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First Alkane Biomarker Results for the Reconstruction of the Vegetation History of the Carpathian Basin (SE Europe)

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Karpatenbecken
Quartär
Löss
Paläoboden
Biomarker

Contents

Erste Ergebnisse von Alkanen als Biomarker für die Rekonstruktion der Vegetationsgeschichte des Karpatenbeckens (Südost-Europa)

Zusammenfassung

Seit einigen Jahren gibt es zunehmend Studien, die, basierend auf der Untersuchung von fossilen Holzkohlen und Schneckenschalen aus Löss-Paläoboden-Sequenzen im Karpaten-Becken, die traditionelle Vorstellung von weitestgehend baumlosen Steppen während der letzten Kaltzeit in Frage stellen. In der vorliegenden Arbeit präsentieren wir daher erste Alkan-Ergebnisse für rezente Wälder und Grünlandflächen sowie für eine Löss-Paläoboden-Sequenz vom Bačka-Löss-Plateau zwischen Donau und Theiß. Wir diskutieren das Biomarker-Potential der Alkane für die Rekonstruktion der Vegetationsgeschichte und wagen eine erste vorsichtige Interpretation für den letzten glazialen Zyklus.

Abstract

Since several years increasing fossil charcoal and malacological evidence from loess-palaeosol sequences in the Carpathian Basin is questioning the traditional paradigm of treeless full glacial palaeoenvironments. In this paper we present first alkane results from recent forests and grasslands as well as from a loess-palaeosol sequence on the Bačka Loess Plateau in-between Danube and Tisa. We discuss the potential of the alkane biomarkers for the reconstruction of the vegetation history and provide a first tentative interpretation for the last glacial cycle.

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1. Introduction

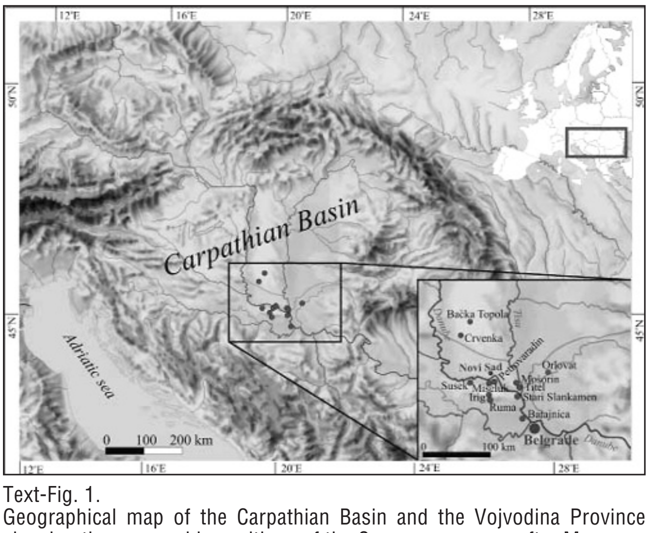
n-Alkanes with 25 to 33 carbon atoms (nC25-nC33) and a strong odd-over-even predominance (OEP) are important constituents of cuticular plant leaf waxes (KOLATTUKUDY, 1976). With the litter-fall they are deposited and stored in soils and sediments, e.g. in aeolian sediments, where they are assumed to be relatively resistant to biogeochemical degradation (CRANWELL, 1981; MEYERS & ISHIWATARI, 1993). Since furthermore different vegetation types reveal distinct alkane pattern and hence a so-called „chemical fingerprint“, alkanes have the potential to serve as biomarkers. For instance, they are used to differentiate between autochthonous (lacustrine) and allochthonous (terrestrial) organic matter (OM) in lake sediments (BOURBONNIERE et al., 1997; FICKEN et al., 2000; MÜGLER et al., 2008) or to reconstruct vegetation histories (CRANWELL, 1973; SCHWARK et al., 2002; ZECH, 2006; ZECH et al., 2008).

During the last years, loess-palaeosol sequences from SE Europe have gotten more and more in the focus of Quaternary scientists aiming at establishing pedo-, magneto- and chronostratigraphies (BUGGLE et al., 2008; BUGGLE et al., submitted; FUCHS et al., 2007; MARKOVIC et al., 2006; MARKOVIC et al., 2008) and at reconstructing palaeoenvironments and palaeoclimate (MARKOVIC et al., 2005; SÜMEGI & KROLOPP, 2002; WILLIS & ANDEL, 2004). And there is increasing fossil charcoal and malacological evidence from loess-palaeosol sequences in the Carpathian Basin questioning the traditional paradigm of treeless full glacial palaeoenvironments. However, up to now studies using n-alkanes for the reconstruction of the vegetation history are missing.

2. Study Area and Pedostratigraphy

Large areas of the Carpathian Basin (Pannonian Basin) are covered with loess, often forming discontinuous plateau uplands between the alluvial plains of the rivers Danube, Tisa, Sava and Tamiš. Close to the town Crvenca about 60 km northwest of Novi Sad in the Vojvodina Region, a loess-palaeosols sequence of about 10 m height is exposed in a brickyard situated on the southwestern edge of the Bačka Loess Plateau (Text-Fig. 1).

A first pedostratigraphical description and first geochemical, grain-size and magnetic results are provided by MARKOVIC et al. (2008). Accordingly, the Crvenca exposure reflects the last interglacial-glacial cycle with an about 2 m thick and clay-rich „V S1“ palaeosol (the prefix „V“ refers to the standard Pleistocene loess-palaeosol stratigraphy in Vojvodina) forming the bottom. The overlaying about 8 m thick „V L1“ loess is interbedded by a weakly developed interstadial palaeosol complex („V L1S1“) and the top of the loess-palaeosol sequence is formed by the modern topsoil („V S0“).



Text-Fig. 1.
Geographical map of the Carpathian Basin and the Vojvodina Province showing the geographic positions of the Crvenca exposure after MARKOVIC et al. (2008).

3. Material and Methods

During a field campaign in November 2007, the Crvenca exposure was refreshed and cleaned by digging about 1 m wide and 0.5 m deep trenches. Sampling for biomarker analysis was conducted by taking mixed samples every 25 cm, resulting in totally 43 samples. Additionally, 12 samples for luminescence dating were taken from the exposure. Manuscripts dealing with a detailed description of the stratigraphical/pedological/geochemical/magnetic features and with the luminescence results, respectively, are in preparation.

In order to characterise the modern vegetation types with respect to their alkane pattern, mixed litter and topsoil samples were taken from several sites of the Fruska Gora Mountains about 10 km south of Novi Sad (*Quercus* and *Fagus* forests) and the Titel Loess Plateau about 25 km east of Novi Sad (grass and herb vegetation) (Text-Fig. 1).

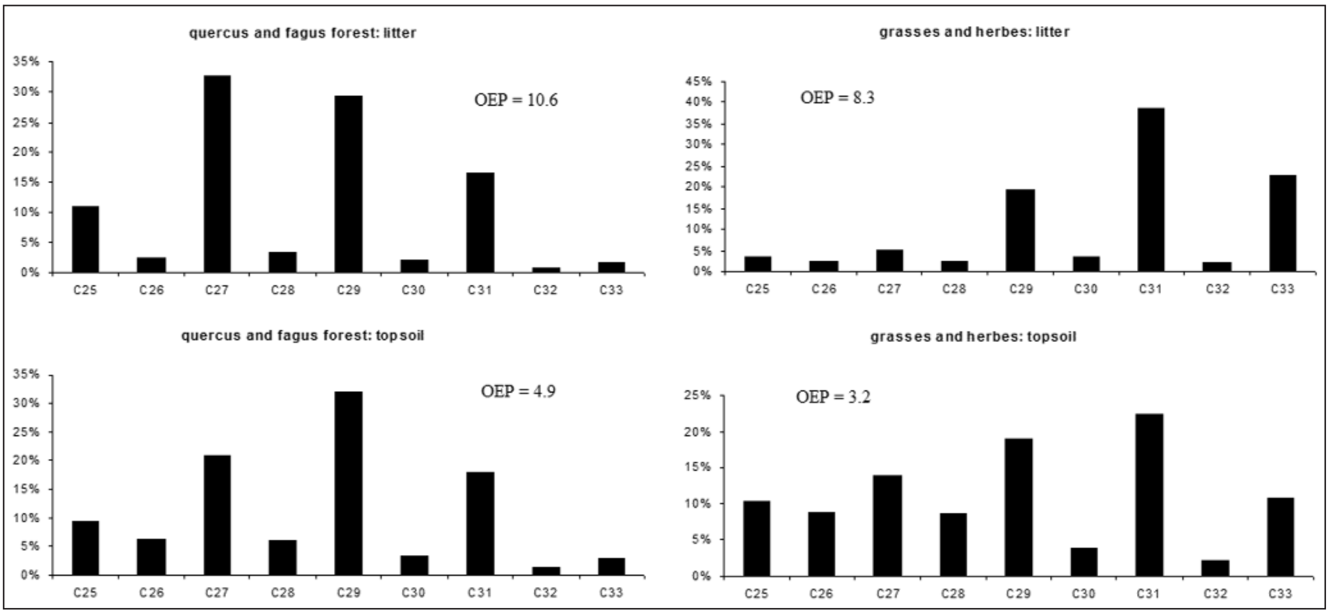
Sample preparation of the n-alkanes was carried out at the University of Novi Sad, Serbia, and at the University of Bayreuth, Germany, using a modified method after ZECH & GLASER (2008). Free lipids were extracted with methanol/toluene (7/3) using Soxhlet apparates and subsequently concentrated using rotary evaporation. The lipid extracts were purified on columns filled with deactivated (5 %) silica (2 g) and deactivated (5 %) aluminium oxide (2 g). n-Alkanes were eluted with 45 ml hexane/toluene (85/15). Quantification was performed on an HP 6890 GC equipped with a flame ionisation detector (FID). 5α-Androstan and Hexatriacontane (nC36) were added as internal and recovery standards, respectively.

4. Results and Discussion

4.1. n-Alkane Pattern of Recent Vegetation and Soils

Text-Fig. 2 shows the n-alkane pattern obtained for the litter and topsoil samples collected from *Quercus* and *Fagus* forests on the Fruska Gora Mountains versus samples from grasslands on the Titel Loess Plateau. On the one hand, they all reveal a strong odd-over-even predominance (OEP = (C25 + C27 + C29 + C31 + C33) / (C26 + C28 + C30 + C32)), which is typical for cuticular plant leaf waxes. Lower OEP values, i.e. more balanced alkane distribution patterns as observed for the topsoils in comparison to the fresh biomass (Text-Fig. 2), are often interpreted in terms of OM degradation (WIESENBERG et al., 2004). On the other hand, it is striking that the respective litter and topsoil samples are not identical: for instance, in the fresh forest litter the alkane C27 dominates, whereas in the topsoil the alkane C29 dominates and the topsoil of the grasslands is characterised by a percentage increase of the shorter alkanes C25-C28. This might be attributed to either an input of microbial or root biomass input or to biodegradation (WIESENBERG et al., 2004).

Despite of these variations, it is overall valid that in the forest there dominate the n-alkanes C27 and C29, whereas in the grassland there dominates C31, and C33 is abundant, too. These results are in agreement with findings from other studies (CRANWELL, 1973; SCHWARK et al., 2002; ZECH, 2006; ZECH et al., 2008) and suggest that alkane ratios can be used to differentiate between forest and



Text-Fig. 2.
n-Alkane distribution patterns of litter and topsoil samples, collected from *Quercus* and *Fagus* forests on the Fruska Gora Mountains and from grasslands on the Titel Loess Plateau, respectively.

grassland vegetation. In the next chapter we will therefore present several alkane-ratios for the Crvenca loess-palaeosol sequence in order to discuss their potential for the reconstruction of the vegetation history of the Bačka Loess Plateau.

4.2. n-Alkane Ratios of the Crvenca Loess-Palaeosol Sequence

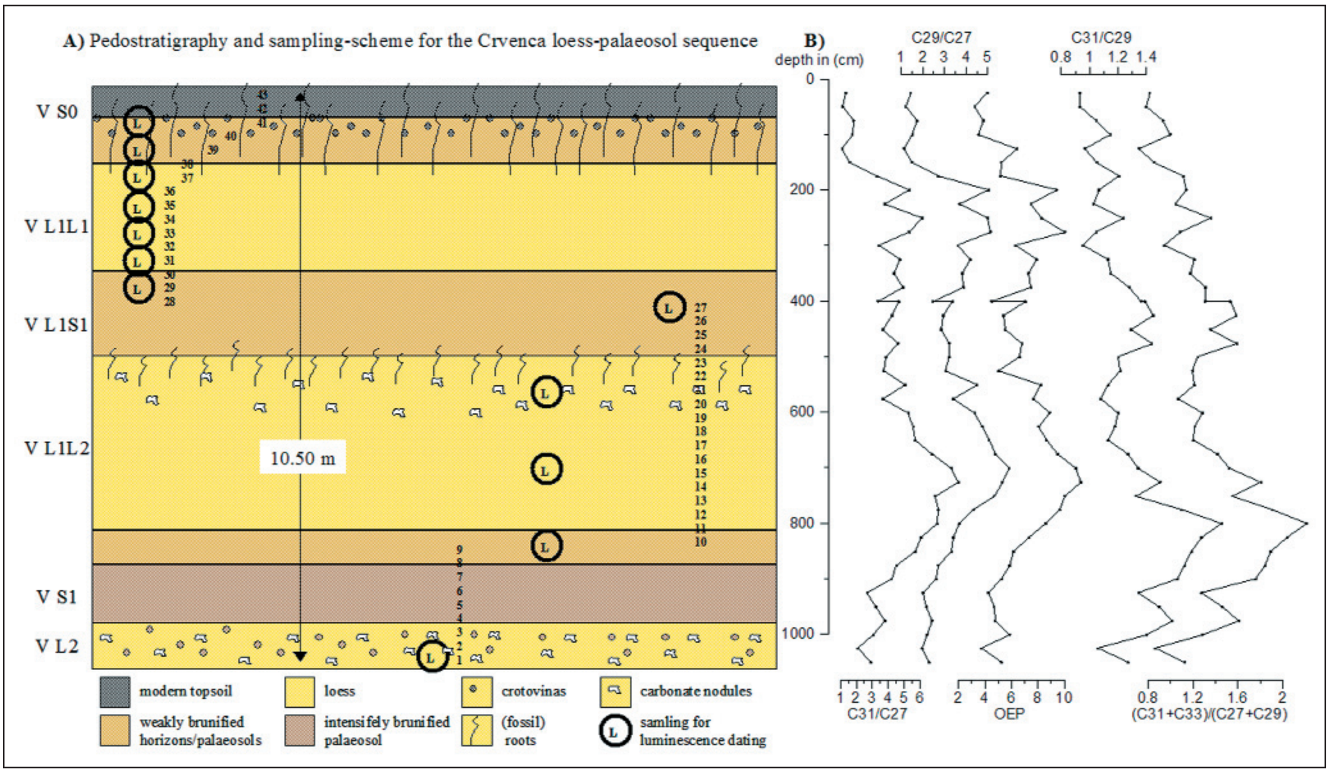
According to Text-Fig. 2, the ratio C31/C27 – already applied e.g. by SCHWARK et al. (2002) and ZECH at al. (2008) – should be a powerful proxy to distinguish between OM derived from forests versus OM derived from grasslands. The depth function of this ratio for the Crvenca loess-palaeosol sequence reveals large variations in the range from 1.1 to 8.5 with maxima for the loess units „V L1L1“ and „V L1L2“ (Text-Fig. 3). Although the exact chronostratigraphy has to await the results from the luminescence analyses, these maxima could be roughly interpreted in terms of cold and steppic environments prevailing during the Marine Isotope Stages (MIS) 2 and 4. On the contrary, lower C31/C27 ratios for the „V S1“ and „V L1S1“ palaeosols suggest an increased contribution of trees during MIS 5 and MIS 3. The dramatic decrease at the transition from „V L1“ to „V S0“ (Text-Fig. 3) could possibly reflect a Holocene reforestation on the Bačka Loess Plateau.

Looking only at the alkane distribution patterns of the recent vegetation with C29 being nearly as abundant as C27 in forest litter (C29/C27 = 0.9) but being clearly more abundant in grasses/herbs (C29/C27 = 3.6) (Text-Fig. 2), the palaeobotanic interpretation deduced from the C31/C27 ratio might be confirmed by the C29/C27 ratio, too (R = 0.9) (Text-Fig. 3). However, there arise doubts when considering additionally the C29/C27 ratios in the recent topsoils: probably due to degradation effects or input of microbial, root or other biomass, the ratios become very similar (1.5 versus 1.4) and do no longer allow to distinguish between forest and grassland soils (Text-Fig. 2). Indeed, both the ratios C29/C27 and C31/C27 correlate significantly with the OEP (R = 0.93 and 0.87, respectively) (Text-Fig. 3), the latter being assumed to be a proxy for OM degradation. Hence the variations in the depth functions of C29/C27 and C31/C27 may not only be interpreted in terms of vegetation changes but also in terms of OM degradation in topsoil/palaeosols versus OM preservation in loess.

An alkane ratio, which is less effected by biodegradation and still differing largely enough between forest and grassland (0.6 in litter and 0.6 in topsoils versus 2.0 and 1.2, respectively) in order to try a reconstruction of vegetation changes, could be C31/C29 (Text-Fig. 2). Its depth function for the Crvenca loess-palaeosol sequence resembles strongly (R = 0.96) the one of the alkane ratio (C31 + C33)/(C27 + C29) and would allow a different palaeoenvironmental interpretation compared to the one made above: trees disappeared in the course of the last interglacial and grassland clearly dominated at the beginning of MIS 4. While loess deposition continued („V L1L1“), trees became more abundant again until grassland spread again during MIS 3 formation of „V L1S1“ (maxima in the alkane ratios). The variations of the alkane ratio depth functions in „V L1L1“ and „V S0“ indicate that the vegetation cover ever since then was characterised by smaller fluctuations with a changeable contribution of trees even during the Last Glacial Maximum. This scenario would be in agreement with fossil charcoal and malacological evidence from the Carpathian Basin provided for instance by MARKOVIC et al. (2007), SÜMEGI & KROLOPP (2002), WILLIS & ANDEL (2004) and WILLIS et al. (2000).

5. Conclusions and Outlook

First alkane biomarker results from the Vojvodina, Carpathian Basin, were presented for *Quercus* and *Fagus* forests and grasslands as well as for a loess-palaeosol sequence. The alkane distribution patterns of the recent vegetation and topsoils suggest that alkanes may serve as biomarkers for distinguishing between OM derived from forests versus OM derived from grassland. However, biodegradation could strongly affect the chemical fingerprint. Though the alkane ratios C31/C27 and C29/C27 allow a palaeoenvironmental interpretation of the Crvenca loess-palaeosol sequence nourishing the traditional paradigm of cold steppic environments during MIS 4 and the LGM, the ratios correlate significantly with the OEP, the latter being an alkane biodegradation proxy. Arguing that the ratios C31/C29 and (C31+C33)/(C27+C29) are less affected by



Text-Fig. 3.
A: Pedostratigraphy and sampling scheme for the Crvenca loess-palaeosol sequence.
B: Depth functions for different n-alkane ratios and the OEP.

degradation, we propose to use them instead for the reconstruction of the vegetation history. Accordingly, grassland dominated at the end of the last interglacial and the beginning of the „V L1“ loess deposition (MIS 4) as well as during the formation of the „V L1S1“ interstadial palaeosol. Ever since then trees contributed varyingly to the soil OM even during the LGM.

Ongoing work focuses on including up to now contradictory results from needle tree study sites and on quantifying the degradation effect on alkane ratios by studying litterbag samples. Furthermore, the biomarker results have to be put in a closer context with other methodological approaches in order to improve our understanding of the palaeoenvironments and palaeoclimate of the Carpathian Basin.

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