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Environmental changes in southeastern Europe over the last 450 ka: Magnetic and pedologic study of a loess-paleosol profile from Kaolinovo (Bulgaria)

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In Memory of Didier Bourlès, Prof. at CEREGE, who made this work feasible.

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A B S T R A C T
Magnetic properties are sensitive paleoenvironmental proxies frequently used in studies of loess paleosol profiles. Understanding precisely the magnetic recording of soil responses to environmental and climatic changes needs combining pedologic data and geophysical proxies. Here we present a new high-resolution study of a 450 ka old loess-paleosol profile from low Danube loess area at Kaolinovo (NE Bulgaria). The profile consists of Holocene soil S0 on top, three paleosol units (S1, S2, S3) and the intercalated loess horizons L1 to L4. Mineral magnetic and rock magnetic data together with pedological parameters (particle size distribution, total, crystalline and amorphous iron, soil organic carbon, total nitrogen, cation exchange capacity, carbonate content) show systematic variations in response to environmental changes. Principal component analyses carried out separately on magnetic mineralogy, rock magnetic and pedological variables reveal the complex response of loess paleosol sediments to changes in source material and climate. The observed sharp shift in coercivity of mineral magnetic carriers at depth of the third loess L3 marks the change from low-coercivity mineral assemblages in older units to higher coercivity in the last three loess paleosol couplets (L1–S0, L2–S1, L3–S2). This boundary is related to both dust source change and increased climate aridity. The observed spikes in concentration-dependent magnetic parameters in the lowermost part of the profile and particular magnetic and pedologic signature of the oldest deposits (S3–S4 pedocomplex) suggest that it may result from tephra additions in the studied loess-paleosol sequence, tentatively correlated to cryptotephra layers in other terrestrial archives in the region like Tenaghi Philippon and lake Ohrid sedimentary sequences. This work demonstrated that using PCA tool for studying the significance and objective inter-relationships of multiple mineralogical, mineral magnetic and pedological characteristics along depth of loess — paleosol profiles is an exemplary approach for revealing the underlying sedimentary and environmental processes.

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1. Introduction
Loess paleosol sequences are widespread Quaternary deposits at mid-latitudes. They have primary aeolian origin and have been formed as a result of glacial/interglacial climate oscillations (Pye, 1995; Muhs, 2013; Maher, 2016). Soils within these sedimentary sequences developed over periods of increased weathering and climate amelioration at stable surface conditions during time windows of several tens of thousands of years (Past Interglacials Working Group of PAGES, 2016). Subsequent soil burial under increasing sedimentation of new aeolian dust material during glacial inception detached the soil from the zone of active near-surface geochemical and microbiological processes (Sheldon and Tabor, 2009; Retallack, 2019). Thus, paleosols formed and preserved information on past environments. The low Danube loess
area is part of the European loess belt, linking Eastern and Western Eurasian loess deposits and already allowed documenting paleoenvironmental changes down to 800 ka (Balescu et al., 2003; Radan, 2012; Jordanova et al., 2008).

Detailed multidisciplinary studies on loessic paleosols as environmental archives are still rare (Jia et al., 2020). Experimental rock magnetic methods have been applied to identify the magnetic carriers of paleoclimate signal and characterize soils that form under typical interglacial climatic regimes. These approaches provide useful diagnostic information to constrain models of soil development and understand future soils formation under global climatic change. Even though magnetic measurements detect predominantly the strong magnetic iron oxides in soils, which constitute merely up to 3 wt% of the total Fe content (Cornell and Schwertmann, 2003), their characteristics and concentration variations along loess-paleosol sequences permit to track changes in local environmental conditions (Maher, 2011).

In our study we show that joined geophysical magnetic and pedological (paleo)soil studies give valuable input for revealing the formation conditions and role of strongly magnetic iron oxides (magnetite, maghemite) in development of specific pedo-features. This approach is developed to identify the interactions between sedimentological processes of aeolian dust deposition, climate change and soil formation. The objective is to test if the utilization of the complex multi-parameter approach in magnetic and geochemical characterization of the studied loess-paleosol sequence allows to explore the driving mechanisms behind the environmental correlations and reconstructions, utilizing single property such as low field magnetic susceptibility.

Moreover, we demonstrate that the underlying reason for the systematically weaker magnetic enhancement of older paleosols S3 and S4 arises from the combined effects of changes in the grain size of the parent loess material, and strong change in the magnetic coercivity and concentration of antiferromagnetic hematite fraction.

2. Study area

Lower Danube area is surrounded by the Carpathians and Balkan mountain chains to the north – northwest and south, and by the Black Sea to the East (Fig. 1a). This topographic setting controls the distinct palaeoclimatological and geomorphic conditions under which loess-paleosol sequences formed since 800 ka. Jipa (2014) outlined the evolution of low Danube loess deposits, emphasizing on the gradation of textural classes related to the distance from the Danube river and the role of Carpathian/Balkan range as a source of detrital inputs. The Kaolinovo site is located at the southernmost part of the continuous loess cover in NE Bulgaria (Evolgiev, 2007) (Fig. 1b). The area is characterized by undulating relief with an overall amplitude of up to 100 m, cut by deeply incised old river valleys (~50 m of incision), having generally a north-south orientation. The terrain is typical karstic with low groundwater table.

The studied Quaternary loess sequence lays on kaolinitic clays deposits filling karstic depression developed in Low Cretaceous limestones. Fragmentary gravel beds are also present below the loess complex. The total thickness of the Kaolinovo’s loess-paleosol sequence is 23.4 m exposed in an open pit quarry exploited for kaolin extraction (Figs. 1S, 2S and 3S from Supplementary information). It consists of seven loess horizons (L1 to L7 from top to bottom), interbedded by paleosol complexes numbered according to the European loess stratigraphic scheme (Marković et al., 2015). In the present study we focused on the uppermost 12 m deposits, covering the Holocene soil at the top (S0), first loess L1, first paleosol S1, second loess L2, second paleosol S2, the third loess L3, and the paleosol complex below (S3 and S4).

Present-day climate is warm oceanic (Cfb) according to the updated Koppen-Geiger climate classification (Peel et al., 2007). According to the long term meteorological data from nearby meteorological stations, mean annual temperature is 10.3 °C with monthly maximum in July–August and monthly minimum – in January–February. Mean annual precipitation is 575 mm, with maximum in May–June and minima in March and September (Fig. 4S).

Natural vegetation cover is mainly steppe – forest (Vassilev and Apostolova, 2013), represented by grasses, bushes and patchy forests, which cover the undulating landforms. Nowadays, agriculture in Shumen region covers 52% of the surface. According to the “Atlas of soils in Bulgaria” (Koynov et al., 1998), Podzolized Chernozems (Degraded Chernozems) are the main soil type around the quarry, classified as Phaeozems in WRB classification system (IUSS Working Group WRB, 2015).

3. Sampled sections

Two loess sections were sampled in the Kaolinovo quarry, one in 2011 and the other in 2017–2019.

3.1. 2011 sampling campaign

The first sampling campaign was carried out in 2011 on the north-facing wall of the Kaolinovo quarry (Fig. 1S). The samples were collected every 5 cm over the whole loess-paleosol complex, except within an inaccessible 3 m thick interval (between 13 and 16 m). The lower part of section (19–23.5 m depth) is composed of thick reddish paleosol complex, the oldest loess horizon L7 and red clays overlaying the kaolinitic clays below (Fig. 1S). Block samples from least weathered levels of the three uppermost loess horizons have been collected for luminescence dating (Balescu et al., 2020).

3.2. 2017–2019 sampling campaigns

In 2017–2019, continuous sampling at 2 cm resolution was performed along the south-facing wall of the quarry down to 12 m depth (Figs. 2S and 3S). Cleaning the outcrops was done by hand tools removing approximately 1 m thick layer to collect about 300 g of fresh material per sample. Detailed profile’s description is provided in Table 1S.

4. Methods

4.1. Laboratory magnetic measurements

The samples were air dried in laboratory, gently crushed and passed through a 2 mm sieve. Magnetic susceptibility of the bulk material was measured on MFK – 1 A susceptibility bridge (AGICO, Czech Republic) at 200 A/m field and two working frequencies – 976 Hz and 15,616 Hz. The material was filled into standard 10 cm³ plastic cylinders. Low-field mass specific magnetic susceptibility ($\chi$) is calculated using sample’s weight and the measured susceptibility at lower frequency. Frequency-dependent magnetic susceptibility ($\chi$) is calculated as the difference between the measured susceptibilities at low and high frequencies. This parameter is commonly used as an indicator for the presence of viscous superparamagnetic ferrimagnetic iron oxides (Dearing et al., 1996). Magnetic remanence measurements were performed on cubic samples (2x2x2 cm) prepared by mixing 2 g of dry powdered material with gypsum and water.

Anhysotropic remanent magnetization (ARM) was imparted using a Molspin AF demagnetizer with a 100 mT AF field superimposed on a 0.1 mT DC field. Isothermal remanent magnetization in 2 T field (IRM2T) (considered as saturation isothermal remanence
magnetization) and subsequent −100 mT and −300 mT back fields have been acquired along the z-axis in IM-10-30 pulse magnetizer (ASC Scientific, USA). Magnetic remanences were measured on JR-6A automatic spinner magnetometer (AGICO, Czech Republic) with a sensitivity of $2 \times 10^{-6}$ A/m. The S-ratio was calculated as: IRM$_{300\text{mT}}$/IRM$_{2\text{T}}$ (Thompson and Oldfield, 1986). High-coercivity remanence component HIRM was calculated according to Robinson (1986) as $0.5 \times (\text{IRM}_{2\text{T}} + \text{IRM}_{300\text{mT}})$.

Magnetic hysteresis loops and back field remanence measurements were carried out for every second depth interval (number of
4.2. Pedological analysis

Demagnetization of composite remanence. INRAE soil analysis laboratory (LAS, Arras, France). They consist of:

- Analysis of the magnetic remanences were deduced by coeval analysis using the MaxUnMix software (Maxbauer et al., 2016). The main parameters determined are: the mean coercivity of an individual component ($B_h$), the component saturation magnetic remanence ($M_r$) as percent from the total remanence, and the dispersion parameter (DP) given by one standard deviation in log space.

Stepwise thermal demagnetization of composite remanence induced along the 3 sample’s axes was used as a diagnostic tool for determination of coercivity and unblocking temperatures ($T_{ub}$) of the major magnetic remanance carrying minerals. The composite remanence was acquired consecutively with IRM$_{2T}$ induced along + z axis; IRM$_{0.2T}$ induced along + y axis; and ARM induced along + x axis. The resulting three orthogonal remanence components are: IRM$_{0.2-2T}$; IRM$_{0.1-0.2T}$; and ARM (acquired in maximum AF field of 0.1 T). The thermal demagnetization of this composite remanence was carried out at 19 steps starting from room temperature up to 700 °C in air using a MMTD shielded furnace (Magnetic Measurements, Ltd.; UK). Remanence signal was measured at room temperature after each heating step. The total intensity of each component is represented as a sum of several mineral – specific components, carried by different (ferro)magnetic minerals. These were identified by the observed remanence unblocking temperatures $T_{ub}$ (see part 5.1.). Identified $T_{ub}$s suggest that ARM is carried by magnetite ($mgt$) and maghemite ($mht$) in various proportions. In few levels final $T_{ub}$ of 700 °C of the ARM component point to hematite (hmt) contribution as well. Mineral – specific components building up IRM$_{0.2-2T}$ and IRM$_{0.1-0.2T}$ were determined in a similar way. An example with schematic representation of the approach is given in Fig. 5S.

The origin and type of magnetic minerals carrying the laboratory induced magnetic remanences were deduced by coeval analysis of the fitted components of IRM acquisition curves and thermal demagnetization of composite remanence.

4.3. Statistical analysis

Principal component analysis (PCA) was performed separately on three sets of data:

- i) intensities of the remanence components carried by different iron oxides, identified by 3-axis composite remanence thermal demagnetization, and components determined from IRM acquisition fits for a set of 40 samples. The input variables for the PCA analysis were chosen as follows: mean coercivity $B_h$ of each fitted IRM component (BH-C1, BH-C2, BH-C3, BH-C4); the corresponding relative share of the four IRM components unmixed (C1%, C2%, C3%, C4%); intensities of ARM carried by magnetite and maghemite (ARM$_{mgt}$ + mht); intensities of IRM$_{0.1-0.2T}$ (depicted as IRMs) carried by magnetite and maghemite (IRMs $mgt$ + mht); intensity of IRMs carried by hematite (IRMs hmt); and intensities of ARM$_{0.2-2T}$ (depicted as IRMs) carried by maghemite (IRM$_{mht}$) and hematite (IRM$_{hmt}$). The intensities of ARM and IRMs, carried by strongly magnetic magnetite and maghemite are summed up due to their similar magnetic characteristics and coercivities, which cannot be discriminated by unmixing IRM acquisition curves. The observed unblocking temperatures were not included in the analysis as they are discrete variables. All variables were standardized to have zero mean and a standard deviation of one.

- ii) magnetic parameters measured for the 309 samples along depth of the profile. The following set of 16 magnetic parameters and ratios were included in the analysis: $\chi_x$, $\chi_y$, $\chi_z$, $\chi_{tot}$, ARM, $M_s$, $M_r$, HIRM, IRM$_{2T}$, $\chi_{sat}$/HIRM, ARM/IRM$_{100mT}$, $\chi_{ferri}$/ $M_s$, $B_s$, $B_{re}$, S-ratio, $M_r$/($M_s$ $B_s$/$B_{re}$).

- all pedologic parameters for a set of 35 samples.

Statistical analyses were performed using Statistica 10 (StatSoft Inc.) and xIstal packages.

5. Results

5.1. Mineral magnetic carriers

5.1.1. Acquisition of isothermal remanent magnetization (IRM) and unmixing of coercivity components

The choice of coercivity components’ number assumes that the bulk signal of the samples from (paleo)sol units is composed at least by two medium coercivity components, representing detrital and pedogenic strongly magnetic fractions. A third component should reflect the presence of high-coercivity weakly magnetic phases and, another (fourth) component could be used in fitting the curves at low fields, where we expect the signal from viscous ferrimagnetic grains. Using this approach, most of the IRM acquisition curves are fitted by four components, with exception of several levels from the upper 5 m of the profile, spotting loess material from L1 and L2. Examples for the shapes of typical IRM acquisition curves and the fitted components are given in Fig. 6S. The softer coercivity component (C1) is characterized by low $B_h$ values of 4–9 mT, contributing 1–15% to the total remanence with higher share in paleosol horizons and notable increase at 580–1176 cm depth. The association of high C1 intensity with paleosols suggests that probably C1 originates from pedogenic SP-
viscous SD fraction. In support of such supposition is the observed relationship between the intensity of the C1 component and frequency dependent magnetic susceptibility ($\chi_{FD}$) (Fig. 7S). The correlation is relatively weak and this could be due to possible contribution of multidomain grains to C1, as well as larger experimental errors in IRM measurements at low DC fields (Roberts et al., 2019). Another source of uncertainty may come from the type of the fitting function used (He et al., 2020). The second component (C2) has mean coercivity in the range 15–23 mT and varying contribution (from 20 to 55%) to the total magnetization. The third IRM component (C3) presents a mean Bh value in the range 30–80 mT and contribution between 30 and 70% to the total IRM intensity. High coercivity component (C4) contributes between 3 and 15% to the total IRM and its mean coercivity strongly changes with depth from (650–1800) mT in the upper 6 m to (115–560) mT in the lower part of the profile (6–12 m). Numerical values of the fitting parameters for the samples shown in Fig. 6S are presented in Table 2S.

5.1.2. Stepwise thermal demagnetization of composite remanence

The three orthogonal components reveal different unblocking temperatures ($T_{ub}$) during stepwise thermal demagnetization experiments (examples are given at Fig. 8S). The ARM component shows progressive demagnetization which is unblocked at final $T_{ub}$ of 580 °C except in B2, B3 and B/C horizons of paleosol S2 and B3 of S3 where $T_{ub}$ of 400–450 °C are observed. A different demagnetization behavior is typical for the IRM$_{0.1}$ component (designated IRM$_{C1}$) (Fig. 8S, middle column). Large part of the remanence is sharply unblocked around 250–300 °C. The remaining magnetization then continuously decreases until 700 °C in most samples. The high coercivity component – IRM$_{2-2_T}$ (named IRM$_{C4}$) as remanence signal remaining along the $+z$ axis after consecutive applications of DC fields of 2 T along $+z$ axis and 0.2 T along $+y$ axis shows similar demagnetization behavior with a higher proportion of remanence unblocked at 700 °C. According to Dunlop and Ozdemir (1997), $T_{ub}$ of 580 °C is ascribed to magnetite, $T_{ub}$ of 270–350 °C to maghemite - hematite transformation during heating, and $T_{ub}$ of 700 °C to hematite. We consider the observed $T_{ub}$ of 250 °C on the IRM$_h$ component as representing maghemite as well. Thus, diagnostic mineral magnetic experiments point out to the presence of strongly magnetic magnetite and maghemite with wide grain size distributions, contributing to coercivity components C1, C2 and C3. Hematite is also identified, being involved not only in the high – coercivity fraction, saturated in fields higher than 200 mT, but also in present as low-coercivity fraction, saturated in the field range 100–200 mT.

5.1.3. PCA on remanent components carried out by different iron oxides

The results from the PCA analysis show that 67.5% of data variability is explained by the first two components (Fig. 2). The first component F1 accounts for 43.4% of the total variance and F2 for 24.1%. Fig. 2a shows the projection of variables on F1 x F2 plane. The first component F1 is strongly positively correlated to C3% IRM$_{h-hmt}$, C1%, C4% and IRM$_{h-hmt}$. At the same time, F1 is negatively correlated to the mean coercivity of C3 component (Bh-C3) and the percent contribution of C2 (C2%) (Fig. 2a). The second principal component F2 is mainly correlated positively to ARM$_{mgt}$ + mht and negatively correlated to C3%. The observed sample positions in F1 x F2 components space reveal firm discrimination among different units (Fig. 2b). With respect to F1, mineralogy of the lower part of the profile (loess L3, the deposits below described as A-horizon of S4 and the soil S3) is significantly different from the magnetic minerals from loess units L1 and L2, and the upper (paleo)sols So, S1 and S2. With respect to F2 component we see clear sub-division between loess and (paleo)sols (Fig. 2b).

Depth variations of F1 and F2 along with the corresponding variables, having the highest loadings are depicted in Fig. 3a and b. The major shift in F1 observed at 778 cm depth corresponds to the increase in the intensity of IRM$_{h-hmt}$ and systematically lowered contribution of C2%. F2 component discriminates between loess horizons and paleosols S1 and S2. Variability in the examined data set not explained by the first two components is mainly related to the coercivity of the softest IRM component (Bh-C1) and intensity of the IRM$_h$ component, carried by hematite (IRM$_{h-hmt}$). Their variations with depth are shown in Fig. 3c. Systematically higher intensities of IRM$_{h-hmt}$ start to appear after 7 m depth accompanied by significant drop in coercivities of C2 and C3 components (Fig. 3d).

Thus, F2 component comprises the effect of pedological variability (e.g. loess vs paleosol) with higher maghemite fraction in paleosols as compared to loesses. The first component F1, which accounts for the largest part of data variability, subdivides the
profile in two contrasting parts with respect to the amount and coercivity of hematite, which is probably related to changes in parent loess mineralogy and can be considered as a lithological effect.

5.2. High-resolution depth records of rock magnetic parameters

Concentration-dependent magnetic parameters such as magnetic susceptibility ($\chi$), frequency-dependent magnetic susceptibility ($\chi_{fd}$), ARM, SIRM show synchronous behavior with depth. These parameters are sensitive to the presence of ferrimagnetic fraction in typical domain states. Namely, the superparamagnetic (SP) fraction dominates in $\chi_{fd}$, single domain/vortex state (SD/PSD) fractions - mainly control the ARM (Liu et al., 2012). Pronounced increase of these magnetic parameters are observed in all soils (Holocene soil and the three paleosols) (Fig. 9S) as generally observed in most loess-paleosol sequences (Evans and Heller, 2003; Marković et al., 2015; Maher, 2016).

A PCA analysis was performed on the high-resolution magnetic proxies to discriminate different pedologic units and interpret the observed depthvariations. The results show that first two components account for 75% of the data variance with 64% of F1, and 17% of F2 (Fig. 4). Concentration – dependent magnetic parameters have the highest contribution to F1, influenced by the enriched strongly magnetic fraction formed in-situ during periods of enhanced pedogenesis. Among them, the highest loadings are coming from the magnetic parameters, sensitive to the presence of SP and SSD ferrimagnets ($\chi_{sp}$, $\chi_{ss}$, $\chi_{fd}$, $\chi_{ARM}$, $\chi_{SIRM}$) to the similar contribution from coercive force ($B_c$) and coercivity of remanence ($B_r$) and the ratio $IRM_{2T}/\chi$ (Fig. 4a, Table 3S). The second component F2 is aligned with the ratios $M_r/M_s$ and $B_r/B_c$ and opposes the S-ratio. The distribution of samples in F1 x F2 space is presented in Fig. 4b. Here, the first component F1 discriminates between loess units (aligned with $B_r$, $B_c$, and $IRM_{2T}/\chi$ vectors) and (paleo)soil samples from So, S1, S2 and B1 – B3 horizons of S3. The second component F2 reflects mainly the opposite behavior of $S_3$ - $B_4$, $S_2$ - $A_2$ and $L_4$ with respect to the loess and paleosol samples from the upper units (Fig. 4b). The first two principal components show depth variations, strongly related to the behavior of the variables, giving the highest contribution (Fig. 5a and b). The variability of F1 with the strongest amplitude is best modulated by magnetic susceptibility and coercive force ($B_c$) of the remanence carriers. The second component (F2) reveals depth variability intimately governed by the relative contribution of the high-coercivity ferromagnetic fraction expressed by the S-ratio, and changes in the ratio $M_r/M_s$. This component shows systematic shift from positive to negative signal marked by the third loess ($L_3$) (Fig. 5b). Total variance of the data set, comprised by the magnetic parameters shown on Fig. 4a is guided by those sensitive to the presence of strongly magnetic iron oxides - magnetite and maghemite (Liu et al., 2012). However, even though possessing weakly magnetic signal, (antiferromagnetic) oxyhydroxides are also important environmental proxy parameters. Such a parameter is high-coercivity remanence (HIRM) (Fig. 5c). It shows higher values in three intervals corresponding to $B_2$ horizon of the Holocene soil (So), to all horizons of the S1 paleosol, although HIRM values slightly decrease downward; and to the $B_3$ horizon of S2 paleosol. Magnetic ratios $M_r/M_s$ and $B_r/B_c$ derived from hysteresis measurements, the coercive force ($B_c$) and coercivity of remanence ($B_r$) are utilized widely in classic rock magnetic studies as magnetic domain state and/or mineral sensitive parameters (Dunlop and Ozdemir, 1997; Liu et al., 2012; Roberts et al., 2018, 2019). The three loess horizons are characterized by higher $B_r$ and $B_c$ with especially higher values within the L2 loess horizon (Fig. 5). Similar relative increase in coercivities with maxima at 1180 cm depth, described as $B_4$ horizon of paleosol S2, suggests that this horizon corresponds to a non-fully pedogenized loess unit. Coercivity variations are similar to the ones expressed by the $IRM_{2T}/\chi$ ratio (graph not shown, see the close proximity of the three vectors in Fig. 4a).

5.3. Pedological parameters

Variability in pedological parameters, determined for 34 representative samples from each horizon described in the field, were analyzed by PCA. The 13 variables used for the statistical analysis are: particle-size fractions (as %): <2 $\mu$m, silt, sand; the particle-size indexes GSI and CSI; CaCO3, SOC, Ntot, the ratio C/N; CEC, total Fe ($Fe_{total}$), Crystalline Fe ($Fe_{cryst}$ = $Fe_{cryst}$ – $Fe_{FeO}$); poorly crystalline Fe ($Fe_{P}$). The initial analysis on all samples reveals that the first two components explain 51.9% and 24.4% respectively of the variability in the data (Fig. 6a). The first component is positively correlated to silt and CaCO3 content, and negatively correlated to the fraction <2 $\mu$m, $Fe_{cryst}$ and total iron $Fe_{total}$ (Fig. 6a). The second component is determined by the positive loadings of SOC, $N_{tot}$ and $Fe_{P}$ (Fig. 6a). Depth variations of the first two components along with their most contributing variables are presented in Fig. 7. As far as the highest loadings in F1 and F2 discriminate generally among loess and paleosol samples, we carried out a second PCA on
Fig. 4. PCA results on magnetic parameters and ratios. a) Circles of correlations of first two principle components F1 and F2; b) projection of samples on F1 x F2 plane. Symbols are colored according to the units: black — Holocene soil S0; brown — S1; orange — B and B/C horizons of S2; orange — S2; pink — S3; violet — S4; shades of yellow — loess samples. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)
paleosol samples excluding the Holocene soil and the loess samples for a better discrimination between the paleosol horizons. The two first components of this second PCA explain 77% of the variance, with 50.5% and 27.2% of the variance for the first and second component respectively (Fig. 10S). The distribution of pedological variables in F1 x F2 space replicates the picture, obtained after inclusion of samples from loess horizons and S0. Consequently, the effect of changing SOC composition and stability with time (Sierra et al., 2018) for the “young” carbon pool is not the main source of variability. The samples from all horizons of paleosol S1 are well distinguished from the rest in F1 – F2 space.

6. Interpretation

6.1. Sources, origin and evolution of magnetic signal along Kaolinovo profile

Variations in type and relative abundance of mineral magnetic phases show high dependence on profile’s stratigraphy. The third loess (L3, 750–795 cm) is a critical boundary for all magnetic properties changes, particularly for the type and coercivity of mineral magnetic carriers. Magnetic properties above L3 (So, S1, S2 and loesses L1 and L2) are significantly different from those in the lower part of the profile (L3, S3,4) as shown in Fig. 2b by the first PCA component. This is mainly controlled by variations in relative contribution of C2 component (Fig. 3a) along with changes in coercivities of the second and third IRM components up to 700 cm depth (Fig. 3d). Meanwhile, intra - parametric variations of Bh-C2 and Bh-C3 between loess and paleosols in the upper part of the profile (0–700 cm) are small (Fig. 3d). The largest differences are observed between the upper and lower parts of the profile, from (20–25) mT to (15–17) mT in Bh-C2 and from (55–65) mT to (30–45) mT in Bh-C3, respectively (Fig. 3d). The opposite behavior of C2% and C3% (Fig. 3a, b) with highs and lows in paleosols (loess units) respectively suggests a pedogenic origin of C2% and detrital of C3%. On the other hand, the intensities of the high-coercivity hematite component (IRMh-hmt) are not straightforwardly related to C2 or C3 relative shares. It resembles more C2 behavior in the upper 8 m and switches to C3 in the deeper horizons. In contrast, intensities of IRMh-hmt (Fig. 3b and c) well resemble the changes in the relative share of the detrital C3 component. These relationships suggest detrital hematites as the mineral carriers of the C3 component. Lower coercivities and C3% increase indicates an overall increase in the amount of detrital hematites fraction within the 700–1200 cm interval due to change in the source material (Figs. 2a and 3a-b, d). Mean coercivities of the fourth high-
coercivity component $C_4$ largely change from more than 1000 mT in the upper 6 m to about 100 mT in the interval 8–12 m (Fig. 3d). The $C_4\%$ shows close relation with IRM$_{h-hmt}$ (Fig. 2a), which significantly contributes to $F_1$ component. We therefore propose that the $C_4$ component represents pedogenically produced hematite, involved in IRM$_{h-hmt}$ remanence.

Our interpretations suggest that the first component $F_1$ reflects the interplay between the relative contribution of detrital hematites, associated with properties of the parent loess material, and pedogenically produced hematite, the latter being dependent on the pristine loess mineralogy and grain size. The second principal component $F_2$ (Fig. 3b) is positively correlated to the intensity of ARM$_{mgt}$ and negatively correlated to $C_3\%$ contribution. Consequently, it points out the interactions between pedogenic formation of magnetite-like fractions, carrying ARM and low-coercivity hematite fraction in the parent loess ($C_3$ component carrier). The lowest coercivity IRM component $C_1$ is characterized by coercivities of 3–9 mT, typical for viscous SP magnetite particles of pedogenic origin (Eyre, 1996; Heslop et al., 2015). Its increase in the lower part of the profile (800–1200 cm) reflects the overall

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**Fig. 6.** PCA on pedologic variables. a) Circle of correlations of first two principle components $F_1$ and $F_2$; b) projection of samples on $F_1 \times F_2$ plane. The distribution of samples shows clear grouping: area of loess samples marked by yellow color is shifted towards positive $F_1$ loadings and negative $F_2$ loadings; areas of distribution of the paleosol samples from different horizons of $S_0$, $S_1$, $S_2$, $S_3$ and $S_4$ are spread from positive ($S_0$) towards progressively more negative $F_1$ and $F_2$ loadings. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)
lower coercivity magnetic minerals, both magnetics and hematites. Thus, our magnetic mineralogy results highlight the key role of parent material mineralogy and properties for in-situ formed pedogenic magnetic phases.

7. Discussion

7.1. Chronostratigraphy of the Kaolinovo profile

Magnetic susceptibility permits to correlate the two parallel profiles from the 2011 and 2017/19 campaigns using the low χ values from the upper three loess horizons L1, L2 and L3, and the enhanced χ values in paleosol horizons (Fig. 8). Three post-infrared infrared (PIR-IR) ages were obtained on K-feldspar grains from the three upper loess horizons (L1, L2, L3) in the Kaolinovo 2011 sequence (Balescu et al., 2020). The depth levels corresponding to PIR-IR ages have been transferred from the 2011 profile to the 2017/19 using χ variations between loess and soil horizons. The stratigraphic position of the L1 age corresponds to the local minimum at 1 m depth in the record from 2017/19 profile (Fig. 8). The sharp increase of χ within L2 related to the cryptotephra layer is considered a secure mark for transferring the L2 age. Similarly, least weathered material of 2011 profile from L3 (lowest χ signal) is correlated to the corresponding lowest χ values in the 2017/19 profile.

The PIR-IR age (45 ± 2 ka) in the L1 loess horizon (Balescu et al., 2020) suggests a deposition of its uppermost part during Marine Isotope Stage (MIS) 2. This implies a deposition of the lower part of L1 during MIS4 which is consistent with the absence of a well-defined horizon with enhanced magnetic properties that could correspond to MIS3 within L1 (Fig. 8). The age in the second loess L2 (167 ± 7 ka) ascribes it to MIS6. The age within the L3 loess (296 ± 17 ka) advocate for a deposition during the MIS 8 interval.

The loess — paleosol sequences from the Viatovo quarry (Jordanova et al., 2008), as well as the Zimnicea borehole (Radan, 2012) and Tuzla section (Balescu et al., 2003) from the nearby Romanian plain (for location of the sites see Fig. 1b) provide a useful age constrain thanks to the identification of the Matuyama — Brunhes (M/B) geomagnetic field reversal in the seventh loess unit (L7). The stratigraphic position of the M/B boundary along with the known lock-in-depth problem with geomagnetic field reversal records in loess-paleosol sequences (Spassov et al., 2003) implies a L7 formation during MIS 20 (Fig. 8). The fourth loess L4 is regionally represented by very thin deposit or is generally absent as in the Viatovo quarry where its position corresponds to a massive hard layer of CaCO3 concretions. Similarly, a layer of massive hard CaCO3 concretions was described in the Kaolinovo profile at depth interval 950—1044 cm (see Table 1S and dashed line in Fig. 8). We thus interpret this interval as the remnants of L4 deposited during MIS10 which implies that the lower laying B4 horizon of the S3 paleosol correspond to MIS 11. Accepting such a stratigraphic scheme, the oldest part of Kaolinovo (2017) profile (depth interval 1040—1140 cm) should conform to MIS12 (e.g. ~ 450 ka).

7.2. Change in eolian dust sources

The major source of low Danube loess is the alluvium of the Danube river (Lehmkuhl et al., 2021). Several authors also propose dust sources from the eastern/northeastern sector. According to Buggle et al. (2008), Ukrainian glacioluvial sediments constitute a second source for loess deposited in the lower Danube area. However, those sediments are generally coarse grained, which contradicts our observation of increased fine silt and clay content in L3 and older units (Fig. 7a, c). Stephens et al. (2003) suggests Aral and Caspian sea arid lands as a source for aeolian dust entrainment and transport by easterly winds towards the Black sea. Jipa (2014) proposed Black sea shelf as sedimentary eolian source at low sea level stands during glacial periods. The presence of large dried areas, available for dust deflation, over the Black sea shelf is alleged during isolated Black sea periods. Recent study by Hoyle et al. (2021) on a 400 ka record from NE Black sea sediment core (DSDP site 379) reveals evidences from dinocysts and Sr isotopes that the Black sea was disconnected from the Mediterranean and Caspian seas during MIS5, MIS 8 and MIS10 glacials. This favors sediments from the Black sea shelf as a source for aeolian dust deposition inland and could explain the peculiar magnetic signature of loess units L3 and L4 (the latter identified by the remnant CaCO3 level). However, further geochemical data are required to untangle sediments sources.

Loess horizons are characterized by clay (<2 μm) content comprised between 20 and 30% (Fig. 7a). We attribute such unusually high clay content for loess units to the geographic position of the site located south of the Danube river which is the main source of dust supply in the region (Evlogiev, 2007; Buggle et al., 2008; Jipa, 2014). Similar high clay contents were also observed in the loess horizons of the nearby Viatovo quarry, situated 50 km away.
west from Kaolinovo (Jordanova et al., 2008) (Fig. 1b), and in the loess horizons L1 and L2 from a 40 km long N–S transect perpendicular to the Danube river at Pleven district (central North Bulgaria) (Evlogiev, 2007). In this regional transect, the clay fraction increases southward from 12 to 37% in L1, and from 6-7 to 30% in L2 supporting a dust fining with source distance. A particular feature of the bottom part of L2 is the presence of a subdivision formed by the S2-A horizon. No C-horizon was observed for the paleosol S3. Instead, a less pedogenised horizon rich in silt and showing small increase in CaCO3 content in S3eB3 horizon (960–1020 cm) probably indicates a boundary between the welded S3 and S4 paleosols (see discussion in part 7.2.).

Variability in grain size fractions further reveal particular depth levels, which mark significant change in grain size distribution of the aeolian dust, persisting over certain depth intervals (Fig. 7a, c). The finest material is found within the deepest 4 m of the profile (800–1200 cm). The persistence of consistently high CSI values within S1 paleosol and L1 loess suggests an increased wind intensity and severe glacial conditions during mid to late MIS 6 and MIS 4. Similar pattern was observed in other loess–paleosol records from Central and Eastern Europe (Fitzsimons et al., 2012; Sümegi et al., 2020), from the Ioannina basin, NW Greece, over MIS 6 (Wilson et al., 2021) or in Lake Ohrid record (e.g. Francke et al., 2016). Because the CSI is defined as a ratio of coarse to fine silt fractions, its

Fig. 8. Links between the two profiles sampled in 2011 (a) and 2017 (b) by using magnetic susceptibility variations with depth. Location of the samples from loess horizons L1, L2 and L3 used for PIR – IR dating obtained by Balescu et al. (2020) are indicated; c) Links of magnetic susceptibility records with global stacked LR04 record of benthic δ18O for the last 800 ka (Lisiecki and Raymo, 2005). Warm Marine Isotope Stages (MIS) (odd numbers) are indicated.
variations are not affected by changes in the clay fraction related to pedogenic alterations of the primary loess material. Therefore, the absence of relative CSI minima in the paleosol S1 probably indicates that dust sedimentation had effectively ceased during MIS 5 interglacial. Persistently low CSI values and negative values of F2 component of the PCA on magnetic parameters (Fig. 5) below 800 cm depth suggest less severe climatic conditions during MIS 8 and 10 glacial periods. The limit of our record and age uncertainty prevent to strictly discuss MIS 12. Notable change of depositional settings deduced from CSI variability (Fig. 7c) occurs at the depth interval of the identified cryptotephra layer in L2 loess. Its stratigraphic position above the dated L2 interval (plifeR290 age of 167 ± 7 ka, Balescu et al., 2020) is consistent with the widely observed (crypto)tephra layer in the second loess horizon in loess-paleosol profiles from Central and Eastern Europe (Marković et al., 2015; Antoine et al., 2019; Jordanova et al., 2022). This observation of significantly different hydroclimatic regimes in the region between early (before ca. 162 ka) and mid to late MIS 6 (162–130 ka), with less wind/more rain and more wind/reduced rainfall, respectively, is coherent with previous observations associated with large-scale atmospheric and oceanic reorganizations (e.g. Margari et al., 2010; Roucoux et al., 2011; Wilson et al., 2021).

The third loess horizon L3, identified at 750–790 cm is the thinnest of the whole sequence (40 cm thick) and shows the highest magnetic susceptibility among the sampled loess units. The minimum γ value is 3.69 × 10⁻⁸ m² kg⁻¹ at 780 cm accompanied by relatively high clay content up to 30% (Figs. 5a and 7a). It is worth noting that L3 likely deposited during the small amplitude MIS 8 glacial period (see LR04 on Fig. 8). This loess horizon marks the gradual change in prevailing magnetic mineralogy from low-coercivity magnetically “soft” hematite to increasingly higher proportion of strongly magnetic magnetite at the base of paleosol S2 (Fig. 3) developed during MIS 7.

The absence of non weathered fourth loess horizon (L4) suggests a very weak dust accumulation at Kaolinovo during MIS10, with subsequent complete assimilation of the loess material into soil developed during MIS 9 (S₃). Sole field evidence for loess accumulation is the presence of a layer of large CaCO₃ hard concretions. Better preservation of L₄ loess was seen in a nearby quarry in the area (some 2 km to the west from the studied site). Such missing, or very thin loess horizons corresponding to the glaciations during MIS10 and MIS 8, coincides with the missing or very weak expression of these glacial periods in different records across Europe (Hughes et al., 2019).

7.3. Pedogenic development influenced by changing interglacial environments

The main variability of the pedological parameters opposes clay enriched (paleo)soil horizons against silt-dominated loess horizons (Figs. 6a and 7a). The second component highlights SOC and poorly crystalline iron (Feₐ) in the Holocene soil S₀ (Fig. 6b). Similarity in the distribution of samples in F1 x F2 space before (Fig. 6b) and after removal of those belonging to the Holocene soil and the loess units (Fig. 10S) points out that SOC content has also the highest loading on F2 component for paleosols.

Incorporation of the magnetic data into analysis of paleosols development allows gaining further information on the paleo-climate’s role in shaping their properties and pedogenesis during ancient interglacials.

The sharp change in coercivity of the C4 IRM component (Fig. 3d) at depth of 650 cm together with the weak local minimum seen in magnetic signature between B₂ and B₁ horizons of the paleosol S₂, and abrupt change in HIRM values (Fig. 5) suggest that the lower part of S₂ belongs to a separate soil-forming period, while the uppermost horizons developed on new eolian sediments. Considering chronological constrains, we propose that the formation of the upper (B₁ and B₂) and lower (B₃ and B/C) horizons of S₂ occurred during MIS 7a-c and MIS 7e sub-stages, respectively (Figs. 8 and 9). The higher HIRM values observed in the B₁ horizon (Fig. 5) suggest that the two paleosol horizons have been formed separately, but subsequently merged into a welded profile. This interpretation implies the presence of a discontinuity (hiatus) in the record corresponding to eolian deposition during cold MIS 7 d. Terrestrial records spanning MIS 7 environmental changes in western and central Europe, Turkey and Israel (Columbu et al., 2019) document the establishment of more arid conditions during MIS 7 d, potentially suggesting a short time interval of eolian deposition within S₂ paleosol. The transition between MIS 7 and the following Pleniglacial MIS 6 shows relatively weak magnetic enhancement and increased coercivities (Fig. 5) suggesting the possible development of an incipient soil as already reported in loess-paleosol records from Carpathian and lower Danube loess areas (Marković et al., 2009; Obreht et al., 2019). Such an incipient soil could have developed during a short climate amelioration period at the inception of cold MIS 6 (pollen zone ODS from Sadori et al., 2016; Wilson et al., 2021).

The increasing contribution of pedogenic hematite to the total signal in the lower part of the profile suggests that older interglacials were characterized by warmer climates. A similar regional interpretation was raised from the loess-paleosol profiles of Stari Slankamen (Serbia) and Mircea Voda (Romania) (Buggle et al., 2014; Necula et al., 2015).

The weathering degree of loess material resulting from climatic amelioration events (increased temperature and/or precipitation) are fingerprinted by the frequency dependent magnetic susceptibility and the values of bulk low field magnetic susceptibility. The first loess horizon L₁ deposited during the MIS 2–4 interval exhibits relatively higher magnetic susceptibility (compared to other loess horizons) slowly decreasing towards the base of the unit at 185 cm (Fig. 5). Signs of higher biological activity are also deduced from the abundant presence of crotovinas, root channels and intermixing of the material from upper levels (see profile description in Table 1S). These could be caused by climate amelioration during MIS 3, which is not expressed regionally by mature soils, but rather as incipient soils (Marković et al., 2015; Zeeden et al., 2018). The second loess L₂ is characterized by relatively steady and lowest magnetic susceptibility values of the whole profile (Fig. 5). The mean value (22.7 10⁻⁸ m³ kg⁻¹) observed within the upper part of the unit (380–420 cm) is the lowest in the studied sequence, suggesting low weathering of aeolian dust during the Penultimate glacial (MIS 6). Similar results, pointing to increasing wind intensity towards mid to late MIS 6 are reported by Sümegi et al. (2020) for Udvari core (SW Hungary), suggesting that this is a common feature on a regional scale. Stronger westerly winds associated with lower temperatures and reduced rainfall in the region could be induced by a southward migration of the winter polar front during glacial (or stadial) periods as already pointed out from Black Sea sediments (Wegwerth et al., 2016).

7.4. Kaolinovo mineral magnetic record as potential archive of tephra additions and their role for paleosol development

Fig. 9 shows magnetic susceptibility record along Kaolinovo profile together with the available age constrains from PIR-IR dating (Balescu et al., 2020); depth variations of magnetic
susceptibility along Stari Slankamen stacked record from Serbian loess (Song et al., 2018); dated cryptotephra layers from lake Ohrid (Leicher et al., 2019) and Tenaghi Philippon (Vakhrameeva et al., 2018; 2019; Wulf et al., 2018), and the global δ18O benthic stack (LR04; Lisiecki and Raymo, 2005).

The weak expression of MIS 10 and MIS 8 in Kaolinovo profile is accompanied by subtle irregularities or sharp peaks in magnetic susceptibility variations (marked by filled red ellipses in Fig. 9). These particular features are not related to measurements’ uncertainties but are reflected in different magnetic parameters (χ, ARM, IRM and the ratios ARM/IRM100mT as well as χ/Ms). Recent detailed study on loess-paleosol sequence from central north Bulgaria (Jordanova et al., 2022) revealed that depth variations of anhysteretic remanence (ARM) (resp. anhysteretic susceptibility χarm) is the most sensitive magnetic parameter with respect to identification of tephra additions into loess material. Several sharp peaks although not so intense, in χarm variability along Kaolinovo profile are also identified (Fig. 9). We suggest that they correspond to a record of tephra additions into the eolian sediments, resulting in the formation of cryptotephra layers. These depth intervals have similar stratigraphic position within the profile as the occurrences of tephra layers within Stari Slankamen loess-paleosol stack from the middle Danube basin (Song et al., 2018). These layers were described as tephra by Song et al. (2018) and exhibit clear peaks in magnetic susceptibility record (Fig. 9a). Similarly, Panaiotu et al. (2001) and Balescu et al. (2010) report the presence of tephra layer in the second loess L2 at Mostistea loess-paleosol profile. On Bulgarian territory, a visible tephra layer in L2 was detected only in Suchia kladenetz quarry near Pleven (Jordanova et al., 2022), while at Harletz (Antoine et al., 2019) as well as at Kaolinovo (the present study) it is only identified as cryptotephra layer due to the larger distance to major volcanic provinces from the Mediterranean basin (Fig. 1a). Dated cryptotephra layers for the last 500 ka from two terrestrial archives in the Balkans—lake Ohrid (Leicher et al., 2019)
and Tenaghi Philippou (Philippi peatland, Greece; Wulf et al., 2018; Vakhrameeva et al., 2018; 2019) are also presented on Fig. 9. They show the occurrence of volcanic ash falls. A particularly large part of the Kaolinovo sequence (800–1200 cm, e.g. L3, S3 – S4) may be also affected by these frequent additions of volcanic ashes, which exert strong influence on mineral magnetic carriers and pedological characteristics of these units. The incorporation of volcanic ash material in soil results in fast weathering of the glassy material and production of increased amounts of amorphous iron oxides, allophane, imogolite and halloysite clay minerals (Quantin et al., 1988; Jousselin et al., 2005; Craverio and Churchman, 2016).

Our data of amorphous iron oxides suggest increased amounts of Fe$_o$ at 900 cm depth, corresponding to S$_5$–B2 horizon, which shows anomalous magnetic signature (see above). Moreover, additional inputs of poorly crystalline Fe oxides (ferrhydrite) and leached Al from volcanic ash weathering represent favorable conditions for precipitation of Al-substituted hematites in warm climates (Schwertmann et al., 1979; Lewis and Schwertmann, 1979; Cornell and Schwertmann, 2003). Tsai et al. (2010) also show that increasing temperature lead to transformation of metastable poorly crystalline materials (e.g. allophane, ferrhydrite) into thermodynamically more stable minerals (e.g. kaolinite, hematite) within volcanic ash material in soil.

8. Conclusions

Multi proxy analysis of combined magnetic and pedological properties along Kaolinovo loess-paleosol profile reveals that such an approach provides detailed information on the interplay between loess sedimentation and pedogenesis. Mineral magnetic and rock magnetic data successfully disentangle the response of pedogenic mineral transformations and weathering to changes in source material and the texture of the parent loess (e.g. grain size distribution), climate and possibly can identify intervals with additions of volcanic ash particles. We demonstrated that the incorporation of a detailed analysis on the type and coercivities of mineral magnetic remanance carriers is a powerful tool for revealing changes in the dust source and the relative importance and interplay between aeolian dust deposition and pedogenesis. Moreover, we show that using PCA in the analysis of magnetic data is a robust approach for discriminating the roles played by various environmental factors on the formation of the bulk signal. Depth changes in concentration dependent magnetic parameters (χ, Ζ, ARM, IRM$_{2T}$) reflect the content of strongly magnetic magnetite/ maghemite carriers, clearly distinguishing non weathered loess from pedogenized units. On the other hand, pedological parameters discriminate paleosols from loess units through opposing silt – dominated texture classes in loess to clay – dominated pedosol horizons. Thus, concentration changes of strongly magnetic iron oxides along loess-paleosol sequences can be considered as proxies for relative variations in sedimentary texture, e.g. silt to clay fractions.

CRediT statement

Diana Jordanova (DJ) - Original Draft Preparation, Conceptualization, Formal analysis, Supervision, Funding acquisition, Project administration. Quentin Simon (QS) - Writing - Review & Editing, Conceptualization, Visualization, Conceptualization. Sandra Balescu (SB) — Investigation, Writing - Review & Editing, Neli Jordanova (NJ) - Writing - Review & Editing, Conceptualization, Daniel Ishlyamski (DI) — Investigation, Formal analysis. Bozhurka Georgieva (BG) - Investigation, Formal analysis. Didier Bourles (DB) - Conceptualization. Adrien Duvierv (AD) - Investigation. Sophie Cornu (SC) - Writing - Review & Editing, Conceptualization, Methodology, Formal analysis, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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