

Field-reversal versus self-reversal hypothesis: Alterations of the Fe-Ti magnetic minerals and an origin of reversed RM of volcanics

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Abstract: A study has been conducted for the relation among the processes, mainly the so called maghemitization of Fe-Ti magnetic minerals, origin of remanent magnetization (RM) and the self-reversed RM of the Neogene intermediate volcanics. The presented suggestions are based mainly on previous laboratory induced self-reversed partial thermoremanent magnetization (PTRM) of the Neogene andesites and rhyolites from about 177 localities. The results have shown that the dominant carriers of magnetic properties are the products of the maghemitization of original titanomagnetites (Ti-Mt) in the Neogene intermediate rocks. From all so far obtained results, including those published in this article, it is evident that the self-reversed PTRM was acquired only by the samples which possessed the two magnetic Fe-Ti phases evidenced by the Curie temperatures. One Fe-Ti phase with the $T_C \approx 555$ to 585°C contained also an original phase. This, the so called titanomaghemite (Ti-Mgh) phase was created due to maghemitization of the original Ti-Mt and in most cases it has carried by *in situ state* reversed RM of chemico-viscous (CVRM) origin. The Ti-Mgh phase was nearly disappeared and the original Ti-Mt phase was revealed after heating of the sample to 700°C and successive cooling - on the cooling thermomagnetic curve. The self-reversed CVRM and in laboratory field induced PTRM was acquired by the rocks by the magnetostatic interactions between these two magnetic phases. In this process, the second magnetic titanomaghemite (Ti-Mgh) phase must start in the so called superparamagnetic (SP) state. When maghemitization takes place in nature, the exterior of the Fe-Ti grain being more highly oxidized compared to the interior core. The properties of the core are similar to the starting material apart from those resulting from a change in composition alone. An altered mantle of the grain consists of unblocked regions with the high susceptibility of a superparamagnet, and which will screen the magnetic moment of the core, and the magnetization of the assemblage will be reduced. There has been revealed a completely new possible mechanism of an acquisition of the self-reversed CVRM in intermediate volcanic rocks due to their maghemitization under the atmospheric conditions in the field.

Key words: maghemitization of Fe-Ti minerals, self-reversal magnetism

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1. Introduction

In the past *Orlický (1998)* studied the carriers of magnetic properties of neovolcanic rocks. He has proposed a general view that the main magnetic minerals in these rocks are the titanomagnetites ($\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$) and in minor position the titanohematites ($\text{Fe}_{2-x}\text{Ti}_x\text{O}_3$, x varies between 0.0 to 1.00, depending mostly on oxidation conditions). Diverse chemico-physical conditions (partial pressure, temperature, presence or lack of oxygen, composition of magmatic gases, speed of the ascent and cooling of magma, presence or lack of magmatic water and steam, etc., have dominantly influenced the development and a state of magnetic minerals.

In paleomagnetism, there has been commonly an assumption that the RM of volcanic rocks is dominantly of the thermoremanent (TRM) origin. This idea follows from the theory (the basic theoretical principles have been described e.g. by *McElhinny (1973)*, *Stacey and Banerjee (1974)*, *McElhinny and McFaden (2000)* and by many other authors). The theory has predicted that the TRM has been preserved up to the present. With respect to such prediction the stable component of the RM of volcanics has been interpreted as the primary TRM from the time of origin of the respective rocks. In such a way also the previous paleomagnetic results of volcanics from central and eastern Slovakia were interpreted (*Orlický, 1979*). In this paper I will outline the basic features and related magnetic properties of altered magnetic minerals of neovolcanic rocks from Central Slovakia.

2. Experimental works and an interpretation of the results

Methodical setting: In the previous works it has been outlined that most of basaltic and andesitic rocks contain the titanomagnetite (Ti-Mt) solid solutions in various stages of their oxidation, as the dominant magnetism carriers. The original magnetic minerals have a tendency to be easily altered in favour of the more oxidized Fe-Ti oxides, and as a consequence, the original RM of these rocks has been changed with regard to different environmental conditions in the field. I have applied the following analytical methods to study the magnetic minerals of the rocks under investigation: the basic method is the measurement of the change of magnetic

susceptibility (κ) of the separated magnetic fraction with the temperature (Curie temperature measurements of magnetic minerals). By means of this method were measured the samples from more than one thousand localities from Slovak volcanic areas. The apparatus and basic methodical procedures have been described in *Orlický (1990)*; The scanning microscopy and the electron microprobe analysis: They were realized by Dr. F. Caňo, Slovak Geological Institution of Dionýz Štúr, Bratislava; X-ray diffraction method. It was realized by Dr. B. Toman, Geological Institute of SAV, Bratislava. The Mössbauer spectroscopy: It was realized by Prof. J. Lipka, Slovak Technical University, Bratislava. These analytical methods were applied to limited number of samples of rocks. The magnetic susceptibility (κ), natural remanent magnetization (NRM) of rocks and its stability against the thermal demagnetization were studied also. Only about 16 samples have been selected to present their results in this article. The position of the sampled locality is delineated by the geographical coordinate φ_L and λ_L , both in $^\circ$. The studied rocks come from andesitic bodies of different petrography. According to Wikipedia-free encyclopedia the andesitic volcanoes generally only occur above subduction zones.

Previously, there were depicted the paleomagnetic results (the direction of stable RM and Koeningsberger ratio) in a modified map (*Orlický, 1979*). Originally there was made an interpretation of the results only on the basis of a stable direction of RM of rocks of individual localities. The individual petrographical types of rocks or rocks of individual complexes or formations, probably of the same geological development, have been frequently characterized by normal and reversed polarities of RM, but the direction of the RM of the rocks of all localities does not coincide with some preferable direction of the field, but a large scatter of the direction of RM was evidenced. It has been evidenced that the magnetic properties of these rocks, including the direction of RM are intensively influenced by the alteration of their magnetic minerals. One of the dominant alteration process is the so called maghemitization of the Fe-Ti oxides at low or high temperatures. The effect of this process may be effectively studied by the measurements of the change of magnetic susceptibility (κ) of the rock with temperature (Curie temperature measurements). This method can detect any variations of κ with temperature and so also the presence of small magnetic particles in the sample. According to Landau and Lifshitz in (*Hubert and Schäfer, 1998*),

only the small particles may show a variation of their magnetic parameter with temperature. The results of additional physical analyses of rocks were used also. I applied dominantly the results of the Curie temperature measurements with temperature and in minor portion the results of physical analyses. I have inscribed these data inside a free space delineated by the thermomagnetic curve of the respective sample for a briefness and a detection of good correlation with the course of the thermomagnetic curve (Figs .1–8). The data of the partial thermoremanent magnetization (PTRM) of some rocks were gained by inducing of the parallel (practically the same compact rocks) like the presented respective thermomagnetic curve. Considering the alteration state of the respective Neogene rock I studied also the historical young and recent intermediate volcanics from different places of the globe (*Orlický et al., 2003*).

Basic knowledge and some review about the maghemitization process: The process of maghemitization is described in detail by many authors. According to *Stacey and Banerjee (1974)* maghemite ($\gamma\text{-Fe}_2\text{O}_3$) is formed by oxidation of magnetite at low-temperature (150–250° C; a conversion can start also from room temperature). The oxidation is achieved by a topotactic process, the anionic structure is left unchanged - the Fe^{2+} ions diffuse to the surface of the grain, oxidize and form Fe^{3+} ions leaving lattice vacancies. The maghemite possesses peculiar properties. It has a tendency to occur in very small dimension of its grain (mostly not more than one $\mu\text{ m}$) and it is thermodynamically metastable. It converts to more stable rhombohedral hematite structure on heating to temperatures above 350° C. This transition has a monotropic nature, occurring slowly at all values of temperature. In *Stacey and Banerjee (1974)* it is deduced that if a minute amount of hematite is present in the initial magnetite grain, two competitive processes occur. In addition to the slow conversion from magnetite to maghemite there is an autocatalytic growth of hematite, which becomes predominant in a mixed crystal. Because the free energy G_γ of maghemite is greater than G_α of hematite, the transition can take place even at room temperature, if the grain size, impurity content and ambient gas are appropriate. Inversion of maghemite to hematite on heating was indicated by an differential thermal analysis at 555° C, according to *Özdemir and Dunlop (1988)*. From the paleomagnetic point of view it is very important, that the *maghemite* cannot have the TRM, unless it is doped with impurities which

inhibit the transition into hematite. At the same time, if the hematite is derived from maghemite, its magnetization may be of the CRM, or CVRM origin.

The problem of the CRM or CVRM of maghemite - hematite or titanomagnetite - titanomaghemite systems have been studied by many authors: e.g. by: *Hedley (1968)*, *Dunlop (1981)*, *Özdemir (1987)*, *Özdemir and Dunlop (1983, 1985, 1988, 1989)*, *McClelland (1987)*; *McClelland and Goss (1993)*.

Readman and O'Reilly (1970) studied an oxidation of transformation of the titanomagnetites ($\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$) for $x = 0.2$, $x = 0.5$, $x = 1.0$, in the interval 100 to 900° C. The reaction kinetics were studied by heating wet ground Ti-Mt at constant temperature between 200 and 300° C. According to the authors if a true order of the reaction is assumed of $n = 1$ the variation of the reaction constant gives activation energies of 1.5, 1.4 and 1.2 eV/molecule for samples with $x = 0$, 0.2 and 0.4, respectively. The time constant for the oxidation of the samples was of the order 10^6 year at room temperature. According the author's deduction the derived constant could be regarded as a lower limit for Ti-Mt-es occurring naturally in rocks. This means that the Ti-Mt-es present in the rocks have a chance to be altered in favour of titanomaghemites and successively to hematites during approximately one million of years at the atmospheric temperatures.

Brown and O'Reilly (1988) studied the effect of low temperature oxidation the TRM Ti-Mt $\text{Fe}_{2.4}\text{Ti}_{0.6}\text{O}_4$ carrying samples. Some results of the experimental study may be applied also for more oxidized Ti-Mt-es. They revealed that when maghemitization takes place in nature, microstructural change accompanies the compositional change. The exterior of the grain being more highly oxidized comparing it with the interior core. The properties of the core are taken to be similar to the starting material apart from those resulting from a change in composition alone. According to the authors an altered mantle of the grain consists of unblocked regions with the high susceptibility of a superparamagnet, which will screen the magnetic moment of the core and the magnetization of the assemblage will be reduced. The authors presented the observed dipole moment of a spherical inclusions surrounded by permeable shell, applying the mathematical formulae according to *Stephenson (1975)*.

Experimental results have proven that dominant types of magnetiza-

tion in neovolcanic rocks are the chemical (CRM) and the chemico-viscous (CVRM) magnetization. CRM is produced when a secondary magnetic mineral grows to stable single-domain (SD) size during an alteration of parent mineral in the presence of a magnetic field. Commonly it overprints part, or a whole primary remanence of rocks. According to *Özdemir and Dunlop (1988)* the CRMs acquired during the transformation of a magnetic parent mineral within 100°C of the Curie temperature seem to have an acquisition mechanism similar to that of viscous remanent magnetism (VRM), which is produced by prolonged exposure to a field without grain size change. At ordinary temperatures, VRM is acquired by a small fraction of SD grains just above the superparamagnetic (SP) threshold diameter d_s for thermal stability, whereas CRM, in the simplest case (J_s) is blocked practically in all grains as they grow beyond d_s to possibly quite large terminal sizes. In this situation, CRM should be more intense and more resistant to demagnetization than VRM. With heating, the thermal stability of a particle decreases, until at the unblocking temperature T_{UB} , the particle becomes SP and its remanence disappears. Equivalently, d_s increases with rising temperature until at T_{UB} it has swept through the sample size spectrum and destabilized all particle remanences. At temperatures just below T_{UB} , a large fraction of the grains have d just above d_s and readily acquire VRM. If a new phase grows at this temperature, its terminal size will likewise be just above d_s . The CRM it acquires by growing through d_s will be continuously augmented by VRM. The size controlled CRM and time controlled VRM processes merge. It is generally assumed in paleomagnetism that chemical remagnetization of rocks or viscous or thermoviscous remagnetization are distinct processes.

The results of rock samples - the young and the historical volcanics: Firstly I selected the historical age hornblende-biotite andesites of the Kaimeno-Chorio locality from Greece (Fig. 1). They have normal polarity of RM of TRM origin. They are of high magnetic and directional stability against the thermal demagnetization. We see from the curves that the magnetic minerals are characterized by gradual increase of κ from -196°C to -150°C which indicates a presence of Ti-Mt near to magnetite (Fe_3O_4) in the composition. In the interval from 25 to 350°C we see again an increase of κ . In this interval there is a transition of non-stoichiometric magnetite to maghemite ($\gamma\text{-Fe}_2\text{O}_3$). But soft increase of κ corresponds to gradual

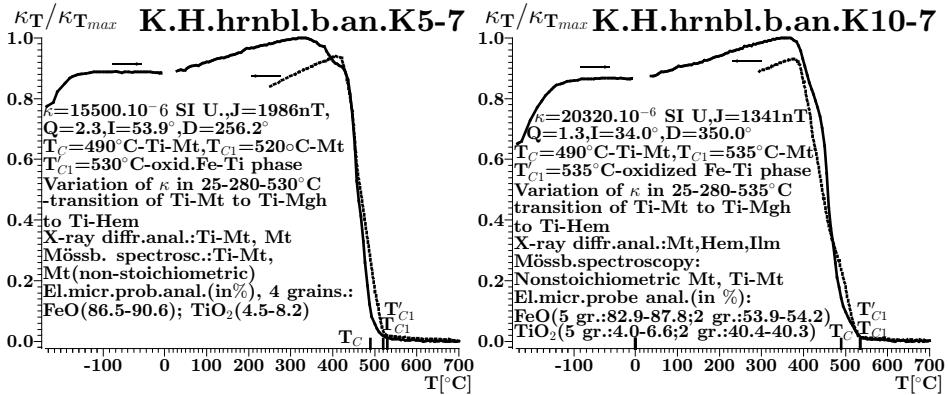


Fig. 1. Thermomagnetic curves of the Fe-Ti oxides of historical age samples K.H.K5-7 and K.H.K10-7 of hornblende biotite andesites from Kaimeno Chorio locality from Greece ($\varphi=37.618^\circ$, $\lambda=23.332^\circ$). Samples originally of only normal RM of TRM origin; φ , λ - geographical coordinates, κ_T , $\kappa_{T_{max}}$ - magnetic susceptibility at temperature T (κ_T); maximum susceptibility ($\kappa_{T_{max}}$); T_C , T'_{C1} - Curie temperatures. \rightarrow , \leftarrow - heating, cooling of the sample, respectively.

creation of small magnetic particles of maghemite in the system. In the interval from 350 to 530°C there is a sharp decrease of κ , which corresponds to transition of maghemite to hematite ($\alpha\text{-Fe}_2\text{O}_3$). The X-ray diffraction method and the Mössbauer spectroscopy detected also non-stoichiometric magnetite in the samples. But in some samples also more oxidized Fe-Ti oxides - hematite and ilmenite were analyzed except of Ti-Mt-es by the electron micro probe method.

It has been evidenced from the results of young volcanics (*Orlícký et al., 2003*). The hornblende-biotite andesites from Greece (Methana Peninsula, Kaimeno chorio, age cca 2 250 years; the results of two samples are in Fig. 1); Italy (Vesuvius, leucitic tephrite, age cca 100 years, Lipary Mount, Canneto town - obsidian, age cca 9 000 to 10 000 years); Haruna Mount - central Japan, rhyodacite, eruption in 1,400; USU volcano, Japan, volcanic ash, eruption in March, 2 000; Pinatubo-Olongapo, Phillipines, dacite ash eruption in 1991; Mazama Mount, Crater Lake, Oregon State, USA, dacite (calkaline magma), cca 10 000 years old; Rainer Mount, Washington State, USA - andesite, cca 20 000 years old have contained dominantly the titanomagnetites (Ti-Mt-es; $\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$), except of Ilmenite hematites (Ilm-Hem-es) and small portion of more oxidized Fe-Ti oxides. The Ti-Mt-

es are of compositional parameter in the range of $x \approx 0.14$ to 0.257 ; with the Curie temperatures from 455 to 510°C . Exceptionally in dacite of USU volcano a small portion of more oxidized Fe-Ti oxides is present. They are of own experimental experience. From the results of the change of magnetic susceptibility with temperature it is evident that after heating of the sample to 700°C the cooling curve does not follow strictly the original heating curve but softly is shifted to higher temperatures. It is nearly reversible also in its high level. Generally, in rhyolites and dacites (higher content of SiO_2) an oxidation of original Fe-Ti oxide takes place easier than in the andesites.

3. Short geological description of rocks

According to *Konečný and Lexa (1984)*, in the central zone of the Štiavnica stratovolcano there are the Neogene volcanics of the I-st stage - complex of intravolcanic and subvolcanic intrusions (andesites and andesite porphyres), and in a large area there is a complex of pyroxene and hornblende pyroxene andesites. The complexes of the I-st stage are intensely propylitized. There were collected volcanics from 46 localities. The relicts of the Badenian stratovolcano are also in Kremnické vrchy Mts. They are termed as the Zlatá studňa formation. The volcanics from 16 localities were collected from this formation.

The products of the Studenec formation, the hornblende-biotite andesites have shown dominantly the normal RM in the SW, S and SE areas, in the northern and SW areas are detected mostly the rocks with the reversed RM. The direction of RM of rocks has shown a large scatter. Some results have been published by *Orlický (2001)*. Additionally applied experimental works - measurements of the change of magnetic susceptibility (κ) with temperature (Curie temperature measurements), X-ray diffraction analyses, the Mössbauer spectroscopy, electron microprobe analyses have provided very useful information and they allowed to make a more precise interpretation of the results.

The results of the selected volcanic rocks - an analysis of geological units with respect to their possible alterations: The Neogene intermediate volcanics are more oxidized than the above described young and recent intermediate volcanics. The basic magnetic Fe-Ti oxides of recent, young, or historical age are characterized by lower Curie temperatures

of about $T_C \approx 60^\circ \text{C}$ in average than those of Neogene age andesites. Their titanomagnetites (Ti-Mt-es) differ in compositional parameter $x \approx 0.05$ in average.

In any case the composition and related Curie temperatures of the Neogene andesites have not reflected the original state of their magnetic minerals. We can deduce that the difference in the selected characteristics mentioned above have reflected the alteration of magnetic Fe-Ti minerals of the Neogene volcanics under normal atmospheric conditions during their survival from an origin up to the present. It could be a very surprising idea and completely new knowledge from the paleomagnetic point of view. What type and which magnetic Fe-Ti minerals have a tendency to be altered in a such easy way in nature? I have stressed many times that the titanomagnetites have a strong tendency to be altered. From the accessible literature it is clear that a basic type of alteration of magnetite including the Ti-Mt into the more oxidized Fe or Fe-Ti phases, so called maghemitization occurs.

Previously I described the petrography of individual volcanic formations or complexes in detail, mostly according to *Konečný and Lexa (1984)*. The Neogene intermediate volcanics originated in the interval of 15 to about 9 million of years (My). The volcanic process did not proceed continually, but within some episodes. So, some previously consolidated volcanic units were subsequently disturbed. They were repeatedly reheated by newly formed volcanic magmas or volcanic bodies, namely by intrusive bodies in subvolcanic level. Their originally formed Fe-Ti oxides were altered and their magnetic properties were changed. Owing to this process also an original RM of contacted rocks was remagnetized.

As an example I can characterize the extrusive and effusive products of the Štiavnica stratovolcano in the Central Slovakia. It is an assemblage of pyroxene andesites, andesite porphyry, intrusive diorites and diorite porphyry, effusive complex of pyroxene and hornblende-pyroxene andesites, complex of extrusions of hyperstene-hornblende andesites. Whole complex is tectonically dislocated. Most of volcanic products of the stratovolcano are named as the Undivided complex of the I-stage (*Orlický, 2001*). According to *Konečný and Lexa (1984)* an origin of the stratovolcano with the range of the caldera $18 \times 22 \text{ km}$ was in the Upper Badenian. The caldera subsequently subsided into the lower levels. The subsidence of the caldera was accompanied by an explosive and extrusive activity of the biotite-hornblende

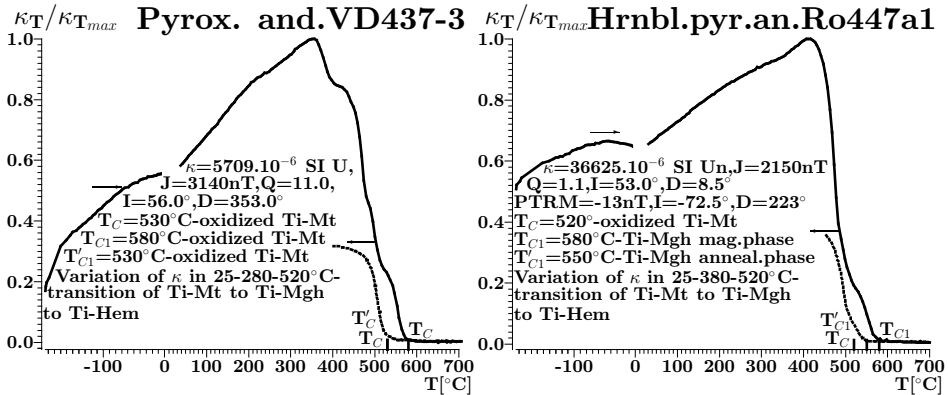


Fig. 2. Thermomagnetic curves of the Fe-Ti oxides of the pyroxene andesite jvd437-3 ($\varphi = 48.544^\circ$, $\lambda = 19.462^\circ$) and the hornblende pyroxene andesite jro447a1 ($\varphi = 48.523^\circ$, $\lambda = 19.372^\circ$) of the Velká Detva formation and Rohy formation respectively. Both samples come from rock of normal RM; but in the sample jro447a self-reversed PTRM was induced after laboratory magnetization in normally oriented field in the interval 700 to 520° C. The magnetostatic interactions between original magnetic phase and that of more oxidized phase was a cause of the self-reversed PTRM in the sample (other explanations see in Fig. 1).

andesites and their various petrographical modifications. They are dominantly accumulated within the Štiavnica caldera. It is composed of large extrusive domes and subordinate pyroclastic flow deposits and epiclastic volcanic rocks - Studenec formation. Beyond the margins of the caldera the formation extends only as filling of radially oriented valleys. In a parallel way an intrusive activity of the silica-diorite and granodiorite porphyrites in subvolcanic levels took part in this area. The subsidized complexes of rocks were areally propylitized. The above described geological units underwent intense alterations. According to geological map of *Konečný and Lexa (1984)* the intrusive bodies are located in the central part of the Štiavnica caldera and are surrounded by the products of the Studenec formation.

The magnetic and mineralogical characteristics of selected neovolcanics: With respect to relatively high age of neovolcanics (15-9 MY) we cannot expect that their magnetic minerals have preserved themselves in the state as they were at their beginning. Generally they have surely survived a dramatic alteration during their existence, dominantly by the so called maghemitization. Exceptionally we can find a sample with only small alterations of original Fe-Ti oxides. Two examples are in Fig. 2. Orig-

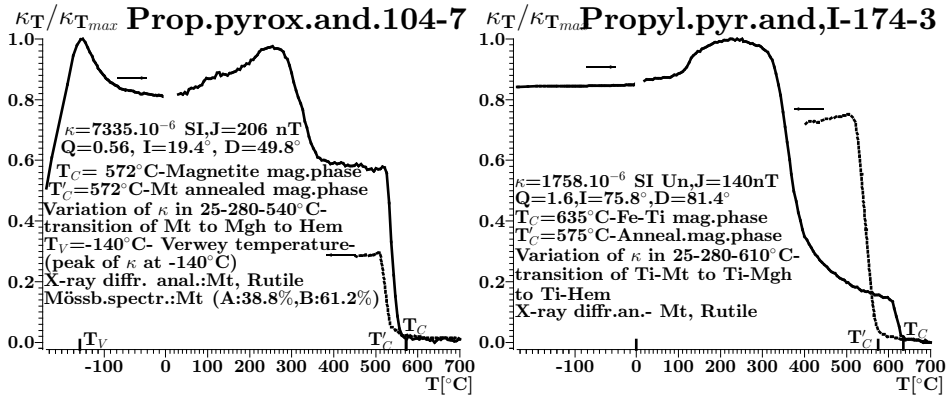


Fig. 3. Thermomagnetic curves of the propylitized pyroxene andesite samples i-104-7 ($\varphi = 48.483^\circ$, $\lambda = 18.750^\circ$), i-174-3 ($\varphi = 48.445^\circ$, $\lambda = 18.883^\circ$), both of normal RM (other explanations see in Fig. 1).

inally there were only more oxidized Ti-Mt-es in the rocks (the phases with $T_C = 530$ and 520° C, respectively), but gradually there took place an alteration of Ti-Mt in favour of Ti-Mgh with T_C near to 580° C (less in the rocks represented by jvd437-3 sample, more intense in those represented by jro447a1 sample. Generally, if there is present only the Ti-Mt there is gradual increase of κ from -196° C to about 450° C, as in Fig. 2, sample jvd437-3. If there is also Ti-Mgh an increase of κ is softer, namely in the low temperature interval, as in the sample jro447a1. Both hornblende pyroxene andesites have normal RM but after laboratory magnetization in normally oriented field self-reversed PTRM was induced in the sample jro447a in the interval 700 to 520° C. The magnetostatic interactions between original magnetic phase and that of more oxidized phase was a cause of the self-reversed PTRM in the sample.

The representatives of the first - undivided propylitized phase:

We see from the curve that the magnetic mineral is characterized by gradual increasing of κ from -196° C to -140° C (Verwey temperature, Fig. 3, sample i-104-7). This behaviour corresponds to the presence of multidomain magnetite (Fe_3O_4) in the sample. In the interval from 25 to 280° C we see again an increase of κ . In this interval there is a transition of magnetite to maghemite ($\gamma\text{-Fe}_2\text{O}_3$). But an increase of κ corresponds to a creation of small magnetic particles of maghemite in the system. This phenomenon has been known from the measurements in air and in vacuum (Orlícký, 1988).

In the interval from 280 to 540° C there is a sharp decrease of κ , which corresponds to the transition of maghemite to hematite (α -Fe₂O₃). Then we see a sharp decrease of κ from 540° to 572° C in Fig. 2. This behaviour corresponds to a presence of non-stoichiometric magnetite in the sample. A presence of magnetite was detected also by the X-ray diffraction method and by the Mössbauer spectroscopy (see in Fig. 3). The Mössbauer analysis has proven also a presence of magnetite. As we know the magnetite is an inversion spinel. At room temperature Fe³⁺ ions occupy the tetrahedrally coordinated (A) sites and both Fe³⁺ and Fe²⁺ ions occupy the octahedral (B) sites. In the two magnetic sublattices Fe³⁺[Fe³⁺, Fe²⁺]O₄²⁻ A position of Fe³⁺ and octahedrally coordinated Fe³⁺, Fe²⁺ cations the orientation of spins is antiparallel - in the ferrimagnetic state. In the magnetite above the transition temperature, Fe²⁺ and Fe³⁺ ions are randomly distributed on the B-sites which makes electron hopping between B-site iron ions energetically easy (we see that in the tetrahedrally coordinated A-site the content of Fe³⁺ ions is 38.8 %, while in octahedrally coordinated B-site the content of both Fe³⁺ and Fe²⁺ ions is 61.2%, nearly of the theoretical value, 2 times as in A site), see in Fig. 3.

In the intrusive rocks there is a petrological chance for the magnetite to originate directly in magma and during its rise - (they were consolidated below the earth's surface; see in *Orlický, 2001*). Many localities of the first phase with propylitized rocks contain the pyroxene andesites of the extrusive or effusive origin. During the stadium of propylitization the sulphate liquids accompanied this volcanic process. The Fe sulphides originated in the volcanic rocks. We know that the Fe sulphides are transformed into Fe oxides, mostly in favour of magnetite. Very important is that these two types of magnetites are of the multidomain structure. They carry very low RM of the CRM origin, dominantly of normal polarity. This knowledge can be supported also by the results of silica diorites and monzonodiorites of the Kalinka intrusive formation (age cca 14 MY) from the borehole KON-1 from the Javorie volcanic field. The dominant magnetic mineral of 72 samples from the interval 850 to 1800 meters is magnetite of multidomain structure. Low intensity RM of normal polarity with the inclination $I = 66.6^\circ$ of the samples is probably of CVRM origin (*Orlický, 1986*).

The Fe-Ti oxides of propylitized pyroxene andesite of i-174-3 sample (Fig. 3) were mostly altered to rutiles (TiO₂) and small amount of magnetite ac-

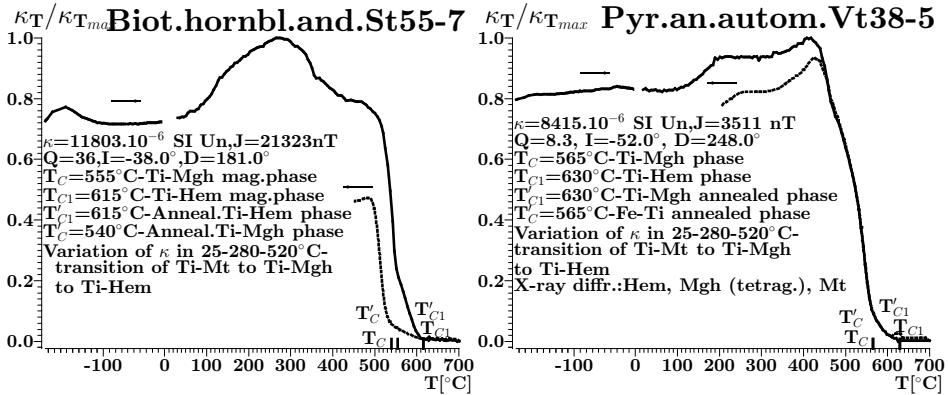


Fig. 4. Thermomagnetic curves of the biotite hornblende andesite St-55-7 $\varphi = 48.542^\circ$, $\lambda = 18.943^\circ$ and the pyroxene andesite Vt-38-5 $\varphi = 48.567^\circ$, $\lambda = 18.714^\circ$ of the Studenec formation and the Vtáčnik formation, respectively. The samples in situ state are of the reversed RM; normal PTRM after laboratory magnetization (other explanations see in Fig. 1).

ording to the analyses. But the most oxidized phase of the sample, with $T_C = 635^\circ\text{C}$ corresponds to the presence of hematites. These rocks carry normal RM with very low intensity of NRM of CRM and CVRM origin. Such intense alterations of original Fe-Ti oxides are quite rare and in our volcanic areas are represented by about 7 localities. The rocks are always of normal RM.

The rocks containing the hornblende and/or biotite minerals: In the biotite-hornblende andesite St-55-3 (Fig. 4) there is a magnetic Ti-Mgh phase of the $T_C = 555^\circ\text{C}$, which carries the self-reversed CVRM and the Ti-hem magnetic phase of $T_C = 615^\circ\text{C}$, which carries the normal CRM. An entire CVRM is of $I = -38.0^\circ$ and $D = 181.0^\circ$. The second magnetic phase with $T_C = 615^\circ\text{C}$ was created during reheating of the volcanic body during additional volcanic activity by contacted melted lava flow or extrusive body. In the sample Vt-38-5 and in the biotite-hornblende andesites of the samples 102-13 and 156-6 (Fig. 4) and in the pyroxene-hornblende andesite of the samples B1-25-2 and B1-33-1 (Fig. 5) there existed more complex oxidation. *Stacey and Banerjee (1974)* deduced that if a minute amount of hematite was present in the initial magnetite (also in Ti-Mt) grain, two competitive processes occurred. In addition to the slow conversion from magnetite to maghemite there is an autocatalytic growth of hematite, which becomes

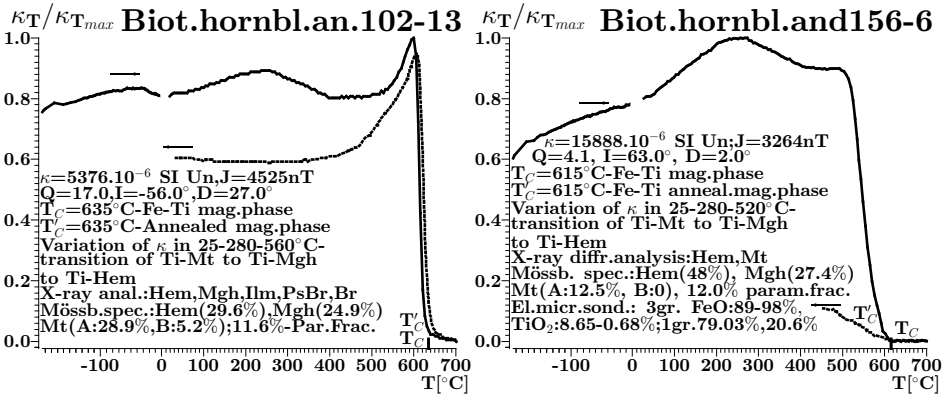


Fig. 5. Thermomagnetic curves of the Fe-Ti oxides of the biotite hornblende andesites St102-13 ($\varphi = 48.482^\circ$, $\lambda = 18.745^\circ$), St156-6 ($\varphi = 48.451^\circ$, $\lambda = 18.966^\circ$) of the Studenec formation. The sample St102-13 is of the reversed inclination and normal declination of RM. The sample St156-6 is of normal RM (other explanations see in Fig. 1).

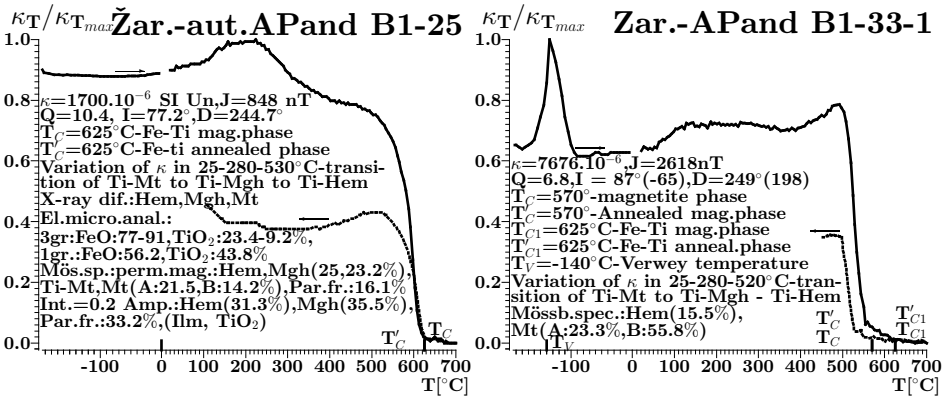


Fig. 6. Thermomagnetic curves of the hornblende pyroxene andesites B1-25 and B1-33 from a large quarry near Žarnovica ($\varphi = 48.518^\circ$, $\lambda = 18.743^\circ$). The sample B1-25 carry normal inclination and reversed declination of RM. The in situ RM of the sample B1-33 is of normal polarity of RM, which is carried by magnetite of the secondary origin in the sample. The reversed RM is carried by the secondary Fe-Ti oxides in the sample. This is appeared after thermal demagnetization of the samples (other explanations see in Fig. 1).

predominant in a mixed crystal. We see from the Curie temperatures and the results of the analyses that there is hematite in the samples except of Ti-Mgh and Mt. In the sample Vt-38-5 there are two magnetic phases, one

with $T_C = 565^\circ\text{C}$, and the second one with $T_C = 630^\circ\text{C}$. The cooling curve is nearly reversible to the heating curve. In the sample 102-13 (Fig. 4) there is present Hem(55%), Mgh(29%) and Ilmenite. The Curie temperature is $T_C = 635^\circ\text{C}$, with a reversible value on the cooling curve which detects only one magnetic phase. This rock has the reversed inclination and normal declination of CVRM. The sample 156-6 contains Mt(13%), Hem(48%) and Mgh(27%); one magnetic phase is determined by the $T_C = 615^\circ\text{C}$. It is the same also on cooling curve.

The hornblende pyroxene andesites in Fig. 6 comes from one of 45 individual places of the large quarry near Žarnovica Village. The samples were studied by *Orlický (2002)*. The height of the quarry from bottom to top was about 220 metres. The samples of rocks from the twenty five places (all from the top to about 120 m below) have shown a negative inclination of NRM, while the samples from 9 places (from the bottom of quarry and about 70 m above) have shown a positive inclination of NRM. The samples with negative inclination of NRM are characterized by the $T_C \approx 610$ to 625°C , see e.g. in Fig. 6, B1-25-2, containing Hem(25%), Mgh(23%), Mt(36%), Ti-Mt(16%) and ilmenite. The samples with positive inclination of NRM (in Fig. 6, B1-33-1) have shown very expressive phase with $T_C \approx 570^\circ\text{C}$, and so called Verwey transition temperature of $T_V = -145^\circ\text{C}$. The magnetic phase corresponds to magnetite. Magnetic phase with the $T_C \approx 625^\circ$ corresponds to more oxidized Fe-Ti oxides. The magnetic phases contain Mt(56%), Mgh(23%), Hem(15%), Ti-Mt(6%) and ilmenite, according to Mössbauer analysis. In the rocks of this quarry were detected also Fe-sulphides (pyrite). While the Mgh Hem and Ilm-es originated due to oxidation of original Ti-Mt within the whole volcanic body, non-stoichiometric magnetite arose by transformation of the Fe-sulphides to the Fe-oxides. Evidently, secondary magnetite is a carrier of positive polarity of RM of samples, mostly from the lower levels of the volcanic body when a leakage of sulphuric liquids was more protected and a precipitation of the Fe-sulphides inside the body occurred. Thermal dissociation of sulphur from the Fe-sulphides and its replacement by oxygen can be actual not only at temperatures over 350°C (which is quite a known process) during heating and cooling of volcanic body, but also at atmospheric conditions on the earth's surface during post volcanic time. The positive RM carried by magnetite is of CVRM origin. The reversed RM, also of CVRM origin is

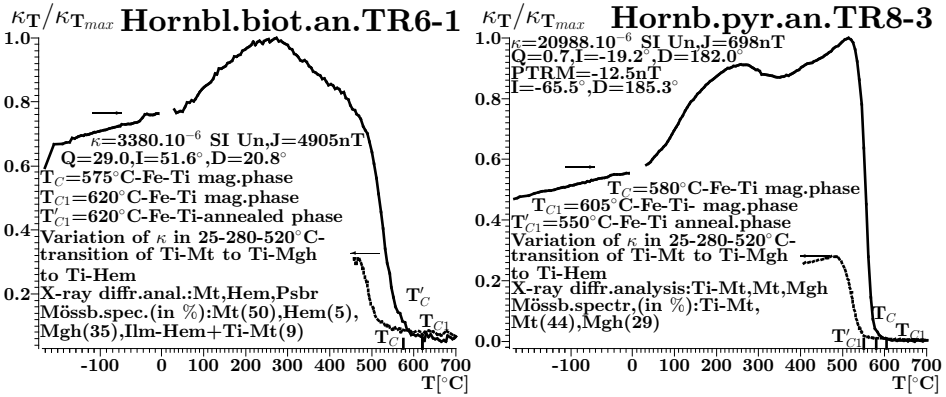


Fig. 7. Thermomagnetic curves of the Fe-Ti oxides of the hornblende biotite andesite TR-6-1 ($\varphi = 48.587^\circ$, $\lambda = 19.392^\circ$) and hornblende pyroxene andesite TR-8-3 ($\varphi = 48.582^\circ$, $\lambda = 19.387^\circ$) both from the Rohy formation from the Javorie and Pořana volcanic area (other explanations see in Fig. 1).

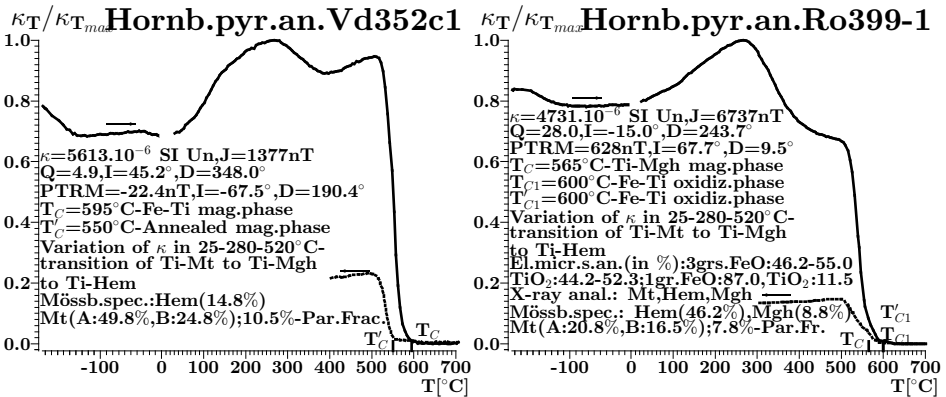


Fig. 8. Thermomagnetic curves of the Fe-Ti oxides of the hornblende pyroxene andesites VD352c1 ($\varphi = 48.623^\circ$, $\lambda = 19.387^\circ$) and Ro399-1 ($\varphi = 48.583^\circ$, $\lambda = 19.373^\circ$) of the Velká Detva formation and the Rohy formation, respectively. The sample VD352c1 carries normal RM, but reversed PTRM after laboratory magnetization. The sample Ro399-1 carries reversed RM, but normal PTRM after laboratory magnetization (other explanations see in Fig. 1).

linked with oxidized Ti-Mt to Ti-Mgh magnetic phase within the volcanic body.

Hornblende pyroxene andesites from the Javorie and Poľana volcanic fields: The results of the study of the hornblende pyroxene andesites are shown in Figs. 7, 8. The sample TR-6-1 was altered by autometamorphic effect. We see that there are two phases in the rock. One, with $T_C = 575^\circ$, corresponded to Mt and Mgh, the second one with $T_{C1} = 620^\circ$ C, corresponded to Hem and other Fe-Ti oxidized components. The positive RM, probably of TRM or CVRM origin is carried by the second magnetic phase of $T_{C1} = 620^\circ$ C. In the sample TR-8-3 there are two magnetic phases. One, dominant with $T_C = 580^\circ$ C corresponding to Ti-Mgh and only small portion of the second phase with $T_{C1} = 605^\circ$ C. The reversed RM of CVRM origin is carried by the Ti-Mgh phase with $T_C = 580^\circ$ C. There was induced also self-reversed PTRM in a parallel sample in the normally oriented laboratory field. We see from the thermomagnetic curves that after heating to 700° C the cooling curve follows in parallel way with the temperature axis up to $T'_C = 550^\circ$ C. The difference between T_C and T'_{C1} is about 30° C. An acquisition of the self-reversed PTRM of the sample Vd352c1 (Fig. 8) was realized by the similar way as in the sample TR-8-3 (Fig. 7). But the sample was originally of normal RM, probably of CVRM origin before its magnetization in the normal laboratory field. The inclination and declination of PTRM of the rock are nearly antiparallel to ambient magnetizing field. The sample R0399-1 (Fig. 8) has a reversed RM of low inclination of CVRM origin, which was linked with the Ti-Mgh phase of $T_C = 575^\circ$ C. But the PTRM induced in the laboratory field was only of normal orientation, coinciding with the direction of laboratory field. This is quite clear from the thermomagnetic curve, because the created PTRM is carried by more oxidized phase containing dominantly hematite.

4. Generalized knowledge

I presented the results of my investigation of the self-reversal origin of the reversed RM of rocks in many publications *Orlický et al. (2000)*, *Orlický and Funaki (2000, 2001, 2002)*, *Orlický (2001, 2002, 2002a, 2002b, 2002c, 2002d, 2003, 2003a, 2004, 2004a, 2005, 2006, 2006a, 2006b, 2007, 2008)*. From the cited publications follows that together about 290 samples of andesites and the rhyolites were subjected to laboratory magnetization

in normally oriented magnetic field of intensity $H = 48\mu\text{T}$. The samples from about 177 localities acquired the self-reversed partial thermoremanent magnetization (PTRM). The self-reversed PTRM was acquired only by the samples which possessed the two magnetic Fe-Ti phases, very expressively evidenced by the Curie temperatures. One Fe-Ti phase with the $T_C \approx 555$ to 585° , contained also an original phase. The second magnetic phase was created due to maghemitization of original Ti-Mt and in most cases it has carried the *in situ state* the reversed RM of CVRM origin. The Ti-Mgh phase was nearly disappeared and the original Ti-Mt phase was revealed after heating of the sample to 700°C and successive cooling - on the cooling thermomagnetic curves. The self-reversed CVRM and in laboratory field induced PTRM was acquired by the rocks by the magnetostatic interactions between these two magnetic phases. In this process, the second magnetic titanomaghemite (Ti-Mgh) phase must start in the so called superparamagnetic (SP) state. The original Ti-Mt phase was probably in the magnetically ordered state, with the thermodynamically stable domain structure.

No one studied sample with only one magnetic phase acquired the self-reversed PTRM during the laboratory magnetization. If there were also the two magnetic phases in the sample, one of them was highly oxidized (T_C over 590°C), and no magnetic phase corresponding to primary Ti-Mt phase after the heating to 700°C and successive cooling was visible on cooling curve, only the positive PTRM was induced in the sample.

I present some sentences of *Brown and O'Reilly (1988)* for this process to be more understandable. The authors revealed that when maghemitization takes place in nature, microstructural change accompanies the compositional change. The exterior of the grain being more highly oxidized comparing it with the interior core. The properties of the core are taken to be similar to the starting material apart from those resulting from a change in composition alone. According to the authors an altered mantle of the grain consists of unblocked regions with the high susceptibility of a superparamagnet, and which will screen the magnetic moment of the core and the magnetization of the assemblage will be reduced.

The suggestions and some inspirations concerning the self-reversal RM are the topic of this article. The andesitic and rhyolitic intermediate rocks from Kremnické vrchy Mts., and from eastern Slovakia volcanic fields are similar to those presented from Central Slovakia volcanic fields. In all so

far studied rocks a stable component of RM corresponds to CVRM origin and the reversed RM of these rocks is of the self-reversal origin. All these results can be very useful for an establishment a more comprehensive theory to describe completely the self-reversal process in magnetization of rocks. The experimental results presented in this article have very clearly shown that except of mechanism of self-reversal process of the reversed RM applied to the famous Haruna dacites from Japan (*Ishikawa and Shiono, 1963*) and other Ilm-Hem bearing acidic rocks (*Orlický and Funaki, 2002; Prévot et al., 2001*) and an acquisition of the self-reversal RM in basaltic samples (*Krásá et al., 2005; Orlický and Funaki, 2008*) there has been revealed a complete new possible mechanism of an acquisition of the self-reversed CVRM in intermediate volcanic rocks due to their maghemitization under the atmospheric conditions in the field. Unfortunately, this process cannot be correctly reproduced in the laboratory during one or two centuries because of very slowly ongoing alteration in atmospheric conditions. But may-be we try it under higher temperatures in the future.

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