Catena 117 (2014) 4–22

Contents lists available at ScienceDirect

Catena

journal homepage: www.elsevier.com/locate/catena

Iron mineralogical proxies and Quaternary climate change in SE-European loess–paleosol sequences

Björn Buggle [a,b,*], Ulrich Hambach [a], Karoly Müller [c], Ludwig Zöller [a], Slobodan B. Marković [d], Bruno Glaser [e]

[a] Chair of Geomorphology, University of Bayreuth, D-95440 Bayreuth, Germany
[b] Department of Geography, Justus-Liebig University Gießen, Senckenbergstr. 1, 35390 Gießen, Germany
[c] Soil Physics Department, University of Bayreuth, D-95440 Bayreuth, Germany
[d] Chair of Physical Geography, Faculty of Sciences, University of Novi Sad, Faculty of Sciences, Trg Dositeja Obradovića 3, 21000 Novi Sad, Serbia
[e] Soil Biogeochemistry, Martin-Luther-University Halle-Wittenberg, von-Seckendorff-Platz 3, 06120 Halle, Germany

ARTICLE INFO

Keywords:
Rock magnetism
Diffuse reflectance spectroscopy
Pleistocene
Paleoclimate
Loess
Paleosols

ABSTRACT

The loess–paleosol sequences Batajnica/Stari Slankamen (Serbia) and Mircea Voda (Romania) represent key archives for the climate and landscape development of the middle and lower Danube Basin during the last 700,000 years. For deciphering the Quaternary climate evolution in these regions, the Batajnica/Stari Slankamen and Mircea Voda sites are for the first time studied by a multi-proxy approach based on iron mineralogical parameters. Changes in the iron mineralogical composition are identified and characterized by rock magnetic investigations, diffuse reflectance spectroscopy (DRS) and Munsell color based proxies. The results show that environmental conditions during mid- and early Middle Pleistocene interglacials were more favorable for hematite formation, suggesting a more oxidizing pedoclimate as in the more recent interglacials. This is also reflected in a gradual increase of the anhysteretic remanent magnetization vs. saturation isothermal remanent magnetization (ARM/SIRM) ratio. In the studied profiles changes in this ratio can be linked to a preferential hematitization of coarse-grained ferrimagnetica and relates to warmer climate conditions and a more extended estival dry period. At the same time, rock magnetic parameters indicate a preferential destruction of fine-grained magnetic particles in older paleosols resulting from seasonal excess moisture.

A progressive cooling and decrease of rainfall during the Middle and Late Pleistocene is evidenced not only for interglacial pedocomplexes but also for glacial loess layers. This finding is in line with previously published proxy records of silicate weathering and clay formation at these sites and similar trends reported from other sites in the European steppe belt. Relating iron mineralogical proxies to paleopedological characteristics and proxies of silicate weathering, additionally a change in the seasonal pattern of the interglacial temperature and precipitation regime from a Mediterranean type to a steppe type climate is revealed, highlighting the potential of such a multi-proxy approach.

Possible triggers for this paleoenvironmental evolution are discussed, as well, finally highlighting a "Quaternary uplift hypothesis", which best could explain the inferred trend of cooling, aridification and increasing continentality. Accordingly, changes in atmospheric circulation and rain shadow effects induced by small-scale uplift of European mountain belts (Alps, Carpathians, Dinaric Alps) would provide a driving mechanism for the westward extension of the Eurasian steppe belt into Central and SE-Europe during the Quaternary.

1. Introduction

Loess–paleosol sequences (LPSs) comprising several glacial–interglacial cycles are widely spread in the European steppe belt along the Danube River in Hungary, Serbia, Bulgaria and Romania. Their potential as paleoclimate archives has been proven in previous studies. Pattern of paleoenvironmental proxy records has been correlated across Eurasia to well established climate archives, the loess sites of Central Asia and China, as well as to marine records of the global ice volume (e.g. Balescu et al., 2010; Bronger, 2003; Buggle et al., 2009; Jordanova and Petersen, 1999a; Jordanova et al., 2007; Marković et al., 2006; Panaiotu et al., 2001). Besides the pollen sequence from the Velay region (France) (de Beaulieu et al., 2001; Reille et al., 2000), as well as Ioannina and Tenaghi Philippon (Greece) (Tzedakis and Bennett, 1995; Tzedakis et al., 2006), quasi-continuous terrestrial records for the Late and Middle Pleistocene climate in Europe can only be provided by these archives. Essentially the sites Batajnica and Stari Slankamen (middle Danube — i.e. Pannonian Basin) and Mircea Voda (lower Danube Basin) have been regarded as key sections comprising at least 700,000 years of climate history (Buggle et al., 2009; Marković

* Corresponding author at: Department of Geography, Justus-Liebig University Gießen, Senckenbergstr. 1, 35390 Gießen, Germany. Tel.: +49 (0) 641 99 36252.
E-mail address: Bjoern.Buggle@uni-bayreuth.de (B. Buggle).

0341-8162/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.catena.2013.06.012

et al., 2009, 2011). Hitherto, paleoclimatic research on these sites focused on paleopedological proxies such as micromorphological indicators of soil development intensity, mineralogy of silicates, grain size parameters or geochemical based weathering indices (Buggle et al., 2013; Buggle et al., 2009; Kostić and Protić, 2000; Marković et al., 2008, 2009). These proxy records revealed a gradual decrease of silicate weathering intensity and pedogenic clay formation during the Middle and Late Pleistocene going along with a change in paleosol typology from fossil (rubified) Luvisols and (rubified) Cambisols to fossil steppe soils. As reviewed in Buggle et al. (2013) similar trends can be also traced in the Northern Black Sea region. The observed patterns have been predominantly interpreted in terms of increasing aridification and/or cooling, reflecting the westwards expansion of the Eurasian steppe belt during the Quaternary (Buggle et al., 2013). However, existing data still leave open for discussion whether it is a change in the absolute annual sum of precipitation and/or temperature or rather a change in the seasonal distribution of rainfall. Therefore, the objective of the present study is to provide further evidences in helping to elucidate this issue by means of iron mineralogical investigations.

On the one hand, the amount of iron oxides formed during pedogenesis reflects soil formation intensity. Therefore, chemical as well as rock magnetic based iron mineralogical proxies such as the dithionite-soluble iron fraction (Fed) (e.g. Ding et al., 2001; Guo et al., 1996) or the bulk magnetic susceptibility (χ) and frequency-dependent susceptibility ($\chi_{fd(\%)}$) (e.g. Avramov et al., 2006; Evans and Heller, 2001, 2003; Maher and Thompson, 1995) are widely applied as proxies for pedogenesis intensity in loess–paleosol studies. On the other hand, formation and stability of different iron minerals and their grain size fractions depend on (soil-) environmental conditions such as soil water content, reduction potential of soil water (Eh), pH, presence of organic ligands, soil temperature and seasonal variations of these parameters (Cornell and Schwertmann, 2003; Orgeira and Compagnucci, 2006; Thompson and Oldfield, 1986). Hence, the assemblage of pedogenic iron minerals can be a sensitive indicator also for changes in amount and seasonal distribution of precipitation. The presence of an intense warm–dry period, for example, promotes formation of hematite and can be reflected in soil color proxies of hematite (Bronger, 1976; Kämpf and Schwertmann, 1983; Torrent et al., 1983; Vidic et al., 2004; Yaalon, 1997). Goethite, in contrast, is the more stable iron species under cooler and wetter conditions or with high humus content such as in steppe soils (Cornell and Schwertmann, 2003). Yet, quantification of hematite and goethite using visually measured soil color proxies, X-ray diffraction technique and Mössbauer spectrometry is either not very precise or time-consuming (Ji et al., 2002; Post et al., 1993; Torrent and Barrón, 1993). Recently transfer functions have been developed allowing a fast and more precise determination of the hematite and goethite contents and hematite vs. goethite ratio in loess and paleosols via diffuse reflectance spectroscopy measurements (Ji et al., 2002; Torrent et al., 2007). Furthermore, rock magnetic techniques are frequently applied to gain insight in the assemblage of iron oxides in soils and sediments (e.g. Jordanova and Petersen, 1999a,b; Liu et al., 2007; Panaiotu et al., 2001). They allow for example to identify gleyzation and reductive dissolution of fine grained magnetic oxides, which characterizes periods of excess soil moisture (Thompson and Oldfield, 1986), or help to identify hematitization of maghemite, indicative for dry periods with strongly oxidizing conditions (Torrent et al., 2006, 2007). Hence, multi-proxy approaches involving rock magnetic and spectroscopic investigations are proposed to infer paleoclimatic information from iron mineralogy (Torrent et al., 2007; Vidic et al., 2004). Here, we present one of the first multi-proxy approaches on European loess–paleosol sequences involving such a combination of a dual rock magnetic and spectroscopic mineralogical analysis.

Concerning the profiles Mircea Voda, Batajnica and Stari Slankamen, the only existing record relating to iron-mineralogy, is the bulk magnetic susceptibility record presented by Buggle et al. (2009) and Marković et al. (2009, 2011) and a basic rock magnetic characterization of Mircea Voda recently published by Necula and Panaiotu (2012). These authors found an increase in interglacial peak magnetic susceptibility from the modern soil to marine isotope stage (MIS) 9, reflecting enhanced formation of ferrimagnetica with higher intensity of pedogenesis. Buggle et al. (2009) hypothesized that the decrease of χ in older paleosols results from dissolution of highly magnetic susceptible particles of superparamagnetic size (SP) ($\sim<30$ nm) due to increasing excess of rainfall. The evaluation of this hypothesis via more comprehensive rock magnetic analyses is a further objective of the present study.

2. Material and methods

2.1. The sites and sampling

The regional settings of the sites have been described previously (Buggle et al., 2008, 2009). Briefly, the sections Batajnica (44° 55′ 29″ N, 20° 19′ 11″ E) and Stari Slankamen (45° 7′ 58″ N, 20° 18′ 44″ E) are situated at the banks of the River Danube 15 and 45 km upstream of Belgrade in the Serbian part of the Pannonian Basin. The climate of this area can be characterized as Cfb type climate with a mean annual precipitation (MAP) of 683 mm and mean annual temperature (MAT) of 11.9 °C (station Belgrade). Rainfall maximum is in June (90 mm/month) and a second maximum occurs in December (58 mm/month) (Fig. 1). According to the definition of Walter (1974), there is a dry period of 1 month (August).

The Mircea Voda site is located in the Dobrudja plateau, about 13 km east of the Danube River in Romania (44° 19′ 15″ N, 28° 11′ 21″ E). With 11.5 °C MAT but only ~400 mm MAP (climate station Constanta), this area is considerably dryer than the Serbian locations (Fig. 1). Two rainfall maxima of similar magnitudes occur in June and in November (~40 mm/month). The climate is of Cfa type with a dry period from ~May to October and a period of drought from ~July to September according to Walter (1974) criteria.

Due to ground water influence at the older part (>MIS 9) of the Batajnica section and a major hiatus in the younger part of the Stari Slankamen section, Buggle et al. (2009) built a composite LPS from the MIS 1 to MIS 9 sequence of Batajnica and the MIS 10 to MIS 17 sequence of Stari Slankamen. In the following, we refer to this composite sequence as "Batajnica/Stari Slankamen" LPS. Both, the LPS Batajnica/Stari Slankamen and Mircea Voda comprise more than six major loess–paleosol couples corresponding to glacial–interglacial cycles. Paleopedological descriptions of these sites are available in Conea (1969), Bronger (1976), Bronger (2003), Marković et al. (2009, 2011) and Buggle et al. (2013). The chronostratigraphy was established by Buggle et al. (2009) and Marković et al. (2009) and confirmed by Timar et al. (2010), Balescu et al. (2010), Schmidt et al. (2010), Marković et al. (2011, 2012). The nomenclature of chronostratigraphic units follows the "S–L" system used in Chinese loess–paleosol sequences (see Buggle et al., 2009).

For the present study, we focus on the uppermost six major loess–paleosol couples corresponding to the last 17 MIS. Pedocomplexes were sampled continuously and at least three representative samples were taken from each intercalated loess unit. Details on sampling strategy are described in Buggle et al. (2008, 2009). Samples were stored in airtight plastic bags and dried at 40 °C in the laboratory.

2.2. Rock magnetic proxies: measurement and background

For rock magnetic measurements the dried material was filled into 6 cm^3 plastic boxes and subsequently compressed and fixed with cotton wool before closing the lid in order to prevent movement of sediment particles during the measurements. The sediment mass served as normalizer. The low field magnetic susceptibility was measured in an AC-field of 300 A/m at 875 Hz using the AGICO KLY-3-Spinner-Kappa-Bridge (AGICO, Brno, Czech Republic) and is given as mass-specific susceptibility