Paleoclimate and weathering of the Tokaj (Hungary) loess–paleosol sequence

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ABSTRACT

The Tokaj loess–paleosol sequence (Northeast Hungary) is a well-studied site in Southeast Europe where detailed paleoenvironmental reconstructions of the Quaternary have been carried out. In this study, the geochemical composition of samples from the upper part of the sequence (45–21 ka) was analyzed and a variety of commonly used weathering indices and element ratios were applied to estimate weathering intensity, a common semi-quantitative proxy of paleoclimatic conditions. Further, similarities and differences between these weathering indices and their sensitivity to changes in paleoclimatic conditions were assessed. Results indicate that all of them accurately track changes in weathering intensity and are, with minor exceptions, very similar to each other.
Based on different transfer functions for major and trace element concentrations (XRF), mass-specific magnetic susceptibility (X) and stable carbon isotopic (δ^{13}C) data, mean annual paleotemperature and mean annual paleoprecipitation for the time intervals of paleosol formation (45–27 ka) and dust deposition (27–21 ka) were calculated. Results differ depending on the respective transfer function and method but agree with (X-, δ^{13}C-based), or slightly overestimate (XRF-based), previously published paleoclimate data of the region. XRF- and δ^{13}C-based results converge to a mean annual temperature (MAT) range of 8.5–10 °C (paleosol) and 8–9 °C (loess) and a mean annual precipitation (MAP) range of 700–900 mm a^{-1} (paleosol) and 550–700 mm a^{-1} (loess). X-based results are most consistent with literature data and yield MATs of 8.4 °C (paleosol) and 6.6 °C (loess) and MAPs of 300–500 mm a^{-1} (paleosol) and 220 mm a^{-1} (loess).

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1. Introduction

Loess–paleosol sequences are important terrestrial archives of Quaternary climate changes (An et al., 1990; Catt, 1991; Catt et al., 2000; Porter, 2001). Loess is a primarily silt-sized, clastic, aeolian sediment (Pye, 1995) that accumulated as dust blown out from alluvial plains of large rivers, deserts or foreland areas of ice sheets during the Pleistocene cold periods (Smalley and Leach, 1978; Smalley et al., 2009). During interstadials and interglacial, when warmer and more humid climate prevailed, dust deposition decreased and environmental conditions favored weathering and soil formation (Kemp, 2001). Hence, loess–paleosol sequences reflect Pleistocene climatic and environmental development and dynamics.

The major elemental geochemical composition of loess and paleosol samples generally reflects paleoweathering conditions, which may be quantified using simple element ratios and more complex weathering indices (WIs). WIs serve different purposes — they may be used to differentiate stratigraphic units, such as paleosols, allow for the comparison of sediment samples over space and time, or provide semi-quantitative information on weathering intensity, which is directly linked with paleoclimate (humidity, temperature, seasonality, etc.) (e.g. Sheldon and Tabor, 2009). Despite the debate about the reliability of these indices (Li and Yang, 2010; Xiao et al., 2010; Buggle et al., 2011), many applications can be found in the literature, mainly, but not limited to, Quaternary loess and/or paleosols in Europe (Kovács, 2007; Újvári et al., 2008; Buggle et al., 2011; Kühn et al., 2013; Vancampenhout et al., 2013; Újvári et al., 2014), North and South America (Goldberg and Humayun, 2010; Hall and Penner, 2013; Meier et al., 2014), China (Chen et al., 1999; Xiong et al., 2010; Baumann et al., 2014), Southern Arabia (Pietsch and Kühn, 2012) and Siberia (Zech et al., 2008). However, despite the large number of published weathering indices and their application in paleosol–loess studies, researchers still lack reliable recommendations as to which (and how many) weathering indices to apply in a loess–paleosol study. With the exception of Buggle et al. (2011) who provide theoretical considerations about the choice of a suitable index, and Baumann et al. (2014), who focus on permafrost-affected soils, we are not aware of a comprehensive, systematic comparison and evaluation of the available indices.

Yet weathering indices may not only serve to describe paleoweathering intensity, but also to quantify paleoclimate parameters, i.e. mean annual temperature (MAT) and mean annual precipitation (MAP), via specifically calibrated empirical transfer functions (Sheldon and Tabor, 2009). Although having been published for

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several years, transfer functions based on weathering indices (Sheldon and Tabor, 2009), magnetic susceptibility (Maher et al., 1994, 2003; Han et al., 1996) and stable carbon isotopes (Nordt et al., 2007) are still to gain more attention in loess–paleosol research, especially for Southeast Europe since most studies have been conducted elsewhere (Kühn et al., 2013; Meier et al., 2014).

Against this background, our study focuses on a loess–paleosol profile in Tokaj, Northeast Hungary, where detailed paleoclimate reconstructions have been carried out (e.g. Sümegi and Hertelendi, 1998; Rudner and Sümegi, 2001; Sümegi and Rudner, 2001; Sümegi and Krolopp, 2002; Schatz et al., 2011, 2012, in press). The goals are:

(a) to apply a variety of geochemical weathering indices to describe weathering intensity
(b) to assess and compare similarities and differences between these weathering indices, as well as their sensitivity to changes in paleoclimatic conditions in order to provide recommendations for the choice of a suitable weathering index, and
(c) to apply transfer functions to derive MAT and MAP estimates from different proxy records and to discuss and compare the results with local climate data from the literature and the results of global climate models.

The results of this study will broaden our understanding of the late Quaternary paleoclimate of Southeast Europe and may serve as an encouragement of future applications of these methods to examine and quantify paleoclimate records at other locations.

2. Principles of weathering indices and paleoclimate transfer functions

2.1. Weathering indices

Traditional, multi-element weathering indices (Table 1) are calculated from the concentrations of several mobile and immobile elements, thus providing a (semi-)quantitative measure of mineral weathering. They are usually based on the enrichment of Al and the depletion of cations as Ca, K, Na or Mg. Common multi-element WIs are Σbases/Al ratio (Retallack, 2001) and, more recently, the Paleosol Weathering Index (PWI, Gallagher and Sheldon, 2013). Other ratios are based on a more limited selection of elements (Al, K, Na, Ca) to focus on the weathering behavior of the feldspar group. An advantage of these feldspar indices is the fact that all index elements are hosted in the same mineral group, which helps minimizing the effects of variations in mineralogy. Common feldspar indices are the widely used Chemical Index of Alteration (CIA, Nesbitt and Young, 1982) and the Indices A and B after Kronberg and Nesbitt (1981).

In order to exclude potential effects arising from the inconsistency in K weathering, as discussed in Harnois (1988), several indices without K were developed, most prominently the Chemical Index of Weathering (CIW, also called CIA-K, Harnois, 1988), which is the K-free equivalent of the CIA, and the Plagioclase Index of Alteration (PIA, Fedo et al., 1995), a further modification of CIA and CIW that adjusts for Al contained in K-feldspar and results in pure plagioclase weathering. The WI after Yang et al. (2006) index uses Ti instead of Al as a refractory element and has been developed specifically for loess–paleosol studies, whereas WI-1 and WI-2 after Darmody et al. (2005) have not been widely applied to loess and paleosols yet.

Due to problems associated with determining the correct amount of silicate-bound Ca, indices that do not rely on Ca might be preferable, such as the index of Feng (1997) or the Chemical Proxy of Alteration (CPA, also known as CIW′, Cullers, 2000; Buggle et al., 2011), which factors out both Ca and K, thus attempting to avoid all potential biases due to these cations.

Trace element indices are the last group of weathering indices commonly employed in paleosol–loess studies. Both Ba/Sr and Rb/Sr represent leaching behavior during weathering, with Ba and Rb being less soluble than Sr. Potential weakness in these indices are the limited understanding and ambiguous behavior of Rb and Ba in the sediment (Kronberg et al., 1979; Nesbitt et al., 1980; Gallet et al., 1996; Sheldon and Tabor, 2009), grain-size dependence and the fact that variable and

Table 1
Overview of weathering indices and empirical climate transfer functions for MAT, MAP and mean July temperature (MJT): a) Mollisol-specific, b) Inceptisol-specific, c) forest soil-specific, d) $X_{B-C} = $ [(mean mass-specific magnetic susceptibility X of B horizon) − (mean mass-specific magnetic susceptibility X of loess)], X [10^{-8} m^3 kg^{-1}], e) $X = $ mean mass-specific magnetic susceptibility of B horizon or loess, and f) the δ^{13}C transfer function results in a mean July paleotemperature (MJT) which needs to be converted to MAT (see Section 4.2 for details).

		Equation	Reference
Weathering index			
Multi-element	CIA	$=[Al / (Al + Na + Ca^* + K)] * 100$	Nesbitt and Young (1982)
	Index A	$=(Si + Ca^* + K + Na) / (Al + Si + Ca^* + K + Na)$	Kronberg and Nesbitt (1981)
	Index B	$=(Ca^* + Na + K) / (Al + Ca^* + Na + K)$	Kronberg and Nesbitt (1981)
	PWI	$=[(4.20 * Na) + (1.66 * Mg) + (5.54 * K) + (2.05 * Ca)] * 100$	Gallagher and Sheldon (2013)
	Σbases/Al	$=(Ca^* + Mg + Na + K) / Al$	Retallack (2001)
K-free	CIW (CIA-K)	$=[Al / (Al + Na + Ca^*)] * 100$	Harnois (1988), Maynard (1993)
	PIA	$=[(Al − K) / (Al + Ca^* + Na − K)] * 100$	Fedo et al. (1995)
	YANG	$=(Ca^* + Na + Mg) / Ti$	Yang et al. (2006)
	WI-1	$=(Si + Ca^*) / (Fe + Ti)$	Darmody et al. (2005)
	WI-2	$=(Si + Ca^*) / (Fe + Ti + Al)$	Darmody et al. (2005)
Ca-free	CPA (CIW′)	$=[Al / (Al + Na)] * 100$	Cullers (2000) and Buggle et al. (2011)
	FENG	$=(Al + Fe) / (Na + K + Mg + P)$	Feng (1997)
Trace element	Ba/Sr		
	Rb/Sr		
Climate parameter			
XRF-based	XRF1-MAP	$=-259.3 Ln(\Sigma bases / Al) + 759$	Sheldon et al. (2002)
	XRF2-MAP[a]	$=-130.9 Ln(Ca / Al) + 467$	Sheldon et al. (2002)
	XRF3-MAP	$=221.1 e^{0.0179 * (CIA-K)}$	Sheldon et al. (2002)
	XRF1-MAT[b]	$=46.9(Al / Si) + 4$	Sheldon (2006)
	XRF2-MAT	$=-18.5 * [(K + Na) / Al] + 17.3$	Sheldon et al. (2002)
	XRF3-MAT[c]	$=-2.74 Ln(PWI) + 21.39$	Gallagher and Sheldon (2013)
MS-based	X1-MAP[d]	$=222 + 199 \log (X_{B-C})$	Maher et al. (1994)
	X2-MAP[e]	$=-22.7 + 11.6X - 6.7 * 10^{-2}X^2 + 1.9 * 10^{-4}X^3 - 1.9 * 10^{-7}X^4$	Han et al. (1996)
	X3-MAP[d]	$=86.4 * Ln(X_{B-C}) + 90.1$	Maher et al. (2003)
	X-MAT[e]	$=-2.4 + 0.2X - 1.1 * 10^{-3}X^2 + 2.7 * 10^{-6}X^3 - 2.7 * 10^{-9}X^4$	Han et al. (1996)
δ^{13}C-based	δ^{13}C-MJT[f]	$=[0.685(\delta^{13}C) + 34.9]$	Nordt et al. (2007)