Study of the Ti-Mt phases of the artificial samples: The contribution to the solution of the source of the intense RM of volcanic rocks

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

Abstract: The laboratory acquired detrital remanent magnetization (DRM) was studied on the artificially prepared titanomagnetite (Ti-Mt) containing samples. The titanium-rich Ti-Mt-es are able to acquire only very low values of DRM, despite the natural basalts possessed extremely high values of magnetic susceptibility (κ). The Q ratio has attained the values of about 0.5 to 6.0. This fact has proven an idea about the superparamagnetic SP-like behaviour of the titanium rich Ti-Mt-es. Similar SP-like behaviour have shown the samples with the non-completely developed low-temperature oxidized Ti-Mt phase. Natural basalts of this group have relative low values of κ and Q ratio. The highly-temperature oxidized Ti-Mt-es carry very high intensities of DRM so the derived Q-ratio is also high. The stability of DRM of highly oxidized Ti-Mt-es against the thermal effect is relatively high, comparable with the stability of NRM natural basaltic rocks. From the experimental works it has followed that intensity and stability of RM depend on the domain state of Fe-Ti oxides, so there have been involved also some comments about the domain structures of the titanium-rich Ti-Mt-es in this article.

Key words: the Ti-rich and oxidized titanomagnetites, artificial samples, the sources of viscous remanent magnetization of rocks

1. Introduction

The volcanics, including the volcano-sedimentary rocks are the subject of the paleomagnetic investigation on the whole Globe. The paleomagnetic method is based on the study of remanent magnetization (RM) of rocks, unfortunately some problems about the types of RM have not been

[1] Dúbravská cesta 9, 845 28 Bratislava, Slovak Republic; e-mail: geoforky@savba.sk

fully solved. The examples of possible source of intense marine magnetic anomalies have been presented on the basis of study of continental basalts from Slovak volcanic fields by *Orlický (2005)*. The experimental works have proven that when the oxidation of the rich-titanium titanomagnetites in basalts has taken place below 150°C with the presence of ambient magnetic field, basaltic rocks acquired low intensity CRM, mostly lower than their original RM. But when the oxidation takes place over 150°C (low, or high-temperature oxidation) the VRM (the chemico-viscous RM) of basalts is several times more intense than the RM of rocks before their oxidation. This VRM is always of positive direction. The author has proposed that the basaltic magma of the central part of rift system preserved its temperatures at higher level and cooled a longer time than the thin lava flows on the flanks of the system. So, the alterations of the Ti-Mt-es took place at higher temperatures in the central sizable body, comparing it with the thin lava flows when the temperatures are supposed to be expressively lower. These different temperature oxidation conditions resulted also in the acquisition of different intensity of VRM (or CRM) of basaltic rocks with the generation of different intensities of marine magnetic anomalies.

From the previous works has followed that the VRM of basalts is the dominant source of intense marine magnetic anomalies. As we have known there is not an effective way to differentiate the proportions of individual types of magnetizations and their carriers within the assemblages of natural remanent magnetization (NRM) in the *in situ rocks*. But we can face our attention to the individual types of magnetizations on the artificially prepared samples. There is possible to arrange an acquisition of the TRM, PTRM, VRM and the detrital RM (DRM) of the artificial Ti-Mt containing samples in the laboratory simulated conditions. In this stage of laboratory works I have preferably arranged an acquisition of DRM of artificially prepared samples. Their study is a subject of this article.

2. Experimental

Preparation of artificial samples and basic measurements

The samples were prepared by grinding the original (*in situ volcanics*) in ceramic bowl. The ground material of the samples was sieved to preserve

Tab. 1. Magnetic characteristics and magnetic Fe-Ti minerals of artificial samples and basaltic rocks from southern Slovakia.

Name of locality	Artificial samples			Original samples			Petrography	Mag.mineral
	$\kappa \times 10^6$ SI Un.	DRM	Q	$\kappa \times 10^6$ SI Un.	NRM	Q		
Borehole KON-1	7583	1298	3.4	44564	454	0.2	M.diorite	Mt(MD)
Mašková2ac1-04	5023	925	3.7	53552	4938	1.8	Basalt	TiMt(SP)
Mašková2aSI-04	5794	1171	4.04	45398	3745	1.6	Basalt	TiMt(SP)
Mašková1a-IIIS	1245	237	3.8	7805	1832	4.7	Basalt	TiMt(ltox)
Mašková1a-1-3S	2605	3481	26.7	6706	1827	5.4	Basalt	TiMt(ht/ltox)
Mašková1a-1-7S	3857	3422	17.7	5924	1803	6.1	Basalt	TiMt(ht/ltox)
Črep-3	6321	1894	6.0	34917	19262	11.1	Basalt	TiMt(htox)
Dunivá hora3	3924	4706	24.0	23800	24780	20.8	Basalt	TiMt(htox)
Ostrá skala 1	1339	1292	19.3	25118	25863	21.0	Basalt	TiMt(htox)
Steb.skala2-2	1930	616	6.3	33775	6180	3.7	Basalt	TiMt(ltox)
Fiľak.Kov.2-4	1968	869	8.8	19050	8610	9.0	Basalt	TiMt(ht/ltox)
Zaboda 3	3235	3729	23.1	26601	19172	14.4	Basalt	TiMt(htox)
Ratka SE-1-1	2051	536	5.1	35473	2509	1.4	Basalt	TiMt(ltox)
Čirinč1	2648	781	5.9	16172	1798	2.2	Basalt	TiMt(ltox)
Veľ.Dravce2	5641	4769	16.9	25895	749	0.6	Basalt	Ti-Mt/Ilm-Hem
Husina3-1	3266	6424	39.3	28309	613	0.4	Basalt	TiMt/Ilm-Hem
Poličko1-1	7429	9324	25.1	28409	860	0.6	Basalt	TiMt/Ilm-Hem
NE of Šavol1	2542	1791	14.1	19413	848	0.9	Basalt	TiMt/Ilm-Hem
Konrádovce2	5323	2811	10.6	11069	942	1.7	Basalt	TiMt/Ilm-Hem
Podrečany2	2673	1836	13.7	13320	3046	4.6	Basalt	TiMt/TiMgh
Šomoška3A-2	308	646	42.0	8282	1157	2.8	Basalt	TiMt/TiMgh
Soví hrad3-2	1141	330	5.8	4412	2245	10.0	B.breccia	Ilm-Hem
Malý Kamenec4	2799	3871	27.7	7649	5599	14.6	Rhyolite	Mt+Hem(PSD)
Velký Kamenec1	6312	4916	15.6	9546	1665	3.5	Rhyolite	Mt+Hem(PSD)

κ–bulk magnetic susceptibility; NRM, VRM–natural remanent magnetization (NRM), detrital remanent magnetization (DRM) in nano Tesla (nT); Q–Koenigsberger ratio; M.diorite-monzonodiorite, the sample was collected from the depth of 1327 m of the borehole KON-1; B.breccia-basaltic breccia; Mt-magnetite; TiMt-titanomagnetite; TiMgh-titanomaghemite; Hem-hematite; Ilm-Hem-ilmenohematite; MD-multi-domain; PSD-pseudo-single-domain; SP-superparamagnetic; lt–low-temperature; ht–high-temperature; ox-oxidized;

the sizes of the grains under 30 μm. The bar permanent magnet was used to separate the magnetic fraction from the ground material. The magnetic grains were fixed in nonmagnetic gypsum. The powdered gypsum was permanently mixed with the magnetic fraction and water in the ceramic bowl. This mixture of an appropriate consistency was poured out into the plastic form of the cylindrical shape with the diameter of 25 mm and height of 22 mm. Above mentioned procedures including the drying of the samples on the free air were made at the room temperature with the presence of ambient magnetic field of the intensity of about 50 μT. During the preparation and drying of the samples the direction of the field was respected. In a such procedure only detrital remanent magnetization (DRM) was acquired in the sample (the previous types of RM might have been preserved in individual grains, but due to completely new alignment of the grains in artificial sample in the direction of ambient laboratory field, the total magnetic moment of the sample was oriented nearly in the direction of the ambient magnetic field). After the samples were drained the magnetic susceptibility (κ) and the remanent magnetization (RM) were measured (by the susceptibility meter KLY-2, JR-4 and JR-5 spinner magnetometers, respectively). The results are in the Tab. 1. The thermal demagnetization and the measurements of the change of κ with the temperature of selected samples were done (Figs 1, 2).

The interpretation of the results

In the previous work (*Orlický, 2005*) interpreted the high magnetic intensities of RM by existing VRM of the secondary magnetic phases (of low or high temperature oxidation) in basalts. Above it has been noted that there is a difficulty to precisely identify a type of magnetization in the natural rocks. In the Tab. 1, there are the basic magnetic data of the artificially prepared samples and those of natural basalts. An inducing of detrital remanent magnetization of all artificial samples was realized at the same conditions.

The explanation of the differences in individual samples:
– The sample of the monzonodiorite from the depth of 1327 m of the borehole KON-1. The artificial sample acquired very low value of intensity of

DRM, despite its high κ. The Q coefficient (the relation of DRM/κ) is very low. Similar behaviour have shown also the natural monzono-diorite samples from large vertical interval of the borehole. The carriers of magnetic properties in these samples are the magnetites of the multidomain structure.
– Very softly oxidized titanium-rich titanomagnetites Mašková 2ac1-04, 2aSI-04 (Tab. 1). The natural (in situ) samples have shown very high values of κ. Despite this fact, the intensity of the DRM (and Q) are extremely low (similar behaviour have shown also the additionally prepared artificial samples of such type of basalts). Such types of the Ti-Mt-es have behaved similarly like the superparamagnetic (SP) particles, in which the domain structure has not been developed. This is the reason for what they acquired only very low intensities of DRM (an idea about the SP behaviour of Ti-rich Ti-Mt-es has been published by (*Orlický 2004, 2005; Orlický et al., 2005*).
– Low-temperature oxidized phase: Mašková1a-IIIS (and basaltic samples Mašková 1-1-3S and Mašková 1-1-7S, in Tab. 1) containing not-completely low temperature oxidized Ti-Mt phase and Podrečany2, Šomoška 3A-2, containing completely low-temperature oxidized phase. These samples are characterized by low κ. It is not due to lack of magnetic Fe-Ti oxides, but owing to specific magnetostatic interactions and anisotropy, which occurred during low temperature oxidation of original Ti-Mt-es in the field.
- Oxidized Ti-Mt samples Mašková 1-1-3S and Mašková 1-1-7S. Magnetic fraction for preparation of these artificial samples was separated from the basaltic samples which were thermally demagnetized up to 650°C (Fig. 2). After complete demagnetization the intensity of NRM was nearly zero. Before thermal demagnetization only low-temperature oxidized phase was present in basaltic samples. From Fig. 2 it follows that there is an intensive change of magnetic susceptibility from laboratory temperature to 650°C due to oxidation of original Ti-Mt-es. These oxidized Ti-Mt-es, probably of a pseudo-single domain structure are able to acquire relatively high intensities of DRM during an alignment of individual particles in the field (according to the theory - in *McElhinny (1973)* the intensity of DRM of a sample is proportional to the intensity of magnetization of individual grain. I need to comment that NRM of original grains was thermally demagnetized to nearly zero value). Both, the DRM and Q of original basalts have not shown high values. Low value of κ of original basalts has pointed out that there was high portion of low-temperature oxidized magnetic phases except

of low portion of SP phase in original samples.
– The examples of induced DRM of 18 artificial samples in Tab. 1 and further 20 additionally prepared artificial samples (not-presented) have shown that the intensity of DRM depends on the presence or absence of oxidized magnetic phases. If there is a high portion of oxidized Ti-Mt phase (preferably high-thermally oxidized phase) an acquisition of high intensity DRM has occurred. Any presence of rich-titanium Ti-Mt phase of SP like behaviour decreases the intensity of DRM of the samples. We see from Tab. 1 that in many cases there are discrepancies in relations of DRM of artificial samples and NRM and Q coefficients of in-situ original basalts. The original basalts (despite of high portion of oxidized phase) of low Q values have possessed the reversed RM. This reversely oriented RM has lowered the value of VRM (VRM is of positive polarity) due to vector summa of both these components. In the artificially prepared samples only a positive polarity DRM was induced, which has corresponded to the direction of an ambient geomagnetic field.

Stability of DRM against the thermal demagnetization

There are two examples of thermal demagnetization of DRM in Figs 1, 2. We see the following:
– the DRM of artificial sample Mašková 2ac1-04 has acquired only very low intensity (DRM= 925 nT, and very low value of Q) after its magnetization in the field of intensity H = 50 μT despite of high value of κ. After its demagnetization the DRM was dominantly destroyed up to 250°C. The direction of DRM (inclination and declination of DRM) was relatively well preserved in the interval from room temperature to cca 250°C (up to Curie temperature of the Ti-Mt). In the interval over 250°C to 600°C there has been preserved only negligible portion of DRM. The direction of DRM has shown very large dispersion. As has been noted above these magnetic Ti-Mt has behaved as the SP-like material so an acquiring of low (or no) remanent magnetization is in a very well correspondence with the theory. We can find such behaviour of VRM also in natural in-situ basalts containing the titanium-rich titanomagnetites.
– Oxidized Ti-Mt artificial sample Mašková 1-1-3S has acquired relatively high intensity of DRM (DRM = 3481 nT and a high value of Q was derived) after its magnetization in the field of intensity H = 50 μT, despite

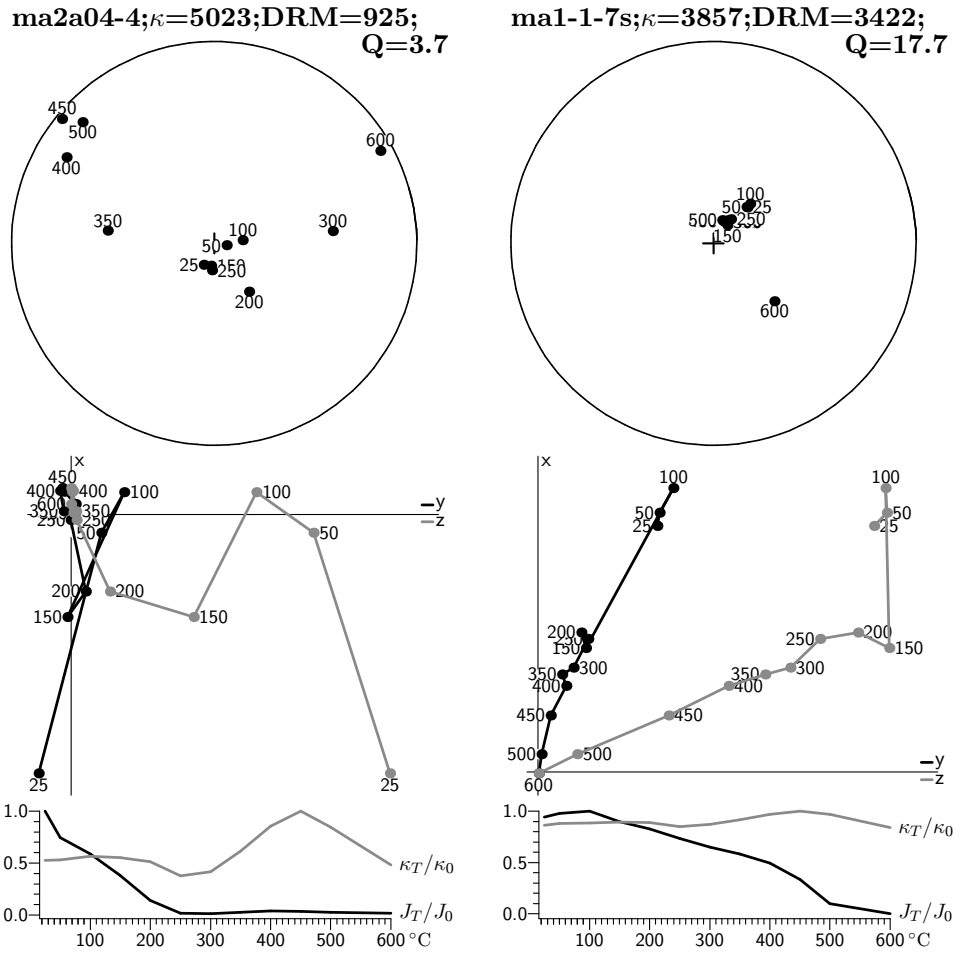

Fig. 1. Thermal demagnetization of the artificial samples ma2a04-4 and ma1-1-7s; stepwise heating to 600°C; Zijderveld diagrams and stereographic projections; • (○) means positive (negative) polarity of RM; κ_T (κ_0) - magnetic susceptibility at T (at 25°C, respectively); J_T (J_0) - remanent magnetization at T (at 25°C, respectively).

of low value of κ. The intensity of DRM and its direction were preserved after its thermal demagnetization in the interval from room temperature to Curie temperature of oxidized Ti-Mt phase, cca of 550°C). As it has been noted above the magnetic fraction of this artificial sample was separated

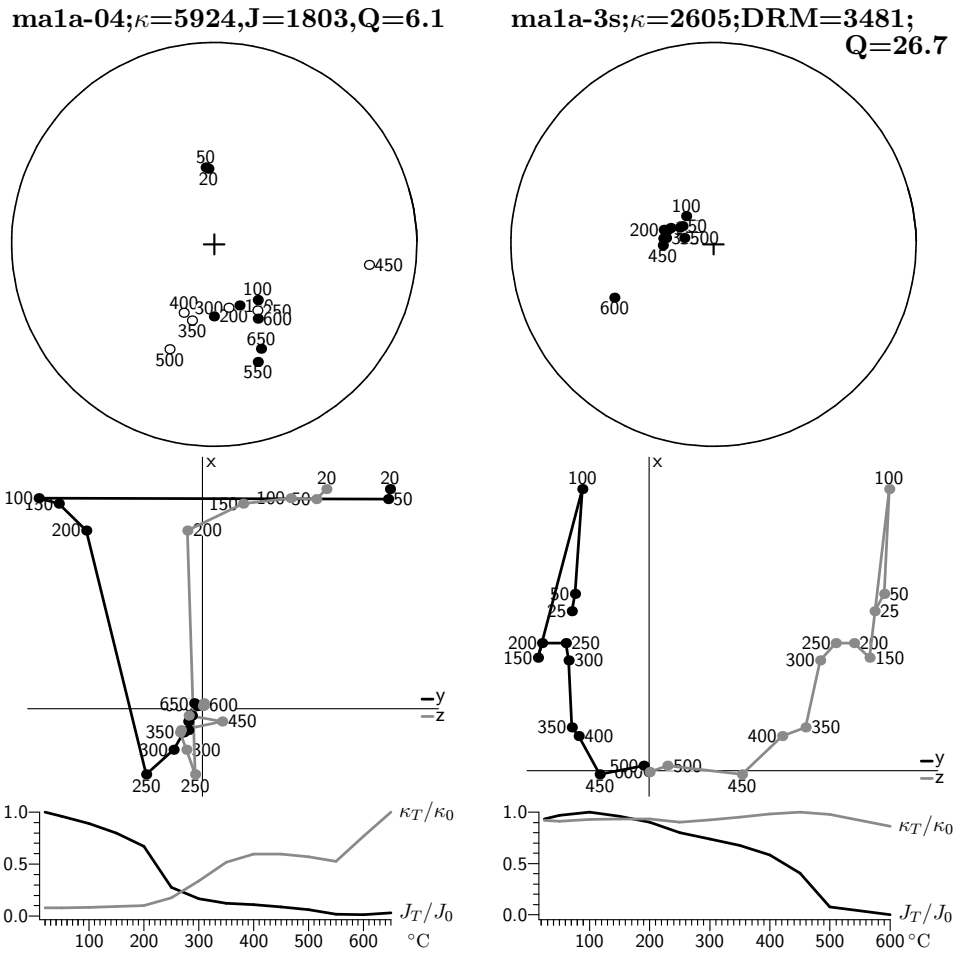

Fig. 2. Thermal demagnetization of natural basaltic sample ma1a-04 and artificial sample ma1a-3s; stepwise heating to 600°C; Zijderveld diagrams and stereographic projections; • (○) means positive (negative) polarity of RM; κ_T (κ_0) - magnetic susceptibility at T (at 25°C, respectively); J_T (J_0) - remanent magnetization at T (at 25°C, respectively).

out from the sample of basalt, which was thermally demagnetized to 600°C, so the original Ti-Mt was completely oxidized. But we see in the Tab. 1 that the original (in-situ) basalt of the sample Mašková 1-1-3S has shown relatively low value NRM, Q and κ. There was present a low-temperature

oxidized Ti-Mt phase which is commonly characterized by lower magnetic characteristics (*Orlický, 2004*). The results of the thermally tested artificial samples Mašková 1-1-3S and Mašková 1-1-7S (and not presented Mašková 1a-6s) have proven that the stability of DRM of the rocks with the oxidized Ti-Mt-es against the thermal effect is comparable with that of NRM (NRM has commonly involved VRM, CRM and TRM) in natural basalts.

3. Discussion and conclusions

The titanium-rich Ti-Mt-es are able to acquire only very low values of DRM, despite the natural basalts possessed extremely high values of magnetic susceptibility (κ). The Q ratio has attained the values of about 0.5 to 6.0. This fact has proven an idea about the superparamagnetic (SP) like behaviour of the titanium rich Ti-Mt-es. Similar SP-like behaviour have shown the samples with the non-completely developed low-temperature oxidized Ti-Mt phase. Natural basalts of this group have relative low values of κ and Q ratio. The highly-temperature oxidized Ti-Mt-es carry very high intensities of VRM so the derived Q-ratio is also high. Very surpassing is a fact that the stability of DRM of highly oxidized Ti-Mt-es in artificial samples against the thermal effect is comparable with the stability of NRM natural basaltic rocks. From the experimental works it has followed that intensity and stability of RM depends on the domain state of Fe-Ti oxides, so there have been involved also some comments about the domain structures of the titanium-rich Ti-Mt-es in this article.

A short comment about the domain structure in Ti-rich titanomagnetites and about an idea concerning the SP-like behaviour of these type of the Ti-Mt-es was presented by *Orlický (2004)* and *Orlický et al. (2005)*. *Orlický (2004)* has commented that the Ti-rich Ti-Mt-es have not developed domain structure. He has also proposed that during the oxidation of these Ti-Mt-es the domain structure is supposed to be developed.

The study about the domain structure in Ti-rich Ti-Mt-es of the Tertiary basalts was referred by *Soffel (1977)*. *Appel et al. (1990)* studied the basalts using the magneto-optical Kerr effect in natural grains of Ti-Mt-es (T_C about 240°C). According to the authors the internal stress in naturally occurring Ti-Mt-es is high and varies strongly in amount and directions

within short distances. *Halgedahl (1987)* has referred that intermediate to high x values Ti-Mt-es largely exhibit complex patterns with a distinctly non cubic style, although simple patterns of broadly-spaced, roughly planar walls are sometimes observed. Undoubtedly, complex patterns in Ti-rich compositions result from stress. Very different domain pattern styles observed through the titanomagnetite series indicate the increasing importance stress with titanium content.

The magnetic domain state of synthetic titanomagnetites including titanium rich ones has been investigated through a study of their susceptibility and hysteresis over a wide temperature range by *Radhakrishnamurthy et al. (1981)*. They have proposed that while the magnetite easily forms multidomains (MD), titanomagnetites in the range TM30-TM100, even when coarse-grained do not exhibit magnetic properties expected from the MD structure and hence do not seem to occur dominantly in the MD state. Therefore the samples in the mentioned TM range probably form chiefly single domains (SD) or spin clusters. Whether single domains behave like a stable SD fraction or a superparamagnetic (SP) fraction depends upon their blocking temperatures (T_B) being greater or less than the ambient temperature. A peak at the κ-T curve of sample, containing single domains may reflect the maximum contribution to κ from superparamagnetism of the single domains at these temperatures. In that case the gradual shift of the κ peak towards lower temperatures in the range TM30 - TM100 might indicate a decrease of the maximum T_B corresponding to variation in SD/SP threshold sizes which are related to changes in other parameters such as the decrease of T_C. For TM70 the κ peak has been found to lie straightly above 300 K and hence, according to their interpretation most of single domains in this material exhibit superparamagnetism at room temperature.

A preliminary simple model for the domain state of Ti-rich Ti-Mt-es has been published by *Appel and Soffel (1984)*. Following the idea of the model, particles of MD grain size should consist of multidomain, single domain and spin cluster regions. The consequence is the decrease of the effective grain size (division into subvolumes) and an enhanced importance of spin rotation processes. According to the authors the micromagnetic state will be comparable with the conditions in magnetic sponges (cold-pressed and partially sintered magnetic powders). Domain patterns on Ti-rich TiMt-es show typically uniaxial anisotropy very similar to those of amorphous metals. They

can be interpreted as caused by locally variable compressive and tensional internal stress.

According to *Appel and Soffel (1985)* domain structure observations showed that at room temperature T-rich Ti-Mt-es normally developed a non-classical domain structure characterized by a very complicated domain pattern. Possible explanations are: mineralogical inhomogeneity of the specimens, inhomogeneous anisotropy field, causing a locally varying preferential direction of the spontaneous magnetization. Possible source of anisotropy are stress, magnetocrystalline and shape anisotropy. The general occurrence of bent domain walls, the varying intensity of the Bitter lines and the local sensitivity on external stress indicate the existence of an inhomogeneous anisotropy field, in amount and direction. Consequently, the preferential direction of the spontaneous magnetization and the specific domain wall energy should fluctuate and prevent the development of a classical domain configuration. Complicated domain patterns will arise from the locally varying anisotropy conditions. Mainly the spontaneous magnetization should be oriented in the direction defined by the local anisotropy (apart from the domain walls). Depending upon certain anisotropy conditions, the development of true domain structures may even be impossible in part of the crystals. The most probable cause for the formation of complicated domain patterns is the existence of an inhomogeneous stress field. Of course, the magnetocrystalline and shape anisotropy will not vanish, but superpose the stress anisotropy.

Small, including the SP particles contain no domain pattern even if they are commonly called single-domain particles. In low-anisotropy materials there is an intermediate range in which continuous micromagnetic vortex states, rather than classical domains, prevail. Even if anomalous, continuous magnetic microstructures do not look like domains, this does not mean that domain models, in which continuous transitions are replaced by domains and walls, are useless. The principal problem in small-particle magnets is their orientation. While magnets consisting of larger particles can be readily oriented in a field before compaction, this becomes increasingly difficult with decreasing particle size. Non-oriented permanent magnets cannot achieve large values of the energy product and can be applied in low-cost bonded materials only. The domain patterns inside single-domain particles are impossible or at least unstable, in contrast to the large grains of

nucleation-type magnets *Hubert and Schäfer (1998)*.

All above mentioned knowledge about the domain structure of the Ti-rich Ti-Mt-es has not directly supported the idea about the SP behaviour of these Fe-Ti oxides, but in the presented results the induced very low intensity DRM of artificial samples containing the Ti-rich titanomagnetites has supported it very clearly.

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References

Appel E., 1987: Stress anisotropy in Ti-rich titanomagnetites. Physics of the Earth and Planetary Interiors, **46**, 233–240.

Appel E., Soffel H. C., 1984: Model for the domain state of Ti-rich titanomagnetites. Geophys. Res. Lett., **3**, 189–192.

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

Appel E., Hoffmann V., Soffel H. C., 1990: Magneto-optical Kerr effect in (titano) magnetite, pyrrhotite and hematite. Phys. Earth Planet. Inter., **65**, 36–42.

Halgedahl S. L., 1987: Domain pattern observations in rock magnetism: progress and problems. Phys. Earth Planet. Inter., **46**, 127–163.

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.

McElhinny M. W., 1973: Palaeomagnetism and plate tectonics. Cambridge, at the University Press.

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., Lipka J., Tóth I., 2005: An explanation of some effects of the titanomagnetite solid solutions ($Fe_{3-x}Ti_xO_4$) based on the magnetic susceptibilities, the Curie temperature measurements, and the Mössbauer spectra measurements. Contr. Geophys. Geod., **35**, 1, 79–94.

Orlický O., 2005: An origin and the source of extreme high intensity of natural remanent magnetization (NRM) of oxidized titano-magnetite bearing basaltic and andesitic rocks. Contr. Geophys. Geod., **35**, 2, 95–112.

Radhakrishnamurty C., Likhite S. D., Deutsch E. R., Murthy G. S., 1981: A comparison of the magnetic properties of synthetic titanomagnetites and basalts. Phys. Earth Planet. Inter., **26**, 37–46.

Soffel H. C., 1977: Domain structure of titanomagnetites and its variation with temperature. Adv. Earth Planet. Sci., **1**, 45–52.