1979). In this figure the sample number increases as the grain size of titanomagnetite becomes smaller. The observed particle sizes are shown in this figure. The results of Ozima and Sakamoto (1971) for $x = 0.7$ are also shown in the same figure. Their trend, with a sharp rise in Curie temperature, coincides with the trend of the samples No. 1 to No. 10. They are almost on the stoichiometric titanomagnetite solid-solution line, so that they can be interpreted as the phase of separated Fe-rich titanomagnetite in high-temperature oxidation: Ti-rich titanomagnetite $+ O_2 \rightarrow Magnetite_{ss} + Ilmenite_{ss}$ where $Magnetite_{ss}$ and $Ilmenite_{ss}$ are Fe-rich spinel and Ti-rich rhombohedral phases, respectively (Buddington and Lindsley 1964). For large grains the oxidation stage, that is the diffusion time of cations on oxidation may differ. However, in the present study Figure 2
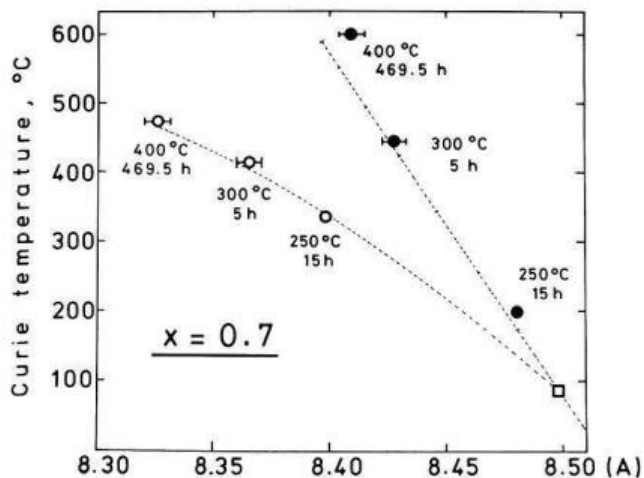
Table 1. Grain size distribution of titanomagnetite ($x = 0.7$)

Sample	Number of grains	Grain size
0.7 TM a precipitated part (2)	114	1.14 ± 0.71 μm
0.7 TM ground in an agate mortar	459	0.84 ± 0.92
0.7 TM a precipitated part (1)	283	0.72 ± 0.57
0.7 TM ball-milled for 36.17 h	432	0.57 ± 0.33

Fig. 3. Results of heat treatment in air for $x=0.7$ titanomagnetite. Temperatures and length of heating are medicated on the figure. Two samples, one is ball-milled (*open circles*) and the other is ground in an agate mortar (*solid circles*), were used
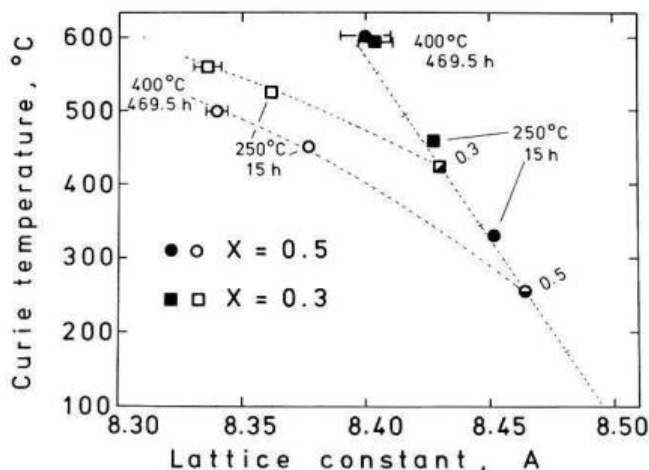

Fig. 4. Results of heat treatment in air. Temperatures and length of heating are marked. Four samples were prepared, two titanomagnetite compositions ($x=0.3$ and 0.5) and for each composition one is ball-milled (*open circles* and *squares*) and the other is ground in an agate mortar (*solid circles* and *squares*)

is interpreted supposing that the diffusion time of cations on oxidation is the same.

Samples with grain sizes between 0.72 ± 0.57 µm (No. 11) and 1.14 ± 0.71 µm (No. 7) reach almost the same position in Figure 2 when they are heated under the same conditions. However, the sample with grain size of 0.57 ± 0.33 µm (No. 12) was oxidized and lay on the low-temperature oxidation line. Therefore, it can be concluded that a titanomagnetite sample ($x=0.7$) decomposes as a result of heating if its grain size is greater than 0.7 to 0.8 µm. This indicates that there is a critical grain size in low-temperature oxidation. The critical size is about 0.7 to 0.8 µm in the case of $x=0.7$ titanomagnetite in a laboratory condition. The ball-milled titanomagnetite, and that ground in an agate mortar, behave in quite a different way when they are heated in air.

To show this distinction more clearly, six samples were prepared: they had three titanomagnetite compositions ($x=0.3$, 0.5 and 0.7) and for each composition one was ball-milled and the other was ground in an agate mortar. They were heated in air successively at 250° C for 15 h, at 300° C for 5 h (only for $x=0.7$) and at 400° C for 469.5 h. The results for $x=0.7$ titanomagnetite and $x=0.3$, 0.5 titanomagnetites are shown in Figures 3 and 4, respectively.

The ball-milled samples were oxidized along the oxidation line of Nishitani (1979) (Fig. 1). On the other hand, samples which were ground in an agate mortar were decomposed or separated to an iron-rich stoichiometric titanomagnetite (spinel phase) and a hemo-ilmenite (rhombohedral phase) by heating. Rhombohedral phases are seen clearly in a chart from an X-ray diffractometer. These experiments indicate that, by observing lattice constants and Curie temperatures before and after heating, it can be determined whether either the low-temperature oxidation process or the decomposition process dominates in oxidation of titanomagnetites.

Ozima and Sakamoto (1971) prepared titanomagnetite samples using an agate mortar and therefore their grain size was probably greater than the critical size of 0.7 to 0.8 µm. As a result, decomposition processes occurred and a sharp rise in Curie temperature was observed as shown in Figure 2. On the other hand, the grain size of samples used by Readman and O'Reilly (1972) was estimated to be about 0.1 µm by the broaden-

ing of X-ray peaks. Therefore, generally the same trend of oxidation process was obtained as in the present experiment. The slight but significant difference between the present and their results probably indicates the uncertainty in the determination of x and/or z values (Nishitani 1979).

Low-Temperature Oxidation in Submarine and Subaerial Basalts

Grains of titanomagnetites in oceanic basalts are usually smaller than 10 µm, and a large number of grains finer than 1 µm exist (Lowrie 1974; Irving 1970). Continental basalts contain much larger magnetic minerals and the particle size commonly ranges up to 100 µm or more (Storetvedt et al. 1978).

In the previous section it was shown that the grain size controlled the state of low-temperature oxidation. This effect may appear in the difference between the oxidation states of oceanic basalts and those of continental basalts. Low-temperature oxida-
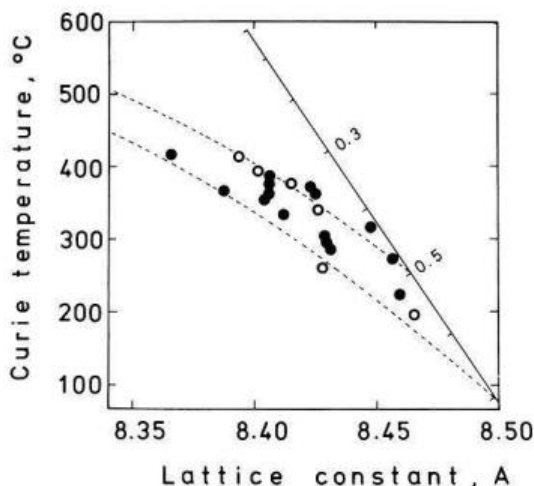

Fig. 5. Relationship between lattice constants and Curie temperatures of titanomagnetites extracted from submarine basalts (*solid circles*) and subaerially erupted basalts (*open circles*). Subaerial basalts were confined to only low-temperature oxidation products
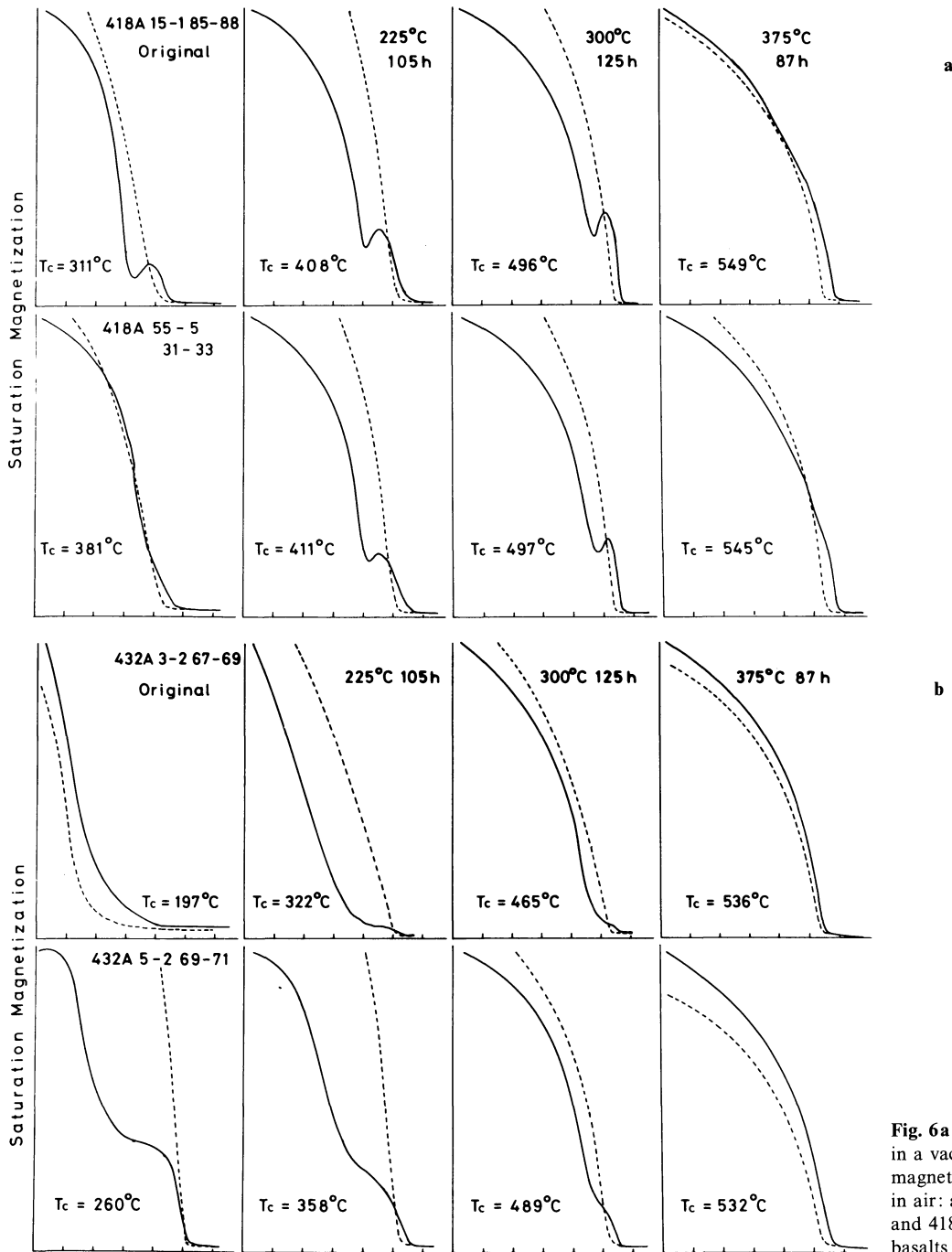
Fig. 6a and b. Thermomagnetic curves in a vacuum (below 1×10^{-5} Torr) for magnetic minerals which were heated in air: **a** submarine basalts (418A 15-1 and 418A 55-5), **b** subaerially erupted basalts (432A 3-2 and 432A 5-2)

tion is affected by other factors such as temperature and f_{O_2}. In this study we pay attention only to the effect of grain size.

Oxidation experiments were carried out on magnetic minerals, obtained by the Deep Sea Drilling Project (DSDP) legs 51, 52, 53 and 55. The samples of Legs 51, 52 and 53 are submarine basalts which originated at a Mid-Atlantic ridge-type spreading center about 100 m.y. ago (Donnelly et al. 1980), while those of Leg 55 are, although now completely submerged, subaerially erupted basalts from the Hawaiian hotspot with ages between 55 and 65 m.y. (Jackson et al. 1980).

Sixteen samples from Holes 417D and 418A (Legs 51, 52 and 53), and six samples from Holes 430A and 433C (Leg 55) were selected and magnetic minerals were separated using a hand magnet. The samples of Legs 51, 52 and 53 basalts were ran-

domly selected, while those of Leg 55 were preferentially selected from those that have undergone only slight high-temperature oxidation and later subjected to varying degrees of low-temperature oxidation. Most of the Leg 55 samples show only the effects of high-temperature oxidation, and their Curie temperatures and lattice parameters were close to those of magnetite (Kono 1980). The relationships between Curie temperatures (T_c) and lattice constants (A) are shown in Figure 5.

It is clear from Figure 5 that most of the data of submarine basalts (solid circles) in a T_c vs. A diagram are confined between two oxidation lines of $x = 0.5$ and 0.7 and various oxidation states exist. This indicates that the magnetic minerals are titanomaghemites with a narrow range of x (0.5–0.7) provided that all magnetic minerals contain no impurities. Analysis with the
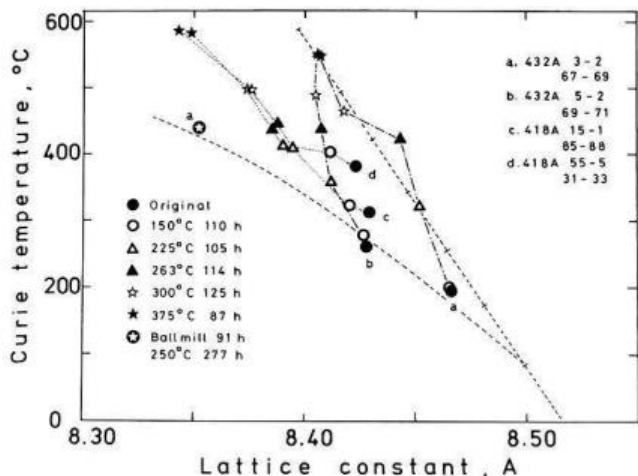
Fig. 7. The effect of heat treatment of magnetic minerals of submarine basalts (418A 15-1 and 418A 55-5) and subaerially erupted basalts (432A 3-2 and 432A 5-2) on the Curie temperature – lattice constant curves. Sample codes, and preparation: conditions are keyed on the figure

microprobe is necessary for exact investigation. The effect of Mg or Al on the magnetic properties of titanomagnetites has been investigated (Nishitani 1981; O'Donovan and O'Reilly 1977a, b). However, lattice constants and Curie temperatures of titanomaghemites containing Mg or Al over the whole range of x have not been reported at the present stage. Therefore the effect of impurities is not considered in this study.

Four magnetic minerals were selected and heated in laboratory conditions. As submarine basalts, 418A 15-1 85–88 and 418A 55-5 31–33 were chosen, which have relatively low z values (Hamano et al. 1980). 432A 3-2 67–69 and 432A 5-2 69–71 were chosen as subaerially erupted basalts because they have low oxidation state and high ulvospinel ratio (Kono 1980). The separated magnetic minerals were heated in air for about 100 h at various temperatures. Thermomagnetic curves are shown in Figure 6. These curves were obtained using a magnetic balance under a magnetic field of 5.5 kOe. All the samples were heated in a vacuum (below 1×10^{-5} Torr) for thermomagnetic analysis up to about 650° C. The change of lattice constants and Curie temperatures of the extracted titanomagnetites as a result of heat treatment are summarized in Figure 7.

The samples 418A 15-1 and 418A 55-5 show similar trends in Figure 7. However, experimental points for 418A and 432A show a different trend as the treatment temperature increases. 432A samples show a sharp rise in Curie temperature, indicating that they are decomposed into Fe-rich titanomagnetite and hemo-ilmenite (high-temperature oxidation). 418A samples show a trend similar to the ball-milled samples, that is, low-temperature oxidation processes seems dominant. However, 418A samples do not follow the low-temperature oxidation line completely, because they contain a slight high-temperature oxidation product. It appears that low-temperature oxidation occurs at the grain size of the magnetic minerals of 418A, but that it does not occur at the grain size of the magnetic minerals of 432A under laboratory conditions.

If small grain size is essential for low-temperature oxidation to occur, 432A samples may also be low-temperature oxidized when their grain size becomes small enough. The magnetic minerals of 432A 3-2 were ball-milled for 91 h and heated for 277 h at 250° C. The result of this heating is also shown in Figure 7. It is evident from this figure that low-temperature oxidation

occurred under the same conditions because the particle size is now smaller than before. Though the sizes of these magnetic minerals were not measured, they are probably less than 0.5 μm, by analogy to other ball-milled samples. It can be concluded from above experiments that the size of the magnetic minerals is one of the controlling factors in low-temperature oxidation.

The sizes of the magnetic minerals were measured only in the samples 418A 55-5 and 432A 5-2 using an electron microscope. The grain sizes which were determined from the photograph of the electron microscope are 1.47 ± 0.83 μm ($N=31$) for 418A 55-5 and 2.11 ± 1.25 μm ($N=30$) for 432A 5-2. As the numbers of grains counted are extremely small, the mean size is not very reliable and likely to contain some error. The magnetic minerals were separated using a hand magnet after they were ground in an agate mortar in a slurry of ethyl alcohol, so that magnetic minerals were probably smaller than the real size in a rock. Magnetic minerals in subaerial basalts in particular, are much larger than the observed value. Nevertheless, it may be concluded that the grain size effect is one of the reasons why oxidation states are relatively low in subaerially erupted basalts and why very severe oxidation states ($z \sim 1.0$) are observed in submarine basalts.

The difference in grain sizes of samples 418A and 432A is not so pronounced. However, 418A samples showed a tendency to low-temperature oxidation, while 432A samples were separated by heating. Particle sizes of 432A samples are greater than the critical size of low-temperature oxidation, therefore only high-temperature oxidation occurs. The effect of ball-milling reduces their grain sizes to less than the critical size. On the other hand, in 418A samples, high-temperature oxidation as well as low-temperature oxidation occurs, because their particle sizes are widely spread.

Ozima and Sakamoto (1971) showed that self-reversal of J_s (saturation magnetization) occurred during progressive low-temperature oxidation if the samples did not suffer initial high-temperature oxidation. They showed that initial conditions such as high-temperature oxidation might influence low-temperature oxidation. Samples which suffered high-temperature oxidation might resist the process of low-temperature oxidation. Therefore, in a re-heating process, subaerially erupted basalts may reveal this difficulty of low-temperature oxidation as a result of high-temperature oxidation.

Conclusions

As a result of experiments on samples of controlled grain size, it has been shown that there is a critical size for low-temperature oxidation in laboratory conditions. The critical size may vary under other conditions, such as those realized in nature. If titanomagnetites smaller than the critical size are heated at moderate temperatures (100–400° C), they are low-temperature oxidized. If the size of a titanomagnetite is greater than the critical size, it decomposes to Fe-rich titanomagnetite and hemo-ilmenite as a result of heating. This citical size is $0.7 \sim 0.8$ μm for $x=0.7$ titanomagnetite. Through this experiment, it has been revealed that the main difference between the results of Ozima and Sakamoto (1971) and Readman an O'Reilly (1972) can be explained in terms of grain size. However, the results of Readman and O'Reilly (1972) do not completely coincide with those of a detailed study (Nishitani 1979).

Magnetic minerals were separated from submarine basalts and subaerially erupted basalts, and lattice constants and Curie temperatures have been measured. In Curie temperature vs. lat-

tice constant diagrams, magnetic minerals of submarine basalts are in the range $0.5 < x < 0.7$ and $0 < z < 1.0$. The oxidation state (z) of the magnetic minerals of subaerial basalts, restricted to low-temperature oxidation products, is less than 0.6. The low-temperature oxidation proceeds in submarine basalts, but unmixing occurs in subaerial basalts as a result of heating. The magnetic minerals of subaerial basalts are also low-temperature oxidized when their grain size is made small enough. It can be concluded from above experiment that the grain size of the magnetic minerals is one of the controlling factors of low-temperature oxidation.

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