DIAGENETIC CONTROLS ON DISTRIBUTION OF METHYL- vs. PHENYL-DERIVATIVES OF POLYCYCLIC AROMATIC COMPOUNDS

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Factors controlling the relative abundance of polycyclic aromatic compounds (PACs) in geological environments have not been well understood yet. Some alkylated PACs can be formed by diagenetic methylation/transmethylation of parent unsubstituted molecules. Many unsubstituted PACs originate from thermal oxidative decomposition and combustion of organic materials and fossil fuels. Others like e.g. cadalene and retene are undoubted biomarkers. In contrary to the alkylated and unsubstituted PACs a few studies deal with phenylpolyarenes (Marynowski *et al.*, 2002). Herein, phenylated PACs are investigated in regard to their origin and distributions in geological samples.

In a rock sequence characterised by the uniform organic matter source the factor controlling the type of PACs derivatives is redox condition during diagenesis. This can be best shown in samples from the North-Sudetic Syncline, Poland, collected in the Konrad copper mine, which represent the lowermost Zechstein section. For example, the dominating dibenzofuran derivatives differ depending on the sample position in the section. In the samples representing diagenesis upon low oxygen fugacity containing pyrite, galena and chalcopyrite, methyldibenzofurans (*m/z* 182) significantly dominate (Fig. 1a), while in the samples representing higher oxygen fugacity as revealed by presence of hematite, anhydrite, and e.g. chalcocite, phenyldibenzofurans (*m/z* 244) prevail (Fig. 1b). Both alkyl and phenyl derivative series are characterised by the same relative abundance of the corresponding positional isomers. The dominant are 4-methyl and 4-phenyldibenzofurans, followed by 2-, 1- and 3- derivatives (Fig. 1). Interestingly, for the other common PACs, e.g. phenantherne and dibenzothiophene, both series of the corresponding alkyl and phenyl positional isomers distribution are strikingly similar. This may suggest the same controls on the distribution of both series.

Changes in oxygen fugacity log fO_2 arising from anhydrite precipitation or dissolution and pyrite/hematite oxidation/reduction is able to cause large changes in hydrocarbon speciation (Fig. 1). Those samples, which contain the higher amounts of phenyl derivatives (Fig. 1b) are also characterised by very low yields of aliphatic fractions containing mainly short chain *n*-alkanes (Püttmann *et al*., 1989). This is indicative for hydrolitic hydrocarbon

disproportionation operating during diagenesis due to large organic matter-water interfaces with small HC/water ratios in the proximity of permeable sandstones. Reaction governing the PACs distribution is demethylation. Moreover, in such aqueous environments relatively well water-soluble benzene is ubiquitous and can serve as source of phenyl species.

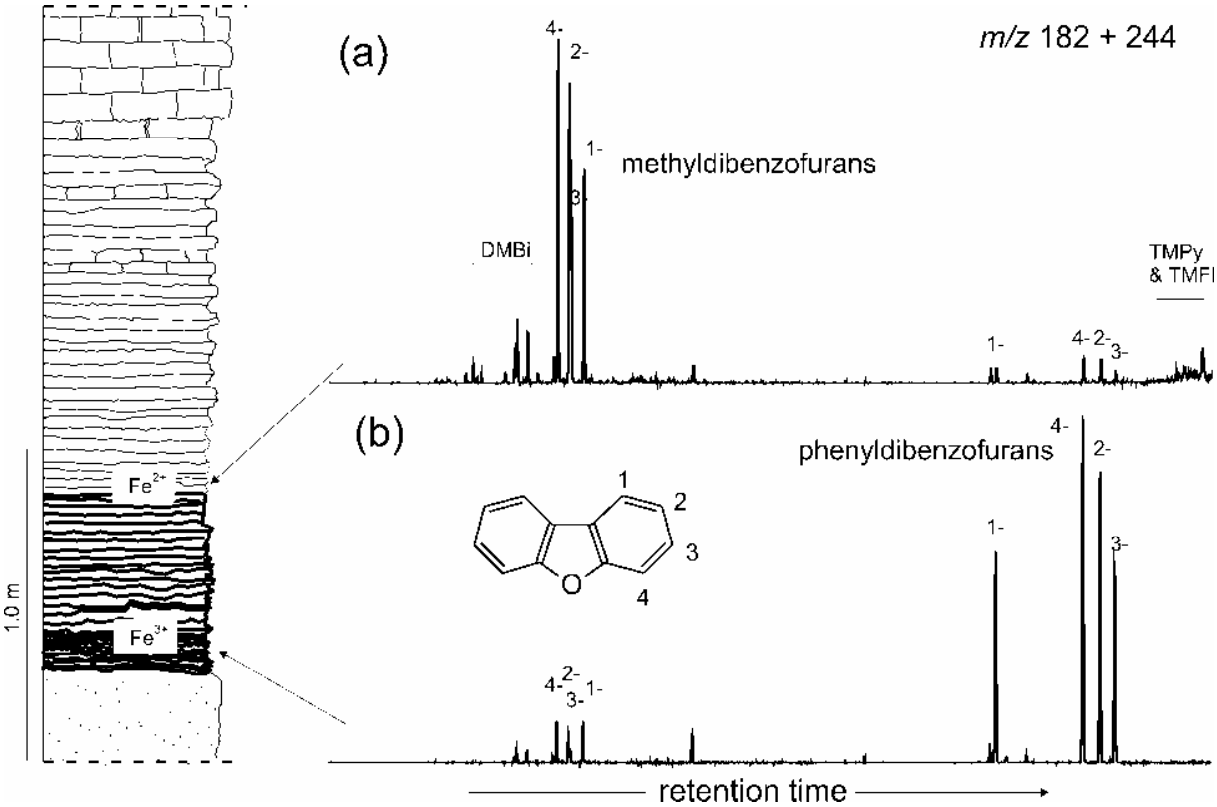

Figure 1. Shift of the prevailing dibenzofuran derivatives from methyl- (*m/z* 182) to phenyldibenzofurans (*m/z* 244) on approaching the redox boundary downward in stratigraphic column of the lowermost Zechstein (the Konrad Mine) (DB-35MS column). DMBi – dimethylbiphenyls, TMPy – trimethylpyrenes and TMFl – trimethyfluoranthenes.

In contrast, the long chain *n*-alkanes in the upper part of the rock sequence seems not to be effected by hydrocarbon disproportionation as suggested by slight predominance of odd over even carbon molecules, indicating that the prevailing reaction responsible for hydrocarbon distribution took place in environments with higher HC/water ratios. The prevailing substituting groups of PACs are methyl species (Fig. 1a). Summarising, the similarities in distribution of alkyl and phenyl PACs derivatives of a given parent PAC molecule is controlled by the similar molecule positional reactivities.

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