

GEOCHROMATOGRAPHIC SEPARATION OF ORGANIC TRACERS USING A NATURAL DRAUPNE (KIMMERIDGE CLAY) SOURCE ROCK COLUMN

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Introduction

The earliest stage of petroleum movement in a natural system is called primary migration. It comprises both the flow of petroleum within a source rock, as well as the discharge of oil and gas into surrounding carrier bed or reservoir units, a process that is termed expulsion. Compared to secondary migration, which has been studied intensely, primary migration so far received comparatively little interest. Previous research has, however, demonstrated that primary migration occurs along with molecular fractionation between asphaltene-/resin-rich source rock bitumens and hydrocarbon-rich oils (Mackenzie et al., 1983; Leythaeuser et al., 1984, 1988). Geochromatographic interactions, i.e. selective adsorption, partitioning into organic matter, ion exchange with minerals, and size exclusion/molecular sieving have been discussed as potential reasons for such fractionation effects (Krooss et al., 1991). Here, we conducted a chromatographic retardation experiment comprising source rock material from mature parts of the Upper Jurassic Draupne (Kimmeridge Clay) Formation to examine the influence of geochromatography on selected organic tracers representing frequently applied organic geochemical proxy molecules. To our knowledge, this was the first time that a chromatographic experiment involved natural, oil-window mature source rock material.

Procedures

A 2 ml stock solution containing selected organic tracers was passed gravitationally through a chromatographic column (20 cm x 1 cm, 15 cm filling height) loaded with ground, excessively pre-extracted (ASE, Soxhlet), and 10% water-saturated oil-window mature Draupne source rock material via a synthetic oil. The composition of the synthetic oil reflected the basic composition (saturates, aromatics, heteroatomic compounds) of a natural crude. Altogether, 32 fractions (0.8 to 8 ml) were collected and quantitatively analyzed by gas chromatography-mass spectrometry (GC-MS) after addition of 10 µl of 9-phenylcarbazole (10 µg/ml) to each fraction as internal standard.

Results and discussion

Fig. 1 illustrates the results of the experiment. Summarized, our data demonstrate a geochromatographic fractionation of the tracer stock solution and therefore selective retention of certain organic compounds in the source rock column, due probably to molecular interaction with minerals (particularly clays) and/or kerogen. Although not fully comparable to a natural petroleum system, the observations have important implications concerning primary migration. In particular, the results indicate a preferential expulsion/migration of dibenzofurans, phenanthrenes, and dibenzothiophenes over carbazoles, a stronger retention of nitrogen-exposed vs. (partially) nitrogen-shielded C₂ carbazoles, and a faster migration of benzo[a]- relative to benzo[c]carbazole. Moreover, alkylated carbazoles were shown to elute earlier than

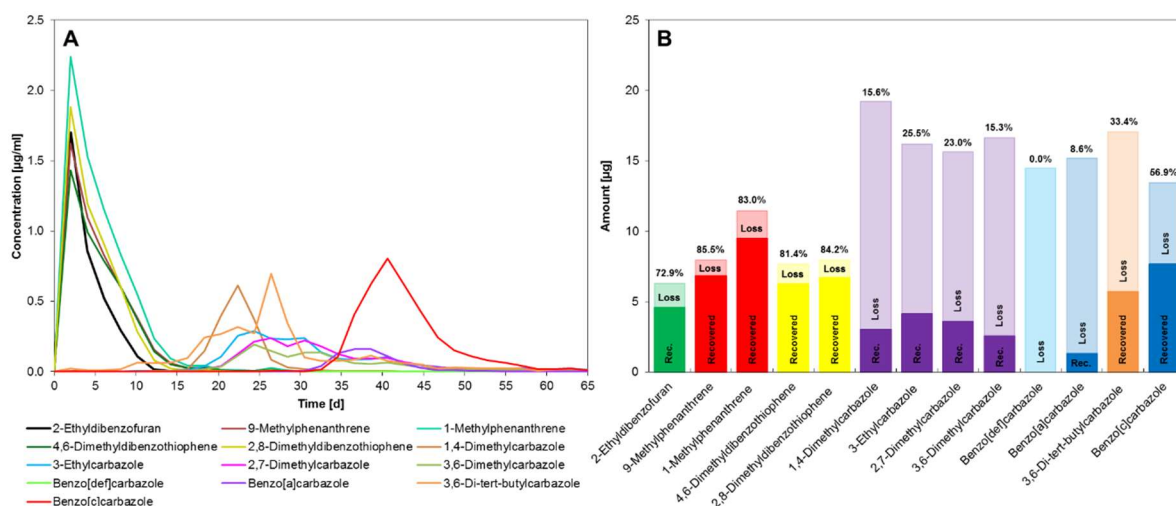


Fig. 1. Results of the geochromatographic retardation experiment comprising natural Draupne (Kimmeridge Clay) source rock material. A: Concentrations of tracer molecules in the eluates over time. B: Mass balance approach with the recovery rates of the added tracers given above the columns.

benzocarbazoles, whereby the migration speed appears to depend on the degree of alkylation, as suggested by the relatively early occurrence of the highly alkylated 3,6-di-tert-butylcarbazole compared to its less alkylated analogues. Benzo[def]carbazole was not detected in the eluates, indicating strong retardation by the source rock column. Also, no significant fractionation between 9- and 1-methylphenanthrene was found. A mass balance approach revealed that overall 72.9% of the dibenzofuran, between 83 to 86% of the phenanthrenes, and around 81-85% of the dibenzothiophenes were successfully recovered. By contrast, carbazoles were generally much stronger retained, likely because of intense molecular interaction with mineral surfaces and/or organic material. Remarkably, despite the later occurrence in the eluates, substantially higher quantities of benzo[c]- (56.9%) compared to benzo[a]carbazole (8.6%) were recovered. With respect to natural systems, this implies that the first oil expelled into a secondary migration system likely has a very high benzocarbazoles ratio (Larter et al., 1996), which then continuously decreases over time. To complete the mass balance approach, we are currently demineralizing (hydrofluoric acid) and subsequently solvent extracting (dichloromethane) parts of the column to release mineral-bound tracers. Additional geochromatographic experiments similar to that presented here are necessary to provide further insights into molecular redistribution processes during primary migration. For example, future retardation experiments could comprise additional organic tracers (e.g. *n*-alkanes, *iso*-alkanes, biomarkers, alkylated vs. non-alkylated compounds), different or mixed source rock material, and/or modified experimental conditions (pressure, temperature). Moreover, it would be interesting to flow a natural crude oil through the column.

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