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Low-temperature behavior and memory of iron-rich titanomagnetites (Mt. Haruna, Japan and Mt. Pinatubo, Philippines)

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Abstract

We report low-temperature remanence and memory of octahedral crystals of titanomagnetite from Mt. Haruna, Japan and Mt. Pinatubo, Philippines. The crystals have Curie temperatures of 460–490°C, indicating a low Ti content ($0.11 \leq x \leq 0.16$). Saturation isothermal remanence (SIRM) produced at 20 K decreased rapidly in warming through the isotropic temperature, 42 K $\leq T_i \leq$ 55 K, where the first magnetocrystalline anisotropy constant K_1 changes sign and momentarily vanishes. 96–99% of the original SIRM was demagnetized at T_i and none was recovered in recooling from 300 K to 20 K. SIRM produced at 300 K decreased continuously in the course of zero-field cooling, leveling out around T_i. On rewarming to 300 K, 45–60% of the initial SIRM was recovered. This memory or recovered remanence is very large compared to that of magnetite and must be due to domain walls that are more strongly pinned, probably magnetostrictively by crystal defects, which are common in natural crystals. The present low-temperature experiments provide a quick, non-destructive method of identifying iron-rich titanomagnetites in soils, sediments and rocks.

Keywords: iron-rich titanomagnetite; low-temperature cycling; magnetic memory; Haruna dacite; Pinatubo dacite; multidomain titanomagnetite

1. Introduction

The main remanence carriers in almost all continental and submarine igneous rocks are titanomagnetites, $Fe_{3-x}Ti_xO_4$, $0 \leq x \leq 1$. According to electron microprobe and magnetic studies, titanomagnetites in oceanic and continental basalts are titanium-rich, with Ti mol% $x \approx 0.6$. Iron-rich titanomagnetite (IRT), on the other hand, is typical of felsic volcanics and pyroclastics, such as the Haruna dacite and the andesitic and dacitic pumices of Pinatubo and Nevado del Ruiz volcanoes. Most published work on these rocks focuses on their ferrimagnetic hemoilmenites, which have the remarkable property of self-reversal [1–3]. Electron microprobe analysis suggests, however, that the main iron oxides in these pumices are IRTs, with a narrow composition range $0.1 \leq x \leq 0.2$ [3,4]. The IRT grains are in the multidomain (MD) size range and dominate the magnetic properties. IRTs also occur in some volcanic flows

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[5,6], diabase dykes [7], and ash-flow tuffs [8], as well as in the transition zone and sheeted dike complex of the oceanic crust (e.g. DSDP Hole 504B [9]).

IRTs are generally identified by their Curie temperatures T_C of 450–560°C, which are lower than $T_C = 580$°C for magnetite. An alternative method of recognizing IRTs is low-temperature cycling (LTC) of a saturation isothermal remanent magnetization (SIRM) produced at very low temperature and continuously monitored during zero-field warming to room temperature and cooling back to low temperature. Sudden loss of remanence in warming through a characteristic temperature T_i is diagnostic of Ti-poor titanomagnetites with compositions $0.04 \leq x \leq 0.4$ [10]. T_i is an isotropic point at which the first magnetocrystalline anisotropy constant K_1 changes sign and momentarily becomes zero.

There is a wealth of published work on the Verwey transition of natural and synthetic magnetite in single domain, pseudo-single domain and MD size ranges. However, in spite of the common occurrence of IRTs in nature, their low-temperature properties have been little studied. Tucker [11] studied single crystals of synthetic titanomagnetites with $0.52 \leq x \leq 0.7$ and found that remanence transitions and the characteristic peak in the susceptibility curve became less pronounced with increasing Ti content. Moskowitz et al. [10] found a strong dependence of low-temperature saturation remanence on the Ti content in synthetic titanomagnetites with $0.05 \leq x \leq 0.6$. The SIRM produced at 5 K for IRTs with $x < 0.4$ decreased sharply at an isotropic temperature in the course of zero-field warming. In iron-poor titanomagnetites with $x > 0.4$, remanence transitions were not as sharp and broadened with increasing Ti content.

The present experiments are on natural single crystals of IRT from the Haruna and Pinatubo dacites. SIRMs were produced both at 20 K and at 300 K, and were continuously monitored in warming–cooling and cooling–warming cycles between these temperatures. Warming a low-temperature SIRM is a good method of identifying IRTs. Cooling a room-temperature SIRM not only has diagnostic value but also has potential as a paleomagnetic cleaning technique. It serves to remove a large part of the remanence due to loosely pinned domain walls, thereby isolating the stable remanence.

2. Sample characterization

Magnetic measurements were made on titanomagnetites extracted from dacite tuffs of Mt. Haruna, Japan and from dacitic pumices of Mt. Pinatubo, Philippines. The titanomagnetite crystals were 0.1–0.6 mm on edge and the eight {111} faces of the octahedron were flat and smooth. X-ray unit-cell edges were determined using a Debye–Scherrer camera with Fe–Kα radiation on one representative crystal from Haruna (H-4) and Pinatubo (P-2). Independent estimates of the unit-cell dimensions were made from (111), (220), (311), (400), (333,511) and (440) reflections. The spinel unit-cell edge for H-4 was $a = 8.409 \pm 0.004$ Å. A similar result, $a = 8.403 \pm 0.002$ Å, was found by Uyeda [1] for Haruna titanomagnetites. Crystal P-2 had $a = 8.406 \pm 0.007$ Å. The Ti content (or ulvospinel fraction) x was obtained by comparing our cell-edge data with the calibration curve of O'Reilly [12] for pure synthetic titanomagnetites. The X-ray cell parameters correspond to $x = 0.16$ and 0.13 for H-4 and P-2, respectively. However, naturally occurring titanomagnetites contain other impurities such as Mn, Mg, Al, Cr and Zn in small quantities. The major cations, diamagnetic Mn^{2+} and Al^{3+}, reduce the cell edge when they replace Fe^{2+} and Fe^{3+} [13–15]. Therefore, the estimated x values of 0.13 and 0.16 for the Pinatubo and Haruna titanomagnetites are upper limits.

High-field thermomagnetic curves measured with a vibrating-sample magnetometer (VSM) gave Curie temperatures T_C of 450–475°C for Haruna and 480–488°C for Pinatubo titanomagnetites (Fig. 1). These T_C values allowed an independent estimate of x for the present titanomagnetites by comparison with the T_C data of Stephenson [16]. The x values estimated in this way were 0.11–0.13 for Pinatubo and 0.14–0.16 for Haruna titanomagnetites. The presence of impurities such as Al^{3+}, Mn^{2+} and Mg^{2+} would re-

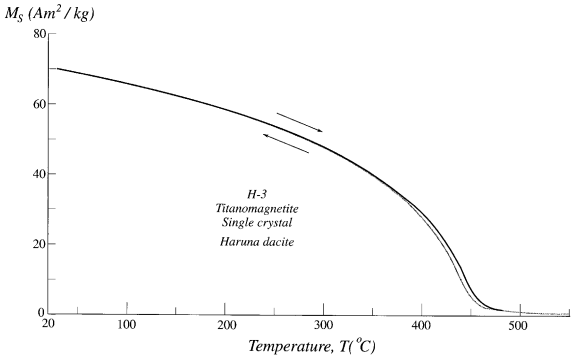

Fig. 1. Strong-field (1.5 T) thermomagnetic curve for a titanomagnetite crystal from the Haruna dacite.

duce T_C as well as cell-edge values, so that again these estimates of x are upper limits for the Ti content. Bina et al. [3] carried out electron microprobe analyses on 10 titanomagnetite crystals extracted from Pinatubo pumices and found that the major impurities are Al^{3+} and Mg^{2+}. Their analysis gave a Ti content $x = 0.095 \pm 0.002$. Another microprobe study [4] reported a slightly higher value, $x = 0.12$, for Pinatubo titanomagnetites.

Room-temperature hysteresis parameters were measured for 12 Haruna and Pinatubo titanomagnetite crystals with a VSM. The observed saturation magnetization M_s was 68–72 Am^2/kg for Haruna and 73–76 Am^2/kg for Pinatubo crystals. These values are lower than the expected 75 and 80 Am^2/kg for pure synthetic TM15 and TM11, respectively [12,17]. The low M_s values of our titanomagnetites are probably the result of impurities such as chlorite or biotite, which are common inclusions in natural titanomagnetites.

The hysteresis curves have ramp-like shapes, with low coercive forces H_c of 66 μT to 0.96 mT and saturation remanence ratios M_{rs}/M_s of 0.001–0.01 (Fig. 2), indicating MD behavior. The susceptibility $\chi = dM/dH$ is essentially constant with respect to H over the range $0 \leq M \leq 0.68 M_s$, above which domain rotations begin to contribute to the approach to saturation (Fig. 2). The demagnetizing factor N, which characterizes the internal field of an MD grain, was determined as $N_{cgs} = 1/\chi = 3.44$ from the data of Fig. 2. The value estimated from $N \approx H_c/M_{rs}$ [18]

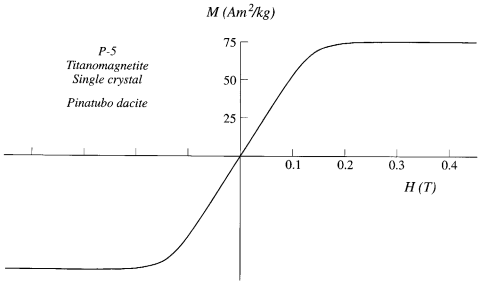

Fig. 2. Typical saturation hysteresis loop measured at room temperature. The ramp-like form of the hysteresis loop indicates MD behavior.

for the same crystal is 3.42, in good agreement with the value from the slope of the hysteresis ramp.

3. Low-temperature remanence measurements

Low-temperature measurements were made on five crystals between 20 and 300 K with an MPMS-2 SQUID magnetometer at the Institute for Rock Magnetism, University of Minnesota. Titanomagnetite crystals were given an SIRM at 20 K in a field of 2.5 T, and then cycled in zero field to 300 K and back to 20 K. All samples showed a remanence transition at 43–54 K (projected intersections between the linear data trends below and above the transition; Figs. 3 and 4). Following Moskowitz et al. [10], we interpret

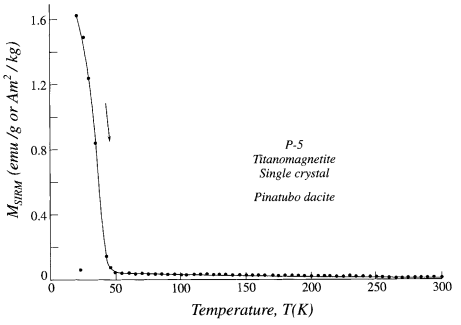

Fig. 3. Zero-field warming curve of SIRM of single-crystal titanomagnetite from the Pinatubo dacite during warming from 20 K to 300 K. A sharp decrease in remanence around 44 K marking the isotropic point is diagnostic of IRT. The single point at 20 K is the memory after cooling from 300 K.

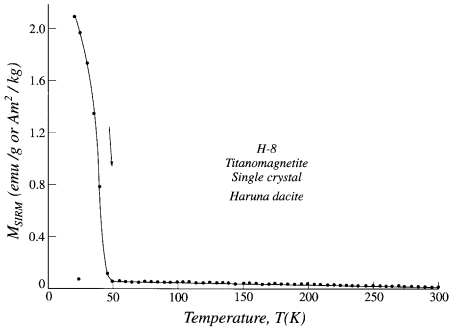

Fig. 4. Zero-field SIRM warming curve of single-crystal titanomagnetite from the Haruna dacite. The warming curve is very similar to that of P-5 (Fig. 3). At the isotropic point $T_i = 46$ K, 97% of the original SIRM has been demagnetized.

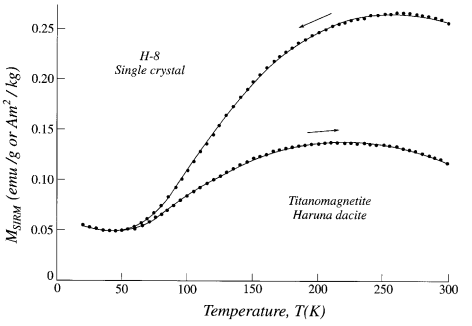

Fig. 5. Temperature variation of room-temperature SIRM of a Haruna titanomagnetite crystal during zero-field cooling from 300 K to 20 K and zero-field warming back to 300 K. The isotropic point is less well defined compared to that of the SIRM warming curve in Fig. 4. At room temperature, 46% of the initial SIRM has been recovered.

these transitions to be isotropic points. Although $K_1 = 0$ has only been measured for $x = 0.05$ and 0.10 (both of which gave $T_i \approx 90$ K [17,19]), extrapolation of the K_1 data for $x = 0.18$ and 0.19 suggests an isotropic point at or below 50 K for these compositions. At T_i, 96–99% of the initial SIRM of our crystals was demagnetized. The remaining remanence decreased slightly during warming from 60 to 300 K but this loss was regained during cooling. The SIRM memory after recooling to 20 K was essentially the same as the SIRM remaining at 50–60 K in the original warming. Thus, SIRM produced at low temperature in our MD IRTs is almost completely demagnetized during warming through T_i and no memory of the demagnetized fraction is recovered in recooling through the transition.

The titanomagnetite crystals were given a new SIRM in a field of 2.5 T at 300 K, then cooled to 20 K and warmed back to 300 K in zero field. The resulting LTC curves (Figs. 5 and 6) are very different from the LTC curves for low-temperature SIRM (Figs. 3 and 4). The remanence at first increased with cooling, reaching a broad peak around 250 K, and then decreased gradually with cooling to the isotropic temperature, 42 K $\leq T_i \leq$ 55 K. The isotropic point is marked by a shallow minimum in the remanence curve, but is less sharply defined than in the warming curves of low-temperature SIRM. At T_i, 50–80% of the room-temperature SIRM was demagnetized for both Haruna and Pinatubo titanomagnetites. The fraction that demagnetizes in cooling to T_i is presumably responding to the changing $K_1(T)$ and resides in loosely pinned domain walls. In warming from 20 K to T_i, the behavior was completely reversible. Warming above 50 K resulted in an increase in SIRM, followed by a broad maximum around 220 K, and then a smaller, more gradual decrease between 220 and 300 K. At room temperature, 45–60% of the original SIRM was recovered. Despite their different origins and x values, all the Pinatubo and Haruna titanomagnetite crystals had similar LTC curves and similar intensities of SIRM and SIRM memory.

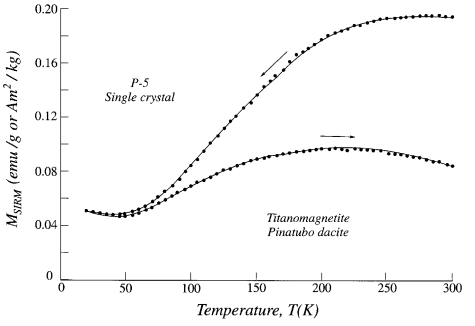

Fig. 6. Zero-field cooling and warming curves for SIRM produced at 300 K in a crystal of titanomagnetite from the Pinatubo dacite. The room-temperature SIRM memory of 44% is very similar to that of the Haruna titanomagnetite crystal (Fig. 5). This probably reflects the defect concentration in these natural crystals.

4. Discussion

The substitution of Ti^{4+} in stoichiometric magnetite results in an equal increase in Fe^{2+} concentration, which in turn strongly affects the magnetic and physical properties, such as T_C, M_s, H_c, and cell-edge parameter a. It is generally accepted that all Ti^{4+} ions are located in octahedral sites and an equal number of Fe^{3+} ions change into Fe^{2+} ions, in order to preserve charge neutrality [20]. According to the O'Reilly and Banerjee [21] model, in the region of composition $0.2 \leq x \leq 0.8$, each new Fe^{2+} ion enters a tetrahedral site, so that both sublattices are occupied by Fe ions of mixed valence. The Fe^{2+} ions cause a cubic expansion of tetrahedral sites, resulting in a trigonal distortion of the cubic geometry of the octahedral sites [22,23]. Large values of magnetocrystalline anisotropy and magnetostriction with increasing x at low temperatures [24] are associated with this distortion.

For compositions $0 \leq x \leq 0.2$, cation distributions are governed by the preference of Fe^{3+} for tetrahedral sites, as in magnetite, where Fe^{2+} ions enter octahedral sites and Fe^{3+} ions occupy both sublattices. However, even a small number of Ti^{4+} ions in octahedral sites produce significant changes in the magnetic properties. A Ti^{4+} content $x \geq 0.037$ results in the disappearance of the Verwey transition [25]. Thus, any sharp transition in SIRM warming curves for titanomagnetite compositions $0.037 \leq x \leq 0.2$ must be an isotropic point, not a crystallographic phase transition.

Multidomain titanomagnetite crystals from the Haruna and Pinatubo dacites undergo important changes in remanence at the isotropic point. Low-temperature SIRM drops irreversibly to near zero in warming across T_i, with almost no recovery in the second crossing (Figs. 3 and 4). Room-temperature SIRM has entirely differently LTC behavior, changing continuously during cooling to T_i, behaving reversibly during cooling and warming below T_i, and recovering a partial memory of the lost remanence in warming above T_i (Figs. 5 and 6). Another interesting observation is that low-temperature SIRM was 8–11 times more intense than room-temperature SIRM. Low-temperature SIRM below the isotropic point must therefore have a different domain structure than SIRM produced at room temperature.

We interpret these contrasting properties to be the result of differences in anisotropy and magnetostriction below and above T_i. Our results superficially resemble LTC curves measured for pure magnetite, and we can gain some insight from models proposed for magnetite. However, there are some major differences:

1. In IRTs of the compositions that we have studied ($0.11 \leq x \leq 0.16$), there is no crystallographic phase transition analogous to the Verwey transition T_V in magnetite.
2. IRTs show no jump in magnetization in cooling through their remanence transitions, whereas in magnetite remanence jumps across T_V are a property of both fine and coarse grains [26–29].
3. Room-temperature SIRM memories after LTC are three to five times larger for our titanomagnetite crystals than for magnetite crystals of similar size [26,28].

In magnetite, the large SIRM and sharp transition observed when approaching T_V from below are due to the very high anisotropy of the low-temperature monoclinic phase. The low-temperature phase of IRTs is presumably cubic. Nevertheless, the only plausible explanation for our observations is strong pinning of domain walls out of equilibrium with the self-demagnetizing field $\boldsymbol{H_d}$, both at 20 K when intense SIRM is produced and during warming to T_i. We thus postulate that K_1 and/or the magnetostriction constants λ_{111} and λ_{100} have much higher values below T_i than above. There are no measurements of these parameters below 77 K, but extrapolation of the data for $x = 0.18$ suggests a zero point in K_1 at approximately the observed T_i and strongly increasing values of λ_{100} [17].

Above T_i, wall pinning is weaker. This explains why SIRM produced at room temperature is much less intense than low-temperature SIRM: $\boldsymbol{H_d}$ can more effectively move domain walls after the magnetizing field is turned off. Weak pinning also explains the continuous change in remanence, ultimately down to 20–50% of the original SIRM, as our crystals are cooled to T_i. This gradual change is due to progressive movements of do-

main walls re-equilibrating in response to $\boldsymbol{H}_{\mathbf{d}}$. The movements may be reversible (walls moving within shallow potential wells around defects) or irreversible (walls jumping between potential wells). Wall width is proportional to $|K_1|^{-1/2}$ [30], so that as $|K_1|$ decreases with cooling, walls become broader and are less effectively pinned by localized defects [31]. The role of magnetocrystalline anisotropy in wall pinning and displacement is indicated by the humps in the cooling and rewarming curves around 220–250 K, in the same temperature range where $|K_1|(T)$ reaches a maximum for titanomagnetites with $0 \leq x \leq 0.18$ [17].

Below T_i, $|K_1|$ increases and so does λ_{110} for $x = 0.18$ [17]. Changes in the surviving 20–50% of the SIRM are reversible and minor because the pinning is stronger: walls are narrow and move small amounts within deep potential wells. These walls whose remanence is not destroyed by cycling through T_i must be pinned magnetoelastically, probably by arrays of dislocations, which are common in natural titanomagnetite crystals. λ_{111} and λ_{110} are unlikely to be zero at the K_1 isotropic point [17,23] and magnetoelastic anisotropy thus remains important at this temperature.

In warming from T_i to room temperature, about one-third of the remanence lost in cooling was regained. The warming curve resembles a scaled-down replica of the cooling curve, showing that a substantial fraction of the soft (easily moved) domain walls never escaped from their pins but moved reversibly in local potential wells. If these walls had jumped irreversibly in the direction of $\boldsymbol{H}_{\mathbf{d}}$, i.e. toward a demagnetized state, during cooling, they could not jump back in opposition to $\boldsymbol{H}_{\mathbf{d}}$ during warming. Similarly, in stepwise LTC of magnetite to progressively lower temperatures, changes down to 180–200 K have been observed to be mainly reversible and magnetoelastically controlled, while larger changes in further cooling were mainly irreversible and due to $K_1(T)$ [32,33].

It has been speculated that residual remanence which remains undemagnetized in crossing a transition serves to renucleate part of the 'lost' softer remanence on recrossing the transition [26]. This is not a viable model of magnetic memory in our experiments. The undemagnetized remanence at T_i is 0.045–0.050 Am^2/kg whether T_i is first approached from below (Figs. 3 and 4) or from above (Figs. 5 and 6). In our other results (not illustrated), the residual level is as high as 0.13 Am^2/kg but the level is again about the same for a 20-K SIRM warmed through T_i as for a 300-K SIRM cooled through T_i. Yet in the first case, the recovered memory of lost SIRM in cooling back through T_i to 20 K is practically zero, while in the second case about one-third of the lost room-temperature SIRM is recovered on warming.

The SIRM memories at room temperature of the present titanomagnetites were 45–60% (this includes the hard remanence which survives across T_i as well as the recovered soft remanence). The recovery is greater than that of MD magnetites, in which SIRM memories are typically 10–20% [26,28,34]. Substitution of titanium in titanomagnetites must favor a higher proportion of reversible wall movements within potential wells compared to irreversible wall jumps. Since both λ_{111} and λ_{110} increase considerably between $x = 0.10$ and 0.18 [17], the mechanism is likely deeper potential wells and more effective magnetoelastic pinning of walls as the Ti content increases.

5. Diagnostic value of LTC curves of IRTs

Although we do not fully understand the underlying mechanisms, the shapes of LTC curves of IRTs have some diagnostic features that can help in identifying these phases without destructive heating to determine T_C. First, SIRM produced at very low temperature and heated through T_i decreases strongly just below T_i and hardly at all above T_i, allowing an estimate of T_i (in the range $42\ K \leq T_i \leq 55\ K$ for our samples with $0.11 \leq x \leq 0.16$). This behavior was previously observed for synthetic titanomagnetites of this general composition [10] but natural examples were lacking. Second, there is essentially no recovery of SIRM in recooling through T_i, a property not previously documented. The sharpness and irreversibility of this remanence transition provide a sensitive technique for detecting IRTs in rocks

and sediments. The transition temperature T_i is well above the 34 K transition of pyrrhotite [35], although the two transitions might be difficult to separate if coarser temperature steps were used [36].

Cooling–warming cycles of room-temperature SIRM of IRTs are also distinctive. The remanence changes continuously over a broad temperature range, leveling out at T_i and recovering a substantial memory (about one-third of the original remanence) in warming. This memory is two to three times that of magnetites of similar size. The LTC curves also provide information about the temperature variation of the magnetic anisotropies which control the remanence.

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