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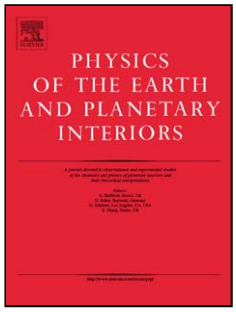

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THERMALLY INDUCED TRANSFORMATION OF MAGNETIC MINERALS IN SOIL BASED ON ROCK MAGNETIC STUDY AND MÖSSBAUER ANALYSIS.

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ABSTRACT

The purpose of this study is to detect thermal transformations of magnetic minerals occurring during thermomagnetic susceptibility analysis based on the example of chernozem soil samples from Ukraine. Rock magnetic methods such as thermal decay of saturation remanent magnetization (SIRM), hysteresis loops and monitoring of magnetic susceptibility (k) during heating from temperature of liquid nitrogen (-196°C) up to 700 °C were used as indicators of magnetic mineralogy, grain size and concentration. In addition, the changes in mineralogy caused by heating were monitored by Mössbauer analysis. The samples were taken from the topsoil and from the loess layer of the unpolluted chernozem profile from the Homutovsky Steppe (East-South Ukraine). SIRM(T) curves and Mössbauer analysis revealed maghemite, hematite and goethite in the topsoil and in the loess. Low- temperature susceptibility experiments showed superparamagentic (SP) - like behaviour in the topsoil and paramagnetic - like behaviour in the loess. The specimens were heated during susceptibility measurements in KLY-3 device from room temperature up to subsequent increasing temperatures: 250 °C, 400 °C, 500 °C, 600 °C and 700 °C. After heating to particular temperature, low temperature experiments, SIRM(T) curves, hysteresis loops and Mössbauer analysis were performed.

Additionally, the sample of topsoil and the sample of loess were heated several times to the increasing temperatures. Mössbauer analysis showed increase of Fe^{2+} ions indicating reduction process during heating. We suggest that in the topsoil, the prevailing transformations are inversion of hydroxides such as goethite and ferrihydrite to magnetite/maghemite which occur at temperature 200 – 450 °C, whereas in the loess reduction of lithogenic hematite to magnetite at temperature above 600°C plays important role. The topsoil and loess do not differ significantly in such pedogenic parameters as pH, total iron content Fe_t or free iron Fe_d. The main differences are in humus and amorphous iron content Fe_o.

Keywords: magnetic mineral, thermal transformations, soil, Mössbauer analysis

INTRODUCTION

The most prominent feature of ferromagnetic minerals (including ferri- and antiferromagnetics) is the Curie (T_c) or Néel (T_l) temperature at which these minerals lose their properties and become paramagnetics. The Curie and Néel temperatures are widely used for identification of ferromagnetic minerals. For this purpose temperature dependence of magnetization acquired in high magnetic field M(T) or temperature dependence of low-field volume specific susceptibility k(T) has been used. In paleomagnetic study, thermal demagnetization of saturation isothermal remanence SIRM(T) or remanence imposed at different field strength in three perpendicular directions are also applied. These measurements provide unblocking temperature values (T_{ub}) at which remanence carried by particular magnetic phase is completely lost. M(T) and k(T) curves are disturbed by alteration of magnetic phases during heating. Compared with M(T), k(T) curves are controlled not only by magnetic mineralogy but also by grain size distribution. SIRM(T) curves although affected by

grain size distribution, are not disturbed by mineralogical changes induced by heating. Thermal alteration are detected during second heating.

Thermal transformations of magnetic minerals occurring during susceptibility measurements often differ significantly from transformations observed during remanence experiments or M(T) measurements. The differences are demonstrated in Figs. 1 and 2 showing several examples of k(T) and SIRM(T) curves for rocks and soil. The thermal behaviour of susceptibility (k) was determined with a KLY-3S kappabridge with a CS-2 furnace device made by the AGICO (Czech Republic). Heating was performed in air. A sample is heated up to the maximum temperature of 700 °C and subsequently cooled to room temperature. Thermal demagnetization of saturation isothermal remanence (SIRM) was carried out with the use of a device made by the TUS, Poland. SIRM was imparted on a sample in the field of 9 T high enough to saturate hard magnetic minerals such as hematite or goethite, and measured during heating up to 700 °C in a magnetic screen.

Figs. 1, 2

As it is seen in Figs. 1 and 2, during heating in SIRM(T) and k(T) experiments different magnetic minerals were created at the end due to specific oxidation – reduction conditions different in both experiments. During M(T) or SIRM(T) measurements oxidation conditions prevail whereas during k(T) experiment reduction takes place.

Although susceptibility changes during heating process did not often provide us with T_c values of magnetic minerals present in a fresh sample, they can be used to better understanding of transformations of the iron oxides present in rocks and soils occurring in reduction conditions. Little attention have been paid to analyze susceptibility changes at high temperature in relation to transformation of magnetic minerals in rocks although Tanikawa et al. (2008) used thermomagnetic susceptibility analysis of core samples from the Chelungpu fault in Taiwan to explain high values of magnetic susceptibility of fault rocks.

In environmental magnetism, monitoring of thermal transformations during k(T) measurements is used by several authors to describe processes occurring in soil during pedogenesis or anthropogenic activities (fires, archeological objects, pollution). Pedogenesis involves a complex series of post-depositional processes related to environmental parameters such as temperature, rainfall, pH or microbial activity. There is still much to learn about the pedogenic processes and their sensitivity to various climatic factors. It is known that in soil pedogenesis leads to breakdown of iron-bearing silicates and clays to produce oxyhydroxides and ferrihydrite. Iron hydroxides transform to ferrimagnetic oxides such as magnetite or maghemite through dehydration process and then to hematite at higher temperature (Cornell and Schwertmann, 2003, Maher, 1998). Several authors (for example Hanesch and Petersen, 1999, Dearing et al., 2001) proposed second mechanism of formation of magnetite from ferrihydrite with the help of iron-reducing bacteria. Magnetite is converted to maghemite through low-temperature oxidation. In nature according to Longworth et al.(1979) this mineral is neither magnetite nor maghemite, but solid solution between them, a cation-deficient magnetite. Özdemir and Banerjee (1982) studying Minnesota topsoil concluded that magnetite is the first strongly magnetic iron oxide produced in pedogenesis. Its concentration and small grain size of superparamagnetic range was responsible for susceptibility enhancement. Magnetite is slowly oxidized in ambient temperature to cation-deficient form and to maghemite at the end. Low-temperature oxidation of magnetite to maghemite is related to paleoclimate conditions and the degree of pedogenesis. Anthropogenic activity is usually connected with coarse- grained magnetite or hematite.

Temperature dependence of magnetic susceptibility has been widely used to determine mineralogy, grain size distribution and stoichiometry of magnetic assembly present in loess/paleosol sequence because it can help better understand pedogenic processes and link them to paleoclimate (Deng et al., 2001, Liu et al., 2004, 2005, 2007). Deng et al. (2001)

investigated magnetic mineralogical changes during thermal treatment of Holocene samples from the Chinese Loess Plateau. The results suggested the stronger pedogenesis caused the higher low-temperature oxidation, the higher content of maghemite, greater susceptibility decrease at 300 –400 °C and weaker susceptibility peak at about 510°C. Lui et al. (2005) examined temperature dependence of susceptibility in argon of Chinese loess/paleosol and stated that the susceptibility loss during heating at temperature 300 – 400 °C is caused by the inversion of pedogenic fine-grained maghemite to hematite. They proposed that the susceptibility loss can be used as a new concentration index of pedogenic SP grains. They suggested that heating up to 700 °C in argon could be in some sense an analogue to the pedogenic processes. According to Liu et al.(2005) " the effect of pedogenesis and thermal treatment on the bulk susceptibility seems to be equivalent…there exists a similarity in two aspects. First, the pedogenesis occurs in a reducing environment. Secondly, the pedogenesis produces a fine-grained assemblage (SP+SD)". Maher et al. (2003a, 2003b) examined pedogenic susceptibility enhancement in soil of Russian steppe and in Chinese Loess Plateau in relation to rainfall. Banerjee (2006) outlined the problem of evaluation separatly the role of abiotic and biotic reduction activity in formation of magnetic enhancement in soil. He believes that this enhancement may be a signature not only of paleorainfall but also of concentration of iron reducing bacteria species and their activity.

In the present paper we focus on the study of thermal transformations of iron oxides and oxyhydroxides in soil which take place during susceptibility measurements. Our interest in the problem arose from the central role they played in environmental magnetic and paleoclimatic study in deciphering of the environmental control on magnetic susceptibility enhancement in topsoil. In our earlier paper (Kopcewicz et al, 2006) we reported the results of Mössbauer spectroscopy used to identify iron oxides responsible for soil magnetism and for changes of the shape of magnetic susceptibility curves observed in the thermomagnetic

124 measurements. The first results justified the use of the laboratory heating process as a means
125 to determine the thermal conversion of iron compounds in the different soil layers and
126 eventually elucidate the problem of the influence of the organic matter on chemical processes
127 which take place during heating.
128
129 EXPERIMENTS
130 The samples were taken from the Ukrainian chernozem soil profile from the Homutovsky
131 Steppe reserve from the topsoil layer 0-10 cm of depth and from the loess layer 120 –130 cm
132 of depth. Table 1 shows chemical characteristics of the samples. They differ in humus content
133 and progress of pedogenesis. Table 1
134 For identification of magnetic minerals the heating curves of saturation magnetization $J_s(T)$
135 and saturation remanence SIRM(T) were used. The saturation magnetization $J_s(T)$ decay
136 curves were measured with the means of a vibrating sample magnetometer in a field of a
137 strength of 0.45 T from 20 °C to 700 °C in paleomagnetic laboratory of the Institute of
138 Physics of the Earth in Moscow. For the topsoil sample the saturation remanence decay curve
139 SIRM(T) during heating showed a phase with $T_{ub} \sim 630$ °C which we interpret as maghemite
140 (Fig. 2). The $J_s(T)$ curve reveals mineral of T_c below 700 °C and weak increase at
141 temperature of about 500 °C indicates formation of small amount of new magnetite. The T_c
142 and T_{ub} were determined from heating curve by the two- tangent method proposed by
143 Grommé et. al. (1969). Magnetic measurements were completed by Mössbauer analysis
144 which shows the presence of maghemite, hematite and goethite. For the loess sample, T_{ub} and
145 T_c are about 690 °C. Mössbauer analysis shows hematite associated with some amount of
146 maghemite and goethite (Kopcewicz et al., 2005).
147 In the case of our samples the heating curves of k(T) demonstrate several mineral
148 transformations (Fig.2). The most common explanation of these curves is as follows: the first

149 small increase of susceptibility at about 220 °C (for the topsoil sample) and 300 °C (for the
150 loess sample) represents dehydration of goethite to hematite. The drop of k between 220 °C
151 and 400 °C or 300 °C and 450 °C, for the topsoil and the loess respectively, is due to
152 transformation of maghemite to hematite. Formation of new magnetite starts from 400 - 450
153 °C. The Curie temperature determined from heating curve is about 590 °C by the two- tangent
154 method proposed by Grommé et. al. (1969) or 570 °C according to the method proposed by
155 Petrovsky and Kapička (2006). Both pointed to magnetite as the main magnetic mineral. The
156 increase of room susceptibility after heating up to 700 °C is 2.6 times for the topsoil and 20
157 times for the loess. It should be noted that in the loess, only small part of magnetite was
158 created below 600 °C. Formation of magnetite occurred predominately above 600 °C. For the
159 topsoil thermally induced mineral changes make impossible determination of the Curie
160 temperature of original minerals. Even for the loess when the changes of k seems moderate up
161 to 600 °C, the Curie temperature determined from heating curve do not represent the original
162 magnetic mineral but is disturbed by newly formed magnetite.
163 To document the sequence of magnetic mineral transformations during the heating process
164 the set of experiments was performed. The scheme of experiments is illustrated in Fig.3. The
165 sample of soil was divided into 5 specimens. Each specimen was heated in KLY-3 device up
166 to different increasing temperature: 250 °C, 400 °C, 500 °C, 600 °C and 700 °C. After
167 heating, low temperature experiments, SIRM(T) curves, hysteresis loops and Mössbauer
168 analysis were performed for each specimen.

Fig. 3

169 The susceptibility behaviour during heating was shown in Fig. 4. For the topsoil sample
170 small alteration occurs after heating up to 250 °C. Dramatic transformation starts at 500 °C,
171 with maximum at 600 °C. For the loess, alteration starts at 400 °C, susceptibility increases
172 slowly with temperature and shows enormous increase after heating up to 700 °C.

Fig. 4

To quantify the degree of irreversibility of thermomagnetic curves, we used the alteration factor A(40) introduced by Hrouda (2003) to characterize the irreversible changes of k. The A(40) index was defined by Hrouda (2003) as follows: $A(40) = 100(k_{Tc,40} - k_{Th,40})/k_{Th,40}$, where $k_{Tc,40}$ and $k_{Th,40}$ are values of total susceptibility at 40 °C during cooling and heating, respectively. The A(40) index described above is shown in Fig.5a. As grain size influence magnetic susceptibility, especially in the range of fine grains, the amount of newly generated strong magnetic phases is better represented by ferrimagnetic contribution to M_s (Fig.5b) calculated from hysteresis loop. The both parameters follow similar courses but the increase of ferrimagnetic content is not so dramatic as in the case of susceptibility. This situation can be explained by creation of SP grains at high temperature which influences strongly magnetic susceptibility.

Fig. 5

SIRM(T) curves of heated specimens (Fig.6) show that significant amount of magnetite was created after heating up to 500 °C in the topsoil samples and after heating up to 700 °C in the loess samples. The "drops" at about 200 °C on SIRM(T) curves obtained for samples previously after heated up to 500°C in k(T) experiment are related to structural features ra than to magnetic phases. They are not seen on k(T) curves and because of that can be interpret as unblocking of unstable remanence carried by fine grains of size just above SD/SP boundary.

Fig. 6

Low-temperature dependence of susceptibility was measured by means of a KLY-3S Kappabridge with a CSL cryostat device made by the AGICO (Czech Republic) during warming samples from the liquid nitrogen temperature (LNT = -196° C) up to room temperature. Susceptibility varies with temperature in complicated manner depending on magnetic mineralogy and also on grain size. Low-temperature experiments provide information about the presence of magnetite and hematite if the Verwey or Morin transitions are observed. The shape of low-temperature curves can provide information about the

Fig. 7

198 contribution of paramagnetic or superparamagnetic grains to the bulk susceptibility
199 (Thompson and Oldfield, 1986; Eyre and Shaw, 1994). Fig. 7 shows low-temperature curves
200 for the topsoil and the loess samples heated previously up to temperatures: 250 °C, 400 °C,
201 600 °C and 700 °C. For the topsoil, first changes were observed for the sample heated up to
202 400 °C when Vervey transition was marked and the shape of curve becomes SD like. For
203 sample heated up to 600 °C and to higher temperatures the curves look like SP behaviour and
204 they differ from that for unheated soil only by presence of magnetite marked by the Vervey
205 transition and higher value of susceptibility. For the loess, first changes were observed after
206 heating to 600 °C when the concave shape of curve becomes almost linear. For the sample
207 heated up to 700 °C, increase of susceptibility and the lack of Verwey transition is an
208 evidence of the presence of SP grains. This observation agrees with our interpretation of
209 variations of the A(40) index and ferromagnetic contribution to M_s.
210 Hysteresis parameters were measured by means of Micro-Mag, AGM device produced by
211 Princeton Measurements Corp. USA with maximum field of 1.4T (Table 2). For the topsoil
212 sample, heating caused increase of M_s, M_r, H_c and H_{cr} starting from temperature of 400 °C
213 with the maximum increase after heating up to 600 °C. For the loess sample, M_s and M_r begin
214 to increase after heating up to 500 °C with the biggest increase after heating up to 700 °C. H_c
215 and H_{cr} decreased. In general, after the heating process, hysteresis parameters, ratios M_r/M_s
216 and H_{cr}/H_c (Table 2) indicate greater contribution of fine grains in heated samples than in
217 fresh material (Day et al., 1977). The contribution of soft and hard material in the topsoil and
218 the loess during heating is demonstrated by the ratio of hysteresis parameters of the topsoil to
219 the respective parameters of the loess (Table 2). In fresh material, the contribution of soft and
220 strong minerals is greater in the topsoil than in the loess whereas at the end of the heating
221 process the loess sample contains more such minerals.

Table 2

Fig. 8, 9

To change the conditions of experiment we applied different mode of heating. The sample of topsoil and the sample of loess were heated in so-called "multi-heating cycles" up to increasing temperatures; 250, 400, 500, 600 and 700 °C in Czech KLY -3S device. The sample was heated up to 250 °C and cooled to room temperature, then heated again to 400 °C and cooled again to room temperature. The heating was repeated up to 700 °C. Changes of susceptibility during succeeding heatings were shown in Fig. 8. When compared with the results of previous experiments one can see that in the case of the topsoil the changes are of similar character only on a smaller scale (Fig. 5b). The loess sample also exhibits similar changes of k until heating up to 400 °C (Fig.8). During heating to higher temperature k(T) curves become almost reversible (Figs. 9 and 5b) with the Curie temperature above 600 °C. SIRM(T) curve of heated topsoil sample shows "decline" at temperature below 200 °C not observed on SIRM(T) curve for fresh sample. For the loess, SIRM(T) curves are practically similar for fresh and heated samples.

MÖSSBAUER MEASUREMENTS

To verify the results obtained during magnetic measurements the Mössbauer spectroscopy was used. Mössbauer measurements were performed for the fresh topsoil and loess samples, for samples heated up to T = 250, 400, 500, 600 and 700 °C (each time starting from room temperature) and for samples heated up to 700 °C in multi-heating process.

First results of the Mössbauer analyses of soil samples heated during measurements of the magnetic susceptibility were reported by Kopcewicz et al.(2006).

The Mössbauer parameters obtained for fresh samples revealed the presence of Fe^{3+}ions in paramagnetic minerals represented by two paramagnetic doublets. One doublet with isomer shift $\delta = 0.36$ mm/s and quadrupole splitting $\Delta = 0.43$ mm/s represented group of minerals named A, and the doublet with $\delta = 0.37$ mm/s and $\Delta = 0.93$ mm/s represented group of

Table 3

minerals called B. The Fe^{2+}-bearing silicate minerals were represented by paramagnetic doublet with δ = 1.08 mm/s and Δ = 2.74 mm/s. Taking into account the value of hyperfine parameters, the paramagnetic doublets (A and B) may originate from Fe^{3+} cations in the oxyhydroxides (ferrihydrite, β-FeOOH and γ-FeOOH), from silicates and/or from iron-containing antiferromagnetic and ferrimagnetic iron oxides in the form of ultra fine particles in superparamagnetic state. Kopcewicz et al. (2005) verified the origin of the quadrupole doublets by performing the Mössbauer measurements at 80 K (LNT) and the results suggested that some part of iron oxides may appeared in the form of ultra fine particles in the superparamagnetic state. Part of Fe^{3+} cations (B) together with Fe^{2+} cations comes most probably from clay minerals. Also magnetically ordered iron oxides (α-Fe_2O_3, α-FeOOH , γ-Fe_2O_3) were identified in the samples. The approximate mineralogical content was determined by relative area (RA) of the Mössbauer spectral components corresponding to each compound (Table 3).

Values of isomer shift and quadrupole splitting, for both minerals A and B, remain relatively similar for samples heated up to 250 °C. After heating up to temperatures higher than 250 °C we observed more pronounced increase in quadrupole splitting values characteristic of distorted crystalline coordination which suggests the beginning of dehydration process (loss of hydroxyl).

The Fe^{3+} cations in minerals described as A which contained OH and/or structural water were significantly affected by the heating. Their content significantly decreases. Ferric and ferrous iron present as structural iron in silicates (minerals B) was more stable. Simultaneously, a steady increase of Fe^{2+} cations content in the paramagnetic components was observed which indicates that transformation process occurred under reduction conditions.

The changes of relative iron content in paramagnetics and relative content of magnetic minerals for the heated topsoil and loess samples identified in the Mössbauer experiment are

shown in Table 3 and Fig. 10. Mössbauer analysis shows that goethite was broken up after heating up to 250°C. Maghemite in soil is extremely stable and transforms to hematite after heating up to 700 °C. In the topsoil sample, content of magnetite increases in the whole heating range. In the loess, magnetite was created by heating up to 400 °C and to 700 °C. However, the Mössbauer analysis made for the topsoil and loess samples heated up to 700 °C in multi-heating process give different picture of chemical changes. Fig. 11 and Tables 4 and 5 show the differences in content of iron compounds depending on the way of heating process. For topsoil sample, in the case of multi-heating process chemical changes had the same character as in the case of singe heating up to 700 °C. It was process of reduction and only amount of Fe^{2+} cations (RA) both, in paramagnetic and magnetic compounds, increased. For loess sample, the chemical changes had completely different character during multi-heating process. The Mössbauer spectrum in Fig. 11c (right) consists of two paramagnetic doublets (Fe^{3+} in minerals A and B), a six line spectrum with the Mössbauer parameters (Table 5) which corresponds to hematite and a weak sextet which likely corresponds to Fe^{3+} cations in maghemite. The Fe^{2+} cations disappeared completely. It suggests oxidation character of the chemical changes in the loess sample during multi-heating process.

DISCUSSION

The susceptibility enhancement in the topsoil is due to formation of strong ferrimagnetic oxides magnetite/maghemite as en effect of pedogenesis.

Pedogenesis starts from weathering of paramagnetic mother clay minerals, amphibolites etc. to form ferrihydrite, and amorphous oxyhydroxide containing Fe^{3+} iron. This iron is reduced to Fe^{2+} by "fermentation" process according to LeBorgne (1960) or due to iron-reducing bacteria (Banerjee, 2006) and combined with the remaining Fe^{3+} ions to form fine-grained magnetite. Finally, magnetite is oxidized to maghemite. Barron and Torrent, (2002) proposed

another mechanism for maghemite creation– slow transformation of ferrihydrite to maghemite at near ambient temperature. Another possibility is dehydroxylation of lepidocrocite which can also lead to maghemite formation. During pedogenesis goethite and hematite are also produced. As a result, topsoil contains goethite and hematite, both pedogenic and lithogenic, fine-grained magnetite and/or maghemite. In well developed soil, for example in the Chinese Loess Plateau, strong ferrimagnetic mineral is neither pure magnetite not pure maghemite but partly oxidized magnetite.

The results of our experiments show that in our samples the starting minerals which can play role in magnetic transformations are iron oxides - maghemite and hematite determined from SIRM(T) curves and from the Mössbauer spectrum. Additionally, hydroxides such as goethite, lepidocrocite (?) and ferrihydrite and amorphous structurally iron- bearing oxyhydroxide were found from the Mössbauer analysis. Although the set of magnetic minerals is the same for both samples, and the content of hematite is similar, the topsoil contains more maghemite and goethite than the loess. SIRM(T) curves and the Mössbauer analysis revealed that the fresh material of both samples did not contain magnetite. According to Liu et al.(2005), the absence of magnetite is a demonstration of the maturity of our soil.

The Mössbauer analysis showed that during thermal experiment (Fig. 10), goethite was dehydrated after heating up to 250 °C, and should transform to maghemite and/or hematite. However, we did not observe increase of these minerals content. For the topsoil, at that temperature small amount of magnetite was created. Özdemir and Dunlop (2000) found that during dehydration of goethite intermediate spinel phase - magnetite was formed. This process can be responsible for magnetite appearance in the topsoil sample. In the loess, thermal transformation of goethite can occur in a different way. Przepiera and Przepiera (2003) have proved that dehydroxylation of precipitated goethite begins at temperature of 200

°C by conversion into amorphous form of hematite (protohematite). As reducing conditions prevail during experiment, after heating up to 400 °C magnetite is created. We observed decrease of susceptibility between 300 – 400 °C. Usually this decrease is explained by conversion of pedogenic maghemite to hematite (Liu et al. 2005). However, the SIRM(T) curves and the Mössbauer analysis did not confirm conversion of maghemite to hematite at temperature range of 300 – 400 °C. Complete conversion of maghemite is observed for both samples at much higher temperature after heating up to 700 °C. We explained the loss of k between 300 and 400 °C as a result of increase of grain size from SP to SD on the basis of low – temperature experiments. In the topsoil, production of magnetite was continued during subsequent heatings. For the loess, magnetite was created at 400 °C and then at 600 °C and higher. According to Cornell and Schwertmann (2003) magnetite can be generated through reduction from lepidocrocite, ferrihydrite and hematite. Barron et al. (2003) proposed that in soil after heating up to 400° C ferrihydrite converts to magnetite and maghemite. Such processes, besides transformation of goethite, can be responsible for production of magnetite at the whole range of temperature in the topsoil and at 400 °C in the loess. Hanesch et al. (2006) studying thermal transformations of goethite, lepidocrocite and ferrihydrite found that the transformations start between 200 and 350 °C for ferrihydrite and lepidocrocite and around 450 °C for goethite. They observed that the presence of organic carbon leads to formation of maghemite or magnetite instead of hematite which is created without organic carbon. In the case of lepidocrocite, organic carbon decreases the transformation temperature and intensifies the effect. The presence of organic carbon intensifies conversion of hematite to magnetite. We observed that in the topsoil the presence of humus lowers temperature at which the increase of Fe^{2+} content and formation of magnetite starts. The temperatures of transformation found by Hanesch et al. (2006) are a little higher than in our experiment. In the loess, organic matter is almost absent. However, the reducing conditions prevail also in the

loess (Table 1). At 700 °C reduction of hematite leads to production of magnetite. In spite of lack of humus, the increase of susceptibility at the end of the heating process is much higher in the loess than in the topsoil (Fig. 5).

When we have compared M_r and M_s intensities for the both samples (Table 2) at the end of experiment, the absolute values turned out to be almost equal. The increase of M_r and M_s caused by the heating process was expressed by the values of remanent and saturation magnetizations ratios measured at room temperature (M_r(RT), M_s(RT)), and after heating up to 700 °C (M_r(700) and M_s(700)). The enhancement (Table 2) is much higher for the loess (33 and 29.5, respectively) than for the topsoil (12.8 and 8.5, respectively) and higher for M_s than for M_r. The difference between the enhancement in the loess and in the topsoil can be related to the degree of pedogenesis. The difference between the enhancement of M_r and M_s can be related to the important contribution of SP grains in loess heated previously to 700 °C. It is confirmed by the shape of k(T) curve obtained in low-temperature experiment.

The high stability of maghemite which converts to hematite at the very high temperature of 700 °C in the both samples – topsoil and loess - is rather unusual for this mineral. Although such high temperature of inversion was reported for loess (Liu et al. 2003) or synthetic samples (Özdemir and Banerjee, 1984), de Boer and Dekkers (1996) found that the coarser grains, the higher inversion temperature appears. Liu et al. (2005, 2007, Deng et al., 2001) reported inversion temperature of maghemite about 300 –400 °C. They correlated the decrease of susceptibility caused by this process with the degree of pedogenesis. Hanesch et al. (2006) stated that maghemite obtained from goethite in the presence of organic carbon does not transform to hematite when heated up to 800 °C. Also Liu et al. (2004) found in Chinese loess/paleosol maghemite which was stable till 700 °C. They stressed that partly oxidized magnetite often occurring in loess/paleosol have different magnetic properties than its fully oxidized form – maghemite.

372 The topsoil and loess in our study do not differ significantly in such pedogenic parameters as
373 pH, total iron content Fe_t or free iron Fe_d. The main differences are in humus and amorphous
374 iron content Fe_o (Table 1). Smaller content of Fe_o indicates less amount of ferrihydrite in the
375 loess than in the topsoil. Almost equal values of M_r and M_s for the both samples at the end of
376 the heating process suggest that pedogenic formation of strong ferrimagnetic minerals
377 observed in the topsoil is limited by the amount of iron in a parent material. Fig. 11
378 The multi-heating experiment indicated that humus play important role in keeping reduction
379 conditions during succeeding heatings. For the loess, reduction conditions were held only at
380 the beginning of experiments during two first heating runs. We suggest that reduction
381 conditions were held due to evaporation of water present in a sample. The oxygen access was
382 hindered be the vapor formed during heating. The observed differences between behaviour of
383 the topsoil and the loess samples during multi-heating process can be explain by different
384 content of organic matter in the samples. In the case of the topsoil humus keeps sufficient
385 amount of water whereas in the loess water is barely enough for two first heating runs. In the
386 case of topsoil the reduction atmosphere is more stable and lasts longer than in the case of the
387 loess layer where the content of organic matter is limited. In the loess sample the multi-
388 heating process changes the atmosphere from reduction to oxidation which has the essential
389 influence on final results of the chemical processes.
390 Summarizing, as the topsoil and loess contain similar amount of hematite we suggest
391 predominantly lithogenic origin of this mineral. The enhanced amount of goethite in the
392 topsoil indicates that the great part of goethite has pedogenic origin probably in association
393 with ferrihydrite in moderate and wet climate. Among the pathway of maghemite formation,
394 oxidation of magnetite is the less probable as no magnetite was revealed in fresh samples.
395 High thermal stability of maghemite points to poor crystallized, transitional form originated

from goethite or ferrihydrite. The role of magnetotactic or iron-reducing bacteria seems rather marginal.

CONCLUSIONS

The experiment can help to trace the alterations of magnetic oxides and hydroxides occurring during the heating process and to determine temperatures at which different transformations take place. The Mössbauer analysis proved that reduction conditions are held during k(T) measurements performed in the Czech KLY –3S device. In single heating process at low temperature of 200 – 450°C, the prevailing transformations are thermal dehydration/ dehydroxylation of hydroxides such as goethite, lepidocrocite and ferrihydrite to magnetite/maghemite, whereas at temperature above 600°C reduction of hematite is the main source of new magnetite. In the topsoil the first process is more important whereas in the loess reduction of hematite to magnetite prevails. The difference in the enhancement of magnetization in the loess and the topsoil can be related to the degree of pedogenesis. The unusual stability of maghemite can be ascribed to specific climate conditions but this suggestion needs confirmation by further study of soil from different climatic zones. The multi-heating process in loess sample change the reduction atmosphere to oxidation one and at the end of thermal transformation only Fe^{3+} bearing compounds were observed. The humus plays important role in keeping reduction atmosphere during the heating process due to enough amount of bounded water.

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RFERENCES

Banerjee, S.K., 2006. Environmental magnetism of nanophase iron minerals: testing the biomineralization pathway. Phys. Earth. Planet. Int. 154, 210-221.

Barrón, V., Torrent, J., 2002. Evidence for a simple pathway to maghemite in Earth and Mars soils. Gochim. Cosmochim. Acta. 66, 2801-2806.

Barrón, V., Torrent, J., de Grave, E., 2003. Hydromaghemite, an intermediate in the hydrothermal transformation of 2-line ferrihydrite into hematite. American Mineralogist. 88, 1679-1688.

Cornell, R.M., Schwertmann, U., 2003. The iron oxides., Wiley-VCH Gmbh&Co. KgaA, Weinheim

Day, R., Fuller M., Schmidt .A, 1977. Hysteresis properties of titanomagnetite: Grain size and composition dependence. Phys. Earth. Planet. Int. 13, 260-267.

Dearing, H.A., Hannam, J.A., Anderson, A.S., Wellington, E.M.H., 2001. Geophys. J. Int.144, 183-196.

De Boer, C.B., Dekkers, M.J., 1996. Grain size dependence of the rock magnetic properties for a natural maghemite. Geophys. Res. Lett. 23, 2815-2818.

Deng, C., Jackson, M.J., Verosub, K.L., Singer, M.J., 2001. Variability of the Temperature-Dependent susceptibility of the Holocene Eolian Deposits in the Chinese Loess Plateau: A Pedogenesis indicator. Phys. Chem. Earth (A). 26, No. 11-12, 873-878.

Eyre, J.K., Shaw, J., 1994. Magnetic enhancement of Chinese loess – the role of γFe_2O_3. Geophys. J. Int. 117, 265-271.

444 Grommé, C.S., Wright, T.L., Peck, D.L., 1969. Magnetic properties and oxidation of iron-
445 titanium oxide minerals in Alae and Makaopuhi lave lakes, Hawaii. J. Geophys. Res.
446 74, 527-5293.
447 Hanesch, M., Petersen, N., 1999. Magnetic properties of recent parabrown-earth from
448 Southern Germany. Earth Planet. Sci. Lett. 169, 85-97.
449 Hanesch, M., Stanjek, H., Petersen, N., 2006. Thermomagnetic measurements of soil iron
450 minerals: the role of organic carbon. Geophys. J. Int. 165, 53-61.
451 Hrouda, F., 2003. Indices for numerical characterization of the alteration processes of
452 magnetic minerals taking place during investigation of temperature variation of
453 magnetic susceptibility. Stud. Geophys. Geod. 47, 847-861.
454 Kopcewicz, B., Kopcewicz**,** M., Jeleńska, M., Hasso-Agopsowicz, A., 2005. Mössbauer
455 Study of Soil Profiles in industrial region of Ukraine. In: Industrial Applications of
456 the Mössbauer Effect. eds: M. Garcia, J. F. Marco, and F. Plazaola, American
457 Institute of Physics, Melville, New York, 378-383.
458 Kopcewicz, B., Kopcewicz**,** M., Jeleńska, M., Hasso-Agopsowicz, A., 2006. Mössbauer
459 study of chemical transformations in soil samples during thermomagnetic
460 measurements. Hyperfine Interact. DOI 10.1007/s10751-006-9332-3.
461 LeBorgne, E., 1960. Influence du feu sur les propriétés magnétiques du sol et sur celles du
462 schiste et du granite. Annales dr Géophysique. 16, 159-195.
463 Longworth, G., Becker, L.W., Thompson, R., Oldfield, F., Dearing, J.A., Rummery, T.A.,
464 1979. Mössbauer effect and magnetic studies of secondary iron oxides in soils. J. Soil
465 Sci. 30, 93-110.
466 Liu, Q.S., Banerjee, S.K., Jackson, M.J., Chen, F.H., Pan, Y.X., Zhu, , R.X., 2003. An
467 integrated study of the grain-size dependent magnetic mineralogy of the Chinese

loess/paleosol and its environmental significance. J Geophys. Res. 108, 2437, doi: 10.1029/2002JB002264.

Liu, Q.S., Banerjee, S.K., Jackson, M.J., Deng, Ch., Pan, Y.X., Zhu, , R.X., 2004. New insights into partial oxidation model of magnetites and thermal alteration of magnetic mineralogy of the Chinese loess in air. Geophys. J. Int. 158, 506-514.

Liu, Q.S., Deng, Ch., Yu, Y., Torrent, J., Jackson, M.J., Banerjee, S.K., Zhu, , R.X., 2005. Temperature dependence of magnetic susceptibility in an argon environment: implications for pedogenesis of Chinese loess/palaeosol. Geophys. J. Int. 161, 102-112.

Liu, Q.S., Deng, Ch., Torrent, J., Zhu, , R.X., 2007. Review of recent developments in mineral magnetism of the Chinese loess. Quat. Sci. Rev. 27, 368-385.

Maher, B.A., 1998. Magnetic properties of modern soils and Quaternary loessic/paleosol: paleoclimatic implications. Palaeogeogr. Palaeoclimatol. Palaeoecol. 37, 25-54.

Maher, B.A., Alekseev, A., Alekseeva, T., 203a. Magnetic mineralogy of soil across the Russian Steppe: climatic dependence of pedogenic magnetic formation. Palaeogeogr. Palaeoclimatol. Palaeoecol. 201, 321-341.

Maher, B.A., Hu, M.Y., Roberts, H.M., Wintle, A.G., 2003b. Holocene loess accumulation and soil development at the western edge of the Chinese Loess Plateau: implications for magnetic proxies of paleorain-fall. Quat. Sci. Rev. 22, 445-451.

Özdemir, Ö., Banerjee, S.K., 1982. A preliminary magnetic study of soil samples from west-central Minnesota. Earth Planet. Sci. Lett. 59, 393-403.

Özdemir, Ö., Banerjee, S.K., 1984. High temperature stability of maghemite. Geophys. Res. Lett. 11, 161-164.

Özdemir, Ö., Dunlop, D.J., 2000. Intermediate magnetite formation during dehydration of goethite. Earth Planet. Sci. Lett. 177, 59-67.

493 Petrovsky, E., Kapička, A., 2006. On determination of the Curie point from thermomagnetic
494 curves. J. Geophys. Res. 111, B12S27, doi: 10.1029/2006JB004507.

495 Przepiera, K., Przepiera, A., 2003. Thermal transformations of selected transition metals
496 oxyhydroxides. J.Therm. Anal. Ca. 74, 659-666.

497 Tanikawa, W., Mishima, T., Hirono, T., Soh, W., Song S., 2008. High magnetic susceptibility
498 produced by thermal decomposition of core samples from the Chelungpu fault in
499 Taiwan. Earth Planet. Sci. Lett. 272, 372-381.

500 Thompson, R., Oldfield, F., 1986. Environmental magnetism. Allen & Unwin, London.

501

502 FIGURES CAPTION

503 Fig. 1. Examples of changes of susceptibility (left curves) and saturation remanence (right
504 curves) during heating for rocks. k_1 – room-temperature susceptibility for fresh sample; k_2–
505 room-temperature susceptibility for heated sample. SIRM(1) - room-temperature saturation
506 remanence for fresh sample; SIRM(2) - - room-temperature saturation remanence for heated
507 sample.

508 Fig.2. Changes of susceptibility (a, b); decay curves of saturation remanence (c, d) and
509 saturation magnetization (e, f) during heating for topsoil and loess samples, respectively.
510 Inlets in left corner of a) and b) curves show full heating – cooling cycle of susceptibility
511 variation. Legend as in Fig. 1.

512 Fig. 3. Scheme of experiments.

513 Fig. 4. Changes of susceptibility during heating of one specimen once to particular
514 temperature (250°C, 400°C, 500°C, 600°C, 700 °C), for topsoil (left curves) and loess (right
515 curves) samples.

Fig. 5. a) Parameter A(40) for samples of topsoil and loess heated in two modes. Full symbols – specimens heated once to particular temperature; open symbols – one specimen heated to increasing temperatures. Circles – topsoil; triangles – loess. b) Content of ferrimagnetic minerals calculated from hysteresis loop.

Fig. 6. Decay curves of SIRM(T) for samples of topsoil and loess heated once to particular temperature.

Fig. 7. Changes of susceptibility during warming from liquid nitrogen to room temperature for samples of topsoil and loess heated once to particular temperature.

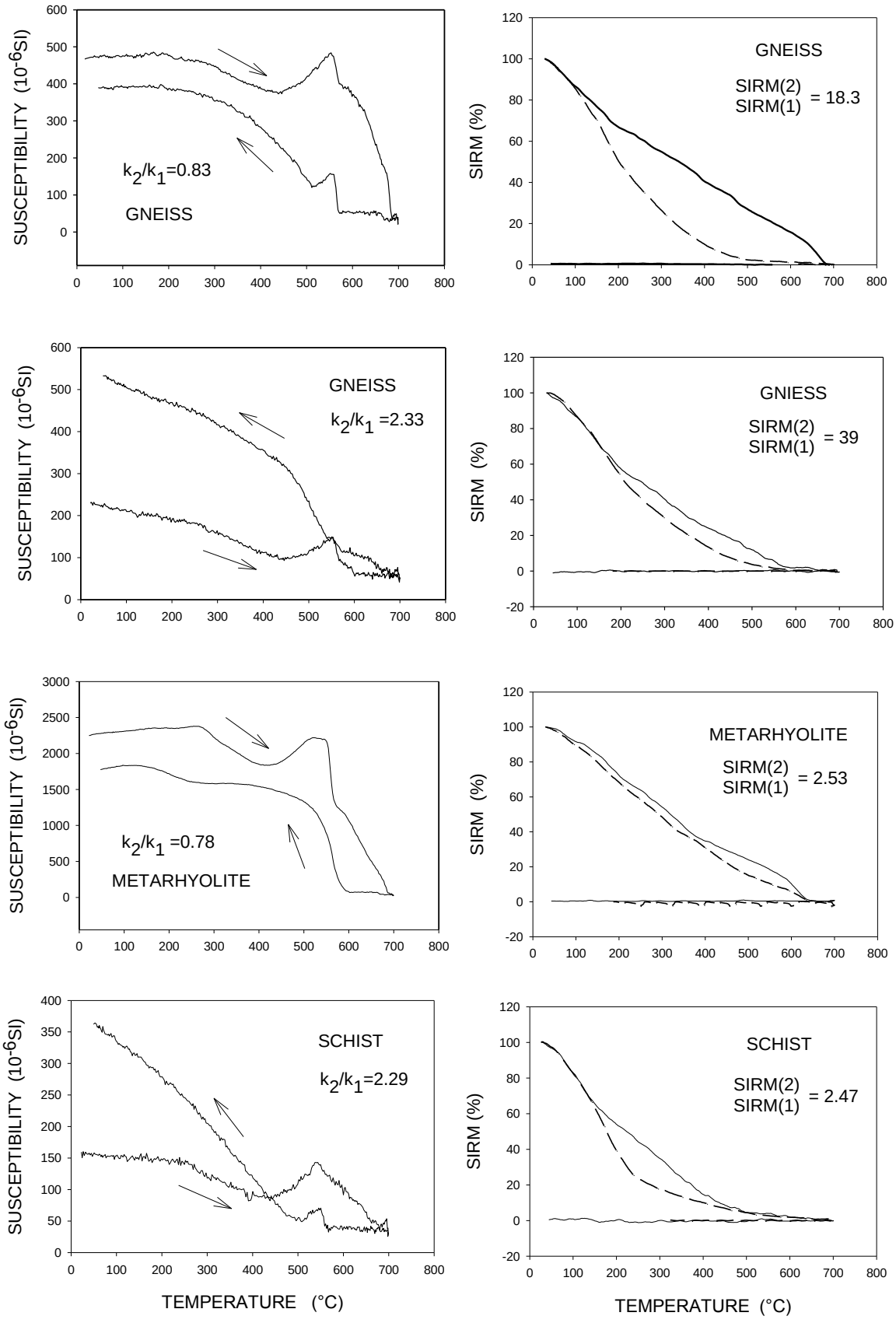
Fig. 8. Changes of susceptibility during multi-heating of specimen to increasing temperatures: 250°C, 400°C, 500°C, 600°C, 700 °C, for topsoil (left curves) and loess samples (right curves).

Fig. 9. Decay curves of SIRM(T) for: a) topsoil and b) loess samples heated previously several times to increasing temperatures (multi-heating process).

Fig. 10. Changes of iron content in paramagnetics (a, b) and in magnetic minerals (c, d) for samples of topsoil and loess heated to particular temperature from room temperature.

Fig. 11. Mössbauer spectra for the topsoil (left diagram) and loess (right diagram) samples measured at room temperature: a – for fresh sample; b – for sample heated from room temperature to 700 °C; c – for sample heated by multi-heating process to maximum temperature 700 °C.

Fig.1



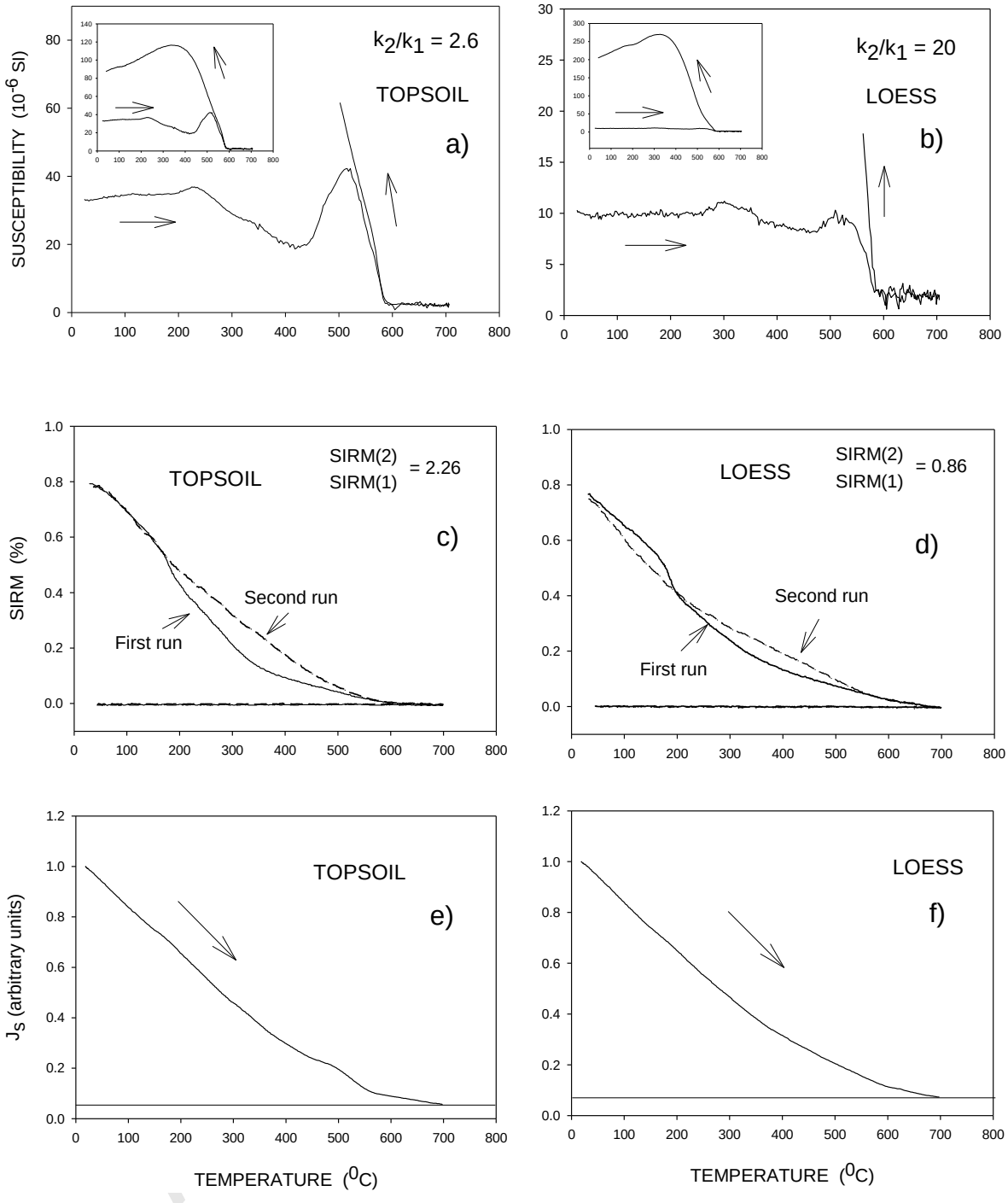
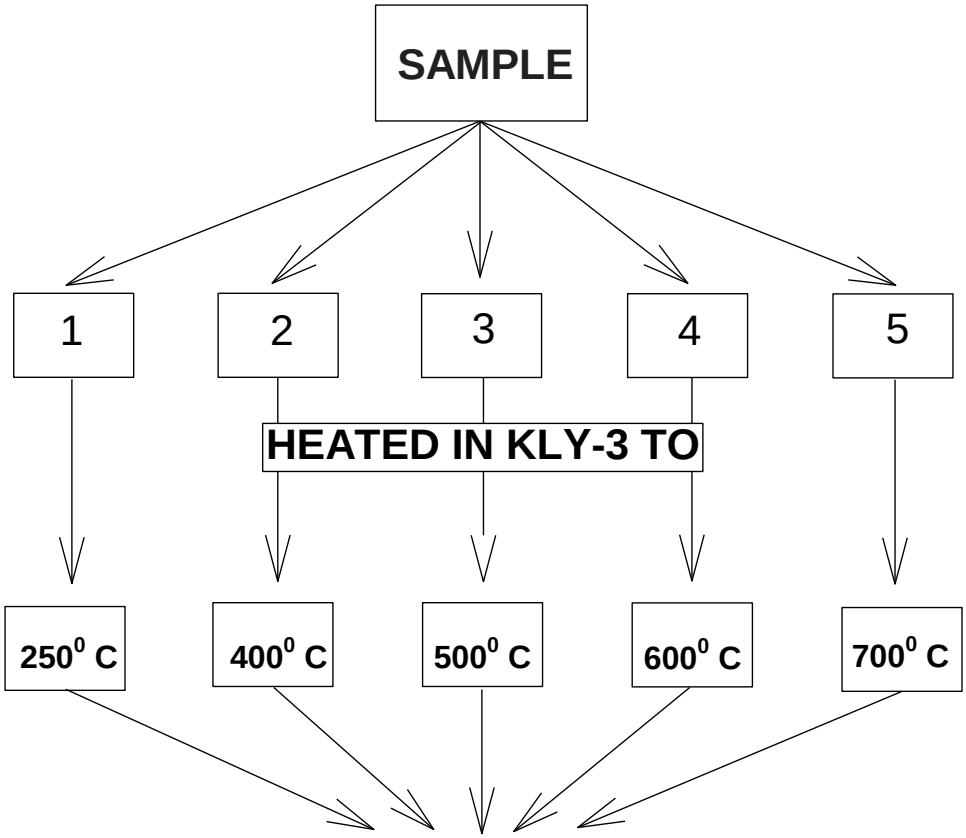


Fig. 2



LOW TEMPERATURE EXPERIMENTS

SIRM (T)

HYSTERESIS PARAMETERS

MOSSBAUER ANALYSIS

Fig. 3.

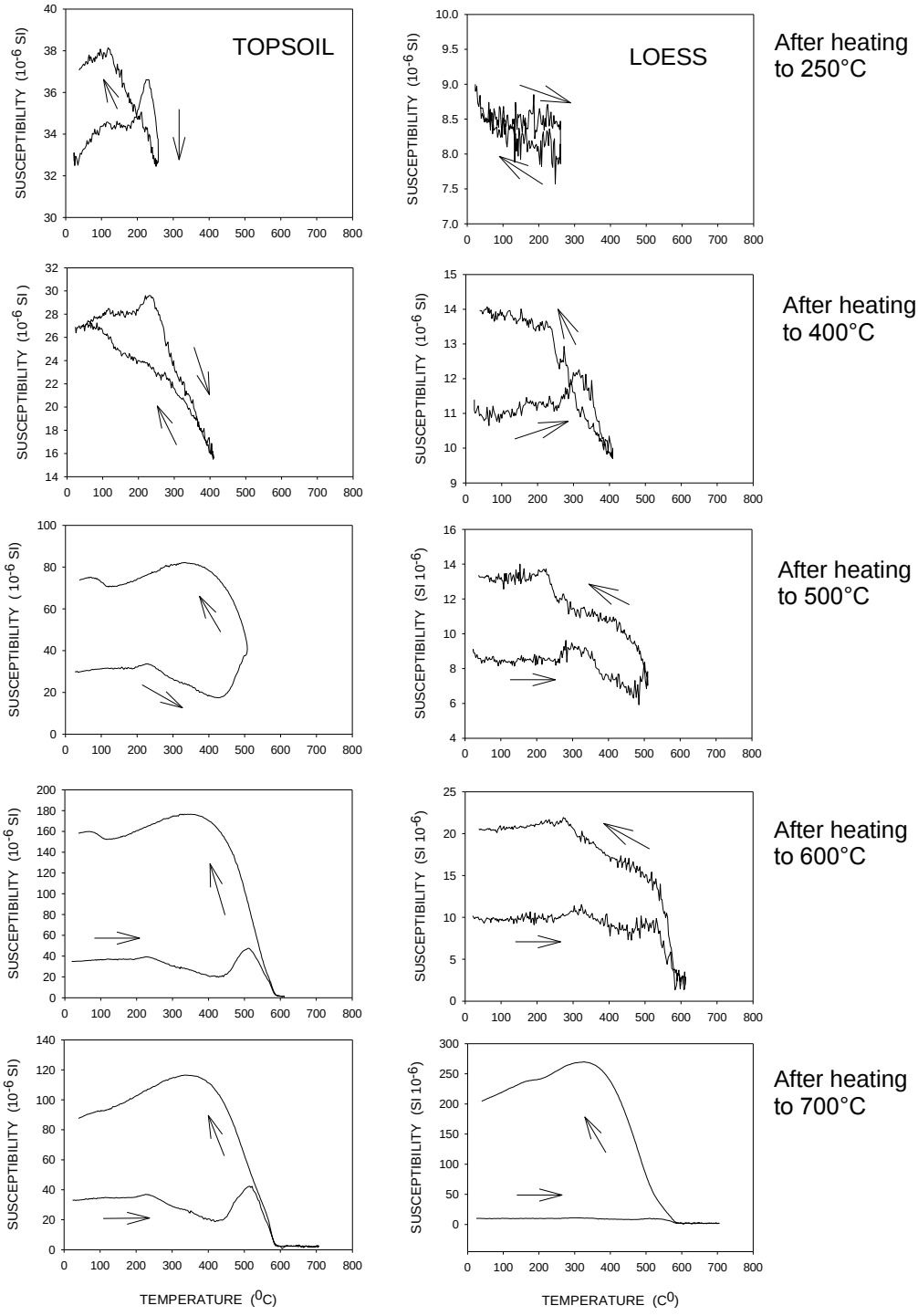
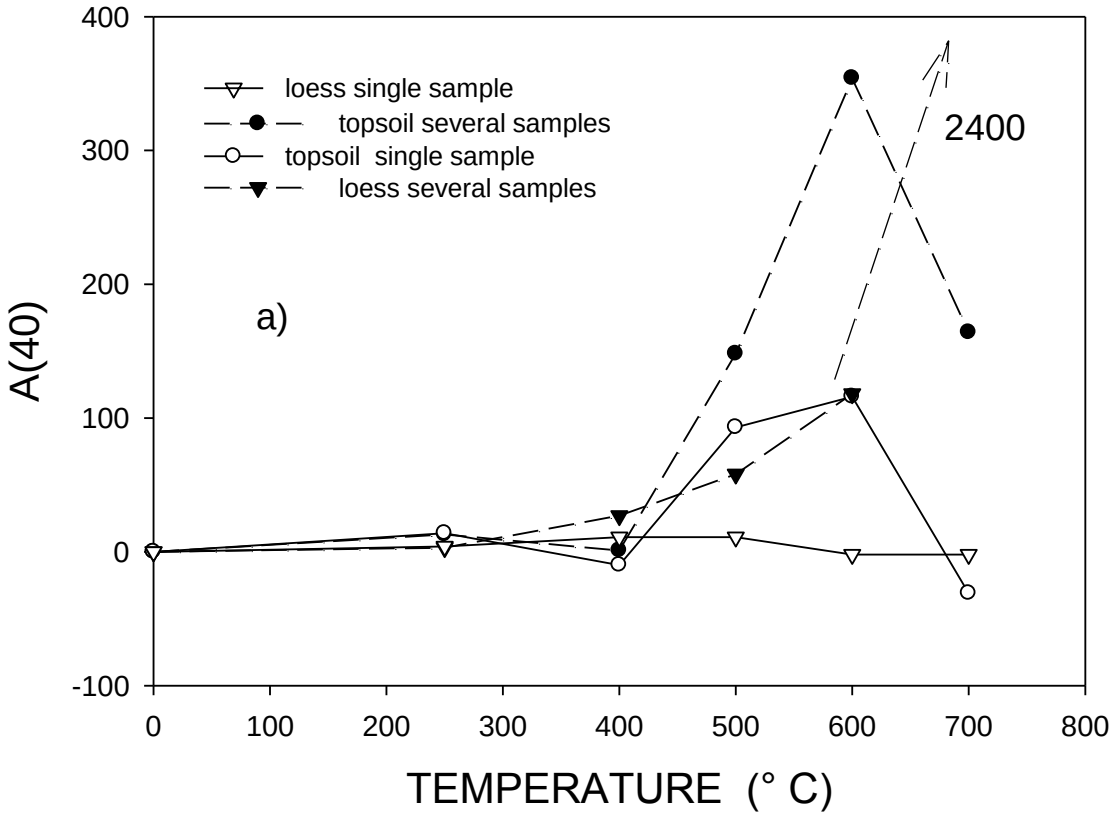


Fig. 4.



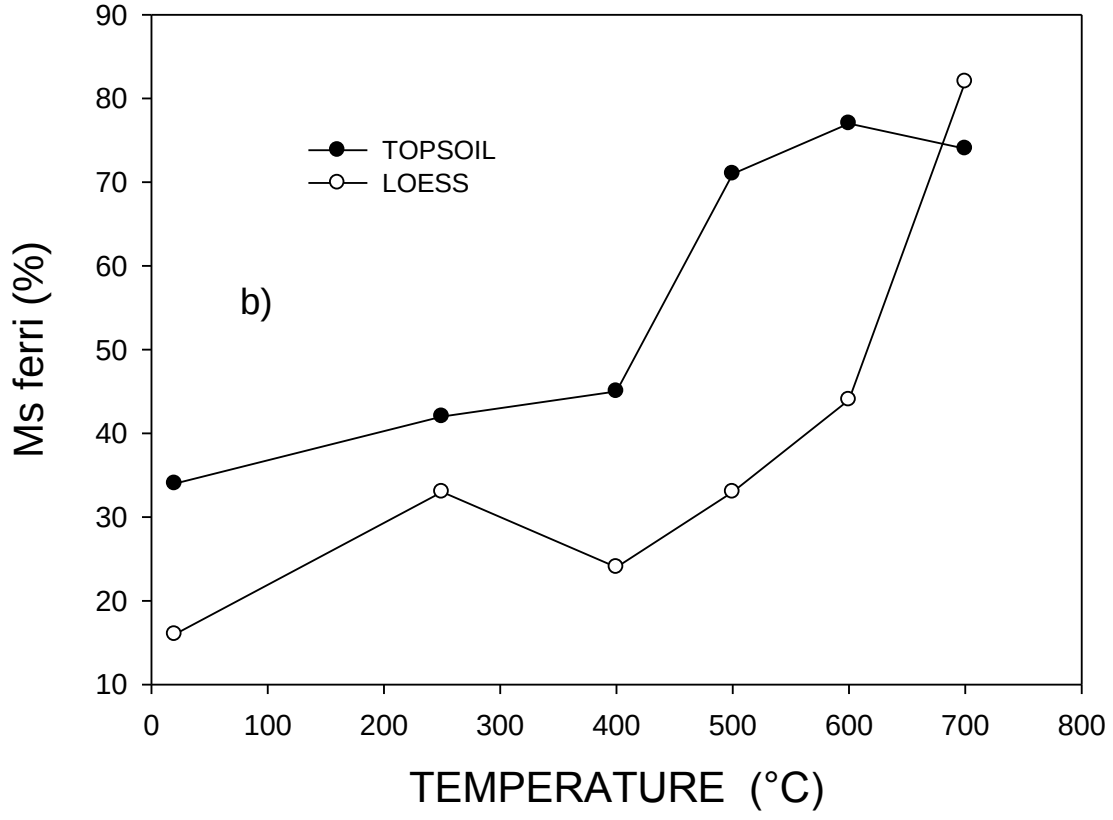


Fig. 5

Fig. 5.

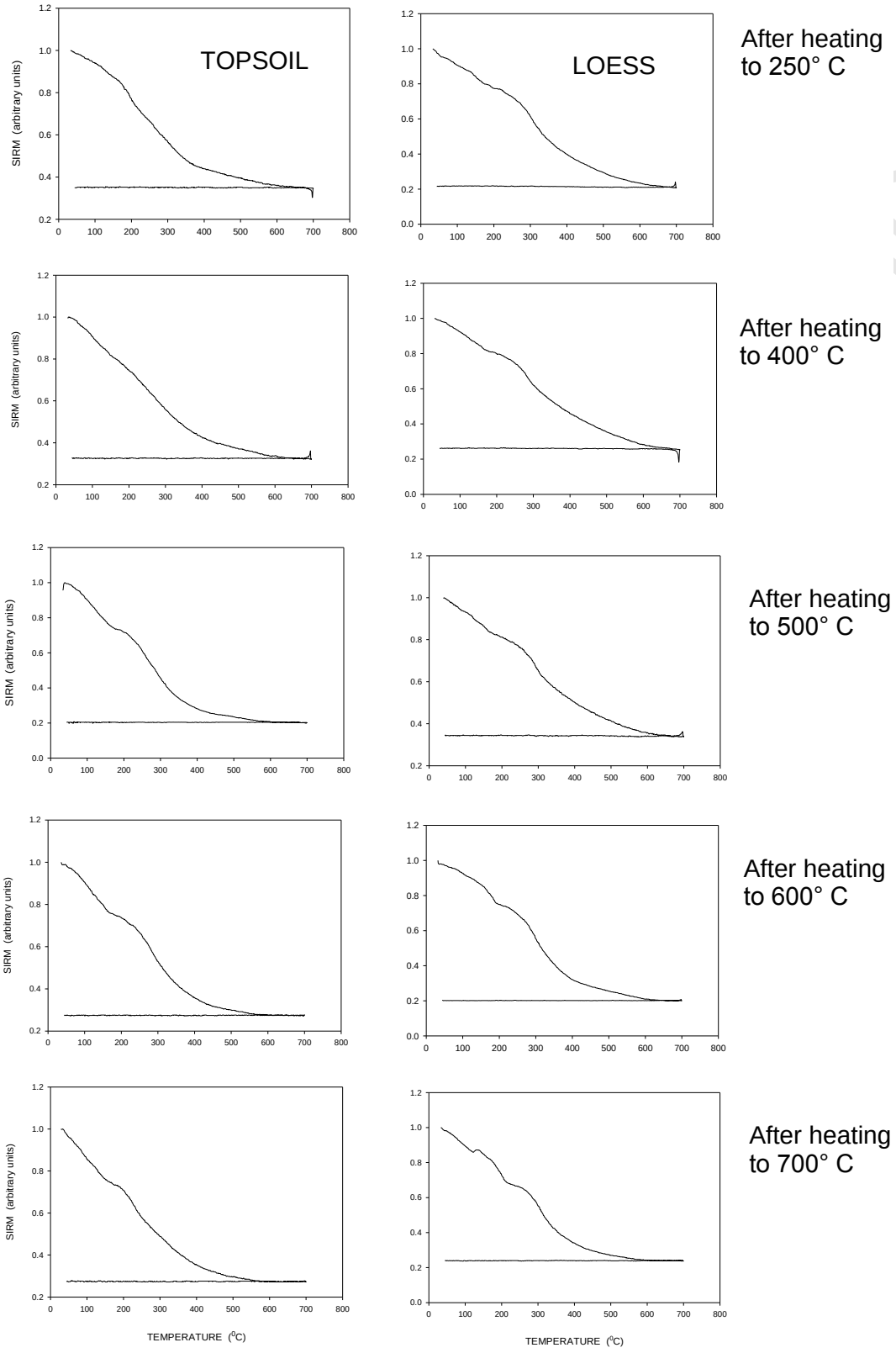
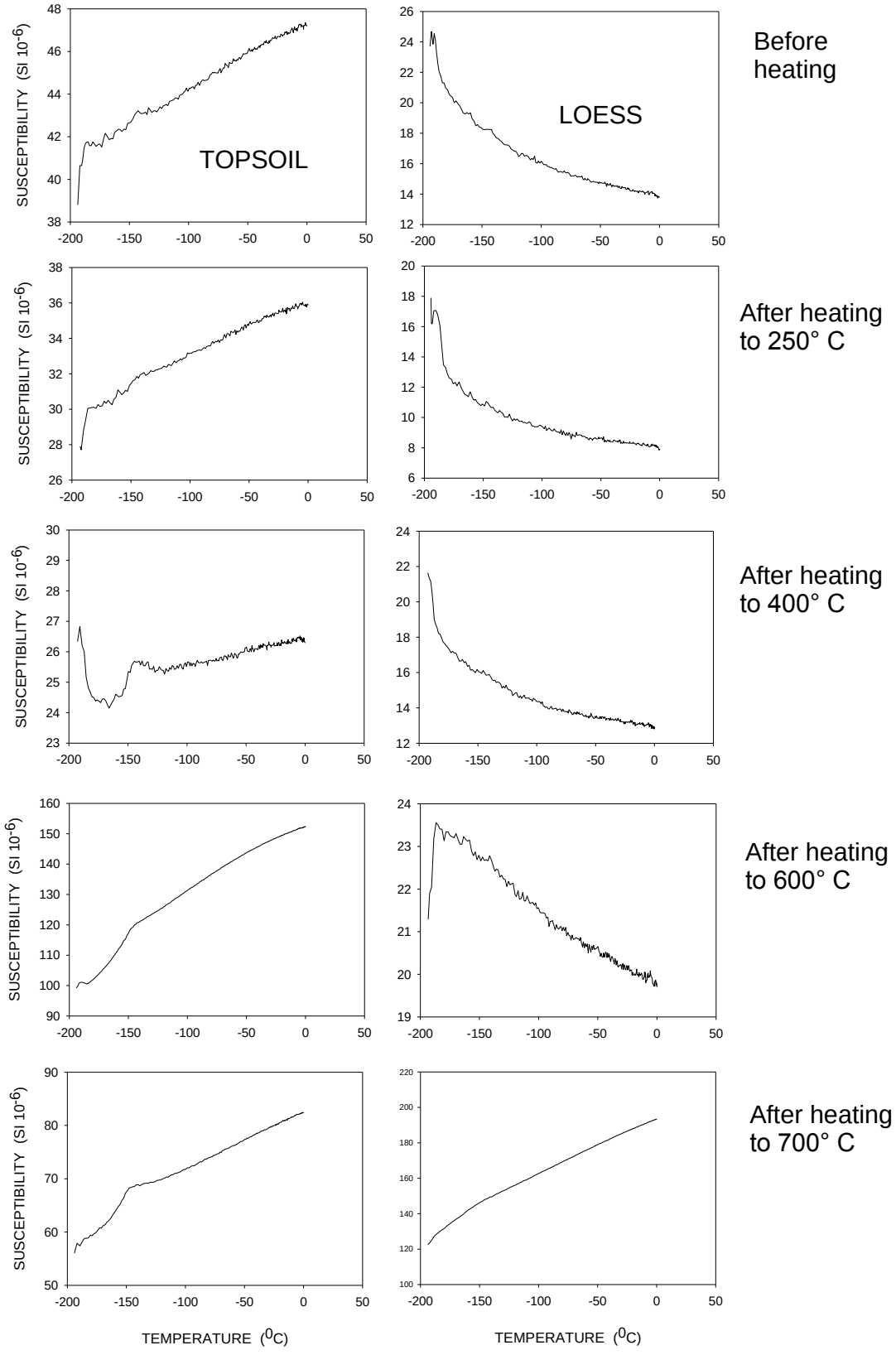


Fig. 6.



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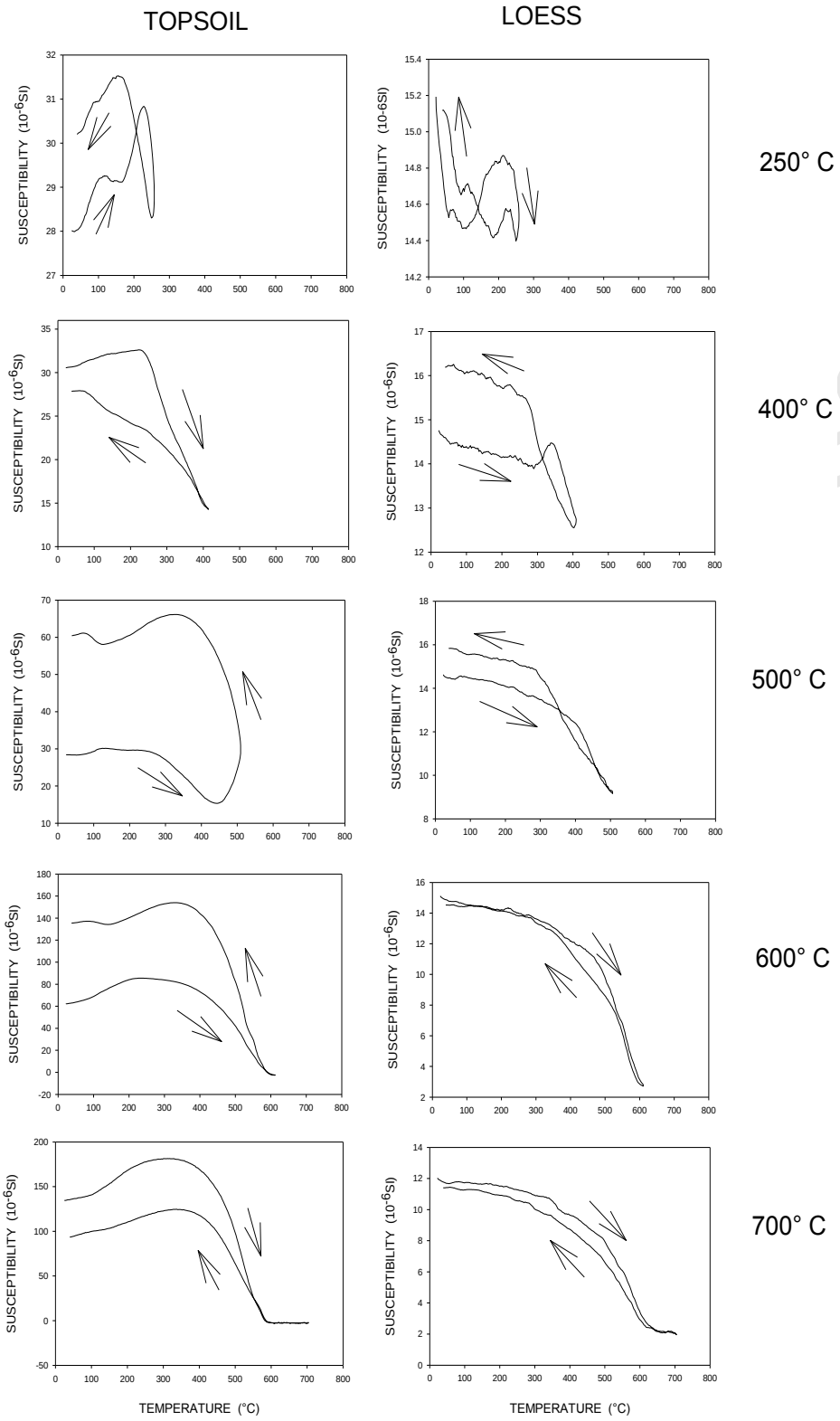

Fig. 8

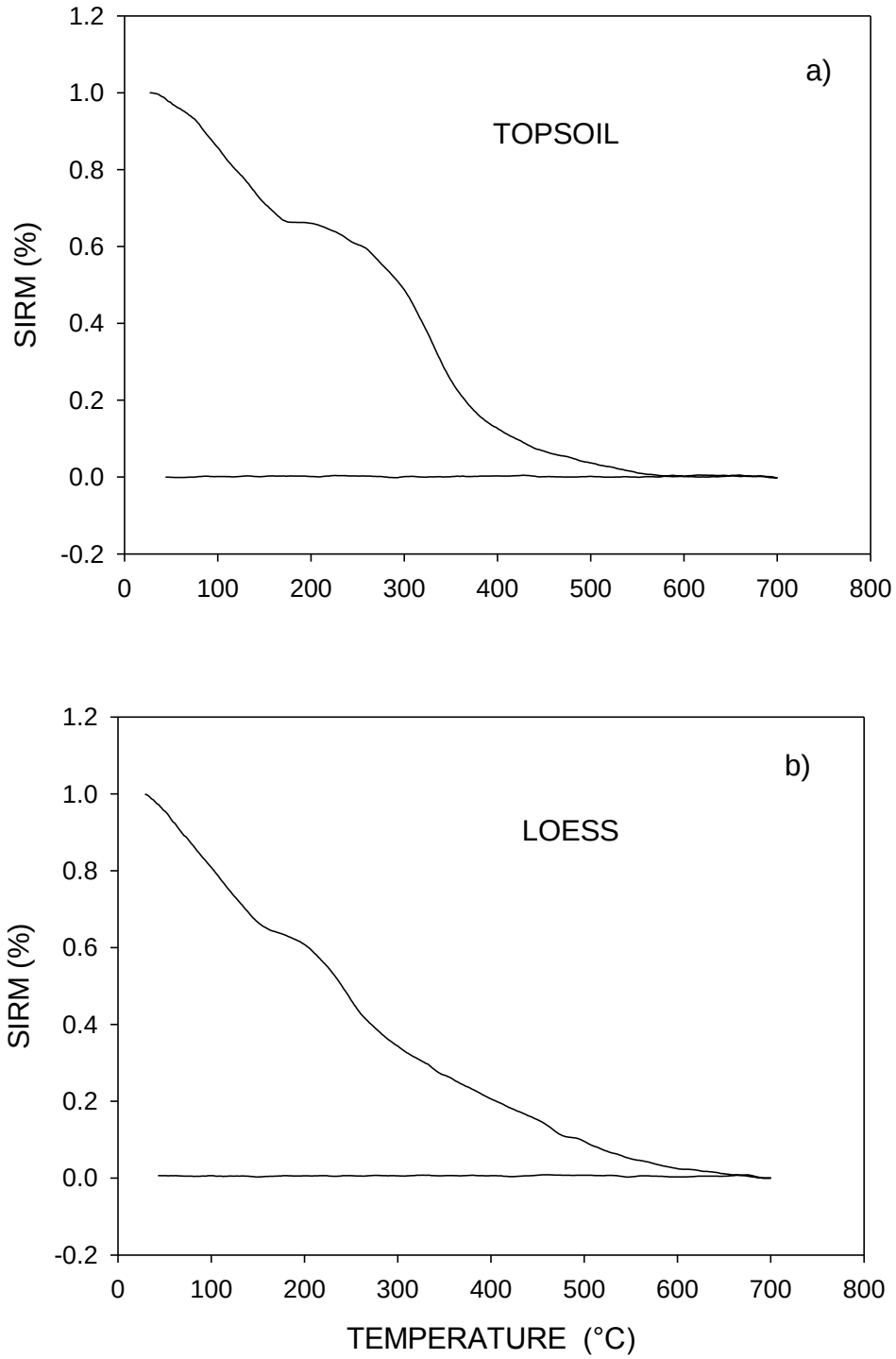

Fig. 9

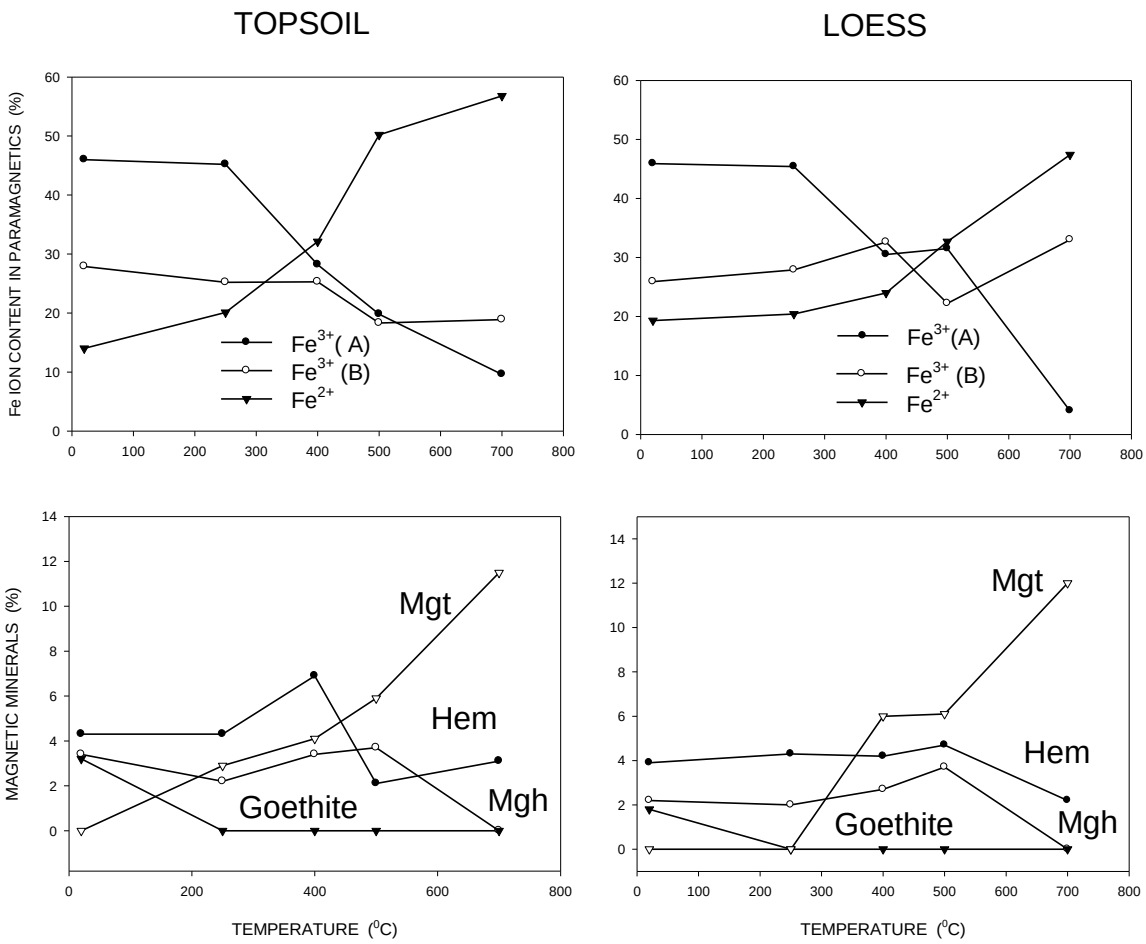

Fig. 10.

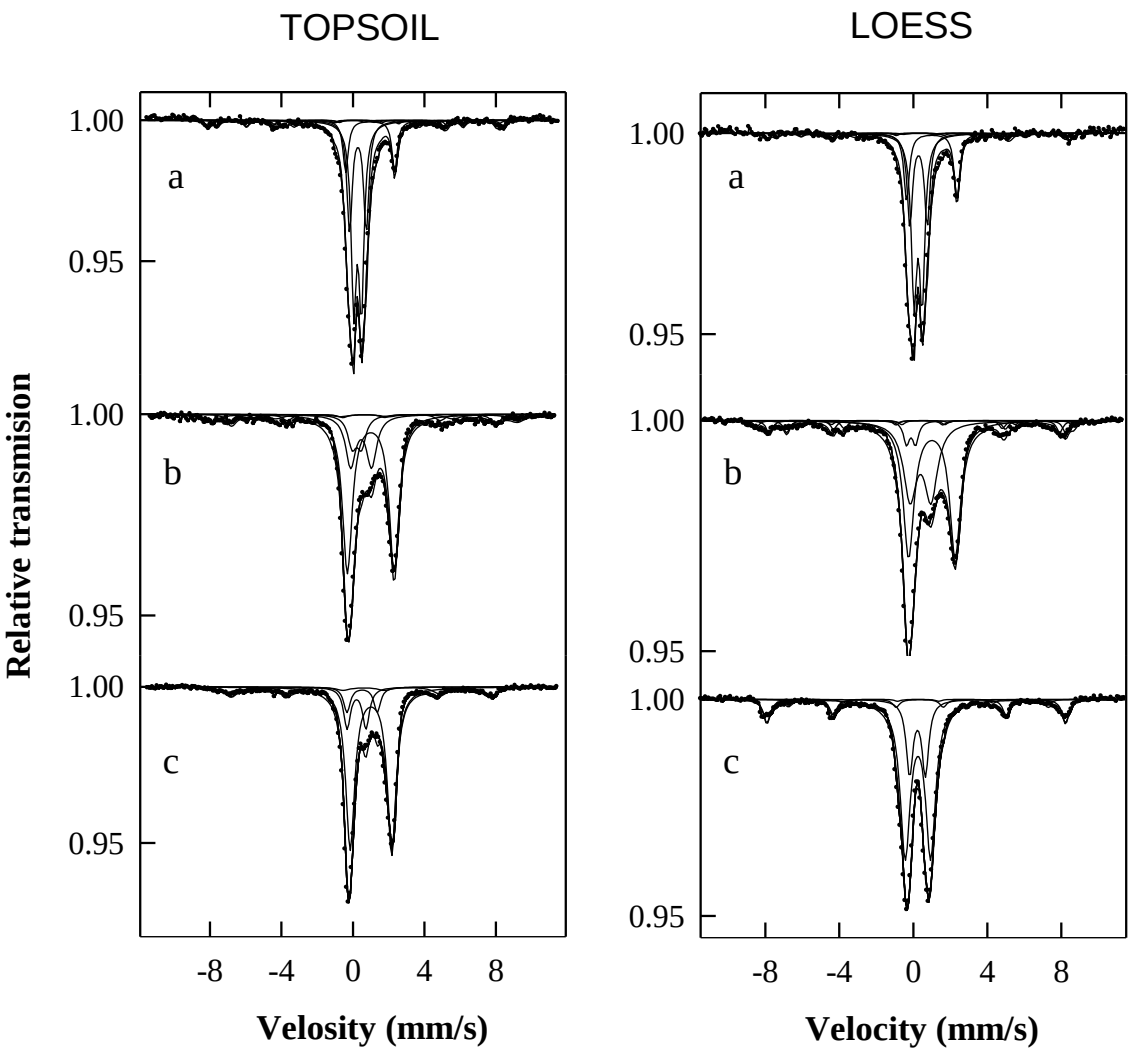

Fig. 11

Table 1. Chemical analysis of topsoil and loess.

Sample	pH	Humus (%)	Fe_{total} (%)	Fe_d (%)	Fe_o (%)	Fe_d/Fe_{total}	Fe_o/Fe_d
Topsoil	7.59	6.87	3.33	0.657	0.095	0.197	0.145
Loess	9.04	0.55	2.74	0.530	0.035	0.193	0.066

Fe_{total} – total content of iron determined by modified Lima-Jackson method (Cornell & Schwertmann 2003); Fe_d - iron extracted with the sodium dithionite, the CBD Mehra-Jackson method (Mehra & Jackson 1960); Fe_o - iron extracted with the acid NH_4 –oxalate, the AAO Tamm method (Mckeague & Day 1966). Fe_d content has become a standard tool for determination of free iron oxides. Fe_o content approximates amorphous or poorly crystalline iron oxides, mainly ferrihydrite. The ratio of Fe_d/Fe_{total} approximates the degree of transformation of original Fe-bearing minerals to pedogenic oxides (Cornell & Schwertmann 2003). The decreasing of the Fe_o/Fe_d ratio approximates the transformation of ferrihydrite to better crystalline oxides. Both ratios serve as indicators of the maturity of a soil.

Table 2. Changes of hysteresis parameters after heating.

T (°C)	RT	250	400	500	600	700	700/RT
Topsoil							
Ms (mAm^2/kg)	37.2	43.3	51.9	204.3	380.0	316.6	8.5
Mr (mAm^2/kg)	6.2	5.8	7.4	46.3	81.2	79.1	12.8
Hc (mT)	8.6	7.7	8.8	15.7	15.4	22.5	2.6
Hcr (mT)	28.4	27.2	31.5	35.4	38.3	50.6	1.8
Mr/Ms	0.17	0.13	0.14	0.23	0.21	0.25	
Hcr/Hc	3.3	3.5	3.6	2.25	2.5	2.25	
Loess							
Ms (mAm^2/kg)	12.4	17.4	18.0	23.9	45.3	365.7	29.5
Mr (mAm^2/kg)	2.5	2.6	2.8	3.9	9.8	82.5	33.0
Hc (mT)	14.0	11.1	10.8	11.0	16.5	12.6	0.9
Hcr (mT)	46.6	35.4	36.8	32.1	38.9	33.7	0.7
Mr/Ms	0.2	0.15	0.15	0.16	0.22	0.22	
Hcr/Hc	3.3	3.2	3.4	2.9	2.4	2.7	
Topsoil (TS) /Loess (L)							
Ms(TS)/Ms(L)	2.5	2.2	2.6	11.8	8.3	0.96	
Mr(TS)/Mr(L)	3.0	2.5	2.9	8.6	8.4	0.87	
Hc(TS)/Hc(L)	0.61	0.69	0.81	1.42	0.93	1.78	
Hcr(TS)/Hcr(L)	0.61	0.77	0.86	1.1	0.98	1.5	

T – heating temperature; RT – room temperature; TS – topsoil; L – loess.
700/RT ratio of respective hysteresis parameter measured for fresh sample and sample heated to 700 °C.

Table 3. Relative area (%) of iron cations and magnetic minerals obtained by the Mössbauer analysis performed at room temperature for samples heated to different temperatures during susceptibility measurements.

T °C	Fe^{3+} (A)	Fe^{3+} (B)	Fe^{2+}	α-Fe_2O_3	γ-Fe_2O_3	α-FeOOH	Fe_3O_4
Topsoil							
RT	46	28	14	4	3	3	-
250	45	25	20	4	2	-	3
400	28	25	32	7	3	-	4
500	20	18	50	2	4	-	6
700	10	19	57	3	-	-	11
Loess							
RT	46	26	19	4	2	2	-
250	45	28	20	4	2	-	-
400	30	33	24	4	3	-	6
500	31	22	33	5	4	-	6
700	4	33	47	2	-	-	12

T – heating temperature; RT – room temperature.

Table 4. Mössbauer parameters for topsoil samples: fresh and heated in different way.

Component	Mössbauer hf parameters	Fresh sample	heated to 700°C	multi-heated up to 700°C
Fe^{3+}minerals (A)	δ[mm/s]	0.36	0.32	0.45
	Δ[mm/s]	0.42	0.52	0.89
	RA[%]	46	10	16
Fe^{3+}minerals (B)	δ[mm/s]	0.38	0.56	0.85
	Δ[mm/s]	0.93	1.27	1.64
	RA[%]	28	19	10
Fe^{2+} silicate	δ[mm/s]	1.10	1.10	1.10
	Δ[mm/s]	2.73	2.62	2.43
	RA[%]	14	57	61
α - Fe_2O_3	δ[mm/s]	0.33	0.42	-
	H_{hf} [T]	51.1	0.50	
	RA[%]	4	3	
γ - Fe_2O_3	δ[mm/s]	0.28	-	-
	H_{hf} [T]	48.6		
	RA[%]	3		
Fe_3O_4 (Fe^{3+})	δ[mm/s]	-	0.74	-
	H_{hf} [T]		53.1	
	RA[%]		5	
Fe_3O_4 ($Fe^{3+}Fe^{2+}$)	δ[mm/s]	-	0.79	0.57
	H_{hf} [T]		45.9	45.1
	RA[%]		6	13
α -FeOOH	δ[mm/s]	0.63	-	-
	H_{hf} [T]	36.8		
	RA[%]	3		

δ – isomer shift; Δ – quarupole splitting, H_{hf} – magnetic hyperfine field
RA – relative area

Table 5. Mössbauer parameters for loess samples: fresh and heated in different way.

Component	Mössbauer hf parameters	Fresh sample	heated to 700°C	multi-heated up to 700°C
Fe^{3+} minerals (A)	δ[mm/s]	0.36	0.32	0.33
	Δ[mm/s]	0.44	0.49	0.85
	RA[%]	46	4	20
Fe^{3+} minerals (B)	δ[mm/s]	0.38	0.49	0.36
	Δ[mm/s]	0.95	1.13	1.37
	RA[%]	26	33	63
Fe^{2+} silicate	δ[mm/s]	1.10	1.10	-
	Δ[mm/s]	2.72	2.52	
	RA[%]	19	47	
α - Fe_2O_3	δ[mm/s]	0.43	0.42	0.36
	H_{hf} [T]	50.8	53.2	50.1
	RA[%]	4	2	13
γ - Fe_2O_3	δ[mm/s]	0.28	-	0.37
	H_{hf} [T]	48.6		48.4
	RA[%]	2		3
Fe_3O_4 (Fe^{3+})	δ[mm/s]	-	0.38	-
	H_{hf} [T]		49.8	
	RA[%]		5	
Fe_3O_4 ($Fe^{3+}Fe^{2+}$)	δ[mm/s]	-	0.64	-
	H_{hf} [T]		45.8	
	RA[%]		7	
α -FeOOH	δ[mm/s]	0.27	-	-
	H_{hf} [T]	38.4		
	RA[%]	2		

Notation as in Table 3.