



Amino Acid Geochronology as an Independent Test of Numerical Dating Methods Applied to Serbian, Romanian and Central Asian Loess Deposits

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*Eurasien
Löss
Äolischer Staub
Atmosphärische Zirkulation*

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Aminosäuren-Geochronologie als unabhängiger Test für numerische Datierungsmethoden für serbische, rumänische und zentralasiatische Lössablagerungen

Zusammenfassung

Paläoklimatische Untersuchungen von Lößsequenzen hängen ganz entscheidend von dem Einsatz numerischer Datierungsmethoden ab. Nur durch sie kann ein verlässliches Altersmodell für die zu untersuchenden hochauflösenden Parameter (z.B. Korngrößen, geochemische Proxies) entwickelt werden. Da allerdings bisher zur Verfügung stehende Methoden sowohl in ihrem Datierungslimit als auch in ihrer methodischen Verlässlichkeit eingeschränkt sind, stellen relative Datierungsmethoden wie die Aminosäuren-Stratigraphie ein unabhängiges Werkzeug dar, um bisherige Altersmodelle zu validieren bzw. das Datierungsspektrum deutlich zu erweitern. Im Rahmen dieser Arbeit wird die Methode erstmalig für den mittel- und zentralasiatischen Raum und mit einer besonders hohen Auflösung für den Raum Südosteuropa eingesetzt.

Abstract

Palaeoclimatic investigations of loess-palaeosol sequences depend on the application of numerical dating techniques, such as radiocarbon and luminescence methods, in order to develop reliable time series for the proxies being studied. Commonly, the utility of luminescence and radiocarbon dating is limited by their applicable dating range or, in the case of many European and Central Asian loess sites, results show a significant age underestimation for samples taken from the last glacial cycle. Relative dating approaches, such as amino acid geochronology, offer an independent assessment of numerical age estimates and assist in the chronostratigraphic evaluation of loess units beyond the range of useful numerical dating methods. In this study we present the first aminostratigraphic results from a Central Asian loess site: the Remisowka loess sequence in southeastern Kazakhstan, as well as new results from the loess sites Stari Slankamen and Mosorin/Titel Plateau in the Vojvodina (Serbia), and also initial results from the loess sequence Mircea Voda (Romania). We measured D/L ratios of glutamic acid, aspartic acid, phenylalanine, valine, and alloisoleucine/Isoleucine in fossil shells of selected terrestrial gastropod genera.

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1. Introduction

Palaeoclimatic investigations of loess-palaeosol sequences depend on the application of numerical dating techniques, such as radiocarbon and luminescence methods, in order to develop reliable time series for the proxies being studied. Commonly, the utility of luminescence and radiocarbon dating is limited by their applicable dating range or, in case of some Central Asian loess sites, results show a significant age underestimation for samples taken from the last glacial cycle (ZHOU ET AL., 1995, MACHALETT et al., 2006). Relative dating approaches, such as amino acid geochronology, offer an independent assessment of numerical age estimates, when results are at or near their methodological limits, and assist in the chronostratigraphic evaluation of loess units beyond the range of useful numerical dating methods. Amino acid geochronology has been successfully applied to fossil gastropod shells from calcareous loess deposits from loess-palaeosol sequences in North America and Europe (OCHES & MCCOY, 1995, 2001; OCHES et al., 1996, 2000), and China (MCCOY et al., 1988; OCHES & MCCOY, 2001).

2. The Method

Amino acid geochronology measures the extent of racemization of amino acids within the carbonate shells of fossil molluscs. Amino acids, which exist in the levorotatory (L-form) optical configuration in living organisms, play an essential role in the biomineralization process of shell formation. Following protein synthesis, amino acids encased within the shell crystal structure, undergo reversible stereochemical inversion, or racemization, to their dextrorotatory (D-form) enantiomers. The rate at which the L to D inversion occurs is primarily a function of environmental temperature, and the extent of racemization, measured by the D/L ratio, is dependent on the amount of time that has passed. Taxonomic factors may significantly influence racemization; therefore sample sets of a single genus are typically analyzed in aminostratigraphic studies. Thus, within a monogeneric suite of fossil shells that have experienced similar post-depositional temperature histories, the D/L ratio measured in individual amino acids can be a useful measure of age. Terrestrial gastropod shells are often abundant and well preserved in loess deposits, making them an ideal system for the application of this method. A detailed review of the principles and applications of amino acid geochronology is available from WEHMILLER & MILLER (2000).

3. First Results

In this study we present the first aminostratigraphic results from a Central Asian loess site: the Remisowka loess sequence in southeastern Kazakhstan, as well as new results from the loess sites Stari Slankamen and Mosorin/Titel Plateau in the Vojvodina (Serbia), and also initial results from the loess sequence Mircea Voda (Romania). We measured D/L ratios of glutamic acid, aspartic acid, phenylalanine, valine, and allsoleucine/soleucine in fossil shells of the terrestrial gastropod genera *Pupilla*, *Pseudonapaeus*, *Leucozonella*, *Helicopsis*, *Vallonia*, *Clausiliidae* and *Succinea* that have been selected for their wide geographic occurrence and reliability and reproducibility in repeated D/L measurements. Taxonomic identification of the sieved fossil snail shells were determined by the comparison with originally described type examples of the Malacozoological Collection at the Museum für Naturkunde of the Humboldt-University of Berlin. The samples were prepared and measured at the Amino Acid Geochronology

Laboratory at the University of South Florida using reverse-phase liquid chromatography, following the method described by KAUFMAN & MANLEY (1998).

The results of amino acid geochronology provide an independent age model for the studied loess series, and their combination with numerical dating techniques allows us to confidently determine the position of the last and the two penultimate interglacial periods in the Serbian, Romanian and Central Asian sequences, casting new light on the chronostratigraphy of the last three glacial cycles in Eurasian loess. On a regional scale the stratigraphic scheme of the loess sequence Stari Slankamen, which was subject to varying interpretations in the past, is verified by the correlation with other aminostratigraphic records from the Vojvodina, in particular from the Titel loess plateau at Mosorin.

We aim to highlight the vast potential of highly resolved multi-proxy investigations, e.g., particle size studies, of the aeolian dust record of terrestrial sediments in combination with different geochronological techniques and chronostratigraphic tools, including luminescence and radiocarbon methods, plus amino acid geochronology. As loess sediments are widespread on the continents and offer palaeoclimatic reconstructions on regional and inter-hemispheric scales, we anticipate that the implementation of new methods will lead to a renaissance in the study of terrestrial climate archives.

References

- KAUFMAN, D.S. & MANLEY, W.F.: A new procedure for determining DL amino acid ratios in fossils using reverse phase liquid chromatography. – *Quaternary Science Reviews*, **17**, 987–1000, 1998.
- MACHALETT, B., FRECHEN, M., HAMBACH, U., OCHES, E.A., ZÖLLER, L. & MARKOVIĆ, S.B.: The loess sequence from Remisowka (northern boundary of the Tien Shan Mountains, Kazakhstan) – Part I: Luminescence dating. – *Quaternary International*, **152/153**, 203–212, 2006.
- MACHALETT, B., OCHES, E.A., FRECHEN, M., ZÖLLER, L., HAMBACH, U., MAVLYANOVA, N.G., MARKOVIĆ, S.B. & ENDLICHER, W.: Aeolian dust dynamics in Central Asia during the Pleistocene – driven by the long-term migration, seasonality and permanency of the Asiatic polar front. – *Geochemistry, Geophysics, Geosystems*, DOI: 10.1029/2007GC001938, 2008, accepted.
- MCCOY, W.D., BRADLEY, R.S., AN, Z.S. & LIU, T.S.: Aminostratigraphy of Chinese loess. – *Abstracts of the American Quaternary Association*, **10**, p. 136, 1988.
- OCHES, E.A. & MCCOY, W.D.: Historical developments and recent advances in amino acid geochronology applied to loess research: examples from North America, Europe, and China. – *Earth-Science Reviews*, **54**, 173–192, 2001.
- OCHES, E.A., MCCOY, W.D. & CLARK, P.U.: Amino acid estimates of latitudinal temperature gradients and geochronology of loess deposition during the last glaciation, Mississippi Valley, United States. – *Geological Society of America Bulletin*, **108**, 892–903, 1996.
- OCHES, E.A., MCCOY, W.D. & GNIESER, D.: Aminostratigraphic correlation of loess – paleosol sequences across Europe. – In: GOOD-FRIEND, G., COLLINS, M., FOGEL, M., MACKO, S. & WEHMILLER, J.F. (eds.): *Perspectives in Amino Acid and Protein Geochemistry*, Oxford University Press, NY, 331–348, 2000.
- WEHMILLER, J.F. & MILLER, G.H.: Aminostratigraphic Dating Methods in Quaternary Geology. – In: *Quaternary Geology: Methods and Applications*, AGU reference shelf, **4**, 187–222, 2000.