

Magnetism and magnetic properties of Ti-rich titanomagnetite and its tendency for alteration in favour of titanomaghemite

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Abstract: The study of the Ti-rich titanomagnetite (Ti-Mt) and the low-temperature oxidized Ti-Mt bearing basalts has been undertaken. High magnetic susceptibility of the Ti-rich Ti-Mt basalts does not correspond to high spontaneous magnetization. The decrease of spontaneous magnetization with increasing content of ulvöspinel is evidenced. The spontaneous magnetization in ferromagnetics and ferrimagnetics originate in the magnetic domains, but the domain structure in the Ti-rich larger Ti-Mt grain sizes is rarely developed. The cause of high magnetic susceptibility of the Ti-rich Ti-Mt stems probably from the molecular field of the two sub-lattice structure of the Ti-Mt.

Alternative explanation: In the low magnetic fields, the permeability of the mixed ferrites increases with increasing temperature and reaches the extreme maximum at the temperature closely below the Curie temperature of material. Similar behaviour have been shown also by the Ti-rich Ti-Mt-es. Rapid decrease of the magnetic crystallographic anisotropy with temperature and the decrease in intensity of the exchange interactions are responsible for this effect. So, the increase of Ti^{4+} ions in the titanomagnetite results in the increase of magnetic susceptibility of the Ti-rich Ti-Mt-es.

The problem of the extremely low magnetic susceptibility in the basalts with low-temperature oxidized phase consists in the following: along with the low-temperature oxidation of Fe^{2+} to Fe^{3+} ion and the formation of vacancies in creating titanomaghemite, the rearrangement of magnetic moments in initial Ti-rich Ti-Mt has taken place. The initial state had a more anti-ferromagnetic arrangement with high content of ulvöspinel of high non-collinearity. High magnetism of the initial Ti-Mt was due to the action of the molecular field. During the above-mentioned process this original state was broken down, and the magnetic susceptibility was rapidly decreased. A completely new ferrimagnetic arrangement of magnetic moments of the sub-lattices has been established in the titanomaghemite.

Key words: Ti-rich titanomagnetites, high magnetic susceptibility, basaltic rocks

1. Introduction

It has been proposed that the ionic reordering in Fe-Ti ferrimagnetics is a dominant source of the reversed RM in basaltic rocks (*Orlický, 2009*). Because the titanomagnetites (Ti-Mt-es) are the dominant carriers of magnetic properties in basalts I present some additional results concerning their magnetic behaviour when they are in the Ti-rich state or if they contain the so-called low-temperature oxidized Fe-Ti phase in the rocks. Many articles have been published so far about the Ti-Mt solid solutions of the sub-continental and the sub-marine basalts. The basaltic layer in sub-marine basalts is the dominant source of the marine magnetic anomalies, because the Ti-Mt-es are either in non-oxidized state, with a high content of Ti, they possess relatively high magnetic susceptibility (κ), or in more oxidized state, they possess a lower κ . Some authors support an idea that in sub-marine basalts the high κ is due to both a larger grain size and a higher content of magnetic minerals (*Prévot and Lecaille, 1979*). These authors have not given any explanation of a high κ of volcanics in an unusual magnetic source in Ti-rich Ti-Mt-es. I tried to account for this problem in the previous paper (*Orlický, 2009*), but it is suitable to expand the previous knowledge by additional results. In this paper the results of the measurements of the artificial and natural Fe and Fe-Ti oxides are presented to describe magnetic properties of Fe-Ti oxides in more exhaustive form.

2. Experimental results

The sub-areal (continental) and sub-marine basalts of varying age have been frequently studied. In paleomagnetic practice the dominant characteristics of rocks have been the NRM, the stability, the direction and an origin of RM of rocks. The volume magnetic susceptibility κ and its relation to the nature of RM of rocks was considered as not so important parameter, and it has been frequently omitted in the paleomagnetic studies. Lately a composition of Ti-Mt-es was frequently studied also. In *Johnson and Hall (1978)*, the average value of a compositional parameter for Ti-Mt-es is given as $x = 0.62 \pm 0.05$ (in the range of $x = 0.54$ to 0.67). The average value x was derived from 397 individual analyses of basaltic samples from Nazca Plate,

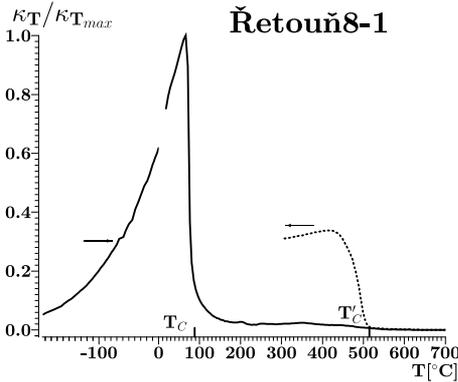
Central Pacific Basin, Mid-Atlantic Ridge, Guadalupe Site, Norwegian Sea, Caribbean Sea, Mid-Atlantic Ridge at 23° N. Paradoxically to the content and the relation of magnetic (magnetite) and non-magnetic (ulvöspinel) constituents in the Ti-Mt solid solutions, the value of κ increases with increasing non-magnetic ulvöspinel in basalts.

From my results (*Orlický, 2002, 2004, 2006, 2008, 2009*) and a new laboratory data, it follows that some samples of basalts have reached very high κ . E.g., one sample from lava neck of Šomoška locality ($\varphi = 48.170^\circ$, $\lambda = 19.842^\circ$) from Southern Slovakia volcanic field: $\kappa = 76\,000 \times 10^{-6}$ SI units and the pycrite basalt sample from Řetoun locality ($\varphi = 50.600^\circ$, $\lambda = 14.143^\circ$) from Bohemian Massif has $\kappa = 84\,750 \times 10^{-6}$ SI units. Except for continental basalts, the high values of κ were detected also in the Ti-rich Ti-Mt bearing sub-marine basalts from the Deep Sea Drilling Program (DSDP) and the Ocean Drilling Project (ODP). Among other basaltic samples of the basalt samples from Hole 504B κ was in the range $72\,848 - 76\,616 \times 10^{-6}$ SI units (*Furuta and Levi, 1989*). Five of 24 samples of low T_C of Ti-rich Ti-Mt basalt samples have the values of κ in the range $65\,300$ to $121\,830 \times 10^{-6}$ SI units (*Johnson and Hall, 1978*). Four of 8 samples of massive plagioclase olivine phyrlic basalts of the Hole 896B (5° N, 84° W) have reached the values of κ in the range of $71\,800 - 103\,700 \times 10^{-6}$ SI units (*Stokking et al., 1996*). 17 samples of the Ti-rich Ti-Mt massive basalts of the Hole 797 from the Japan Sea have reached the mean value of $\kappa = 82\,361$, with a several samples of extreme κ of 90 000, up to $154\,110 \times 10^{-6}$ SI units (*Vigliotti, 1992*).

According to *Hunt et al. (1995)* the basalts have reached the values of volume κ in the range of $250 - 180\,000 \times 10^{-6}$ SI units (the high values of κ belong probably into the group of Ti-rich Ti-Mt-es). We see that the Ti-rich Ti-Mt bearing of low T_C unoxidized basalts have reached extremely high values of volume κ , compared with those of high T_C low-temperature oxidized basalts. The higher content of ulvöspinel in Ti-rich T-Mt-es, the higher value of magnetic susceptibility. If we take into account the individual constituents, the ulvöspinel and the magnetite, the situation is as follows: Ulvöspinel (Fe_2TiO_4) has a Mass susceptibility $\chi = 4\,800 \times 10^{-3} \text{ m}^3\text{kg}^{-1}$, whereas magnetite Fe_3O_4 has χ of $1\,000\,000 - 5\,700\,000 \times 10^{-3} \text{ m}^3\text{kg}^{-1}$, which is 208 to 1 188 times more than that ulvöspinel. We deduce, that high susceptibility of Ti-rich Ti-Mt has a more complex and strange principle.

The temperature dependence of κ of Ti-rich Ti-Mt-es

In Fig. 1 the thermomagnetic curve of Ti-rich Ti-Mt ($x = 0.62; z = 0.2$) of the sample Řetoun 8-1, from Bohhemian Massif ($\varphi = 50.600^\circ, \lambda = 14.143^\circ$; some samples have reached a value of $\kappa = 84750 \times 10^{-6}$ SI units) is shown. We see that there is a rapid increase of κ from -196°C to higher temperatures up to the maximum, and just below the Curie point κ has abruptly fallen down ($T_C = 90^\circ\text{C}$). All samples with $x \geq 0.6$, with low Curie temperature and no low-temperature oxidized phase have shown a similar behaviour like in Fig. 1. But in Fig. 2 there is a thermal behaviour of the low-temperature oxidized Ti-Mt bearing basaltic andesite sample of low Curie temperature of about 160°C ($x = 0.6; z = 0.46$) from central Slovakia volcanic field ($\varphi = 48.451^\circ, \lambda = 18.816^\circ$) with evident increase of



Gr.s.	TiO ₂ (%)	FeO (%)
50	21.20	73.00
8	21.87	72.05
7	20.95	73.85
7	20.99	74.26
6	20.70	76.05

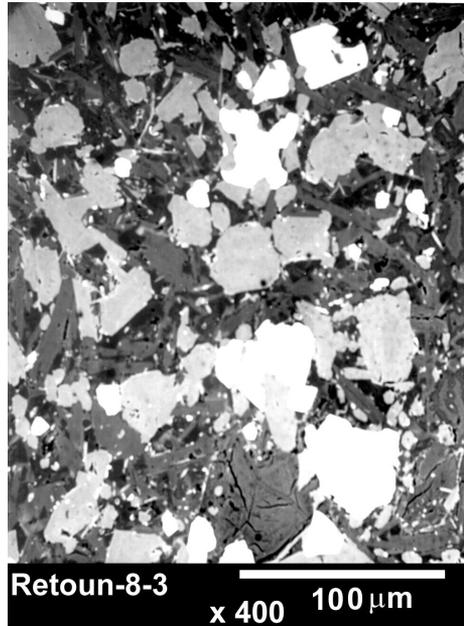


Fig. 1. Thermomagnetic curve, results of microprobe analyses and microphotographs of Fe-Ti grains (mostly of light, or light-dark tint on the image) of the sample Retoun8-1 (8-3); T_C, T'_C – Curie temperatures during heating and cooling (T') respectively of the sample; $\kappa_T / \kappa_{T_{max}}$ – magnetic susceptibility at temperature T , and maximum magnetic susceptibility ($\kappa_{T_{max}}$). Gr.s. – grain size in μm .

magnetic susceptibility of about 15% during heating at constant temperature about 312 °C (measurements were realized in one minute intervals over 60 minutes). This low-temperature oxidized Ti-Mt bearing basaltic andesite has a magnetic susceptibility only of $28\,300 \times 10^{-6}$ SI units. The samples of non-oxidized Ti-rich Ti-Mt bearing volcanics, without a low-temperature oxidized phase, have not shown the behaviour in Fig. 2.

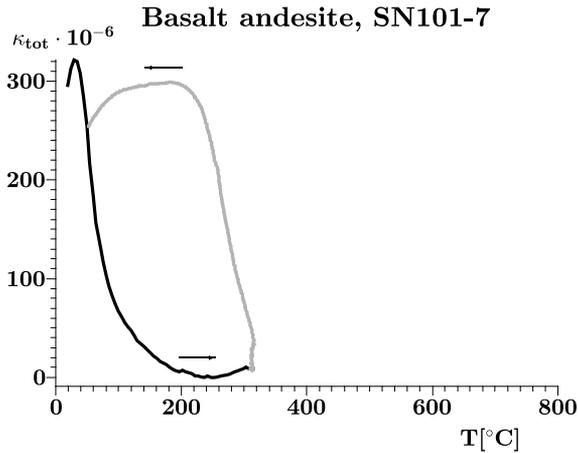


Fig. 2. The change of magnetic susceptibility of low-temperature oxidized titanomagnetite of basaltic andesite sample SN101-7 during heating on air in the interval from laboratory temperature to 312 °C; a measurement of the change of κ at constant temperature during 60 min was performed, and then during cooling to about 45 °C. The basaltic andesite sample comes from central Slovakia volcanic field ($\varphi = 48.451^\circ$, $\lambda = 18.816^\circ$); κ_{tot} – total magnetic susceptibility.

In order to detect the differences in magnetic properties and magnetic behaviour of these two types of Ti-rich Ti-Mt bearing volcanics, I realized a thermal induction of partial thermoremanent magnetization (PTRM) of samples. This was realized in normally oriented magnetic field of intensity $H = 48 \mu\text{T}$ at discrete temperatures (as described in *Orlický, 2009*).

We see that the Řetoun-3 pycritic basalt sample has nearly 3 times higher value of κ than the basaltic andesite sample SN101-7. The former sample does not contain the low-temperature oxidized phase, while the later one contains also the low-temperature oxidized Fe-Ti phase. From Fig. 3 it is evident that in both samples there is an expressive decrease of PTRM, in

An induction of PTRM of compact basaltic samples, Figs. 3, 4, and the artificially prepared magnetite and maghemite samples, Fig. 5

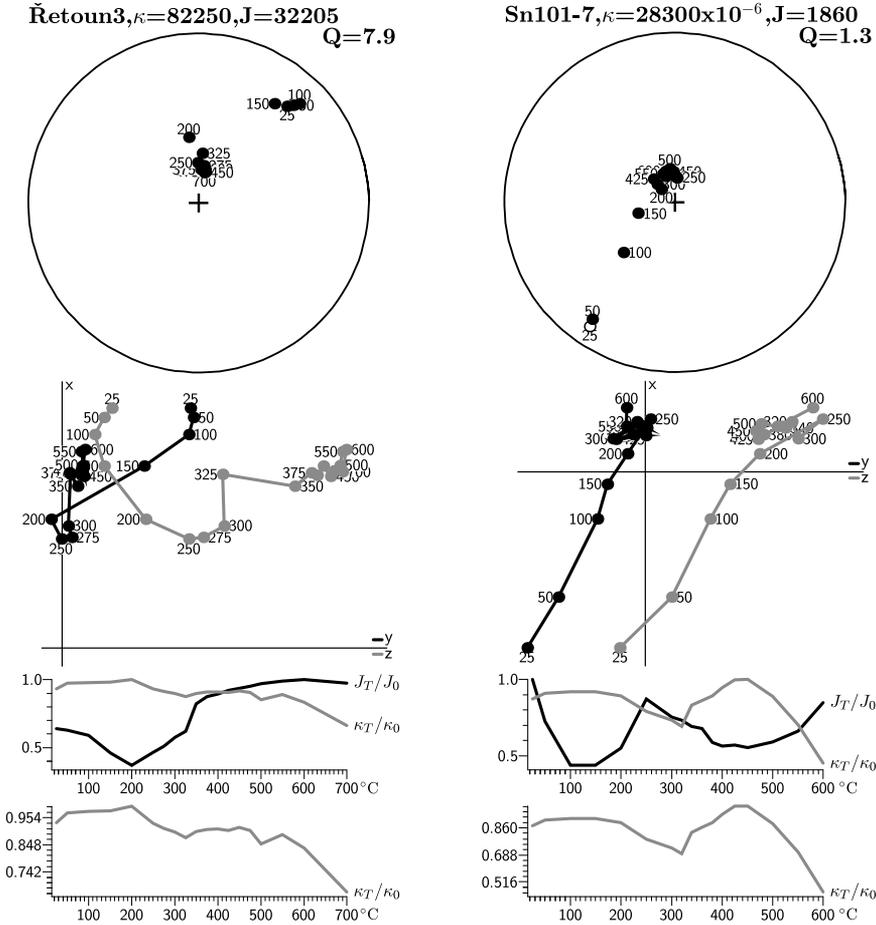


Fig. 3. Thermal induction of PTRM and the change of magnetic susceptibility at different temperatures for sample Retoun-3 (pyritic basalt with normal polarity of RM) and the sample SN101-7 (basaltic andesite with reversed polarity of RM). Zijderveld diagrams and stereographic projections; ● (○) – positive (negative) polarity of RM; κ - magnetic susceptibility (above the pictures: the κ is $\times 10^{-6}$ SI units, and remanent magnetization J is in nano Tesla (nT)); κ_T at T, κ_0 – at 25 °C; J_T (J_0) – remanent magnetization at T and at 25 °C, respectively; Q – Koenigsberger ratio. The separate curve at the bottom represents the change of κ with temperature for the respective sample.

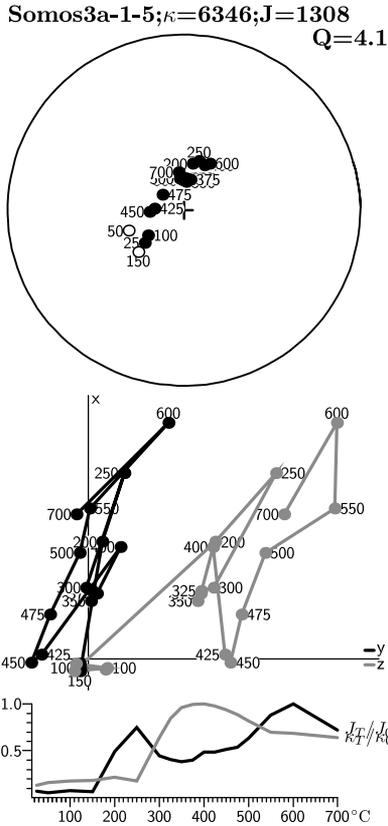


Fig. 4. Thermal induction of PTRM and the change of magnetic susceptibility at different temperatures for the intensely altered Fe-Ti minerals of the basalt sample Šomoška3a1-5 with a reversed polarity of RM. Zijderveld diagrams and stereographic projections; for the explanation of symbols see Fig. 3.

the intervals 25–200 and 25–120 °C, respectively. This effect is not only due to the presence of high portion of viscous remanent magnetization (VRM) in total NRM, but mainly due to low magnetic stability of RM in the mentioned temperature intervals. In the higher temperature intervals the behaviour of PTRM of samples is different. In the sample of Řetoun-3 pyritic basalt there is an increase of PTRM of about 1.5 times of its original value from 200 °C to 350 °C and then follows a gradual increase of PTRM up to 700 °C. From Fig. 3 it is evident that there is a gradual decrease of κ (with

some fluctuations) in the mentioned interval. In the nature the Ti-rich Ti-Mt bearing volcanics of such behaviour will acquire a very high values of PTRM and a relatively stable positive direction of RM. The decrease of PTRM of the basaltic andesite of the Sn101-7 sample is about 0.4 times its original value in the interval 25 to 110 °C (Fig. 3). From 110 °C to about 250 °C there is a sharp increase of PTRM and then a decrease of PTRM from 250 °C to 400 – 450 °C, and then an increase of PTRM up to 600 °C. The change of magnetic susceptibility of this sample is the following: in the interval 25 to 200 °C it is effectively constant, then it gradually decreases to 320 °C, then it abruptly starts to increase to 450 °C, where it reaches a maximum. From this value it gradually decreases down to 600 °C (Fig. 3). The Ti-Mt bearing volcanics, with low-temperature oxidized phase present and with above-described behaviour of PTRM and κ with temperature, will acquire a reversed RM by self-reversal mechanism in the nature. This self-reversal reversed RM is of the chemical – CRM origin with a relatively low magnetic and directional stability. During the thermal tests in a fully compensated external field it is removed in the interval up to 450 °C.

The sample Šomoška3a1-5 contains the low Curie temperature Ti-Mt phase with Curie temperature of $T_C = 220$ °C, the inversion phase with T_{inv} of 365 °C and the third phase with T_C of 580 °C. The samples contain highly oxidized Ti-Mt-es (titanomaghemites, Ti-Mgh-tes). We can infer that the maghemitization taken place in these basalts. The degree of oxidation z of individual samples is in the range from 0.45 to more than 0.6 (it has been derived from Curie temperatures of individual samples). A volume magnetic susceptibility of individual samples from the locality in question has reached a value from 2855 to about $22\,650 \times 10^{-6}$ SI units. This is significantly different comparing it with that of unoxidized Ti-rich Ti-Mt-es. The dependence of the acquired PTRM and magnetic susceptibility on temperature is similar to those of the above-described basaltic andesite sample Sn101-7 in Fig. 3. Particularly important is a sharp increase of κ from about 250 °C to 400 °C.

The cause of very low values of κ in Ti-Mgh bearing basalts

In order to explain the different behaviour of non oxidized Ti-rich Ti-Mt and that of maghemitized, low-temperature oxidized Ti-Mt bearing basalts, I studied the relatively poor magnetite, separated from the silica diorite

porphyry of the borehole KON-1, from central Slovakia volcanic field and the synthetic maghemite, which was produced in the Přerov's laboratory in Czech Republic. The detailed description, data concerning the Curie temperatures and Mössbauer spectra of these Fe-oxides are presented in *Orlický (1988)*.

In Fig. 5. a gradual decrease of PTRM for magnetite from 25 to 300 °C is detected. From 300 to 350 °C there is a very sharp decrease of PTRM to the level of about 0.1 of its initial value of NRM. Over 350° to 700° there are only neglectable changes of PTRM. There is only a slight increase of κ from 25 to 350° and then there is an abrupt decrease of κ to 400° and over 400 to 700° there is only a gradual decrease of κ . This effect corresponds to maghemitization of magnetite. These changes can take place usually over 150°, depending on a purity of magnetite and the presence of some nuclei of maghemite. Generally maghemite is formed by the low-temperature (150 – 250 °C) oxidation of magnetite. Because of the instability, single crystal larger than 1 μm can rarely be synthesized or found in nature. The oxidation is achieved by a topotactic process, in which because anionic (oxygen) structure is left unchanged; the Fe^{2+} ions diffuse to the surface of the grains, oxidize and form Fe^{3+} ions, leaving lattice vacancies. If the diffusion can proceed unhindered, one microcrystal of magnetite will be completely transformed to maghemite without an additional new crystal of maghemite being formed (*Stacey and Banerjee, 1974*). The described process of oxidation is similar also for the Ti-Mt, except for the presence of the Ti ion in this mineral. We see that the PTRM of maghemite sample is very stable in the interval from 25 to 550 °C and then falls down very sharply. In the same way κ is changed also with temperature (Fig. 5). No extraordinary increase of κ in both artificially prepared samples appeared in the interval of 300 to 450°, which is typical for the Ti-Mgh-tes – low-temperature oxidized Ti-Mt-es. We can say that the presence of Ti^{4+} ion in the Ti-Mt is decisive and it extremely influences the magnetic behaviour of the Ti-rich Ti-Mt and that of the Ti-Mgh.

From the thermomagnetic curve in Fig. 4 we see that this basalt sample contains partly oxidized Ti-Mt phase of $T_C \approx 220 - 230$ °C and the second magnetic phase with a so-called inversion temperature. This starts from about 360 to 370 °C and reaches maximum peak of κ at about 465 to 530 °C during continual heating of the sample in air. This inversion phase

has usually achieved the Curie temperature at about 580 °C. A similar behaviour of κ can to seen for parallel samples in Fig. 2 during step-wise ther-

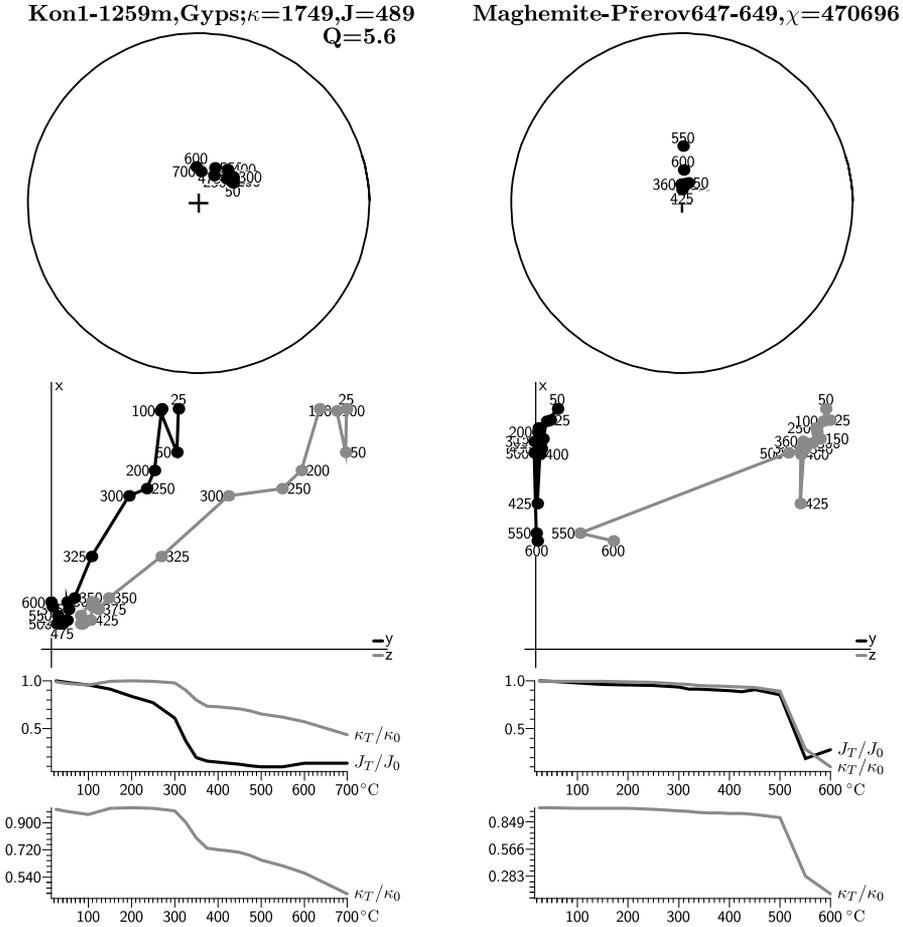


Fig. 5. Thermal inducing of PTRM and the change of magnetic susceptibility at different temperatures of artificially prepared samples of magnetite (separated magnetic fraction and fixed in gypsum) from silica diorite porphyry of borehole Kon-1, from the depth of 1259 m, and synthetic maghemite produced in the laboratory in Přerov and then fixed in gypsum. Zijderveld diagrams and stereographic projections; χ represents the mass magnetic susceptibility of synthesized maghemite in $10^{-3} \text{m}^3 \text{kg}^{-1}$. The separated curve at the bottom for the respective samples represents the change of κ with temperature with overtopped relation. Explanation of other symbols see in Fig. 3.

mal treatment of the sample Šom.3A2-2, also for the induction of PTRM of the sample Somos3a-1-5. A reflection of the presence of an inversion phase started in both samples with the increase of κ in the interval from approximately 360 °C. But while the maximum κ is about 530 °C for the sample Šom.3A2-2 during thermal treatment, the maximum of κ about 400 °C was achieved for the Somos3a-1-5 during induction of PTRM of the sample. This difference in maximum κ is associated with the degree of oxidation of the samples. As was commented above the temperature at the maximum of κ coincided with the minimum of the induced PTRM, which was influenced by a self-reversed component acquired during thermal treatment.

X-ray powder diffraction analysis of the oxidized Ti-Mt Ti-Mgh bearing basalt of the Šomoška 3a-1-6 sample was performed by Dr. Dobročka from the Electrotechnical Institute of the Slovak Academy of Sciences Bratislava, Slovakia (*Orlický et al., 2008*). The results of the analysis are: hematite – α -Fe₂O₃ with $a = 5.036 \text{ \AA}$, ilmenite FeTiO₃ (both of rhombohedral structure); maghemite- γ -Fe₂O₃ $a = 8.35150 \text{ \AA}$, titanomagnetite Fe_{2.4}Ti_{0.6}O₄ (both of cubic structure); pseudorutile Fe₂Ti₃O₉ $a = 2.86670 \text{ \AA}$ (hexagonal structure).

Shortly about the Ti-rich titanomagnetites

The titanomagnetites are the ionic compounds in which the iron ions (Fe³⁺ and Fe²⁺) carry net magnetizations (spin moments) proportional to the number of the unpaired electron spins on each iron (Banerjee in *Lindsley, 1991*). The Ti-rich Ti-Mt-es do not behave as completely magnetically ordered magnetic minerals. They are composed from magnetite, Fe₃O₄(Fe³⁺[Fe²⁺, Fe³⁺]O₄²⁻) and ulvöspinel, Fe₂TiO₄(Fe²⁺[Fe²⁺, Ti⁴⁺]O₄²⁻). Both members of the titanomagnetite have the inverse spinel structure. While the magnetite is a ferrimagnetic mineral, the ulvöspinel, as a second end member of the Ti-Mt has an antiferromagnetic order, with a Curie temperature $T_C \approx -153 \text{ °C}$, according to *Hunt et al. (1995)* (which is a critical temperature for a second order transition). Ulvöspinel has Fe²⁺ ions in both the tetrahedral A and octahedral B sites (see above in square brackets, and in Fig. 6 for the two models). On cooling to temperature below liquid nitrogen temperature (–196 °C), lattice distortions set in which have been variously identified as Jahn-Teller distortion of tetrahedral Fe²⁺ and as the effect of unquenched orbital angular momentum of octahedral

Fe^{2+} . The chief effect of this distortion is a phenomenally large magnetic anisotropy. Ulvöspinel has a non-collinear structure. It has been noted above that at low temperature the ulvöspinel shows a highly anisotropic magnetization. Magnetocrystalline anisotropy and magnetostriction arise from spin-orbit coupling of ionic magnetic moments, resulting in crystallographically controlled easy and hard direction magnetization (*Hunt et al., 1995*). If this resulted from octahedral Fe^{2+} ions, the preferred (or easy) alignment of individual Fe^{2+} spins would be along the cubic [111] axis while the tetrahedral Fe^{2+} spins would point along [100] axis, the easy axis for the single crystal as a whole. Furthermore, since a negative intra-sublattice superexchange interaction is present in the B sites of spinel, one can postulate a triangular arrangement in a magnetic cell in which two tetrahedral Fe^{2+} spins will point along [100] while the opposed two octahedral Fe^{2+} will form a slightly misaligned v-shaped pair. This arrangement will result in a net weak magnetization along [100] axis of the crystal.

In order to explain a source of high κ of Ti-rich Ti-Mt-es we can apply the Akimoto and Néel-Chevallier models of a probable distribution of Fe and Ti ions in titanomagnetite – $\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$ (Fig. 6). We see that non-magnetic Ti^{4+} ions are placed only in octahedral B sublattice in both models within the whole 0.0 to 1.0 x - compositional parameter interval. In the scheme the content of Fe^{2+} Fe^{3+} ions is following: According to Akimoto model (up) the content of an anisotropic Fe^{2+} ($3d^6$) ion with a magnetic moment of $4\mu_B$ (Bohr Magnetons) in B site is constant in the whole x composition interval and 1/2 of the whole magnetic moment is compensated with that in the A site (partly ferrimagnetic order of A regarding to B positions). But there is no contribution of this moment to κ with increasing of x in the Ti-Mt. The magnetic Fe^{3+} ($3d^5$) with $5\mu_B$ decrease by the same way with x for both A and B positions. Due to antiparallel orientation of A and B magnetic moments, the resultant moment is of zero value. There is also no contribution to κ with increasing of x in the Ti-Mt. According to Néel-Chevallier model (down) the Fe^{3+} ($3d^5$) ion with the moment of $5\mu_B$ is distributed in B and A positions but its resultant content decreases with x composition interval. For Fe^{2+} ($3d^6$) ion and magnetic moment of $4\mu_B$ increases with x up to $x = 0.5$ in B position, but from this content then is present also in A position and partly compensated the resultant moment of the whole crystalline lattice of the Ti-Mt. Generally, there is no contribution

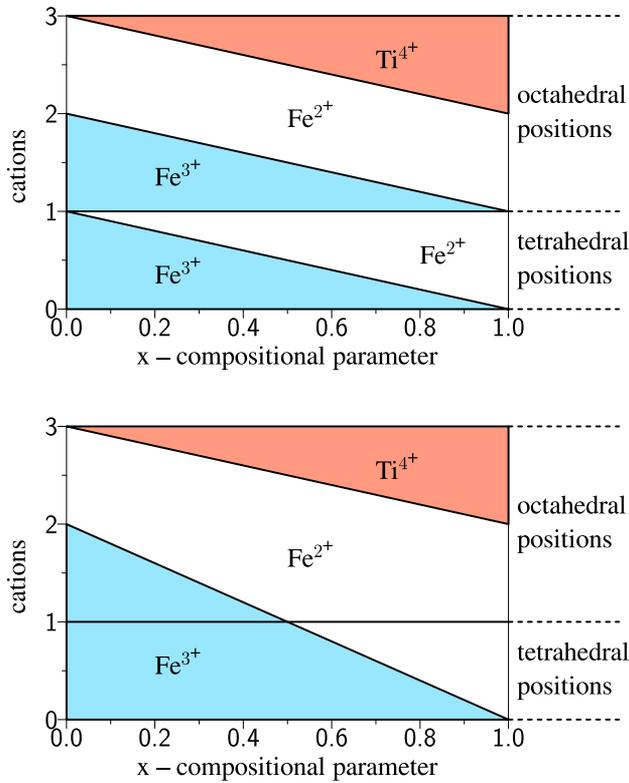


Fig. 6. Scheme of the distribution of Fe and Ti cations in the crystalline tetrahedral (A) and octahedral (B) sublattices of the titanomagnetite for the Akimoto (up) and the Néel-Chevallier (bottom) models (scheme was taken from *Kropáček, 1986*).

of magnetic moments of the Fe^{3+} ion to the increase of κ with increasing of x composition in the Ti-Mt. We need to find another source which makes κ to increase with increasing of the ulvöspinel (or Ti^{4+}) content in the Ti-Mt. Very important is a fact that the spontaneous magnetization of Ti-Mt decreases with increase of content of ulvöspinel. If it is extrapolated to 0° K of the Ti-Mt decreases with increasing of content of Ti and for $\text{Ti} = 0.7$ is only $0.75 \mu_B$ (Bohr Magnetons), while for the magnetite (Fe_3O_4) it is $4 \mu_B$ per molecule and that for $0.2 \leq x \leq 0.8$ the extra Fe^{2+} ions resulting from Ti substitution enter A-sites preferentially, leaving Fe^{2+} content of B-sites unchanged if extrapolated to 0° K (*Stacey and Banerjee, 1974*).

3. Discussion and conclusions

Own experimental results and those previously published have shown that the high value of magnetic susceptibility of the Ti-rich titanomagnetites cannot be ascribed to high spontaneous magnetization, because there is evident decrease of spontaneous magnetization with increase of content of ulvöspinel. Moreover, the previous results have shown that the domain structure in the Ti-rich larger Ti-Mt grain sizes is not well developed. According to theory, a source of the spontaneous magnetization of ferromagnetic or ferrimagnetic minerals is assumed to be in the magnetic domains (each of the domain is spontaneously magnetized to saturation by virtue of a strong molecular field, according to *Stacey and Banerjee, 1974*). If the domains are missing, no spontaneous magnetization can be created.

Explanation based on the change of the magnetic crystallographic anisotropy with temperature

According to *Brož (1962)*, in the low magnetic fields, the permeability (μ) of the mixed ferrites (the solid solutions of the inverse ferrites), increases with increasing of temperature and it reaches the extreme maximum at the temperature closely to that of the Curie temperature. Such behaviour have been detected also in the Ti-rich Ti-Mt-es. This effect is due to the rapid decrease of the magnetic crystallographic anisotropy with temperature. With the increasing of divalent ions in the ferrite, intensity of the exchange interactions decreases, which results in a decrease of the Curie temperature of the ferrite. Similar situation arises also in the Ti-rich Ti-Mt-es. If we increase a portion of Ti^{4+} ions in the Ti-Mt (Ti^{4+} ions have only small magnetic moments) the magnetic susceptibility of the Ti-Mt increases. We have known that there is a direct proportionality between μ and κ ($\mu = 1 + 4\pi\kappa$). So, the increase of the Ti^{4+} ions in the titanomagnetite results probably in an increase of magnetic susceptibility. According to *Appel (1987)*, domain patterns on Ti-rich Ti-Mt-es show a typically uniaxial anisotropy, very similar to those of amorphous metals. They can be interpreted as being caused by locally variable compressive and tensional internal stress. According to *Halgedahl (1987)*, intermediate to high x-value Ti-Mt-es largely exhibit complex patterns with a distinctly non-cubic style. Undoubtedly, complex patterns in Ti-rich compositions result from stress. Thus the very different

domain pattern styles observed throughout the Ti-Mt series indicate the increasing importance of stress with titanium content. Whether this stress is intrinsic or an artifact of the surface preparation methods still remains a topic of debate. There is also other aspect: From the study of *Readman et al. (1967)* it follows that while the orbital angular momentum in the octahedral B site the Fe^{2+} ion is only partially quenched, the Fe^{2+} ion in the tetrahedral A site is fully quenched. The result is that while the A-site Fe^{2+} ion in ulvöspinel has a magnetic moment of $4\mu_B$, the magnetic moment in B-site Fe^{2+} ion due to spin and some orbital momentum is $4.5\mu_B$. According to *Hunt et al. (1995)* the magnetocrystalline anisotropy and magnetostriction arise from spin-orbital coupling of ionic magnetic moments, resulting in crystallographically controlled easy and hard directions of magnetization. The magnetocrystalline anisotropy energy (E_k) for a cubic crystal is proportional to empirical anisotropy constants K_1 , K_2 and the direction cosines of magnetization with respect to the principal cubic axes, according to equation:

$$E_K = K_1(\alpha_1^2\alpha_2^2 + \alpha_2^2\alpha_3^2 + \alpha_3^2\alpha_1^2) + K_2(\alpha_1^2\alpha_2^2\alpha_3^2).$$

The anisotropy constants depend on mineral composition, crystal structure, temperature and pressure, but are independent of grain size.

More complex explanation of high κ of Ti-rich Ti-Mt bearing volcanics, and their tendency to be easily altered needs to take into account the basic principles of magnetism. Evidently, this problem is linked with a presence or deficiency of domain structure in these Ti-Mt-es. According to *Orlický and Funaki (2008)*, the Ti-rich Ti-Mt-es have shown only rarely developed domain structure. The large grains of the Ti-rich Ti-Mt-es were characterized as the paramagnetic ones. Similar idea was supported also by *Soffel (1978)*, who suggested that the large amount of optically observed Ti-rich Ti-Mt grains are paramagnetic at room temperature, with no domain structure. From a preliminary model for the domain state of Ti-rich Ti-Mt-es it follows that the particles of multidomain (MD) grain size should consist of MD, single domain (SD) and spin cluster regions. The consequence is a decrease of the effective grain size (division into subvolumes) and an enhanced importance of spin rotation process (*Appel and Soffel, 1984; 1985*).

From experimental results it follows that there is very strong dependence of magnetic susceptibility (κ) of Ti-rich Ti-Mt-es on temperature. κ

decreases from the maximal value (nearly at room temperature) down to the liquid nitrogen temperature ($-196\text{ }^{\circ}\text{C}$) and on the other side to that of Curie temperature (mostly slightly above $100\text{ }^{\circ}\text{C}$). This is not a characteristic behaviour for the magnetically ordered materials of the thermodynamically well-developed domain structure. Landau and Lifshitz (in *Hubert and Shäffer, 1998*) proposed that the magnetic materials with a developed domain structure are athermal – not temperature dependent. We have shown that the spontaneous magnetization occurred within the domain structure of magnetic material. So, if there is no domain structure, no source for magnetism has existed in such a system.

We know that ferromagnetism, antiferromagnetism, and ferrimagnetism may exist only for the atoms in which some of the internal electron orbit is occupied by the electrons only partially in the 3d or 4f orbits, when the spin moments are not fully compensated. A further condition is an effective relation of some parameter of a lattice to the radius of the respective orbit (*Brož, 1962; Vonsoukij, 1971*). While in the ferromagnetics there is only one lattice, in the antiferromagnetics and ferrimagnetics, the atoms or ions create two lattice modes, called sub-lattices. The existence of unpaired electron spins on the respective electron orbits of the atom is not sufficient condition to generate the magnetism (ferromagnetism, antiferromagnetism and ferrimagnetism). The second very important condition is a function of the internal molecular field. It acts in such a way that it leads to a parallel alignment of magnetic moments in the atom in partial areas of magnetic material. The origin of the field is in the existence of the exchange forces of a quantum origin which act among the electrons of the neighbouring atoms. The energy of these quantum forces is of about $2 \cdot 10^{-14}$ erg/atom. It severely overtops the effect of magnetic forces acting mutually among the electrons. The exchange energy is dependent on the distance of the atoms, among which their electrons interacted. If their distance is too large, the energy is too low to align the magnetic moments parallelly and the matter becomes paramagnetic. If the distance corresponds to that of distance of atoms in the crystal, the exchange forces orient the spins of electrons parallel – a positive orientation. A further reduction of the distance between atoms leads to an increase of the exchange forces. In some very small – critical distance the exchange forces fall to a zero level. Further reduction of distance between atoms leads to a stage of the negative interaction and

the spins become oriented antiparallel. So, either the antiferromagnetic – fully compensated, or the non-fully compensated – ferrimagnetic ordering of magnetic moments can be established. If the resultant magnetic moment of a crystal – or the elementary magnetic lattice is zero, then the compensated ferrimagnetism – the antiferromagnetism has occurred.

The basic condition for the existence of the ferrimagnetic behaviour of the respective mineral is a presence of ions with non-zero magnetic moments in both mineral sublattices. In this system the magnetic configuration contains two ferromagnetic sub-lattices bonded mutually antiparallely, one to each other. If the magnetic moments of both sub-lattices are equal to each other and the sum of the magnetic moments is zero – the magnetic structures are as *antiferromagnetics*. The ordered structures with the resultant moment $M = M_B - M_A$ different from zero are as *ferrimagnetics*. For the ferrimagnetics there is a characteristic spontaneous magnetization. In the ferrimagnetics the magnetization is a vector sum (M_S) of magnetizations (M_1, M_2) of the two antiparallel sub-lattices: $M_S = [M_1 - M_2]$. The thermal dependence of M_S must of course be expressed separately for M_1 and M_2 of individual sub-lattices, because M_1 and M_2 can have very different temperature dependences. According to Néel (1948) model, M_B sub-lattice magnetization (I_{SB}) then has a stronger temperature dependence than the M_A sub-lattice (I_{SA}). This can lead to a reversal of spontaneous magnetization at a *compensation point* (θ). This is consistent with a model in which the strongest superexchange coupling is the negative one (i.e., antiparallel) A-B interaction and the smaller B-B interaction between B-site iron atoms is also negative one. The negative B-B interaction hastens thermal disorder (Stacey and Banerjee, 1974). From the three different types of the exchange interactions the AB interaction is the strongest one, and its exchange integral is always negative. It always makes the antiparallel orientation of magnetic moments of individual sublattices. The AB interaction is as an example of the indirect exchange. With regard to large distance between neighbouring metallic ions, a direct exchange effect is very weak. The indirect exchange is interfaced by the negative oxygen's ions. They create some *bridges*, and they make possible, the electrons, which make the non-zero magnetic moments of the metallic ions of the A sublattice, to be approached to the respective electrons of the metallic ions of the B sublattice and so to integrate with them. Because A and B sublattices are neither magneti-

cally nor crystallographically equivalent (they contain different numbers of ions and different quality types of non-zero ions), the resulting spontaneous magnetic moment of these sublattices is different and equal to a difference between magnetic moments of both individual sublattices.

The magnetism and some magnetic effects of the Ti-rich Ti-Mt-es are probably due to the action of the molecular field and indirect interactions of Fe^{2+} and Ti^{4+} ions in the octahedral B crystalline lattice with that of O^{2-} ions. The increase of the content of Ti^{4+} ions in the Ti-Mt leads to the increase of distance between Fe^{2+} and Ti^{4+} ions and so, to the increase of the cubic cell edge of the Fe-Ti mineral. The increase of the cubic cell edge with a content of Ti in the Ti-Mt-es has been determined by the X ray diffraction analyses of Ti-Mt-es (the cubic cell edge $a = 8.50 \text{ \AA}$ for the TM80, but $a = 8.42 \text{ \AA}$ for the TM20, according to *Grommé et al. (1979)*). An increase of the a/r relation results in an increase of the magnetism in the ferromagnetic material ($a =$ cubic cell edge; $r =$ radius of the internal not-fully occupied orbit of magnetic ion).

In the Ti containing oxides there is a problem of their magnetic state. E.g. in ilmenite (FeTiO_3) the Ti^{4+} ion has a diamagnetic state (*Goode-nough, 1963*). Generally, in spinels $\text{Fe}^{2+}[\text{Fe}^{2+} \text{Me}^{4+}]\text{O}_4$, like ulvöspinel ($\text{Fe}^{2+}[\text{Fe}^{2+}\text{Ti}^{4+}]\text{O}_4$) the compounds are supposed to be the ferrospinels, not ferrispinel (it is evidenced that an increase of κ is linked with the increase of Ti^{4+} in the B sublattice in the Ti-rich Ti-Mt solid solution. The structure may behave as the ferromagnetic material, with respect to dominant presence of only B sublattice, while A sublattice is in a negligible portion). This means that they have other magnetic behaviour than Ti-Mt at lower x . There is also the problem of determination of magnetic moments of Ti-rich Ti-Mt-es and the problem of a basic state.

The images presented so far about the magnetic structures of the Fe-Ti oxides relied on the macroscopic observations and magnetic characteristics of the minerals in question. The neutron diffraction is capable to detect directly a diffraction picture of the distribution of magnetic moments of the Fe active and Ti ions in the antiferromagnetics and ferrimagnetics. Unfortunately I have not succeeded when contacting the foreign specialists to realize such a study of separated natural Ti-Mt-es in the past. Very important question is the determination of energy of basic state of antiferromagnetics and ferrimagnetics. In the common ferromagnetics (with only

one crystalline lattice) there exists a maximum magnetic saturation (full parallel ordering of magnetic atomic moments) at absolute zero temperature, except for negligible mutual magnetic influence of excited electrons. An arrangement of positioning (distribution) of the spins into the nodes of the crystalline lattice is considered usually as a basic state (at 0 K). But this state does not correspond to the minimum of the energy of the interaction of spins of the system itself, and it cannot be realized in the sense of the quantum mechanics principles, applying for a description of the system the Heisenberg's hamiltonian, according to *Vonsovskij (1971)*. These difficulties have not allowed to establish a complete theoretical solution of the origin of the high magnetic susceptibility of the Ti-rich titanomagnetites.

From the laboratory measurements of the temperature change of PTRM and magnetic susceptibility of natural magnetite and synthetic maghemite it is evident that the PTRM of maghemite sample is very stable in the interval from 25 to 550 °C and then falls down very sharply. In the same way κ varied with temperature (Fig. 5). No extraordinary increase of κ in both artificially prepared samples appeared in the interval of 300 to 450°, which is typical for the Ti-Mgh-tes (low-temperature oxidized Ti-Mt-es). We can say that a presence of Ti^{4+} ion in the Ti-Mt and the creation and rearrangement of the magnetic moments of A and B sub-lattices are the decisive phenomena. They have influenced extremely the magnetic behaviour of the Ti-rich Ti-Mt and that of the Ti-Mgh.

When Ti-Mt-es in nature are oxidized at low temperatures ($\leq 300 - 400$ °C), especially in the presence of hydrothermal solutions, cation-deficient spinels (Ti-Mgh-es) are formed in which some vacancies appear in the iron cation sites, according to Banerjee, in *Lindsley (1991)*. They constitute important carriers of natural remanent magnetization of submarine pillow basalts, responsible for the larger part of linear marine magnetic anomalies. Among sub-aerial basalts, occasionally reversed polarity of NRM has been observed, resulting from the presence of Ti-Mgh-es. Starting with a given cation distribution for Ti-Mt-es, it is possible to follow the changes in their net ferrimagnetism (M_S per molecule) with oxidation, and predict when such a process will cause a self-reversal of magnetization of basalt after prolonged titanomaghemitization. Because these minerals are metastable and invert rapidly on heating to a magnetite-ilmenite intergrowth, such self-reversals are difficult to reproduce in the laboratory.

The experimental results have shown that except of oxidization of Fe^{2+} to Fe^{3+} ion and leaving vacancies in the creating titanomaghemite, the rearrangement of magnetic moments in original Ti-rich Ti-Mt during the low-temperature oxidation of the titanomagnetite started first. Ulvöspinel has a non-collinear structure. Due to its high content in the Ti-rich Ti-Mt, the initial magnetic state is more antiferromagnetic. But this state starts to change in favour of the ferrimagnetic state. During this process a breakdown of the initial magnetic state of the Ti-rich Ti-Mt was identified. This was a cause of the extreme lowering of magnetic characteristics, including the magnetic susceptibility in the altered Ti-Mt.

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