Fe-Ti MAGNETIC MINERALS OF BASALTIC ROCKS: A STUDY OF THEIR NATURE AND COMPOSITION

OTO ORLICKÝ[1], FRANTIŠEK CAŇO[2], JOZEF LIPKA[3], ANNA MIHALIKOVÁ[2] and BORIS TOMAN[4]

[1] Geophysical Institute, Slovak Academy of Sciences, Dúbravská cesta 9, 842 24 Bratislava

[2] Dionýz Štúr Institute of Geology, Mlynská dolina 1, 817 04 Bratislava

[3] Department of Nuclear Physics and Technology, Slovak Technical University, Mlynská dolina, 812 19 Bratislava

[4] Geological Institute, Slovak Academy of Sciences, Dúbravská cesta 9, 842 26 Bratislava, Czecho-Slovakia

Abstract: The magnetic Fe-Ti oxides of basaltic rocks of different ages from Central Slovakia, Bohemian Massif, Syria and Nigeria have been studied by electron-microprobe analysis, X-ray powder diffraction, Mössbauer spectroscopy, and by fully automated measurements of the change of magnetic susceptibility (κ) of the samples in the range -196 to 620 °C. The compositions of dominant magnetic phases, also oxidation parameter z of Fe-Ti oxides of basaltic rocks under study have been evaluated and derived, comparing our laboratory data with those published by other authors. A following compositions and oxidation parameters z of Fe-Ti oxides of four selected groups of basaltic rocks are supposed to be actual:
- $Fe_{2.3}Ti_{0.7}O_4$ - $Fe_{2.4}Ti_{0.6}O_4$ ($z \approx 0.15 - 0.35$)
- $Fe_{2.28}Ti_{0.72}O_4$ - $Fe_{2.62}Ti_{0.38}O_4$ ($z \approx 0.12 - 0.32$)
- $Fe_{2.95}Ti_{0.05}O_4$ - Fe_3O_4 (+ Fe_2O_3)

A solution of the nature of Fe-Ti oxides is supposed to be very problematic. In true multi-domain particles of the samples κ should be approximately constant over a rather extended temperature interval. Many authors have concluded that the properties of all compositions are consistent with multi-domain structure. Surprisingly, titanomagnetites with low Curie temperatures exhibit a variation of κ with temperature. These titanomagnetites have shown a characteristic cusps behaviour, which is typical for spin-glasses. It means that actual temperature dependence of κ for coarse-grained high-titanium titanomagnetites is quite different from that, expected for large multi-domain grains.

Key words: basaltic rocks, Fe-Ti oxides, composition, domain structure.

The titanomagnetites (TM) are the most common carries of magnetism in basaltic rocks. They have a variable composition between magnetite (Fe_3O_4) and ulvospinel (Fe_2TiO_4). Both of these minerals have a cubic crystal structure which allows a complete solid solution, the TM-serie ($Fe_{3-x}Ti_xO_4$) to exist between them. The change in composition from magnetite towards ulvospinel is marked by an increase in size and distortion of the cell, also by a change of magnetic and other characteristics. None of common magnetic minerals, including the titanomagnetites and their end members - magnetite and ulvospinel are stable with respect to oxidation by air oxygen. Two main alteration processes determine the state of the Fe-Ti oxides in basaltic rocks. These proceses have been termed deuteric oxidation, which is active between 800 °C and 500 °C during initial cooling, and regional hydrothermal alteration, acting between 0 °C and 300 °C during post-eruptive burial of younger material (Ade-Hall et al. 1971). Both of these processes can produce a multiplicity of new phases (which are supposed to be mutually different in their domain structures) from initially homogeneous TM in basaltic rocks. The detection of these new phases in the TM is supposed to be rather problematic.

We have applied a variety of laboratory techniques to understand the nature, composition and the origin of natural Fe-Ti oxides from diverse basaltic rocks. The rocks of different ages were collected from outcrops of volcanic complexes from Central Slovakia, from Bohemian Massif, from north and north-eastern Nigeria and from Syria. The localities under consideration are drawn on the sketch map in Fig. 1.

Applied laboratory methods and basic results

Petrographical analyses and electron-microprobe analyses (by JEOL microscope) were performed in the laboratories of the Dionýz Štúr Geological Institute, Bratislava. X-ray diffraction analyses by Philips PW 1420 X-ray spectrometer and PW 1150 diffractometer were carried out in the Laboratory of the Geological Institute of the Slovak Academy of Sciences in Bratislava. Mössbauer spectroscopy was performed in the Laboratory of the Nuclear Physics Dept. of Slovak Technical University in Bratislava. The Curie temperatures determinations and the measurements of the change of magnetic susceptibility (κ) of powdered magnetic fraction of rock sample influenced by the temperature, also other measurements of magnetic properties of rocks were carried out in the Laboratory of the Applied Geophysics in Bratislava. Basic data about basaltic rocks are summarized in Tab. 1. All other results are presented in Tabs. 2, 3 and depicted in Figs. 2 - 10.

Microscopy revealed Fe-Ti oxide grains in all investigated samples. The Fe-Ti oxides in the samples Brehy-B2/1, Syr.-12/3, RK-2-1/2, RK-1-2/1 and BP-4-1/1 contain also ilmenite lamellae on the base of microscopic analyses. This mineral originated

probably by high temperature oxidation of TM in these rocks.

The electron microprobe analysis was realised by analyser JEOL, equiped by the EDAX system. The results of chemical composition of Fe-Ti grains of polished rocks are presented in Tab. 2. The content of Cr, Al and Mn was analysed besides of Fe-Ti ions in studied rocks (Cr_2O_3 - 0.01 - 0.81 %, Al_2O_3 - 0.05 - 3.0 %, MnO - 0.11 - 1.34 %). A compositional parameters of TM have been evaluated on the base of Fe/Ti ratio, according to Reidar et al. (1982). They are in the range x = 0.5 - 0.73. Also ilmenite-like lamellae is supposed to be present in several Fe-Ti grains of the sample B2/1, Syr. 12/3, RK-2-1/2, RK-2-1/5A and BP-4-1/1.

Fig. 1. Sketch map of selected areas and localities.

a - Central Slovakia (localities: B-2 - Brehy, Š.V. - Šibeničný vrch Hill, STR.N.101); b - Bohemian Massif (localities: Obr.2 - Obrnice, ret.8 - Retoun, SMR-12 - Smrečiny, Klim.13 - Klimberg); c - Syria (localities: S-3, S-6, S-9, S-12); d - Nigeria (localities: RK-1 - Runka - northern part, RK-2 - Runka - southern part, JP-2 - Jos Plateau, BP-1, BP-2, BP-3, BP-4 - Biu Plateau).

A following procedure has been used to prepare the samples for further applied methods: the samples of basaltic rocks were grinded and powdered in non-magnetic mortar. They were ground under alcohol to prevent oxidation. Magnetic grains were then separated from non-magnetic material with permanent bar magnet. The purity of the sample was verified ordinarily by microscope.

The results of X-ray powdered diffraction analysis are presented in Tab. 2. We see that only a qualitative interpretation of X-ray diagrams were made. But using both, the compositional parameters x of TM, which were evaluated on the base of results of electron microprobe analyses and the knowledges presented by Hamano (1989), also a lattice parameters *"d" of studied TM were derived. Hamano (1989) studied a lattice parameters of synthetic TM with x* values 0.0, 0.3, 0.7 and 1.0 respectively at the temperatures 25 up to 700 °C. He derived an empiric equation for lattice parameter *"d"*

Table 1: Magnetic characteristics of basaltic rocks of different ages (in million years - M.Y.)

Table 1

Designation of locality, number of sample	Geographical coordinates of loc.		Petrograph. description	Age of rock (M.Y.)	$\kappa \times 10^6$ (SI)	NRMP (nT)
	φ_L°	λ_L°				
CENTRAL SLOVAKIA						
STR. N. 101/7	48.451	18.816	Basaltic and.		28 362	3 693
Brehy B2	48.409	18.650	Nepheline basanite	0.5 ± 0.16 by K/Ar	9 025	6 286
Brehy B2/4	"	"	"	0.13 - 0.22	55 125	6 320
Brehy B2/16	"	"	"	according to geol. data	38 650	5 460
Š.V. 2/1	48.593	18.879	Aphanitic basalt.	Panonian	11 900	3 433
Š.V. 2/3	"	"	andesite	age	14 009	17 682
Š.V. 2/4	"	"	"	"	25 981	67 673
Š.V. 2/5	"	"	"	"	25 833	38 112
Š.V. 2/6	"	"	"	"	11 314	24 227
Š.V. 2/10	"	"	. "	"	10 574	35 450
BOHEMIAN MASSIF						
Obrn. 2/1	50.428	13.757	Olivine basalt	Quaternary	46 350	13 767
Klim. 13/2	50.541	15.321	"	to Tertiary age	40 350	4 375
Ret. 8/2	50.600	14.143	Picrite basalt	"	90 813	1 303
Smr. 12/2	50.632	15.279	Olivine basalt	"	23 225	7 807
SYRIA						
S-3/3	35.380	36.160	Spilite	119.83 ± 4.6	58 363	7 866
S-6/3	35.380	36.160	Albitized hyalobasalt	119.85 ± 2.65	72 279	4 952
S-6/5	"	"	Albitized basalt	"	17 500	7 024
S-8/1	35.000	36.260	Albitized hyalobasalt	109.27 ± 4.2	18 727	24 570
S-8/2	"	"	Olivine basalt	99.15 ± 3.66	66 589	5 286
S-12/3	34.770	36.300	Olivine basalt		28 540	4 202
NIGERIA						
RK-1-2/1	12.505	7.186	Nepheline basanite	121.0 ± 2.0	43 508	26 142
RK-1-3/1	"	"	"	"	36 487	19 673
RK-1-6/1a	"	"	"	"	34 422	16 339
RK-2-1/4	"	"	"	163.0 ± 3.0	15 718	59 979
RK-2-1/5a	"	"	"	"	42 275	10 043
RK-2-1/7a	"	"	"	"	44 093	96 456
RK-2-1/8b	"	"	"	"	41 844	178 870
JP-2	9.700	8.467	Olivine basanite	0.8 to 5.0	25 113	5 740
BP-2	10.636	12.152	Olivine basalt	"	28 355	4 390
BP-3	19.600	12.216	"	"	26 317	4 369
BP-4	10.573	12.232	Albitized olivine basalt	"	21 756	7 627

κ - volume magnetic susceptibility (in SI units), NRMP - natural remanent magnetic polarization (in nano-Tesla, nT).

$$d(\mathring{A}) = (8.395 + 8.5 \times 10^5 T + 7.5 \times T^2) + (0.14 - 6.0 \times 10^5 T)x$$

The equation expresses the overall variation of lattice constant with temperature and compositional parameter x. (T is given in °C, the lattice constant is given in Angström). This equation including a graphically evaluated variations of a lattice constant versus x (for a different temperatures) may be used for the determination of chemical composition of titanomagnetites and titanomaghemites of synthetic and natural samples, according to Hamano (1989). The lattice constants of our investigated samples of TM are supposed to be in the range d = 8.455 - 8.489 $\mathring{A}$ *(for x* = 0.3 - 0.73) using the equation according to Hamano (1989), for 20 °C.

X-ray powdered diffraction of several samples in question (from Nigeria) was carried out also in the Laboratory of Applied Physics, Technical University of Denmark, in Lyngby (Lipka et al. 1988). Evaluated unit cells of some samples are following: d = 8.463 $\mathring{A}$ and 8.524 $\mathring{A}$ for samples BP-1 (*x* ≈ *0.5*) and RK-1 (*x* ≈ *0.7*) respectively.

Mössbauer spectroscopy most of samples was realised at

Table 2: The results of X-ray powder diffraction, electron-microprobe analyses and Mössbauer spectroscopy of magnetic minerals of basaltic rocks.

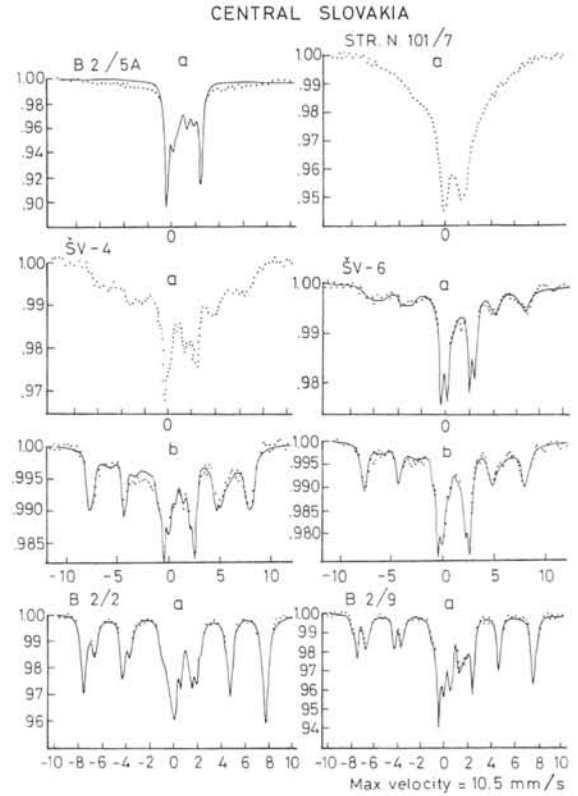| Designation of the sample	X-ray diffraction analyses	Mössbauer spectroscopy	Number of positions	FeO(%) average min. max.	TiO₂(%) average min. max.
				CENTRAL SLOVAKIA	
STR. N. 101/7	$Fe_{3-x}Ti_xO_4$		4	73.06 / 72.49 73.41	25.24 / 24.58 25.78
Brehy B2/1	Fe_3O_4; Fe_2O_3 / Fe_2TiO_5	Fe_3O_4; / $\alpha-Fe_2O_3$ / $\gamma-Fe_2O_3$	4 / 1	80.43 / 70.34 89.34 ; 51.45 / 47.62	18.53 / 9.22 29.47
Brehy B2/4			5	78.41 / 78.02 78.67	20.93 / 20.41 21.57
Brehy B2/16			5	74.92 / 73.48 76.64	23.92 / 22.42 25.63
Sib. vrch S. V. 2/1	Fe_3O_4; $\alpha-Fe_2O_3$		5	67.94 / 66.71 68.47	29.30 / 28.71 30.22
S. V. 3/2	$FeTiO_3$		5	73.81 / 73.23 74.44	24.07 / 23.31 24.63
S. V. 10/2			5	73.73 / 71.73 75.97	24.58 / 23.08 26.16
				BOHEMIAN MASSIF	
Obrnice 2/1	Fe_3O_4; $\alpha-Fe_2O_3$		5	75.37 / 74.81 75.82	23.77 / 23.27 24.37
Klimberg 13/1	Fe_3O_4; Fe_2TiO_5		5	76.49 / 75.36 78.13	20.96 / 20.04 22.37
Retoun 8/2	Fe_3O_4; Fe_2TiO_4		5	73.84 / 72.05 76.05	21.14 / 20.70 21.87
Smrečiny 12/3			5	78.07 / 76.53 79.21	20.20 / 18.90 21.91
				SYRIA	
Syr. 3/8			5	74.45 / 74.07 75.01	24.82 / 24.17 25.20
Syr. 3/11	Fe_3O_4; Fe_2TiO_4 / $\alpha-Fe_2O_3$		5	81.18 / 86.39 87.71	10.39 / 10.16 10.76
Syr. 6/5	Fe_3O_4; $FeTiO_3$	Fe_3O_4; Fe_2TiO_4	5	70.38 / 69.79 70.64	25.53 / 24.27 27.23
Syr. 8/2	Fe_3O_4; Fe_2TiO_4 / Fe_2O_3; $FeTiO_3$	Fe_3O_4; Fe_2TiO_4	5	74.27 / 72.55 75.58	24.58 / 22.50 25.68
Syr. 12/3	Fe_3O_4; Fe_2TiO_4 / $\alpha-Fe_2O_3$	Fe_3O_4 / $\alpha-Fe_2O_3$	4 / 1	72.84 / 68.96 77.33 ; 48.44	25.49 / 22.49 28.76 ; 50.63
				NIGERIA	
RK-2-1/2	$Fe_{3-x}Ti_xO_4$		4 / 1	74.83 / 72.98 77.95 ; 48.06	24.41 / 21.48 25.99 ; 51.60
RK-2-1/5A	$Fe_{3-x}Ti_xO_4$ / $\alpha-Fe_2O_3$; TiO_2 / $FeTiO_3$; Fe_2TiO_5		3 / 2	74.48 / 72.95 75.43 ; 48.72 / 48.45 48.98	24.89 / 23.82 26.61 ; 50.84 / 50.45 51.23
RK-2-1/7	"		5	76.06 / 63.56 85.03	23.63 / 14.97 36.05
JP-2-2/2	Fe_3O_4; $\alpha-Fe_2O_3$ / $FeTiO_3$	Fe_3O_4; $\alpha-Fe_2O_3$ / $\gamma-Fe_2O_3$	5	72.54 / 70.17 75.35	26.01 / 24.16 28.42
BP-2-2/1	$Fe_{3-x}Ti_xO_4$	Fe_3O_4; $FeTiO_3$	5	74.31 / 73.42 74.87	23.35 / 17.38 25.25
BP-3-3/4	$Fe_{3-x}Ti_xO_4$ / $FeTiO_3$; $\alpha-Fe_2O_3$	Fe_3O_4; $\alpha-Fe_2O_3$ / $FeTiO_3$; $\gamma-Fe_2O_3$	5	74.65 / 72.07 76.36	23.25 / 22.72 24.09
BP-4-1-1	$\alpha-Fe_2O_3$ / Fe_3O_4	$\alpha-Fe_2O_3$; Fe_3O_4 / $\gamma-Fe_2O_3$; $FeTiO_3$	4 / 1	89.33 / 87.92 91.77 ; 45.39	8.66 / 6.32 11.39 ; 54.46

Fig. 2. Mössbauer spectra of magnetic Fe-Ti oxides of individual samples of basaltic rocks. **a** - at room temperature; **b** - at the temperature of liquid nitrogen. B2/5A - designation of the locality/number of the sample.
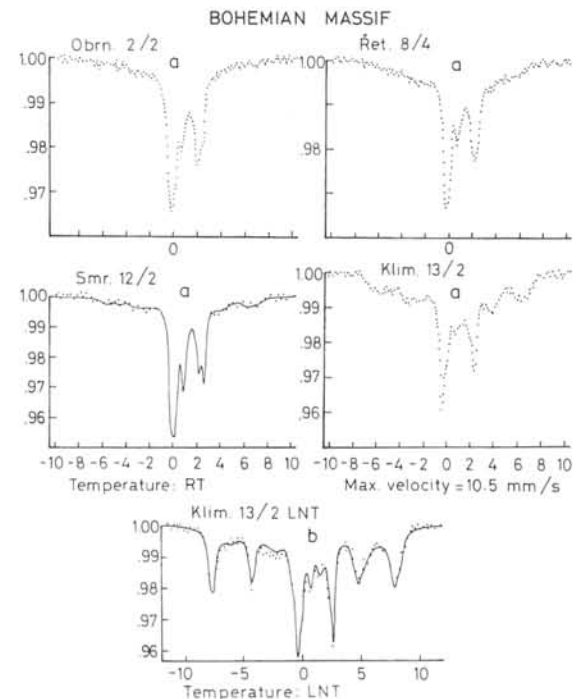
Table 3: The results of Mössbauer spectroscopy; computed compositions of Fe and Fe-Ti oxides of selected basaltic rocks.

Designation of sample	Fe_3O_4 $Fe_{3-x}Ti_xO_4$ %	Field (MA/m)	$\alpha-Fe_2O_3$ $\gamma-Fe_2O_3$ %	Field (MA/m)	Paramagnetic particles Fe^{2+} %	Fe^{3+} %
Brehy B2/2	29.0	38.86				
	34.9	36.35	6.1	40.30	19.0	11.0
Syria 3/12	17.2	37.46				
	9.2	35.92	-	-		
	18.6	34.60			26.3	21.0
	7.7	31.78				
Syria 12/3	16.8	38.75				
	18.0	36.29	13.0	40.48	22.5	29.7
Nigeria JP-2-2/4	22.0	38.88	5.7	40.93		
	12.0	36.74			23.5	20.3
	12.8	35.97	3.7	39.75		
Nigeria BP-2-2/4	9.6	38.58				
	4.0	37.73				
	22.1	35.84	-	-	17.4	37.2
	9.6	32.84				
Nigeria BP-3-3/5	19.7	38.52	7.9	40.83		
	19.6	36.28	5.5	39.60	17.3	17.9
	6.4	35.56	5.0	40.25		
Nigeria BP-4-4/1	23.6	38.85	14.7	40.98	4.9	14.4
	7.2	36.91	35.1	40.29		

Fig. 3. For explanation see Fig. 2 (LNT - liquid nitrogen temperature).

Mössbauer spectroscopy most of samples was realised at room temperature, but several samples were studied also at absorber temperature of liquid nitrogen (-196 °C). The spectra were reco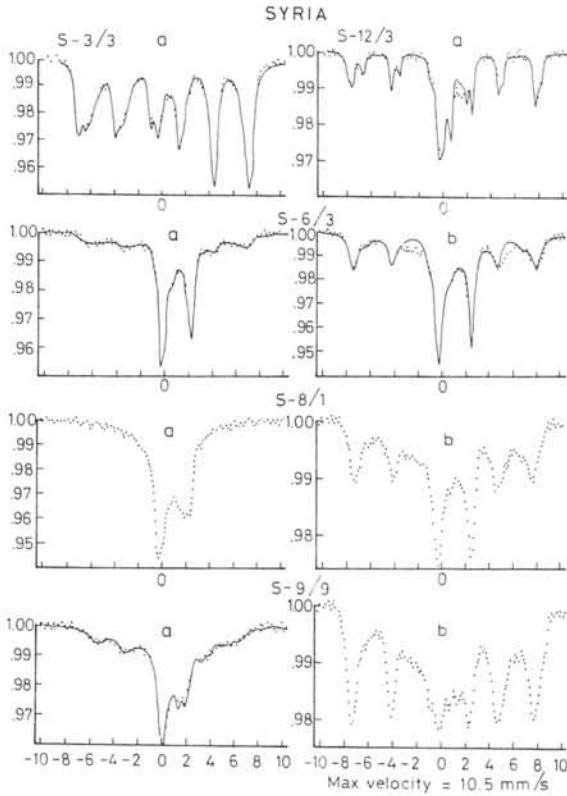rded us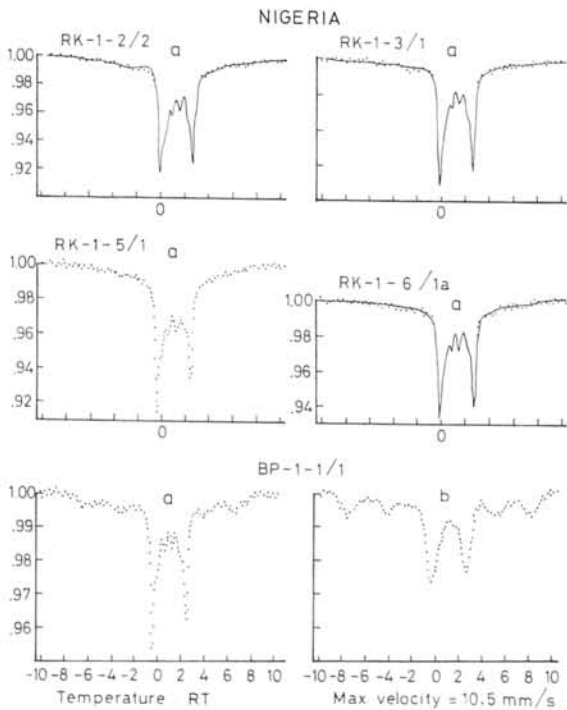ing a constant acceleration spectrometer with a source of 1.5 GBq ^{57}Co in rhodium. Isomer shifts are given relative to that of the α-Fe absorber at 25 °C. Most of Mössbauer spectra were fitted, using a least squares technique.

Mössbauer spectra of studied Fe-Ti oxides are in Figs. 2 - 6. The composition of the titanomagnetites and titanomaghemites is presented in Tabs. 2 and 3. Magnetic components in the spectra most of studied samples of TM - solid solutions at room temperature have shown very broad, non-Lorentzian lines (see examples in Figs. 2 - 6), whereas the spectra of samples B2/2, B2/9, Syr. 3/3, Syr. 12/3, JP-2-2/4, BP-2-2/4, BP-3-3/5, and BP-4-4/1 (Figs. 2, 4, 6) showed characteristic two-sextet pattern of the spectra, which correspond to a presence of magnetite-like magnetic minerals. A broad lines of Mössbauer spectra of analyzed TM-solid solutions, especially an investigated temperature dependece of Mössbauer spectra of several samples (e.g. samples from loc. RK-1 and RK-2) suggested a behaviour which is typical for materials containing superparamagnetic microcrystals with broad distributions in particle size. The results of application of an external magnetic field excluded presence of superparamagnetic particles in studied rocks (Lipka et al. 1988). The problem of correct interpretation of Mössbauer spectra of TM-solid solutions with high content of titanium was solved by measurements of synthetic Fe-Ti oxides of known composition of magnetite and ulvospinel by Banerjee et al. (1967, 1967a). Local variations in hyper-fine field produce very broad lines in the Mössbauer spectra of Fe-Ti inverse spinels. A complications arise due to variable local-site symmetry, caused by the disordering of cations on the octahedral sites of TM-solid solutions, and hence variable hyper-fine field. Quadrupole splitting and isomer shift can be detected on the Mössbauer spectra, according to Banerjee et al. (1967, 1967a). Radhakrishnamurty et al. (1982) have noted that the hyper-fine lines becoming less and less clear as the Ti content increases. They have supposed that it is due to local magnetic inhomogenity.
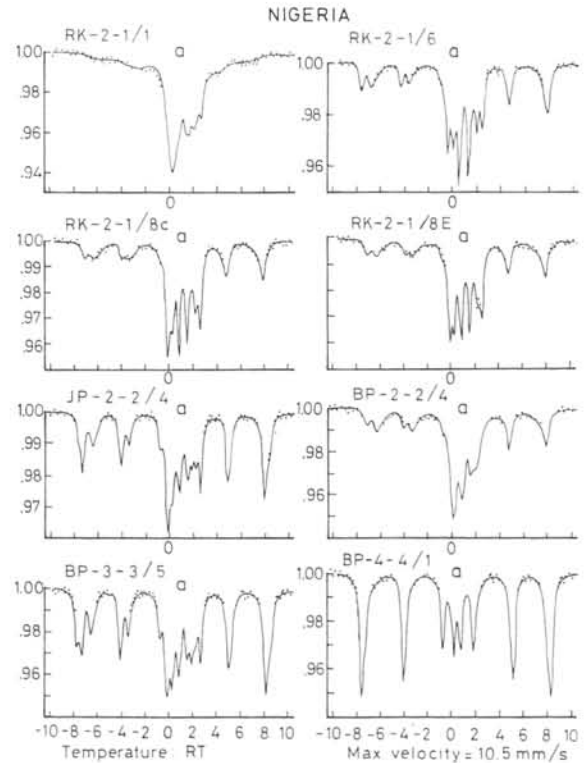

Fig. 4. For example see Fig. 2.

Fig. 5. For example see Fig. 2.

Fig. 6. For explanation see Fig. 2.

troscopy of several samples of Fe-Ti oxides obtained at the temperature of liquid nitrogen (LNT). The six-line components exhibit a magnetic hyper-fine field about 48 Tesla. The relative areas of a paramagnetic components decrease with decreasing temperature, whereas the area of magnetically split components increase. We know that there is present a part of magnetite in TM-solid solutions. Magnetite undergoes a cubic-to-orthorombic crystallographic transition on cooling through -155 °C. At -196 °C, where an electron-hopping between Fe^{2+} and Fe^{3+} ions on the octahedral sites does not occur, so that the observed spectrum is the sum of that from Fe^{2+}, which is broad and similar to that of Fe_2TiO_4, and Fe^{3+}, which is an almost spherically symmetrical ion and gives sharp lines as it is not so sensitive to the random environment (Banerjee et al. 1967). Direct evaluation of a portion of both ulvospinel and magnetite in titanum-rich TM-solid solutions have not been made from the Mössbauer spectra obtained at room and LNT temperatures respectively. We might of course comment that the room temperature paramagnetic Mössbauer spectra with non-Lorentzian lines of several samples are rather similar to those published by Banerjee et al. (1967, 1967a) and by Radhakrishnamurty et al. (1982) for synthetic ulvospinel and for TM with high content of ulvospinel respectively. Only rough estimates of compositional parameter x of TM have been made, comparing our Mössbauer spectra with those given by Bhaduri (1982). They are between $x \approx 0.5$ - 0.7, which seems to be quite in a good agreement with those which were evaluated from electron microprobe results.

Several investigated samples of Fe-Ti oxides of basaltic rocks showed two-sextet pattern of Mössbauer spectra at room temperature (see Tab. 3). The composition of these samples correspond to cation-deficient titanomagnetites (titanomaghemites). Similar composition of magnetic minerals of mentioned basaltic rocks were confirmed also by the results of electron microprobe analyses (higher content of Fe, which is due to high-temperature oxidation of original TM) also by the results of X-ray powder diffraction analyses (see Tab. 2). Rough estimates of compositional parameters x of mentioned samples could also be evaluated by comparing our Mössbauer results with those given by Bhaduri (1982) (e.g. $x < 0.2, x < 0.1$ for samples JP-2 and BP-2 respectively, according to Lipka et al. 1988).

Measurements of magnetic susceptibility (κ) changes of Fe-Ti oxides induced by temperature: A fully automated apparatus for the study of magnetic minerals has been emloyed. The apparatus and detailed procedures of measurements have been described by Orlický (1990). The preselected rate of heating of the sample was 3 °C/min. Most of samples were measured in air at the room temperature from -196 °C to 620 °C and at 20 °C to 620 °C respectively (Figs. 7 - 10, full lines). Several samples were measured in vacuum ($\approx 10^{-4}$ to 10^{-5} Torr) at the temperature from 20 °C to 620 °C (Figs. 7, 8, 10, dashed lines). Some samples (placed into a quartz ampoule; vacuum $\approx 10^{-4}$ to 10^{-5} Torr) were heated up to 850 °C in the furnace and kept there about 2 hours at the constant temperture 850 °C. The samples were then measured after their cooling (Figs. 7, 8, 10; dotted lines). Evidently diverse behaviour of κ-T curves is registered if a heating of the sample takes place with a presence of air oxygen or in vacuum.

Thermomagnetic curves show that natural Fe-Ti oxides contain mostly two or more magnetic phases. We have compared - κ-T curves of dominant magnetic phases of our Fe-Ti oxides with those published by Radhakrishnamurty et al. (1981) for synthetic titanomagnetites of known composition (in a range x = 0.0 - 1.0). This procedure can help us to evaluate a composition of titanomagnetite especially with low Curie temperature (T_C),

which are characterized by very broad, non-Lorentzian Mössbauer's lines. (An interpretation of Mössbauer spectra with non-Lorentzian lines is very problematic.) We have tried to estimate also an oxidation parameter "z" comparing our data (T_C and x) and temperature behaviour of Fe-Ti oxides with those published by Nishitani & Kono (1989) and Özdemir (1987) for synthetic titanomagnetites of known z. The samples of Fe-Ti oxides presented in Figs. 7 - 10 might be grouped by a following fashion (considering their T_C and the shape of κ-T curves):

- The samples B2/11, B2/16, B2/5A, Šib.v.1/1, STR.N.101/7, Obr.2/1, Klim.13/1, Ret.8/1 (Figs. 7, 8; full lines-1) contain dominant magnetic phase of low T_C ($T_C \approx 80$ - 230 °C) and second magnetic one of very low content with $T_C \approx 570$ °C. Derived composition: $Fe_{2.3}Ti_{0.7}O_4$ - $Fe_{2.4}Ti_{0.6}O_4$ ($z = 0.15$ - 0.35).

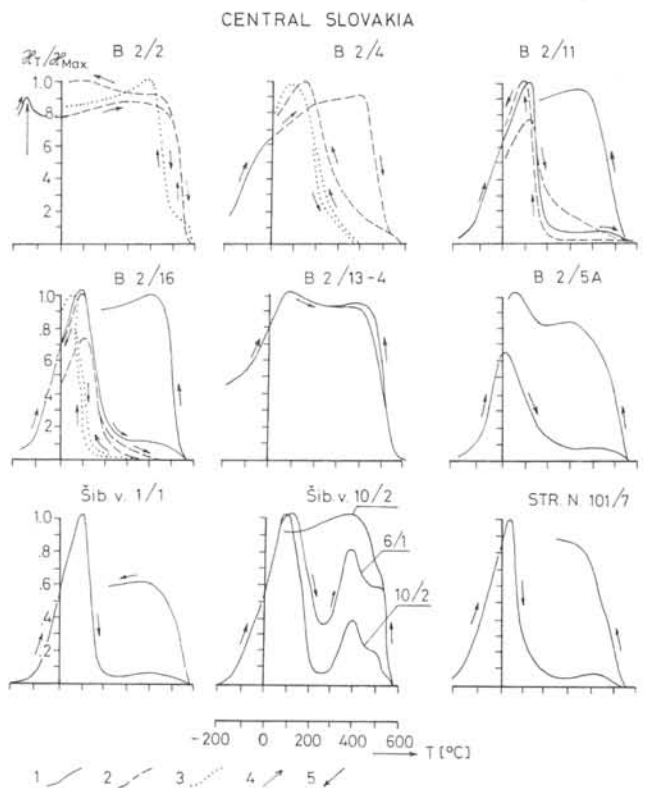- The samples Šib.v.6/1, Šib.v.10/2, Syr.3/8, Syr.6/5, Syr.8/1,

Fig. 7. The variation of magnetic susceptibility (κ) of magnetic Fe-Ti oxides with temperature. B2/2 - designation of the locality/number of the sample.

1 - measurements with the presence of air oxygen; 2 - measurements in vacuum ($\sim 10^{-5}$ Torr); 3 - measurements in vacuum ($\sim 10^{-5}$ Torr) after temperature treatment of the sample at constant temperature 850 °C; 4 - heating of the sample; 5 - cooling of the sample.
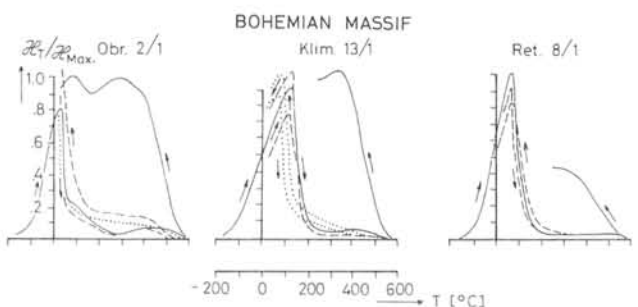

Fig. 8. For example see Fig. 7.

- The samples Šib.v.6/1, Šib.v.10/2, Syr.3/8, Syr.6/5, Syr.8/1, RK-1-6, RK-2-1/4 (Figs. 7, 9, 10; full lines-1) are characterized by magnetic phase of low T_C ($T_C \approx 80 - 260\ °C$), but a second phase has been revealed at $T > 300\ °C$ in these samples. The increasing of κ the sample at $T > 300\ °C$ has been termed as inversion of Fe-Ti oxide according to Özdemir (1987). Derived composition: $Fe_{2.28}Ti_{0.72}O_4 - FW_{2.62}Ti_{0.38}O_4$ ($z \approx 0.12 - 0.32$).

- The samples B2/4, B2/13-4, Syr.3/3, RK-2-1/8, RK-2-1/7 (Figs. 7, 9, 10). The Curie temperature of dominant magnetic phase is about $T_C \approx 520 - 570\ °C$. The magnetic phase of low T_C has not been revealed in these samples. Derived composition: $Fe_{2.95}Ti_{0.05}O_4$.

- The samples B2/2, Syr.12/3, JP-2-2/2, BP-2-2/2 (Figs. 7, 9, 10), have a dominant magnetic phase with $T_C \approx 580\ °C$. There is also registered the Verwey transition temperature about $T \approx -150\ °C$ on the thermomagnetic curves. Derived composition: $Fe_3O_4 (+ Fe_2O_3)$.

Also other magnetic phases have been identified by applied thermomagnetic method besides of described dominant phases, but their composition has not been derived.

The κ-T curve of the sample BP-4-4/2 is anomalous with respect to the samples mentioned above. Besides of cation-deficient titanomagnetites also ilmenito-hematites with $T_C \approx 250\ °C$ are supposed to be present in this sample (Fig. 10, BP-4-4/2).

The compositions of Fe-Ti oxides under study which have been evaluated from the results of electron-microprobe analysis ($Fe_{2.27}Ti_{0.73}O_4 - Fe_{2.5}Ti_{0.5}O_4$), X-ray diffraction analysis and Mössbauer spectroscopy ($Fe_{2.3}Ti_{0.7}O_4 - Fe_{2.5}Ti_{0.5}O_4$) are supposed to be in a good agreement with those derived from thermomagnetic measurements.

Discussion and conclusions

The composition of the titanomagnetites of basaltic rocks under study, their oxidation paramenter z, and in some cases also their lattice parameters have been evaluated from the results of applied diverse laboratory methods. There are presented also basic magnetic characteristics (κ and NRMP) of basaltic rocks of different ages in Tab. 1. We see that very comprehensive information about Fe-Ti oxides might be gained from the results of the measurements of the change of κ of the sample influenced by temperature. It can be seen in Figs. 7 - 10, that the shape of κ - T curves of the titanomagnetites with low T_C is very peculiar. These materials seems to show a characteristic cusps behaviour, which is typical for spin-glasses. Radhakrishnamurty et al. (1981) have discussed also an idea, that for a composition range $x = 0.3$ - 1.0 the titanomagnetites are not affectively in a multi-domain state and their magnetic behaviour in some cases resembles that attributed to spin-glasses. We see that the nature of the titanomagnetites is not clear. Clark & Smidt (1982), Soffel & Appel (1982), Soffel et al. (1982) studied synthetic stoichiometric titanomagnetites in detail. Senanayake & McElhinny (1982) studied properties of natural titanomagnetites of basaltic rocks. They concluded that the properties of all compositions are consistent with multi-domain structure. We know that in true multi-domain particles the magnetic susceptibility should be approximately constant over a rather extended temperature interval according to Stacey & Banerjee (1974). Surprisingly, titanomagnetites with low Curie temperature exhibit a variation of κ with temperature (Figs. 7 - 10). Radhakrishnamurty & Deutsch (1974), Murthy et al. (1976), Radhakrishnamurty et al. (1977, 1978, 1979, 1981), Deutsch & Pätzold (1976, 1980) and Deutsch et al. (1981) have questioned the applicability of the multi-domain model to titanomagnetites having $x > 0.3$, and have proposed an alternative explanation of the properties for these compositions in terms of single-domain and superparamagnetic particles. Lipka et al. (1988) studied the titanomagnetites of some basaltic rocks from Nigeria. The results of Mössbauer spectroscopy with an application of external magnetic field have shown that the samples do not contain small superparamagnetic particles. It can be seen that there is the apparent conflict concerning the nature and domain structure of titanomagnetites. It is evident that the actual temperature dependence of κ for coarse-grained high-titanium titanomagnetites is quite different from that expected for large multi-domain grains.
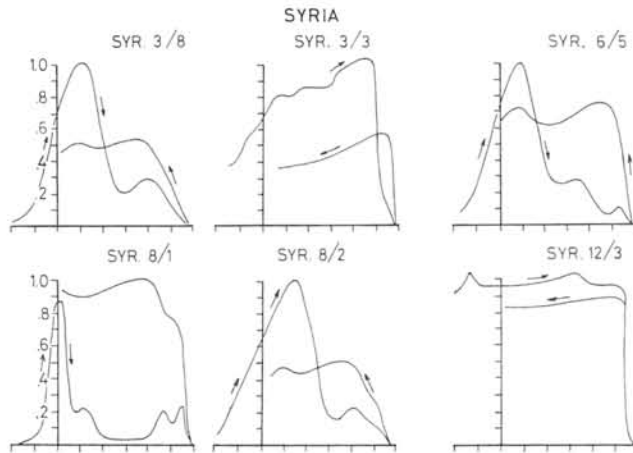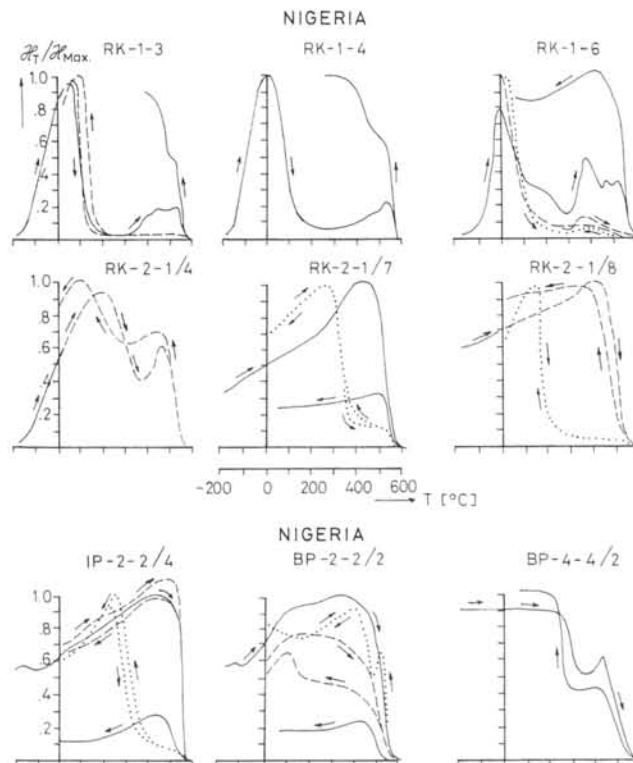

Fig. 9. For example see Fig. 7.

Fig. 10. For example see Fig. 7.

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