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A study of the self-reversal process of rhyodacites from Haruna volcano, Japan and those from the 1991 Pinatubo eruption, Philippines

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Abstract: The results of the study of young rhyodacites (erupted in 1400 year) from the Haruna area (Japan) and from the 1991 Pinatubo eruption (Philippines) are presented. The experimental works have proven that the *Fe-Ti ferrimagnetic-antiferromagnetic phase* is the carrier of the self-reversed remanent magnetization in these rocks. The theoretical solution of this problem has been outlined, but has not yet been accomplished.

Key words: The Fe-Ti ferrimagnetic-antiferromagnetic phase, the sole carrier of the self-reversed remanent magnetization in the Haruna and Pinatubo rhyodacites

1. Introduction

In nature the rocks with the reversed direction of remanent magnetization (RM) with respect to today's orientation of the geomagnetic field are very frequently present. A case when the reversed RM was revealed in very young rhyodacites (erupted in 1400) of Haruna locality in Japan, during the period of normal direction of the geomagnetic field was very surprising. Many authors had started the studies of the rocks with reversed RM long time ago: *Nagata et al. (1952); Nagata and Akimoto (1953); Uyeda (1955, 1958); Ishikawa (1958); Nagata and Uyeda (1959); Nagata (1961, 1963); Ishikawa and Syono (1963).* Some results are reviewed in *Stacey and Banerjee (1974).* The studies of the Haruna rhyodacites were undertaken by *Orlický et al. (2000), Orlický and Funaki (2000), Orlický and Funaki (2001); Ozima and Funaki (2000).* The results of these studies pointed out on the existence of a very important phenomenon - the self-reversal of RM

in the rocks. An enrichment of the knowledge in this field has been gained by the studies of dacites from Shasta Mts. (*Nord and Lawson, 1992*), the study of self-reversed TRM by *Hoffman (1992)* and by many other authors. In recent time (in 1991) the Pinatubo volcano (Philippines) erupted, which produced also the rhyodacite carrying the reversed RM. The self-reversed TRM of Pinatubo rhyodacites was studied by *Ozima et al. (1992)*, *Hoffmann and Fehr (1996), Bina et al. (1999), Goguitchaischvili and Prévot (2000), Prévot et al. (2001), Orlický and Funaki (2002).* The results outlined many useful explanations about the sources and mechanism of the self-reversal RM, but many details of this point remained unrevealed.

I study the self-reversal of RM of young and old continental volcanics from different places of the Globe. I have revealed that the main source of the reversed RM of the self-reversal origin are the Fe-Ti ferrimagnetic - antiferromagnetic phases, which have frequently occurred during either their primary in appearance volcanics, or during their low or high temperature alterations in post volcanic time in the field (e.g. in *Orlický (2009)*; in the low-temperature oxidized Fe-Ti oxide bearing basalts the antiferromagnetic phase with $T_N \approx 450\,^\circ$C was evidenced in all samples with the reversed RM).

As has been mentioned above, the previously studied rhyodacites are very suitable objects to make an enrichment of the current knowledge about the self-reversal problem. For this perspective I studied again the rhyodacite samples from Haruna and Olongapo localities. The results of this study are the subject of this paper.

2. The results of laboratory experiments

I select the following results about the Haruna rhyodacites published in *Orlický et al. (2000)*, *Orlický and Funaki (2000, 2001)*:

1. The results of thermal demagnetization of natural samples: twenty four natural samples from three individual Haruna localities (signed 1, 2, 3; in *Orlický et al. (2000)*) were observed under different conditions. All samples from the locality 1/1 showed the normal polarity of RM (declination $D = 67.4^\circ$, inclination $I = 38.1^\circ$), after demagnetization to 475 °C. The reversed RM was detected in interval 475 to 600 °C.

The samples from other localities (2,3) pointed out only the reversed RM after thermal demagnetization.

2. Laboratory-induced thermoremanent magnetization (TRM) in the field of 48 μT in the samples was realized after their heating at 700 °C and cooling to room temperature (keeping at 700 °C during 60 minutes). The TRM in 7 samples was induced within the interval of 700–25 °C. The samples were oriented in the direction of ambient field. The samples were then thermally demagnetized. A following polarity of TRM was detected: six samples showed reversed polarity in 25–250° interval, and relatively low value of TRM of normal polarity in 250–380 °C interval, then very low value of reversed TRM was detected in the interval 380–550 °C. In only one sample the low values of reversed TRM were achieved in the interval of 25–250 °C; in 250–500 °C interval, the normal polarity of TRM was detected.
3. In 24 samples of Haruna dacite the partial thermoremanent magnetization (PTRM) was induced according to a procedure described in *Orlický et al. (2000)*. After demagnetization of samples in magnetic vacuum at 700 °C temperature an annealing of magnetic phases was made during 60 minutes. Then the PTRM was induced, in 40 °C interval during 20 minutes, in the range of 630 to 50 °C. In other temperature intervals the ambient field was fully compensated. Except of PTRM the measurements of the change of magnetic susceptibility (κ) was measured at each step. Generally, the reversed PTRM was induced in the samples between cca 550 to 400 °C and then between 320 to 50 °C intervals. The normal PTRM was mostly induced in the intervals between 400–320 °C or over 550 °C. While the samples of rocks from locality No. 1 acquired the normal PTRM (some of them were only of normal polarity for whole 630 °C interval) more frequently, the rock samples from localities No. 2 and No. 3. acquired only the negligible values of normal PTRM and dominantly only reversed PTRM was induced in the 530 to 50 °C interval.

The results of an additional study of original Haruna rhyodacite rocks and that of Pinatubo volcano rhyodacite ash fixed in gypsum

An induction of PTRM in eight natural samples of rhyodacites and the

Laboratory-induced PTRM of original rhyolite dacite samples from Haruna locality

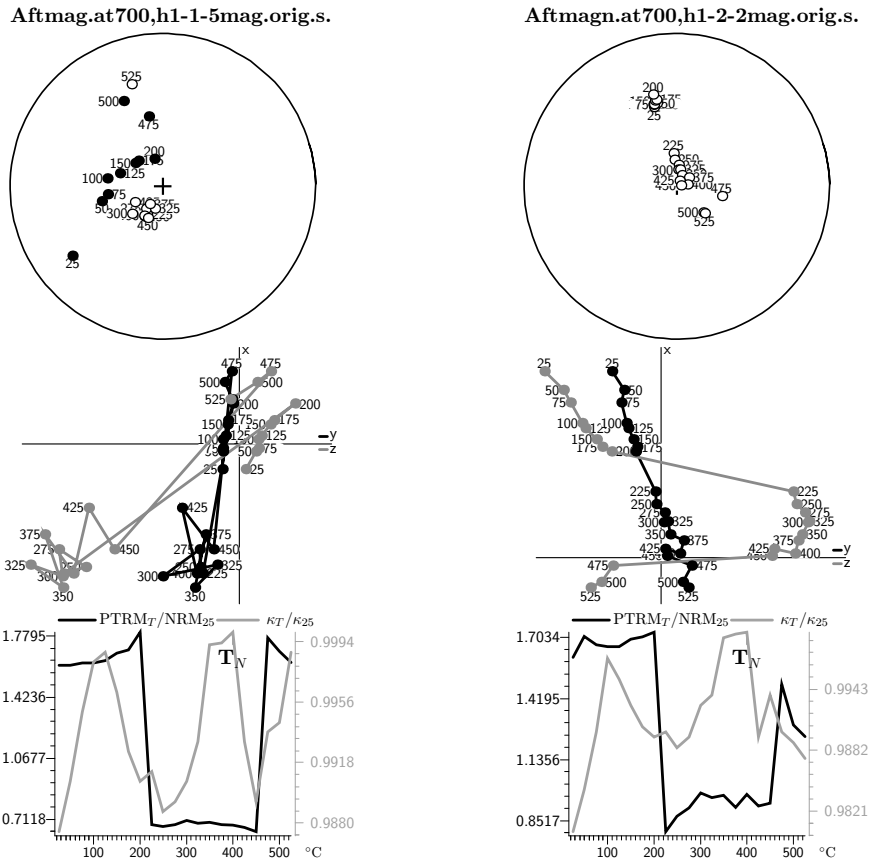

Fig. 1. The results of inducing of PTRM and the change of magnetic susceptibility of samples h1-1-5 and h1-2-2 at different temperatures. Zijderveld diagrams and stereographic projections; • (○) - positive (negative) polarity of PTRM; κ- magnetic susceptibility; κ_T at T, κ_{25}-at 25 °C; PTRM$_T$ - partial thermoremanent magnetization at temperature T; TRM$_{25}$ - thermoremanent magnetization induced in the field of $H = 0.48$ μT during 60 min. heating at 700 °C and successive cooling of the sample to laboratory temperature. T$_N$ - Néel temperature of Fe-Ti antiferromagnetic phase.

two artificially prepared samples with the Ilm-hem and the Ti-Mt fraction (separated from original samples) and fixed in gypsum from Haruna local-

Laboratory-induced PTRM of original rhyolite dacite samples from Haruna locality

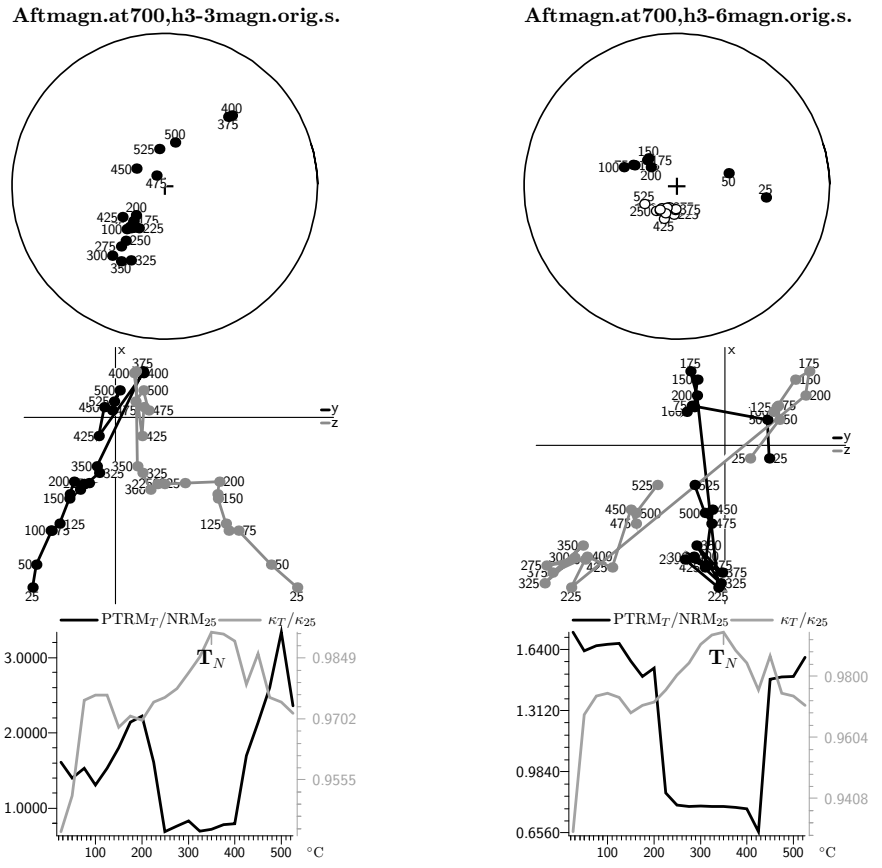

Fig. 2. The results of inducing PTRM and the change of magnetic susceptibility of samples h3-3 and h3-6 at different temperatures. Zijderveld diagrams and stereographic projections. For explanations, see Fig. 1.

ity and the two samples from Olongapo locality (Pinatubo eruption) of the rhyodacite ash fixed in gypsum was performed. All samples were heated to 700 °C, and then the TRM was induced in the field of intensity 48 μT in all samples, during cooling from 700 °C to room temperature. In 8 natural rhyodacite samples from Haruna locality the PTRM was induced in the field

Measurement of the change of magnetic susceptibility of magnetic Fe-Ti fraction of rhyolite dacite samples from Haruna locality

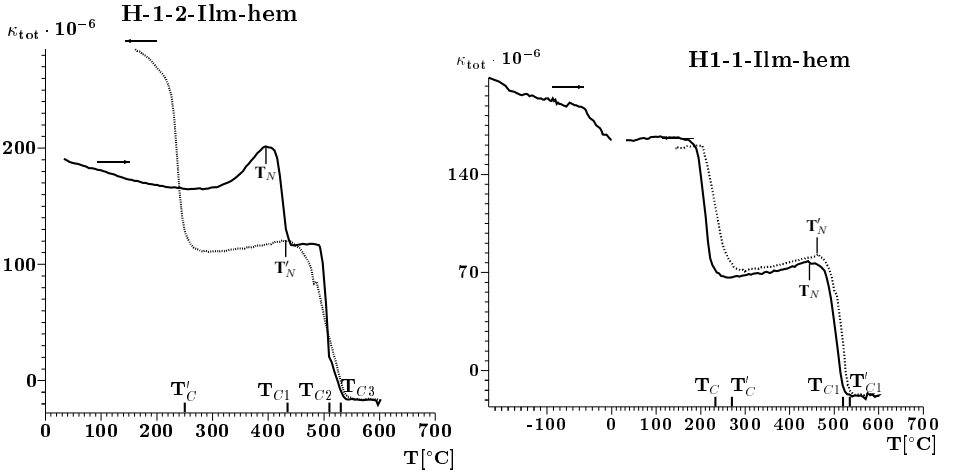

Fig. 3. Thermomagnetic curves of samples (the measurements of the change of magnetic susceptibility-κ with temperature): sample H1-2-Ilm-hem was separated as a weaker magnetic fraction from the coarse grinded original rhyolite dacite without any heating; sample H1-1-Ilm-hem was separated from the coarse grinded original rhyolite dacite during its heating at 350 °C. The Ti-Mt was separated from heated magnetic fraction by permanent magnet. T_C - T_{C2}, T'_C - T'_{C1} - Curie temperatures detected during heating and cooling of samples, respectively. T_N, T'_N - Néel temperatures of Fe-Ti antiferromagnetic phase detected during heating and cooling of samples, respectively.

of intensity 48 μT during heating of the samples at 20 steps (25 °C step, in the range 50–600 °C). The heating of samples at each step and inducing of PTRM took 30 minutes. After cooling of the samples the PTRM of samples was measured at room temperature. At the same time a change of κ was measured after cooling the samples (Figs. 1, 2). The artificially prepared samples were thermally demagnetized (Figs. 4, 5). The intensity of PTRM of samples was computed with respect to sign (plus or minus) of individual x, y, z components).

The role of magnetic susceptibility in magnetic Fe-Ti phases

Previously only little attention was paid to the magnetic susceptibility (κ) in the studied rocks. But the measurement of κ of rocks is decisive for the detection of any changes in magnetic minerals during their temperature

treatment, moreover the antiferromagnetic and ferrimagnetic phases except of the Curie points can be identified. From Figs. 1, 2, 4, 5 (and from the results of other 4 studied samples) we see that very conspicuous changes of κ have been evidenced after heating and successive cooling of samples. E.g. in the sample h1-1-5 there is an increase of κ from 25 °C with a maximum at 140 °C, followed by a decrease to minimum at 240 °C. This behaviour corresponds to a presence of ilm-hem phase with Curie temperature $T_C \approx$ 240–250 °C, when comparing these results with those pictured in Fig. 3. From cca 240 °C there is an increase of κ with a maximum at 400 °C (an increase of κ of sample corresponds to a change of about 225×10^{-6} SI Units in this interval). Afterwords, a sharp decrease in κ is detected. The increase of κ with the maximum at about 400 °C corresponds to the *antiferromagnetic phase* with the Néel temperature of $T_N \approx 400$ °C; at this temperature there is a complete antiparallel magnetic moment arrangement in magnetic Fe-Ti phase. Such, or very similar behaviour of κ with T_N temperature was evidenced in all natural samples of Haruna dacites.

3. Results

The results of only four samples are shown in Figs. 1, 2, but similar magnetic behaviour have been detected for other 4 samples from Haruna locality. A complete self-reversed PTRM (all x, y, and z components were reversed) in a whole 25–600 °C interval attained the samples h2-2, h2-3 h3-3a and h3-5 and partly the sample h2-3. The PTRM of the sample h3-3 acquired only the positive z component in the interval 25–600 °C, but the reversed x, y components in 350–600 °C interval (Fig. 2). The sample h1-2-2 attained also only non-complete reversed PTRM (Fig. 1), similarly to the sample h3-6 (Fig. 2). The sample h1-1-5 shows a positive (+) x and z components of PTRM from 25 to 200 °C, then all components (x,y,z) of PTRM are of the reversed sign (complete self-reversal) with intensity 1060 nT at 225 °C. As we see from Fig. 1 the similar reversed values of PTRM were acquired in the 8 intervals between 225 to 450 °C. At 475 °C and 500 °C a normal PTRM was acquired, and an increase of normal value of intensity of PTRM was detected. In the interval 525–600 °C the reverse PTRM was acquired again. Previously other types of temperature treatment and inducing of

the TRM in the same sample were realized. The sample was kept under the magnetic vacuum in the course of a cooling from 700 °C to 630 °C, and below the lower limit of temperature interval, the TRM was induced in the field of intensity $H = 48$ μT (in the intervals 630–590 °C, successively in 630–550 °C and in the last run in 630–70 °C interval). The results showed that the TRM of the h1-1-5 sample attained the reversed polarity (and low, about 350 nT value of the reversed intensity of PTRM) only within very narrow interval 140–80 °C. Below 80 °C and over 140 to 600 °C only normal TRM of sample h1-1-5. Similar behaviour of TRM was detected also for other samples of the h1-1 locality. While these results have pointed out only very rare acquisition of the self-reversed TRM, the reversed PTRM of the same sample was induced in the large temperature interval, and on the contrary the normal polarity of PTRM was induced very rarely. The TRM of samples from localities No. 2 and No. 3 was dominantly of the reversed polarity, and if there is the normal TRM in some temperature intervals it is of low intensity. The results have shown that the Fe-Ti magnetic minerals in natural Haruna volcanic body were dispersed very heterogeneously and they have a different level of their magnetic state. This property has been reflected in magnetic characteristics of individual samples. Some of them have shown the reversed RM and others only normal RM after their thermal cleaning, especially after the inducing of TRM or PTRM in the samples, despite they were collected from the narrow places, or the same place.

The evidence of the most effective temperature interval for inducing of the self-reversed PTRM of samples

The artificial samples were prepared for laboratory study. The ilm-hem and Ti-Mt were separated from Fe-Ti fraction of natural Haruna rhyodacite and that of the rhyodacite ash from Olongapo locality (I remind that no physical separation is such effective to separate the ilm-hem from Ti-Mt perfectly, because some grains are intergrowth). The magnetic fractions were then fixed into the cylindrical-shape samples from gypsum. The samples were heated to 700 °C and the TRM was induced according to the procedure described above. The samples were then stepwise thermally demagnetized (Figs. 4, 5).

From the stereographic projection of sample H12-Il-He it is evident that except of normal TRM detected at 570 °C, in all other steps the TRM re-

mained reversed (Fig. 4) during thermal demagnetization. We see a gradual increase of TRM from 25 to 240 °C followed by a sharp decrease of the curve TRM_T/TRM_{25} (Fig. 4). This can delineate the first phase with the blocking temperature about 350 °C. There is also a second phase in the sample, with the blocking temperature about 560 °C. We see a gradual decrease of κ_T/κ_{25} up to about 315 °C followed by an increase of κ with maximum about 435 °C. The decrease of κ continues to about 575 °C (Fig. 4). The first phase corresponds probably to ilm-hem, the second phase to the antiferromagnetic phase with Néel temperature T_N about 435 °C. This phase contains probably both the ilm-hem and the Ti-Mt solid solutions, taking into account the results of natural samples and the results of Curie temperature measurements of separated Fe-Ti fractions. The magnetic behaviour is different in the sample with Ti-Mt fraction (Fig. 4, sample H12-Ti-Mt). From the stereographic projection it is evident that only at 570 and 600 °C the TRM is reversed, but in other 11 temperature steps (25–500 °C) the TRM of the sample is of normal polarity. The TRM_T/TRM_{25} curve shows a gradual decrease up to about 435 °C, and then follows a sharp decrease of the curve with a blocking temperature of about 570 °C (a different slope of the curve at about 500 °C outlined a presence of other phase in the sample). We see from the curve κ_T/κ_{25} that in 25 to about 210 °C interval there is a gradual decrease of magnetic susceptibility, but from 210 °C to about 350 °C there is a sharp increase of κ with maximum at 350 °C. I assume that this temperature corresponds to T_N of the antiferromagnetic phase. Then there is a decrease of κ up to 440 °C (T_N of antiferromagnetic phase), then it sharply decreases down to 500 °C (T_C of ferrimagnetic phase) and after that an increase of κ is present.

In the stereographic projection of sample Ol-Il-He, except of normal TRM at 600 °C, the TRM remained reversed in all other steps of thermal demagnetization (Fig. 5). Very smooth increase of TRM from 25 to 240 °C and then a sharp decrease of the curve TRM_T/TRM_{25} is present for this sample. It corresponds to the first phase with the blocking temperature of about 400 °C. The second phase has the blocking temperature of about 560 °C. A smooth decrease of κ_T/κ_{25} up to about 280 °C (it corresponds to T_C of ilm-hem phase) and then an increase of κ with maximum about 435 °C (it corresponds to T_N of antiferromagnetic phase) is evident. Then it is followed by the decrease of κ to about 575 °C (Fig. 5). The second

phase with Néel temperature T_N about 435 °C contains probably both the ilm-hem and the Ti-Mt solid solutions. The magnetic behaviour is different in the sample with Ti-Mt fraction (Fig. 5, sample Ol-Ti-Mt). From the stereographic projection it is evident that in 25 to 250 °C interval the TRM of the sample is reversed after demagnetization, but in other 7 temperature intervals (in 300–600 °C) the TRM of the sample is of normal polarity. The TRM_T/TRM_{25} curve shows a complicated shape like in the sample of H-Ti-Mt (Fig. 4). Soft changes, gradual decrease up to about 435 °C, and then a sharp decrease of the curve with a blocking temperature about 570 °C (a different slope of the curve at about 500 °C outlined a presence of other phase in the sample) are evident. The curve of κ_T/κ_{25} shows its decrease up to about 200 °C. After this point there is a sharp increase of κ with a maximum about 340 °C of the sample (Fig. 5, sample Ol-Ti-Mt). The decrease of κ to about 500 °C and then an increase of κ up to 580 °C and then decrease was detected. The dominant portion of Ti-Mt magnetic mineral and a minor portion of ilm-hem magnetic mineral are present in this sample. Despite there is probably present also the antiferromagnetic phase in this sample, we were not able to visualize it, because of very conspicuous increase of TRM in the interval about 340 °C (we see a very intense increase of TRM; but if there is an antiferromagnetic phase we cannot expect an inducing of high TRM in this point).

The source of the self-reversed RM in rhyodacites

According to electron microprobe analyses, the titanomagnetite (Ti-Mt) grains were detected in the two polished samples. No ilmenite-hematite (ilm-hem) grains were detected. But the results of the Curie temperature measurements revealed also the ilm-hem in Fe-Ti fraction of rocks samples. The Fe-Ti fraction separated from original sample at room temperature contained the two Fe-Ti magnetic minerals. One with Néel temperature (T_N) = 420 °C (of antiferromagnetic state) and the other with (T_C) = 515 °C (Fig. 3). During heating to 600 °C and successive cooling of the sample on air, the original Fe-Ti mineral was divided into the ilm-hem with the Curie temperature (T_C) of 230 °C and the second Fe-Ti magnetic mineral containing the antiferromagnetic phase with (T_N) = 440 °C and a Ti-Mt phase with T_C = 520 °C. I separated a Fe-Ti magnetic fraction at temperature 350 °C and it was successively measured. The two magnetic phases

Thermal demagnetization of artificially prepared samples from Haruna locality

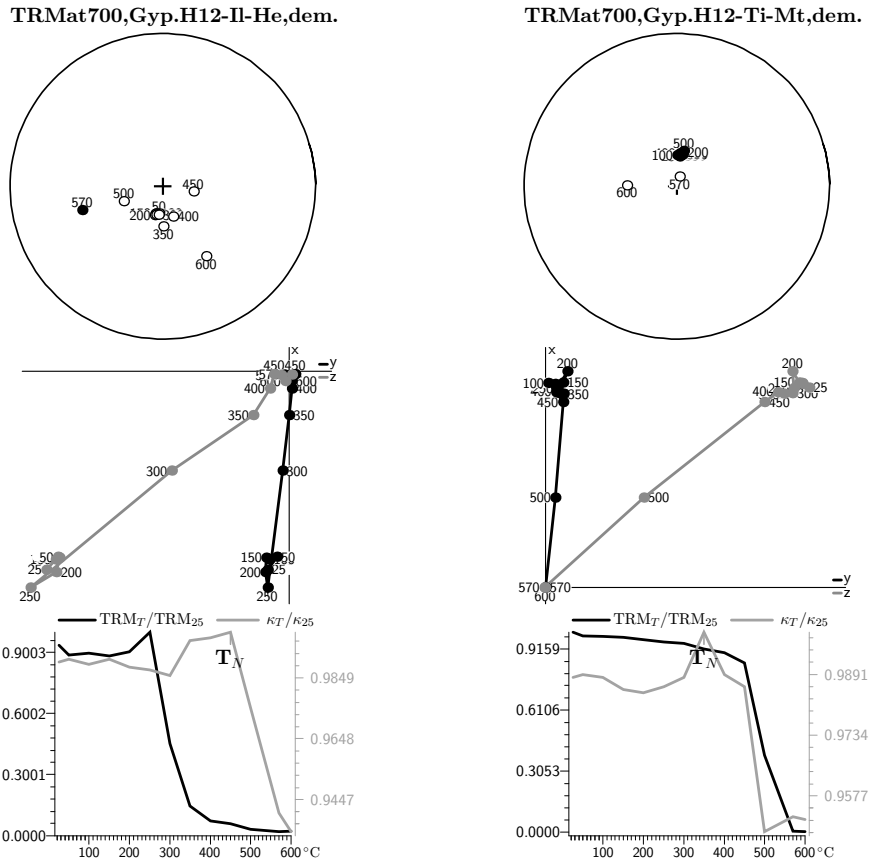

Fig. 4. Thermal demagnetization of samples H12-Il-He, H12-Ti-Mt and the change of magnetic susceptibility at different temperatures. Zijderveld diagrams and stereographic projections; • (○) - positive (negative) polarity of RM; κ - magnetic susceptibility. κ_T at T, κ_{25} - at 25 °C; TRM - thermoremanent magnetization at temperature T and at 25 °C, respectively. T_N - Néel temperature of the Fe-Ti antiferromagnetic phase.

were detected during heating and cooling of this sample, the Ilm-hem with $T_C = 240\,^\circ$C, Fe-Ti antiferromagnetic phase with $T_N = 440\,^\circ$C and Ti-Mt phase with $T_C = 520\,^\circ$C, during heating and with two phases ($T_C = 530\,^\circ$C and $T_N = 440\,^\circ$C and Ilm-hem with $T_C = 270\,^\circ$C during cooling of the

Thermal demagnetization of artificially prepared samples from Olongapo locality

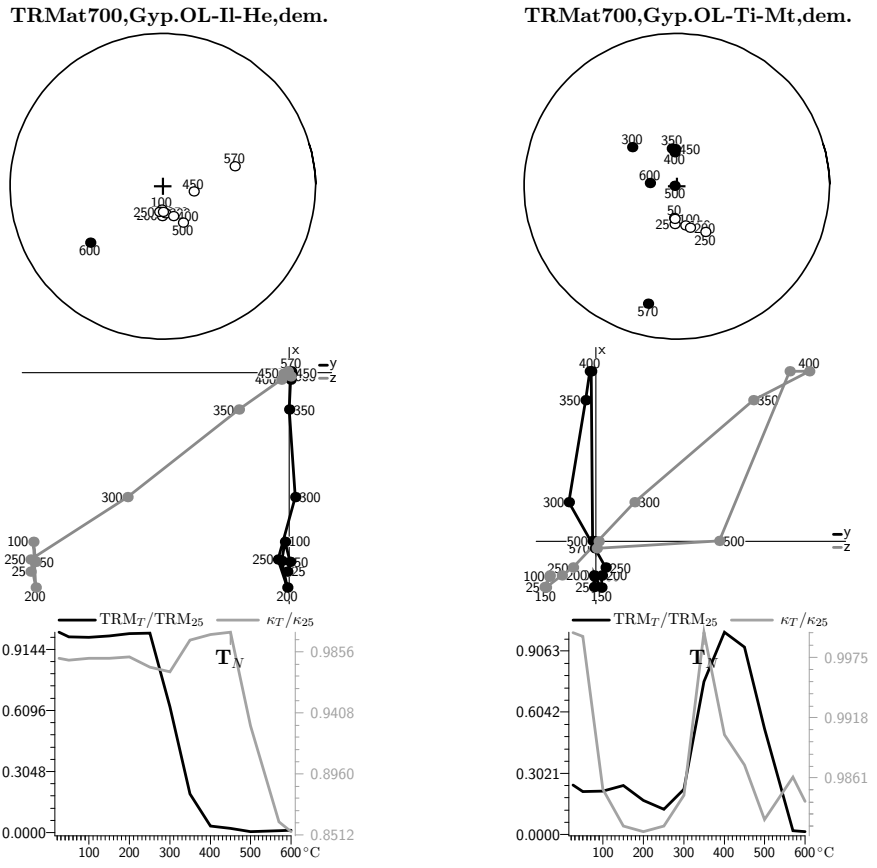

Fig. 5. Thermal demagnetization and the change of magnetic susceptibility of samples OL-Il-He and OL-Ti-Mt at different temperatures. Zijderveld diagrams and stereographic projections. For explanations, see Fig. 4.

sample (Fig. 3). The ilm-hem phase is supposed to be screened in natural rhyodacites and it could be revealed after the heating of the sample. The antiferromagnetic phase is present in natural rhyodacites, also in the rhyodacite samples after their heating on air.

The results of Pinatubo dacite ash, presented in *Orlický and Funaki (2001; 2002)*: According to the electron microprobe analysis, the ilm-hem

grains and the Ti-Mt grains were detected in one artificially prepared polished sample. The T_C of the Ilm-hem is 270 °C and that of Ti-Mt is 520 °C during heating and cooling of the sample. The Curie temperature of ilm-hem is higher than that of ilm-hem sample of Haruna locality. One can assume that the temperature of volcanic material of Pinatubo eruption was higher, or it took a longer time, compared with the results of the Haruna rhyodacite volcano. Both the ilm-hem and Ti-Mt magnetic minerals were found in natural samples after their emplacement in the field.

4. Discussion and conclusions

The previous suggestions about the magnetic sources of the self-reversed RM of Haruna and Pinatubo rhyodacites

Previously, many authors tried to find the sources of the self reversed RM of the Haruna and the Pinatubo rhyodacites. The results of the first authors lead to the proposal that the main carriers of RM is ilmenite-hematite but magnetite-ulvöspinel was also present in these rocks. The ratio of the Mag-Usp phase to ilm-hem phase in the Haruna rocks was approximately 100 to 1 (*Nagata et al., 1953; Uyeda, 1958*). However, the authors ascribed the dominant remanence signal to the ilm-hem phase. *Uyeda (1955)* ascribed the acquirement of the self-reversed TRM of the rhyodacite to a magnetic interaction between two phases (two phase model; the crystal consists of ultrafine intergrowths of disordered - antiferromagnetic and ordered - ferrimagnetic phases, that is the x-phase and the self-reversing phase, respectively) of different Curie temperatures both with intermediate compositions in the ilm-hem solid solution series. The author assumed that both coexisting phases have the same chemical composition, what is considered as an insufficiency of this model. According to *Nagata (1963)* the ability to acquire the self-reversed TRM consists in the existence of the order-disorder boundary and the ferrimagnetic - antiferromagnetic arrangement in the magnetic Fe-Ti phases. It was quite clear from the results that such arrangement would be dependent and sensitive to the thermal treatment of the respective samples. The study of self-reversal of RM of natural rhyodacite samples was gradually replaced by a study of SR of RM on artificial samples containing Ilm_{50}-Hem_{50} in $xFeTiO_3$-(1-x) Fe_2O_3 solid

solution (*Ishikawa and Syono, 1963*). The authors found that this composition has shown the order-disorder transformation of the atomic arrangement of Ti and Fe ions. The disordered specimen is parasitic ferromagnetic with the crystal symmetry R3C, while the ordered one is ferrimagnetic with the crystal symmetry R3. The reverse TRM is therefore expected to be closely related to the order-disorder transformation of this system. The authors have believed that the phenomenon of the self-reversal TRM of the rhyodacites of the Haruna volcano could be satisfactory explained by their so called *the antiphase-contact-two phase model*. They suggested that the reverse TRM is found to be the result of an antiparallel superexchange interaction between the magnetic moment of the Fe-rich metastable phase which is created around the ordered structure in the process of development of the order. The TRM requires not only that the bulk of the sample be ordered and ferrimagnetic but also that it contains a second phase the x phase, that need to have some specific properties. According to *Nagata et al. (1959)* they proposed that this metastable phase has a tendency to disappear, if the crystal reaches an equilibrium. They assumed that the ordered phase has the Curie temperature of about 230 °C, disordered phase about 20-30 °C less than the ordered phase and the metastable Fe-rich phase reaches variable values of the Curie temperatures, depending on the development of order in the system (they predicted the Curie temperatures in the range of 280 to about 325 °C). The striking result is that the reverse TRM exists in the intermediate state and it is not found in either the fully ordered or fully disordered state. They suggested that the reverse TRM is the result of anti-parallel coupling between the magnetic moments of the ordered phase and an Fe-rich metastable phase. Moreover the x-phase must be atomically in antiphase with respect to the ordered phase in order that the resultant magnetic moments of the two phases can be aligned antiparallel through the superexchange interaction.

Nord and Lawson (1992) studied the dacites from Shasta Mts. According to the authors twin boundaries consist of only a few atomic layers, and may pin down thin unconventional 180° magnetic domain walls which cannot move. Thus, although multidomain (MD), the magnetic structure of crystals could exhibit high coercivity, as was observed for both synthetic and natural hemoilmenites. *Lawson et al. (1981)* present the electron diffraction data which indicate the ease to which short-range compositional fluc-

tuations can form within certain samples via spinodal decomposition within the ilm-hem solvus. *Hoffman (1992)* suggested that it is a kinetic process of cation ordering, rather than exsolution, that controls the mechanism of self-reversal. Given that cation domain boundaries act as the more Fe-rich x phase controlling the mechanism of self-reversal, one immediately is drawn to the question of the actual magnetic spin alignment mechanism. Because the ferrimagnetic moment measured in ordered specimens is relatively strong, it may appear reasonable to assume that both the direction of magnetization of the x phase as well as that of the (net) reverse RM in each crystal lie along the line of spin alignment. However, as we will now see, simple considerations are inconsistent with this contention. First, the x phase possesses, relative to the bulk, ordered material, an imperceptible magnetization. Since cation domain boundaries are interwoven through each grain separating antiphase cation distributions, they need to be, on average, cation-disordered with zero net magnetization, that is, provided the Fe spins are collinear. Nevertheless, if we make the assumption that the Fe spins within the boundary material to magnetically align (during cooling) along the direction of an externally applied field, further cooling through the Curie temperature of the adjacent ferrimagnetic (cation-ordered) material would produce, through superexchange, a zero ferrimagnetic moment. That is, only material on one side of the boundary will acquire a net ferrimagnetic magnetization opposite to the applied field. In order for a perfectly aligned reverse RM to be realized by both cation-ordered domains, superexchange interactions through the boundary material require a complex spin structure not unlike a magnetic domain wall. However, the central observation is that the x phase has a higher Curie temperature than the ferrimagnetic bulk phase and thus is the first phase to magnetically order on cooling. The energetics associated with such a complex spin arrangement within the boundary material likely preclude its development at temperatures above the Curie point of the ferrimagnetic phase. In brief, the basic spin alignment mechanism through which the x phase controls the acquisition of reverse TRM in ferrian ilmenites has yet to be adequately understood.

The studies of self-reversed TRM by *Hoffman (1992)* and the results of the study of the 1991 Pinatubo rhyodacite products (*Hoffmann et al. (1996), Bina et al. (1999), Ozima et al. (2002), Goguitchaischvili and Prévot (2000), Prévot et al. (2001), Orlický and Funaki (2002)* brought

contributions to an interpretation of self-reversal problem. According to *Ozima et al. (1992)* the source of the self-reversed TRM in the 1991 Pinatubo dacite pumice is ilm-hem with $T_C = 280\,^\circ$C, but also the titanomagnetite (Ti-Mt) with $T_C = 480\,^\circ$C is present. The mechanism of an origin of the self-reversal is similar to that of the Haruna dacite pumice. *Hoffmann and Fehr (1996) and Bina et al. (1999)* detected three magnetic phases: ilm-hem ($T_C = 250\,^\circ$C; of two phases $y = 0.52$; $y = 0.54$) and Ti-Mt ($T_C = 480\,^\circ$C) in the dacite of Pinatubo volcano. The ilm-hem particles display chemical zonation. A ferrimagnetic phase is in the central part and the weakly ferromagnetic phase is at the crystal margin. The self-reversal is due to exchange coupling between these two phases.

Goguitchaichvili and Prévot (2000) revealed on the large, single crystal of hemoilmenite (y close to 0.54) that the directions of natural remanent magnetization (NRM), saturation isothermal magnetization and TRM all lay in the basal plane, regardless of the direction of the applied field. They proposed new but very specific model in which they integrated some previous theoretical considerations of *Hoffman (1992)*, including the results of domain pattern observations of *Hoffmann and Fehr (1996)* and *Bina el al. (1999)*. They proposed that the studied crystals of hemoilmenite contain the ferromagnetic core which is surrounded by the antiferromagnetic matrix with weak ferromagnetism. The ferrimagnetic core consists of coalescent cation ordered domains in magnetostatic interactions with each other. In their model this ferrimagnetic core plays no role in the TRM self-reversal, because of its overall multidomain behaviour. The cation ordered domains of SD-like behaviour are dispersed within the cation disordered antiferromagnetic matrix of multidomain magnetic structure. The matrix acquires a normal (extreme small) TRM between 250 and 200 °C. The ferrimagnetic cation ordered SD have an average Curie temperature about $T_C = 180\,^\circ$C. The ferrimagnetic SD-like regions acquire a strong reversed TRM below 180 °C as a result of superexchange coupling with a matrix. *Ozima and Funaki (2001)* studied single crystals of Haruna dacite pumice. They found that both ordered ferrimagnetic and disordered weak ferrimagnetic phases in the hemoilmenite crystals coexist in single crystals without distinct structures. Accordingly, the essentials of self-reversal TRM could not be related to the structure but the coexistence of two intergrown hemoilmenite phases with different compositions and magnetism in single crystals, one being or-

dered and the other disordered weakly ferromagnetic phase, irrespective of the structure. In other words, the coexistence of two phases in a single crystal of hemoilmenite must be essential for the acquisition of self-reversal TRM of hemoilmenite bearing Haruna rhyodacite.

Very complex interpretation of the existing results was presented by *Prévot et al.(2001)*. One of very important intricacies is a comparison of the results obtained for synthesized hemoilmenites with those of natural samples. There are the indications from transmission electron microscopy (TEM) observations that the structure of cation-ordered domains in synthetic hemoilmenite is quite distinct from natural samples (*Prévot et al., 2001*). The authors made a study of self-reversal on natural samples from Pinatubo dacitic pumice. Their TEM observations and thermomagnetic measurements lead to a proposal of the three-phase model. They proposed that the highly coercive thermoremanence provides information not about the strong magnetic cation-ordered crystal cores, but rather about the nano-sized magnetic carriers observed by TEM in the weakly magnetic mostly cation-disordered regions. The authors claimed that three mineralogical phases comprise the weakly magnetic macrocrystals of the Pinatubo hemoilmenite:

1. A self-reversed cation ordered phase, magnetically dominating the thermoremanence. Since the self-reversed TRM is assumed to be blocked by a normally magnetized higher Curie temperature phase, the destructive temperature (about 270 °C; of $y \approx 0.54$) of this negative component should correspond to its Curie point.

2. A normally magnetized partially cation-ordered phase. The magnetic moment of this phase is presumably blocked by a higher Curie point aureole (the destructive temperature about 380 °C; this corresponds to a composition $y \approx 0.35$).

3. A cation-disordered phase, antiferromagnetic, with presumed spin canting, which is the dominant phase seen in TEM in the weakly magnetic hemoilmenite macrocrystals and weakly magnetic regions of zoned macrocrystals (it corresponds to $y \approx 0.53$). This phase was not observable during thermomagnetic runs. Thus, its Curie temperature (or Néel point) was unmeasurable (this disordered phase should have a Curie

temperature about 200 °C). This indirectly determined value assumes that the embedded cation-ordered nano domains have no pronounced effect on the chemical composition of the disordered matrix, a reasonable assumption given the TEM observed volumetric importance of the disordered phase relative to the tiny ordered domains in the weakly magnetic regions (some local Fe-ion enrichment can be expected only along the contact between these two phases).

According to the above mentioned authors, the x phase is not detectable. But these disordered, so called x, phase and ordered self-reversing phase have been the subject of a debate up to the present. But in my results it has been emphasized that in both Haruna and Pinatubo rhyodacites the ferrimagnetic-antiferromagnetic phase corresponding to the self-reversing phase was revealed.

The self-reversed Fe-Ti magnetic phase

A review of the previous opinions on the source and the mechanism of the self-reversal acquisition of reversed RM in the ilm-hem bearing rhyodacites was presented. But my new results have shown that instead of the so called x-phase (a responsible source for the self-reversing process), the ferrimagnetic-antiferromagnetic Fe-Ti phase has been revealed on the basis of the measurements of the change of magnetic susceptibility with temperature. Very important knowledge is that the state of Fe-Ti magnetic minerals is very sensitive to a temperature treatment. The intensity of TRM of samples depends on the duration of heating and inducing of TRM. The results obtained on the synthetic ilmenite-hematite samples are somewhat different from those obtained in the original samples from Haruna locality.

The presence of the antiferromagnetic phase with $T_N \approx 400\,^{\circ}C$ in natural rhyodacites from Haruna area and $T_N \approx 440\,^{\circ}C$ in the artificially prepared samples of the Fe-Ti fraction from both Haruna and Pinatubo rhyodacites have been revealed (I assume that the differences in Néel points are due to different temperature treatment with the samples). The phase closely at $T \leq T_N$ (below the T_N) corresponds to the ferrimagnetic Fe-Ti phase. This fact of course means that this system is composed from the two-sublattices of active Fe-ions. We need to take into account that the ilm-hem is of the rhombohedral structure, so we need to find an explanation how and by which way the total self-reversed TRM has occurred. This *ferrimagnetic-antiferromagnetic phase* is the only source of the self-reversed

RM in the studied rhyodacites from Haruna area and Pinatubo volcano. The ferrimagnetic-antiferromagnetic phase is present in original samples, and also in the samples after their heating on air. This is a completely new approach to explanation to the source of the self-reversed RM in the ilm-hem bearing acidic dacites from the above mentioned localities.

The precise mechanism for an origin of the self-reversed RM is not presented in this article. The Fe-Ti crystals of the antiferromagnetics and the ferrimagnetics belong to the ion crystals in which there are active Fe ions. There are the mutual magnetic exchange interactions in these systems. These exchange forces have resulted in a creation of the so-called axes of quantization, along which the spontaneous magnetic moments of magnetic particles are oriented. It is quite predictable that both magnetic sub-lattices in the Fe-Ti system are magnetized not by the same way under the presence of the external magnetic field. The reversed RM takes place preferably in one sub-lattice which possesses the lowest magnetic free enthalpy (as the appropriate thermodynamic potential) at the moment of developing the ferrimagnetic-antiferromagnetic phase. The magnetic sublattice can be understood as the electron with its spin magnetic moment, with respect to the quantum physical principles. Despite the existence of the self-reversal RM of the above studied rocks has been proven by experimental works, its theoretical understanding will require further effort of scientists.

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