

# A strange antiferromagnetic phase has controlled the magnetic and paleomagnetic properties of the Fe-Ti inversion spinel bearing rocks on the whole Earth globe

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**Abstract:** The magnetic characteristics of Fe and Fe-Ti magnetic mineral bearing rocks of young, through recent, quaternary, mesozoic to palaeozoic age have been studied. I have discovered a strange antiferromagnetic phase (AFMP) in Fe and Fe-Ti magnetic minerals of about 288 samples from 78 localities of volcanic rocks and of about 346 samples of the sedimentary rocks. The AFM phase has played a very important role in magnetism and paleomagnetism of rocks. I have considered that an evolution of the AFM phase started probably after solidification of magnetic minerals during post magmatic process and it has gradually followed during survival of minerals on the Earth's surface. The AFMP can be found in different evolutionary stages, from a beginning stage to completely developed stage. The indicated AFMP has the Néel temperature ( $T_N$ ), in the range from 350 °C to 485 °C, mostly around 450 °C in the samples under study. I have deduced that one can find the rocks in the two basically different aggregations: 1) The rocks containing so called the *pseudo original phase state* magnetic minerals, where the AFM phase is absent, and 2) The rocks containing the *transformed phase state* magnetic minerals, where the AFM phase is present. The AFM phase coexists with the ferrimagnetic phases in large range of temperatures and disappears at  $T_N$ . The AFM phase has a strong relations with magnetic properties, including the polarity of RM of rocks. The rocks with a completely developed AFM phase have always reversed RM. The AFM phase bearing rocks have possessed lower values of magnetic susceptibility ( $\kappa$ ) comparing them with the Fe and Fe-Ti minerals bearing rocks, where the AFMP is absent. The self-reversed partial thermoremanent magnetization (PTRM) was induced in many samples of volcanic rocks, applying a normally oriented geomagnetic field in the laboratory. In all these rocks was present the AFM phase. The rocks without the AFM phase have always normal RM. I can propose that the reversed RM of the AFMP containing magnetic minerals bearing rocks has been generated by the self-reversal process in nature.

**Key words:** pseudo original phase state, mineral bearing rocks, normal remanent magnetization, transformed phase state, antiferromagnetic phase, reversed remanent magnetization

## 1. Introduction

I refer to my previous works (*Orlický, 2004, 2008, 2009, 2010, 2011*), where I tried to account for the different magnetic characteristics of unoxidized (stoichiometric) and those of low-temperature oxidized titanomagnetites. I gathered the data by studying the rocks of different petrography from very young, recent, quaternary, tertiary, mesozoic, and palaeozoic rocks. No complete solution of the problem has been finished so far. The most frequent magnetic minerals in the rocks are the Fe-Ti solid solutions, the titanomagnetites (Ti-Mt-es,  $\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$ ) and the titanohematites (Ti-hem-es,  $\text{Fe}_{2-x}\text{Ti}_x\text{O}_3$ ), which are commonly termed as the ilmenite-hematites (Ilm-Hem-es). They have been largely studied by many authors as the carriers of magnetic and paleomagnetic properties of rocks. Many specialists have considered these minerals very stable, which have survived in the field in unchanged state from their origin up to the present. I studied the magnetic minerals of large collections of rocks in the past. My long term experience has shown that only few percentage of magnetic minerals have probably survived in original state. I have revealed that the magnetic minerals have undergone a dramatic transformations not only in a chemical composition, but mainly in their microstructural state. The magnetic susceptibility ( $\kappa$ ) and natural remanent magnetization (NRM) have corresponded then to a transformed state. An arise of a strange phenomenon has accompanied this transformation process in the field (*Orlický, 2011*). I have indicated it as the antiferromagnetic phase (AFMP). According to *Harrison and Putnis (1999)* the most important *internal* processes with respect to NRM acquisition are magnetic ordering, cation ordering, and subsolvus exsolution. The most important mechanism is the interaction between magnetism and microstructure of magnetic mineral for increasing the stability of NRM of rock. Microstructure describes the size, shape, orientational relationship and spatial distribution of the phases and defects which form an individual mineral. I have deduced that one can find the rocks in the basically two different aggregations: 1) the rocks containing so called the *pseudo*

*original phase state* magnetic minerals, where the AFMP phase is absent, and 2) the rocks containing the *transformed phase state* magnetic minerals, where the AFMP phase is present. The AFMP phase has appeared as a consequence of the transformed processes. Why the *pseudo-original phase state*, and why the *transformed phase state* of magnetic minerals? We do not know the true evolutionary history of Fe-Ti oxides. Their basic Fe and Ti ions survived originally inside the Earth's Mantle under the totally different conditions (pressure and temperature), than after a crystallization as the Fe-Ti solid solutions at the Earth's surface. The internal processes – the cation ordering, magnetic ordering, subsolvus exsolution and external low-temperature oxidation of Fe-Ti oxides have involved more factors which have influenced the state of a final mineral product. We will see below, that e.g. the tholeiite basalt from contemporary Kilauea volcano has contained the three Ti-Mt phases. One Ti-rich phase with  $T_C \approx 125^\circ\text{C}$ , the second one with  $T_C \approx 420^\circ\text{C}$ , and the third one with  $T_C \approx 560^\circ\text{C}$ . The two latter phases originated due to oxidation during cooling of basaltic magma at the Earth's surface. When there is a lack of oxygen in hot magma during cooling, only phase of original state with Ti-rich Ti-Mt should occur. We see the differences also in contemporary volcanic rocks from the Etna volcano. While the basaltic scoria from the 1982 eruption contains dominantly Ti-rich Ti-Mt phase with  $T_C = 250^\circ\text{C}$  and more oxidized Ti-Mt phase with  $T_C = 500^\circ\text{C} - 550^\circ\text{C}$ , the basalts from the 1983 eruption contain dominantly the Ti-Mt phase with  $T_C = 565^\circ\text{C}$ , corresponding to non-stoichiometric magnetite. All these phases correspond to the primary magnetic minerals. Because the whole assemblage of non oxidized and oxidized Ti-Mt-es, and more phases are there in firstly cooled rocks, it is more convenient to denote them as the *pseudo-original phase state* magnetic minerals. The *transformed phase state*, containing also the AFMP phase, originated due to the transformation of previous magnetic minerals.

The results have shown that most of magnetic minerals of rocks have been partially or intensely transformed in the field. In volcanic, sedimentary and metamorphic rocks, the magnetic minerals have undergone the transformation. The original Fe and Fe-Ti minerals in the rocks have been transformed from their *pseudo-original phase state* to *transformed-phase state* with the presence of the AFMP. This AFMP has imparted to magnetic minerals completely different magnetic properties in the rocks, including the self-reversed

orientation of remanent magnetization (RM), dominantly of chemical origin (CRM). The AFMP is characterized by marked increase of  $\kappa$  with a peak at about 450 °C, corresponding to the Néel temperature ( $T_N$ ). The rocks with the minerals of the *pseudo-original phase state* have not shown a presence of the AFMP. The presence of the AFMP may be detected by magnetic methods. I will present the examples of magnetic behaviour and magnetic characteristics of the *pseudo-original phase state* and the *transformed phase state* containing magnetic minerals of volcanic and sedimentary rocks in experimental chapter of this article to distinguish their magnetic properties and their magnetic behaviour.

## 2. Experimental results

### A short review of methods applied

The magnetic minerals of rocks were studied using the basic method for detection of a change of magnetic susceptibility ( $\kappa$ ) with temperature – Curie temperature measurements of samples. The first prototype of the apparatus, combined with KLY-2 susceptibilytometer for high temperature and low temperature measurements was used (*Orlický, 1990*). Some samples were measured by F. Hroudá and M. Chadima, Agico, Brno, using the CS-4 instrument in high temperature interval. The thermal demagnetization and the thermal magnetization of rocks with parallel measurements of a change of magnetic susceptibility with temperature were used as the basic and the most frequently applied methods. Except for compact natural rocks there were measured also artificially prepared samples, either from volcanic ash, or from the grinded rocks which were fixed in non-magnetic gypsum of a cylindrical form (a preparation of sample must be realized in zero magnetic field, not to acquire a DRM). The detailed procedures of magnetic methods were described by *Orlický (2009)*. The results of magnetic measurements were complemented by the X-ray diffraction analysis, realized by B. Dobročka, Electrotechnical Institute of SAS, Bratislava. The measurements of the differential scanning calorimetry (DSC) were realized by E. Illeková, Institute of Physics SAS, Bratislava. The study of hysteresis properties and the magnetic domain structure of magnetic minerals of rocks were realized by M. Funaki, National Institute for Polar Research, Tokyo, Japan (see *Orlický and Funaki, 2008*).

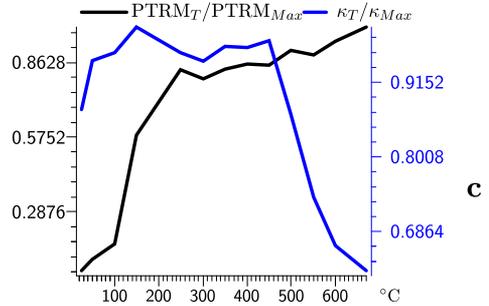
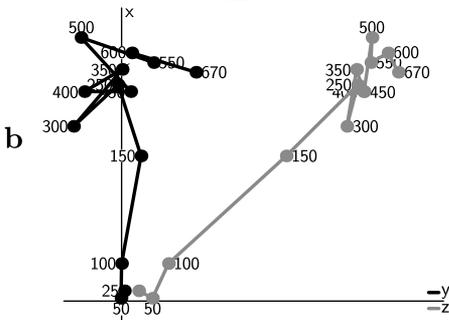
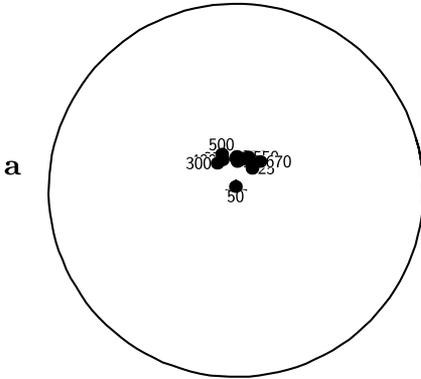
## I. Volcanic rocks

### The basaltic rocks with magnetic minerals of the pseudo original phase state

**The tholeiite basalt of the 1971 eruption** (Fig. 1) and three samples, all from the Hawaii area, coordinates: 19.430° N, 195.290° W, basaltic sample from the 1984 eruption and two basaltic scoria samples, one from the 1982, and other from 1972 eruption were studied (*Orlický, 2009a*). A tholeiite basalt contains the Ti-rich Ti-Mt with  $T_C = 125^\circ\text{C}$ , and more oxidized Ti-Mt phases with  $T_C = 420^\circ\text{C}$  and  $560^\circ\text{C}$  respectively. Only fluent increase of PTRM up to  $650^\circ\text{C}$  was detected during magnetization of these rocks. No AFMP was revealed during this process. Similar behaviour have been shown also the basalts of the Etna Volcano, 1982, 1983, 1984 and basaltic ash of 2010 eruptions. The basalts from the 1983 eruption (37.73° N, 15.00° E) contain predominantly the Ti-Mt phase with  $T_C = 565^\circ\text{C}$ , corresponding to non-stoichiometric magnetite. Basaltic scoria from the 1982 eruption (Zafferani locality) contains predominantly the Ti-rich Ti-Mt phase with  $T_C = 250^\circ\text{C}$  and more oxidized Ti-Mt phase with  $T_C = 500^\circ\text{C} - 550^\circ\text{C}$ . Six additional samples were studied. Two of them were prepared from the basaltic ash erupted in 2010. The results have shown that the Fe-Ti magnetic minerals are of the *pseudo-original phase state*, without the AFMP phase. A fluent acquirement of PTRM dependent on the magnetic phases was detected in these samples during magnetization in the laboratory (Fig. 1).

**The nepheline basanite of Putikov vršok locality:** The sample of nepheline basanite of Putikov vršok locality comes from the individual place of among 22 locations of large volcanic lava flow, defined by coordinates 48.410° N, 18.650° E (Fig. 3). This nepheline basanite body is the youngest one among volcanics of the Western Carpathian Mts. The age of the volcano is 0.22 – 0.13 m.y., according to *Šimon and Halouzka (1996)*, or  $0.53 \pm 0.16$  m.y. according to *Konečný et al. (1995)*. The samples from only few locations of collected 22 positions have shown a fluent acquirement of RM during thermal laboratory magnetization dependently on the magnetic phases (Fig. 2). The samples from most locations (12) have shown the signs of the consequence of the cation ordering, magnetic ordering and subsolvus exsolution process. Some magnetic minerals are in (*transformed-*

Kilauea2, basalt,  $\kappa=48875$ , NRM=11050  
 $Q=5.7$



Tab. Tholeite Basalt

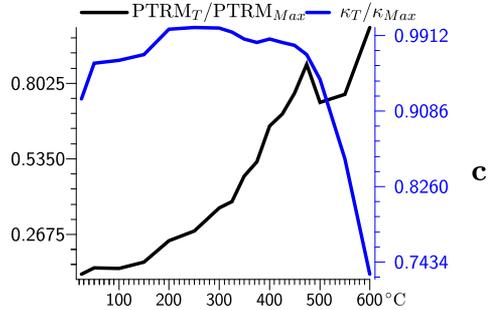
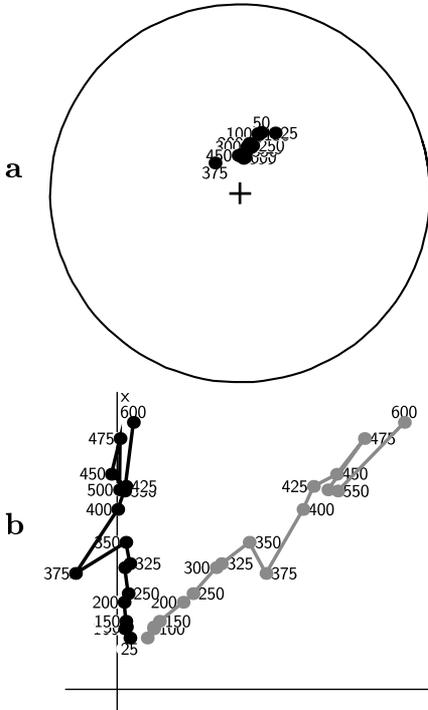
Temp, °C	$\kappa \times 10^{-6}$ SI units	PTRM, (mA/m)	Q
25	48875	11050	5.7
50	53091	18999	8.9
100	53727	29910	14.0
150	55970	106481	47.6
200	53727	152310	71.0
300	53024	146083	69.0
350	52657	152954	72.6
400	54228	156651	72.2
450	54798	155674	71.0
500	48505	166117	85.6
550	41375	162885	98.4
600	37224	172390	115.8
670	35048	182482	130.2

Fig. 1. Stereographic projection, Zijderveld diagram, temperature dependence of partial thermoremanent magnetization (PTRM) and magnetic susceptibility ( $\kappa$ ) of tholeite basalt (magnetic minerals of *pseudo-original phase state*). The Kilauea volcano, the 1971 eruption, coordinates:  $\varphi_L = 19.430^\circ$  N,  $\lambda_L = 195.290^\circ$  W; The descriptions and explanations: **a** – stereographic projection;  $\bullet$  – normal polarity,  $\circ$  – reversed polarity of RM; **b** – Zijderveld projection of RM vector onto a horizontal plain (y) and a vertical plain (z); **c** – black curve –  $PTRM_T - PTRM$  at temperature T,  $PTRM_{Max}$  – maximum PTRM; blue curve – a change of  $\kappa$  of sample;  $\kappa_T - \kappa$  at temperature T,  $\kappa_{Max}$  – maximum value of  $\kappa$ ;  $T_N$  – Néel temperature; mA/m – milli Ampere over meter;  $\varphi_L, \lambda_L$  – geographical coordinates of locality in  $^\circ$ .

*phase state*). The results for one sample are shown in Fig. 9.

**The olivine basalt of the Locality Blhovce-Buda:** I studied the 1.73 m.y. old olivine basalt from lava flow of Blhovce Buda locality, coordinates:  $48.266^\circ$  N,  $19.957^\circ$  E. This basaltic body belongs to rare basalts of normal

Put.vrs., B2-2-3, neph.bas.,  $\kappa=19462$   
 NRM=6411, Q=12.1



Tab. Put.vrs., B2-2-3

Temp, °C	$\kappa \times 10^{-6}$ , SI units	PTRM, (mA/m)	Q
25	19462	6411	12.1
50	20288	7561	11.7
100	20288	7476	11.5
150	20363	8572	13.1
200	20488	12452	18.5
250	23563	14262	21.1
300	21113	18357	27.2
325	21013	19411	28.9
350	20850	24654	37.3
375	20763	26612	40.1
400	20838	32997	49.5
425	20763	35274	53.1
450	20700	38984	58.9
475	20480	44143	67.3
500	19913	37289	58.5
550	18075	38768	67.0
600	15413	50075	101.5

Fig. 2. Stereographic projection, Zijderveld diagram, temperature dependence of PTRM and  $\kappa$  of nepheline basanite (magnetic minerals of *pseudo-original phase state*). Putikov vršok locality, coordinates 48.410° N, 18.650° E. For further description and explanation see Fig. 1.

polarity of RM in the Cerová vrchovina Highland in Southern Slovakia. The magnetic mineral of this basalt is non-stoichiometric magnetite of the Curie temperature  $T_C = 580^\circ\text{C}$  and Verwey temperature  $T_V = -155^\circ\text{C}$ . It has shown quite well developed magnetic domain structure (Fig. 5.), relatively high coercive force  $H_C = 333.7$  Oe and remanent coercive force  $H_{RC} = 605.8$  Oe. The following minerals were detected in this sample by

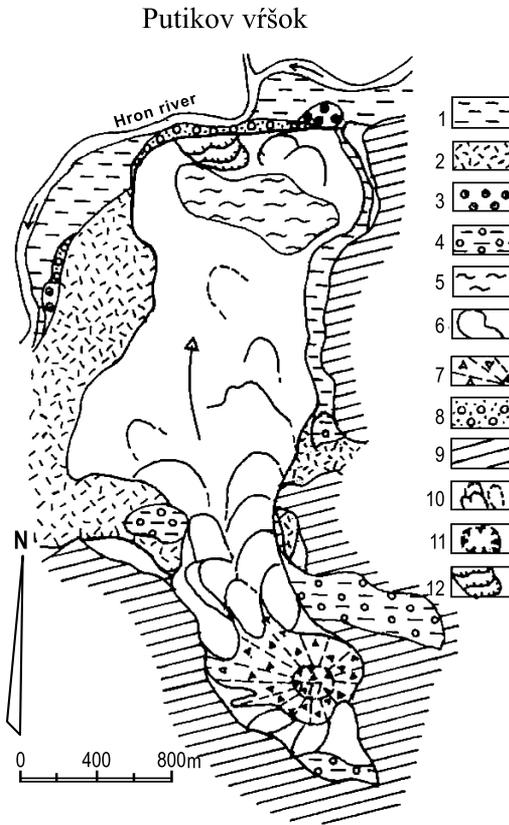


Fig. 3. Locality Putikov vršek Hill, B2 (48.410° N, 18.650° E): a cinder cone with lava flows; The 22 collected samples coming from the quarry of the nepheline basanite lava flow (explanation 6, 12); the age of the volcano: 0.22 – 0.13 m.y., or  $0.53 \pm 0.16$  m.y.; Explanations: 1 – fluvial sediments; 2 – polygenetic colluvial sediments; 3 – fluvial sandy gravels and sands; 4 – fluviolacustrine loams with gravels; 5 – aeolian loess fossil soils; 6 – nepheline basanite lava flows; 7 – pyroclastic rocks of a cinder cone; 8 – fluvial sandy gravels (Late Riss); 9 – underlying volcanic rocks – undifferentiated (Badenian); 10 – margins of individual lava flows; 11 – supposed crater rim; 12 – quarry; (Konečný et al., 1999).

X-ray diffraction analysis: magnetite (Mt)  $\text{Fe}_3\text{O}_4$  of Fc-cubic lattice,  $a = 8.39410 \text{ \AA}$ ; maghemite (Mgh)  $\gamma\text{-Fe}_2\text{O}_3$ , primitive (P) cubic,  $a = 8.35150 \text{ \AA}$ ; hematite (Hem)  $\alpha\text{-Fe}_2\text{O}_3$ , rhombohedral,  $a = 5.035 \text{ \AA}$ ; iron-titanium oxide  $\text{FeTiO}_3$ , rhombohedral; titanomagnetite (Ti-Mt)  $\text{Fe}(\text{Fe}_{1.24}\text{Ti}_{0.61}\text{O}_4)$ , Fc-cubic,  $a = 8.46600 \text{ \AA}$ , Fd-3m; pseudorutile  $\text{Fe}_2(\text{TiO}_3)_3$ , hexagonal; rutile  $\text{TiO}_{0.91202}$  tetragonal. As we see from Fig. 4 a gradual increase of PTRM with temperature, attaining a high  $Q = 157$  at  $700 \text{ }^\circ\text{C}$ , corresponding to thermoremanent magnetization. The runs of  $\kappa$  and PTRM with temperature correspond to the *pseudo original phase state* magnetic mineral which has not been attacked by subsolvus exsolution during its survival in the field.

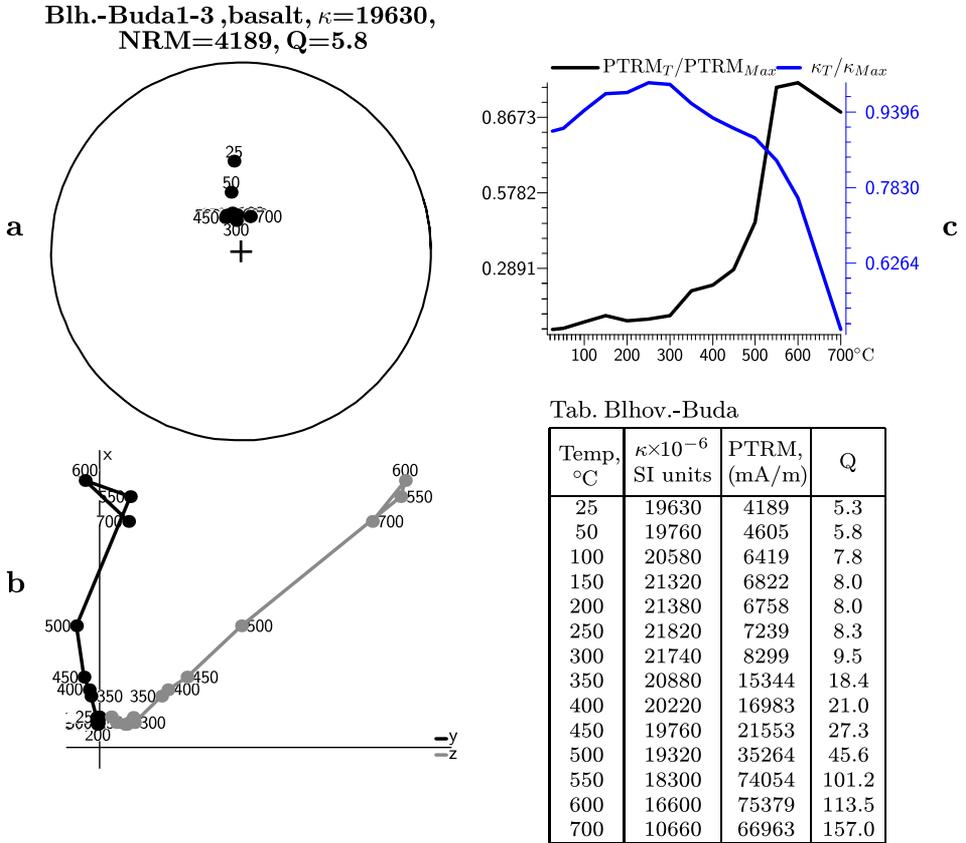


Fig. 4. Stereographic projection, Zijderveld diagram and temperature dependence of PTRM and  $\kappa$ , olivine basalt (magnetic minerals of *pseudo-original phase state*), Blhovce Buda locality, coordinates 48.266° N, 19.957° E. For further description and explanation see Fig. 1.

**The andesite basalt of the Malužiná area:** The andesite basalt belongs into the series of the Palaeozoic melaphyres which were previously studied by *Orlický (2003)*. The coordinates of the locality are 48.983° N, 19.783° E. The age of basalt is 270 m.y. The magnetic minerals of this andesite basalt are of the *pseudo original phase state*. Most of melaphyres contain a large associations of magnetic minerals with high-temperature oxidized Ilm-Hemtes. These types of minerals have carried mostly extremely stable reversed

RM of low  $\kappa$ , but of very high NRM. I considered these minerals as an apriory secondary. I chosen the samples of high  $\kappa$  of normal polarity of RM (in Orlický, 2003), when I have predicted only low intense alterations in the rocks. According to the previous analyses and lately analysed samples, there are the Ti-Mt-es dominantly present, with some small portion of non-stoichiometric magnetite, low portion of hematite and ilmenite. These minerals were detected by the Curie temperature measurements, by the electron microprobe analyses and by the Mössbauer spectroscopy. We see from Fig. 6, that  $\kappa$  and PTRM behaviour with temperature corresponds to the *pseudo original phase state* magnetic mineral which has not been attacked by the transformation process during its survival in the field. The PTRM of the sample gradually increases with temperature during magnetization process. The andesite basalts from other two localities in this area have shown a similar magnetic behaviour. The AFMP was revealed in several sedimentary rocks of the Palaeozoic age.

### The rocks with magnetic minerals of the *transformed phase state*

**The recent basaltic andesite from the Telica Volcano, Nicaragua:** two samples were studied. One comes from boulder and the second one from the lava flow (12.603° N, 86.845° W). The results of one sample are in Fig. 7. Two ferrimagnetic phases with  $T_C = 250^\circ\text{C}$  and  $T_{C2} = 520^\circ\text{C}$  and one

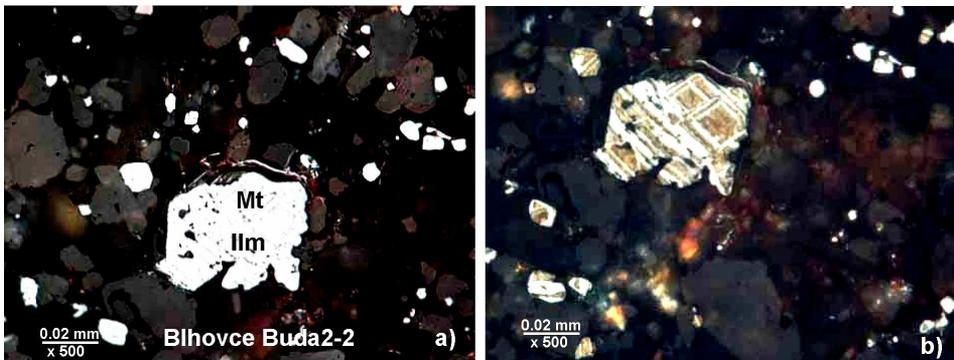


Fig. 5. Olivine basalt Blhovce-Buda; **a)** (in picture) – light microscopy of Fe-Ti grains of the sample; **b)** (in picture) – light microscopy of Bittern-Pattern technique domain structure of Fe-Ti grains of the sample.

Maluzina, 214-4, and.basalt, 270 m.y.,  
 $\kappa=32040$ , NRM=10085, Q=7.9

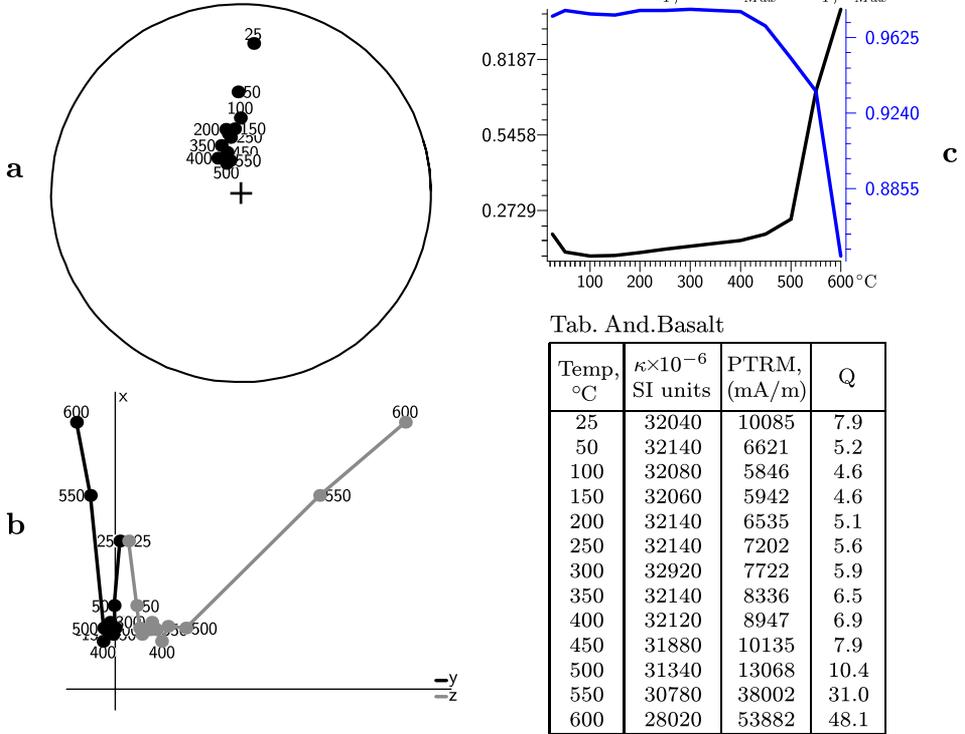


Fig. 6. Stereographic projection, Zijderveld diagram and temperature dependence of PTRM and  $\kappa$ , andesite basalt (magnetic minerals of *pseudo-original phase state*), Malužiná area, coordinates 48.983° N, 19.783° E, age 270 m.y.. For further description and explanation see Fig. 1.

AFMP with  $T_N = 350^\circ\text{C}$  contains the sample from the boulder body. In the sample from lava flow there are two ferrimagnetic phases with  $T_C = 390^\circ\text{C}$  and  $T_{C1} = 570^\circ\text{C}$ , all corresponding to Ti-Mt solid solutions, but the last one supposed to be more oxidized. The AFMP is there as well of  $T_N = 375^\circ\text{C}$  in the sample from lava flow. The basaltic lava flow is older (eruption in 1520 year) than that of the larger boulder body, which erupted 1999–2000. We see from results that there are the differences in basic volume  $\kappa$  and NRM of samples. These values are of higher level in boulder body than in lava flow samples. There are differences also in  $T_N$  values.

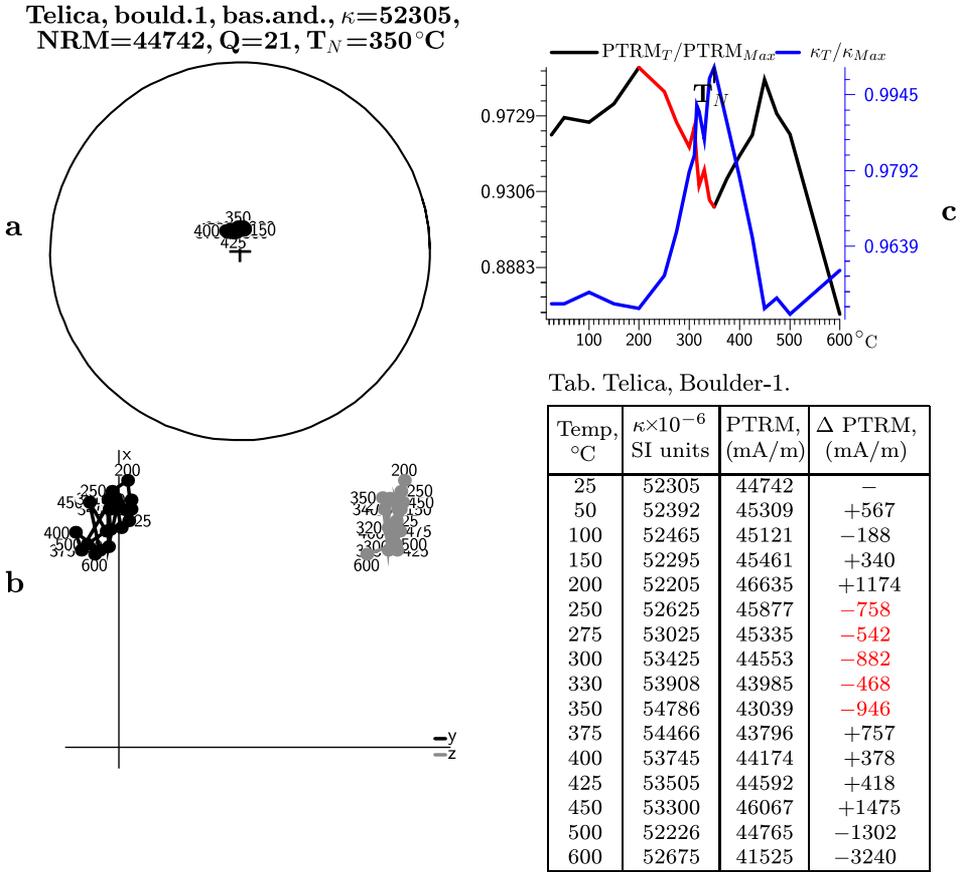


Fig. 7. Thermal magnetization of the sample of basaltic andesite from the boulder of the Telica Volcano, Nicaragua, coordinates 19.430° N, 135.290° W; stereographic projection, Zijderveld diagram and temperature dependence of PTRM and  $\kappa$  of sample.  $\Delta$  PTRM – difference between a previous and a subsequent PTRM value; red part of the PTRM curve – interval of an acquisition of the self-reversed PTRM; red numbers in the table – the increments of the reversed PTRM between the two consecutive temperature intervals. For further description and explanation see Fig. 1.

The AFMP has evolved in such a young basaltic andesites, so the *transformed phase state* magnetic minerals prevail in these Ti-Mt solid solutions.

**The olivine basalt samples of locality Šomoška:** The samples are of the age 4.06 m.y. (Fig. 10). The artificially prepared sample Šomoška1a1-5G

**BrehyB2-11-3, nepheline basanite,**  
 $\kappa=48625$ ,  $NRM=5355$ ,  $Q=2.8$

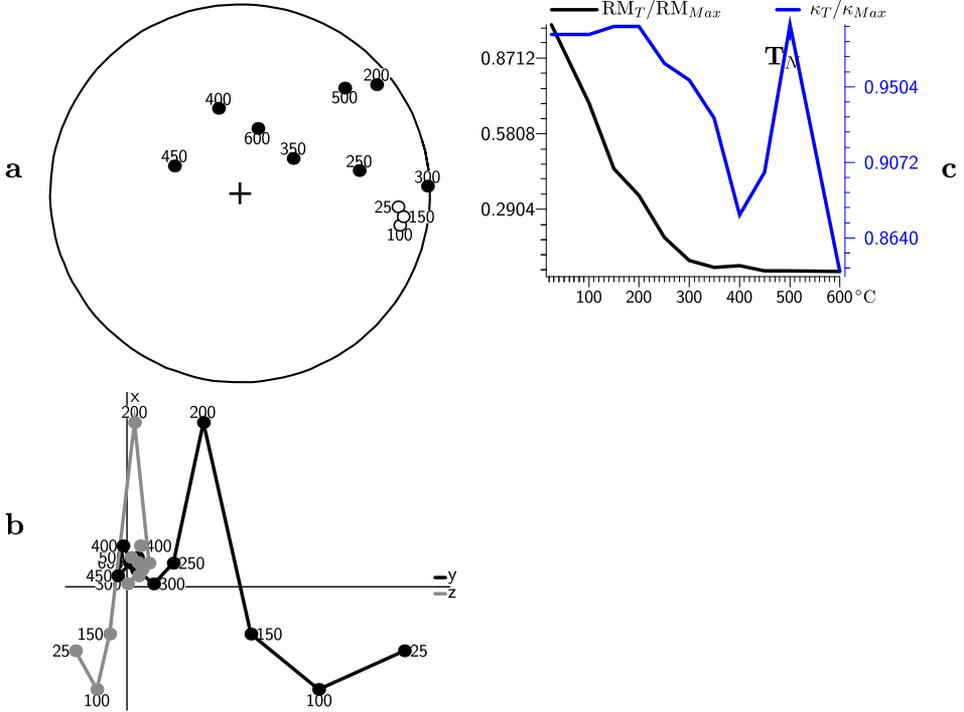
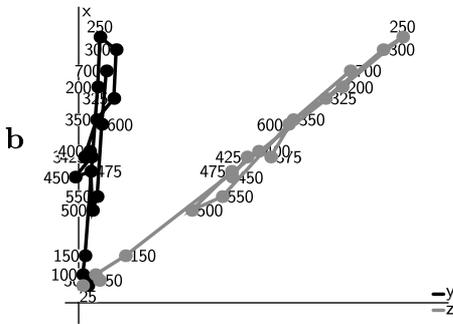
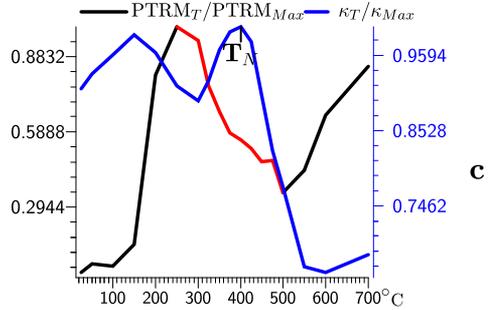
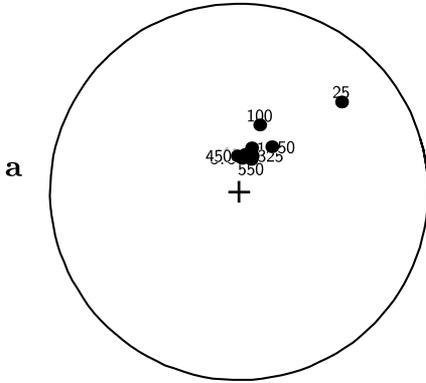


Fig. 8. Thermal demagnetization of the sample B2-11-3 (magnetic minerals of the *transformed phase state*), from nepheline basanite lava flow of the Putikov vršok, coordinates 48.410° N; 18.650° E; stereographic projection, Zijderveld diagram and temperature dependence of PTRM and  $\kappa$  of sample. For further description and explanation see Fig. 1.

comes from the top of the neck body, with the minerals of (*pseudo original phase state*), and the sample somoska3 with the minerals of (*transformed phase state*) comes from the lava dyke. Neck body: Eight samples were studied. The volume  $\kappa$  reached relatively high values in the range of 48000 to  $62123 \times 10^{-6}$  SI units. The magnetic phases with Curie temperatures of  $T_C = 120^\circ\text{C}$ ,  $T_{C1} = 230^\circ\text{C}$  and  $T_{C2} = 560^\circ\text{C}$ , corresponding respectively to Ti-rich Ti-Mt, low-temperature oxidized Ti-Mt and more oxidized Ti-Mt in the neck body were detected. The results of X-ray diffraction analysis of magnetic fraction of sample Šomoš1/3 are: Ti-Mt of a com-

Put.vrs. B2-11-2,  $\kappa=44100$ , NRM=585,  
 $Q=0.33$ ,  $T_N=400^\circ\text{C}$



Tab. Put. vrš. B2-11-2

Temp, °C	$\kappa \times 10^{-6}$ SI units	PTRM, (mA/m)	$\Delta$ PTRM, (mA/m)
25	44100	585	–
50	45100	1092	+507
100	46400	966	–126
150	47775	2275	+1309
200	46550	12410	+10135
250	44275	15283	+2873
300	43260	14456	–827
325	44650	11730	–2726
350	46775	10192	–1538
375	47950	8953	–1239
400	48325	8522	–431
425	47325	8016	–506
450	43625	7205	–811
475	39825	7264	+59
500	37375	5355	–909
550	31900	6704	+1349
600	31500	9977	+3273
700	32725	12902	+2925

Fig. 9. Thermal magnetization of the sample B2-11-2 (magnetic minerals of the transformed phase state), from nepheline basanite lava flow of Putikov vřšok, coordinates 48.410° N, 18.650° E; stereographic projection, Zijderveld diagram and temperature dependence of PTRM and  $\kappa$  of sample. For further description and explanation, see Figs. 1 and 7.

position  $\text{Fe}_{1.24}\text{Ti}_{0.61}\text{O}_4$ , Fc-face-centered-cubic of a unit cell parameter  $a = 8.46600 \text{ \AA}$ ; maghemite  $\gamma\text{-Fe}_2\text{O}_3$ , primitive P-cubic  $a = 8.3515 \text{ \AA}$ ; hematite  $\alpha\text{-Fe}_2\text{O}_3$ , rhombohedral,  $a = 5.03560 \text{ \AA}$ ,  $b = 5.03560 \text{ \AA}$ ,  $c = 13.74890 \text{ \AA}$ , R-3c; pseudorutile  $\text{Fe}_2(\text{TiO}_3)_3$ , hexagonal; rutile  $\text{TiO}_{0.91202}$ , tetragonal. About 22 Fe-Ti grains (size 3 to  $48 \mu\text{m}$  in diameter), of two samples Somoska1-5c and

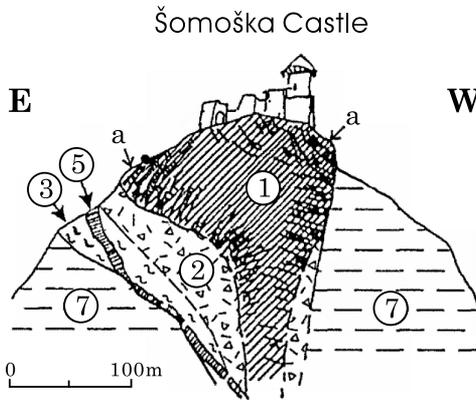


Fig. 10. Locality Šomoška Castle, coordinates 48.170° N, 19.842° E. The figure and the geological explanations are according to *Konečný et al., (1999)*. The lava neck of alkaline basalt with small lava dyke; the age: 4.06 m.y.; the investigated samples come from 5 places on open western flank and from the top near of the castle (see 1 and a), and from 4 places of small lava dyke (see 5). Explanations: a – beds composed of sand material derived from underlying sediments; 1 – lava neck, 2 – tuff breccia, 3 – scoria cone, 5 – lava dyke, 7 – Early Miocene sediments.

Somoška1-5d have shown a well evolved domain structure, studied by the Bitter Pattern technique. These results have outlined a presence of spontaneous magnetization in these Fe-Ti oxides. Most samples collected from the lava neck body have shown a fluent increase and then a decrease of  $\kappa$  during thermal demagnetization or magnetization of rock samples. But in some of them also the AFMP behaviour appeared (Fig. 13). The lava dyke: Nine samples were studied. The volume magnetic susceptibilities of samples are in the range of 2855 to  $36123 \times 10^{-6}$  SI units with an average value of  $13850 \times 10^{-6}$  SI units, which is lower than in the samples from the neck body of the same locality. The Curie temperatures of  $T_C = 230^\circ\text{C}$  (Ti-rich Ti-Mt) and  $T_{C2} = 560^\circ\text{C}$  correspond more oxidized Ti-Mt of the sample. The results of X-ray diffraction analysis of magnetic fraction of sample Šomoška1-6 are: Ti-Mt of a composition  $\text{Fe}_{1.24}\text{Ti}_{0.61}\text{O}_4$ , Fc-cubic,  $a = 8.46600 \text{ \AA}$ ; maghemite  $\gamma\text{-Fe}_2\text{O}_3$ , P-cubic,  $a = 8.3515 \text{ \AA}$ ; hematite  $\alpha\text{-Fe}_2\text{O}_3$ , rhombohedral,  $a = 5.03560 \text{ \AA}$ ,  $b = 5.03560 \text{ \AA}$ ,  $c = 13.74890 \text{ \AA}$ , R-3c; iron-titanium oxide –  $\text{FeTiO}_3$ , rhombohedral,  $a = 5.14120$ ,  $b = 5.14120$ ,  $c = 14.22500 \text{ \AA}$ , R-3; pseudorutile  $\text{Fe}_2(\text{TiO}_3)_3$ , hexagonal, rutile  $\text{TiO}_{0.91202}$ ,

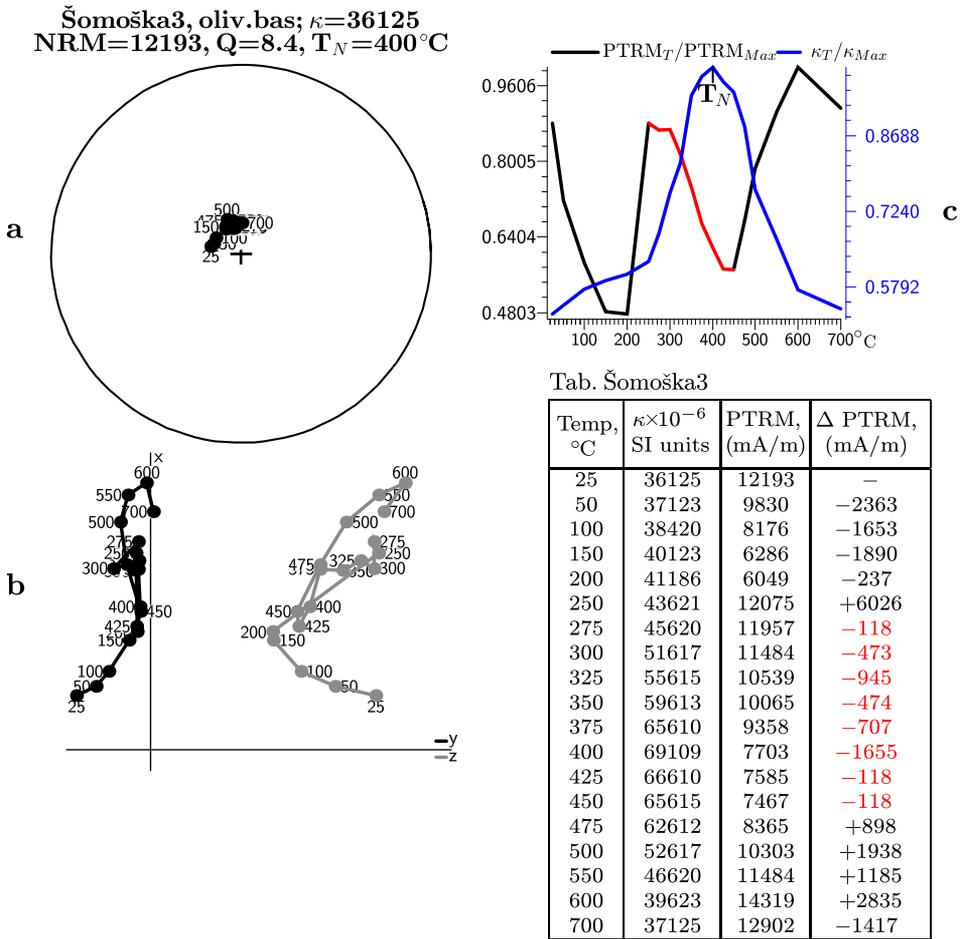
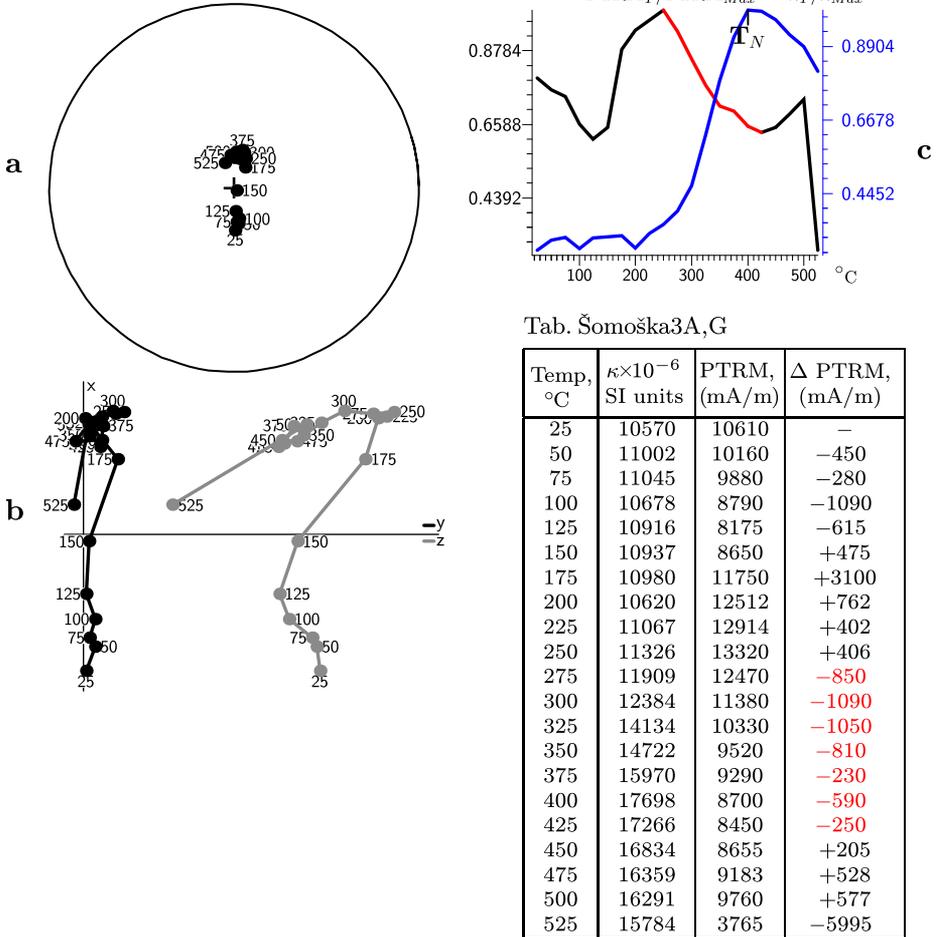


Fig. 11. Thermal magnetization of sample Šomoška3 (magnetic minerals of the *transformed phase state*), from olivine basalt lava dyke of the Šomoška locality, coordinates (see in Fig. 10); stereographic projection, Zijderveld diagram; temperature dependence of PTRM and  $\kappa$  of sample. For further description and explanation see Figs. 1 and 7.

tetragonal. About 26 Fe-Ti grains, size 1 to  $26\mu\text{m}$  in diameter of sample Somoska3A1-6 have shown a quite good evolved domain structure, studied by the Bitter Pattern technique (Fig. 15). These results have outlined a presence of spontaneous magnetization in these Fe-Ti oxides. The 9 samples of lava dyke body (including the artificially prepared sample, Fig. 12)

Somos3A,G.,  $\kappa=10570$ , RM=10610, Q=25,  
 $T_N=400^\circ\text{C}$



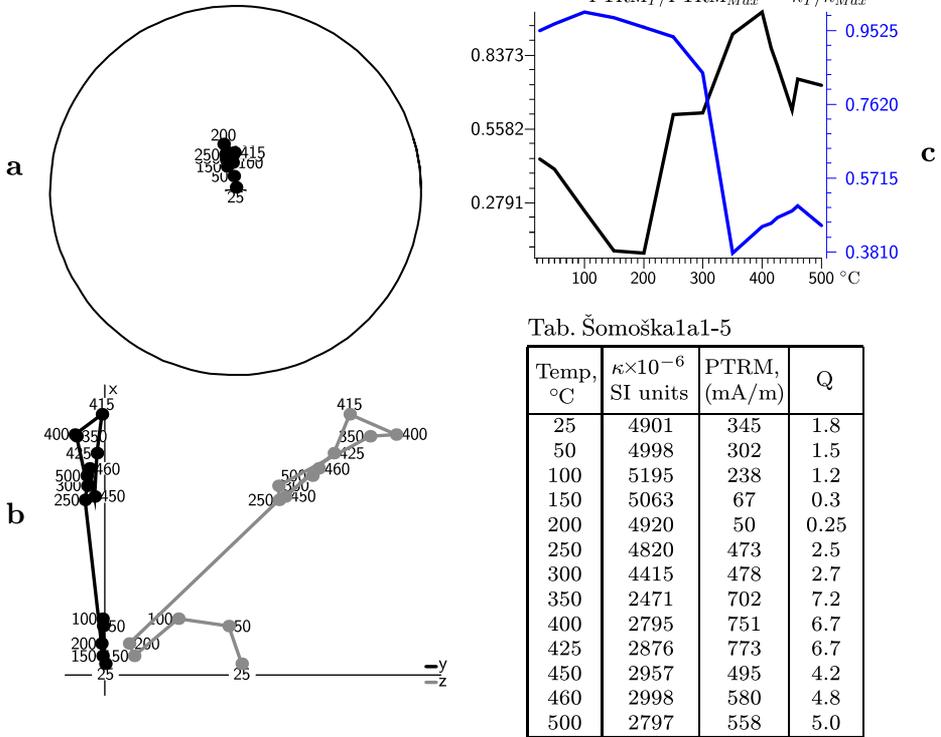
Tab. Šomoška3A,G

Temp, °C	$\kappa \times 10^{-6}$ , SI units	PTRM, (mA/m)	$\Delta$ PTRM, (mA/m)
25	10570	10610	—
50	11002	10160	−450
75	11045	9880	−280
100	10678	8790	−1090
125	10916	8175	−615
150	10937	8650	+475
175	10980	11750	+3100
200	10620	12512	+762
225	11067	12914	+402
250	11326	13320	+406
275	11909	12470	−850
300	12384	11380	−1090
325	14134	10330	−1050
350	14722	9520	−810
375	15970	9290	−230
400	17698	8700	−590
425	17266	8450	−250
450	16834	8655	+205
475	16359	9183	+528
500	16291	9760	+577
525	15784	3765	−5995

Fig. 12. Thermal magnetization of the artificially prepared sample Somart-3 (magnetic minerals of the *transformed phase state*), from olivine basalt lava dyke of the Šomoška locality, coordinates (see in Fig. 10); stereographic projection, Zijderveld diagram; temperature dependence of PTRM and  $\kappa$  of sample. G (in the picture) means in gypsum fixed magnetic grains. For further description and explanation see Figs. 1 and 7.

have shown a presence of the AFMP phase with  $T_N \approx 400^\circ\text{C}$  to  $485^\circ\text{C}$ . The similar behaviour of these minerals was detected by the Curie temper-

Somoška1a1-5G,  $\kappa=4901$ , NRM=345, Q=1.8



Tab. Šomoška1a1-5

Temp, °C	$\kappa \times 10^{-6}$ , SI units	PTRM, (mA/m)	Q
25	4901	345	1.8
50	4998	302	1.5
100	5195	238	1.2
150	5063	67	0.3
200	4920	50	0.25
250	4820	473	2.5
300	4415	478	2.7
350	2471	702	7.2
400	2795	751	6.7
425	2876	773	6.7
450	2957	495	4.2
460	2998	580	4.8
500	2797	558	5.0

Fig. 13. Thermal magnetization of artificially prepared sample Šomoška-1a1-5G (magnetic minerals of the *pseudo- original phase state*), from olivine basalt lava neck of the Šomoška locality, coordinates (see in Fig. 10); stereographic projection, Zijderveld diagram and temperature dependence of PTRM and  $\kappa$  of sample. G (in the picture) means in gypsum fixed magnetic grains. For further description and explanation see Fig. 1.

ature measurements of sample Šomoška3a (Fig. 14). The effect of AFMP behaviour was identified also by the differential scanning calorimetry and specific heat ( $C_p$ ) measurements of the sample, with a maximum of  $C_p$  (the heat released during phase decomposition) at about 490 °C (Fig. 14). Generally, the rocks containing the AFMP phase have shown relatively low coercive force (HC of 50 Oe) and remanent coercive force (HRC of 150 Oe), comparing it with that of magnetite containing basalts without AFMP behaviour (HC of 334 Oe) and (HRC of 606 Oe). Olivine basalts from the

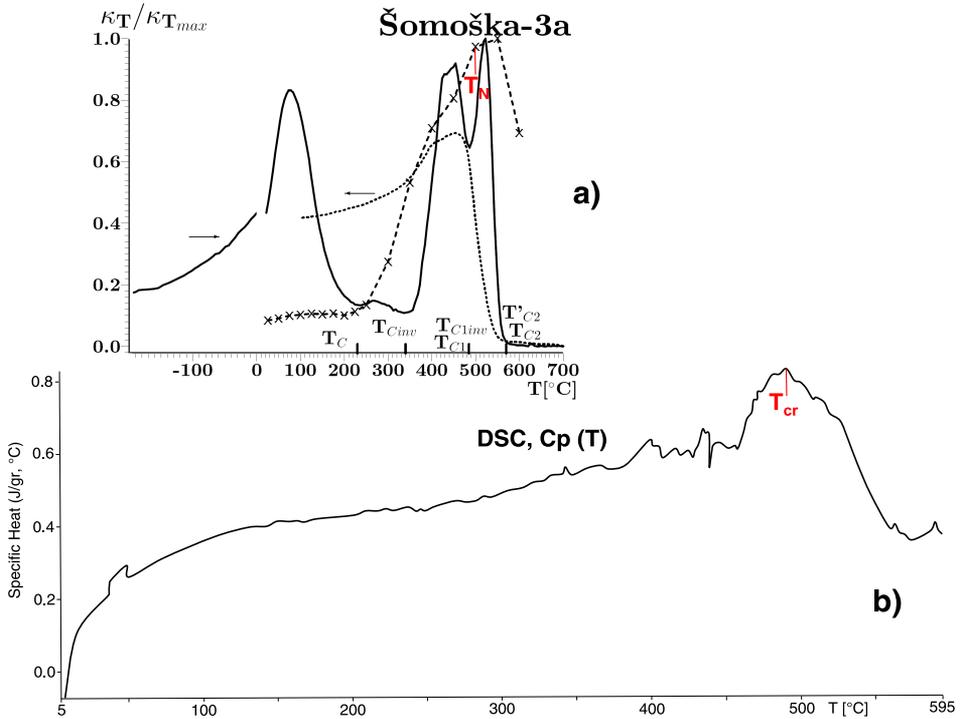


Fig. 14. **a)** The change of magnetic susceptibility of sample during continual heating and cooling (Curie temperature measurements) and during stepwise heating (dashed line with crosses);  $\kappa_T$ ,  $\kappa_{T_{max}}$  – magnetic susceptibility at the respective temperature ( $\kappa_T$ ) and at  $T$  with maximal magnetic susceptibility  $\kappa_{T_{max}}$ ;  $T_C$ ,  $T_{C1}$ ,  $T_{C2}$  – Curie temperatures of ferrimagnetic phases;  $T_N$  – Néel temperature of antiferromagnetic phase. **b)** The differential scanning calorimetry (DSC) and continual measurements of the change of the specific heat ( $C_p$ ) measurements of sample of olivine basalt from Šomoška 3A locality with temperature;  $T_{cr}$  – critical temperature.

neck body and the lava dyke body are probably of the same age, but their microstructural evolution has been rather different.

**The volcanics from Greece:** The biotite hornblende andesites of historic age from the Kaimeno Chorio Volcano (37.618° N, 23.332° W), Methana Peninsula, age 250 years b.c., olivine basanites from Microthebe (39.24° N, 22.25° E, age 1.5 m.y.), Porphyrion (39.42° N, 22.23° E, age 1.5 m.y.) and Achilleion (38.38° N, 22.21° E, age 3.0 m.y.) were studied (Orlický, 1986;

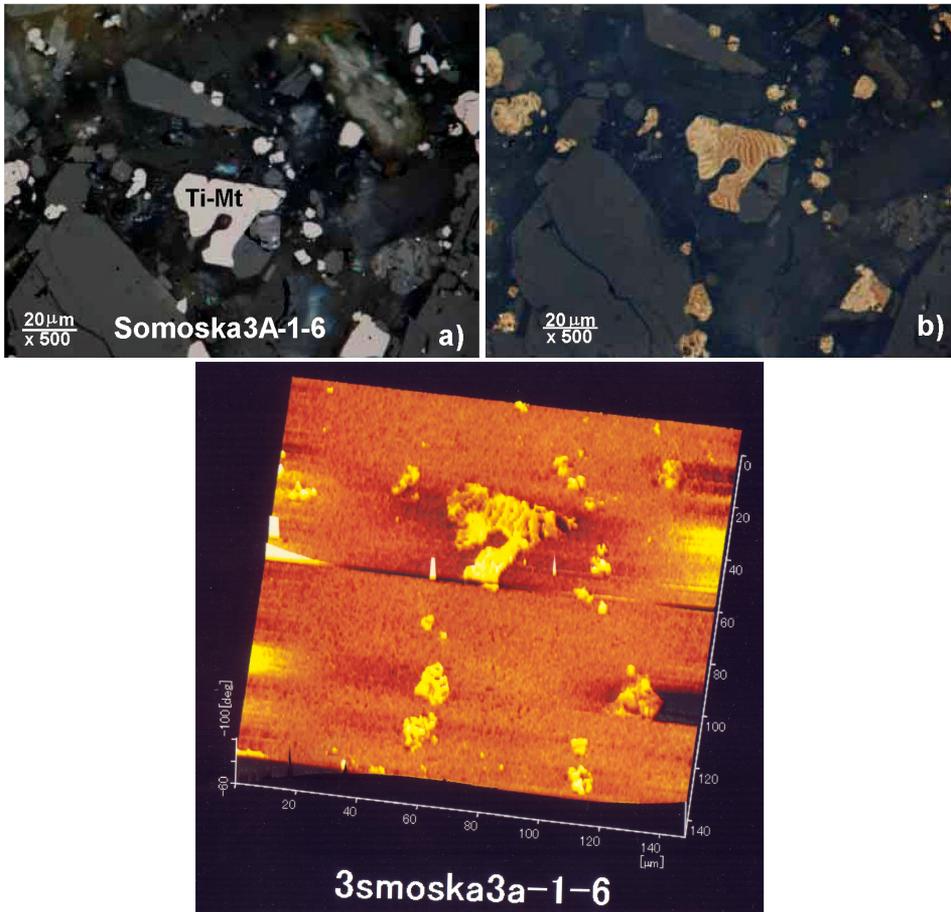


Fig. 15. Olivine basalt Šomoška3a-1-6; **a)** (in picture) – light microscopy of Fe-Ti grains of the sample; **b)** (in picture) – light microscopy of domain structure of Fe-Ti grains of the sample. Picture on bottom: the magneto force microscopy (MFM) image of domain structure of Fe-Ti grains of the sample of the Šomoška locality.

*Orlický et al., 1988*). As has been shown in Fig. 16, the sample k-4d has AFMP (not in complete stage) of  $T_N = 450^\circ\text{C}$ , except for phases with  $T_C = 490^\circ\text{C}$ ,  $520^\circ\text{C}$ . The AFMP was detected also in the sample k-8-4, but its volume portion with respect to whole of Ti-Mt one is very small. In low temperature interval also small portion with more Ti in Ti-Mt was detected.

Table 1. Basalts containing the magnetic minerals with AFMP, from central and southern Slovakia

Name of locality	Geographical coordinates		Age [m.y.]	N	$\kappa \times 10^{-6}$ [SI units]	NRM [mA/m]	$T_C$	$T_N$
	$\varphi_L$	$\lambda_L$						
5-Devičie	48.317	19.030	8.0	11	25307	9251	160	450
6-Podrečany	48.399	19.608	6.44	18	13320	2437	220	450
7-Podrečany	48.390	19.625	6.44	5	21612	7694	220	450
8-Mašková	48.320	19.575	7.17	14	41750	2440	140	450
11-13-Čirinč	48.318	19.848	?	26	16172	1438	140	450
19-Bulhary	48.288	19.862	1.6	14	27220	754	220	450
25-Veľ.Hradište	48.283	19.714	5.43	9	47887	1622	270	450
26-Črep	48.265	19.955	4.10	7	34917	15410	220	450
28-Maar	48.267	19.956	–	7	35395	1125	260	450
30-Stebl.skala	48.250	19.986	4.63	7	33775	4944	140	450
31-E of St.skala	48.267	19.965	1.4	8	28915	2628	150	450
34-Zaboda	48.226	19.987	2.03	6	26601	15338	150	450
37-Veľký kopec	48.217	19.926	1.92	6	21057	2882	240	450
39-E of Hajnačka	48.185	18.985	2.58	6	24557	674	150	450
42-Dun.hora	48.176	19.871	1.3	3	23800	24780	224	450
42a-Dunivá hora	48.176	19.871	1.3	4	16725	1008	280	450
45-Šomoška	48.162	19.849	4.06	4	8282	926	230	450

m.y. – million year; N – number of samples;  $\kappa$  – bulk magnetic susceptibility; NRM – natural remanent magnetization; mA/m – milli Ampere/meter;  $T_C$  ( $^{\circ}\text{C}$ ) – Curie temperature;  $T_N$  ( $^{\circ}\text{C}$ ) – Néel temperature. The samples have also a second Fe-Ti ferrimagnetic phase with  $T_C \approx 550^{\circ}\text{C}$ .

A transition of original Ti-Mt to Ti-Mgh in the interval  $360^{\circ}\text{C} - 460^{\circ}\text{C}$  was detected during Curie temperature measurements. I have shown the results of only one tested sample (Fig. 11) from large collection of 44 samples. Taking into account the level of  $\kappa$  of sample as a measure of a change of magnetic mineral, we see the following: the studied samples come from 11 individual positions of extrusive andesite body. Their average  $\kappa$  is in the range from 5063 (loc. k-4) to  $20320 \times 10^{-6}$  SI units (all samples from other positions have shown a higher values of  $\kappa$ ). The AFMP of magnetic minerals has evolved better as in other 10 positions (e.g. AFMP is not present in

Table 2. The basaltic andesites containing the AFMP, Kremnické vrchy, Čtiavnické vrchy, Streda nad Bodrogom

Name of locality	Geographical coordinates		Age [m.y.]	N	$\kappa \times 10^{-6}$ [SI units]	NRM [mA/m]	$T_C$	$T_{C1}$	$T_N$
	$\varphi_L$	$\lambda_L$							
101-7	48.451	18.816	8.8	4	28300	1488	185	565	450
Šib. vrch7-1	48.317	18.030	8.8	11	25307	9251	220	560	450
Šib. vrch.f.,30a	48.584	18.625	8.8	4	19179	178	250	570	380
Šib. vrch.f.,31a	48.584	18.625	8.8	6	21687	365	240	565	400
Vlč. vrch.f.,27	48.757	18.972	8.8	4	12875	6022	260	565	450
Vlč. vrch.f.,28	48.757	18.976	8.8	5	18588	5123	300	555	450
Vlč. vrch.f.,30	48.754	18.960	8.8	?	14225	3099	320	565	450
Vlč. vrch.f.,32	48.753	18.982	8.8	?	10550	1261	–	575	450
1Ad,Str.n.Bodr.	48.38	21.76	LS	8	7921	462	220	520	450

m.y. – million year; N – number of samples;  $\kappa$  – bulk magnetic susceptibility; NRM – natural remanent magnetization; mA/m – milli Ampere/meter;  $T_C$  (°C) – Curie temperature;  $T_N$  (°C) – Néel temperature.

sample k9-2; Table 3). As was outlined in the introduction, olivine basalts of Microthebe and Porphyriion localities (1.5 m.y.) have shown a presence of AFMP, but in the olivine basanite of the locality Achilleion (3.0 m.y.) there has not been evolved the AFMP. The results of mineralogical study of samples by light microscopy, electron microscopy and Mössbauer spectroscopy are in *Orlický et al. (1988)*.

### The incidentally found volcanic rocks in the Canary Island Areas, in the North western part and in the Southern part of the USA:

In my previous works the contemporary, historical and recent volcanic rocks were studied (*Orlický et al., 2003; Orlický, 2009*). The low-temperature oxidized Fe-Ti phase of rocks were a subject of interest. Firstly I will show the results of non-oriented sample of very young, 20000 years old andesite from Rainier volcano (46.85° N, 121.842° W), from the Cascade Range of the North Western Part of the USA. The andesite contains two oxidized Ti-Mt phases, one with  $T_C \approx 495^\circ\text{C}$  (dominant portion), and the second one of  $T_{C1} \approx 555^\circ\text{C}$  (minor portion). The results of X-ray diffraction analysis of sample Rainier2-2 are: Ti-Mt of a composition  $\text{Fe}_{1.24}\text{Ti}_{0.61}\text{O}_4$ ,

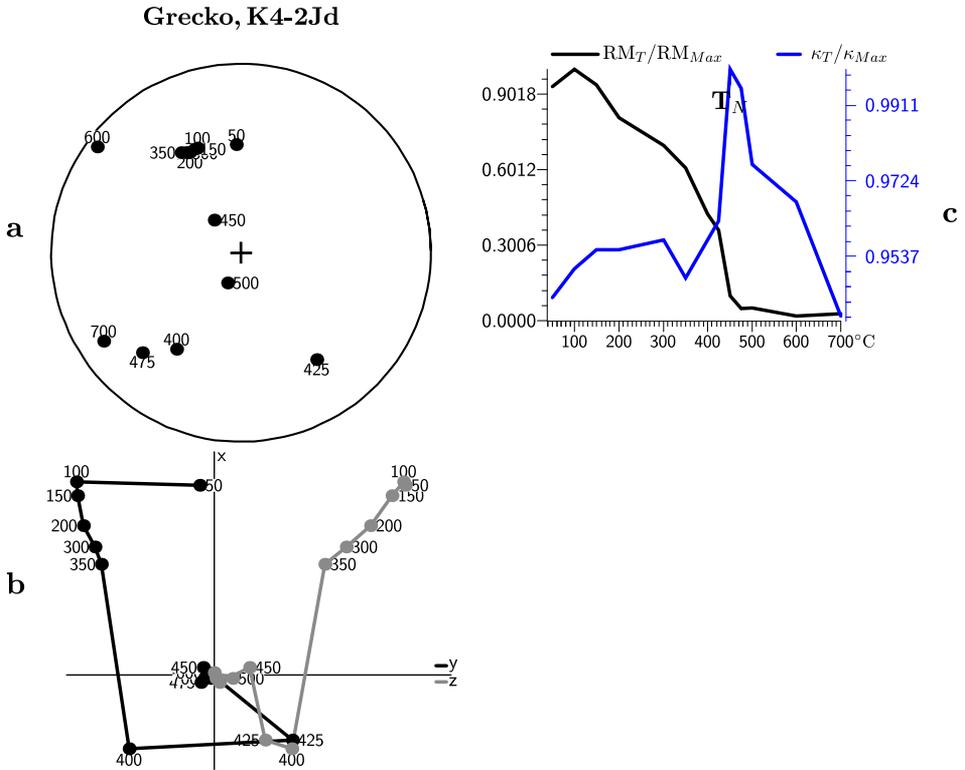


Fig. 16. Stereographic projection, Zijderveld diagram, temperature dependence of PTRM and  $\kappa$  of biotite amphibole andesite sample from the extrusive body of the Kaimenochorio Volcano, the coordinates 37.618° N, 23.332° E, Greece. For further description and explanation see Fig. 1.

Fc-cubic,  $a = 8.46600 \text{ \AA}$ ; Ti-Mt  $\text{Fe}_{2.75}\text{Ti}_{0.25}\text{O}_4$ , Fc-cubic,  $a = 8.42370 \text{ \AA}$ , Fd-3m; Maghemite  $\gamma\text{-Fe}_2\text{O}_3$ , P-cubic,  $a = 8.3515 \text{ \AA}$ ; Iron-titanium oxide –  $\text{FeTiO}_3$ , rhombohedral,  $a = 5.14120$ ,  $b = 5.14120$ ,  $c = 14.22500 \text{ \AA}$ , R-3; Pseudorutile  $\text{Fe}_2(\text{TiO}_3)_3$ , hexagonal; Ilmenite  $\text{FeTiO}_3$ , rhombohedral,  $a = 5.08317$ ,  $b = 5.08317$ ,  $c = 14.02561 \text{ \AA}$ , R-3. The results have shown that there evolved smaller portion of original mineral in favour of AFMP. This phase is magnetically involved in the Fe-Ti ferrimagnetic phases and so the AFMP has a very strong effect on the whole magnetic behaviour of the rock. Moreover, we see from stereographic projection (Fig. 17), a) a dif-

Table 3. Magnetic characteristics of samples of biotite-hornblende andesites of the Kaimeno Chorio Volcano, the coordinates 37.618° N, 23.332° E, Greece (for explanation and description see Table 1)

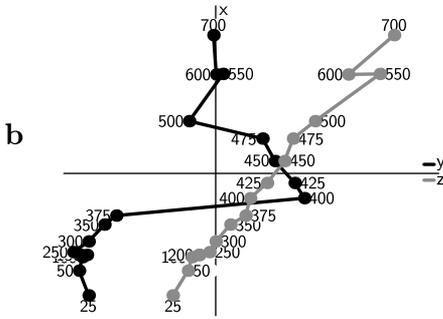
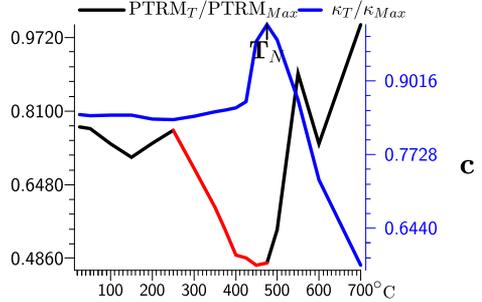
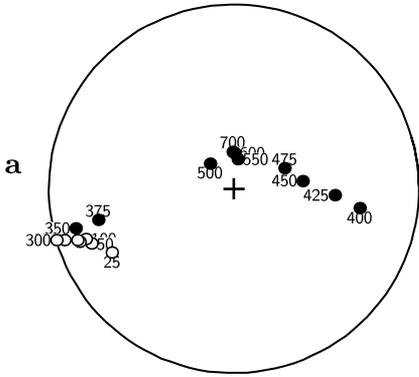
Sample	$\kappa \times 10^{-6}$ [SI units]	PTRM [mA/m]	Q	$T_N$ [°C]	$T_C$ [°C]
k3-2	13917	4930	7.8	410	551
k3-3	13420	4171	7.8	450	553
k5-2	1550	1589	2.6	450	535
k5-6	13313	9010	17.0	480	535
k7-5	6250	1364	5.4	410	540
k9-2	17375	6533	9.4	–	563
k10-5	15600	1226	2.0	425	540
k11-4	14900	844	1.4	400	543

ferent directional behaviour of PTRM during magnetization of the sample. Whereas the reversed polarity of PTRM is in the interval 25 °C–350 °C (temperatures before the  $T_N$  of AFMP), PTRM of only normal polarity was induced beyond the  $T_N$  critical point. There has been detected an extreme decrease of PTRM in the interval 250 °C to 475 °C (from 30524 to 18890  $\mu\text{A/m}$ ). We see from Fig. 17 (Table Rain2), that there is a conspicuous increase of  $\kappa$  (from 26575 to  $31875 \times 10^{-6}$  SI units) in this interval. Similar magnetic behaviour has been shown also by samples of dacite from Crater Lake Mazama Mount and rhyodacite and dacite from the St. Helens Volcano, both of very young age (Table 4). The sample Crater Lake2-3 has  $T_C = 480$  °C (dominant) and  $T_C = 565$  °C (minor portion); X-ray analysis: Magnetite  $\text{Fe}_3\text{O}_4$ , Fc-cubic,  $a = 8.39410$ , F-43m; Maghemite  $\gamma\text{-Fe}_2\text{O}_3$ , Fc-cubic,  $a = 8.35150$ ; Ti-Mt  $\text{Fe}_{2.75}\text{Ti}_{0.25}\text{O}_4$ , Fc-cubic,  $a = 8.42370$ , Fd-3m; The results of the samples of three very young volcanic eruptions from the Cascade Range of the North Western Part of the USA have shown a presence of AFMP. The magnetic minerals are in the *transformed phase state*.

In two basaltic scoria samples of the age about 700 k.y. to 12 m.y from the places near small cinder cone of the Death Valley, USA (36.308° N, 117.08° W) was revealed AFMP with  $T_N = 410$  °C.

Two samples of basaltic obsidian, two samples of basaltic scoria from the Tenerife Volcano (28.109°–28.289° N, 16.668°–16.808° E), one basaltic

Rain2, and.  $\kappa=26850$ ,  $NRM=30804$ ,  $Q=29$ ,  
 $T_N=475^\circ\text{C}$



Tab. Rain.2

Temp, °C	$\kappa \times 10^{-6}$ , SI units	PTRM, (mA/m)	$\Delta$ PTRM, (mA/m)
25	26850	30804	—
50	26775	30660	-124
100	26825	29326	-1334
150	26825	28152	-1174
200	26625	29421	+1269
250	26575	30524	+1103
300	26750	27165	-3359
350	27025	23779	-3386
375	27100	21805	-1974
400	27225	19594	-2211
425	27600	19328	-266
450	30925	18720	-608
475	31875	18890	+170
500	31025	21831	+2941
550	27675	35498	+13667
600	23225	29357	-6141
700	18463	39763	+10406

Fig.17. Thermal magnetization of andesite sample, Rainier Volcano (magnetic minerals of the transformed phase state), coordinates 46.85° N, 121.842° W; stereographic projection, Zijderveld diagram; temperature dependence of PTRM and  $\kappa$  of sample. For further description and explanation see Figs. 1 and 7.

sample from the Fuente Ventura Volcano and two basaltic samples from obscured place, all from the Canary Islands. The Ti-rich Ti-Mt with  $T_C = 190^\circ\text{C}$ , Ti-Mt with  $T_C = 520^\circ\text{C}$  and more oxidized phase with  $T_C = 600^\circ\text{C}$  are present in one sample of basaltic scoria. Only fluent increase of RM up to  $650^\circ\text{C}$  was detected in the 5 rocks during magnetization. No AFMP was detected during this process. But in two basaltic rocks the AFMP with

Table 4. Magnetic characteristics of samples of dacite from Crater Lake volcano (42.993° N, 122.008° W) of the Mount Mazama and dacite to rhyodacite from the St. Helens Volcano (46.184° N, 122.184° W), the USA

Sample	Type of rock	Age of rock	$\kappa \times 10^{-6}$ [SI units]	PTRM [mA/m]	Q	$T_N$ [°C]	$T_C$ [°C]	$T_{C1}$ [°C]
Cratlak3	dacite	10000	6100	3587	14.7	450	480	565
StHel2	rhyodacite	in 1980	3050	1160	9.5	450	390	520
StHel3	dacite	in 1980	4620	2347	12.7	480	–	–

Explanations:  $\kappa$  – volume magnetic susceptibility; NRM – natural remanent magnetization; Q – Koeningsberger ratio;  $T_p$  – partitioning temperature dividing the ferrimagnetic phase from that of antiferromagnetic phase;  $T_N$  – Néel temperature of antiferromagnetic phase;  $T_C$ ,  $T_{C1}$  – Curie temperatures of ferrimagnetic phases.

$T_N = 475^\circ$  was indicated. No increase of PTRM in the interval around this critical temperature was indicated. While the magnetic minerals of first types of rocks behave like the *pseudo-original phase state*, the last named basalts, containing the AFMP, have shown as the *transformed phase state* magnetic minerals.

### Some volcanics and sediments from the volcanic fields of Štiavnické vrchy Mts., and from foreign localities

There were identified the *transformed phase state* magnetic minerals of glassy pyroxene andesites with the AFMP phase in the 7 localities of the BaĽan formation, in andesites, including the tufs and tufites around the Brhlovce locality, in several localities of the Drastvica formation from Štiavnické vrchy Mts., Orlický (2003b), also in several Miocene basalts from the Bohemian Massif (Orlický, 2002), in the Cretaceous and Jurassic basalts from the Syrian Arab Republic and from Nigeria and Sudan Republic (Orlický, 2003a,b).

## II. Sedimentary rocks

According to the theory, the depositional remanent magnetization (DRM) arises, when magnetized grains are aligned with the earth's magnetic field during sedimentation (Stacey and Banerjee, 1974). Thus grains with magnetic minerals which originated in an igneous rock, in which they acquired

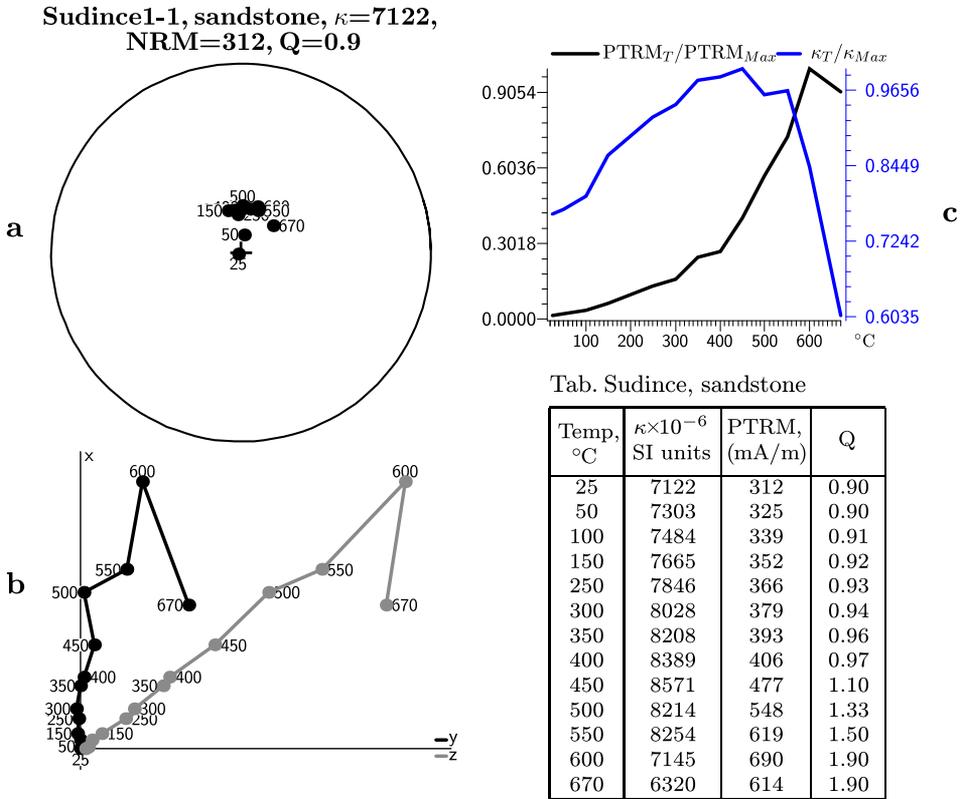


Fig. 18. Stereographic projection, Zijderveld diagram and temperature dependence of PTRM and  $\kappa$ , sandstone, (magnetic minerals of *pseudo-original state*), locality Sudince, coordinates 48.266° N, 19.957° E, Badenian age. For further description and explanation see Fig. 1.

a RM, may impart to a sediment in which they are deposited a DRM which has high magnetic stability, but it is less intense. The magnetic minerals have included very frequently the AFMP in sedimentary rocks. Their magnetic behaviour is more complex, compared with volcanic rocks. The AFMP has markedly influenced the original DRM, mainly in the temperature interval from 25 to  $T_N$ , during either thermal demagnetization or magnetization of rocks. I tested hundreds of samples of sediments: sandstones, clays, claystones, tufts and tuffites, conglomerates, hyaloclastites and limestones. I have shown an example of magnetic behaviour of the sandstones in Fig. 19.

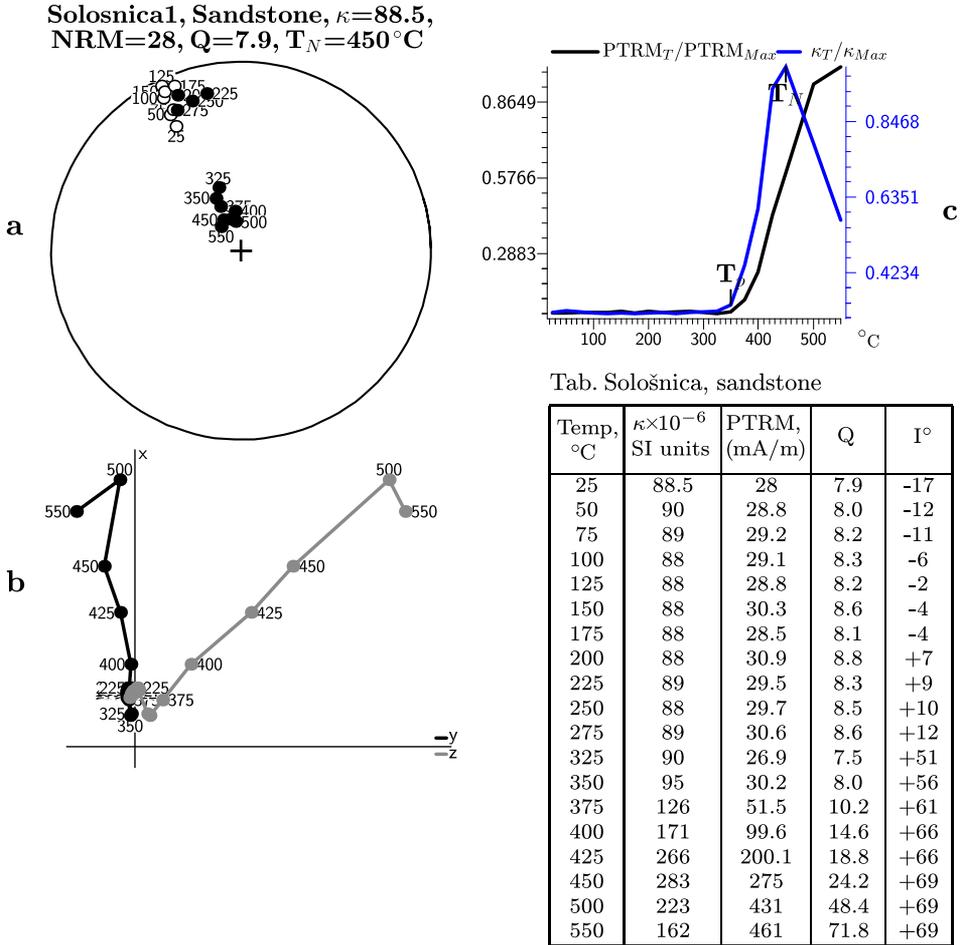


Fig. 19. Stereographic projection, Zijderveld diagram and temperature dependence of PTRM and  $\kappa$ , sandstone, (magnetic minerals of *transformed phase state*), locality Sološnica, coordinates  $48.4654^\circ\text{N}$ ,  $17.231^\circ\text{E}$ , Egemburgian age (24 m.y).  $I^\circ$  – inclination of PTRM of sample. For further description and explanation see Fig. 1.

### The sandstone of the Drastvica Formation, Locality Sudince

The Badenian age samples are from the locality defined by coordinates ( $48.211^\circ\text{N}$ ,  $18.892^\circ\text{E}$ ). An example of the *pseudo-original phase state* magnetic minerals is shown in Fig. 18. The sandstone sample contains Ti-Mt,

non-stoichiometric magnetite with small portion of hematite, according to the Curie temperatures  $T_C = 425$ ,  $T_{C1} = 560$  and  $T_{C2} = 610$  °C (Orlický, 2003a).

### The sandstone of the Locality Sološnica

The sandstone samples from the locality, coordinates 48.4654° N, 17.231° E have non-stoichiometric magnetite with small portion of hematite, according to the Curie temperature measurements. The X-ray diffraction (XRD) analysis showed the Bragg peaks corresponding to magnetite,  $\text{Fe}_3\text{O}_4$ , Fc-cubic,  $a = 8.49100$  Å, Fd-3m, and peaks corresponding to wustite  $\text{FeO}_{0.9020}$ , Fc-cubic,  $a = 12.9000$  Å. XRD was done also for a parallel sample after heating up to 650 °C (after the AFMP disappeared). There were detected a bit different Bragg peaks in both Mt and Wustite, but no other types of magnetic minerals were detected after heating the sample.

### 3. Discussion and conclusions

The presented results have been based on my whole professional experience in a study of the magnetic properties of rocks and their magnetic minerals, from about 1964 up to now. A form of evaluation of results, mainly a selection of target figure of work, has been focused for summarization of magnetic properties of rocks with the characteristic magnetic behaviour, regardless their age and petrography. I think that the interpretation of the results has enriched our realistic point of view on a source of very diverse magnetic and paleomagnetic properties, including the source of the reversed polarity of RM of rocks containing the cubic inverse spinel magnetic minerals. The theoretical background of the above described results and a final interpretation of the processes mentioned above will be presented in another article in the near future. There is missing also a topic concerning the rhombohedral magnetic mineral bearing rocks in this paper, which will be published in a separate article as well.

The results have allowed to distinguish the rocks into the two distinct aggregations: I) the rocks containing so called the *pseudo original phase state* magnetic minerals, where the AFMP phase is absent, and II) the rocks con-

taining the *transformed phase state* magnetic minerals, where the AFMP phase is present.

- I. The first group represents the rocks which contain the magnetic minerals that have not been transformed by the internal processes (cation-ordering, subsolvus exsolution and magnetic ordering) during their survival on the earth's surface. I have presented above only four examples of *pseudo-original phase state* behaviour of magnetic minerals in volcanic rocks, and only one example of sedimentary rock, but there are rocks of hundreds of localities with such magnetic behaviour in my database. But a relative portion of rocks with the *pseudo-original phase state* behaviour of magnetic minerals is lower, compared with those which were attacked by the internal processes and the external low-temperature oxidation. Their characteristic feature is that they have the higher values of  $\kappa$  than those transformed by the internal processes, compared to the rocks of the same petrography. Moreover, they carry only normal polarity of RM, regardless of the age of the rock. The properties of this first group have not been particularly considered in this article. The results of laboratory experiments have shown that the rocks without any AFMP phase were fluently magnetized and that volcanic rocks have acquired relative high values of TRM at temperatures near the Curie temperature of the respective magnetic mineral of rock. This has been achieved regardless of the age of the rock. Similar fluent magnetization was achieved in the sedimentary sandstone from the Sudince locality.
- II. The rocks containing the *transformed phase state* magnetic minerals have been described in more detailed form in this article. A dominant reason is that they have contained the AFMP, which played a decisive role in a magnetic behaviour of the rocks. Now, I do not know a precise chemico-physical composition and a microstructure of this phase itself, but these rocks behave as follows:
  1. Initio nascent state: The antiferromagnetic phase (AFMP) has begun during phase transition of the *pseudo-original phase state* ferrimagnetics, two sub-lattices containing magnetic minerals. In volcanics and sedimentary rocks it has started probably in a parallel way with low-temperature oxidation of ferrimagnetic Fe and

Fe-Ti inversion spinels (in the titanomagnetites – Ti-Mt), in a state, when the primary minerals became unstable. An evolution of the AFMP is a consequence of the internal processes of the cation ordering, magnetic ordering, and subsolvus exsolution and low-temperature oxidation of magnetic minerals. The cation ordering produces a complex distribution of cations among tetrahedral and octahedral sites as a function of temperature and composition (in the titanomagnetites the exchange of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  between the tetrahedral and octahedral sites can occur simply by the transfer of an electron). Exsolution in intermediate compositions yields very fine scale coherent intergrowths of magnetite-rich and magnetite-poor phases. The magnetic ordering in the magnetite-rich compositions yields a ferrimagnetic structure below the Curie temperature with magnetic moments on octahedral sites aligned antiparallel to those on tetrahedral sites. An added complication occurs in this system due to the ability of  $\text{Fe}^{2+}$  cations in the solid solution to be oxidized to  $\text{Fe}^{3+}$ . Oxidation at low temperature produces a metastable defect spinel (titanomaghemite – TiMgh) where the excess positive charge due to the formation of  $\text{Fe}^{3+}$  is balanced by cation vacancies occurring predominantly on octahedral sites (*Harrison and Putnis, 1999*). The subsolvus exsolution in intermediate compositions leads to the break-down of the homogeneous solid solution into two-phase intergrowth of Fe-rich and Ti-rich phases (*Harrison and Putnis, 1999*). The crystal structure of a spinel consists of an approximately cubic closed packed arrangement of the oxygen anions with the cation occupying 1 tetrahedral (A) site and 2 octahedral (B) sites per formula unit.

2. Most of Fe and Fe-Ti inversion spinels of rocks have undergone the transformation process during their survival in the field and the AFMP has evolved, according to my results. I identified the AFMP in 288 volcanic samples from 78 localities and altogether in 346 samples of sedimentary rocks. The AFMP has been proven also in the dacite pumice from the Haruna Volcano, Japan, and in the dacite ash from the 1991 Pinatubo eruption, Phillipines (*Orlický, 2011*). The results have shown that the evolution of the

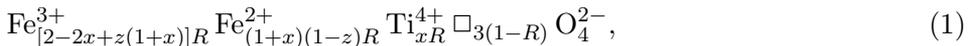
AFMP in the magnetic minerals of rocks is an ubiquitous process. A characteristic feature of the AFMP containing rocks is that they are not able to be fluently magnetized in the laboratory. One can assume that a similar situation occurred under the magnetization of rocks by geomagnetic field in nature.

3. In the minerals of some rocks the AFMP has not been evolved enough to provide unambiguous magnetic behaviour. Some previous magnetic Fe and Fe-Ti minerals have been partially transformed, but other have preserved their original stage. The AFMP can be found in a different evolution stage, from a starting stage to completely developed stage. The partially transformed Fe-Ti oxides are in the nepheline basanites of the Putikov vršek lava flow (Figs. 8, 9), in olivine basalts of Šomoška locality (Fig. 13, lava neck), olivine basalts of localities Obrnice, Řetoun, Klimberg, Smrečiny, all from Bohemian Massif, from localities Syr8-3, Syr9-2, from the Syrian Arab Republic (*Orlický, 2005*), in the historic age volcanic rocks from Greece, in non oriented volcanic rocks from the Canarian Islands and from the west northern part and from southern part of the USA. There were AFMP phases revealed also in the magnetic minerals of basalts of the Sites 794 and 797 from the Japan Sea (*Orlický et al., 2014*).
4. An evolution of the AFMP in the field has followed through the range of lower temperatures including the atmospheric temperatures at around of 25 °C.

### **The characteristic features of the AFM phase**

What is the chemical composition and a structural state of the AFM phase? The AFMP bearing magnetic mineral of rocks have been so far studied as a whole assemblage, without any separation of only that part with the AFMP behaviour itself. The magnetic minerals of the olivine basalt lava dyke of the locality Šomoška (Fig. 9) were studied by the more complex way. All results of magnetic measurements have been presented above. A presence of the AFM phase with  $T_N \approx 400\text{ °C} - 485\text{ °C}$ , (mostly around of 450 °C) by magnetic measurements has been proven in these basalts. The effect of AFMP behaviour was identified also by the differential scanning calorimetry

and specific heat ( $C_p$ ) measurements of the sample, with a maximum of  $C_p$  at about 485 °C (the heat release during phase decomposition). The Curie temperatures of  $T_C = 230$  °C, and  $T_{C2} = 560$  °C correspond respectively to low-temperature oxidized and more oxidized Ti-Mt ( $T_{C2} = 560$  °C of the body). Both these Fe-Ti ferrimagnetic phases coexist with that of the AFM phase. The results of X-ray diffraction analysis of magnetic fraction of the sample Šomoš3A1-6 detected the Ti-Mt of a composition  $\text{Fe}_{1.24}\text{Ti}_{0.6}\text{O}_4$ , Fc-cubic,  $a = 8.46600$  Å; maghemite  $\gamma\text{-Fe}_2\text{O}_3$ , P-cubic,  $a = 8.3515$  Å; hematite  $\alpha\text{-Fe}_2\text{O}_3$ , rhombohedral,  $a = 5.03560$  Å,  $b = 5.03560$  Å,  $c = 13.74890$  Å, R-3c; iron-titanium oxide –  $\text{FeTiO}_3$ , rhombohedral,  $a = 5.14120$ ,  $b = 5.14120$ ,  $c = 14.22500$  Å, R-3; and other Fe-Ti minerals pseudorutile  $\text{Fe}_2(\text{TiO}_3)_3$ , hexagonal; rutile  $\text{TiO}_{0.91202}$ , tetragonal. The Ti-Mt  $\text{Fe}_{1.24}\text{Ti}_{0.6}\text{O}_4$  and maghemite  $\gamma\text{-Fe}_2\text{O}_3$  are as the main compounds but the precise titanomaghemite composition has not been derived. An oxidation parameter  $z$  (see in formula (1)) was not determined. A composition presented in literature may be as follows:



where  $R = 8/[8 + z(1 + x)]$  and  $0 \leq x \leq 1$ . This formula does not reflect the AFMP ordering of the respective samples. The intermediate number of vacancies may be present in a molecule of the Ti-Mgh. In the titanomaghemite the  $(\text{Ti}^{4+} + \text{Fe}^{2+})$  replaces  $2\text{Fe}^{3+}$  in maghemite. So, an appropriate arrangement of  $\text{Fe}^{2+}$   $2\text{Fe}^{3+}$  active ions,  $\text{Ti}^{4+}$  ions and  $\square$  vacancies in B and A sublattices may be in a state when the magnetic moments of A and B sublattices are antiparallel. Such Ti-Mgh may have the antiferromagnetic ordering. The AFMP has then a high magnetoresistance.

**How do the ferrimagnetic phases interact with that of AFM phase in the rock?:** The examples of laboratory magnetizations (the PTRM inducing) of 5 samples in the laboratory field of normal orientation are in Figs. 7, 9, 11, 12, 17. The  $\kappa$  behaviour (blue curve), Curie temperature measurements and X-ray analyses suggested that there are present the ferrimagnetic Fe-Ti oxides except of the antiferromagnetic phase in the samples. The AFM phase does not carry any magnetization and it is not able to be magnetized by the external field. The AFM phase coexists together with the ferrimagnetic phases up to the  $T_N$  temperature of the respective rocks. The AFMP phase disappears beyond the  $T_N$  temperature during heating of

the sample. We see from Figs. 7, 9, 11, 12, 17, that at the beginning of magnetization the Ti-rich Ti-Mt bearing rocks are partly demagnetized due to thermal effect. A sharp increase of PTRM starts at about 100 °C–125 °C, 200 °C, reaching a maximum at about 200 °C, 250 °C, 275 °C, 300 °C (black part of PTRM curve). We see a sharp decrease of the PTRM in Figs. 7, 9, 11, 12, 17 (red part of the PTRM curve in the respective Figures, and red negative  $\Delta$  PTRM increments in the respective Tables). This sharp decrease of PTRM corresponds to an acquirement of the self-reversed PTRM during stepwise heating and cooling of samples of rocks. This sharp decrease of the PTRM follows mostly up to the Néel temperature ( $T_N$ ) of the respective sample. This behaviour clearly reflects the magnetic interactions of the Fe-Ti ferrimagnetic phases with that of the antiferromagnetic phase. No self-reversed acquirement of the PTRM occurred at higher temperatures after the AFMP disappeared, despite the ferrimagnetic phase of  $T_C$  about 560 °C is present in the samples.

### **A mechanism of the self-reversed acquirement of RM of rocks**

A very complex magnetic behaviour of magnetic minerals of rocks was shown in the examples above. The magnetic susceptibility increases very sharply with a maximum representing the Néel temperature of the AFM phase of rock. In a parallel way an induced PTRM gradually decreased in the same temperature interval. Whole laboratory magnetizing procedure was realized under a presence of normally oriented geomagnetic field. The ferrimagnetic materials are highly susceptible, easily penetrable by magnetic force-lines (photons) of geomagnetic field. The antiferromagnetic phase has a high magnetoresistance and create unpenetrable environment for the force-lines (photons) of geomagnetic field (magnetic field in general). A characteristic feature of the AFMP containing rocks is that they are not able to be fluently magnetized in the laboratory. One can assume that a similar situation has occurred under the magnetization of rocks by geomagnetic field in nature.

There was not possible to derive a correct composition and a geometry of both the ferrimagnetic Fe-Ti phase and that of antiferromagnetic Fe-Ti phase of magnetic minerals concerned. We can deduce that the AFM phase and the ferrimagnetic phases are supposed to be involved in a cluster, in which the ferrimagnetic phases coexist with that of the AFM phase in a large range of temperatures. I have respected the results of magnetic behaviour

of magnetic minerals during laboratory inducing of the PTRM of rocks. The ferrimagnetic Fe-Ti minerals acquired the self-reversed PTRM in the interval of temperatures when the ferrimagnetic phases have coexisted with the antiferromagnetic phase. I can suggest that the AFM phase reflects the magnetic force-lines (photons) in a reversed direction with respect to the normally oriented magnetizing field and so the ferrimagnetic Fe-Ti phase of the sample is able to acquire the self-reversal remanent magnetization. No total reversed thermoremanent magnetization (TRM) of the respective samples was induced under the applied laboratory process. But previously an inducing of the self-reversal PTRM of the artificially prepared samples (the grinded basaltic grains were fixed in non-magnetic gypsum) was realized. In these samples the PTRM was induced only at concrete temperature. During heating and cooling of the sample the magnetic field was fully compensated. During this process the sample Maar3-4kG received the reversed PTRM =  $-29$  mA/m, and the sample Velkop2-4kG received the reversed PTRM =  $-80$  mA/m, both at at  $500^{\circ}$  C (in *Orlický, 2009*).

I described above that an evolution of the AFM phase is a gradual process and it takes place a realtive long time in the field. The magnetization of rocks is also more complex process in the field. All magnetic minerals of rocks, including those in a nascency state (in a nucleation state) are under a permanent influence of geomagnetic field. Each molecule of a growing ferrimagnetic minerals, including those belonging to AFM phase have been involved into the magnetizing process in the field. So, there are very specific conditions in the field, which is not so easy to simulate in the laboratory. So, an origin of the self-reversed RM of rocks my be quite common process in nature.

I studied the domain structure of some rocks *Orlický and Funaki, 2008*. The Fe-Ti grains of basaltic sample Somoska3A1-6 have shown a quite good evolved domain structure, studied by the Bitter Pattern technique. It is quite surprise, because in the minerals of antiferromagnetic arrangement no magnetic domains could be present (*Stacey and Banerjee, 1974*). Generally, the rocks containing the AFM phase have shown relatively low coercive force and remanent coercive force comparing it with that of dominantly magnetite containing basalts, without AFMP behaviour.

*Özdemir (1987)* has proposed that a metastable Ti-Mgh inverts to a multiphase intergrowth when heated above  $250^{\circ}$  C –  $300^{\circ}$  C, that the inversion is

an intrinsic property of Ti-Mgh-es, whether heating is in air or in vacuum. The peak of magnetic parameter around of  $400\text{ }^{\circ}\text{C}$ – $450\text{ }^{\circ}\text{C}$  is due to the first stage inversion product. Its height increases with increasing degree of oxidation. On cooling, this product inverts to the final stable product, which should be a spinel phase close to stoichiometric Ti-Mt plus a rhombohedral phase close to ilmenite. 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 superparamagnetic (SP), or nearly SP-size subgrains. The spinel phase in the intergrowth was near-stoichiometric Ti-Mt or magnetite. The rhombohedral (inversion) phase included ilmenite, hematite, anatase, and pseudobrookite. The composition of the final inversion product depends on the *compositional parameter*  $x$  and a *degree of oxidation*  $z$ .

In the rocks with non-completely evolved AFMP, an increase of the PTRM is either hampered around  $T_N$ , or it is similar in behaviour to that on Fig. 9., where the PTRM extremely decreases in the interval from  $250\text{ }^{\circ}\text{C}$  ( $300\text{ }^{\circ}\text{C}$ ) to about  $450\text{ }^{\circ}\text{C}$  ( $500\text{ }^{\circ}\text{C}$ ) during magnetization of the sample. In such rocks several parts of a respective body (volcanic or sedimentary) have shown the reversed RM (partly reversed RM), other parts of the body have shown normal polarity of RM. For this reason no unique level of the PTRM acquirement has been achieved in the temperature interval beyond the  $T_N$  temperature. After a transformation of previous magnetic minerals and evolution of the AFMP, when it has been completed, the only reversed RM has been induced in the rocks. From this idea it follows that some rocks of normal polarity of RM today will acquire the reversed RM in normally oriented geomagnetic field in future, in a time when the AFMP in the minerals will be completely evolved.

In many articles of other authors some relations between a type of magnetic mineral and that of anomalous magnetic behaviour of the rock were identified. The authors interpreted it mostly by a presence of Fe-sulphides and their alterations in favour of magnetite due to temperature treatment behind the temperature  $300\text{ }^{\circ}\text{C}$ ,  $350\text{ }^{\circ}\text{C}$  to  $600\text{ }^{\circ}\text{C}$ . I present some examples in a more detailed fashion. *Lagrou et al. (2004)* and their explanation: sulphides were considered as the main magnetic remanence carriers in the rocks, despite they have not been identified by the classical technique. The authors deduced that the failure to detect them may be due to the low

concentration of these minerals, the small grain size, and the close physical relation with pyrite. Experiments have shown that above 370 °C the orientation of the magnetic remanence becomes erratic and that additional heating does not provide additional polarity information. During thermal demagnetization, an increase in the remanence signal is observed at about 270 °C, suggesting thermally induced mineral transformations. Indications of these transformations are also found in the thermomagnetic curves, as described in the next section. Measured at room temperature, it remains constant up to 320 °C after each heating step followed by a marked increase starting at approximately 360 °C and up to 500 °C–550 °C, and finally a strong decrease between 550 °C and 680 °C. An increase in susceptibility between 360 °C and 500 °C was explained in terms of the thermally induced growth of magnetite through oxidation of pyrite. The strong decrease of susceptibility above 550 °C can be attributed to further oxidation of magnetite into hematite.

Except basaltic rocks, *Vigliotti (1992)* studied also the finer grained silty claystones from the Site 797 from the Yamato Basin. The author proposed that the two vectors of primary and secondary components were exactly opposite each other, so during thermal cleaning the intensity of the remanence increased, reaching in one sample at 200 °C a value of 376 % with respect to the NRM intensity. From the stereographic projections of these sedimentary rocks it is evident that the polarity reversed in the range of 220 °C to 400 °C (in one sample) and from 100 to 480 °C (the second sample, see at page 919, *Vigliotti, 1992*). The magnetic minerals of these sediments from the Site 797 were studied by *Torri et al., 1992*: The sediments are of early Miocene or older in age. According to authors a thermal demagnetization often showed a confusing pattern in the vector-demagnetization diagrams at temperatures higher than 300 °C. This pattern corresponds to an increase in initial susceptibility measured right after the thermal treatment of samples. Samples reached a maximum  $\kappa$  mostly at 450 °C. The ratio of  $\kappa_{450}/\kappa_{25}$  was used as a characteristic parameter. Samples of high  $\kappa_{450}/\kappa_{25}$  ratio tend to display an irregular pattern in the vector-demagnetization diagrams. The hump at about 450 °C in curves of thermal change of  $\kappa$  can be explained by the production of new magnetic minerals during heating. The mixture of pyrrhotite and titanomagnetite is dominant. Magnetite is more dominant in the samples of lower part of the hole. The strong-field magnetization of

the bulk sample decays rather monotonically (showing paramagnetic curve) up to 350 °C. Then is a sudden increase between 350 °C to 500 °C, which decrease to 0 °C by about 600 °C. Upon cooling the curve is irreversible. The polarity of RM of sedimentary rocks of the Hole 797 was measured by *Vigliotti (1992)* and by *Tamaki et al. (1990)*. Some of these sedimentary rocks are of normal, others of the reversed polarity. Commonly the rocks do not create a regular polarity intervals with respect to a depth's level. A similar explanations of the above-mentioned anomalous magnetic behaviour is described also by the authors *Lesič et al. (2007)*; *Márton et al. (2004)*; *Márton et al. (2006)*; *Scholger and Stingl (2004)*; *Torii (1995)*. The described magnetic behaviour fully corresponds to that of behaviour of the antiferromagnetic phase in the magnetic minerals of the rocks, according to my idea, presented above.

An explanation which is based on the transformation of Fe-sulphides in favour of Fe-oxides (namely magnetite) requires a short comment. I studied the natural Fe-sulphides (pyrrhotites, pyrrhotite + sphalerite + chalcopyrite, marcasite, pyrite + sphalerite) by the Curie temperature measurements, completed by the Mössbauer spectroscopy results (*Orlický, 1988*). Yes, part of Fe-sulphide transforms into the magnetite if there is enough of oxygen in environment. In any case the magnetic susceptibility is mostly of higher level after heating and successive cooling of the sample on air, than the level of  $\kappa$  before heating of the sample. But an increase of  $\kappa$  does not take at 450 °C as a maximum, but closely to Curie temperature of magnetite and its level is preserved also after cooling of the sample. The resultant mineral has more complex composition after heating to 700 °C and its cooling to room temperature. E.g. the samples of pyrrhotites were in partly disordered state and they were enriched by magnetite before their heating. After their heating (5 °C/min) and cooling to room temperature, more ordered and clear pyrrhotite with  $T_C = 320$  °C was created. It is usual to find the quenched sulphides in nature. When annealed at temperatures of the order of 300 °C, two processes occur simultaneously. First, the disordered vacancies in the intermediate  $\text{Fe}_{1-x}\square_x\text{S}$  approach ordered arrangement producing a net ferrimagnetic moment in previously antiferromagnetic materials. Secondly, the different chemical phases are homogenized to produce a single chemical composition with a common vacancy concentration (*Stacey and Banerjee, 1974*).

The authors *Irving (1970)*, *Kelso et al. (1996)*, *Kirkpatrick (1979)*, *Lowrie et al. (1973)*, *Marshall and Cox (1972)*, *Petersen (1979)*, *Petersen et al. (1979)*, *Zhou et al. (2001)*, *Xu et al. (1997)* have accepted the idea that the main cause of decrease of magnetic characteristics in submarine basalts is the transformation of titanomagnetite to titanomaghemite (maghemitization of Ti-Mt oxides) during low-temperature oxidation of Ti-Mt oxides. Now it would be very useful to study also the presence of the AFMP phase in the Fe-Ti minerals of rocks to make a complete interpretation of the results.

I can deduce now that an extraordinarily important thing is a strange phenomenon, that the antiferromagnetic phase has been discovered. This AFMP has been evolved in the cubic inverse spinel magnetic minerals bearing volcanic and sedimentary rocks. In such rocks the AFMP has controlled the magnetic properties, including an origin of the reversed remanent magnetization in the rocks on the whole Earth. The mechanism of an origin of the reversed RM and the interactions of the AFMP with other ferrimagnetic phases will be presented in a more complex fashion and supplemented by the theoretical background in separate article. Also more complex interpretation of the results of the sedimentary rocks in a planned future paper will be completed. My previous interpretations, based on the dominant portions of some types of magnetic minerals, Ti-rich Ti-Mt-es, magnetites, hematites (*Orlický, 2010, 2010a,b*), of only normal polarity of RM, and those, of low-temperature oxidized Ti-Mt-es, of the reversed RM (*Orlický, 2011, 2012*) could be precised on the basis of new results.

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