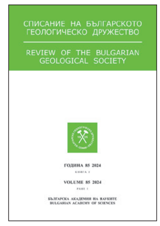
СПИСАНИЕ НА БЪЛГАРСКОТО ГЕОЛОГИЧЕСКО ДРУЖЕСТВО,
год. 85, кн. 1, 2024, с. 67–70

REVIEW OF THE BULGARIAN GEOLOGICAL SOCIETY,
vol. 85, part 1, 2024, p. 67–70



Insights into floral and climatic changes from biomarker and isotopic composition of land plant organic matter – A review

Achim Bechtel, Doris Groß

Department of Applied Geosciences & Geophysics, Montanuniversität Leoben, Peter-Tunner-Str. 5, A-8700 Leoben, Austria; E-mail: Achim.Bechtel@outlook.de

Обзор на възможностите за използване на биомаркерите и изотопния състав на органичните вещества на сухоземните растения за изучаване на растителни и климатични промени

Ахим Бехтел, Дорис Грос

Департамент по приложни геонауки и геофизика, Минен университет Леобен, Peter-Tunner-Str. 5, A-8700 Leoben, Austria; E-mail: Achim.Bechtel@outlook.de

Резюме. Биомаркерите и изотопният състав на въглищата и растителните тъкани дават възможност за определяне на растителната група и условията на палеосредата. Съдържанието, разпределението и стойностите на d^{13}C в листните восъчни липиди (т.е. *n*-алкани) се различават между покритосеменните и голосеменните растения. Терпеноидните въглеводороди се използват за оценка на приноса на голосеменните спрямо покритосеменните растения. Влиянието на промените в привноса на голосеменни/покритосеменни растения върху d^{13}C на въглищата може да се преодолее като се изучава изотопния състав на остатъци от фосилизирана дървесина. Покритосеменните и голосеменните показват подобно H-изотопно фракциониране между *n*-алкани и вода. Поради различни биосинтетични пътища, дитерпеноидите показват по-ниски стойности на d^{2}H в сравнение с тритерпеноидите, получени от покритосеменни растения. Разликите в средногодишните количества на валежите влияят върху d^{13}C на общата органична маса на листата. Ковариациите в d^{13}C и d^{2}H на липидите отразяват промените в наличността на вода за растенията. Температурните вариации на базата на разклонени глицерол-диалкил-глицерол-тетраетери (brGDGTs) и d^{2}H стойности на *n*-C_{29} алкан от седиментите на езерото Ван разкриват топъл и влажен климат по време на междуледникови периоди и по-хладен и по-сух климат по време на ледникови периоди. Въз основа на метилирането на разклонените GDGT е наличен калибриран палеотермометър за торф и лигнити.

Ключови думи: *n*-алкил-липиди, терпеноиди, лигнити, стабилни изотопи, условия на палеосредата.

Abstract. Biomarkers and isotopic composition of coal and plant tissue enable insights into floral assemblage and paleoenvironment. Abundance, distribution, and d^{13}C values of leaf wax lipids (i.e. *n*-alkanes) differ between angiosperm and gymnosperm plants. Terpenoid hydrocarbons are used to assess the contributions of gymnosperms versus angiosperms. The influence of varying contributions of angiosperms and gymnosperms on d^{13}C of coal can be overcome by the analyses of fossil wood remains for their isotopic composition. Angiosperms and gymnosperms show similar H-isotope fractionation between *n*-alkanes and water. Diterpenoids yield lower d^{2}H values compared to angiosperm-derived triterpenoids, due to different biosynthetic pathways. Differences in mean annual precipitation affect d^{13}C of bulk leaf organic matter. Co-variations in d^{13}C and d^{2}H of lipids reflect changes in water availability to the plants. Temperature variations, based on branched glycerol dialkyl glycerol tetraethers (brGDGTs), and d^{2}H values of *n*-C_{29} alkane from Lake Van sediments reveal warm-humid climate during interglacials and cooler and drier climate during glacials. Based on the methylation of brGDGTs, a calibrated paleothermometer is available for peats and lignites.

Keywords: *n*-Alkyl-lipids, terpenoids, lignite, stable isotopes, paleoenvironment.

Introduction

Biomarker and stable isotope systematics in coal and fossil wood provide valuable information for the reconstruction of floral assemblage and paleoenvironmental changes. The presence of biomarker characteristic for plant families of specific climatic requirements is useful as paleoclimatic proxy (Žatková et

https://doi.org/10.52215/rev.bgs.2024.85.1.67

al., 2023). Carbon isotope analyses have been used to reconstruct changes in the isotopic composition of upper ocean and atmospheric carbon reservoirs (Farquhar et al., 1989; Gröcke et al., 1999; Arens et al., 2000), as well as climatic changes (e.g. temperature, humidity) via water-use efficiency of land plants (Lücke et al., 1999; Edwards et al., 2000; van Bergen and Poole, 2002). The analysis of hydrogen isotope composition of leaf wax lipids is a promising tool to reconstruct climatic changes during Earth's history (Sachse et al., 2012).

Biomarkers and vegetation

The reconstruction of paleoclimate based on stable isotope ratios of coal and fossil wood requires corrections for effects of variations in floral assemblage (Bechtel et al. 2008). The ratio of diterpenoids versus non-hopanoid triterpenoids and differences in the concentration and distribution of leaf wax lipids have been shown to reflect varying contributions of gymnosperms and angiosperms to peat formation (Bechtel et al., 2002; Diefendorf et al., 2011). However, differences in the contents of terpenoids lead to overestimation of the contribution of evergreen plants (e,g., conifers) to peat formation (Diefendorf et al., 2012). The relative proportions and concentrations of abietane-type and tetracyclic diterpenoids may enable to distinguish between the dominant contribution of Cupressaceae, Podocarpaceae, and Pinaceae (Diefendorf et al., 2019). A significant change in the ratios of diterpenoids specific for gymnosperms versus angiosperm-derived triterpenoids has been obtained from studies on numerous lignites and subbituminous coals throughout the Cenozoic of central Europe (Bechtel et al., 2008). The results are in agreement with paleobotanical records, indicating that broadleaved evergreen vegetation extended to almost 60° N during the Paleocene and Eocene. At the end of the Eocene, a decrease in both mean annual range of temperature and mean annual temperature resulted in northern European vegetation represented by temperate deciduous and coniferous forests (Wolfe, 1980).

Factors affecting C- and H-isotope ratios of land plant biomass

Compound-specific isotope analyses on biomarkers offer the possibility to trace changes in isotopic composition of source-specific compounds (e.g., leaf wax lipids, diterpenoids from conifer resins, angiosperm-derived triterpenoids) over Earth´s history. The production of organic matter (OM) by different kinds of plants has been shown to influence the isotopic (C-, H-) composition of bulk OM and plant lipids (Lane, 2017; Bechtel et al., 2019). Furthermore, degradation of plant tissue affects the isotopic composition of the biomass due to differences in $d^{13}C$ of plant constituents (e.g., cellulose, lignin) and their different resistance to decomposition (Schleser et al., 1999; Bechtel et al., 2008). Angiosperms show higher isotopic discrimination of leaf OM against atmospheric CO_2 (D_{leaf}) and increased biosynthetic fractionation of *n*-alkanes (e_{lipid}) than gymnosperms, resulting in a $d^{13}C$ difference in *n*-C_{29} (Diefendorf et al., 2011). In contrast, angiosperms and gymnosperms show similar H-isotope fractionation between *n*-alkanes and water (Chikaraishi and Naraoka, 2003). Minor differences in carbon isotopic fractionation during biosynthesis of *n*-alkanes may be used to detect the contribution of different conifer families (Diefendorf and Freimuth, 2017).

Fossil wood remains from angiosperms or gymnosperms, identified based on biomarker composition, can be used to overcome the influence of varying contributions on $d^{13}C$ on plant OM in paleoclimate reconstruction (Bechtel et al., 2008). The effect of decomposition on $d^{13}C$ of fossil wood can be minimized by the analyses of extracted cellulose (Schleser et al., 1999; Bechtel et al., 2020a). Differences in isotopic composition of biomarkers (e.g., *n*-alkanes, diterpenoids, triterpenoids) are caused by different biosynthetic pathways (Chikaraishi et al. 2004).

C- and H-isotope ratios of plant lipids and climate

In a recent study of lignite seams from the Cenozoic coal basins of the Primorye region (Far East, Russia), parallel fluctuations in mean $d^{13}C$ values of long-chain *n*-alkanes, diterpenoids, and angiosperm-derived triterpenoids with age trends of carbon isotopic composition of the ocean-atmospheric CO_2 were obtained. The results argue for a major influence of changes in the isotopic composition of atmospheric CO_2 on $d^{13}C$ of plant OM over the Cenozoic (Bechtel et al., 2020b).

Beside variations in d^{13}C of atmospheric CO_2, changes in mean annual precipitation have been reconstructed based on the carbon isotope composition of leaf wax lipids (i.e. *n*-alkanes) from coals and sediments. A significant increase in d^{13}C of total leaf OM under dry conditions was obtained in a study by Diefendorf and Freimuth (2017). Based on correlations between d^{13}C and d^{2}H of *n*-C_{29} alkane, and between d^{13}C of cellulose and d^{2}H of *n*-C_{29}, water availability most probably governs the isotopic composition of fossil wood OM from lignite deposits of the Konin Basin in Poland (Bechtel et al., 2020a).

The hydrogen isotope composition of leaf wax lipids is mainly linked to the hydrogen isotope composition of regional rainwater, reflecting changes in air temperature and precipitation/evaporation ratios (Schefuß et al., 2005; Sachse et al. 2012). It has been shown that d^{2}H most likely records the hydrogen isotopic composition of plant growth water and thus, may act as a proxy for air temperature, water availability and evapotranspiration. Geochemical proxies for changes in mean annual air temperature (MAAT), based on branched glycerol dialkyl glycerol tetraethers (brGDGTs), revealed temperature variations during glacials/interglacials within the Lake Van area (Turkey). brGDGT-based temperature variations and d^{2}H values of *n*-C_{29} alkane from sediments of Lake Van, deposited during MIS 3 to MIS 1, indicate warm-humid climate during interglacials, and cooler and drier climate during glacials (Stockhecke et al., 2021).

Paleoclimatic proxies for peat and lignite

The distribution of bacterial branched GDGTs (brGDGTs) has been investigated from 96 peatlands around the world with a broad MAAT and pH range (Naafs et al. 2017). It could be shown that the degree of cyclisation of brGDGTs is positively related to pH, and the degree of methylation of brGDGTs is positively correlated with MAAT. Based on the peat-specific calibration (Naafs et al. 2017), the potential exists to use brGDGTs in peats and lignite to reconstruct terrestrial climate during the Cenozoic. Recently, the application of this paleothermometer on mid-lattitude (45-60°) lignite deposits resulted in the reconstruction of MAATs during early Paleogene (56-48 Myr) between 23 and 29°C (Naafs et al., 2018). However, a high uncertainty of ± 4.7 °C has to be considered.

Acknowledgements**:** Financial support by the Bulgarian Research Fund (contract KP-06-H64/5), the National Science Centre Poland (Project No. 2017/27/B/ST10/00001), and the Swiss National Science Foundation (SNF grants 200020_143340, 20FI21_124972 and 200021_124981), as well as by the Austrian Science Foundation (FWF Project Nos. P16251-N11 and I 2068-N29) is gratefully acknowledged.

References

Arens, N.C., A.H. Jahren, R. Amundson. 2000. Can C3 plants faithfully record the carbon isotopic composition of atmospheric carbon dioxide? – *Paleobiology*, *261*,137–164; https://doi.org/10.1666/0094-8373.

Bechtel, A., R.F. Sachsenhofer, I. Kolcon, R. Gratzer, A. Otto, W. Püttmann. 2002. Organic geochemistry of the Lower Miocene Oberdorf lignite (Styrian Basin, Austria): its relation to petrography, palynology and the paleonvironment. – *Int. J. Coal Geol*., *51*, 31–57; https://doi.org/10.1016/S0166-5162(02)00079-4.

Bechtel, A., R. Gratzer, R.F. Sachsenhofer, J. Gusterhuber, A. Lücke, W. Püttmann. 2008. Biomarker and carbon isotope variation in coal and fossil wood of Central Europe through the Cenozoic. – *Palaeogeogr., Palaeoclimatol., Palaeoecol*., *262*, 166–175; https://doi.org/10.1016/j.palaeo.2008.03.005.

Bechtel, A., M. Widera, M. Woszczyk. 2019. Composition of lipids from the First Lusatian lignite seam of the Konin Basin (Poland): Relationships with vegetation, climate and carbon cycling during the mid-Miocene Climatic Optimum. – *Org. Geochem*., *138*, 103908; https://doi.org/10.1016/j.orggeochem.2019.103908.

Bechtel, A., M. Widera, A. Lücke, D. Groß, M. Woszczyk. 2020a. Petrological and geochemical characteristics of xylites and associated lipids from the First Lusatian lignite seam (Konin Basin, Poland): Implications for floral sources, decomposition and environmental conditions. – *Org. Geochem*., *147*, 104052; https://doi.org/10.1016/j.orggeochem. 2020.104052.

Bechtel, A., I.Y. Chekryzhov, B.I. Pavlyutkin, V. Nechaev, S. Dai, S.V. Vysotskiy, T.A. Velivetskaya, I.A. Tarasenko, W. Guo. 2020b. Composition of lipids from coal deposits of the Far East: Relations to vegetation and climate change during the Cenozoic. – *Palaeogeogr., Palaeoclimatol., Palaeoecol*., *358*, 109479; https://doi.org/10.1016/j.palaeo.2019.109479.

Chikaraishi, Y., H. Naraoka, 2003. Compound-specific dD–d^{13}C analyses of *n*-alkanes extracted from terrestrial and aquatic plants. – *Phytochemistry*, *63*, 361–371; https://doi:10.1016/S0031-9422(02)00749-5.

Chikaraishi, Y., H. Naraoka, S.R. Poulson. 2004. Carbon and hydrogen isotopic fractionation during lipid biosynthesis in a higher plant (Cryptomeria japonica). – *Phytochemistry*, *65*, 323–330; https://doi.org/10.1016/j.phytochem.2003.12.003.

De Jonge, C., E.C. Hopmans, C.J. Zell, J.-H. Kim, S. Schouten, J.S. Sinninghe Damsté. 2014. Occurrence and abundance of 6-methyl branched glycerol dialkyl glycerol tetraethers in soils: implications for palaeoclimate reconstruction. – *Geochim. Cosmochim. Acta*, *141*, 97–112; https://doi.org/10.1016/j.gca.2014.06.013.

Diefendorf, A.F., E.J. Freimuth. 2017. Extracting the most from terrestrial plant-derived *n*-alkyl lipids and their carbon isotopes from the sedimentary record: A review. – *Org. Geochem*., *103*, 1–21; https://doi.org/10.1016/j.orggeochem. 2016.10.016.

Diefendorf, A.F., K.H. Freeman, S.L. Wing, H.V. Graham. 2011. Production of *n*-alkyl lipids in living plants and implications for the geologic past. – *Geochim. Cosmochim. Acta*, *75*, 7472–7485; https://doi.org/10.1016/j.gca. 2011.09.028.

Diefendorf, A.F., K.H. Freeman, S.L. Wing. 2012. Distribution and carbon isotope patterns of diterpenoids and triterpenoids in modern temperate C_3 trees and their geochemical significance. – *Geochim. Cosmochim. Acta*, *85*, 342–356; https://doi.org/10.1016/j.gca.2012.02.016.

Diefendorf, A.F., A.B. Leslie, S.L. Wing. 2019. A phylogenetic analysis of conifer diterpenoids and their carbon isotopes for chemotaxonomic applications. – *Org. Geochem*., *127*, 50–58; https://doi.org/10.1016/j.orggeochem.2018.11.007.

Edwards, T.W.D., W. Graf, P. Trimborn, W. Stichler, J. Lipp, H.D. Payer. 2000. $\delta^{13}C$ response surface resolves humidity and temperature signals in trees. – *Geochim. Cosmochim. Acta*, *64*, 161–167; https://doi.org/10.1016/S0016-7037(99)00289-6.

Farquhar, G.D., J.R. Ehleringer, K.T. Hubick. 1989. Carbon isotope discrimination and photosynthesis. – *Annu. Rev. Plant Physiol. Plant Mol. Biol*., *40*, 503–537.

Gröcke, D.R., S.P. Hesselbo, H.C. Jenkyns. 1999. Carbon-isotope composition of Lower Cretaceous fossil wood: Ocean-atmosphere chemistry and relation to sea-level change. – *Geology*, *27*, 155–158; https://doi.org/10.1130/0091-7613(1999)027<155:CICOLC>2.3.CO;2.

Lane, S.C. 2017. Modern *n*-alkane abundances and isotopic composition of vegetation in a gymnosperm-dominated ecosystem of the southeastern U.S. coastal plain. – *Org. Geochem*., *105*, 33–36; https://doi.org/10.1016/j.orggeochem. 2016.12.003, 2017.

Lücke, A., G. Helle, G.H. Schleser, I. Figueiral, V. Mosbrugger, T.B. Jones, N.P. Rowe. 1999. Environmental history of German Lower Rhine Embayment during the Middle Miocene as reflected by carbon isotopes in brown coal. – *Palaeogeogr., Palaeoclimatol., Palaeoecol., 154*, 339–352; https://doi.org/10.1016/S0031-0182(99)00122-4.

Naafs, B.D.A., G.N. Inglis, Y. Zheng, M.J. Amesbury, H. Biester, et al. 2017. Introducing global peat-specific temperature and pH calibrations based on brGDGT bacterial lipids. – *Geochim. Cosmochim. Acta*, *208*, 285–301; https://doi.org/ 10.1016/ j.gca.2017.01.038.

Naafs, B.D.A., M. Rohrssen, G.N. Inglis, O. Lähteenoja, S.J. Feakins, et al. 2018. High temperatures in the terrestrial mid-latitudes during the early Paleogene. – *Nature Geoscience*, *11*, 766–771; https://doi.org/10.1038/s41561-018-0199-0.

Sachse, D., I. Billault, G.J. Bowen, Y. Chikaraishi, T.E. Dawson, et al. 2012. Molecular paleohydrology: interpreting the hydrogen-isotopic composition of lipid biomarkers from photosynthesizing organisms. – *Annual Review Earth Planetary Science*, *40*, 221–249; https://doi.org/10.1146/annurev-earth-042711-105535.

Schefuß, E., S. Schouten, R. R. Schneider, 2005, Climatic controls on central African hydrology during the past 20,000 years, – *Nature*, *437(7061)*, 1003–1006; https://doi.org/10.1038/nature03945.

Schleser, G.H., J. Frielingsdorf, A. Blair. 1999. Carbon isotope behaviour in wood and cellulose during artificial aging. – *Chem. Geol.*, *158*, 121–130; https://doi.org/10.1016/S0009-2541(99)00024-8.

Stockhecke, M., A. Bechtel, F. Peterse, T. Guillemot, C.J. Schubert. 2021. Temperature, precipitation, and vegetation changes in the Eastern Mediterranean over the last deglaciation and Dansgaard-Oeschger events. – *Palaeogeogr., Palaeoclimatol., Palaeoecol*., *577*, 110535; https://doi.org/10.1016/j.palaeo.2021.110535.

van Bergen, P.F., I. Poole. 2002. Stable carbon isotopes of wood: a clue to palaeoclimate? – *Palaeogeogr., Palaeoclimatol., Palaeoecol.*, *182*, 31–45; https://doi.org/10.1016/S0031-0182(01)00451-5.

Wolfe, J. A. 1980. Tertiary climates and floristic relationships at high latitudes in the northern hemisphere. – *Palaeogeogr., Palaeoclimatol., Palaeoeol.*, *30*, 313–323; https://doi.org/10.1016/0031-0182(80)90063-2.

Žatková, L., R. Milovský, A. Bechtel, D. Starek, R. Pipík, J. Šurka. 2023. *n*-Alkane and terpenoid fingerprints of modern biomass producers unveil floral changes recorded in postglacial alpine lake sediments, Tatra Mountains, Slovakia. – *Org. Geochem.*, *184*, 104672; https://doi.org/10.1016/j.orggeochem.2023.104672.

Постъпила на 20.04.2024 г., приета за печат на 29.05.2024 г.
Отговорен редактор Йоцо Янев