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EARLY RESTRUCTURING PROCESSES OF COALY ORGANIC MATTER AS REVEALED BY LC- AND GC-MS ANALYSIS OF THE BITUMEN FRACTION

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This study develops alternative methods to evaluate restructuring processes of coaly organic matter (OM) during early to moderate maturation. Although different hetero-compound fractions are analysed, the focus is on changes to the aromatic compound composition of the extractable OM. Therefore, we introduce LC-MS, in addition to GC-MS analysis, as a rapid and efficient method to follow molecular maturity trends.

The idea behind our studies is to ascertain the influence of maturation-induced restructuring processes of OM on the release of low molecular weight (LMW) compounds (e.g., CO_2, acetate, methane, hydrogen, etc.) from terrestrial bitumen as substrates for the deep biosphere.

Studies are performed on a series of Cretaceous–Cenozoic humic coals within the New Zealand Coal Band that comprises a relatively restricted range of coaly organofacies. The selected samples cover a maturity range from Suggate rank [Rank(S_r)] 0 (peat; R_o c. 0.25%) to 12 (high volatile bituminous; R_o c. 0.8%) (Suggate, 2000); i.e., up to the maturity threshold for oil expulsion (Sykes and Snowdon, 2002).

Bulk geochemical data already indicate complex OM reorganisation with increasing maturation. Asphaltenes, for instance, show a clear decrease from peat to high volatile bituminous coal. In contrast, no trend is observed for total maltene amounts, indicating that processes such as insolubilisation (i.e. incorporation into the kerogen) occur mainly between the kerogen and asphaltene fractions. This inference is supported by changes between maltene fractions obtained from Iatroscan screening.

Our application of aromatic hydrocarbon analysis by LC-APCI-MS is based upon the chromatographic separation of aromatic compounds according to the number of aromatic rings due to charge-transfer interactions (e^- donor/acceptor). Results show that variations in aromatic compound patterns and concentrations are related mainly to the stage of maturity and only to a minor extent to organofacies variation. One obvious maturity trend is a general shift in molecular aromaticity, i.e. an overall increase in the number of aromatic rings, although concentrations of tri- and tetra-aromatic biomarkers decrease due to either degradation or insolubilisation. In contrast, monoaromatic biomarkers first increase at early maturation stages, possibly as a result of formation from aliphatic or polar precursors, before decreasing at c. Rank(S_r) 5–6 (sub-bituminous; R_o 0.38–0.43%). This decrease coincides with the start of generation of polyaromatic hydrocarbons (PAH) from kerogen at Rank(S_r) 5–6. The amounts of PAH increase with maturity and thus follow the expected trend also with regard to the enhanced occurrence of PAH containing 3, 4 and 5 aromatic rings. Screening for highly condensed PAH (>7 aromatic rings) by LC-APCI-MS was carried out on different polar HMPLC fractions (Willsch et al., 1997) but none were detected for the studied maturity range.

Results of GC-MS analysis on individual terpenoid groups further confirm increasing ring aromatisation from Rank(S_r) 5–6. For example, the degree of aromatisation within ß- and α-amyrin, and abietane derivatives first decreases and then increases from Rank(S_r) 5–6.

Initial evaluation of hetero-functional alkyl compound distributions shows that with increasing maturity polar compounds are degraded, and at higher maturities acids and esters are generated. We observed significant changes in alkyl compound proportions of different polarity, with a decline from 58% *n*-alcohols in a low mature sample to 3% in a slightly more mature sample. These changes in the proportions of functionalised alkyl compounds are considered to be primarily maturity related and may be the result of the incorporation of specific compounds such as alcohols and fatty acids into asphaltenes and/or kerogen during early maturation, similar to processes described for higher ranks (Larter et al., 1979).

Further investigation of the proportional changes in the molecular composition of coal bitumen should allow interpretation of OM restructuring during maturation and with that, estimation of the concomitant release of LMW compounds, with regard to their potential to provide substrates for the deep biosphere.

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