Inducing the partial thermoremanent magnetization: The study of the domain structure and the hysteresis properties of the Fe-Ti bearing minerals in basalts from southern Slovakia, West Carpathian Mts.

O. Orlický
Geophysical Institute of the Slovak Academy of Sciences[1]

M. Funaki
National Institute of Polar Research[2]

A b s t r a c t : The basalts of the Pleistocene to Quaternary age were investigated. The partial thermoremanent magnetization (PTRM) in original and artificially prepared samples was induced in the geomagnetic field of the intensity H $\approx 48\mu$ T. The domain structure and the hysteresis properties of some selected samples were studied as well. The basalts from 87% of investigated localities have shown the reversed, or partly reversed remanent magnetization (RM). One group of these types of basalts contains dominant, or only small portion of Ti-rich titanomagnetites (Ti-Mt-es), altogether with the titanomaghemite (Ti-Mgh) phase. The second large group of basalts contains dominantly the Ti-Mgh-es, the Ti-Mt-es and more oxidized derivates are in minor portion. They are exclusively of the reversed RM, probably of the self-reversed origin. In the two artificial basalt samples with the Ti-rich Ti-Mt-es and Ti-Mgh phase, a reproducible self-reversal PTRM was induced in the positive geomagnetic field. Many other artificial samples have shown a strong tendency for the acquisition of the self-reversed PTRM. The source of the self-reversed PTRM in these basalts is supposed to be the secondary magnetic phase of the titano-maghemite composition, which has shown a behaviour of small magnetic particles. The basalts with the normal polarity of RM contain dominantly a highly oxidized phase, close to magnetite with hematite in composition, but also the ilmenite is present in these basalts, according to microscopical and Bittern Pattern (BP) observations. From Šomoška locality, the basalts contain also the Ti-rich Ti-Mt-es, but the normal RM is linked to the more oxidized Fe-Ti phase. These types of basalts acquired only normal polarity of PTRM. In the Ti-rich Ti-Mt bearing basalts the domain structures are developed mostly in the rock

[1] Dúbravská cesta 9, 845 28 Bratislava, Slovak Republic; e-mail: geoforky@savba.sk
[2] Kaga, Itabashi, Tokyo 173-8515, Japan; e-mail: funaki@nipr.ca.jp

samples which contain high-temperature oxidized Fe-Ti phases, except for an original low Curie temperature phase.

Key words: Small particle-like behaviour, of the Fe-Ti oxides, Ti-Mgh phase, the self-reversed remanent magnetization

1. Introduction

So far, in many intermediate volcanics: andesites, basaltic andesites and rhyolites of the Neogene age, the reproducible self-reversal partial thermo remanent magnetization (srpTRM) was induced in the laboratory field of normal polarity and the intensity of H $\approx 48\mu$ T. Together, the samples from about 177 localities from central and eastern Slovakia acquired a srpTRM of the intensity in the range of 2.0 to about 200 nT (*Orlický, 2001, 2002, 2002a, 2002b, 2002c, 2003, 2003a*). Similarly, the srpTRM in selected acidic types of volcanics of Eocene to Miocene age from the Bohemian Massif was induced in the laboratory (*Orlický, 2002d*). An interpretation of the reversed, or partly reversed RM of the Neogene volcanic and volcano sedimentary rocks of central Slovakia was made on the basis of non-complete self-reversal origin in *Orlický (2003b)*. In recent time the partial and total srTRM was studied in the rhyodacite of the Haruna Volcano from Japan (*Ozima and Funaki, 2001; Orlický et al., 2000; Orlický and Funaki, 2000* and the dacite ash of Mount Pinatubo from Philippines (*Ozima et al., 1992; Bina et al., 1999; Orlický and Funaki, 2001, 2002; Prévot et al., 2001)*.

The carriers of the self reversal TRM of the Haruna and the Pinatubo rocks are the Ilmenite-hematites of the range $Ilm_{45}Hem_{55}$. In a recent time the srpTRM was induced in two Ti-rich Ti-Mt bearing basalts from southern Slovakia, in *Orlický (2006)*. Considering an idea about the self-reversal origin of the reversed RM of volcanic rocks a realistic interpretation of magnetic and paleomagnetic results of basalts from southern Slovakia was presented by *Orlický (2006a)*. The basalts were categorized into 6 groups, according to the different Fe-Ti magnetic phases and their magnetic properties. The basalts from 33 localities (87% of all studied ones) have possessed the reversed RM. It has been suggested that the reversed RM of the respective basalts originated by the self-reversal mechanisms, according to *Orlický*

(2006a). So far, no progressive background about the self-reversed origin of RM of rocks has been established in paleomagnetism. We present the results of the magnetization of natural and artificial samples by the laboratory magnetic field, the results of microscopical observations, the domain structure studies, as well as the hysteresis studies of selected basaltic rocks.

2. Laboratory experiments and basic results

The basic magnetic measurements, the Curie temperature studies, the thermal demagnetization and an inducing of the PTRM of rocks were performed in the Paleomagnetic laboratory of the Geophysical Institute of the Slovak Academy of Sciences, Bratislava, Slovak Republic. All technical work concerning the study of the domain structure of magnetic minerals of basalts and the microscopical observations and hysteresis properties of rocks was realized in the Laboratory of the National Institute of Polar Research, Tokyo, Japan. We studied the basaltic rocks from all localities depicted in Fig. 1. The results are documented only for the selected collections of rocks. The following groups of basalts are documented: Ti-rich Ti-Mt-es, the basalts with a partly altered Ti-Mt-es; these basalts have been characterized dominantly by the reversed RM or by an anomalous direction of the RM. The basalts come from the localities: 6,7,8,25,28,30,31,32,33,37,42,45(3A), see Fig. 1. Also the basalts from the locality Devičie - No. 5 ($\varphi_L = 48.306°$, $\lambda_L = 19.103°$) belong to this group. Into the group of basalts, with more oxidized Fe-Ti oxides of normal RM, belong the samples from the localities Blhovce-Buda-24, Šomoška-43,44 and Ostrá skala-33. They contain a highly oxidized Ti-Mt-es, with non-stoichiometric magnetite. In the third group are the basalts of 11 localities with the Ti-Mgh-es (Šavoľ, Poličko, Husina), all exclusively of the reversed RM (8 from the relatively large lava flow with the radiometric age of about 1.16 to 1.6 Ma, two from Ratka localities-27,29 and Pohanský vrch-40).

An inducing of the PTRM of the samples in the magnetic field of the positive polarity and the intensity of H $\approx 48\mu$ T.

The samples for an inducing of PTRM in the laboratory:

a./ Original basaltic samples: Most of samples of a cylindrical shape were demagnetized by AF field of about 400 mT before the PTRM was induced.

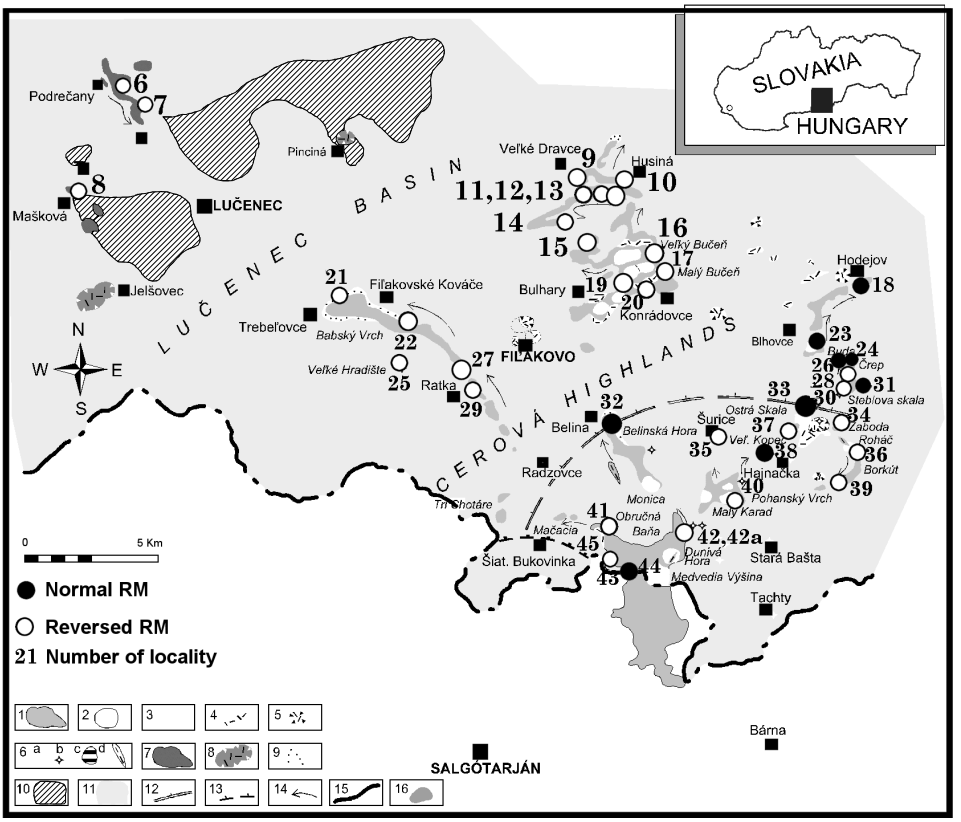

Fig. 1. A sketch map (according to *Konečný et al., 2001*; modified by authors of this article) - the distribution and forms of the Late Miocene to Early Quaternary alkaline volcanics in southern Slovakia; Podrečany basalt Formation - early Pliocene (7–lava flows; 8–maar), the names and numbers of the investigated localities: Podrečany-6,7, Mašková-8; Cerová basalt Formation, Middle Pliocene - Pleistocene (1–lava flows; 2–scoria cone, 3–agglomerates; 4–lapilli tuffs; 5–maar; 6–eruptive centres - 6a-diatreme, 6b-neck, 6c-extrusion, 6d-dyke); the names and numbers of the investigated localities: Husina-10, Poličko-14, Blhovce-Buda-24, Veľké Hradište-25, Maar-28, Steblová skala-30, East of Steblová skala-31, Belinská skala-32, Ostrá skala-33, Veľký kopec-37, Dunivá hora-42, Šomoška-43,44, Šomoška-45(3A). 9–state boundary.

They were then held in the container of high magnetic permeability, to protect them against any influence of the external magnetic field.

b./ Artificial samples: They were prepared from a grinded material of the same larger samples as the original basalts. The grinded material was

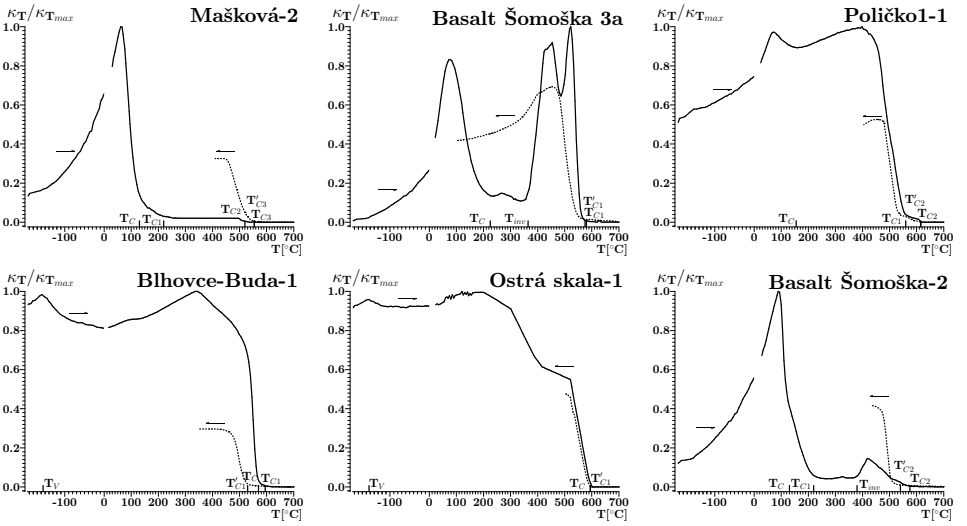

Fig. 2. Thermomagnetic curves of samples from the localities Mašková (Fig. 1: loc. 8, age = 7.17 Ma); Šomoška (loc. 45 [3A]; age = 4.06 Ma); Poličko (loc. 14); Blhovce Buda (loc. 24, age = 1.73 Ma); Ostrá skala (loc. 33, age = 2.6 Ma); Šomoška (loc. 43,44, age 4.06 Ma); $\kappa_T/\kappa_{T_{max}}$ – magnetic susceptibility at temperature T, and maximum magnetic susceptibility; T_{C1-3} – Curie temperatures; T_V - Verwey transition temperature.

fixed in a non-magnetic gypsum and shaped into a cylindrical form. The mixing of the respective material with gypsum and water were carried out either inside of compensated magnetic field, or inside of above named container, to protect them against non wanted magnetization by external field. After the samples were dried up in the free air, they were then held in the container. But some samples acquired low, probably viscous RM, despite the above described protection. An inducing of the PTRM at the following temperature steps was applied: 50, 100, 150, 200, 300, 350, 400, 450, 500, 600, 700° C. The samples were placed on the holder of the non-magnetic furnace. They were oriented in the positive direction of H - component of the field. A speed of heating of the samples was about 3°/min. During about 20 min. the magnetization was realized at the concrete temperature ($T_{concr.}$). The samples were then cooled to laboratory temperature. The RM of the samples was measured by the spinner magnetometer JR-5 at room temperature. The change of magnetic susceptibility (κ) was measured by the susceptibility meter KLY-2, after each laboratory treatment of the samples (See Figs. 3–7).

I.) The original basalts (natural basalts) and the artificial samples (in the figures labelled as Gyps, or Gs): The magnetic field was active (not compensated) during heating to $T_{concr.}$, and cooling of the samples to laboratory temperature. An inducing of the PTRM in the artificial samples was realized in order to have the samples without any previous RM and to know if the magnetic behaviour of these samples is the same or similar to original ones.

II.) The second selected collection of artificial samples (in the figures labelled as kG), was subjected to laboratory magnetic field only during inducing of the PTRM at the $T_{concr.}$. The heating up to $T_{concr.}$, and cooling down to the laboratory temperature of the samples from the $T_{concr.}$ were realized in a fully compensated external magnetic field. This procedure allowed to induce the PTRM only at the $T_{concr.}$, and no other components of PTRM are involved in the samples below $T_{concr.}$ to laboratory temperature. The results are depicted in Figs. 3–7.

The reason for the magnetization of the samples from the lower to higher temperatures is as follows: In the field the hot magma cools from high temperatures to atmospheric temperature. The temperature of a basaltic magma reaches about 1200° C, in some cases more, before it cools on the Earth's surface. We have known that dominant carriers of magnetism in basaltic rocks are the Fe-Ti oxides, mostly the Ti-Mt-es. These minerals are very sensitive to oxidation in free air, namely at high temperatures. It means that if we apply a procedure of their cooling from high temperatures to room temperature during laboratory experiment, the original composition of Ti-Mt-es would be either completely or partly destroyed and transformed into the non-precisely defined oxidized Fe-Ti oxide (mostly of high-oxidation Fe-Ti product, and the laboratory PTRM of the sample would be completely overprinted by the phase, corresponding to this product). This unfavorable effect can be partly suppressed by heating and cooling of the samples either in high vacuum, or to proceed from lower laboratory temperature gradually to higher temperatures.

Because all investigated basalts contain the Fe-Ti oxides, we can present something about the Ti-Mt-es. Dominant magnetic minerals in basalts are the titanomagnetites and their oxidized derivates. The ilmenite-hematites are less frequent than the dominant magnetism carriers in the basalts. We can assume that Fe-Ti minerals in a nascent state arose as a very tiny par-

ticles. They were then modified into the heterogeneous assemblage of a qualitatively, and in the grain size different Fe-Ti oxides. These different properties influenced also the magnetic behaviour of the basalts. The Ti-Mt-es were recently considered as the multi-domain ferrimagnetic minerals. *Orlický (2004)* revealed that the Ti-rich Ti-Mt-es behave as the SP-like materials. Many magnetic grains in the basalts have properties corresponding to small magnetic particles. They have only rarely thermodynamically stable domain structures. From the results of continual measurements of temperature dependence of κ of the Ti-rich Ti-Mt-es (in Fig. 2) we see that the minimal κ lies at about $-196°$, while the maximum value is in the range of about 50 to 100° C. The Curie temperature for the magnetic phase with low T_C is at about 120 to 190° C. The κ has evidently changed with the temperature. For more complex view about the Ti-rich Ti-Mt-es, a preliminary simple model for the domain state of Ti-rich Ti-Mt-es has been published by *Appel and Soffel (1984, 1985)*. An idea is described also in *Orlický (2007)*. A presence of the single-domain and superparamagnetic (SP) Ti-rich Ti-Mt-es was detected in young ocean-floor basalts, especially in their glassy matrix by *Zhou et al. (1997)*. *Radhakrishnamurty et al. (1981)* also revealed the SP particles in basalts.

An acquisition of the self-reversed RM of the Ti-rich Ti-Mt bearing basalts.

We can demonstrate the process of acquisition of the PTRM by a thermal inducing of the samples in the magnetic field of the intensity H$\approx 48\mu$ T in the laboratory. We see from the Zijderveld diagrams (Figs. 3, 4) that the projection of the end vector of RM to both xy and xz planes has decreased its value and has an opposite (reversed) direction with respect to the original magnetized direction of PTRM up to about 300° C, and that after about 500° C. It means that in this interval, direction of acquired PTRM is reversed. A minimum value of the PTRM is about 1/3 of the value at 300° C. Namely, in the interval about 450° C the self-reversed PTRM has been induced. We can support such behaviour with the results of several artificial samples containing the Ti-rich Ti-Mt-es and secondary titano-maghemite (Ti-Mgh) phase. They acquired the self-reversed PTRM during inducing in the laboratory (Figs. 3, 4). The sample Maar3-4kG acquired the reversed PTRM= -36 nT at 500° C (Fig. 3), and the sample Velkop2-4kG acquired

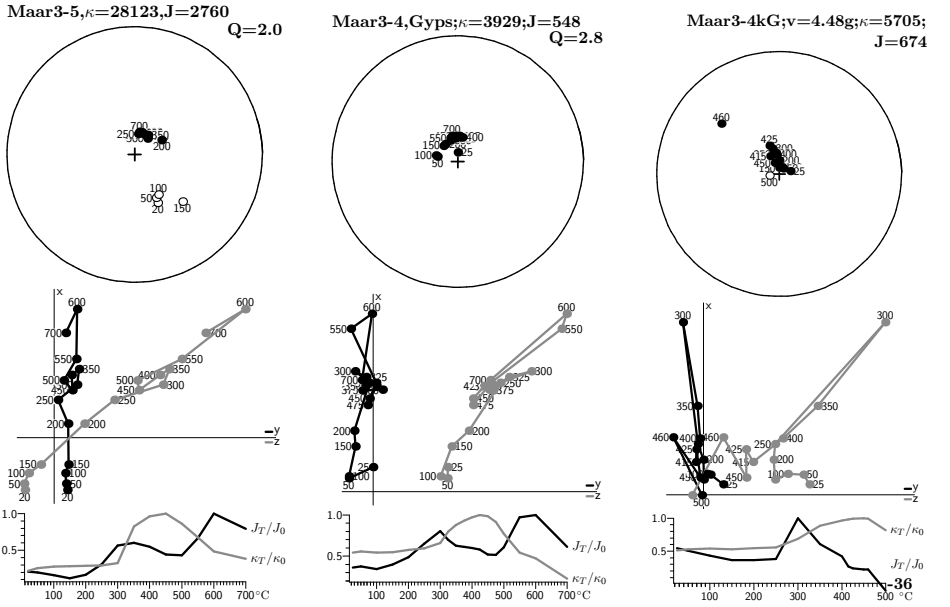

Fig. 3. Thermal inducing of samples: Maar (loc. 28; reversed RM of rocks); Maar 3-5 - natural basalt sample; Maar 3-4, Gyps - artificial sample - grinded basaltic sample fixed in gypsum; Maar 3-4 kG- artificial sample as under Gyps - heating and cooling of the sample in fully compensated field (k); Zijderveld diagrams and stereographic projections; • (○)-positive (negative) polarity of RM; κ- magnetic susceptibility (above the pictures: the κ is x 10^{-6} SI Units, and remanent magnetization J is in nanoTesla (nT)); κ_T at T, κ_0- at 25° C; J_T (J_0)- remanent magnetization at T and at 25° C, respectively; v–weight of basalt grains (g - gram) within a gypsum cylindrical sample.

the reversed PTRM= −100 nT at 500° C (Fig. 4). The samples from further three localities exhibited strong tendency for the acquisition of the reversed PTRM by the self-reversal mechanisms. The results in Figs. 3, 4 (labelled as kG) have shown that this self-reversed PTRM is generated at around 450° C, or very close above this temperature. The artificial samples, which were prepared from basalts from the localities with originally normal RM have never acquired the reversed PTRM during the above mentioned inducing. By the self-reversal behaviour are characterized not only the samples of basalts presented in Figs. 3, 4, but the basalts of all other 9 localities (Podrečany-6,7, Mašková-8; Veľké Hradište-25, Steblová skala-30, East of Steblová skala-31, Dunivá hora-42, Šomoška-45(3A) and Devičie-5). We see from the results that while the behaviour of the induced PTRM is very sim-

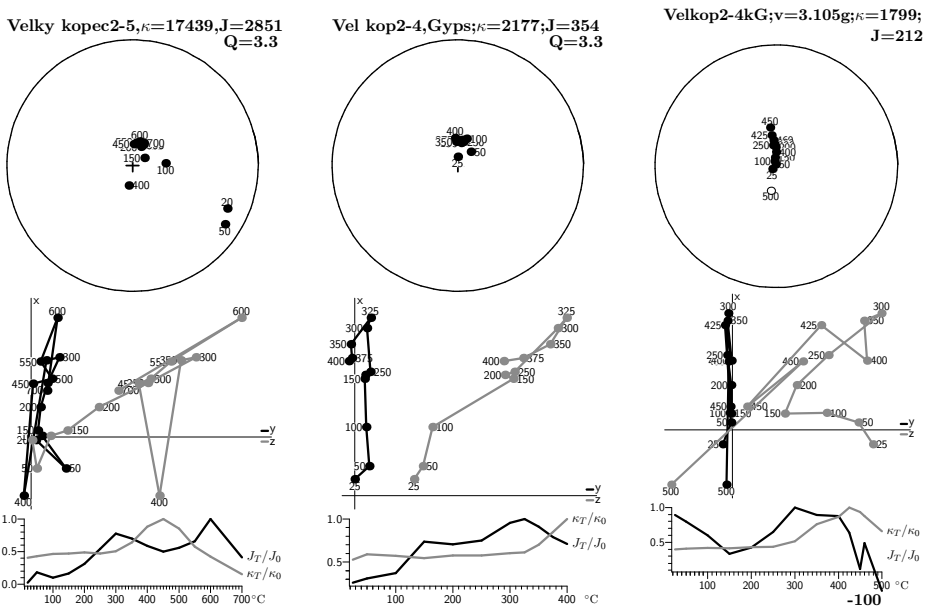

Fig. 4. Thermal inducing of PTRM of the samples: Veľký kopec (loc. 37, age = 1.92 Ma; reversed RM of rocks); Veľký kopec2-5 - natural basalt sample; Velkop2-4, Gyps - artificial sample - grinded basaltic sample fixed in gypsum; Velkop2-4 kG- artificial sample as under Gyps; PTRM induced at concrete temperature, other treatment in fully compensated external magnetic field; other description and explanations as in Fig. 3.

ilar or the same for the natural basalts and for the I. group, while for the group II., it is quite different. The artificial samples, in which the PTRM was induced only at the concrete temperature, and in other temperature intervals during heating or cooling of the samples, the PTRM was not induced. There has appeared strong tendency to acquire the reversed PTRM by the self-reversal mechanism.

We can comment that during the original volcanic activity the process of cooling of basaltic magma proceeded from higher to lower temperatures in the field, from about 1200° to atmospheric temperatures. In the laboratory, the magnetization of the samples was realized in the opposite direction, from lower to higher temperature intervals. The magnetization of magnetic minerals of cooling magma takes place in the permanent geomagnetic field of the intensity H $\approx 50\mu$ T.

In the Ti-Mt bearing compact basalts from 13 localities and in the ar-

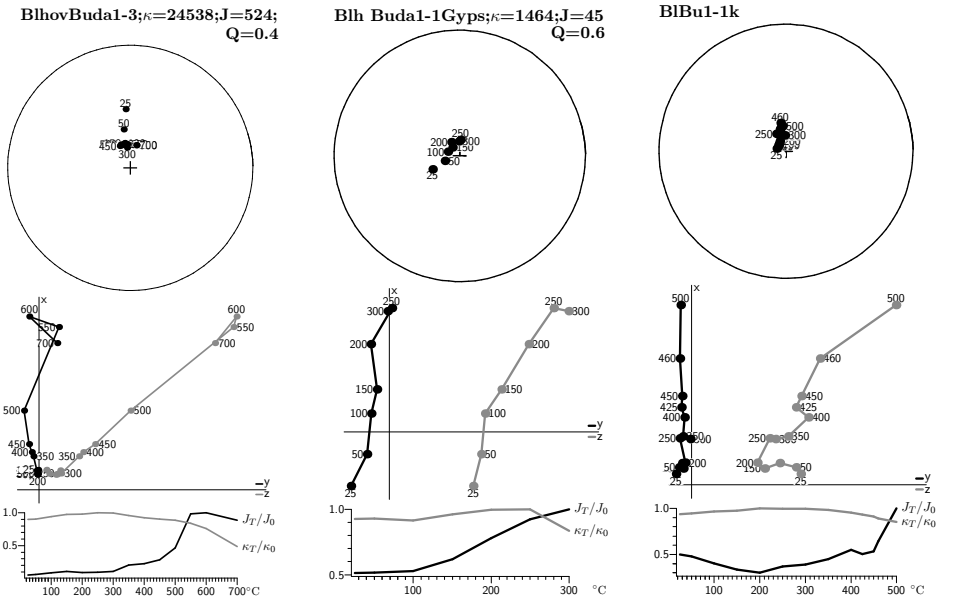

Fig. 5. Thermal inducing of PTRM the samples: Blhovce Buda (loc. 24, age = 1.73 Ma; normal RM of rocks); BlhovBuda1-3 - natural basalt; Blh Buda1-1 Gyps - artificial sample - (grinded basaltic sample fixed in gypsum); Bl Bu1-1k - artificial sample as under Gyps - PTRM induced at concrete temperature; other treatment in fully compensated external magnetic field; other description and explanations as in Fig. 3.

tificial samples (see part of text under II.), there is gradual decrease of PTRM in the interval 25 to about 150 - 200° C. This decrease of the PTRM corresponds to demagnetization of residual RM due to destroying of the domains, probably of the first paramagnetic phase of the samples (this phase is documented with the Curie temperature measurement of the T-rich Ti-Mt samples; as in Fig. 2). In the interval 150 (200), mostly to about 300° C a conspicuous increase of PTRM (in some cases more than 10 times of an initial value of RM) of the samples was acquired. This PTRM is acquired probably by the low temperature oxidation – the second magnetic phase. In the basalts, originally of the reversed RM, in interval from 300 to about 475° C (500° C), there was detected very intense decrease of PTRM in the samples, with a minimum value, mostly at about 450° C. In the compact basalts and the artificial samples an increase of κ is evident over the temperature of 300° C. The κ reaches the maximum value - the superparamagnetic

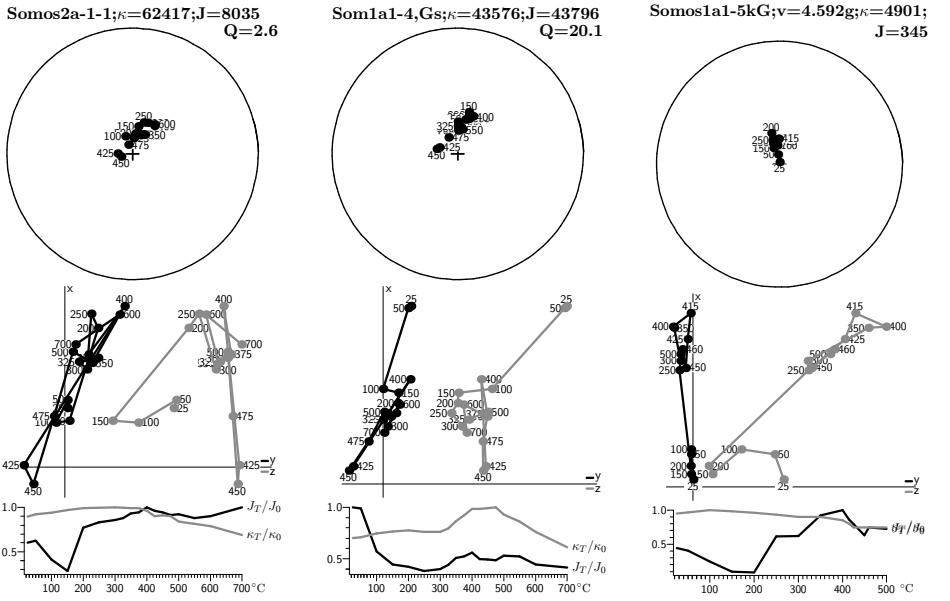

Fig. 6. Thermal inducing of PTRM of the samples: Šomoška (loc. 43,44, age = 4.06 Ma; normal RM of rocks); Somos2a-1-1 - natural basalt sample; Som1a1-4,Gs - artificial sample - grinded basaltic sample fixed in gypsum; Somos1a1-5 kG- artificial sample as under Gs; PTRM induced at concrete temperature; other treatment in fully compensated external magnetic field; other description and explanations as in Fig. 3.

thermally activated effect - magnetic viscosity, mostly at about 450° C and after that it decreases. The described effect at about 450° C coincides with the minimum value of PTRM of the samples. What is very important, such behaviour of κ has occurred for a dominant number of basaltic samples containing the Ti-rich Ti-Mt-es with a secondary Ti-Mgh phase (cca 120 samples from central and southern Slovakia and many samples from abroad). The source of the mentioned exceptional behaviour is the superimposed - the third Ti-Mgh magnetic phase. This magnetic phase originated probably by an original thermal oxidation of some portion of Ti-rich Ti-Mt-es, during initial cooling of basalt magma in the field. After laboratory thermal treatment of such samples, further portion of the Ti-Mt-es are oxidized, together with that of original third phase itself, and more pronounced SP effect was registered on the curve of the change of κ of the sample with temperature. After 450° C an increasing of PTRM up to about 600° C was detected. The

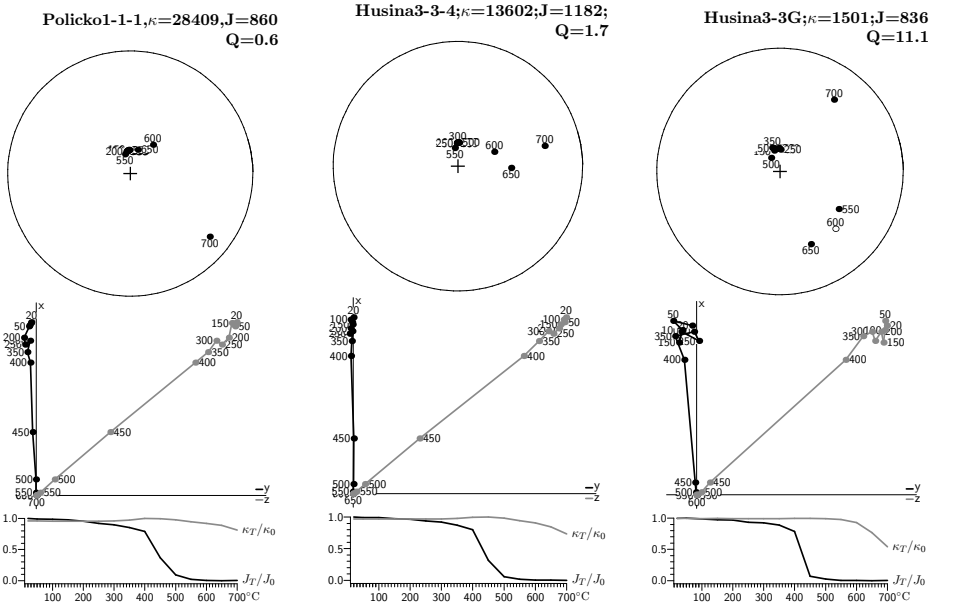

Fig. 7. Thermal inducing of PTRM of the samples Poličko (loc. 14) and Husina (loc. 10); both of the reversed polarity of RM; (Poličko1-1-1 and Husina3-3-4 - natural basalt samples; Husina3-3G - artificial sample - grinded basaltic sample fixed in gypsum); other description and explanations as in Fig. 3.

most oxidized product with the Ilm-Hem-es is created at these temperatures.

The detailed study of an oxidation of the natural and the artificial Ti-rich Ti-Mt-es was performed by *Özdemir (1987)*. According to the author a metastable Ti-Mgh inverts to a multiphase intergrowth when heated above 250-300° C. After an inversion, an increase in magnetic viscosity and the change of other parameters reflect the subdivision of originally single domain (SD) homogeneous Ti-Mgh grains into SP, or nearly SP-size subgrains. The spinel phase in the intergrowth was near-stoichiometric Ti-Mt or magnetite, and the other phases included ilmenite, hematite, anatase, and/or pseudobrookite.

We can deduce that there are present three Fe-Ti magnetic phases over 300° C temperature treatment in the Ti-rich Ti-Mt bearing basalts. The first one, the remnants of the paramagnetic low Curie temperature phase, the second one – low temperature oxidized Fe-Ti phase (with the thermodynam-

ically stable domain structure) and the third Ti-Mgh with a superparamagnetic-like behaviour magnetic phase. This phase carries only self-reversed RM in the rocks. There are probably developed the flower and vortex configurations; the classical domain structures are in minor portion in this SP phase. When we induce the PTRM of the samples only at the temperatures over 300 to 500° C, and a protection against the magnetization of the second phase with the compensation of the field during heating and cooling of the artificial samples is arranged, the resulted PTRM for the third phase would be reversed, or very near to reversed polarity.

In the basalt of the Šomoška neck (Šomoška2a-1-1 and Šomoška1a-1-4; whole neck of normal RM) very near values of the PTRM were induced in the interval above 300° C. Only moderate increase of PTRM is in the interval 400 to 700° C. No conspicuous decrease of the PTRM was detected in the interval from 300 to about 475° C (500° C). We assume that there are the low and highly temperature oxidized Ti-Mt phases with a quite well thermodynamically stable domain structure in this type of basalt. The magnetization in this phase takes place dominantly through the domain wall movement.

A behaviour of the Ti-rich Ti-Mt-es, like described above has been proven also by the results of *Pan et al. (2006)*. The authors studied the Thellier-Coe paleointensity of Al-substituted Ti-Mt-es of basalts. They revealed that between 300 and 460° C specimens acquire thermoremanence with a direction antiparallel to the external field direction, leading to intensity decreases.

We assume that the Ti-rich Ti-Mt bearing basalts from the world-wide localities will have the properties and behaviour as has been described above.

A study of domain structure of the Fe-Ti oxides of basalts by the Bittern Pattern method

We have dealt with the three groups of basalts: basalts with the Ti-rich Ti-Mt-es and their softly oxidized derivatives, basalts with the minerals close to magnetite oxides in composition and basalts with the dominant Ti-Mgh composition. In order to know more about the nature of the RM of the respective basalts, the domain structure of the magnetic grains of basalts was detected. A conventional Bitter-pattern (BP) technique was used to observe the mentioned domain structure. The samples were polished by

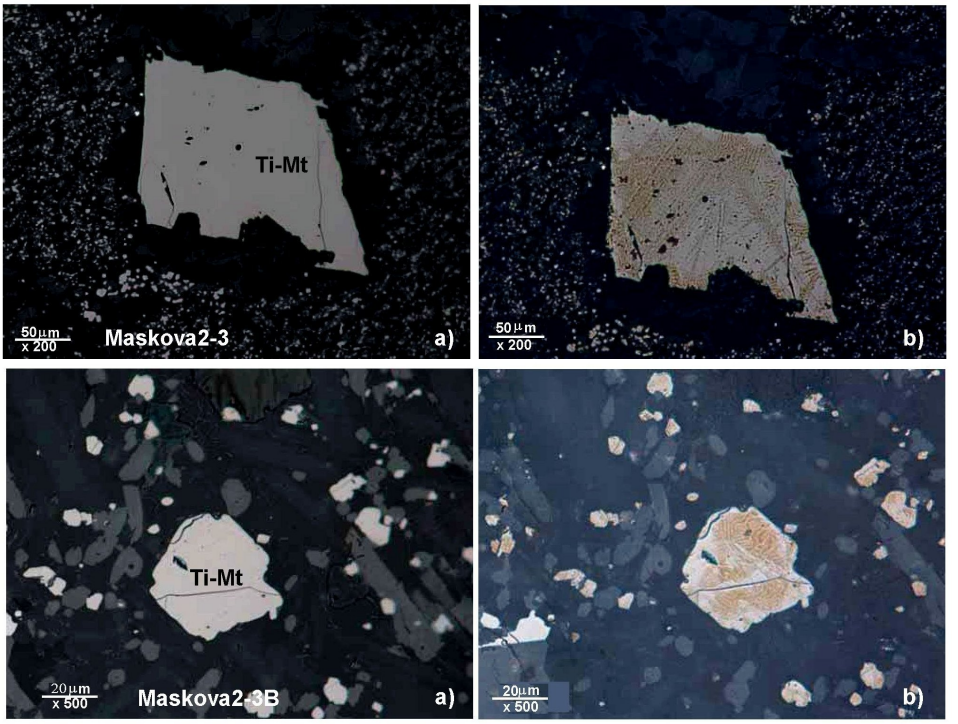

Fig. 8. The microphotographs of the ore microscopy (a) and the visualization of the domain structures by the Bitter Pattern method (b). The titanomagnetite (Ti-Mt) grains of the basalt samples Mašková2-3 and Mašková2-3B.

diamond paste of 1.0 micro-meter (μm) and then they were polished by colloidal silica paste of about 0.1 μm in diameter, in order to remove the distortion. A magnetic colloid was used as a medium for the visualization of the domain structure. All procedures were applied at the laboratory temperature. The results of ore microscopy observations [a] and the images of the BP technique [b] are in Figs. 8–11.

Evaluation of the microscopical observations and the results of the Bitter-pattern method

In the rocks, there is an assemblage of Fe-Ti minerals of various composition, and various grain sizes of the magnetic particles. Before obtaining the microscopical and the BP results, there were previous proposals about

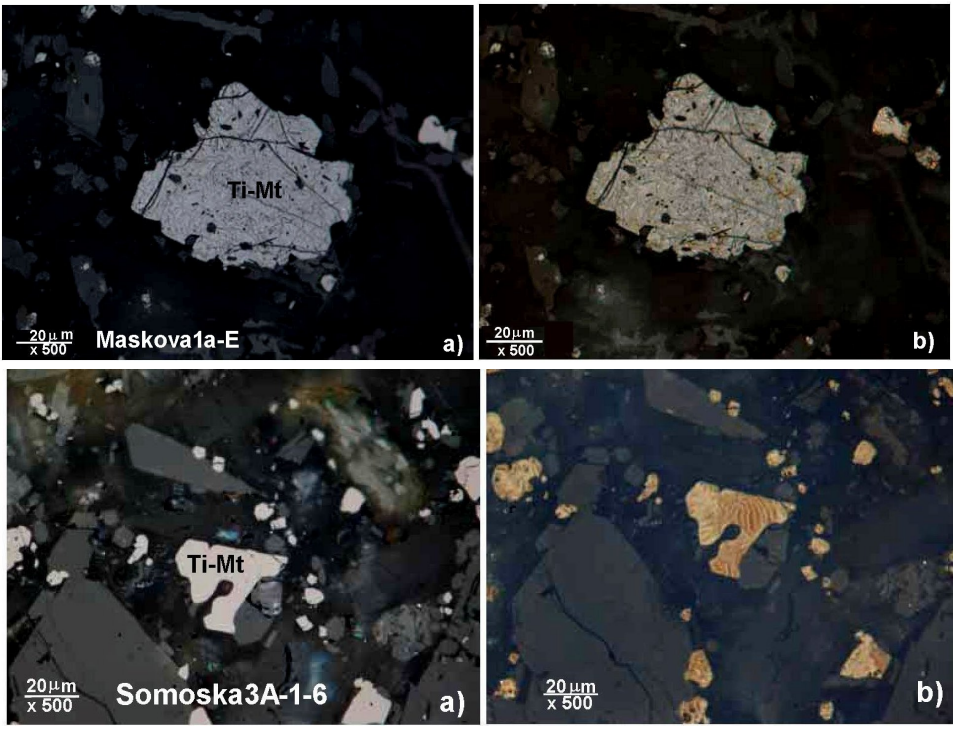

Fig. 9. The titanomagnetite (Ti-Mt) grains of the basalt samples Mašková1a-E and Šomoška3A1-6. The basic description see in Fig. 8.

the magnetic state of the Ti-rich Ti-Mt-es of basalts (*Orlický, 2004, 2006*). For the samples of Maskova2-3 and Maskova2-3B (Fig. 8) it was suggested that the Ti-rich Ti-Mt-es are in the paramagnetic, more probably in SP state. The results of the measurements of the temperature dependence of the change of κ reflected a contribution of all magnetic minerals present in the sample. But by the BP method we are able to detect a domain pattern only at several polished grains on the surface of the sample. Moreover, in the BP procedure, it is necessary to select an orientation of the polished surface of the magnetic grain with respect to the so called magnetic easy axis. When the mentioned condition is not fulfilled, then the results are supposed to be not as correct as they need to be. The magnetic domains cannot be seen in all cases, in spite of well polished magnetic grain. When the magnetic grain is cut along the easy axis, the domain structures appear.

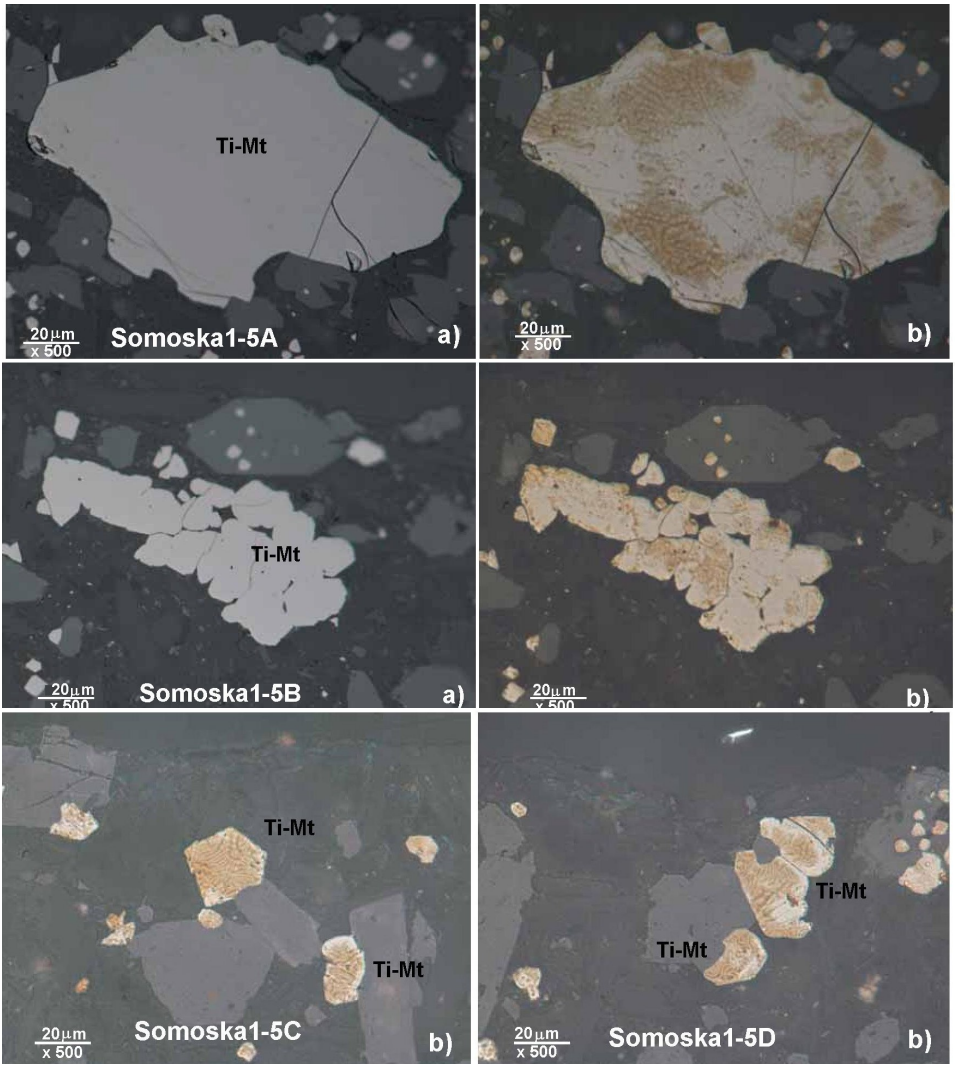

Fig. 10. The titanomagnetite (Ti-Mt) grains of the 4th positions of the basalt samples Šomoška 1-5. The individual positions have not been uniformly oriented during observation. A maze like domains have appeared in the grains of all 4th positions. A preferable orientation of domains of the grains within the individual positions is supposed to be rather uniform. The basic description see in Fig. 8.

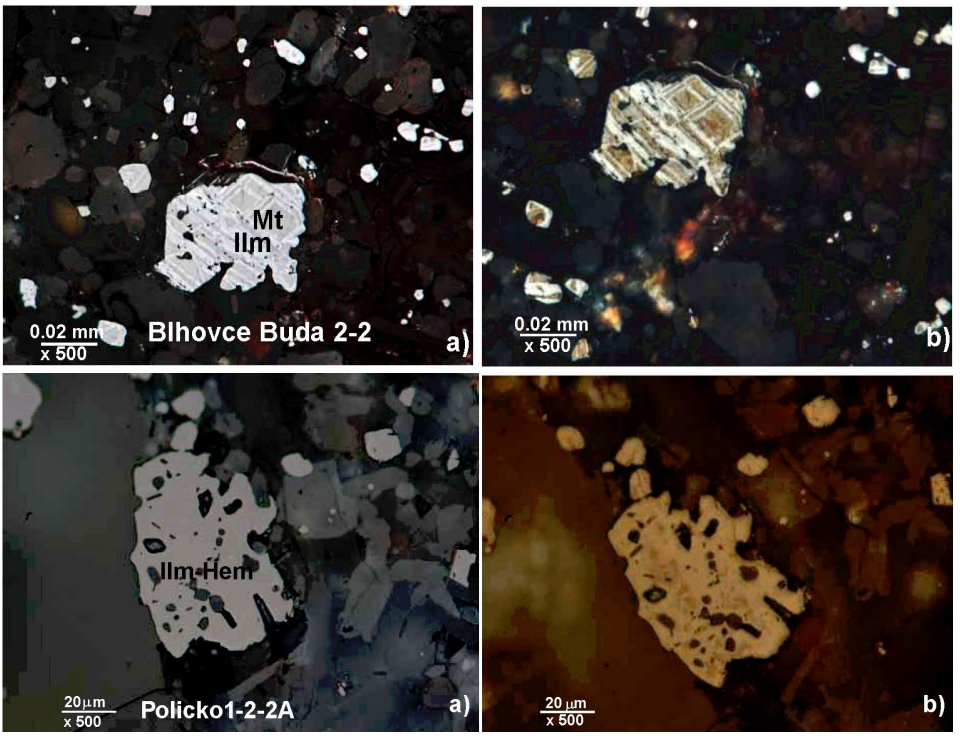

Fig. 11. The microphotographs of the ore microscopy (a) and the visualization of the domain structures by the Bitter Pattern method (b). The magnetite (Mt, as a shadow ribbons) and the ilmenite (Ilm, as a white ribbons) were revealed by the ordinary polarized light microscopy (a) in the Blhovce Buda 2-2 sample. The hematite (Hem) grains are present also in these basalt samples.

But if the surface is perpendicular to the easy axis, the domain structure does not show clearly. In such cases, only few domains, or no domains are visible in the Fe-Ti grains. We see from Fig. 8 that the large Ti-Mt grain of about 250 μm in diameter of the Mašková2-3 is surrounded by many tiny disseminated Fe-Ti grains. There are no typical domains in the Mašková2-3 sample. Only rarely a magnetic fluid is attracted along the basic structure of the Fe-Ti minerals of this large grain (b). A maze like domains are present in the larger Ti-Mt grain (of about 50 μm in diameter) of Mašková2-3B sample (b). A preferential direction of the domains in the upper part of the grain is supposed to be in a rather perpendicular position to that of the

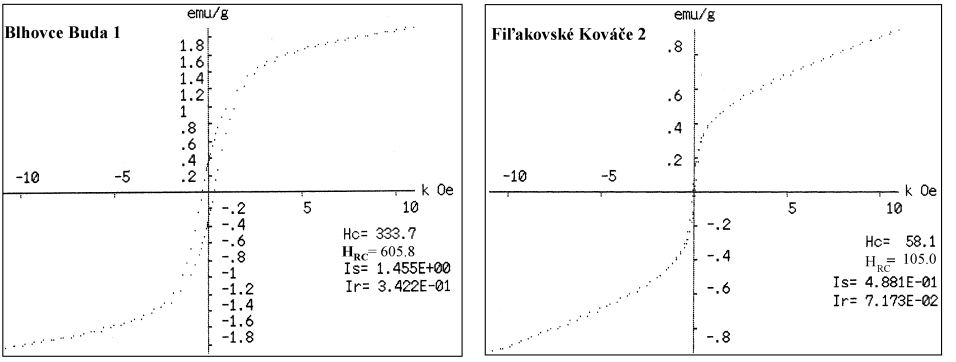

Fig. 12. Magnetic hysteresis loops of basalt samples Blhovce Buda 1, and Fiľakovské Kováče 2. Explanations: emu–electromagnetic units; g–gramme; k Oe–kilo Oerstedt; H_C(Oe), H_{RC}(Oe)–coercive force (in Oe), remanent coercive force (in Oe), respectively; I_s–saturation magnetization; I_r–remanent magnetization.

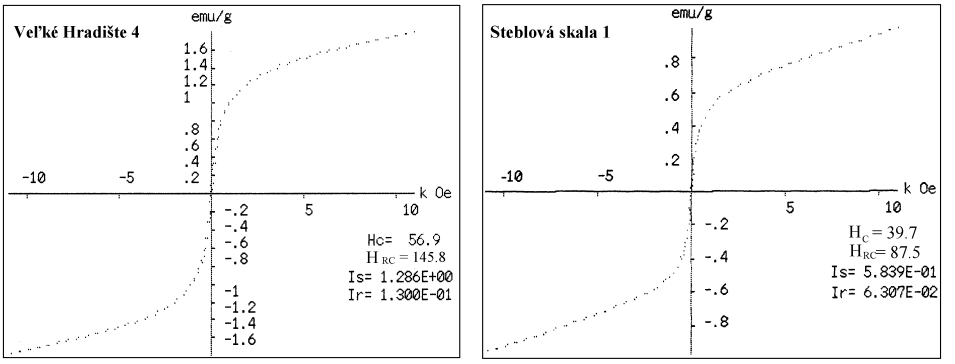

Fig. 13. Magnetic hysteresis loops of basalt samples Veľké Hradište 4, and Steblová skala 1. Explanations see in Fig. 12.

lower part of the grain surface. An arbitrary selected large grain of Ti-Mt (of about 80 μm in diameter) of the Maskova1-E (Fig. 9b) has no domain pattern. Only rarely a magnetic fluid is attracted along the basic structure of the Fe-Ti minerals (b). Maybe, the surface of the grain was not along the easy axis, but this lack of domains can be also due to paramagnetic like behaviour of minerals. In Fig. 9 the Somoska3A-1-6 sample comes from the outcrop which is very near, cca 50 m on the southern part, from the bottom of a very large basaltic body of Šomoška (in Fig. 10 labelled as Somoska1-5). In the Somoska3A-1-6 sample, selected grain of cca 40 μm in diameter has

shown a maze type of domain structure (Fig. 9b). A preferential direction of the domains in the left position of the grain is supposed to be in a rather perpendicular shape to the domains in the right part of the grain surface. In Fig. 10 there are presented the results for the titanomagnetite (Ti-Mt) grains of the 4th positions of the basalt samples Somoska1-5. The individual positions have not been uniformly oriented during observation. A maze like domains have appeared in the grains of all 4th positions. A preferential alignment of domains of the grains within the individual positions is supposed to be rather uniform (longer side of domains is mostly oriented in one direction). On the one larger Ti-Mt grain (cca 150 μm in diameter) of the sample Somoska1-5A the domains are mostly on the outer part, but in all other Ti-Mt grains of the samples Somoska1-5B-D they are concentrated also in the central parts of the grains. In the Fig. 11 are the Fe-Ti oxide of the Blhovce Buda2-2 sample and the Policko1-2-2A sample. The Blhovce Buda2-2 sample corresponds to basalts with a presence of intergrowth of the magnetite (gray ribbons on the picture) and ilmenite (white ribbons on the picture). They appeared under polarized light microscopy image. The gray magnetite ribbons evidently attracted the magnetic fluid, but no typical domains were visualized. In the white ilmenite ribbons no attracted magnetic fluid and no visualized domains were detected (Fig. 11 b). The detected structure of a large, cca 0.06 mm in diameter grain is arranged dominantly in the linear geometry. It has not corresponded to preferred RM direction, because other surrounded grains have a linear geometry in other directions. In the Policko1-2-2A basalt sample, the Fe-Ti oxide grain, cca 100 μm in diameter, does not show the visualized domain structure. A part of the grain surface has accumulations of magnetic fluid. Or, a studied grain does not contain the Ilm-Hem? In the Ilm-Hem-es of $Fe_{2-y}Ti_yO_3$; y$\approx$ 0.54 and 0.53, respectively, *Prévot et al. (2001)* suggested the nanophase self-reversal model, in which the nano-sized (20-40 nm) regions would behave in a SP fashion in magnetically uncoupled to advanced material. Summarizing the results we have deduced: on the basis of the change of κ of basalts with the temperature the Ti-rich Ti-Mt grains behave dominantly as the paramagnetic particles. They have only rarely the developed domain structure. This can be supported by *Soffel (1978)*, who suggested that large amount of the optically observable Ti-rich Ti-Mt grains are paramagnetic at room temperature, with no domain structure. We know that lack of visualized

domain structure in BP results can be influenced also by a fact that a polished surface of the grain does not lie in the easy axis of the magnetic Fe-Ti oxide. We can deduce, that in the Ti-rich Ti-Mt bearing basalts the domain structures develop mostly in the rock samples which contain either the low, or high-temperature oxidized Fe-Ti phases, except of an original low Curie temperature phase. In the samples, originally of the reversed RM, there are mostly the domains of a non-uniform orientation (there are parts of Ti-Mt grains with a perpendicular direction of domains). In the samples, originally of normal RM, there is nearly uniform orientation of domains. *Soffel (1978)* studied also variation of domain structure with temperature. For the basalts with low Curie temperatures, if there is a domain structure at room temperature, after heating to + 70° C in the earth's magnetic field, most of the domain configuration is destroyed.

The hysteresis properties of selected samples

The results of the hysteresis properties (Figs. 12,13) have shown a decreasing of coercive force (H_C) and the remanent coercive force (H_{RC}), which follows in the sequence from Blhovce Buda (the most oxidized phases) → Veľké Hradište → Fiľakovské Kováče → Steblová skala (dominant are the Ti-rich Ti-Mt-es). The derived RM (J_r) of the samples decreases also, but the saturation magnetization (J_s) is lower for the Fiľakovské Kováče sample than for that of Steblová skala. We can deduce that both the H_C and the H_{RC} increase for the basalts with increasing of the oxidized phase in the sample. We can anticipate that the lowest H_C and H_{RC}, also other mentioned above parameters will be for the basalts of the locality Mašková2-3, with the largest portion of the Ti-rich Ti-Mt-es. The H_C and H_{RC} of Fe-Ti oxide and Ti-Mgh bearing basalts will be probably of the values similar to Blhovce-Buda sample.

3. Discussion and conclusions

The basalts of the Pleistocene to Quaternary age were investigated. The basalts from 87% of investigated localities have shown the reversed, or at least anomalous partly reversed RM. Most of reversely magnetized basalts contain either dominant, or at least small portion of Ti-rich Ti-Mt-es, together with more oxidized Ti-Mgh phase. They have also a tendency to be

magnetized by the self-reversal mechanism in the normally oriented magnetic field. In the original Ti-rich Ti-Mt bearing basalts the reversed RM survived mostly to about 450° C during thermal demagnetization. The κ reached the maximum value mostly at 450° C during temperature treatment. Similar behaviour has been shown also by the Ti-rich Ti-Mt bearing basalts of the localities from abroad and the basaltic andesites, as well as other intermediate andesites containing residual portions of the Ti-rich Ti-Mt-es from central and eastern Slovakia volcanic fields. It is very important that the minimum PTRM has been acquired by the samples at the temperatures corresponding to maximum values of κ. In one large group of basalts from 11 localities, dominantly the Ti-Mgh-es, the carriers of reversed RM are present. The basalts of normal RM are represented by the localities Blhovce-Buda-24, Ostrá skala-33 (containing only more oxidized, close to magnetite Fe-Ti phases), and Šomoška 43,44 (containing the Ti-rich Ti-Mt and more oxidized Fe-Ti phases). The normal RM of the mentioned basalts is linked with the more oxidized phase. The basalts, dominantly with the Ti-Mgh phases, exclusively of the reversed RM, are represented by those from Husina-10 and Poličko-14 localities.

– We see large inconsistency between the level of the RM of natural basalts and that acquired during magnetizing process in the laboratory field. The intensity of the reversed RM of Ti-rich Ti-Mt bearing compact basalts (after removal of viscous RM) is on average of 1700 nT. This value was derived from the data of about 73 samples of basalts from different localities. The RM of these rocks is supposed to be of thermoviscous origin. This RM is linked with a presence of more oxidized Ti-Mgh secondary magnetic phase. The average value of PTRM of basalts (induced at 450° in the laboratory) is $\approx$ 7673 nT. A relation between this intensity of PTRM $\approx$ 7673 nT and that of average value of RM $\approx$ 1700 nT (originally magnetized in the field) is a multiplication factor of 4.5. This 4.5 times higher intensities of the PTRM of rocks were acquired at the laboratory field intensity H $\approx 48\mu$ T, during only about 20 min. But a cooling of basaltic magma in the field took place probably for a very long time, and the intensity of the geomagnetic field was approximately very close to that applied in the laboratory. It has been predicted, that the intensity of the geomagnetic field of positive and reversed polarity (if any) in a balanced state and at the same geographical position should

be approximately very similar. If the magnetizing mechanisms, a quality and magnetic properties of magnetic minerals of rocks in the field were similar as those in the laboratory, the intensities of RM of both collections of samples should have been approximately the same. Despite the investigated samples have different age (from 1.16 to 8.0 Ma), the values of the original intensities of the reversed RM of basalts from individual localities are very close. It is hard to believe that the intensity of the geomagnetic field in the time of acquiring the reversed RM was about 4.5 times less than that of today. So, the low intensity of reversed RM of the respective basalts could be attributed to magnetization by the self-reversal mechanisms.

– In the low Curie temperature Ti-rich Ti-Mt-es there is evident a strong κ variation with temperature. This variation corresponds to paramagnetic (near to SP magnetic phases) phase, without a presence of a thermodynamically stable domain structure. Such phases behave as the small magnetic particles. According to Landau and Lifshitz in (*Hubert and Schäfer (1998)*, only the small particles may show a variation of their magnetic parameter with the temperature. The magnetic particles with the developed thermodynamically stable domain structure are athermal. The results of BP method have proven a presence of domain pattern in some Ti-rich Ti-Mt grains in our samples. We see that the domain structures are more frequently present in the basalts containing a high-temperature oxidized Fe-Ti phases, except of an original low Curie temperature of Ti-rich Ti-Mt phase. Under some conditions, also a non-balanced, very weak RM can be acquired by the low Curie temperature phases, but it can be so that the Ti-Mt grains with the domain structure belong to the more oxidized phase in the respective basalts. The samples, originally of the reversed RM, have mostly the domains of nearly non-uniform orientation, while the samples originally of normal RM have mostly domains of uniform orientation. The results of the study of magnetic parameters and those, which were obtained by BP method, are not fully consistent with respect to the detection of some magnetic Fe-Ti phases. The limitations cannot be specified now.

– From the study of the hysteresis properties it follows that the coercive force, the remanent coercive force, and other hysteresis parameters in-

crease for the basalts with increasing the portion of the oxidized phase in the sample.

The most important knowledge is that the rocks are able to acquire the reversed RM by the self-reversal mechanisms, and that this phenomenon is linked with a presence of small magnetic particles in the rocks. So far, no relevant theory has been established to explain the self-reversal origin of the RM of rocks. Now we can start with describing some elementary principles, which can be additionally extended into a more progressive theory with regard to the self-reversal magnetization of rocks. In the physics of magnetization of the artificial magnets the small magnetic particles play a very important role. According to *Hubert and Schäfer (1998)*, if a particle is too small, no domain structure will develop. For such particles the behaviour in magnetizing field will have other theoretical ground than in the particles with the thermodynamically stable domain structure. Above a certain size an inhomogeneous magnetization state with a low average magnetization takes over. This state is not more continuously related to the uniformly magnetized state. The initial high-remanence or single-domain configuration is called the flower state. The low remanence state, which has a lower energy beyond the single-domain limit, is called the curling or vortex state. If a small particle is first saturated at high field and the field is then reduced, it will in general switch at some point to opposite magnetization direction, or to some other state closer to equilibrium. The saturated state is usually metastable on approaching the equal energy limit, it cannot switch without some excitation as long as there is an energy barrier. The barrier may be overcome by thermal activation. This leads to magnetic viscosity and thermally induced loss of magnetization - superparamagnetism. While the magnets consisting of larger particles can be readily oriented in a field before compaction, this becomes increasingly difficult with decreasing particle size. According to *McElhinny and McFadden (2000)* there are the most important viscous effects in rock magnetism which may arise from thermal activation of domains. The thermoremanence in independent single-domain grains follows from the state of superparamagnetism. In the absence of an applied field, the magnetic moment (θ) of a uniaxial single-domain (SD) grain can take up two orientations of equal minimum energy, $\theta = 0$ or $\theta = 180°$. The potential barrier between two

positions is represented by the positions of maximum energy that occur at $\pm 90^\circ$ and has value $E_r = vK$; *v-particle volume, K-anisotropy constant.* The thermal fluctuations of energy $E_t = kT$; *k-Boltzman's constant, T-absolute temperature*, are capable of moving the magnetic moment from one minimum to the other if $E_t \geq E_r$, i.e., if $kT \geq vK$. For a given value of T there must always be some grains of volume v, for which the thermal fluctuations are large enough to cause the moment to change spontaneously from one position to the other. If an assemblage of identical grains has an initial moment M_0, then under these conditions it will decay exponentially to zero according to the relation: $M_t = M_0$ exp (-t/τ); M_t is the moment remaining after time t and τ is relaxation time of the grains. The τ is related to both E_r and E_t as

$$\tau = \frac{1}{f}\exp\left(\frac{E_r}{E_t}\right) = \frac{1}{f}\exp\left(\frac{vK}{kT}\right)_T, \tag{1}$$

where $f = 10^9 s^{-1}$. The anisotropy constant K is related to the microscopic coercivity B'$_c$. Then

$$\tau = \frac{1}{f}\exp\left(\frac{vB'_cM_s}{2kT}\right)_T, \tag{2}$$

where B'$_c$ and M_s are their values at temperature T. This has important implications related to the magnetic stability of rocks. The grains are rendered unstable by thermal agitation, and on application of weak field, they quickly reach equilibrium with this field. The moment so acquired is called equilibrium magnetization, which on removal of the field quickly dies away at a rate determined by the relaxation time. Grains such as these are said to be superparamagnetic (SP). The τ becomes small when T is large, also when v is small. For each grain of volume v there is then a *critical blocking temperature* T_B, at which τ becomes small, but which might also be below the Curie temperature. Similarly at any given T, there is a *critical blocking volume*, v_B at which τ becomes small. Since the characteristic time for thermal activation is a strong function of temperature, it follows that as magnetic body cools, so it passes through a narrow temperature range over which there is dramatic change in the rate of thermal activation. Thus at a particular temperature single domains may undergo frequent spontaneous (thermally excited) reversals

of magnetization, but at a temperature only slightly lower, the average time for reversals becomes much longer than the time scale of observation. They thus change quite suddenly from the SP state to a stable, permanently magnetized state. The temperature at which this occurs, assumed to be sharp, is referred to as the *blocking temperature* T_B. The effective blocking temperature is a function of cooling rate, being lower for slow cooling, since blocking temperature is really the temperature at which the relaxation time for thermal activation becomes longer than the time scale of cooling.

The RM depends on the material parameters, as well as on the size and shape of the magnetic particle. Frequently, small magnetic particles are used to achieve the high intensity and stability of artificial magnets. In magnetism and paleomagnetism we are concerned with the RM of magnetic minerals in volcanic, sedimentary and metamorphic rocks. During the creation and alteration of rocks, the different types and grain sizes, including SP particles of Fe-Ti, or Fe magnetic minerals are created. Below the superparamagnetic limit (critical size of the particle) the small magnetic particles may continually reverse their magnetization direction due to thermal agitation (*Bode et al., 2004*). For microscopic single-domain particles, the coercivity can reach high values, since the state of reversed magnetization has first to be nucleated. Such particles exhibit a high stability of the magnetization (*Braun, 1993, 1994*). This fact renders them suitable for information storage in recording media, and as constituents of rocks they preserve the value of the local magnetic field as the temperature has dropped below the blocking temperature of the particle.

In many types of rocks the reversed RM has been generated by the self-reversal mechanisms, not by the reversed geomagnetic field. The presented results have provided only the experimental background for further achievement of more successful establishment of the theory for the self-reversal origin of the reversed RM of the rocks.

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References

Appel E., Soffel H. C., 1984: Model for the domain state of Ti-rich titanomagnetites. Geophys. Res. Lett., **11**, 189–192.

Appel E., Soffel H. C., 1985: Domain state of Ti-rich titanomagnetites deduced from domain structure observations and susceptibility measurements. J. Geophys., **56**, 121–132.

Bina M., Tanguy J. C., Hoffman V., Prévot M., Listanco E. L., Keller R., Fehr K. Th., Goguitshaichvili A. T., Punongbayan R. S., 1999: A detailed magnetic and mineralogical study of self-reversed dacite pumices from the 1991 Pinatubo eruption (Philippines). Geophys. J. Int., **138**, 159–178.

Bode M., Pietzch O., Kubetzka A., Wiesendanger R., 2004: Shape-Dependent Thermal Switching Behavior of Superparamagnetic Nanoislands. Phys. Rev. Letters, **92**, 6, 067201-1–067201-4.

Braun H. B., 1993: Thermally Activated Magnetization Reversal in Elongated Ferromagnetic Particles. Phys. Rev. Letters, **71**, 21, 3557–3560.

Braun H. B., 1994: Statistical mechanics of nonuniform magnetization reversal. Phys. Rev. B, **50**, 22, 16501–16521.

Hubert A., Shäffer R., 1998: Magnetic Domains. The Analysis of Magnetic Microstructure. Springer Berlin, Hidelberg, New York, Barcelona, Budapest, Hong Kong, London, Milan, Paris, Singapore, Tokyo, 685 p.

Konečný V., Balogh K., Orlický O., Lexa J., Vass D., 2001: The evolution of Neogene-Quaternary alkali basalt volcanism in Western Carpathians (Slovakia). Session Carpathians, Poster. Pancardi 2001, II. Abstracts, CP-11.

McElhinny M. W., McFadden P. L., 2000: Paleomagnetism. Continents and Oceans. Academic Press. San Diego, San Francisco, New York, Boston, London, Sydney, Tokyo, 386 p.

Orlický O., 2001: Field-reversal versus self-reversal hypothesis: Paleomagnetic properties and magnetic mineralogy of the Neogene andesites of central Slovakia (Part I). Contr. Geophys. Geod., **31**, 4, 653–681.

Orlický O., 2002: Field-reversal versus self-reversal hypothesis: Paleomagnetic properties and magnetic mineralogy of the Neogene andesites of central Slovakia (Part II). Contr. Geophys. Geod., **32**, 1, 1–40.

Orlický O., 2002a: Field-reversal versus self-reversal hypothesis: Paleomagnetic properties, magnetic mineralogy and the reproducible self-reversal RM of the Neogene andesites from the Javorie and Poľana mountain range (Part III). Contr. Geophys. Geod., **32**, 2, 91–128.

Orlický O., 2002b: Field-reversal versus self-reversal hypothesis: Paleomagnetic properties, magnetic mineralogy and the reproducible self-reversal PTRM of the Neogene andesites from the Kremnické vrchy mountain range (Part V). Contr. Geophys. Geod., **32**, 4, 309–333.

Orlický O., 2002c: Field-reversal versus self-reversal hypothesis: Paleomagnetic properties, magnetic mineralogy and the reproducible self-reversal PTRM of the Neogene

andesites from the East-Slovak Lowlands, Zemplínske vrchy Mts., and the Slanské vrchy Mts., (Part VI). Contr. Geophys. Geod., **32**, 4, 359–373.

Orlický O., 2002d: Field-reversal versus self-reversal hypothesis: Paleomagnetic properties, magnetic mineralogy and the reproducible self - reversal RM of the Eocene to Miocene age volcanic rocks from Ceské Stredohorí Mts. North Bohemia (Part IV). Contr. Geophys. Geod., **32**, 2, 129–149.

Orlický O., 2003: Field-reversal versus self-reversal hypothesis: Paleomagnetic properties, magnetic mineralogy and the reproducible self-reversal PTRM of the Neogene andesites of the Vihorlat Mts. (Part VII). Contr. Geophys. Geod., **33**, 1, 57–76.

Orlický O., 2003a: Field-reversal versus self-reversal hypothesis: Paleomagnetic properties, magnetic mineralogy and an origin of the reversed RM of the Neogene rhyolites from central and eastern parts of Slovakia (Part VIII). Contr. Geophys. Geod., **33**, 2, 77–97.

Orlický O., 2003b: A study of magnetic properties and magnetic mineralogy of the Neogene volcanic and volcano-sedimentary rocks from central Slovakia. Contr. Geophys. Geod., **33**, 2, 111–126.

Orlický O., 2004: Magnetic mineralogy and anomalous magnetic susceptibilities of basalts from Central and Southern Slovakia. Contr. Geophys. Geod., **34**, 3, 227–249.

Orlický O., 2006: Field-reversal versus self-reversal hypothesis: The Ti-rich titanomagnetite bearing basalts and their partly self-reversed thermoremanent magnetization induced in the laboratory field. Contr. Geophys. Geod., **36**, 2, 171–188.

Orlický O., 2006a: A realistic interpretation of magnetic and paleomagnetic data: A study of basalts from Southern Slovakia. Contr. Geophys. Geod., **36**, 2, 201–227.

Orlický O., 2007: An exceptional role of small magnetic particles in magnetism and paleomagnetism of rocks. Contr. Geophys. Geod., **37**, 4, 331–358.

Orlický O., Funaki M., Pagáč P., 2000: Study of the self-reversal thermoremanent and partial thermoremanent magnetization of the Haruna dacite from central Japan. Contr. Geophys. Geod., **30**, 4, 323–342.

Orlický O., Funaki M., 2000: An origin and mechanism of the self-reversal TRM or PTRM of rocks. A study of the Rhyodacite from the Haruna Locality (Japan). Geol. Carpathica, **51**, 203–204.

Orlický O., Funaki M., 2001: Magnetic study of individual Fe-Ti oxides separated from the rhyodacite of the Haruna volcano (Japan) and the dacite ash of Mount Pinatubo (Philippines). Contr. Geophys. Geod., **31**, 3, 537–556.

Orlický O., Funaki M., 2002: Study of laboratory induced self-reversed thermoremanent magnetization and the Fe-Ti oxides of the dacite ash from the 1991 Pinatubo eruption (Philippines). Stud. Geophys. Geod., **46**, 527–544.

Ozima M., Funaki M., Hamada N., Aramaki S., Fujii T., 1992: Self-reversal of thermoremanent magnetization in pyroclastics from the 1991 eruption of Mt. Pinatubo, Philippines. J. Geomag. Geoelectr., **44**, 979–984.

Ozima M., Funaki M., 2001: Magnetic properties of hemoilmenite single crystals in Haruna dacite pumice revealed by the Bitter technique, with special reference to self-reversal of thermoremanent magnetization. Earth Planets Space, **53**, 111–119.

Özdemir Ö., 1987: Inversion of titanomaghemites. Physics of the Earth and Planetary Interiors, **46**, 184–196.

Pan Y., Liu O., Deng Ch., Qin H., Zhu R., 2006: Thermally induced inversion of Al-substituted titanomagnetite in basalts: Evidence for partial self- reversal. J. Geophys. Res., **111**, B12S29, doi:10,1029/2006JB004576.

Prévot M., Hoffman K. A., Goguitchaichvili A., Doukhan J. C., Shcherbakov V., Bina M., 2001: The mechanism of self-reversal of thermoremanence in natural hemoilmenite crystals: new experimental data and model. Physics of the Earth and Planetary Interiors, **126**, 75–92.

Radhakrishnamurty C., Likhite S.D., Deutsch E.R., and Murthy G.S., 1981: A comparison of the magnetic properties of synthetic titanomagnetites and basalts. Physics of the earth and Planetary Interiors, **26**, 37–46.

Soffel H. C., 1978: The reliability of palaeomagnetic data from basalts with low Curie temperatures ($T_C \leq 90^\circ$ C). Physics of the Earth and Planetary Interiors, **16**, 38–44.

Zhou W., Van der Voo R., Peacor D. R., 1997: Single-domain and superparamagnetic titanomagnetite with variable Ti content in young ocean-floor basalts: No evidence for rapid alteration. Earth and Planetary Science Letters, **150**, 353–362.