

# STUDY AND DETECTION OF MAGNETIC MINERALS BY MEANS OF THE MEASUREMENT OF THEIR LOW-FIELD SUSCEPTIBILITY CHANGES INDUCED BY TEMPERATURE

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**Abstract:** There are presented in the article: a block diagram of the fully automated apparatus for the study and detection of magnetic materials, short review about basic magnetic minerals and experimental results gained by the mentioned measuring system.

**Key words:** fully automated apparatus, magnetic minerals.

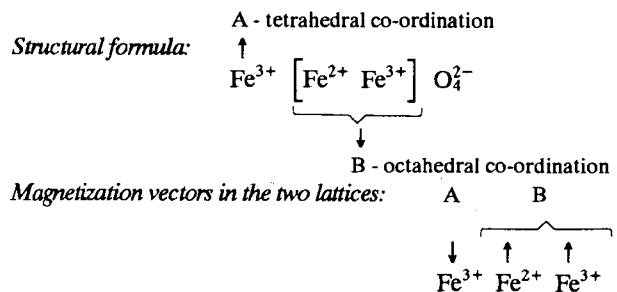
## Introduction

Recently a fully automated apparatus for the study and detection of magnetic minerals of rocks has been designed and completed (Orlický 1990). The measurement is based on the change of the initial magnetic susceptibility ( $\kappa$ ) with temperature. The apparatus comprises the KLY-2 Kappabridge, the furnace supplied with the equipment which moves the furnace into and out of the pick-up coil of the KLY-2, the control and measuring unit controls furnace movement, measuring of a sample temperature. The apparatus (CS-1 or CS-2) is produced and completed nowadays by the Geofyzika, a.s. Brno. The block diagram of the original measuring system see in Fig. 1. The temperature range of the original apparatus is 20 - 850 °C. There is possible to use a special makeshift cooling system for measurement in the low-temperature interval in range 20 °C down to -190 °C in the apparatus. Magnetic susceptibility of a sample is measured in a fixed position of the furnace (or of special cooling system) inside the pick-up coils. The temperature increase and decrease (in the high temperature interval) is automatically controlled according a chosen regime. The Curie temperatures ( $T_C$ ) can be determined from the thermomagnetic curve, each  $T_C$  characterizing a specific magnetic component in the sample. Phase transitions and chemical alternations of the materials can be also detected.

I present in this article some knowledge about basic magnetic minerals and the experimental results gained by the method mentioned above. There are commented below also the results of the Mössbauer spectroscopy (MS) for individual minerals. MS was realized and all results of this method were evaluated by Prof. Ing. J. Lipka, DrSc., Slovak Technical University, Electrotechnical Faculty, Mlynská dolina, Bratislava.

## Basic description of individual magnetic minerals and their characteristic phenomena

**Magnetite ( $Fe_3O_4$ )** - magnetite is a cubic mineral. It has an inverse spinel structure. The cations are located in two lattices A and B, the A sites in four-fold co-ordination with oxygen ions and B sites in six-fold co-ordination.



it means that magnetite is the ferrimagnetic mineral.

Above the transition temperature,  $Fe^{2+}$  and  $Fe^{3+}$  ions are randomly distributed on the B sites which makes, "electron hopping" between B site iron ions energetically easy (Stacey & Banerjee 1974).

- Curie temperature ( $T_C$ ) of the stoichiometric magnetite is  $T_C = 580$  °C;

- Magnetite undergoes a cubic-to-orthorhombic crystallographic transition on cooling through -155 °C (Verwey transition -  $T_V$ ). The crystallographic transition is accompanied by a magnetic isotropic point (an expressive increasing of the mag-

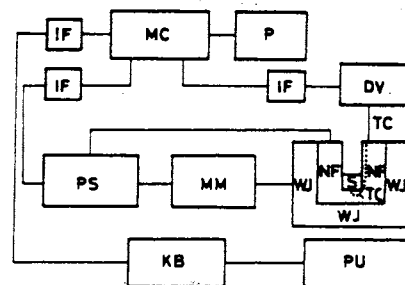


Fig. 1. Block diagram of the measuring system.

MC - microcomputer; P - printer; IF - interface; DV - digital voltmeter; PS - electric power source; MM - movement mechanism; NF - non-magnetic furnace; TC - Pr-PtRh - thermocouple; WJ - cooling water jacket; S - sample; KB - Kappabridge KLY-2; PU - pick-up unit of the Kappabridge.

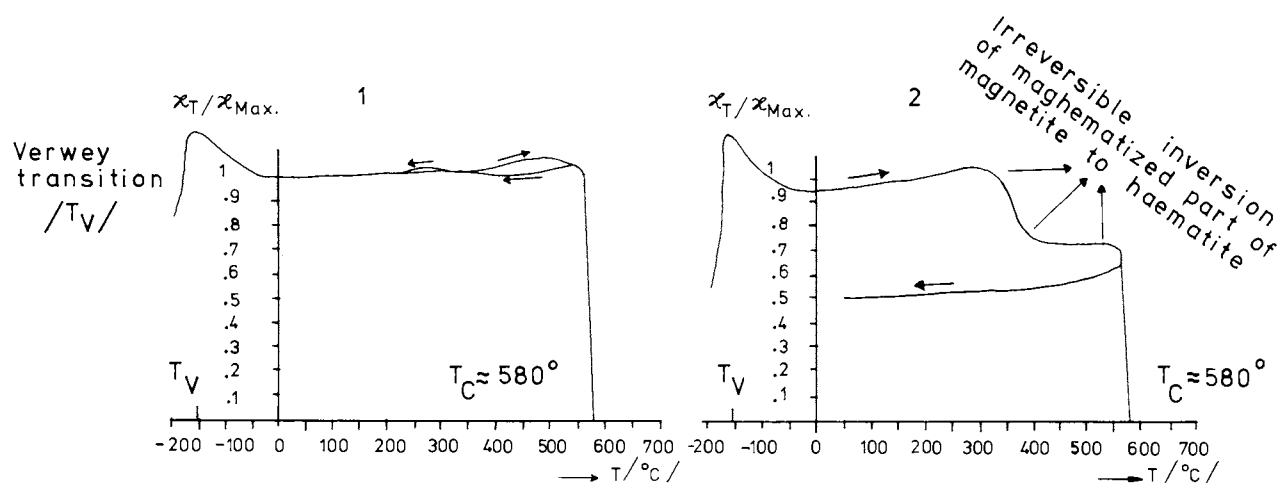


Fig. 2. Thermomagnetic curves of magnetites. 1 - Gellivara, Sweden; 2 - Sobotín, Czech Republic., →, ← - heating, cooling of the sample.

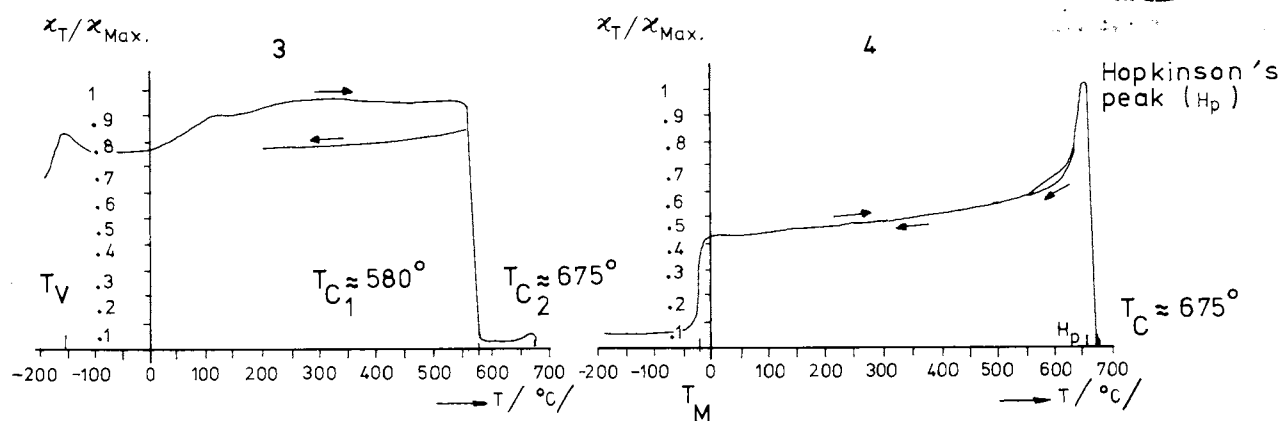


Fig. 3. Thermomagnetic curves of haematites. 3 - Gellivara, Sweden; 4 - Minar Gerais, Brazil., →, ← - see as in Fig. 2.

netic susceptibility ( $\kappa$ ) at  $T \approx -155^\circ\text{C}$ ; magnetocrystalline anisotropy constant,  $K_1 = 0$ ):

– Magnetite is a metastable magnetic mineral. A gradual alteration of the magnetite can take place at normal atmospheric conditions. Non-stoichiometric magnetite with a presence of the vacancies ( $\square$ ) is created due to the alteration of the original one. This process can be described by the formula:  $\text{Fe}^{3+}[\text{Fe}_{1-\delta}^{2+} \text{Fe}_{1+2\delta/3}^{3+} \square_{\delta/3}] \text{O}_4^{2-}$ ;  $0 \leq \delta \leq 1$ . As a final product of above mentioned alteration is the maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ), ( $\delta = 1$ ). This reverts to  $\alpha\text{-Fe}_2\text{O}_3$  irreversibly on being heated.

We see that three phenomena can be detected on the thermomagnetic curves of the magnetic samples. Two quasi pure magnetite samples were studied. 1 - Gellivara, Sweden, and 2 - Sobotín, Czech Republic (Fig. 2). Both of magnetites are characterized by  $T_C \approx 580^\circ\text{C}$  and Verwey transition temperature  $T_V \approx -155^\circ\text{C}$ . While magnetite - sample 1 is rather stable (thermomagnetic curves during heating and cooling are practically the same, stoichiometry of this magnetite has been confirmed also by MS), magnetite - sample 2 reveals decreasing of  $\kappa$  in the interval  $360^\circ\text{C} - 570^\circ\text{C}$ , due to irreversible alteration of maghemitized part of magnetite to haematite (low degree of non-stoichiometry has been confirmed also by MS).

**Haematite** ( $\alpha\text{-Fe}_2\text{O}_3$ ) - haematite is a rhombohedral mineral. Iron atoms in haematite are all in octahedrally co-ordinated (B)

sites. The lattice is made up of layers of oxygen ions and layers of cations in six-fold co-ordination parallel to the crystal axis. The oppositely magnetized  $\text{Fe}^{3+}$  ions in the two sub-lattices are canted at small angle and give rise to a small saturation magnetization. The spin alignment is antiferromagnetic, but the antiferromagnetism is imperfect. At low temperatures haematite is antiferromagnetic. In addition to spin canted ferromagnetism, there is an additional component which arises from the interaction between the antiferromagnetism and lattice defects or impurities. This defect ferromagnetism is observable below  $-20^\circ\text{C}$  and between  $680^\circ\text{C}$  and Néel point of  $725^\circ\text{C}$ . Defect ferromagnetism is sensitive to structure, and it is altered by stress or heating (McElhinny 1973). Spin-canted remanence is very resistant to thermal as well as to alternating-field demagnetization (Dunlop 1970).

– Curie temperature of the haematite is  $T_C \approx 675^\circ\text{C}$ ;

– At temperatures below about  $-20^\circ\text{C}$  intrinsic weak ferromagnetism disappears (this effect is named as Morin transition; the Morin transition is a point of magnetic isotropy ( $K = 0$ ) in haematite, according to Stacey & Banerjee (1974).

Sample 3 - Gellivara, Sweden, and sample 4 - Minar Gerais, Brazil (Fig. 3) are quasi pure haematites according to MS. We see that there are two magnetic phases in sample 3. Both - Curie temperature  $T_C \approx 580^\circ\text{C}$  and Verwey transition temperature

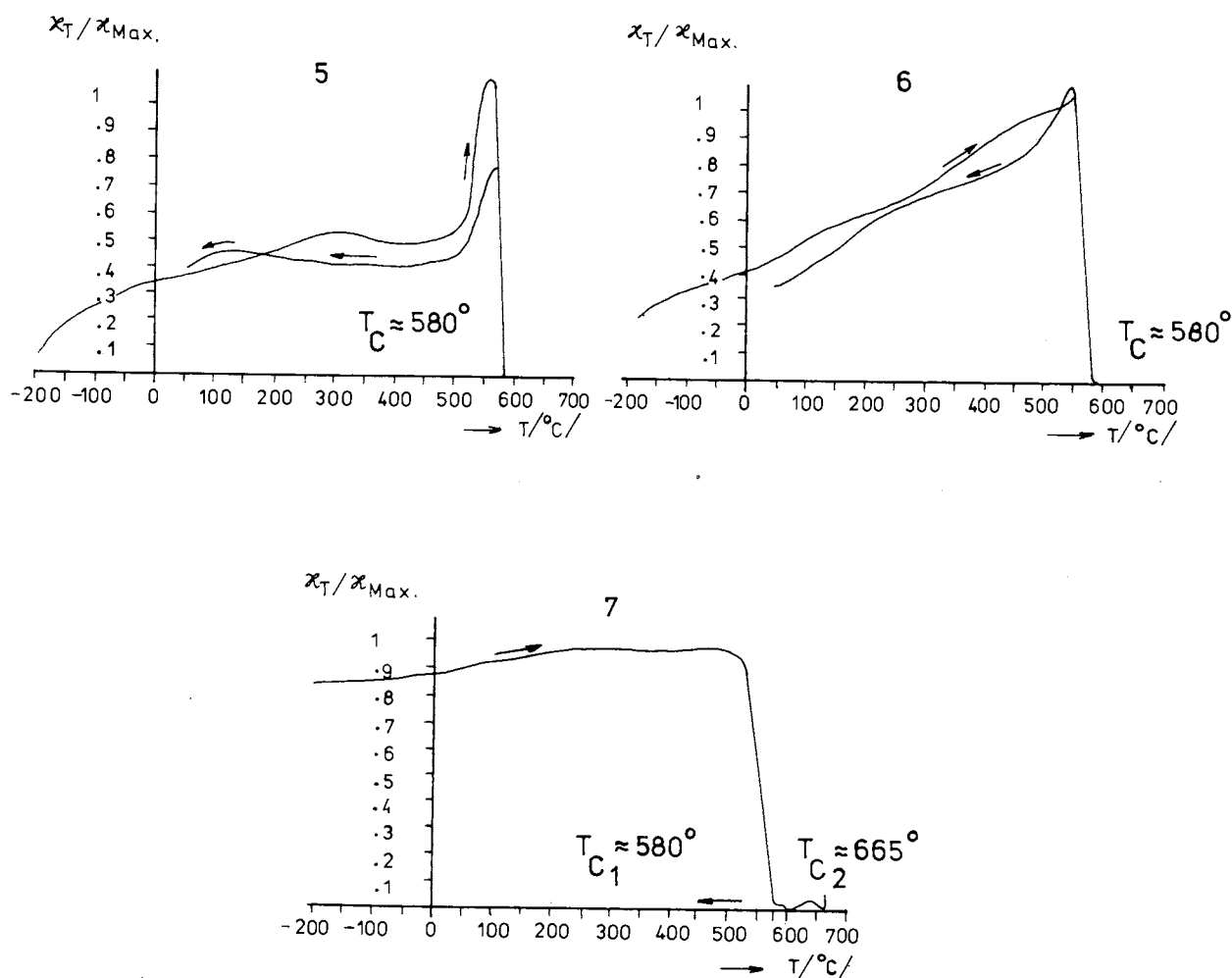


Fig. 4. Thermomagnetic curves of synthetic maghemites. 5 - maghemite Bayer; 6 - maghemite Pferov 236 (samples 5 and 6 were measured in vacuum  $10^{-5}$  Torr.); 7 - maghemite Pferov 647 - 649 (sample 7 was measured at the air).  $\rightarrow$ ,  $\leftarrow$  - see as in Fig. 2.

$T_V \approx -150^\circ C$  correspond to magnetite; magnetic phase with  $T_C \approx 675^\circ C$  corresponds to haematite. When we consider a saturation magnetization of magnetite ( $480 \text{ emu} \cdot \text{cm}^{-3}$ ) and haematite ( $2.2 \text{ emu} \cdot \text{cm}^{-3}$ ) and relations of both components on the thermomagnetic curve of sample 3, there is only about 7.9 % of magnetite in the haematite sample 3 - Gellivara, Sweden. Sample 4 - Minar Gerais, Brazil contains only haematite with  $T_C \approx 675^\circ C$  and Morin transition temperature  $T_M \approx -20^\circ C$ . There is also Hopkinson's peak ( $H_p$ ) at  $T \approx 660^\circ C$ . We see at the same time, that there is residual  $\kappa$  below  $T_M$  of the sample 4. It means that this haematite is not complete antiferromagnetic at low temperatures, below Morin transition. This phenomenon corresponds to "defect ferromagnetism" of the haematite sample 4 - Minar Gerais, Brazil.

**Maghemite** ( $\gamma - \text{Fe}_2\text{O}_3$ ) - maghemite is a cubic mineral. It has an inverse spinel structure similar to magnetite, but has a defective lattice. Elementary lattice of maghemite is possible to describe by a formula  $\text{Fe}_{8/3}^{3+} \square_{1/3} \text{O}_4$ . Maghemite is formed by the low-temperature oxidation of magnetite. One third of the original  $\text{Fe}^{2+}$  sites becomes vacancies ( $\square$ ). The crystal structure is therefore not exactly spinel, but tetragonal, due to the vacancy superlattice. The most important property of the maghemite is that it is thermodynamically metastable and converts to the

more stable rhombohedral haematite structure on heating to temperatures above  $350^\circ C$  (a transition depends upon grain size, water content, foreign ion impurities, etc. Stacey & Banerjee 1974). Because of this, it has not been possible to determine  $T_C$  of maghemite. Various extrapolation methods have been used to determine the  $T_C$  of maghemite. ( $T_C \approx 750^\circ C$ , Brown & Johnson 1962;  $T_C \approx 750^\circ C$ , Banerjee & Bartolin 1970; Stacey & Banerjee 1974;  $T_C \approx 675^\circ C$ , McElhinny 1973).

Three synthetic samples were studied. Samples: 5 - maghemite - Bayer; 6 - maghemite - Pferov-236; 7 - maghemite - Pferov-647-649 (Fig. 4). Two of them (sample 5 and 6) were sealed in vacuum ampoules (vacuum  $10^{-5}$  Torr.). Sample 7 - Pferov-647 - 649 was measured with a presence of air oxygen. We see from thermomagnetic curves, that Curie temperatures of main magnetic phases of all three samples are  $T_C \approx 580^\circ C$ . But there has not been detected Verwey transition at  $T_V \approx -155^\circ C$ . It means that Curie temperature  $T_C \approx 580^\circ C$  do not corresponds to magnetite in the samples measured at the air or in vacuum. There is gradual decreasing of  $\kappa$  of all three samples from ca.  $20^\circ C$  down to liquid nitrogen temperature. There was detected also the haematite according to Curie temperature  $T_C \approx 665^\circ C$  in the sample 7 - Pferov-647 - 649. Sample 5 and 6 contained maghemite with about 35 % cobalt ferrite before tempera-

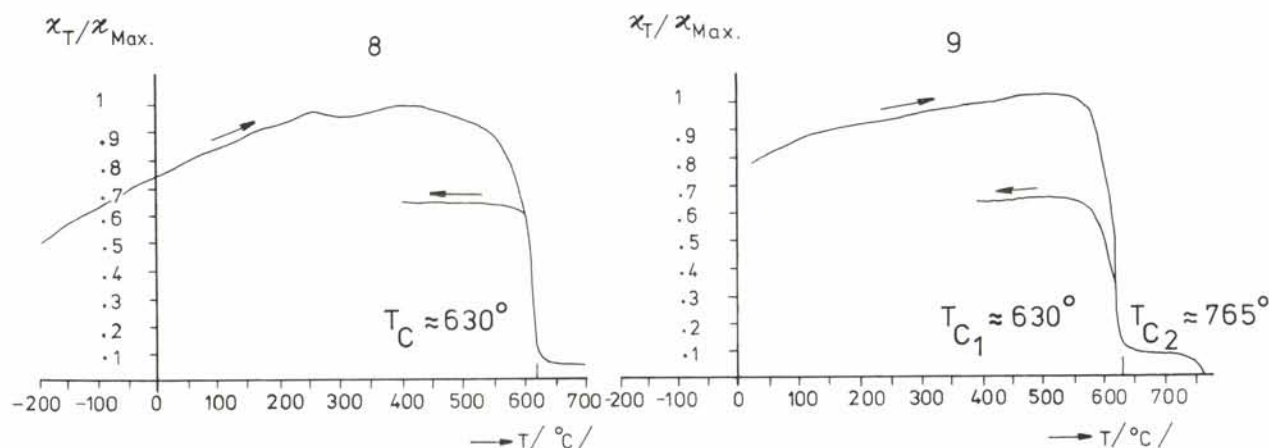


Fig. 5. Thermomagnetic curves of impactite from Chile. 8 - first measurement of the sample to 700 °C; 9 - repeated measurement of the sample to 780 °C. →, ← - see as in Fig. 2.

ture treatment, according to Mössbauer spectroscopy. Sample 7 was quasi pure maghemite before our measurements according to MS. Samples 5 and 6 were analyzed by MS also after temperature treatment (heating and cooling of the samples during Curie temperature measurements in vacuum). Quality of sample 5 was changed according to MS. Maghemite to non-stoichiometric magnetite was transformed. We see from the thermomagnetic curves that there are differences between the shape and amplitudes of thermomagnetic curves during heating and cooling of the sample 5. Thermomagnetic curves during heating and cooling of the sample 6 are practically the same. This behaviour point out that quality of the original maghemite has not been changed. Results of the Mössbauer spectroscopy have not confirmed qualitative changes of the sample 6 - maghemite - Pferov-236 after temperature treatment. (The rate of heating and cooling during fully-automated measurements of change of  $\kappa$  for all studied samples was 5 °C/min). There has not been detected evident decreasing of  $\kappa$ , e.g. on the thermomagnetic curve of the sample 7 up to 535 °C. We see that haematite is evidently detected over 630 °C by increasing of  $\kappa$  (probably the Hopkinson's effect) and decreasing of  $\kappa$  at  $T_C \approx 665$  °C. The haematite which originated from the maghemite Pferov-647 - 649 is supposed to be complete antiferromagnetic at room temperature.

**Impactites** are materials which originated due to an interaction of cosmic bodies (meteorites) with the surface rocks of the Earth. The consequences of the interaction are thermal and pressure attacks of the materials (shock metamorphose - welding on and melting of the materials). Sometimes is there present also meteoric iron in the impactites.

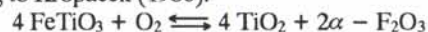
There are two thermomagnetic curves of the impactites from Chile in Fig. 5. Sample 8 - first measurement and sample 9 - repeated measurements with the sample which was heated up to 700 °C during former measurement. We see from thermomagnetic curve sample 8, that first decreasing of is about 300 °C. Curie temperature of main magnetic phase is  $T_C \approx 630$  °C. There is residual of the impactite in the interval 630 - 700 °C. This has shown that there should be present a third phase in the sample. Repeated measurements (sample 9) have revealed that there is present also magnetic phase with  $T_C \approx 765$  °C. Impactite contains maghemite (as the dominant magnetic mineral), nickel, and substituted magnetite according to Mössbauer spectroscopy. We see from Fig. 6 that nickel

(from Nickel Plant Sereď, Slovak Republic) has Curie temperature  $T_C \approx 360$  °C.

Curie temperature  $T_C \approx 630$  °C corresponds to maghemite in the samples 8 and 9 (Fig. 5), but there is a discrepancy towards an idea concerning the conversion of maghemite to haematite during heating. This maghemite is supposed to be relatively resistant to temperature treatment. This stability of maghemite is probably a reflection of peculiar conditions during impact processes. Magnetic phase with  $T_C \approx 765$  °C (Fig. 5, sample 9) corresponds to meteoric iron in the impactite.

Gradual increasing of  $\kappa$  from liquid nitrogen temperature to about 250 °C corresponds probably to ordering vacancies in maghemite influenced by temperature. (This explanation can be accepted also for the samples of maghemites which have been presented before).

**Ilmenite** ( $\text{FeTiO}_3$ ) - ilmenite is a perfect antiferromagnet. Elementary lattice consists of two  $\text{Fe}^{2+}$  ions,  $\text{Ti}^{4+}$  ions and six  $\text{O}^{2-}$  anions. Néel temperature ( $T_N$ ) of pure antiferromagnetic ilmenite is  $T_N = -205$  °C. Ilmenite is nonstable mineral at normal conditions. Slow oxidation of ilmenite takes place at air oxygen, according to Kropáček (1986).



There are present also solid solutions of ferroilmenites in nature.

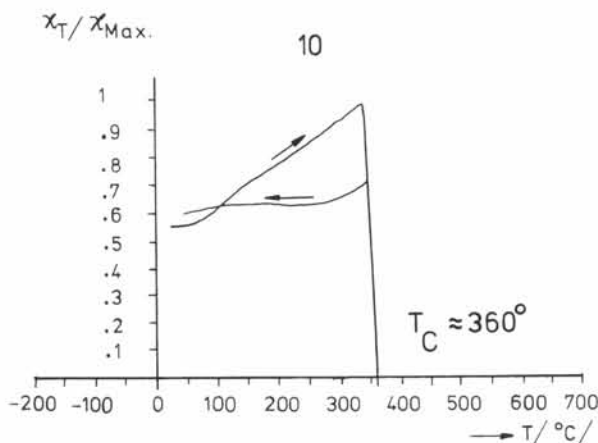
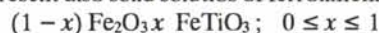


Fig. 6. Thermomagnetic curve of nickel from Nickel Plant Sereď, Slovak Republic. →, ← - see as in Fig. 2.

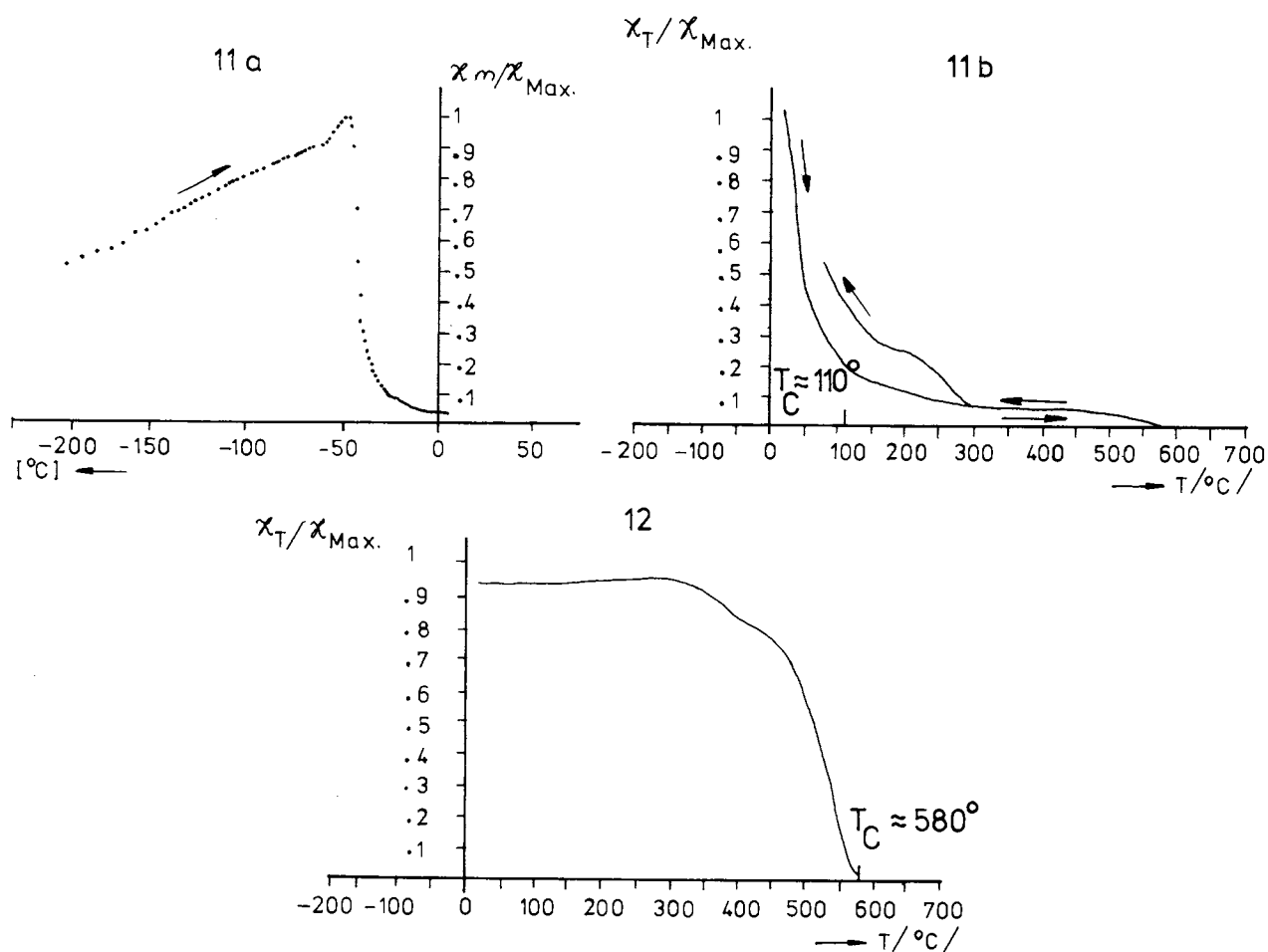


Fig. 7. Thermomagnetic curves of "ilmenites". 11 - Jizerská lúka, Czech Republic (11a - in low temperature interval, 11b - in high temperature interval); 12 - Dolné Bory, Czech Republic (ilmenite is interthrown in pegmatite).  $\rightarrow$ ,  $\leftarrow$  - see as in Fig. 2.

These solid solutions are not stable at normal atmospheric temperatures. They usually desintegrate to two-phases: ferrian-ilmenite phase and titanohaematite phase (Kropáček 1986).

Thermomagnetic curves of two "ilmenite" samples are presented in Fig. 7. Sample 11 - Jizerská lúka, sample 12 - Dolné Bory (both from Czech Republic). Thermomagnetic curves of sample 11 are drawn separately for low-temperature interval ( $-195$  -  $3$  °C) - curve 11a, and for high-temperature interval ( $20$  -  $700$  °C) - curve 11b (Fig. 7).

We see from thermomagnetic curve 11a that there is extreme increasing  $\kappa$  of sample at  $T \approx -45$  °C (from  $440 \times 10^{-6}$  SI units at room temperature to  $20073 \times 10^{-6}$  SI units at  $T \approx -45$  °C). This behaviour is anomalous and corresponds probably to unknown phase-transition of the investigated "ilmenite". We see that strong ferrimagnetic properties of the unknown inter-phase have been acquired in the interval  $-196$  °C to  $-45$  °C. Main magnetic phase of the sample has  $T_C \approx 110$  °C (see Fig. 7, sample 11b). There is supposed to be present a mixture of haematite, maghemite and substituted magnetite, according to Mössbauer spectroscopy, or magnetite, according to X-ray diffraction analysis in the sample "ilmenite" - Jizerská lúka. I suppose that these data are not sufficient to reveal extremely anomalous behaviour of ilmenite in question influenced by temperature. Phase with  $T_C \approx 320$  °C originated after heating and cooling. We see from Fig. 7 - sample 12, that main magnetic

phase of "ilmenite" Dolné Bory has  $T_C \approx 580$  °C. Mössbauer spectrum of the sample 12 - Dolné Bory corresponds to pure ilmenite. Magnetic phase with  $T_C \approx 580$  °C corresponds probably to magnetite. We suppose that there have been taken place slow oxidation of ilmenite to haematite at the beginning of the formation of the mineral association in the pegmatite. But part of this haematite was at the same time (or later) reduced to magnetite.

**Pyrrhotite** ( $\text{FeS}$ ;  $\text{Fe}_{0.875}\square_{0.125}\text{S}$ ) - pyrrhotite is the iron-deficient sulphide. The vacancies in pyrrhotite form an ordered structure and are commonly located preferentially in alternate iron layers normal to the hexagonal symmetry axis of  $\text{FeS}$ . There are commonly present intermediate sulphides which have different vacancy concentration in nature. For vacancy concentration less than 0.125 per molecule, a disordered arrangement is obtained if the material is quenched from high temperatures (Stacey & Banerjee 1974). When reheated slowly, however, there is enough thermal energy at about  $200$  °C for the vacancies to order. The disordered vacancies in the intermediate  $\text{Fe}_{1-x}\square_x\text{S}$  phases approach ordered arrangement, producing a net ferrimagnetic moment in previously antiferromagnetic materials.

- Curie temperature of pyrrhotite  $\text{Fe}_7\text{S}_8$  is  $320$  °C.

There is also hexagonal  $\text{FeS}$  sulphide troilite which is of course antiferromagnetic. Pyrite ( $\text{FeS}_2$ ) is a paramagnetic sulphide.

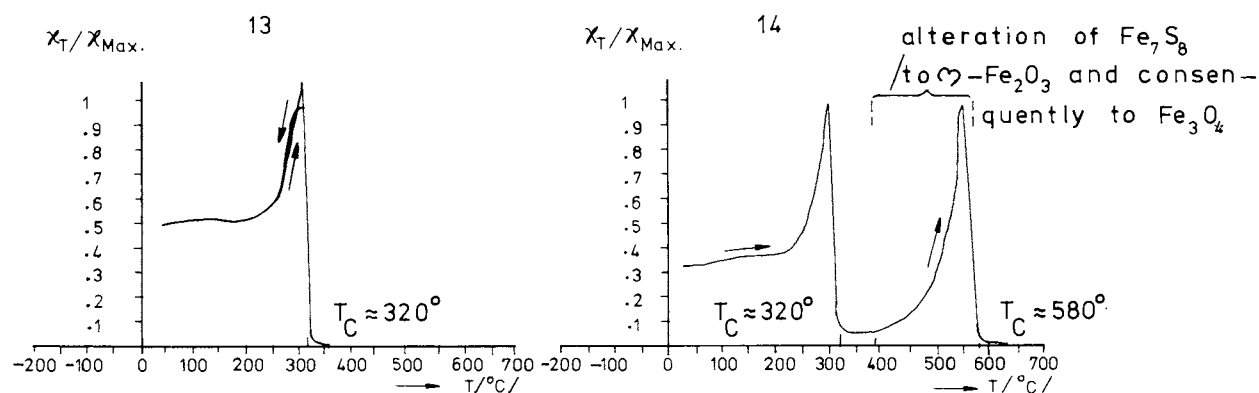


Fig. 8. Thermomagnetic curves of ferrimagnetic pyrrhotite ( $\text{Fe}_7\text{S}_8$ ). 13 - Zlaté hory, Czech Republic; 14 - pyrrhotite from diorite porphyry of the borehole Strechov-1, depth 822 m, Slovak Republic.  $\rightarrow$ ,  $\leftarrow$  - see as in Fig. 2.

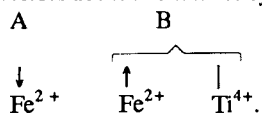
Two samples of ferrimagnetic pyrrhotite  $\text{Fe}_7\text{S}_8$  were studied (Fig. 8). One of them (sample 13) coming from Zlaté Hory - northern Moravia - Czech Republic), second one (sample 14) was separated from diorite porphyry of borehole Strechov-1 (depth 822 m) - eastern part of the Slovak Republic). Sample 13 was heated and measured to 350 °C and cooled to room temperature (Fig. 8, sample 13). Preselected rate of heating and cooling of the sample was 4.5 °/min. We see that there is evident Hopkinson's peak at about 300 °C ( $T_H$ ) and Curie temperature  $T_C \approx 325$  °C. The shape of thermomagnetic curves for heating and cooling differ very slightly at temperatures around of the Hopkinson's peak. It has shown that no phase or chemical transitions or pyrrhotite take place. Studied sample 13 seems to be one-phase ferrimagnetic  $\text{Fe}_7\text{S}_8$  pyrrhotite, according to Mössbauer spectroscopy.

Sample 14 was measured to 650 °C (Fig. 8, sample 14). Behaviour of thermomagnetic curve to ca. 350 °C is rather the same like for sample 13. The Hopkinson's peak (around 300 °C and  $T_C \approx 325$  °C) revealed that this sulphide is supposed to be  $\text{Fe}_7\text{S}_8$  pyrrhotite). We see from thermomagnetic curve sample 14 that there is evident alteration of original sulphide to other magnetic mineral with Curie temperature  $T_C \approx 580$  °C after heating over 405 °C. Despite  $T_C \approx 580$  °C ( $T_C \approx 580$  °C corresponds to magnetite) this magnetic phase corresponds probably to inter-phase product  $\eta$  -  $\text{Fe}_2\text{O}_3$  according to X-ray diffraction analyses realized by other specialists. This inter-phase oxide is of course able to convert to magnetite and haematite during long-term heating of the sample.

**Magnetite - ulvospinel series (titanomagnetites -  $\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$ )** - these solid-solutions are the most common magnetic minerals in basaltic rocks. In the magnetite-ulvospinel series there is complete solid solution at temperatures in excess of 600 °C. At lower temperatures the solid solution is much more restricted and there is a tendency for the two phases to exsolve. The ionic replacement in this solid solution series takes the form (according to McElhinny 1973):  $2\text{Fe}^{3+} \rightleftharpoons \text{Fe}^{2+} + \text{Ti}^{4+}$ .

Magnetite is ferrimagnetic. Ulvospinel is paramagnetic at room temperature and antiferromagnetic at low temperatures. As in all spinels, the cations are located in two lattices A and B in the ulvospinel.

*Magnetization vectors in the two lattices of ulvospinel:*



The oxidation of titanomagnetites takes place at temperature 600 - 1000 °C during initial cooling of magma and is not due to weathering. The oxidation during cooling tends to proceed first through the production of ilmenite lamellae and then progresses towards the pseudobrookite series (McElhinny 1973). Titanomagnetite can be produced from titanomagnetite during low-temperature oxidation. Magnetization can take place either during the late stages of the initial cooling or perhaps during subsequent weathering, according to McElhinny (1973).

The examples of four thermomagnetic curves of Fe-Ti magnetic oxides from basaltic rocks of the Central Slovakia are in Fig. 9. There is many samples of basaltic rocks with the titanomagnetites (TM) of low Curie temperature, like in the sample Bz-B2/17, Fig. 9. The composition of these TM-es is supposed to be in the range  $\text{Fe}_{2.5}\text{Ti}_{0.5}\text{O}_4$  -  $\text{Fe}_{2.3}\text{Ti}_{0.7}\text{O}_4$ . There are also TM-es in basaltic rocks with two magnetic phases (Fig. 8, Bz-131/7) or with three magnetic phases (Fig. 9, Bz-Devčie P-95B). Presence of ulvospinel in TM-es is supposed to be characterized by a relative sharp decreasing of  $\kappa$  in low-temperature interval, down to liquid nitrogen temperature. (Ulvospinel is paramagnetic at room temperature and antiferromagnetic at low temperature, see Fig. 9, Bz-B2/17, Bz-131/7, Bz-Devčie-P-95B). Non-stoichiometric magnetite with  $T_C \approx 580$  °C and Verwey transition temperature  $T_V \approx -155$  °C is present in oxides TM of the sample Bz-B2/1 (Fig. 9).

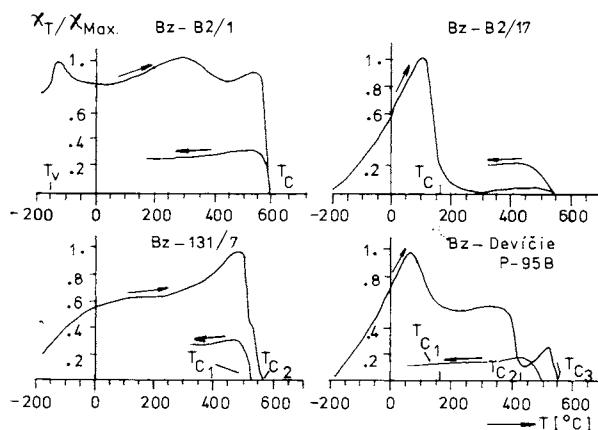


Fig. 9. Thermomagnetic curves of magnetic Fe-Ti oxides from basalts and basanites, Central Slovakia.  $\rightarrow$ ,  $\leftarrow$  - see as in Fig. 2.

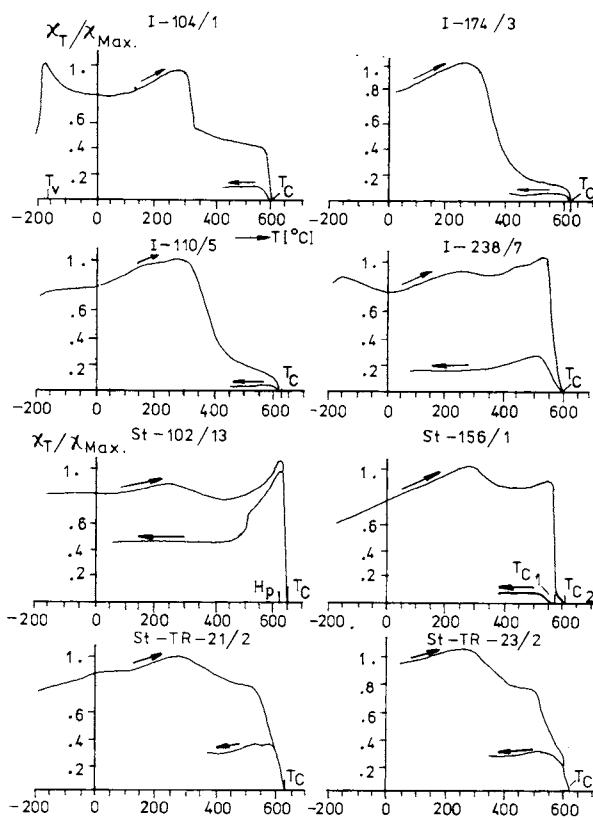


Fig. 10. Thermomagnetic curves of magnetic Fe-Ti oxides from andesitic rocks of the Central Slovakia. →, ← - see as in Fig. 2.

**Titanohaematites ( $\text{Fe}_{2-x}\text{Ti}_x\text{O}_3$ ;  $0 \leq x \leq 1$ )** - solid solution is complete only above  $700^\circ\text{C}$  so that some compositions can be obtained only by quenching from above  $700^\circ\text{C}$ . Slow cooling results in exsolution of haematite-rich and ilmenite-rich components, known as haematite-ilmenites which are quite common in igneous rocks. (Both titanomagnetites and titanomaghemites are inverted into a two-phase intergrowth - spinel and rhombohedral phase, when they are heated over  $700^\circ\text{C}$  and cooled to natural atmospheric temperature. They contain mineral near to magnetite, mineral near to ilmenite and mineral near to haematite). Magnetic minerals of very large groups of Neogene pyroxene andesites and hornblende-amphibole andesites from the Central Slovakia have been studied. There is only several examples of thermomagnetic curves in Fig. 10. Curie temperature  $T_C \approx 580^\circ\text{C}$  and Vervey transition temperature  $T_V \approx -155^\circ\text{C}$  of the sample I-104/1 have shown that this magnetic phase corresponds to magnetite. There is pronounced decreasing of  $\kappa$  in the interval  $300 - 550^\circ\text{C}$  at the thermomagnetic curve of the sample I-104/1. This behaviour corresponds to irreversible conversion of maghemitized magnetite to haematite (we see at the same time that  $\kappa$  after heating and cooling of the sample is expressively lower comparing it with the original state at the thermomagnetic curve during cooling). High content of FeO

and very low one of  $\text{TiO}_2$  was detected by electron-microprobe analysis in most of Fe-Ti grains of the sample. Non-stoichiometric magnetite was revealed by MS of this sample.

Different situation is in the sample I-174/3 (Fig. 10). Curie temperature of the sample is  $T_C \approx 625^\circ\text{C}$ . There is evident intensive decreasing of  $\kappa$  during heating in the interval  $280^\circ\text{C}$  to ca.  $610^\circ\text{C}$  at the thermomagnetic curve of the sample. This behaviour corresponds to irreversible conversion of titanomaghemite to haematite. There is lack of FeO content and dominant content of  $\text{TiO}_2$  in magnetic Fe-Ti grains of the sample, according to electron-microprobe analysis. Sample St-102/13 has Curie temperature  $T_C \approx 645^\circ\text{C}$  and Hopkinson's peak  $T_H \approx 640^\circ\text{C}$ . About 55.5% of  $\alpha\text{-Fe}_2\text{O}_3 + \gamma\text{-Fe}_2\text{O}_3$  is in this sample, according to MS. High content of  $\alpha\text{-Fe}_2\text{O}_3 + \gamma\text{-Fe}_2\text{O}_3$  is also in the sample St-156/1 which has two magnetic phases  $T_{C1} \approx 580^\circ\text{C}$ ,  $T_{C2} \approx 620^\circ\text{C}$ . High content of titanomaghemite is present in this sample. There are two very similar shapes of the thermomagnetic curves of the samples St-TR-21/2, St-TR-23/2 in Fig. 10. They differ only by their Curie temperatures. Higher  $T_C$  of the magnetic phase of the sample St-TR-21/2 ( $T_C \approx 635^\circ\text{C}$ ) corresponds to higher content of  $\alpha\text{-Fe}_2\text{O}_3$ , comparing it with that in the sample St-TR-23/2 with  $T_C \approx 620^\circ\text{C}$ . (It has been confirmed also by MS; we need to note that MS was realized before temperature treatment of analyzed samples). We see that magnetitic susceptibility after heating of Fe-Ti magnetic minerals to  $700^\circ\text{C}$  and their cooling is extremely lower comparing in with  $\kappa$  before temperature treatment. This phenomenon is a reflection of irreversible inversion of maghemitized magnetite or titanomaghemite to haematite due to thermal influence.

## Conclusion

The work described in the contribution shows that the presented fully automated apparatus as well as the laboratory technique used are useful for the study of magnetic materials.

The results of presented individual magnetic minerals have shown that hyperfine differences, chemical alterations, as well as phase transitions of concrete materials are detectable by the method of measurements of the change of the initial magnetic susceptibility ( $\kappa$ ) of the sample (magnetic fraction) influenced by temperature.

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