Palaeoclimatic record from a loess–soil profile in northeastern Bulgaria—I. Rock magnetic properties

Diana Jordanova¹,* and Nikolai Petersen²

¹ Geophysical Institute, Bulgarian Academy of Sciences, Acad. G. Bonchev Str., block 3, 1113 Sofia, Bulgaria. E-mail: vanedi@geophys.bas.bg
² Institut für Allgemeine und Angewandte Geophysik, Ludwig-Maximilians Universität, Theresienstraße 41, 80333 München, Germany

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SUMMARY

A detailed record of mineral magnetic properties of a loess–palaeosol profile comprising seven loess horizons, six interbedded palaeosols and recent soil at the top in NE Bulgaria is analysed. A strong contrast between the soil and loess susceptibilities as well as other concentration-dependent hysteresis parameters is present, similar to the well-documented magnetic characteristics of the Chinese loess (Hus & Han 1992; Maher & Thompson 1992; Heller & Evans 1995; Hunt et al. 1995). The magnetic enhancement of the palaeosol units is caused by very fine-grained pedogenic magnetite with superparamagnetic behaviour. Thermomagnetic analyses on bulk material suggest magnetite and maghemite as the main ferrimagnetic carriers in both soil and loess horizons. Their relative proportions are shown to reflect different palaeoclimatic conditions. Chernozem soils, which include recent soil S₀ and first and second palaeosols S₁ and S₂ developed under steppe vegetation, show a high degree of low-temperature oxidation of the pedogenic magnetite to maghemite. This material is characterized by coercive force $H_c$ showing even higher values than those of the parent loess material. The older palaeosols (S₄ to S₆) were formed during more humid climatic conditions and therefore probably developed as forest types. Rock magnetic data suggest the existence here of only partly oxidized magnetite grains. The behaviour of the thermomagnetic curves, characterized by a kink at 200 °C, may be due to either a release of internal stress (built up as a result of partial low-temperature oxidation) or interactions between two phases.

Key words: Bulgaria, magnetic susceptibility, mineral magnetism, palaeoclimate.

1 INTRODUCTION

There is little doubt that loess–palaeosol sequences can carry a palaeoclimatically driven magnetic record (e.g. Kukla et al. 1988; Heller et al. 1991; Maher & Thompson 1992; Verosub et al. 1993; Heller & Evans 1995). They also provide one of the most complete continental records of geological as well as geomagnetic field history for the last 2.4 Myr (Heller & Liu 1984; Hus & Han 1992). However, in spite of the close correlation between magnetic susceptibility variations of loess/palaeosol sequences and palaeoclimatic $\delta^{18}$O records (Forster & Heller 1994; Forster et al. 1996), the exact magnetic response to climate change is still open to discussion (Maher & Thompson 1991; Eyre & Shaw 1994; Maher & Taylor 1988; Zhou et al. 1990; Oches & Banerjee 1996; Evans et al. 1996; Maher 1998).

The data available so far on rock magnetic characteristics of loess/soil sediments mostly concern the Chinese loess plateau and Central Asia (Hunt et al. 1995; Forster & Heller 1994), regions with a climatic history influenced by the tectonic uplift of the Tibetan plateau or seasonal periodicity of East Asian monsoon activity (Banerjee et al. 1993; Thompson & Maher 1995). Although the loess/soil sequences in Central and Eastern Europe cover shorter time intervals (Forster et al. 1996; Oches & Banerjee 1996), a comparison amongst magnetic characteristics of different sections in temperate continental areas can provide new evidence for the main mechanisms of climatic response of the loess/soil mineral magnetic assemblages.

We present the results of detailed rock magnetic investigations of a 34 m thick loess/palaeosol profile from NE Bulgaria in order to provide information about mineral magnetic characteristics of lower Danube loess deposits (this paper) and their relation to the global and local climatic changes during the last 800 Kyr (Jordanova & Petersen 1999, Paper II).
2 SAMPLING AND METHODS

The loess/palaeosol profile studied is situated in NE Bulgaria, near the village of Koriten (Fig. 1). It consists of seven loess horizons and six palaeosols overlying a complex of red clays developed on Aptian limestones (Evlogiev 1993). The Brunhes/Matuyama boundary found in the seventh loess, L7 (Butchvarova 1993; Hus et al. 1997), is a good time marker for developing the loess stratigraphy and palaeoclimatic reconstructions of the region.

Sampling was carried out on non-oriented core. Samples were taken at 10 cm intervals along a 34 m thick profile. All the experiments were performed on bulk non-separated material, crushed by hand in order to obtain homogeneous material. Hysteresis measurements were carried out on 160 samples using a variable field translation balance (VFTB) at the Geophysical Institute in Munich. The maximum applied field was 600 or 250 mT. Stepwise IRM acquisition was measured using the same instrument up to the maximum field available, followed by a backfield demagnetization. Subsequently, thermomagnetic curves (in an applied field of 45, 21 or 10.5 mT for different samples) up to 700 °C and for cooling back to room temperature were obtained in order to determine the Curie temperature ($T_c$) of 95 samples. A few low-temperature measurements at liquid nitrogen temperature were carried out as well. The low-field susceptibility was measured for each sampling level (342 samples in total) using a dual-frequency Bartington susceptibility meter (0.47 and 4.7 kHz).

3 LOESS ACCUMULATION AND PEDOGENESIS

The initial stages of secondary alteration of dust material, deposited during glacial times, are generally considered to comprise chemical weathering of the unstable primary minerals (olivine, pyroxene, amphibole, mica, feldspar). Such weathering is caused mainly by hydrolysis due to the interaction of water and the atmosphere with the Earth's crust (Stumm & Wollast 1990). The rate of pre-depositional weathering of the material depends on the particular dust source, depositional history (single or multiple) and environmental conditions in the source area (Pye 1987). According to the geological concept of the origin of the Bulgarian loess deposits (Minkov 1968; Evlogiev 1993), at least two transport stages were involved: (1) alluvial deposition of the material carried by the Danube river during pluvial phases of the glacials; and (2) pure aeolian redeposition of the previously formed and subsequently dried alluvial deposits. Consequently, considering the involvement of an alluvial stage of dust transportation, a higher degree of weathering could be expected than for single-stage aeolian loess accumulation. This could partly explain the relatively higher $\text{Al}_2\text{O}_3$ and $\text{Fe}_2\text{O}_3$ contents in the loess of the Danube valley ($\text{Al}_2\text{O}_3$: 15.77 per cent; $\text{Fe}_2\text{O}_3$: 6.03 per cent) compared to those of Central European and western Ukraine loesses (Stoilov 1984) as they are a measure of silicate dissolution and subsequent formation of Al and Fe oxides from liberated ions (Stumm & Wollast 1990). Another specific property of Bulgarian loess is its relatively higher mica content (10–30 per cent) at the expense of feldspar (2–9 per cent). This could be due to the predominance of granitic and pegmatitic rocks in the catchment area of the Danube river (Minkov 1968; Stoilov 1984).

The clay fraction in loess units ($d < 0.002 \text{ mm}$) is dominated by illite (Minkov 1968), whilst palaeosol units are rich in montmorillonite. In situ kaolinite synthesis possibly took place in the oldest palaeosols as a result of a more humid climate in the past. The observed differences in the relative abundance of clay minerals in loess and palaeosols point to pedogenesis.
playing a significant role in the building up of an enhanced clay content. Specific climatic conditions play an important role in this process, as demonstrated for different loess/soil sections in China (Zhengtang et al. 1993; Bronger & Heinkele 1989).

The present-day climate of the area where the studied loess/palaeosol profile is situated is characterized by typical continental temperate conditions with a mean annual temperature of 11 °C and a mean annual precipitation of 556 mm, with maximum rainfall in May–July (Velev 1990). A specific peculiarity of the climate here is the presence of strong northerly winds during the whole year, which leads to hot and relatively dry summers. Under these conditions a typical steppe vegetation is developed. According to the palynological studies of Holocene lakes in the region (Bozilova 1986), steppe vegetation was dominant (Artemisia, Chenopodiaceae, Asters, Poaceae), even during the climatic optimum—the Atlantic period, which took place before about 6000 years ago. Some tree species, mostly Quercus, Corylus, Tilia and Ulmus, are also identified (Bozilova 1986). Under the environmental conditions described above recent chernozem soils are widely spread in the area.

Pedological information about the palaeosol types in NE Bulgaria is scarce. The few available studies concern only the first two paleosols ($S_1$, $S_2$) (Fotakieva 1974; Minkov 1968). According to these studies, $S_1$ and $S_2$ are of chernozem type. The morphological features of older palaeosols ($S_3$ to $S_n$) are characterized by a high clay content, dark brown–red colour, rubification and decalcification. Except for $S_3$, the calcitic horizons of the palaeosols ($S_{n-1}$, the lower 20 cm of the soil’s thickness; $S_3$ and $S_{n-2}$, the lower 100 cm) contain small carbonate nodules and micelli. Consequently, broadleaf forest vegetation probably played a significant role during pedogenesis. Organic matter is an important factor during the pedogenic alteration of parent material. Its transformation into humic acids, fulvic acids or humins strongly depends on the particular type of pedogenesis. In chernozems, developed under steppe vegetation, mainly humic acids are formed. This soil type is characterized by near-neutral acidity (pH 7), a maximum concentration of immobilized humic acids at the soil surface and good drainage. Grey/dark grey forest soils [haplic luvisols according to the FAO classification, Bojadjiev (1994)] are developed on loess parent material in the southern part of the loess cover in Bulgaria. The main reason for the lower pH of these soils is a specific biochemical transformation of canopy material, resulting in the formation of strongly acidic, mobile fulvic acids (Ganev 1990). Water is another strongly acid-promoting factor which replaces bases from the surfaces of primary volcanic and secondary clay minerals with hydrogen ions through hydrolysis.

Humus content in the Bulgarian loess/palaeosol complex is relatively low compared with other sections in Eastern/Central Europe and China, possibly due to the particular climatic conditions, which promote fast and complete transformation of organic matter, although the possibility of truncated humic Ah horizons cannot be ruled out. Typical values for humus content in the recent soil $S_0$ are around 2–2.5 per cent, for $S_1$, 1.3–1.5 per cent, and for $S_2$, 0.1–0.2 per cent (Minkov 1968; Stoilov 1984; Fotakieva 1974). There are no data for older palaeosols because of the progressive decomposition of humus with advanced age, which seriously restricts the reliability of this analysis applied to palaeosols (Bronger & Heinkele 1989).

In most cases, Fe is incorporated into the aluminosilicate minerals as isomorphous substitutions. Therefore, the process of Fe release from aluminosilicates and factors controlling this process are of great importance in understanding the formation of Fe-hydroxides and their further alteration. Acid destruction of clay minerals starts when the pH value drops below 6 (Ganev 1990). Such an environment develops under conditions of increased precipitation and forest vegetation (Jenny 1941). An unambiguous indication that acid destruction of clay minerals has taken place is the presence of exchangeable Al$^{3+}$. The main mineralogical tendency in acid soils is their progressive depletion in montmorillonite and relative enrichment in illite and kaolinite. In contrast, all alkaline or near-neutral soil types such as carbonate, typical and leached chernozems are characterized by the presence of exchangeable bases but not Al. In our particular case the loess material (e.g. parent material) is rich in alkali, so that pH ≤ 6 could be obtained only for grey forest soils—the typical present-day soil type for the most southern part of the loess cover in Bulgaria. Another favourable factor for a strong secondary alteration is the combination of deciduous forest vegetation and more clayey loess material (the clay fraction $d < 0.002$ mm increases from about 10 up to 40 per cent in a southwards direction), which is more susceptible to weathering (Minkov 1968).

During warm climatic periods the role of climate and vegetation becomes increasingly more important for the development of soil properties. According to Schwertmann (1988), Cornell & Schwertmann (1996) and Dearing et al. (1996), in situ formation of a magnetic fraction probably results from an initial ferrihydrite synthesis. The necessary condition for subsequent magnetite formation is the presence of Fe$^{3+}$ ions in pore solution. As a reducing agent for Fe$^{3+}$ appearance these authors as well as Coleman et al. (1993) and Fassbinder et al. (1990) favour the role of Fe-reducing microorganisms. In our opinion, the latter control the initial stages of soil development, characterized by near-neutral conditions. Changes in the environmental conditions from cold glacial to warm interglacial lead to continuous alteration of the rocks into a soil. When a new equilibrium state of the system is achieved, the soil is termed ‘mature’ (Jenny 1941). At the stage of soil ‘maturity’ Fe$^{3+}$ may also originate from organic ligand-promoted chelation of already existing Fe(III) hydroxides due to natural acidification caused by organic matter (Stumm & Wollast 1990). The latter mechanism is more effective in weakly to moderately acid soils (pH < 6) where fulvic acids can migrate downwards and chelate Fe(III) oxides, which are formed more effectively in the lower part of the soil profile.

4 ROCK MAGNETIC RESULTS

4.1 Thermomagnetic analysis

All the loess and soil samples investigated show common behaviour. This behaviour suggests that their magnetic properties are dominated by a magnetite/maghemite mineral assemblage. The loess samples generally have a distinctly lower magnetization than the soil samples. Commonly, the intensity of induced magnetization of soil samples is about three to four times higher than that of loesses. Typical examples of thermomagnetic curves are shown in Fig. 2. A particular situation is observed for the samples from the recent soil $S_0$ (Fig. 2a).
They show the presence of a low-temperature kink at about 120 °C and another at 300 °C. Subsequently, above 400 °C a new strongly ferromagnetic phase appears, which causes an eight-fold increase in magnetization on cooling.

Samples from the unweathered loess horizon L_2 show a distinct thermomagnetic behaviour (Fig. 2c). Due to the presence of magnetic particles with higher coercivity, which are not saturated at lower temperatures in an applied field of 21 mT, the heating curve is initially slightly concave with a final $T_c$ of 590 °C (Fig. 2c). The cooling cycle shows a wider blocking temperature spectrum with almost linear temperature dependence and a net increase in the final magnetization.

Another type of thermomagnetic behaviour is that seen in the older palaeosol units (S_3, S_4, S_5, S_6) (Figs 2d, e and f). Except for S_5, all samples show a decrease in magnetization after heating. The shape of the heating curve could be considered as a combination of two linear segments (20–200 and 200–600 °C). This behaviour is most strongly expressed for samples from S_5 and S_6 (Figs 2e and f). Several samples from the palaeosol horizons and one of the recent soil S_0 (Fig. 2a), show some indications of the presence of oxyhydroxides, probably goethite, according to the small but well distinguished drop in magnetization at 80–120 °C (Fig. 2d). These levels are marked with stars in Fig. 3.
Low-temperature demagnetization down to liquid nitrogen temperature (Fig. 4) is characterized by a continuous increase without an indication of the Verwey transition.

4.2 Hysteresis measurements

Two different VFTB apparatuses were used for the hysteresis measurements. The more sensitive one, on which most of the weakly magnetic loess samples were measured, achieved a maximum field of 280 mT; the other one, on which all the palaeosol samples were measured, achieved a field of 600 mT.

Saturation magnetization ($J_s$), saturation remanence ($J_{rs}$), and the coercive force ($H_c$) were determined from the hysteresis loops. $J_s$ was deduced by extrapolation of the linear parts in

The ratio of the induced magnetization after the thermomagnetic run, $J_{in2}$, to that before the run, $J_{in1}$, ($J_{in2}/J_{in1}$) shows an interesting pattern along the profile (Fig. 3). If only the loess samples are considered, the main experimentally deduced property is the less weathered the loess material is, the more pronounced the magnetization increase is on cooling. The two youngest palaeosol units, S1 and S2, which are of chernozem type, together with the recent soil S0 (also chernozem), show an increase of magnetization after heating ($J_{in2}/J_{in1} > 1$) as well. Samples from the other palaeosol horizons show a decrease of magnetization after heating, commonly of 15–20 per cent (Fig. 3).

Figure 3. Variation of the ratio of induced magnetization after cooling to room temperature ($J_{in2}$) and before heating ($J_{in1}$) deduced from the thermomagnetic runs. Stars mark the levels where $T_c$ values of 80–120 °C were detected.

Figure 4. Low-temperature behaviour of induced magnetization. Applied field: 45 mT.
the high-field portion of the hysteresis loop to \( H = 0 \). The determination of \( J_s \) for the loess samples (measured only up to 280 mT) may therefore lead to slightly lower values (not exceeding 4 per cent, verified by comparing \( J_s \) values obtained for the same sample measured using the two different maximum fields). Hysteresis loops of the older palaeosols, \( S_1, S_2, S_3 \) and \( S_4 \), have slightly wasp-waisted (WWL) shapes. This is typical of all samples measured. The best-expressed WWL shapes are observed for the \( S_1 \) unit.

The controlling role of concentration of the ferrimagnetic fraction on the behaviour of magnetic susceptibility (\( \chi \)), \( J_s \) and \( J_m \) is clearly shown by their linear dependence (Fig. 5). The log-linear dependence is best for the soil samples; loess samples show a higher scatter.

The behaviour of coercivity parameters along the profile—coercive force (\( H_c \)), coercivity of remanence (\( H_{rm} \)) and remanent acquisition coercivity (\( H_{ac} \)) (Fig. 6)—is surprisingly not a straightforward indicator of the presence (or absence) of a low-coercivity pedogenic component, as reported in other studies of loess/soil sediments (Hus & Bater 1993; Forster & Heller 1997). One possible reason could be the relatively low value of the maximum magnetic field available (280–600 mT), which is capable of saturating only the magnetite/maghemite particles (O’Reilly 1984; Thompson & Oldfield 1986). In such a case, relative variations in the coercivity most probably reflect the variability of the domain state of the magnetically soft component. An unexpected mode of \( H_c \) behaviour (Fig. 6) is seen in the upper part of the profile, with comparable coercivities of the first three soil units (\( S_0, S_1, S_2 \)) and the corresponding parent loess horizons (\( L_1, L_2, L_3 \)). Lower in the profile, palaeosol units show lower \( H_c \) values than the underlying loess horizons, with the exception of unit \( L_4 \).

The ratios \( J_{rm}/J_s \) and \( H_{rm}/H_c \), frequently used as a granulometric tool (Day et al. 1977) are not efficient in our case. The \( J_{rm}/J_s \) values in particular show almost no variations along the section, with only a very weak trend of decrease for progressively younger horizons (Fig. 7). \( H_{rm}/H_c \) variations are linked to the stratigraphical changes in the upper part of the profile (\( S_0–L_3 \)), but no clear change is found below \( L_3 \) (Fig. 7).

Fig. 8(a) shows the dependence of the coercivity parameters \( H_c \) and \( H_{ac} \) on susceptibility (\( \chi \)). There is no clear decrease in \( H_c \) with increasing \( \chi \), as would be expected if only the SP fraction played a significant role. On the other hand, the absence of linear \( H_c(H_{ac}) \) dependence (Fig. 8b), especially for soil samples, is obvious, whilst loesses show a significant correlation (\( R^2 = 0.64 \)).

### 4.3 Magnetic susceptibility (\( \chi \)) and its frequency dependence (\( \chi_b(\% \))

Considering the relative enhancement of the palaeosol units as the amplitude of low-field susceptibility (\( \chi \)) variations in Fig. 9, it appears that the \( S_1 \) unit represents the time interval characterized by palaeoclimatic conditions, most favourable for the growth of phases with high susceptibility. It is interesting to note that the low-field susceptibility, normalized by saturation magnetization (\( \chi/\chi_b \)), the ratio widely used as an indicator of the relative variations in SP content (Dunlop 1981; Benerjie 1994; Hunt et al. 1995), also shows maxima in the soil horizons, although less pronounced than the non-normalized values.

Fig. 10 shows the results as a \( \chi/\chi_b \) versus \( \chi_b(\% \) plot. It is obvious that an overlap between palaeosols and loess samples exists only in the \( \chi_b(\% \) interval 3–8 per cent, with the exception of the samples from \( L_4 \). The \( L_4 \) unit is the loess horizon with the most enhanced secondary (pedogenic) alteration. Thus, pedogenesis and loess accumulation can be considered as simultaneous and competing processes (Fine et al. 1995; Forster & Heller 1997).

Further support for the assumption of a certain degree of pedogenesis also in the loess horizons comes from the analysis of the so-called ‘background susceptibility’ (Forster et al. 1994) (Fig. 11a). Fig. 11(b) shows a histogram of susceptibility values with two separate maxima for loess and soil samples. The loess maximum is at 2–3 \( \times 10^{-7} \) m\(^3\) kg\(^{-1}\). When this value is compared with the ‘background susceptibility’ (\( \chi_b \)) obtained from the intersection of the straight line \( \Delta f = \chi - \chi_b \) versus \( \chi_b \) at \( \Delta f = 0 \) (Fig. 11a), a distinctly lower value of \( \chi_b = 1.29 \times 10^{-7} \) m\(^3\) kg\(^{-1}\) is obtained. Since the \( \chi_b \) values are considered to reflect the susceptibility of the initial detrital fraction with no frequency dependence, higher mean susceptibilities of the loess horizons point to the presence of secondary (pedogenic) alteration.

### 5 DISCUSSION

The proper identification of magnetic mineralogy as well as thermal transformations during laboratory heating are of major importance for the subsequent understanding of the behaviour of room-temperature hysteresis properties and susceptibility along the depth of the studied loess/palaeosol profile.

In recent soil (\( S_1 \)), a significant contribution of goethite/ferrihydrite (\( T_g \)) and maghemite (\( T_m \)) could be assumed as an interpretation of the kinks on the thermomagnetic curve at 120 and 350 °C, respectively (Fig. 2a). The subsequent appearance of a strongly magnetic phase (presumably magnetite) during

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**Figure 5.** Linear dependence of concentration-dependent parameters \( J_s, J_c, J_m \). Loess samples are plotted as open diamonds, palaeosol samples as solid circles.
heating to 400–500 °C is evident. The presence of maghemite in S0 is probably promoted by the highly oxidizing surface environment, leading to almost complete low-temperature oxidation of an initial magnetite phase.

Magnetite authigenesis is enhanced in the top levels of the chernozems because of the suitable conditions [higher Fe content due to the intense hydrolysis of primary minerals, high organic matter concentration and high oxidation rate (Taylor et al. 1987)]. As a result, \( \gamma \)-Fe\(_2\)O\(_3\) is relatively poor in Al and other substitutions because exchangeable (free) H\(^+\) and Al\(^{3+}\) ions cannot exist at pH > 6 (Jenny 1941). Under these conditions, rapid oxidation of magnetite to maghemite will occur (Murad & Schwertmann 1993). Subsequently formed \( \gamma \)-Fe\(_2\)O\(_3\) is unstable with respect to heating, due to the absence of isomorphous substitutions, and gamma–alpha transformation occurs, causing a significant drop in the thermomagnetic curve (Fig. 2a). On the other hand, Fe\(^{3+}\) ions, liberated from montmorillonite clay minerals during heating, are placed in a strongly reducing atmosphere due to the combustion of organic matter. In this way, they are easily reduced to Fe\(^{2+}\) and
subsequently oxidized to form a new magnetite phase. This leads to the seven- to eight-fold increase in magnetization after cooling. Such an increase can in part also be caused by the reduction of haematite or oxyhydroxides to form magnetite (Mullins 1977).

At the top of L1, a lower organic content, which is a result of the low migratory ability of the dominating humic acids, probably prevents the appearance of a new strongly magnetic phase during heating. However, the presence of maghemite can also be seen here in the kinks at $T = 350\, ^\circ C$ (Fig. 2b). The existence of $T_e \sim 580\, ^\circ C$ also suggests a magnetite contribution. The simultaneous presence of $\gamma$-Fe$_2$O$_3$ and Fe$_3$O$_4$ combined with significantly higher coercivities in this part of the profile (Fig. 6) supports the idea that maghemite may form a shell around an Fe$_3$O$_4$ core of fine SD/PSD grains, possibly leading to stress-controlled magnetic characteristics (Knowles 1981; Ozdemir & Dunlop 1989; Housden & O’Reilly 1990; Van Velzen & Zijderveld 1995; Van Velzen 1997). This is clearly seen in the behaviour of $H_e$ in the interval 1.5–6.5 m (Fig. 6).

Regarding forest-type pedogenesis, active during the soil formation of older palaeosol horizons ($S_4, S_5, S_6$), a significant amount of kaolinite is highly probable. As kaolinite minerals are characterized by low isomorphous substitutions (including Fe ions) and a low cation adsorption capacity (Young et al. 1992), there is a relative and absolute deficiency of Fe sources for magnetite formation during heating above 400 C. The behaviour of the ratio $J_{in2}/J_{in1}$ (Fig. 3) also reflects these differences in mineral composition (Fe oxides/hydroxides as well as clay minerals) of the different horizons. In the presence of aluminosilicates with a high degree of Fe substitutions in

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Figure 7. Variations of the ratios $J_{rs}/J_s$ and $H_{er}/H_e$ along the profile.

Figure 8. (a) $H_{er}$ and $H_e$ plotted against $\gamma$ values; (b) $H_{er}$ versus $H_e$ values. Loess samples are represented by open diamonds, soil samples by solid circles.
their lattice, these Fe ions may diffuse out and form a new magnetic phase. Such minerals are primary micas and feldspars in unweathered loess samples, and secondary formed montmorillonites in chernozem soils. The older palaeosol units (S3, S4, S6) show only a restricted creation of new magnetic minerals on heating. Indeed, they presumably formed during a more humid climate with a prevailing synthesis of kaolinite clay minerals and has low organic content due to humus destruction with age. In the unit S5, the wealth of non-transformed organics probably leads to values of $J_{a2}/J_{a1} > 1$. Such circumstances would be realized during a significant regression of the Black Sea. A combination of high winter temperatures, high humidity and relatively low summer temperatures favours the appearance of abundant vegetation. Because of these climatic conditions, the transformation of organic remains into humic substances is reduced and thus preserved for a long time after burial of the soil. Another peculiarity, which may play a significant role for the magnetic behaviour of these samples, is the possible presence of Al$^{3+}$ ions in pore solution during the soil development. The presence of exchangeable Al$^{3+}$ in most of the grey forest soils, especially in their textural Bt horizons, is genetically determined (Jenny

Figure 9. Variations of magnetic susceptibility $\chi$, frequency-dependent susceptibility as percentage values ($\chi_{fd}$%) and the ratio $\chi/J_s$ along the profile.
1941) because of a low pH (pH < 6) and more efficient water retention due to the clay illuviation. In such conditions, characterized by an excess of water, slightly acid or neutral pH ~ 6 and slow oxidation rate, Fe$_3$O$_4$ authigenesis is enhanced (Taylor et al. 1987; Maher 1998). In recent studies (Dearing et al. 1996; Cornell & Schwertmann 1996), ferrihydrite is considered as a necessary precursor for subsequent magnetite formation. It is reported to be of poor crystallinity with grain sizes in the range 3–5 nm (Schwertmann 1988; Vandenberghe et al. 1990; Goodman 1994). Subsequent magnetite/maghemite synthesis in the presence of Fe$^{2+}$ ions would result in a sub-micron fraction of SP particles eventually growing to SD/PSD sizes, which would contribute to the remanence signal as well. Ferrihydrite synthesis is favoured by a relatively high organic content and Fe supply (Schwertmann 1988) and consequently the process of magnetite enhancement of soil through ferrihydrite dissolution will be intensified during periods of an optimum combination of temperature, precipitation and evaporation regimes. Such a dissolution process is a result of 'induced hydrolysis', which occurs due to the adsorption of Fe$^{2+}$ ions on to the surface of the poorly crystalline ferrihydrite (Maher 1998). Additionally, the presence of Al-hydroxy cations promotes hydrolysis of Fe$^{2+}$ (Cornell & Schwertmann 1996). Analogous situations are usually encountered during stages of soil 'maturity'; that is, in periods when a sufficient quantity of organic matter has already been accumulated at greater depths. At the same time, higher precipitation leads to higher Fe supply due to the impeded hydrolysis. In such conditions, goethite also will possibly grow out of ferrihydrite. An identification of oxyhydroxides from thermomagnetic curves is difficult intense pedogenesis and weathering. Since goethite and haematite formation are competing processes (Cornell & Schertmann when magnetite (maghemite) is the dominating ferrimineral. If goethite authigenesis is considered to be a result of ferrihydrite dissolution and subsequent nucleation and growth in solution, its appearance is connected with conditions favouring the high reactivity of ferrihydrite. It is obvious from the depths marked in Fig. 3 that usually the upper levels of the palaeosols show $T_c$ values of 120 $^\circ$C, only palaeosols $S_4$ and $S_5$ being characterized by the presence of goethite (with a $T_c$ of 80 $^\circ$C) in the middle or lower parts of the soil. Such a distribution of goethite could be due to the effect of increased organic matter in the upper soil levels (Schwertmann 1988). The $T_c$ value of 120 $^\circ$C obtained points to relatively low Al substitutions (Friedl & Schwertmann 1996), probably as a result of lower amounts of Al available in the soil solution in chernozems (Cornell & Schwertmann 1996). The observed lower $T_c$ of 80 $^\circ$C in the profiles of $S_4$ and $S_5$ could serve as an indication of a subtropical climate, leading to an excess of Al sources as a result of intense pedogenesis and weathering. Since goethite and haematite formation are competing processes (Cornell & Schertmann 1996), factors promoting or impeding goethite appearance should be accounted for. First, lower precipitation temperatures of the initial ferrihydrite phase lead to its high reactivity and an increase in the rate of dissolution (and hence goethite formation). Second, the presence of other compounds, for example increased concentrations of Si in solution, retards the transformation, as does Al. Third, higher levels of Fe$^{2+}$ promote magnetite synthesis instead of goethite (Cornell &
Ultra-fine-grained pedogenic magnetites are very susceptible to low-temperature oxidation, causing the appearance of maghemite shells around the original grains (Ozdemir & Dunlop 1989). This results in stress, which is reduced by heating up to 200°C (Van Velzen & Zijderveld 1995), possibly causing the typical kinks at T ≈ 200°C on the thermomagnetic curves. Such partial low-temperature oxidation is probably promoted by preservation of palaeoclimatic information in loess. The increase in $I_{c}$ in palaeosol units suggests that coarser grains spanning the SD-PSD range are also present. This is in accordance with a number of rock magnetic studies on loess sections around the world (Hus & Han 1992; Hunt et al. 1995; Maher & Thompson 1995; Heller & Evans 1995; Fine et al. 1995; Oches & Benerjee 1996; Forster et al. 1996) and suggests that a single mechanism is responsible for the preservation of palaeoclimatic information in those sequences (Maher 1998).

The significance of grain size and concentration changes of ferromagnetic grains on the observed magnetic behaviour through the palaeosol profile is substantial. Obviously, concentration changes of strongly magnetic maghemite and magnetite, identified by thermomagnetic measurements, determine the observed linear correlation of $I_{c}$ and $I_{a}$ values with susceptibility (Fig. 5). Consequently, the pedogenic fraction is responsible for the magnetic enhancement of palaeosol horizons. At the same time, the amplitude of this enhancement for different units may well reflect variability of both the degree of maghemitization and magnetic grain sizes. Coercivity parameters (Fig. 6) strongly support the predominance of stable near-SD stress-controlled maghemite/magnetite grains in $S_{1}$ and $S_{2}$, leading to relatively lower values of susceptibility and $\gamma_{DS} \%$ (Fig. 9) in comparison with older palaeosol units. In the latter units, a decrease of the effective magnetic grain size of the magnetite core and the maghemite shell down to true SP size is probably responsible for the observed higher $\gamma_{DE} \%$ and lower coercivities (Figs 6 and 9). A significant SP contribution is probably the reason for the observed constricted (wasp-waisted) hysteresis loops for older palaeosols. The $\gamma/I_{c}$ behaviour suggests almost equal SP contributions in $S_{1}$, $S_{2}$, $S_{3}$ and $S_{4}$, with a maximum in $S_{2}$, unlike the non-normalized $\gamma$ values, which show a maximum in $S_{1}$ (Fig. 9).

A close link between susceptibility values and palaeo-precipitation, as proposed for the Chinese loess (Banerjee et al. 1993; Heller et al. 1993; Maher et al. 1994), is not directly applicable here, because the most developed palaeosol $S_{1}$ (probably of forest type) is not the soil with the most enhanced magnetic susceptibility (Fig. 9). Similarly, rock magnetic studies of recent dark grey and grey forest soils in NE Bulgaria, which are also developed on loess material (Jordanova et al. 1997), and the Parabraunerde palaeosol in the Czech Republic (Oches & Benerjee 1996) show lower susceptibility enhancement in comparison with chernozems. Nevertheless, it is clear that there is an overall similar response of European and Chinese loesses to climate fluctuations, but that some specific features of the magnetic recording process in different areas exist.

6 CONCLUSIONS

(1) The magnetic characteristics of Bulgarian loess/palaeosol sediments are broadly similar to those of the corresponding deposits in China, Central Asia and Europe. This suggests that the same driving mechanism for the magnetic enhancement in the soil horizons plays a role over large areas in the temperate belt.

(2) The magnetic enhancement of palaeosol units is caused by magnetite authigenesis, thus being of pedogenic origin. The degree of subsequent low-temperature oxidation of the magnetite...
fraction is closely related to the particular palaeoclimatic conditions. In chernozem soils, developed under steppe vegetation, magnetite is highly oxidized. In older palaeosols which are of forest type, low-temperature oxidation results in the development of composite grains, leading to a decrease in the effective grain sizes and a dominant contribution of the fine-grained SP fraction to the bulk magnetic properties.

(3) Assuming that the relative quantity of SP grains (taken from $I_{oa}/I_{ol}$) is a measure of climate humidity, the $S_3$ unit in the section studied marks the period with the most favourable environmental conditions for magnetite/maghemite authigenesis.

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