

Molecular and isotopic characterization of hydrocarbons: effects of palaeoenvironment and prograde metamorphism

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The changes in organic and isotopic geochemical compositions in sedimentary rocks record the palaeoenvironmental conditions prevailing during sedimentation and the postdepositional physicochemical (P, T, pH, fO₂, fH₂O, catalytic potential of sulfur) transformations. This thesis studies these geochemical changes in a carbonate shelf sequence deposited on the northern shallow-epicontinental Tethys margin. The first part of the thesis aims to reconstruct the palaeoenvironmental conditions that occurred during deposition of the Lower Liassic Frick sediments in the Swiss Jura. The second part evaluates the effects of prograde metamorphism on the organic compounds in the Lower Liassic black shale by studying a complete metamorphic sequence ranging from diagenesis at <100°C in the Swiss Jura (Frick) to amphibolite facies metamorphism at >550°C in the north of the Swiss Alps (Lukmanier). The distribution and δ¹³C values of source-specific hydrocarbons (HCs) in Middle Hettangian to Upper Sinemurian sedimentary rocks of the Frick section indicate higher algal, cyanobacterial and phytoplanktonic productivity upsection. This is associated with a ¹³C-enrichment of cyanobacteria derivatives and kerogen, indicating isotopically heavier dissolved CO₂ in the upper layers of the water column. These geochemical changes are related to increasing oxygenation and depth of the water column. In Middle Hettangian, the occurrence of anaerobic photosynthetic green sulphur bacteria (Chlorobiaceae) derivatives indicates depositional environments with euxinic conditions up to the photic zone, allowing for anaerobic photosynthesis. The ¹³C-depleted hopanoids (-39.5‰) are most likely derived from phototrophic purple sulphur bacteria utilizing isotopically light organic carbon at the base of the aerobic zone. These bacteria may have consumed the H₂S produced by Chlorobiaceae in the deeper layers and thus, sustaining algae, cyanobacteria and dinoflagellate productivity in the upper photic zone. In this sulfur-rich environment, the higher extent of the n-alkyltoluenes isomerization and naphthalenes methylation is related to the ability of sulfur to increase the acidic potential of the source rocks and to promote the transfer of electrons among reactants. The transformations of molecular and isotopic compositions of HCs are clearly related to metamorphism. In the diagenetic samples (<100°C), the occurrence of the thermally less stable terpenoid and steroid isomers such as 17b(H)-trisnorhopane, C₂₉ to C₃₁ 17b(H), 21a(H)-hopanes and 5a(H), 14a(H), 17a(H)-20R C₂₇, C₂₉ steranes are characteristic of immature bitumens. From diagenesis (<100°C) to the medium anchizone (~250°C), the molecular maturity parameters display the expected trend resulting from the combined preferential degradation and generation of individual HCs. From the medium anchizone to the amphibolite facies of metamorphism (~550°C), these parameters display constant values. A progressive increase of the n-C₁₂₋₁₃ / n-C_{total} ratio and ¹³C-enrichment (up to 5.6‰) of the n-alkanes with metamorphism suggests the predominance of β-scission of the C-C bonds during thermal cracking of the long-chain homologs. The predominance of specific HCs in metamorphic samples (> 200°C) such as cadalene, bibenzyl, hydrogenated aromatic compounds, and the increasing relative abundance of C₁₄,

C16 and C18 n-alkylcyclopentanes formed by direct cyclization of kerogenlinked algal or bacterial fatty acids, indicate organic matter transformations occurring in reducing aqueous fluid. The coherence of the maturity parameters and of the C-isotopic compositions of n-alkanes, aromatic compounds, kerogen and the associated bitumen with increasing metamorphism, suggests that indigenous HCs may survive in metamorphic rocks at temperatures above 500°C. The thermal stability of kerogen and associated organic compounds was most likely increased by the presence of reducing aqueous fluid and elevated pressure.