

BIOMARKERS OCCLUDED IN ASPHALTENES AS REVEALED BY MILD OXIDATION OF H₂O₂/CH₃COOH: GEOCHEMICAL IMPLICATIONS

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The previous studies showed that the mild oxidation system, H₂O₂/CH₃COOH, can release the occluded hydrocarbons from asphaltenes without interference from the oxidation treatment. The occluded hydrocarbons can be considered as the components derived from kerogen in early time of oil generation, and little affected by the secondary alteration processes occurring in petroleum reservoir, and then have some special significance in studies of reservoir geochemistry. In this work, the asphaltenes were prepared from the oil (Ym2 from Tarim Basin, China). The occluded hydrocarbons were released by the oxidation system (H₂O₂/CH₃COOH) and studied by gas chromatography-mass spectrometry, and their geochemical significance discussed.

The preliminary experimental results indicated that the occluded component has different characteristics compared with those from free oil and absorbed fraction (from the acetone extracts of the asphaltenes). Plenty of branched alkanes, such as mono-methylalkanes (MMAs), multi-alkylalkanes (MAAs) and alkylcyclanes (ACs) were identified from the occluded component. These branched alkanes showed a wide range distribution of carbon number (C₁₅-C₃₁), dominated within *i*C₁₈-*i*C₂₅. Nevertheless only a small quantity of branched alkanes was found in the free oil and the adsorbed fraction (in Fig.1 (TIC)). Additionally, the biomarker assemblage of these components (free oil, absorbed and occluded ones) also revealed distinct differences among them. Mass fragmentograms of steranes from the occluded component (m/z 217) showed a significant predomination of C₂₇ steranes and relatively low concentration of diasteranes. However, the steranes from the free oil and absorbed fraction were characterised by no predomination of C₂₇ and C₂₉ steranes, or a slight predomination of C₂₉ steranes, and relatively high concentration of diasteranes. In regard to the characteristics of terpanes from these components, as can be seen from Fig. 1 (m/z 191), the terpanes of the occluded component showed a relatively predomination of the low carbon number tricyclic terpanes, and the C₃₀ hopane had a relatively higher concentration than the C₂₉ norhopane. But the terpane distributions of the free oil and the absorbed fraction showed the opposite results.

The occurrences of abundant MMAs, DMAs and ACs in the occluded component in asphaltenes may imply that the crude oil was derived from some lipid-rich precursors (algal or bacteria) that can be formed and preserved in reduction sedimentary-water environment, which is accordant with the prevalent viewpoint that this oil (Ym2) was derived from Cambrian marine source rocks under reduction environment.

The present data cannot explain the above-mentioned differences of biomarker characteristics among the free oil, adsorbed and occluded components. However the differences between the free oil and the occluded components indicated that the occluded hydrocarbons could not be exchanged with the free oil, and maybe preserved some important information little affected by the secondary alteration of petroleum. Likewise, the biomarker distributions have almost the same distribution features, due to exchange between the adsorbed fraction and the free oil. In order to obtain more geochemical information from and get a better explanation for these experimental results, the further work is under way.

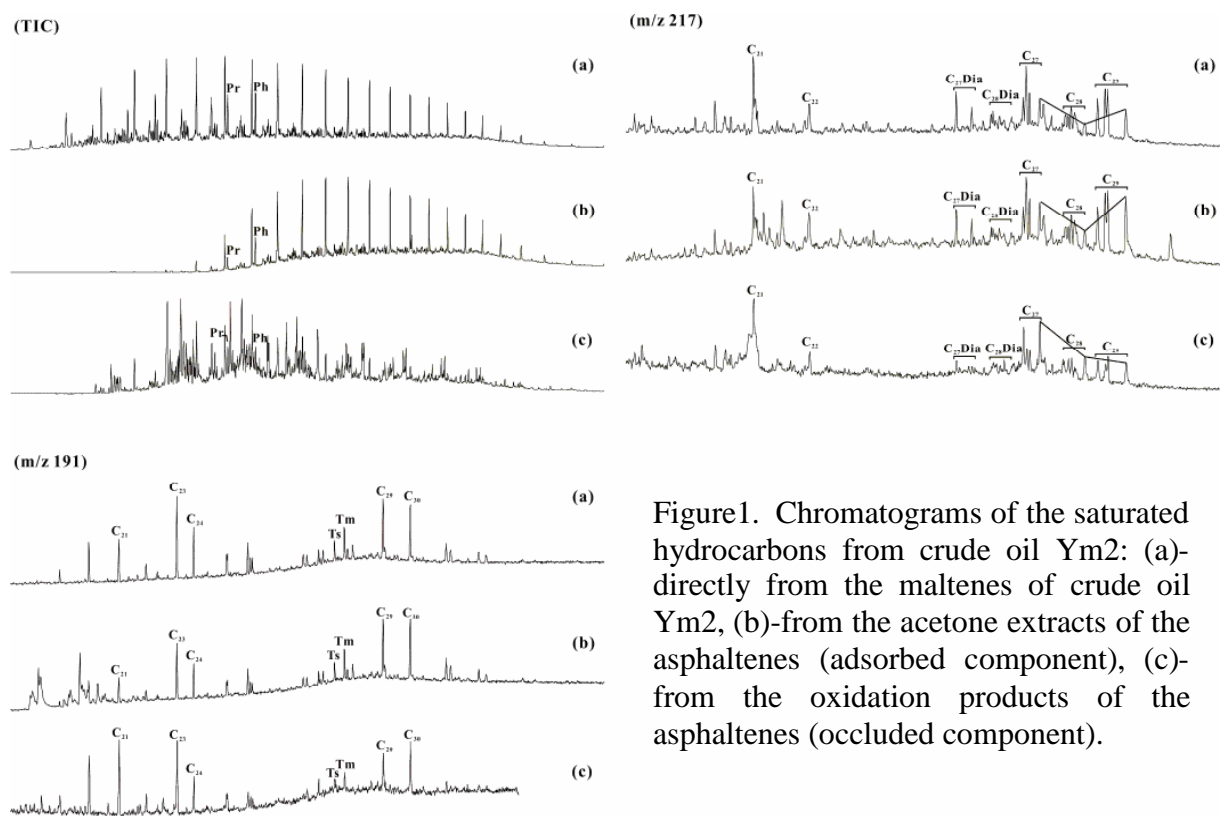


Figure1. Chromatograms of the saturated hydrocarbons from crude oil Ym2: (a)-directly from the maltenes of crude oil Ym2, (b)-from the acetone extracts of the asphaltenes (adsorbed component), (c)-from the oxidation products of the asphaltenes (occluded component).