



Biomarkers as a proxy for unravelling palaeoenvironmental conditions in the Central Paratethys during the Early Oligocene, Vrancea Nappe, Eastern Outer Carpathians, E Romania

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At the Eocene/Oligocene boundary a large, isolated basin called Paratethys arose as an effect of advancing collision of Africa and Eurasia and subsequent Tethys Ocean closure. In the Oligocene, Paratethys basin which stretched from the modern-day Alpine Molasse basin in the west through the Outer Carpathians, Black Sea and Caspian Sea region to the Aral Sea in the east became a suitable setting for the organic matter (OM) accumulation. OM was buried in sediments, named Menilite Shales, deposited in the Central Paratethys, where Carpathian Foredeep basin developed. The Menilite Shales are widely considered as hydrocarbon source rocks, containing wealth of information about this significant Oligocene anoxic event. The aim of this research was to get a detailed insight into the palaeoenvironmental conditions in the Early Oligocene by biomarker examination of the Menilite facies from the representative cross-section of the Vrancea Nappe recording sedimentation in the Carpathian Foredeep basin of the Central Paratethys.

More than twenty samples of finely laminated black, siliceous shales, cherts and bituminous marls were collected near Piatra Neamț city in the Bistrița half-window belonging to the Vrancea Nappe, Outer Carpathians, E Romania and subjected to the organic geochemical analysis. This comprised of Soxhlet solvent extraction in DCM:MeOH (7.5:1 v:v), column chromatography of extracts into aliphatic (in n-hexane), aromatic (in n-hexane:DCM, 9:1 v:v) and polar fractions (in DCM:MeOH, 1:1 v:v), derivatization of polar fractions with MTBSTFA (N-tertbutyldimethylsilyl-N-methyltrifluoroacetamide) and finally GC-MS analysis of all the fractions.

Biomarker composition varies among the samples and indicates diversified OM sources. Dominance of steranes (aliphatic and aromatic) in almost all the samples implies general high level of autochthonous, algal OM production in the basin. Certainly, diatoms were important group of OM producers as inferred from the occurrence of C₂₅ highly branched isoprenoid (HBI) thiophenes. On the other hand, presence of the aromatic conifer biomarkers, like retene or simonellite and odd-over-even long chain n-alkane predominance characteristic for epicuticular leaf waxes point to common admixtures of land plant-derived OM, transported most probably by rivers to the basin.

Reduced sulfur sequestration proceeded mainly via pyrite formation in the water column as derived from the common presence of small pyrite framboids (<5 μm) in the rocks, while early diagenetic sulfur incorporation into OM was limited to HBI precursors and late diagenetic formation of dibenzothiophene and its alkyl homologues.

Temporal photic zone euxinia in the water column was revealed by the occurrence of isorenieratene diagenetic derivatives (aryl isoprenoids) together with Me,_i-Bu maleimides originating from bacteriochlorophyll c, d or e. Both biomarker groups are characteristic for the green sulfur bacteria (Chlorobiaceae) requiring light and reduced sulfur to thrive.

Most of the biomarker-based redox indicators suggest rather suboxic conditions during OM transformation, which contradicts anoxia derived from the specific pyrite framboids distribution dominated by small-sized species. Early diagenesis of precursors from photoautotrophic organisms probably began in the upper oxidized water column, e.g. by photodegradation, limiting precursor reactivity toward reduced sulfur. In contrary, pyrite framboids were formed deeper in the water column near chemocline.