# PALAEOMAGNETISM AND MAGNETIC MINERALOGY OF SELECTED NEOVOLCANIC ROCKS OF THE CENTRAL SLOVAKIA (WESTERN CARPATHIANS)



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Abstract: The contribution briefly summarizes the results of the study of magnetic minerals and palaeomagnetic properties of Pliocene and Pleistocene alkaline basalts and basanites, Neogene andesite and andesite porphyry of the Štiavnica stratovolcano (I-stage) and hornblende-biotite andesites of the Studenec Formation of the Central Slovakia. Magnetism carriers in the basalts are mostly titanomagnetites of a composition  $Fe_25Tia_5O4$ . Pyroxene andesites and andesite-porphyry of the I-stage have been mostly propylized. They contain predominantly magnetic Fe-Ti oxides very near to magnetite-like mineral. Hornblende-biotite andesites of the Studenec Formation contain mostly haematite-ilmenite solid solutions. Magnetism carriers of andesitic rocks of both - the I-stage also the Studenec Formation are supposed to be of secondary origin. A. F. demagnetization tests were mostly used to consider palaeomagnetic stability of rocks, thermal tests were also rarely employed. Succession of the volcanic activity is presented on the base of the polarity of the stable RMP of volcanics using also a combination of radiometric ages of rocks with the polarity time-scale.

Key words: Western Carpathians, Central Slovakia, volcanics, magnetic minerals, palaeomagnetism.

#### Introduction

Volcanic rocks exhibit some magnetic properties due to the presence of various Fe-Ti oxides (mostly of the magnetite-ulvospinel series, magnetite-maghemite series and haematite-ilmenite series) as accessory minerals. The remanent magnetic polarization (RMP) of the accessory minerals can reflects both the direction and intensity of the geomagnetic field in the past, if the magnetization has been acquired at the time the rocks were formed. The mechanism by which the RMP was acquired depends upon the mode of formation and subsequent history of rocks as well as the characterics of the magnetic minerals. The source of the difficulty with respect to the palaeomagnetic point of view lies in the mineral alterations of the magnetic constituents during the existence of rocks in the field. It means that we have very serious interest to recognize if the RMP of rocks is synchronous with the origin of rocks or if has been acquired in the unknown time when the original magnetic minerals were altered. The oxidation of the titanomagnetites ( $Fe_{3-x}Ti_xO_4$ ) takes place during initial cooling of the volcanic rocks. This process tends to proceed first through the production of ilmenite lamellae and then progresses the pseudobrookite series (McElhinny 1973). There is actual maghematization of the titanomagnetites during low-temperature oxidation in the field. This process can take place during the late stages of the initial cooling or perhaps during subsequent weathering of rocks. It cannot take place at high temperatures, because maghemite is metastable and reverts to haematite irreversibly on being heated in the range 280 - 700 °C. It means that maghemite can only exist at low temperature. Both the titanomagnetites and titanomaghemites are inverted into a two-phase intergrowth (spinel phase and rhombohedral phase) when they are heated over 600 - 670 °C

and cooled up to natural - atmospheric temperature. Individual phases of the intergrowth comprise following minerals:

spinel phase: mineral near to magnetite (in composition) containing small quantity of Ti and vacancies and mineral richer in iron than original titanomagnetite (or titanomaghemite);

*rhombohedral phase*: mineral near to ilmenite (less Ti rich in composition than ilmenite), mineral near to haematite in composition, pseudobrookite -  $Fe_2TiO_5$ , and  $TiO_2$ - anatas (according to Readman & O'Reilly 1970).

The existence of such alterations has provoked us to study not only palaeomagnetic characteristics, but also to recognize the magnetic minerals of selected volcanic rocks in detail.

The results of study of rocks of following volcanic complexes and formations of the Central Slovakia are presented in this paper:

- Alcaline basalts and basanites (Bz);

- Selected intrusive, extrusive and effusive products of the Štiavnica stratovolcano - Undivided complex - I stage (I);

- Studenec Formation (St).

Goal of the paper is not to make only an interpretation of stable direction and polarity of RMP of rocks, but to contribute also to the explanation of an anomalous magnetic properties of several rocks under study.

## **Brief description of volcanites**

Alkaline basalts and basanites: Basaltic volcanism in studied area is represented only by smaller volcanic bodies. The youngest basanite lava flows are located near the Nová Baňa and Brehy. Two necks of nepheline basanite are located nerby the Kalvária and Kysihybeľ. Alkaline olivine basalts are located near the Ostrá Lúka, Dobrá Niva and Devíčie (see Fig. 1).



**Fig. 1.** An outline of lithostratigraphic units in the Štiavnické vrchy and Pohronský Inovec mountain ranges. 1-25-designations of palaeomagnetically investigated rocks of localities, or groups of localities. 1-6-basanites and basalts - Bz; 7-14- and esites and and esite porphyry of the I-stage - I; 15-25-hornblende-biotite and esites of the Studenec Form. - St.; other symbols in Fig. 1 see according to Konečný et al. (1983).

Selected intrusive, extrusive and effusive products of the Štiavnica stratovolcano: The Štiavnica stratovolcano is the most extensive volcano in the Central Slovakia volcanic field. Evolution of the volcano proceeded in several stages during the Badenian to Panonian time. Complex is an assemblage of propylitized andensite and andensite porphyry, effusive complex of pyroxene and hornblende-pyroxene andesites, complex of extrusions of hyperstene-hornblende andesites. Complex is tectonically dislocated. Most of volcanic products of the stratovolcano are named as the Undivided complex of the I-stage (first stage, according to Konečný et al. 1983).

Studenec Formation: The Studenec Formation represents products of extrusive and explosive volcanic activity of biotitehornblende andesites and their various modifications, accumulated dominantly within the Štiavnica caldera. It is composed of large extrusive domes and subordinate pyroclastic flow deposits and epiclastic volcanic rocks. Beyond the margins of the caldera the formation extends only as filling of radially oriented valleys. Structural position, microflora from volcanosedimentary rocks and radiometric dating indicate the Upper Badenian to Early Sarmatian age of the formation.

#### Study of magnetic minerals

Four physical and physico-chemical methods were applied for the detection of magnetic minerals and for the recognition of their behaviour if the magnetic minerals were influenced by temperature. Polished rock samples were used for the analysis of magnetic grains by means of electron microprobe analysis. A cube shaped rocks were used for the Thellier method. The preparation of magnetic fraction for the Mössbauer spectroscopy as well as for the measurements of a change of magnetic susceptibility ( $\kappa$ ) of samples influenced by temperature was realized by a following procedure: samples of volcanic rocks were grinded in non-magnetic mortar. Sample was then ground under alcohol to prevent oxidation. Magnetic grains were then separated from non-magnetic material with permanent bar magnet. The purity of magnetic fraction was ordinarily verified by microscope.

*Electron microprobe analysis*. Electron microprobe analysis was realized by analyser JEOL, equiped by the EDAX system, in the laboratory of the Dionýz Štúr Institute of Geology, Bratislava (Caňo, unpubl. data). The microphotographs of the polished samples were realized also (a magnification 40, 400, 600, and in individual cases also 1 500 and 3 000 times), but they are not presented in this paper. The results of the chemical composition of the Fe-Ti grains of selected polished rocks are presented in Tab. 1.

*Mössbauer spectroscopy*. Mössbauer spectroscopy of magnetic fraction was realized at room temperature by a constant acceleration spectrometer with a source of 1.5 GBq <sup>57</sup>Co in rhodium matrix. This method was performed in the laboratory of the Department of Nuclear Physics and Technology, Slovak Technical University, Bratislava (Lipka et al. 1983, 1987, 1988). The Mössbauer spectra were fitted, using a least squares tech-

[	1	d		1	d		[	d			d		I	d
Sample	FeO		TiO2	FeO		TiO <sub>2</sub>	FeO		TiO2	FeO		TiO <sub>2</sub>	FeO	TiO <sub>2</sub>
		(%)			(%)			(%)			(%)			(%)
B2/16		20			8			7			10			6
	76.6		22.4	75.8		23.2	74.3		24.6	74.4		23.8	73.5	25.6
B2/4		30			8			7			7			6
	78.6		21.0	78.7		20.4	78.2		21.2	78.0		21.6	78.6	20.4
B2/1		20			10			9			8			7
	70.3		29.5	84.9		14.6	78.7		20.9	51.5		47.6	89.4	9.2
I-104/1		100			60			70			20			
	93.2		4.4	94.1		3.5	94.9		3.9	0.8		99.2		
I-174/3		50			20			10			9			
	0.4		99.6	3.2		96.1	1.4		98.6	2.2		97.0		
I-238/7		40			25			15			10			
	78.1		18.9	51.0		48.4	77.6		19.1	76.3		21.0		
I-TR-16/1		30			15			8			7			6
	92.3		7.5	50.9		48.6	87.4		12.3	51.9		47.2	87.2	12.8
St-102/13		45			25			15			8			
	92.7		7.0	88.2		11.5	81.8		17.9	80.2		19.0		
St-156/1		100			50			15			8			
	79.0		20.6	89.4		8.7	97.7		0.3	98.4		0.7		
St-TR-13/2		70			15			10			7			
	91.2		8.1	73.9		25.6	88.4		11.1	96.5		3.3		
St-TR-17/1		45		-	30			15			7			
	88.7		10.3	88.0		10.2	83.7		14.8	88.3		10.0		
St-TR-21/2		110			100			35			6			
	92.7		5.6	63.5		35.9	93.2		5.2	93.4		5.1		
St-TR-23/2		30			15			8			6			
	90.8		7.8	82.3		15.6	90.1		8.6	87.7		10.4		
St-TR-24/2		50			35			20			7			
	84.4		14.5	55.1		44.1	93.4		5.3	90.2		8.4		

Table 1: Results of the electron microprobe analysis.

d- the largest size of grain in  $\mu m$ 

nique. The results of the Mössbauer spectroscopy of samples are in Tab. 2. There are included intensities of magnetic hyperfine field of six-line components of spectra as well as volume of corresponding Fe and Fe-Ti oxides in Tab. 2. A and B designate tetrahedral and octahedral positions in magnetite, respectively.

Measurements of magnetic susceptibility changes of samples induced by temperature. A fully automated apparatus for the study of magnetic minerals was employed. The apparatus and detailed procedures of measurements have been described by Orlický (1990). Measurements were realized in air in the temperature interval 20 - 700 °C and in low temperature interval from 20° down to liquid nitrogen temperature (to -196 °C). Results of measurements are in Figs. 2 - 6.

Thellier method. Thellier method is ussually applied for the determination of the palaeointensity of the geomagnetic field on the base of the dual heating and cooling of rock samples. This method of course seems to be rather problematic. The source of the difficulty lies in mineral alteration of the magnetic constituents on laboratory processing. We will try to recognize what kind of magnetic constituents can have a tendency to be altered during heating and cooling of rock, comparing the results of the Thellier method with those gained by other above mentioned methods. It means that we will not to determine a palaeointensity of the field applying the Thellier method. The results of the Thellier method of selected samples are in Figs.7, 8.

Magnetic minerals of alkaline basalts an basanites. Electron microprobe analysis reveals that the analysed content of FeO and TiO<sub>2</sub> in five arbitrary choosen grains of samples B2/16 and B2/4 is relatively homogeneous (Tab. 1). But there are present

Fe-Ti grains of different degree of oxidation in the sample B2/1 (Tab. 1). Some grains of the sample are supposed to be highly oxidized with a presence of Fe-rich mineral, in some grains are minerals with high content of Ti (probably ilmenite), some Fe-Ti grains have not been intensively oxidized in the sample B2/1. Scanning-electron microphotographs of polished samples B2/1, B2/4, B2/16 show that there are present mostly multi-domain grains in the nepheline basanites. Pseudosingle-domain grains are rarely present there in these rocks. There is many samples of the Brehy locality with the TM-es of low Curie temperature (e.g. Fig. 2, B2/11, B2/17, also many other samples, including B2/16). Mössbauer spectra of these TM-es have shown very broad-non-Lorentzian lines. There was not possible to analyse their parameters according to computing program. Only rough estimates of compositional parameter x of the TM-es have been made, comparing our Mössbauer spectra with those presented by Bhadury (1982). The composition of these TM-es is supposed to be in the range Fe25Ti0.5O4 - Fe23Ti0.7O4. Samples of magnetic fraction B2/2 and B2/9 showed two-sextet of room temperature Mössbauer spectra (Tab. 2). The composition of these samples corresponds to the cation-deficient TM-es (titanomaghemites). Non-stoichiometric magnetite is present in the sample B2/2 according to the intensities of effective magnetic field and the relation of the content in the octahedral (B) and tetrahedral (A) position of the spectra (Tab. 2). A magnetic magnetite-like mineral is indicated in the samples B2/1, B2/2 according to both - Curie temperature ( $T_C \approx 580$  °C) and Verwey transition of magnetite (T  $\approx$  -150 °C), see Fig. 2. We see that the TM-es of low Curie temperatures are characterized by a relatively sharp decreasing of the  $\kappa$  in the low temperature interval down to liquid nitrogen temperature (-196 °C). This behaviour is probably a reflection of a presence of ulvospinel in Fe-Ti oxides, which is paramagnetic at room temperature and antiferomagnetic at low temperature. There are present some magnetic phases with an inversion temperatures besides of phases with Curie temperatures in several basaltic rocks (see Fig. 2, Devičie-P-95B at about 450 °C, indicated by increase of the  $\kappa$ ).

Magnetic minerals of andesitic rocks of the Undivided complex. High content of FeO and very low one of TiO2 was detected by electron-microprobe analysis in most Fe-Ti grains of the sample I-104/1. There are of course also Fe-Ti grains with opposite relation of FeO and  $TiO_2$  contents in this sample (Tab. 1). The most of magnetic grains are of large size, corresponding probably to multi-domain state. Mössbauer spectroscopy reveals that there are only two-sextet pattern lines in the spectrum, with the intensities of the effective magnetic field 39.3 (tetrahedral - A position) and 36.8 MA/m (octahedral - B position Tab. 2). These data correspond to a presence of magnetite, but due to the relation B/A contents (1.57, A and B contents see in Tab. 2) it is quite clear, that this magnetite is non-stoichiometric mineral. Both the Curie temperature ( $T_C \approx 580$  °C) and very evident Verwey transition (T  $\approx$  -150 °C Fig. 3) of this sample have confirmed the magnetite. But expressive decreasing of the  $\delta$  magnetic susceptibility in the interval 280° to 560 °C has shown (at the thermomagnetic curve) that a maghematization of the magnetite takes place in the sample (Fig. 3). There were investigated about 60 samples of magnetic fractions of rocks of the Undivided complex by the measurements of the change of their  $\kappa$  influenced by temperature. The behaviour and the main features of the thermomagnetic curves of about 28 samples are the same/or very similar to that of the sample I-104/1.

Different situation is in the sample I-174/3 (Tab. 1, Fig. 3). We see from the Tab. 1 that there is lack of Fe content in the investigated grains. There is dominant quantity of TiO2 in magnetic grains. Grain size most of grains is supposed to be of the multidomain state. The Curie temperature of magnetic fraction of sample I-174/3 is  $T_C \approx 625 \,^{\circ}C$  (Fig. 3). There is evident intensive decreasing of the during heating in the interval 280 °C to cca 610 °C at the thermomagnetic curve of the sample. This behaviour of the is a consequence of irreversible conversion of intensively magnemitized magnetite into the haematite. Such, or very similar behaviour of the thermomagnetic curve (with the  $T_C \approx 625$  °C) has shown also sample I-110/5 (Fig. 3). No evident Verwey transition at the thermomagnetic curve of sample I-110/5 (Fig. 3) has been detected. Such minerals are supposed to be the titanomaghemites with high content of the haematite-ilmenite solid solutions.

Contents of FeO and TiO<sub>2</sub> within individual grains of the sample I-238/7 (Tab. 1) are very near to those detected e.g. in several basaltic rocks. Some of grains have high content of TiO<sub>2</sub>. Multi-domain, mostly pseudo-single-domain, rarely also single-domain Fe-Ti minerals are supposed to be present in this rock according to scanning electron microphotographs. Maghemite, non-stoichiometric magnetite and oxidized titanomagnetites are supposed to be present in the sample I-238/7 (Tab. 2). Magnetic phase with T<sub>C</sub>  $\approx$  580 °C and inexpressive Verwey transition (T  $\approx$  -150 °C) are revealed at the thermomagnetic curve of sample I-238/7 (Fig. 3). This corresponds to magnetite-like magnetic mineral in the sample. Phase with T<sub>C</sub>  $\approx$  620 °C corresponds to the haematite-ilmenite solid solution. There are heterogeneous contents of FeO and TiO<sub>2</sub> in individual grains of sample I-TR-16/1 and I-TR-16/3 (Tab. 1). Rarely single-domain and multi-do-



----, ----heating, cooling of the sample

Fig. 2. Variations of magnetic susceptibility of magnetic fraction of basaltic rocks with temperature (thermomagnetic curves).  $\kappa_{T}$  - magnetic susceptibility of the sample at concrete temperature used;  $\kappa_{Max}$ . - maximum value of magnetic susceptibility of measured sample.

main but mostly pseudo-single-domain grains are supposed to be present in these samples. Different quantities of magnetite, approximately equal amount of haematite are in samples I-TR-16/1, 16/2 (Tab. 2). Maghemite was also detected in the sample I-TR-16/2 by Mössbauer spectroscopy. The shapes of thermomagnetic curves of both samples are different (Fig. 3). Both of these samples have shown magnetic phase with  $T_C \approx 570$  °C and a second one with  $T_C \approx 630$  °C. There is inexpressive Verwey transition in the sample I-TR-16/1. This effect absents in the sample I-TR-16/2 (Fig. 3).

There have been detected various shapes of the thermomagnetic curves of magnetic minerals of rocks of the Undivided complex at Figs.3, 4. Most of results have revealed magnetitelike mineral, rarely have been detected cation deficient titanomagnetites and haematite-ilmenite solid solutions within the rocks of the Undivided complex. Most of these minerals are supposed to be not in their original state. Original Fe-Ti oxides have been probably altered during the propylitization stage of the evolution of the complex.

Magnetic minerals of hornblende-biotite andesites of the Studenec Formation. A prevalence of both - hornblende and biotite silicates in volcanic rocks has indicated that there was higher volume of the water within the magma from which these silicates crystallized. These specific conditions of a formation of minerals should have influenced also on magnetic properties of magnetic



**Figs. 3, 4.** Variations of magnetic susceptibility of magnetic fraction of andesites and andesite porphyry of the I-stage with temperature. The explanations of symbols  $\kappa_{T}$ ,  $\kappa_{Max}$ ,  $\rightarrow$ ,  $\leftarrow$  are in Fig. 2.

Figs. 5, 6. Variations of magnetic susceptibility of magnetic fraction of hornblende-biotite andesites of the Studenec Formation with temperature. The explanations of symbols  $\kappa_{T}$ ,  $\kappa_{Max}$ ,  $\rightarrow$ ,  $\leftarrow$  are in Fig. 2.

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	Parameters of the Mössbauer spectra								
Sample	Mag	$\alpha - Fe_2O_3$	Mag.	$\gamma - Fe_2O_3$	Mag.	Fe <sub>3</sub> O <sub>4</sub>	Mag.	Fe <sub>3-x</sub> Ti <sub>x</sub> O <sub>4</sub>	Dublets
Jampie	field		field		field		field		
	[MA/m]	(%)	[MA/m]	(%)	[MA/m]	(%)	[MA/m]	(%)	_ 21
	[				A	A			$\frac{\text{Fe}^{2+}}{2}$
			1	1	B	B			Fe <sup>3+</sup>
B2/2			40.3	6.1	38.9	29.0			<u>18.6</u>
02/2				1	36.4	35.0			11.4
B2/9	40.7	3.4			38.8	<u>16.0</u>			<u>38.0</u>
5270					36.4	30.5	L	<u> </u>	12.2
I-104/1	T	T	1	<u> </u>	<u>39.3</u>	38.8	Ţ		
1 10 1/ 1					36.8	61.2			L
I-238/7	<u> </u>		40.5	2.5	38.8	<u>33.9</u>	32.8	9.5	
					36.2	48.5			5.6
I-TR-16/1	40.7	10.4	1		<u>38.8</u>	22.7			7.8
					36.4	44.1			15.1
I-TR-16/3	41.0	10.8	39.7	7.4	<u>39.1</u>	28.2			$\frac{25.1}{5.1}$
[ /					37.4	23.3			5.4
1		1			36.3	1	<u> </u>	<u> </u>	
St 102/13	412	29.6	40.5	24.9	39.6	28.9			
31-102/10	11.12			}	38.6	5.2			
				1					11.4
St-156/1	41.2	48.1	40.4	27.4	39.1	3.4			5.1
00100/1					37.9	<u>9.2</u>			6.9
St-TB-13/1	40.9	33.4	40.1	8.3	<u>39.1</u>	<u>18.3</u>	34.9	5.8	<u>14.1</u>
00 110 10,1					36.9	7.8	31.6	4.5	7.7
St-TB-17/1	<u> </u>				38.6	16.0	35.7	39.2	}
			1		<u>38.0</u>	<u>15.9</u>	33.7	11.4	
					37.4	16.6			+
St-TR-17/2	2	1			38.0	22.1	34.2	20.6	8.4
1					35.9	24.2	31.4	18.4	6.3
St-TR-21/2	2 40.8	23.0	40.0	18.9	<u>39.0</u>	29.0			17.1
,	1				35.7	4.5		<u>_</u>	17.1
St-TR-23/1			40.3	24.4	39.2	25.3	34.0	5.5	9.0
1 '					<u>38.1</u>	<u>14.0</u>		l I	0.3
1					36.1	13.5			20.2
St-TR-24/2	2 40.8	21.5	39.7	13.9	38.7	16.2			<u>38.3</u>
1 '	t	1	i	i		1	1		10.5

Table 2: Results of the Mössbauer spectroscopy. A, B - tetrahedral, octahedral positions of fe-ions in the magnetite, respectively.

minerals of rocks in question. There are heterogeneous contents of FeO and TiO2 within the analysed Fe-Ti grains of six polished samples (Tab. 1). Only in the sample St-TR-17/1 are approximately homogeneous contents of FeO and TiO2 in individual analysed grains. Predominantly multi-domain grains, rarely pseudo-single-domain and single-domain grains are present in the samples St-156/1, St-TR-17/1, St-TR-21/2 and St-TR-24/2, but predominantly pseudo-single-domain grains and rarely single-domain and multi-domain grains are present in the samples St-102/13, St-TR-13/2 and St-TR-23/2 according to the scanning electron microphotographs. Dominant quantities of oxidized TM-es are present in the samples St-TR-17/1, 17/2. Maghemites and haematites have not been detected by means of the Mössbauer spectroscopy in samples St-TR-17/1, 17/2 (Tab. 2). Evident presence of oxidized TM-es has been identified also at the thermomagnetic curve of the sample St-TR-17/1 (Fig. 5). The main magnetic phase has shown  $T_C \approx 520$  °C, the secon one  $T_C \approx 570$  °C. There is evident decreasing of the  $\kappa$  in the low temperature interval down to liquid nitrogen temperature at the thermomagnetic curve of the sample St-TR-17/1 (Fig. 5). This decreasing of the  $\kappa$  reflects a presence of the ulvospinel in the Fe-Ti grains. No Verwey transition has been detected at the thermomagnetic curve of mentioned samples.

The results of the Thellier method of samples St-TR-17/1, 17/2 have revealed a very expressive alteration of oxidized TMes during heating (or cooling) of a compact rock sample (Fig. 7). The results of the Thellier method of samples of rocks with a presence of oxidized TM-es are very dependent upon their magnetic state before the beginning of the Thellier procedure (Fig. 7), different behaviour of the thermodemagnetizing and the thermomagnetizing curves of samples St-TR-17/1 and 17/2, despite the samples are petrographically the same and that they comming from the same outcrop (a heating and cooling procedures of both samples were also the same). I assume that most of rocks with oxidized TM-es are not supposed to be convenient for a determination of a palaeointensity of the field. We see from both, contents of FeO, TiO2 and a compositions of Fe-Ti oxides of other six samples (Tabs. 1, 2), that the main magnetism carriers are the haematite-ilmenite solid solutions in these rocks. But there are rarely also Fe-Ti grains with cation-deficient titanomagnenite solid solutions in several rocks. Magnetic minerals most of investigated samples are in highly oxidized state (e.g. sample St-156/1 has 75.5 % of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> + +  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, Tab. 2). There is good correspondence between volume content of  $\alpha$ - $Fe_2O_3 + + \gamma - Fe_2O_3$  and the Curie temperature in some samples. E.g. the sample St-102/13 has  $T_C \approx 645 \,^{\circ}C (\alpha - Fe_2O_3 + \gamma - Fe_2O_3)$ 



Figs. 7, 8. Results of the Thellier method.

RMP - remanent magnetic polarization; PTRMP - partial thermoremanent magnetic polarization; nT - nano tesla; x - demagnetization, magnetization of rock sample, respectively; 150 - coordinates of both magnetized and demagnetized values of sample (in nT) at concrete step of temperature.

= 55.5 %); the Curie temperature of the sample St-TR-24/1 is  $T_C \approx 630 \ ^{\circ}C \ (\alpha - Fe_2O_3 + \gamma - Fe_2O_3 = 35.4 \ \%, \text{ other-paramag-}$ netic  $Fe^{2+}$  and  $Fe^{3+}$  ions are in the dublets of the spectrum). The shapes of the thermomagnetic curves of both mentioned samples are very similar, they differ only by their Curie temperatures (Fig. 5). There are other two very similar shapes of thermomagnetic curves of samples St-TR-21/2 and St-TR-23/2 (Fig. 5). They differ also only by their Curie temperatures. Higher Curie temperature of the sample St-TR-21/2 ( $T_C \approx 635$  °C) corresponds to higher content of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> + +  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, comparing it with those in the sample St-TR-23/2 (Fig. 5, Tab. 2), when more, magnetite-like mineral is present (Tab. 2). There is of course also a discrepancy between the Curie temperature of dominant magnetic phase of the sample St-156/1 and a content of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> (Fig. 5, Tab. 2). Contents of haematite and maghemite is about 75.5 % of Fe-Ti oxides, but Tc of dominant phase is  $T_C \approx 570$  °C; second-minor phase has  $T_C \approx 615$ °C. There is no evident Verwey transition (T  $\approx$  -150 °C, detection of a presence of magnetite) at the thermomagnetic curve. The behaviour of the thermomagnetic curve, as well as a Curie temperature of dominant phase are a reflection of dominant content of maghemite in the sample St-156/1.

We see from Figs. 5, 6 (and from other thermomagnetic curves of about 50 samples) that investigated samples od hornblende-biotite andesites have included a highly oxidized phases with a presence of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>. There are present rarely also oxidized TM-es in these rocks. The main magnetism carriers in the hornblende-biotite andesites of the Studenec Formation are supposed to be the haematite-ilmenite solid solutions, in minor content also cation-deficient TM-es and oxidized TM-es.

Very important resolution results from the investigation of magnetic minerals of the hornblende-biotite andesites, considering whole analysed data. Both - maghemite and haematite are not primary but secondary magnetic minerals which originated during alteration of the titanomagnetites.

We can compare the results of the Thellier method of selected rocks with the results of analyses of their magnetic minerals, and to investigate if in all kinds of Fe-Ti oxides the process of alteration follows on by the same way. Alteration of magnetic minerals is supposed to be a time dependent phenomenon. There are samples of rocks with anomalous behaviour of demagnetizing and magnetizing curves at Figs. 7 and 8 (13/1, 16/2, 17/2, 17/1, 23/1), but some samples have shown quite correct results of of the Thellier method (Fig. 8, 21/2, 24/1, 24/2). I suppose that correct results can be expected only for rocks with a stoichiometric magnetic minerals (magnetite, haematite, titanomagnetite), completely exsolved titanomagnetites and completely exsolved haematite-ilmenite solid solutions, all predominantly in multi-domain state. If there are present individual Fe-Ti grains of different degree of their oxidation in the sample, mostly in

Volcanic	Group,		Mean						Mean coordi-				
complex or	Number of		geographical		I°m	D°m	k	a95	nates of the		$\delta_m$	$\delta_p$	
formation	localities,		coordinates						virtual	pole			
	Number		w <sub>a</sub>	10					$\varphi_{p(N)}$	$\lambda_{r(E)}$			
	of s	ample	s	70							M2)		
Allealine	<u> </u>	1	11	48.41	18.65	58.5	20.3	82	5	72.8	133.4	8	8
Alkaime		<b>^</b>		10.11	10.00	00.0	20.0						
basalts and	2	1	7	48.46	18.92	43.0	83.0	541	3	22.9	96.5	4	3
basanites:	3	1	12	48.46	18.94	69.0	23.0	17	14	74.9	84.8	23	20
(Pleistocene,	4	1	2	48.52	19.03	78.6	357.9	384	13	70.5	16.7	24	22
Pliocene)	5	1	4	48.50	19.07	-54.9	222.2	97	26	56.5	116.1	36	26
	6	1	11	48.32	19.03	-60.8	176.7	59	6	83.1	219.9	9	7
Undivided com-	7	3	33	48.62	18.70	-48.4	142.2	3	107	55.4	268.9	141	92
plex-I-stage: Py-	8	9	62	48.45	18.67	-72.6	214.1	4	31	67.8	70.6	54	48
roxene and horn-	9	7	26	48.47	18.84	-75.8	197.5	2	82	72.5	45.7	152	140
blende-pyroxe-	10	5	19	48.59	18.94	37.7	357.6	15	21	62.5	203.7	25	14
ne andesites;	11	7	50	48.42	18.65	80.8	11.0	13	17	65.9	26.6	33	32
intrusive rocks;	12	6	87	48.37	18.97	83.0	31.3	3	46	59.4	33.0	90	88
(Badenian,	13	10	68	48.43	18.79	68.0	3.3	3	32	86.6	56.1	54	45
Sarmatian)	14	25	154	48.46	18.87	76.2	16.7	4	18	72.2	43.3	34	31
Studenec for-	15	3	21	48.42	18.61	-50.4	210.3	15	24	61.3	134.5	33	22
mation: Products	16	8	28	48.46	18.74	-71.3	165.2	5	34	78.3	333.9	59	51
of explosive, and	17	6	58	48.41	18.71	52.3	282.1	2	55	31.5	304.3	76	52
extrusive acti-	18	3	15	48.39	18.81	-50.5	186.1	3	103	72.3	181.5	139	93
vity of horn-	19	3	16	48.39	18.84	62.6	24.4	4	74	72.6	114.3	116	90
blende-biotite	20	5	24	48.43	18.92	-63.3	246.9	5	40	45.4	87.2	62	49
andesites and	21	8	37	48.42	18.92	66.8	325.1	3	35	67.4	304.6	58	48
their various	22	10	68	48.48	18.96	-54.8	205.6	8	18	67.1	134.4	25	18
modifications.	23	6	34	48.54	18.94	-62.1	204.3	9	23	72.4	116.8	36	28
(Badenian, Sar-	24	19	146	48.47	18.95	69.5	8.5	11	10	82.8	15.4	18	15
matian).	25	1	5	48.58	18.90	25.0	322.0	18	11	42.7	253.6	12	6

Table 3: Palaeomagnetic characteristics of volcanic rocks.

 $I_{M}^{o}$ ,  $D_{M}^{o}$  - mean inclination, mean declination of the RMP of rocks of group localities, or locality, respectively; k - precision parameter;  $\alpha_{95}$  - semiangle of cone confidence for P = 0.05;  $\delta_{m}$ ,  $\delta_{p}$  - dimensions of the reliability oval for pole positions.



Fig. 9. Mean directions of the RMP (a), and mean coordinates of the virtual poles (b), of rocks of localites (1 - 6), or groups of localities (7 - 25), according to Tab. 3.

	Age /My/	Polarity /bounda-	Volcanic rocks /locality.com-	K-Ar age
		ries/	plex,formation	1
	2	<	Basanites, 1, Brehv	0.13-0.22
	• ~			0.53±0.16
	• 4 -			
	•6 -	73		
	.8-			
	1.0-	6.07		
	•2 -	_	Baselts, 5-Do-	
	• 4 -	6.42	brá Niva,6-De- víčie	
	.6-			
	.8-	6.77		
	7.0		Basanites, 3-Ky- sihýbel, 2-Kal-	6.77±0.48
	.2 -	<	várie	7.29±0.41
	. 4 -		_	
	.6 -	7.44		
	.8-	7.81	D	
	8.0	<	sihýbeľ,2-Kal-	8.08±0.58
	.2 -	8.18	váris	
		ã		
	15.0-	15.09	Andesites.Stu-	
	.2 -	15.23	denec formation	15.52±0.67
	.4-			
	.6-	<b> </b> ←	denec formation	15.52±0.67
	.8-			
	16.0-	<	Andesites, Undi-	Bodonion
	.2 -	16,20	. Laca complex	
	.4 -	<	Andesites,Undi- vided complex	Badenian
.	16.6 -	16.50		
			normal revensed	polonity
		······································	of the field	porarity

Fig. 10. Correlation among polarity of the RMP, the age of volcanics and the polarity of the modified time-scale according to Harland et al. (1982).

single-domain or pseudo-single-domain state, we can expect very irregular oxidation of individual Fe-Ti grains during heating or cooling and then an acquired partial thermoremanent magnetization of rock sample is supposed to be anomalous. Different heterogeneous content and composition of Fe-Ti oxides in individual grains of sample as well as their grain size can influence the efficiency of alteration processes besides of the duration of haeting of rocks.

### Palaeomagnetic results

A. F. demagnetization tests were mostly applied to reveal a stable components of the RMP of rocks. Thermal tests were also rarely employed. Direction and polarity of stable components of the RMP are presented as a dominant characteristics coordinates of the virtual poles were also computed.

Palaeomagnetic results are presented in Tab. 3 and in Figs. 1, 9, 10. The results of alkaline basalts and basanites have been presented separately for each locality. The results of rocks of individual localities of the Undivided complex, separately also the results of rocks of individual localities of the Studenec Formation have been grouped into the several larger groups (see Tab. 3). (We can remark that there were grouped into the larger groups only the results of rocks of the same polarity of RMP of those localities which are situated very closely to each other). There are basalts of four localities with normal polarity and basalts of two localities with reverse polarity of the RMP (Tab. 3). Rocks of the Undivided complex have shown normal polarity for 5 groups (53 localities) and reverse polarity of the RMP for 3 groups (19 localities). Products of the Studenec Formation of 5 groups (37 localities) have shown normal polarity and 6 groups (35 localities) reverse polarity of the RMP. There is evident mostly extreme dispersion of the RMP among of individual localities in Tab. 3 (see k and  $\alpha_{95}$ ). Nowdays we dont know a cause of such dispersion of the RMP among of individual localities. But we would like to use these palaeomagnetic data for the palaeoreconstruction of the volcanic area, or for the solution of tectonic problems. We dont know of course what influence consists in an alteration of magnetic minerals on the direction of the RMP, what part of a dispersion of RMP is due to tectonic movement of individual volcanic bodies and what can be as a consequence of the dynamics of the geomagnetic field in the past. We can apply preferentially a polarity of the RMP, using also a combination of radiometric ages of rocks with the polarity time-scale according to Harland et al. (1982) for a magnetostratigraphy of studied rocks. (Radiometric ages of rocks have been used according to Konečný et al. 1983).

The following succession of volcanic activity can be actual, according to data in Fig. 10:

- basaltic activity started in the place of the Kalvária (3) and Kysihýbeľ locality (2) during normal geomagnetic field, in the interval 7.81 - 8.18 or 6.77 - 7.44 Ma in the Central Slovakia;

- we suppose that during the geomagnetic field of reversed polarity originated basalts of the locality Dobrá Niva (5) and locality Devíčie (6) in the interval 6.07 - 6.42 Ma, comparing the magnetic properties and magnetic minerals with those of basalts from Podrečany and Podrečany-Tomášovce;

- nepheline basanite lawa flows near Brehy (loc. 1) has only normal polarity of the RMP. The analytical radiometric age of  $0.53 \pm 0.16$  Ma should not be real because flows occur over the younger Riss terrace, the latter corresponding to the interval 0.13 - 0.22 Ma;

- volcanic products of the Undivided complex with normal polarity were originated during normal polarity of the geomagnetic field in the interval 16.2 - 16.5 Ma, rocks of this complex with reverse RMP originated probably in the reversed interval 15.23 - 16.2 Ma;

- during a reversed interval 15.23 - 16.2 Ma originated probably also hornblende-biotite andesites of the reverse polarity RMP of the Studenec Formation;

- hornblende-biotite andesites of the Studenec Formation of the normal polarity of the RMP originated during normal polarity of the geomagnetic field, probably in the interval 15.09 - 15.23 Ma.

#### Conclusion

The present study deals with magnetic minerals and palaeomagnetic data of the alkaline basalts and basanites, andesitic and andesite-porphyry products of the Undivided - Štiavnica stratovolcano complex, and hornblende-biotite andesites of the Studenec Formation of the Central Slovakia. The magnetism carriers in the alkaline basalts and basanites are mostly titanomagnetites of the composition in the range  $Fe_{2,5}TI_{0,5}O_4$ -  $Fe_{2,3}TI_{0,7}O_4$ . Andesites and andesite-porphyry of the Undivided complex are mostly propylitized. They contain mostly magnetite-like magnetic mineral, but cation-deficient titanomagnetites and haematite-ilmenites are rarely also present in these rocks. Most of these minerals are as a consequence of the alteration of the original Fe-Ti oxides. The hornblende-biotite andesites of the Studenec Formation contain mostly haematite-ilmenite solid solutions, in minor content also the cation-deficient titanomagnetites. There are present relatively high contents of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> in these minerals. These two oxides are not primary, but secondary magnetic minerals. It means, that if the stable RMP is linked with the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> constituents the RMP is of the secondary origin.

Preferentially the polarity of the RMP of rocks was applied, using a combination of the radiometric ages of rocks with the polarity time-scale according to Harland et al. (1982), for the magnetostratigraphy of rocks. The directions of the RMP of rocks have not been applied so far for the palaeoreconstruction of the volcanic area, nor for the solution of tectonic problems.

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