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# Excursions to C<sub>4</sub> vegetation recorded in the Upper Pleistocene loess of Surduk (Northern Serbia): an organic isotope geochemistry study

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**Abstract.** Loess sequences have been intensively studied to characterize past glacial climates of the 40–50° north and south latitude zones. Combining different approaches of sedimentology, magnetism, geochemistry, geochronology and malacology allows the general pattern of the climate and environment of the last interglacial–glacial cycle in Eurasia and America to be characterized. Previous studies performed in Europe have highlighted the predominance (if not the sole occurrence) of C<sub>3</sub> vegetation. The presence of C<sub>3</sub> plants suggests a regular distribution of precipitation along the year. Therefore, even if the mean annual precipitation remained very low during the most extensive glacial times, free water was available for more than 2 months per year. Contrarily, the  $\delta^{13}\text{C}$  record of Surduk (Serbia) clearly shows the occurrence and dominance of C<sub>4</sub> plants during at least 4 episodes of the last glacial times at 28.0–26.0 kyr cal BP, 31.4–30.0 kyr cal BP, 53.4–44.5 kyr cal BP and 86.8–66.1 kyr. The C<sub>4</sub> plant development is interpreted as a specific atmospheric circulation pattern that induces short and dry summer conditions. As possible explanation, we propose that during “C<sub>4</sub> episodes”, the Mediterranean Sea would have been under the combined influence of the following: (i) a strong meridional circulation unfavorable to water evaporation that reduced the Mediterranean precipitation on the Balkans; and (ii) a high

positive North Atlantic Western Russian (NA/WR)-like atmospheric pattern that favored northerlies over westerlies and reduced Atlantic precipitation over the Balkans. This configuration would imply very dry summers that did not allow C<sub>3</sub> plants to grow, thus supporting C<sub>4</sub> development. The intra-“C<sub>4</sub> episode” periods would have occurred under less drastic oceanic and atmospheric patterns that made the influence of westerlies on the Balkans possible.

## 1 Introduction

Loess deposits are important terrestrial sediment records that provide key data for climate reconstruction and the interpretation of past glacial cycles (Kukla, 1977; Guo et al., 2002). Combining multidisciplinary approaches (sedimentology, magnetic properties, geochemistry, geophysics, geochronology, malacology, palynology) allows a general pattern of climatic and environmental evolution in Eurasia and America to be proposed.

In Western Europe, high-resolution study of the Nussloch loess sequence (Germany), supported by a large set of luminescence (OSL, IRSL, TL) and <sup>14</sup>C dates, has allowed correlation of the loess grain size variations and loess–paleosol alternation with the Greenland ice core dust record, which

suggests a global connection between North Atlantic and Western European atmospheric circulations and associated wind regimes (Fuchs et al., 2012; Rousseau et al., 2007). The first attempt to model the impact of the abrupt climate variations of the North Atlantic on dust emissions supports the hypothesis that the North Atlantic millennial-timescale variability is imprinted on Western European loess profiles and points to changes in the vegetation cover as the main factor responsible for the dust emissions, yielding material for millennial-scale sedimentation variations (Sima et al., 2009). Among the multidisciplinary investigations, a recent organic geochemistry study focused on the impact of these abrupt events in terms of precipitation at the key section of Nussloch. Using inverse modeling of  $\delta^{13}\text{C}$  and vegetation, Hatté and Guiot (2005) showed a general glacial precipitation background of  $200\text{ mm yr}^{-1}$  along the last glaciation punctuated by estimated increases of 100 % recorded during interstadial events.

A comprehensive pattern of past Western European mid-latitude atmospheric circulation and interconnection is now emerging, but comparatively few similar high-resolution data on past climate are available for Central Europe. Stratigraphical, paleopedological and chronological studies (Antoine et al., 2009a; Fuchs et al., 2008; Galović et al., 2009; Schmidt et al., 2010; Stevens et al., 2011; Zech et al., 2009) in Serbia have provided information that the Carpathian region and Western European environments were under different atmospheric conditions that resulted in a drier environment throughout the last climatic cycle (Antoine et al., 2009a; Marković et al., 2008). This conclusion was based on grain-size and paleosol analyses, but a more precise interpretation requires appropriate investigation. Indeed, the extent of this dryness, the search for seasonality of the precipitation and the reconstruction of past vegetation appear necessary for providing key elements for understanding the past atmospheric circulation conditions in this area.

Such an issue could be addressed by an organic isotopic geochemistry study, as has already been performed in Western Europe, if properly conducted. Loess sequence is an alternation of typical loess and paleosols. These two distinct facies must be considered separately as they yield different types of information. European interglacial paleosols are associated with several millennia of temperate forest vegetation, no or very weak mineral accumulation, temperate humid climate and are the result of strong and efficient pedogenesis forming organic soils that can reach up to 2 m in depth (Finke, 2012; Finke and Hutson, 2008; Yu et al., 2013). Roots can penetrate the underlying unaltered sediment (Gocke et al., 2010). By carefully cleaning the vertical wall to remove all potential superficial modern vegetation which can also have laterally penetrating roots, and by conscientiously investigating the sediment to identify and to avoid rhizolith tracks, contamination risks are greatly reduced. Nevertheless, by precautionary principle, the isotopic signal of soils and paleosols (including Bt horizon) and the

underlying 1 m of sediment should be regarded only as support of climatic trends, not climatic quantitative information. Conversely, typical glacial loess is a suitable sediment for organic geochemistry studies. It accumulates very quickly during the cold oxygen isotope stage (OIS) and is associated with sparse vegetation and a weak rhizosphere. The presence of centimeter-thick laminated structures recognized in most of the typical loess (Derbyshire and Mellors, 1988; Lautridou, 1985; Schwan, 1986) implies the absence of significant vertical disturbance and a good preservation of the memory of the climatic conditions contemporaneous to the time of deposition.

The lack of conditions favorable to pedogenesis and the dry periglacial environment favor the degradation of organic matter without distortion of the isotopic signal, making typical loess suitable for organic geochemical study (Hatté et al., 1998). Indeed, as corroborated by the very low loess organic content, microbial degradation of the weak and low energetic vegetal input in typical loess during glacial times results in a near-total mineralization of organic matter. This near-complete degradation does not induce isotopic fractionation and the original isotopic signal is preserved. In contrast, flourishing vegetation associated with soils and paleosols provide a large amount of organic matter with a wide range of energetic value. In such an environment, microbes select compounds of high energetic value at the expense of less easily degradable compounds. This results in a selective degradation of organic matter compounds that might bring in isotopic fractionation. In conclusion, the carbon isotopic composition ( $\delta^{13}\text{C}$ ) of organic matter preserved in typical loess sediments nicely reflects the original isotopic signature of the vegetation and, therefore, represents an indicator of paleoenvironmental conditions.

The isotopic signature of vegetation provides information on photosynthetic pathways ( $\text{C}_3$  versus  $\text{C}_4$ ) (Farquhar et al., 1982; O'Leary, 1981) and, thus, on environmental changes that are a prelude to the replacement of one vegetation type by another. Based on physiological studies on plants and on the  $\text{C}_4$  versus  $\text{C}_3$  distribution, a replacement of  $\text{C}_3$  by  $\text{C}_4$  plants occurs when the  $\text{C}_3$  plants can no longer develop because of severe environmental changes, such as changes in altitude, temperature, precipitation and wind along with their seasonal patterns. Ecological niche succession follows the rule of "choice of the stronger". If potential niches of  $\text{C}_4$  and  $\text{C}_3$  plants overlap, the  $\text{C}_3$  plants will prevail. Austin (1985) stated that the ecological niche of  $\text{C}_4$  plants is the potential niche minus the  $\text{C}_3$  overlapping niche.  $\text{C}_4$  plants will expand when  $\text{C}_3$  plants disappear.  $\text{C}_3$  plants need available water for at least 2–3 months, according to the species, to complete a growth cycle. In contrast, most  $\text{C}_4$  plants can complete a growth cycle in less than 2 months with available water (Paruelo and Lauenroth, 1996).

Working at the bulk (plant) scale justifies the use of empirical relationships linking environmental conditions to plant isotopic signatures (concentration and isotopic composition

of atmospheric CO<sub>2</sub>, water availability and, secondarily, temperature, soil type and texture and insolation) previously established at this scale (Lloyd and Farquhar, 1994) and not yet available at the molecular scale.

This study presents new geochemical data obtained from the Surduk loess sequence in Serbia and proposes a new environmental scheme to better understand the past environmental conditions in the south of the Carpathian Basin during the last glacial cycle.

## 2 Location, sampling and methodology

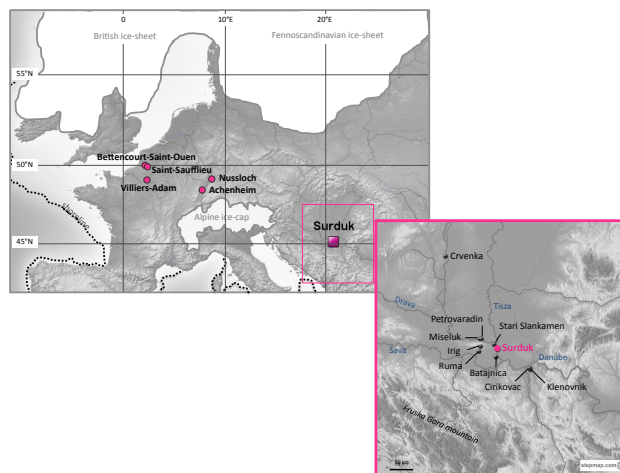
### 2.1 Location

The Surduk loess section is located on the right bank of the Danube River (45°04' N; 20°20' E, ~111 m a.s.l.) in the southeastern part of the Carpathian Basin ca. 30 km northwest of Belgrade, Serbia (Fig. 1), at the southern edge of the European loess belt.

The area is characterized by the occurrence of thick loess–paleosol sequences that mainly outcrop in quarries but also as high loess cliffs along the left bank of the Danube River and at the confluence between the Danube and tributaries, including the Tisa River east of the Titel Plateau (Fig. 1). Today, the site is mostly under a Mediterranean climate influence, with winter occurring from November to February. The average annual temperature is 10.9 °C. In January, the average temperature is –1 °C and in July it is 21.6 °C. The annual rainfall is ca. 690 mm, and there are ca. 120 rainy days (Klein Tank et al., 2002). The area does not undergo very strong seasonality with a dry summer season and/or a long and cold winter (Fig. 2). This implies a region covered by plants with a carbon C<sub>3</sub> fixation pathway. Less than 2 % of vascular plants in southeast Europe are C<sub>4</sub> plants (Pyankov et al., 2010).

### 2.2 Sampling

All stratigraphic studies and high-resolution samplings were carried out on a 20-m-high vertical loess cliff over a period of 15 days. Due to stability and security problems, the upper 3 m of the section was sampled in a trench excavated from the top above the vertical profile. The work began with the careful cleaning (removal of weathered material) of the whole section to provide a highly detailed stratigraphical profile (Fig. 3, stratigraphy). This cleaning step is crucial for organic geochemistry to prevent any pollution by organic material, which can be found, according to the sediment texture, as far as 0.5 m below the exposed surfaces. This material can be the product of bacterial activity in the coarser sediment, nets of burrowing insects or the illuviation of organic compounds in topsoil through cracks. Removal from at least 1 m below the vertical wall reduces the contamination risk. Furthermore, measuring the nitrogen content of the sampled sediment checks a posteriori for the absence of modern organic matter. As nitrogen is mostly linked to amino acids

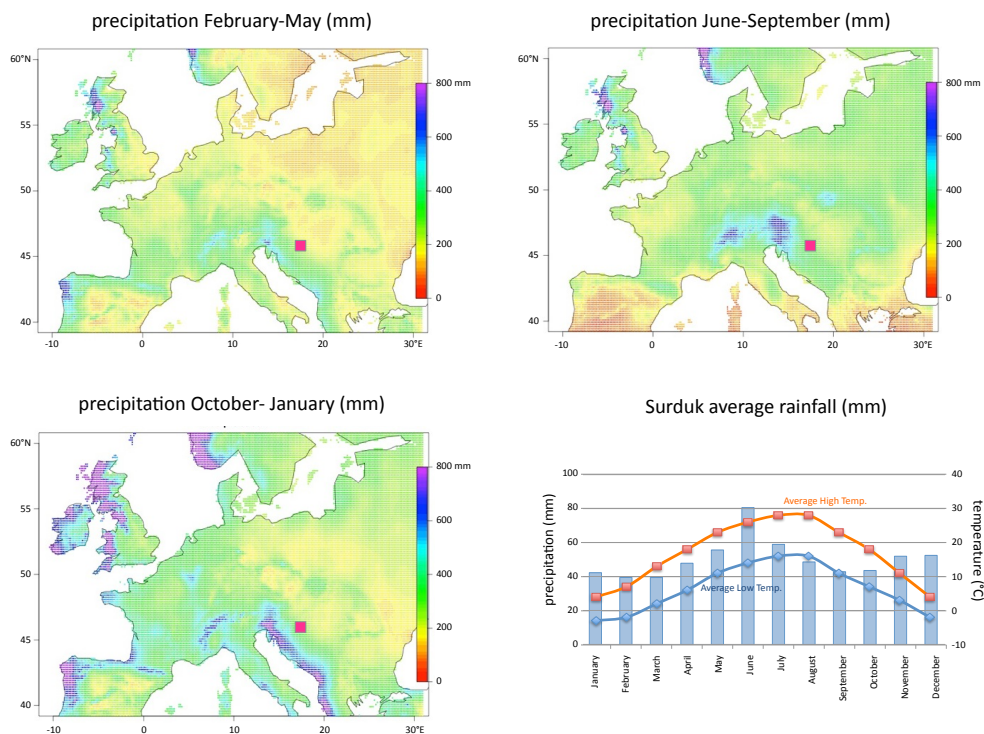


**Fig. 1.** Location of the Surduk loess sequence. Other series relevant to this study and mentioned in text are also shown.

that rapidly decrease with organic matter degradation, a measurable level of nitrogen implies the input of recent organic matter into the sediment.

The sampling methodology used in Surduk for the geochemistry was based on the continuous column sampling (CCS) method developed by the team several years ago when investigating Western European loess sequences. This method consists of cutting a continuous vertical column ( $\pm 5$ –7 cm width) through the whole loess–paleosol sequence, which is then sliced every 5 cm to produce 376 homogeneous samples of sediment. The CCS method allows the geochemistry to be averaged every 5 cm, preventing any gap between the different samples as usually occurs when taking a succession of isolated samples. A single sample was subdivided into four for grain-size, carbon content and  $\delta^{13}\text{C}$  and  $^{14}\text{C}$  determination. This division allows the correlation of independent environmental proxies. More information on the CCS and on the Surduk sampling is available in Antoine et al. (2009a,b).

Sediment sampling is performed while preventing contact with any organic material, which means no hand contact with the sample at any time and no contact with paper or any potential pollutant, including smoking. Samples are preserved in zipper PE plastic Minigrip<sup>®</sup> bags with no VOC emission. We chose to sample a large amount of sediment (approximately 50 g), even though only some 100 mg is necessary for geochemical analysis. This process “dilutes” any potential contamination that would still have subsisted after all the precautions we took. Following this protocol is absolutely necessary for the quality requirement of the investigation of sediment with such a low amount of organic carbon (typically 0.1 % wt) (Gauthier and Hatté, 2008).



**Fig. 2.** Modern annual precipitation distribution in Europe with a focus on Surduk. Upper panels and the lower left panel are for modern cumulative precipitation from February to May (panel upper left), June to September (panel upper right) and October to January (panel lower left). Scale is in mm. Note that the Surduk region (red square) does not undergo dry summer season. Focus on Surduk area (lower right) with the 1946–2006 average precipitation (histogram) and high (orange line) and low (blue line) temperature recorded at Cortanovci (45°09' N, 20°01' E), the closest meteorological station to Surduk.

## 2.3 Geochemistry methodology

The sediment samples were dried at low temperature as soon as possible to ensure safe storage, as recommended by Gauthier and Hatté (2008). After being sieved at 250  $\mu\text{m}$  to remove stones and being homogenized, the sediment then underwent a soft leaching process to remove carbonate using pre-combusted glass beakers, HCl 0.6N at room temperature, ultra-pure water and drying at 50 °C. The samples were then crushed in a pre-combusted glass mortar for homogenization prior to carbon content and  $\delta^{13}\text{C}$  analysis. The handling and chemical procedures are common precautions employed with low-carbon-content sediments.

### 2.3.1 Organic and carbonate content

Two different carbon measurements were performed for every sediment sample: total carbon for the bulk sediments and organic carbon for the leached sediments. Approximately 15 to 20 mg of sediment was weighed in tin cups for measurement (with a precision of 1  $\mu\text{g}$ ). The sample was combusted in a Fisons Instrument NA 1500 Element Analyzer, and the carbon content determined using the Eager software. A standard was inserted every 10 samples. The inorganic carbon content in the bulk sediment was calculated by

assuming that mineral carbon exists only as  $\text{CaCO}_3$ . The results are reported in % weight of carbonate/bulk sediment and in % weight of organic carbon/bulk sediment.

### 2.3.2 Carbon isotopic signature

Analysis was performed online using a continuous flow EA-IRMS coupling, that is, a Fisons Instrument NA 1500 Element Analyzer coupled to a ThermoFinnigan Delta+XP Isotope-Ratio Mass Spectrometer. Two in-house standards (oxalic acid,  $\delta^{13}\text{C} = -19.3\%$  and GCL,  $\delta^{13}\text{C} = -26.7\%$ ) were inserted every five samples. Each in-house standard was regularly checked against international standards. The results are reported in the  $d$  notation:

$$\delta^{13}\text{C} = (R_{\text{sample}}/R_{\text{standard}} - 1) \cdot 1000,$$

where  $R_{\text{sample}}$  and  $R_{\text{standard}}$  are the  $^{13}\text{C}/^{12}\text{C}$  ratios of the sample and the international standard, Vienna Pee Dee Bee (VPDB), respectively. The measurements were at least triplicated for representativeness. The external reproducibility of the analysis was better than 0.1 %, typically 0.06 %. Extreme values were checked twice.

## 2.4 Geochronology methodology

### 2.4.1 IRSL dating

Ten samples were taken for infrared stimulated luminescence dating (IRSL) using copper cylinders ( $\pm 4$  cm diameter), which were hammered into the loess section to avoid any contamination by light-exposed material. Additional material was taken from the 30 cm surrounding every IRSL sample for dose rate determination. The sample preparation of the polymineral fine grain fraction (4–11  $\mu\text{m}$ ), the luminescence measurements and the dose rate determination are explained in detail in Fuchs et al. (2008).

### 2.4.2 $^{14}\text{C}$ dating

Based on the  $\delta^{13}\text{C}$  results, 15 samples were selected for  $^{14}\text{C}$  dating. The  $^{14}\text{C}$  activity evaluation was performed using AMS physical measurements taken at the Australian ANSTO (ANUA numbers), the NSF-Arizona AMS Lab (AA numbers) and the French LMC14 (SacA numbers) facilities. The  $\text{CO}_2$  gas was prepared using three different protocols chosen according to the type of sediment. The protocol from Hatté et al. (2001c) (HCl 0.6 N,  $\text{Na}_4\text{P}_2\text{O}_7$  0.1 M and HCl 1 N at room temperature) was applied for typical loess sediment, whereas either protocol from Hatté et al. (2001b) (HCl 0.6 N,  $\text{Na}_4\text{P}_2\text{O}_7$  0.1 M,  $\text{K}_2\text{Cr}_4\text{O}_7$  0.1 M/ $\text{H}_2\text{SO}_4$  2 N at room temperature) was applied to sediment extracted from gleys under  $\text{N}_2$  flow to avoid possible incorporation of modern  $\text{CO}_2$  during alkali treatment by adsorption on  $\text{Fe}^{2+}$ .

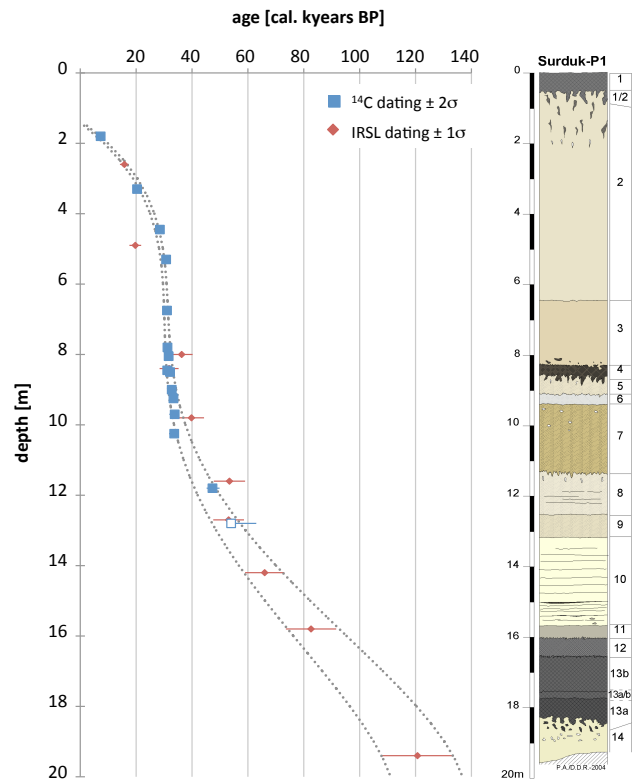
All  $^{14}\text{C}$  measurements were converted to calendar ages using Calib 6.0, which includes the IntCal09 calibration (Reimer et al., 2009).

## 3 Results

### 3.1 Geochronology

All geochronological data are reported in Tables 1 and 2 and are shown with their stratigraphic position in Fig. 3. Within errors, the  $^{14}\text{C}$  and IRSL dates are in good agreement. Some classical discrepancies remain only because  $^{14}\text{C}$  and luminescence dating do not characterize the same event.  $^{14}\text{C}$  dating estimates the time elapsed since the death of the plant that trapped the dust, while luminescence estimates the time elapsed since the grains to be dated were without the influence of sunlight. Both chronologies cannot be directly compared, especially for recent times during which external parameters that are at the origin of the discrepancy may be larger than the uncertainties of the physical measurement (Fuchs et al., 2008).

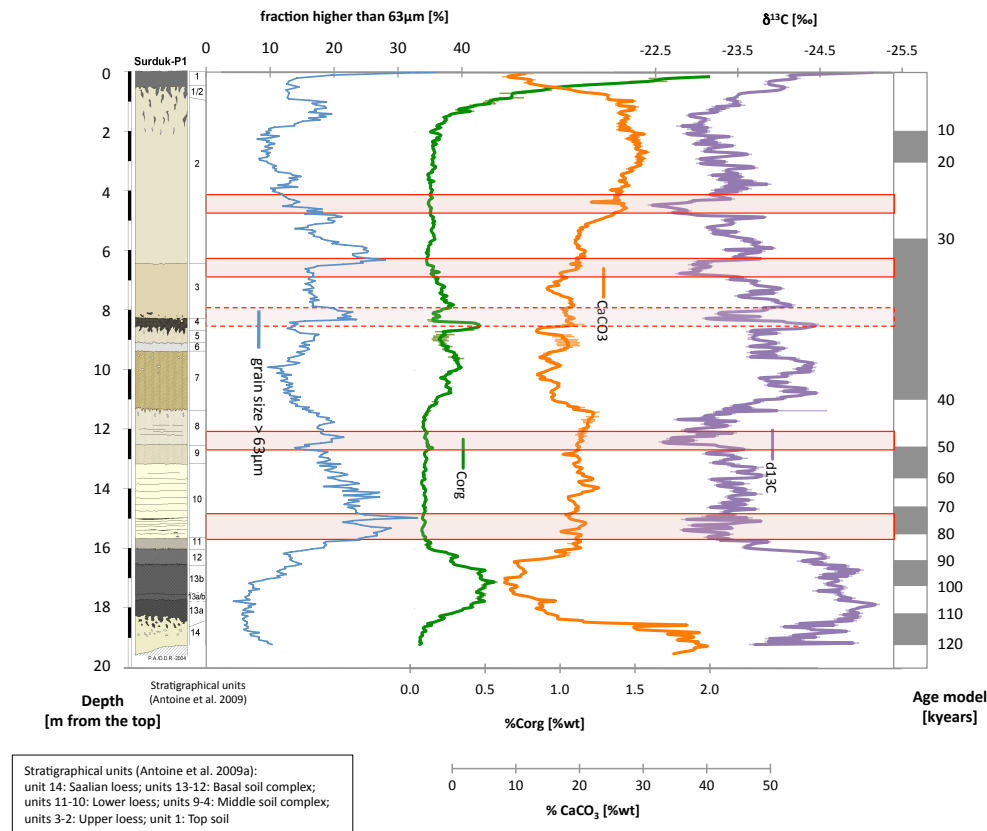
The largest discrepancy between organic radiocarbon and mineral luminescence chronologies occurs between a 400 and 600 cm depth (Fig. 3), where the organic chronology has a relatively uniform sedimentation rate. The mineral IRSL



**Fig. 3.** Stratigraphy and age model of the Surduk loess sequence. Red diamonds are for IRSL dating; the error margin encompasses the 1 sigma variation range (Fuchs et al., 2008). Blue squares represent Calib 6.0 calibrated  $^{14}\text{C}$  dating (Reimer et al., 2009); the error margin encompasses the 2 sigma variation range. The open symbol represents the  $> 53\,000$   $^{14}\text{C}$  conv. year, for which we only have a minimum age. The dotted lines represent an age model envelope that should very likely encompass the chronology of the loess organic accumulation. Major stratigraphic units are 14: Saalian loess; 13–12: basal soil complex; 11–10: lower loess; 9–4: middle soil complex; 3–2: upper loess; and 1: top soil (Antoine et al., 2009a).

would indicate a rupture in the sedimentation at the onset of the major loess accumulation. This discrepancy may be the result of the intrinsic nature of both chronologies: vegetation at the origin of the organic matter used for the analysis of the C chronology was present all along this interval, whereas mineral accumulation occurred by pulses (Sima et al., 2009). The organic chronology is thus smoother than the mineral chronology. Nevertheless, the shift is approximately 9 kyr, and smoothing cannot be the only explanation. Another explanation could be an IRSL underestimate of sample BT141 for reasons so far unknown.

Although the intent of the chronological framework is to place organic geochemical signal in time, we favored the  $^{14}\text{C}$  dating to draw an outline that should encompass the most likely chronological organic framework of the sequence (Fig. 3).



**Fig. 4.** Geochemical data of the Surduk loess sequence. The stratigraphical description is from Antoine et al. (2009a). Blue, green, orange and violet curves represent grain sizes greater than  $63\mu\text{m}$  in %, organic carbon content in % wt, carbonate content in % wt and  $\delta^{13}\text{C}$  of loess organic matter in ‰ vs. PDB, respectively. All data are presented versus depth. On the right axis, a non-linear timescale is presented based on IRSL and  $^{14}\text{C}$  dates. Horizontal bars highlight  $\text{C}_4$  episodes. Major stratigraphic units are 14: Saalian loess; 13–12: basal soil complex; 11–10: lower loess; 9–4: middle soil complex; 3–2: upper loess; and 1: top soil (Antoine et al., 2009a).

We thus face a very high accumulation during the Middle Pleniglacial with 600 cm (from 1050 to 450 cm depth) as an imprint of 10 kyr (between 37 and 27 kyr) corresponding to an average sedimentation rate of  $1.7\text{ mm yr}^{-1}$ . This pattern appears to be unusual, as the highest sedimentation rates are generally observed in European loess during the Upper Pleniglacial ( $\pm\text{OIS } 2$ ) and upper Middle Pleniglacial (OIS 3) (Fuchs et al., 2008).

### 3.2 Geochemistry

All geochemical data are presented in Fig. 4. The organic carbon and carbonate contents are both within the classical ranges observed throughout European loess sequences. These contents respectively vary between 0.2 % wt and 20 % wt, with approximately 4 % wt of organic carbon maximum for modern soil associated with the lowest carbonate content of approximately 8 % wt. The lowest organic content (0.06 % wt) corresponds to the highest carbonate content (40 % wt) during the offset of the penultimate glacial period.

Typical values of the last glacial periods are 0.15 % wt and 20 % wt, respectively.

The  $\delta^{13}\text{C}$  signature in Surduk varies from  $-25.1\text{‰}$  for the roots of the modern soil to  $-22.4\text{‰}$  at a 445 cm depth. Such a scheme is outside the current pattern measured in Western Europe, where isotopic values are always lighter than  $-23.5\text{‰}$ . The heaviest  $\delta^{13}\text{C}$  record during the last glacial time in the Nussloch (Upper Rhine Valley, Germany), Villiers-Adam (Ile-de-France, France), Bettencourt-Saint-Ouen and Saint-Saufflieu (Picardy, France) loess sequences are  $-23.5\text{‰}$ ,  $-23.9\text{‰}$ ,  $-24.1\text{‰}$  and  $-24.1\text{‰}$ , respectively (Hatté, 2000; Hatté et al., 1998).

The isotopic organic record of the Achenheim sequence (Alsace, France) is not considered here, as it was perturbed by both periglacial features and inadequate sample preservation; its highest recorded value was  $-23.1\text{‰}$  (outside the periglacial perturbation) (Hatté et al., 1998). Likewise, we do not consider the  $-16.9\text{‰}$  values obtained by Pustovoytov and Terhorst (2004) in Schattenhausen near Nussloch in some tundra gley horizons, which inexplicably have the lightest  $\delta^{13}\text{C}$  in typical loess.

**Table 1.** Chronological data of the Surduk loess sequence: IRSL age determinations (Fuchs et al., 2008). The first two columns are for sample identification; columns 3 to 5 are for U, Th and K contents; columns 6 and 7 are for effective dose rate (DL) and equivalent dose rate (De); and last columns are for IRSL estimated age ( $\pm 1$  sigma). Further information in Fuchs et al. (2008).

Depth [m]	Sample #	U	Th	K	DL	De	IRSL age	
		[ppm]	[ppm]	[%]	[Gy ka <sup>-1</sup> ]	[Gy]	[yr]	[ $\pm 1\sigma$ ]
2.6	BT 140	3.0 $\pm$ 0.1	9.8 $\pm$ 0.5	1.4	3.2 $\pm$ 0.3	50.4 $\pm$ 2.4	15 800	1600
4.9	BT 141	3.4 $\pm$ 0.1	10.8 $\pm$ 0.5	1.4	4.0 $\pm$ 0.4	77.8 $\pm$ 3.7	19 700	2100
8	BT 142	3.5 $\pm$ 0.1	11.8 $\pm$ 0.5	1.6	4.0 $\pm$ 0.4	145.2 $\pm$ 6.2	36 300	3900
8.4	BT 143	3.5 $\pm$ 0.1	12.5 $\pm$ 0.5	1.6	3.7 $\pm$ 0.4	117.5 $\pm$ 6.1	31 800	3400
9.8	BT 144	3.7 $\pm$ 0.1	12.3 $\pm$ 0.6	1.6	4.1 $\pm$ 0.4	161.6 $\pm$ 9.1	39 800	4500
11.6	BT 145	3.2 $\pm$ 0.1	11.1 $\pm$ 0.4	1.6	3.6 $\pm$ 0.4	190.6 $\pm$ 8.1	53 400	5600
12.7	BT 146	3.1 $\pm$ 0.1	11.1 $\pm$ 0.5	1.6	3.6 $\pm$ 0.4	188.8 $\pm$ 7.7	53 100	5500
14.2	BT 147	3.4 $\pm$ 0.1	11.6 $\pm$ 0.5	1.7	3.8 $\pm$ 0.4	247.9 $\pm$ 10.6	66 000	7000
15.8	BT 148	3.5 $\pm$ 0.1	12.2 $\pm$ 0.5	1.7	3.9 $\pm$ 0.4	321.5 $\pm$ 16.1	82 600	9000
19.4	BT 149	3.0 $\pm$ 0.1	10.5 $\pm$ 0.6	1.4	3.2 $\pm$ 0.3	391.9 $\pm$ 16.4	120 700	12 800

**Table 2.** Chronological data of the Surduk loess sequence: <sup>14</sup>C dating. The specificity of the chemical treatment prior to CO<sub>2</sub> evolution and the <sup>14</sup>C activity measurement is provided in a reference column. The <sup>14</sup>C results are shown as conventional <sup>14</sup>C and calibrated <sup>14</sup>C ages based on the Calib 6.0 calibration (Reimer et al., 2009), for which minimum, maximum and median ages are given.

Depth [m]	Chemistry #	Physical measurement #	Chemical treatment ref.	<sup>14</sup> C conventional age		Calibrated age $\pm 2\sigma$ [3]		
				age [yr]	$\pm 1\sigma$ [yr]	min [yr]	max [yr]	median [yr]
1.8	GifA-050011	ANUA-31418	[1]	6.400	190	6.855	7.620	7.295
3.3	GifA-070129	AA-78959	[2]	17.135	85	20.060	20.555	20.335
4.45	GifA-070128	AA-78958	[2]	23.740	145	28.005	29.025	28.490
5.3	GifA-050013	ANUA-31419	[1]	26.000	330	30.235	31.195	30.735
6.75	GifA-050014	ANUA-31420	[1]	26.500	370	30.455	31.445	31.040
7.8	GifA-080225	SacA-13476	[3]	26.775	530	30.320	32.195	31.210
8.05	GifA-070127	AA-78957	[2]	27.550	175	31.300	32.175	31.635
8.45	GifA-050015	ANUA-31421	[1]	26.640	340	30.605	31.520	31.135
8.5	GifA-050016	ANUA-31423	[3]	27.870	440	31.310	33.180	32.145
9	GifA-080224	SacA-13475	[3]	28.360	645	31.460	34.245	32.740
9.25	GifA-070126	AA-78956	[2]	28.950	180	33.020	34.460	33.355
9.7	GifA-080223	SacA-13474	[3]	29.335	725	31.875	35.125	33.800
10.25	GifA-080222	SacA-13473	[3]	29.145	710	31.805	34.935	33.630
11.8	GifA-070123	AA-78953	[2]	44.025	1.350	45.230	49.850	47.320
12.8	GifA-070124	AA-78954	[2]	> 53 000				

[1]: AAA under air; [2]: AAA under N<sub>2</sub>; [3]: Calib 6.0; [3]: ABOx (see text for AAA and ABOx definitions).

The Surduk  $\delta^{13}\text{C}$  record differs from the other European loess geochemical records not only by the heaviest isotopic episode reaching  $-22.4\text{‰}$  at a 445 cm depth (ca. 28.0–26.0 kyr cal BP) but also by three other episodes of heavy  $\delta^{13}\text{C}$  values recorded at 675 cm ( $-22.8\text{‰}$ , ca. 31.4–30.0 kyr cal BP), 1240 cm ( $-22.6\text{‰}$ , ca. 53.4–44.5 kyr cal BP) and a plateau between 1535 and 1500 cm at  $-22.85\text{‰}$  (ca. 86.8–66.1 kyr BP).

Carbon isotope fractionation by C<sub>3</sub> plants depends on the atmospheric CO<sub>2</sub> concentration and isotopic composition and on the humidity level (Farquhar et al., 1989; O'Leary, 1981). As a consequence the current  $\delta^{13}\text{C}$  range for all

modern C<sub>3</sub> plants of  $[-31; -24\text{‰}]$  (Deines, 1980) might have been shifted towards less negative values during glacial arid periods. Based on a mechanistic vegetation model that simulates carbon isotopic fractionation of vegetal biome, Hatté et al. (2009) showed that isotopic niches of dwarf shrub tundra and shrub tundra, the expected biomes during glacial times, shifted from  $[-32; -28\text{‰}]$  under present conditions to  $[-31; -26.5\text{‰}]$  under glacial times (assuming 220 ppm of CO<sub>2</sub>). Thus, if values lighter than approximately  $-23.5\text{‰}$  were interpreted as exclusively resulting from the degradation of C<sub>3</sub> plants (Hatté et al., 2001a), those of  $-22.4\text{‰}$  to  $-22.85\text{‰}$  likely derive from the degradation of combined



C<sub>4</sub> and C<sub>3</sub> plants. Furthermore, C<sub>4</sub>-derived organic carbon decomposes faster than its C<sub>3</sub> counterpart in mixed C<sub>3</sub>/C<sub>4</sub> environments (Wynn and Bird, 2007), leading to a shift towards more negative values of the sediment organic  $\delta^{13}\text{C}$  by comparison with the plant mixture  $\delta^{13}\text{C}$ . This might be of importance in typical loess environment where mineral accumulation rates are high. Therefore, the presence of C<sub>4</sub> plants can also be invoked for the events recorded at 825 cm ( $-23.1\text{‰}$ ) and at 1200 cm ( $-22.9\text{‰}$ ) that occurred during the 32.9–30.7 cal kyr and 50.4–42.0 cal kyr intervals, respectively.

A C<sub>4</sub>/C<sub>3</sub> plant mixture does not imply that both plants cohabited. Plants with both photosynthetic pathways can have occurred successively during the period represented by the sampling interval, i.e., over ca. 250 yr (in the case of the  $-22.4\text{‰}$  value). As the paleoprecipitation reconstruction by inverse modeling of BIOME4 was only validated for C<sub>3</sub> plants (Hatté and Guiot, 2005), no quantitative paleoprecipitation can be estimated from the  $\delta^{13}\text{C}$  signal.

## 4 Discussion

### 4.1 General last climatic cycle trend

The geochemical records clearly match the classical pattern of the last climatic cycle, with a higher organic carbon content and the lowest  $\delta^{13}\text{C}$  during the equivalent to OISs 5, 3 and 1. The carbonate content follows the same pattern, with a lower carbonate content for warmer episodes (OISs 5, 3 and 1) as the result of carbonate leaching during pedogenesis.

According to both the organic chronology and the  $\delta^{13}\text{C}$  record, Surduk's last interglacial and early glacial periods cover more than 2 m, from a depth of ca. 1850 to 1600 cm (Fig. 3, units 14 to 12). The Upper Pleniglacial covers the upper part of the sequence from 825 cm to the upper top, the uppermost meter being crossed by a few deep root tracks down to 200 cm from the Holocene humic topsoil horizon (Fig. 3, units 3 to 1). The boundary between the Lower and Middle Pleniglacial is more difficult to establish. Fuchs et al. (2008) and Antoine et al. (2009a) placed the limit at approximately 1300 cm (Fig. 3, boundary between units 10 and 9), whereas the organic record would push the climatic pe-  
joration, the equivalent of OIS 4 (boundary between units 8 and 7), to 1150 cm at the offset of the heaviest  $\delta^{13}\text{C}$  values.

Aside from the isotopic excursions toward heavy values, the Surduk loess sequence remains roughly within the same  $\delta^{13}\text{C}$  range as other European loess sequences. This result implies drastic climatic conditions along the last glacial cycle that favored C<sub>3</sub> plants for most of the time. The expected level of precipitation should likely be approximately 200–300 mm yr<sup>-1</sup> with respect to other loess sequences, and the C<sub>3</sub> predominance leads to free meteoritic water distributed along the warm season for most of the last glacial period. The field observation did not provide evidence of a direct effect

of precipitation on the loess deposits through any drainage characteristics. We must consider that vegetation captured all the precipitation.

### 4.2 Excursions toward C<sub>4</sub> plants and climatic significance

Occurrences of C<sub>4</sub> plants are recorded at 26.0–28.0 kyr cal BP, 30.0–31.4 kyr cal BP, 44.5–53.4 kyr cal BP, and 66.1–86.8 kyr. Based on physiological studies and on niche theory (Austin, 1985), C<sub>4</sub> plants expand when C<sub>3</sub> plants disappear. Pyankov et al. (2010) explicitly described the C<sub>4</sub> taxonomic distribution in Europe and its relation to climatic parameters. They summarized their discussion by stating that “the abundance of total C<sub>4</sub> dicotyledons including C<sub>4</sub> *Chenopodiaceae* is correlated with precipitation and aridity but not temperature, whereas the abundance of total C<sub>4</sub> monocotyledons, C<sub>4</sub> *Poaceae* and C<sub>4</sub> *Cyperaceae* is correlated with temperature and aridity but not precipitation.” Today C<sub>4</sub> dicotyledons and C<sub>4</sub> *Chenopodiaceae* represent about 65–75 % of the C<sub>4</sub> plants in the southeastern and Central Europe, i.e., in the present Surduk geographical region and in the likely modern analog region of past Surduk vegetation. This allows us to consider that C<sub>4</sub> dicotyledons and C<sub>4</sub> *Chenopodiaceae* were likely the most abundant C<sub>4</sub> plants and that their emergence was linked to water availability. C<sub>4</sub> plants expand when there are less than 2 months of available water to allow C<sub>3</sub> plants to achieve a complete growing cycle. Available water means “free” liquid water. Snow and frozen water are not available for plant uptake. The occurrence of C<sub>4</sub> plants during at least 4 episodes during the last glacial in Surduk led to the persistence of climatic conditions that were unfavorable to C<sub>3</sub> development.

Three potential scenarios can be proposed to describe the climatic conditions relative to the heavy  $\delta^{13}\text{C}$  episodes: (i) a short and dry summer with less than 2 months of free meteoritic water during the plant growth cycle; (ii) a snowy summer that does not bring free water that would have been directly assimilated by plants; (iii) temperatures less than 0 °C for 8–9 months a year, which would make the permafrost thaw too late and the soil too hard to allow C<sub>3</sub> plant roots to penetrate; or a combination of (iii) with (i) or (ii). In any case, the Surduk results provide evidence of a very strong climatic seasonality that has never been recorded in Western Europe.

Based on the climate reconstructions that derive from European palynological record covering the Last Glacial Maximum, temperatures less than 0 °C for 8–9 months are very unlikely, even for anterior periods. Indeed, the summer temperature, even during this extreme time, is 6 to 10 °C less than the pre-industrial period (Jost et al., 2005; Leng et al., 2012; Lézine et al., 2010; Peyron et al., 1998). With a reference summer temperature of ca. 20 °C (modern summer value), the LGM summer temperature should have been 10 to 14 °C. However, these reconstruction methods were based on assumptions which are not all valid. First, any past

pollen assemblage is assumed to be well approximated by the modern analog, but glacial assemblages lack good modern analogues. As an example, modern analogues for glacial steppe are missing as they are found today in Central Asia under milder winter and warmer summer. Second, plant–climate interactions are assumed to remain constant throughout time. Implicitly this assumes that these interactions are independent of changes in atmospheric CO<sub>2</sub> and daylight, whereas a number of physiological and paleoecological studies (Cowling and Sykes, 1999; Farquhar, 1997; Polley et al., 1993) have shown that plant–climate interactions are sensitive to atmospheric CO<sub>2</sub> concentration and sun exposure. Even considering these restrictions, it is very unlikely that summer temperatures differed by more than 10 °C with these reconstructions. Considering a sinusoidal temperature pattern along the year with the highest temperatures in summer and the coldest in winter, and even considering a very strong seasonality that would have been represented by a sharp sinusoid, pollen reconstructed summer temperature cannot be associated with more than 4–6 months of below 0 °C temperatures. Furthermore, according to Hatté et al. (2009), and ecological niche under low CO<sub>2</sub> concentration at equivalent latitude for biomes expected for glacial periods yields mean annual temperatures lowered by 10–15 °C with respect to the reference point set at 9.5 °C, i.e., mean annual temperatures of –5 to 0 °C. Such a range cannot be associated with more than 6 months of temperature lower than 0 °C. The third hypothesis can thus be ruled out.

Repetitive snowy summers would have been recorded by a specific sedimentological feature (niveo-aeolian laminations), but the feature was not observed here (Antoine et al., 2009a). The second hypothesis can thus be ruled out as well.

The remaining hypothesis suggests dry (and short) summers for times associated with heavy  $\delta^{13}\text{C}$ , which is consistent with malacological studies. To the north (Mišeluk, Marković et al., 2004; and Petrovaradin, Marković et al., 2005) and south (Ruma, Marković et al., 2006; and Irig, Marković et al., 2007) of Fruška Gora mountain, i.e., 30–50 km west of Surduk, the hygrophilous *Succinella oblonga*, which is ubiquitous in the loess north of the Alps under the form “elongata”, was not identified contrary to very abundant steppe taxa, such as *Granaria frumentum*, *Pupilla triplicata*, *Chondrula tridens* and *Helicopsis striata*. These taxa are rarely found in Western European loess series (Moine et al., 2005, 2008, 2011; Rousseau et al., 1990) and are more or less frequent in Central Europe north of the Alps (Frank, 2006; Ložek, 1964), in the Pannonian Basin (Sümegei, 2005), though they are not as common as in the Balkans. In Čirikovac and Klenovnik, about 80 km southeast of Surduk, on the western flank of a north–south elongated relief, similar general observations have been recorded with some differences. *S. oblonga* is poorly represented in Čirikovac, and among steppe taxa only *C. tridens* and *G. frumentum* are abundant, *P. triplicata* and *H. striata* being absent (Mitrović, 2007). However, we must keep in mind that only a single

taxa has been sampled in these last two sites. Other identified species suggest a resemblance with more humid and woody steppe vegetation from Ruma and Irig north of the Fruška Gora mountain. Furthermore, fauna from Požarevac brickyard, a few kilometers north of Čirikovac, indicates an even drier environment than in Irig, for example (Jovanović, 2005; Jovanović et al., 2006).

*n*-Alkane investigations performed for the Crvenka loess–paleosol (North Serbia) sequence show that grasses dominated the vegetation cover during the whole last glacial cycle (Zech et al., 2009). However, Zech et al. (2009) underlined several periods with a presence of trees based on corrected *n*-alkane distribution. The applied correction derives from modern observations of *n*-alkane distribution in vegetation and in the associated litter and topsoil, where they evidenced a modification of the original vegetation *n*-alkane distribution in litter consecutively to degradation that conceals the tree percentage in the original vegetation ratio. The middle paleosol complex likely has undergone a similar degradation effect, but the corrected ratio of trees in typical loess may be overestimated as vegetal organic matter degradation was quite different during glacial times. It is conceivable that as a result of the very drastic conditions and of the weak vegetal input, the original *n*-alkane distribution was better preserved in typical loess than in middle paleosol (high odd-over-even predominance stated by authors in typical loess, i.e., L1Lx units) and thus loess *n*-alkane distribution does not require high correction. This said, the possible occurrence of some trees in protected areas during the C<sub>3</sub> plant interval remains. Few dwarf trees in open grassland, as currently found today in Greenland, may have grown in Surduk area throughout these periods.

Combining the specifications of malacological, organic geochemical and isotopic geochemical investigations yields strong vegetation dynamics during the Middle and Late Pleniglacial, with C<sub>4</sub> episodes highlighted by isotopic geochemistry and short excursions toward mosaic or even forest vegetation elements during C<sub>3</sub> plant periods, as indicated by the subdomination of forest taxa at Petrovaradin during the Late Pleniglacial (Marković et al., 2005) and a few trees (likely dwarf) during glacial periods, as indicated by peaks toward high C<sub>31</sub>/C<sub>27</sub> *n*-alkane ratios at Crvenka (Zech et al., 2009). Isotopic signatures alone that remain within the range of C<sub>3</sub> plants cannot evidence these excursions toward close vegetation. However, the occurrence of periods with C<sub>3</sub> plants interspersed with C<sub>4</sub> episodes is also suggested by palynological investigations that show arboreal vegetation (with likely dwarf trees) at some times of the last glaciation in Romania (~ 300 km north of Surduk) (Willis et al., 2000; Willis and van Andel, 2004).

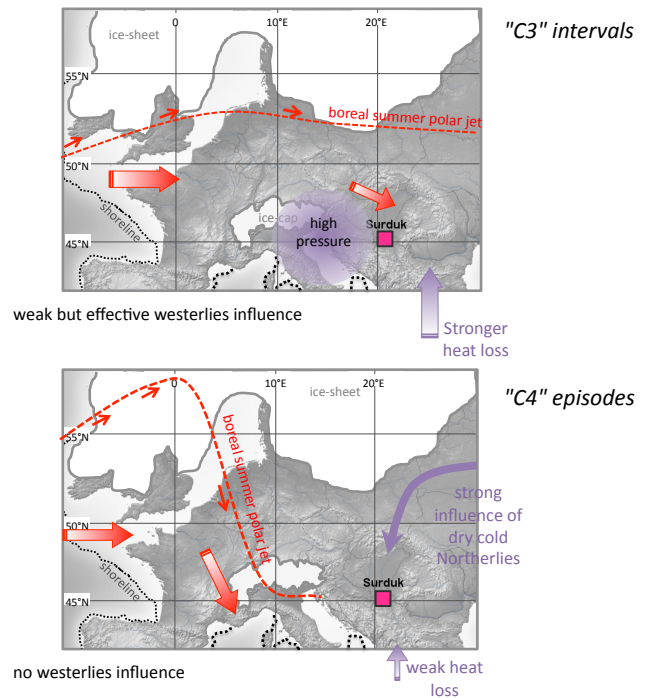
### 4.3 Possible climatic pattern to explain C<sub>4</sub> episodes

The Balkan climate is under the combined influence of the Atlantic Ocean and the Mediterranean Sea, as both contribute

to regional precipitation. An explanation of the summer precipitation ( $C_4$  plants growing season) decline over this part of the eastern Mediterranean Basin can be found in both modern meteorological patterns and past climate studies.

Such an example is related to the Heinrich events (HE). Sierro et al. (2005) showed that HE interrupted the antiphase relationship in deepwater formation between the North Atlantic and Mediterranean because of a large injection of fresh water from melting icebergs at the entrance to the Mediterranean. Lower salinities of Mediterranean surface water resulted in a slowdown of western Mediterranean deepwater overturn, even though cold sea surface temperatures (SSTs) and a drier climate should have resulted in enhanced deepwater. A similar but less pronounced pattern of cold SSTs was revealed in the eastern Mediterranean, where catastrophic arid episodes were connected with Heinrich events as a result of cold water input in the eastern Mediterranean Basin, which reduced evaporation and precipitation on the continent (Bar-tov et al., 2003). The contrast between the strongly reduced SSTs in the western basin and the much less reduced SSTs in the eastern Mediterranean Basin was enhanced during the Heinrich events and favored strong meridional circulation. In the Carpathians, this regime resulted in *less precipitation from the Mediterranean Sea*. The precipitation was even lower for periods that lagged behind the HE or during equivalent Mediterranean meridional circulation-favoring situations.

Another example related to the Last Glacial Maximum (LGM) can be found based on Alpine evidence and SST reconstructions. Several studies (Florineth and Schlüchter, 2000; Kühlemann et al., 2008, 2009) show that the LGM Mediterranean atmospheric pattern consisted of an amplified meridional winter circulation. This pattern would result in a northward extension of the Azores High toward Iceland or Greenland, blocking the moisture supply by the westerlies. The situation was further enhanced by expansion and intensification of the Siberian High in winter and spring during glacial times. The most common glacial situation on the Balkans was thus a replacement of the wet westerlies by this blocking situation that was more frequent than that of today. The northward displacement of the polar jet in summer allowed westerlies over Western Europe but less and less precipitation from west to east. This situation resulted in *lower precipitation brought by westerlies* over the Carpathians and even lower precipitation for periods under the influence of an intense Siberian High. As cold Pleistocene winds move closer to the ground, they are, consequently, more influenced by the topography than during warm periods. The Carpathians can thus deflect original weak westerlies towards the N/NW direction (Sebe et al., 2011). This is in agreement with previous investigations performed in the same area. Based on a mineral geochemistry investigation on the Stari Slankamen loess sequence (Fig. 1), Buggle et al. (2008) show that loess originated from alluvial sediments of the Danube and of weathered products of the Carpathian mountain drained by



**Fig. 5.** Atmospheric pattern explaining  $C_3$  and  $C_4$  episodes. Upper panel: atmospheric pattern effective during  $C_3$  episodes; Surduk is under a weak but effective influence of westerlies, allowing the more than 2–3 months of available water required for the  $C_3$  growth cycle. Lower panel: atmospheric pattern that prevailed during the  $C_4$  episodes; Surduk is under the strong influence of dry and cold northerlies, leading to less than 3 months of available water. Red arrows are from Kühlemann et al. (2009) and violet arrows are from Krichak and Alpert (2005) and Josey et al. (2011).

the Tisza and the Drava rivers. They therefore favored a meteorological pattern with strong influence of N/NW winds. This scenario is in agreement with the enhancement in the frequency of storms from the N/NW, as suggested by Antoine et al. (2009b) based on a sedimentological study, and corroborates the possible predominant dust deposition direction proposed by Marković et al. (2008) for the Surduk area based on a loess thickness investigation. It also fits with the 850 hPa winds reconstructed by Rousseau et al. (2011) and Sima et al. (2013).

An explanation for the occurrence of Surduk “ $C_4$  episodes” can be proposed by looking at modern meteorological patterns and, more closely, at the patterns that are rarely recorded today but could have occurred during glacial times.

The Mediterranean climate is associated with oscillations in sea level pressure, the well-known North Atlantic Oscillation (NAO), which mostly impacts the western part of the Mediterranean Basin, and the East Atlantic/West Russia mode (EA/WR) that plays a key role in the eastern Mediterranean precipitation. The EA/WR is based on two main anomaly centers that today are located over the Caspian Sea and Western Europe. This mode occurs today from fall

to springtime. During the high EA/WR periods, northerly winds predominate over the eastern Mediterranean region. The positive phase of the pattern is characterized by negative-pressure anomalies throughout western and southwestern Russia and positive-pressure anomalies over northwestern Europe. During the EA/WR positive phases, drier than normal conditions are found today in a large eastern region of the Mediterranean Basin (Josey et al., 2011; Krichak and Alpert, 2005). A study by Krichak and Alpert (2005) clearly showed dry and cold northerlies over the Balkans during a high phase (positive EA/WR), leading to dry conditions. Transposed to glacial conditions with the Fennoscandian ice sheet covering the north of Europe, such a circulation pattern would bring very cold and dry air masses over the Balkans. A high positive EA/WR mode would have resulted in *very cold and very dry summer conditions in the Balkans*.

In the present-day climate, a high positive EA/WR mode can persist for several consecutive months, as happened from the winter of 1992/1993 until May 1993. If, during particular intervals of the glacial period, this mode extended throughout the summer, the result would have been very cold and very dry conditions in the Balkans with a duration long enough to hinder the development of C<sub>3</sub> plants and allow the development of C<sub>4</sub> plants.

Put together, these studies suggest a climatic schema that fits with the occurrence of the “C<sub>4</sub> episodes”. During the four episodes (26.0–28.0 kyr cal BP, 30.0–31.4 kyr cal BP, 44.5–53.4 kyr cal BP and 66.1–86.8 kyr), the Mediterranean Basin was dominated by strong meridional oceanic circulation with low evaporation from the eastern basin and a high positive EA/WR mode reducing the influence of westerlies and favoring northeasterlies, both leading to dry and cold summer conditions over the Balkans (Fig. 5b).

Others periods of the glacial record with C<sub>3</sub> plant dominance would then be associated with lower meridional Mediterranean circulation due to a weaker EA/WR mode and/or a less intense Siberian High, allowing westerlies to access the Balkans (Fig. 5a). This situation, which predominated during the last glaciation, could also be connected with the N/NW winds indicated by mineral geochemical (Bugge et al., 2008) and sedimentological (Antoine et al., 2009a) tracers as cold Pleistocene winds moved closer to the ground and consequently were more influenced by the topography than during warm periods. The Carpathians can thus deflect original westerlies (“wet” winds) towards the N/NW direction (Sebe et al., 2011).

## 5 Conclusions

Geochemical records of the Surduk loess sequence show similarities with other European loess sequences. The loess organic matter  $\delta^{13}\text{C}$  record evidenced dry and/or cold climatic conditions during glacial times with high  $\delta^{13}\text{C}$  values and less drastic conditions during interglacial periods

with low  $\delta^{13}\text{C}$ . Nevertheless, and in contrast to all European loess sequences recorded along the last climatic cycle, with widespread C<sub>3</sub> plant dominance, the organic  $\delta^{13}\text{C}$  record of Surduk is the only glacial record with several unquestionable records of C<sub>4</sub> plants.

This finding suggests a past atmospheric circulation schema over Europe with a focus on Balkan areas. The whole glacial period would be associated with a strong meridional Mediterranean circulation responsible for a low evaporation rate and with an atmospheric situation unfavorable to the influence of westerlies over the Balkans. This situation would have been enhanced during at least four episodes (26.0–28.0 kyr cal BP, 30.0–31.4 kyr cal BP, 44.5–53.4 kyr cal BP and 66.1–86.8 kyr) under a highly positive EA/WR-like atmospheric mode that even reduced the Mediterranean evaporation and westerlies in favor of northerlies over the Balkans. This climatic configuration would have led to short and very dry summer conditions unfavorable to C<sub>3</sub> plant development and, therefore, would have allowed the development of C<sub>4</sub> plants.

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