FIRST EVIDENCE OF GREEN PIGMENTED CHLOROBIACEAE BIOMARKERS FROM CRETACEOUS CRUDE OILS (SERGIPE-ALAGOAS BASIN, BRAZIL)

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The occurrence of isorenieratane and related compounds in Sergipe-Alagoas Basin suggests that the photic zone euxinia (PZE) (i.e., sulfidic environment) dominated the Brazilian marginal basin during the deposition of Cretaceous OM, at least temporarily. The diaromatic carotenoids (e.g., isorenieratane) and aryl isoprenoids are important aromatic hydrocarbons from Sergipe-Alagoas Basin and related Brazilian Cretaceous geological samples (Sousa Júnior et al., 2013) and their occurrence indicates the presence of brown-pigmented green sulphur bacteria (GSB, Chlorobiaceae) (Sinninghe Damsté and Schouten, 2006 and references therein). In this work, the high-temperature comprehensive two-dimensional gas chromatography-time-of-flight mass spectrometry (HT-GC×GC−TOFMS) was applied to the investigation of diagenetic aromatic carotenoids and aryl isoprenoids in Cretaceous crude oils (BSO1−BSO5) from Sergipe-Alagoas Basin, Brazil.

The crude oils (ca. 100 mg) were submitted to activated silica gel column and fractionated in saturated hydrocarbon, aromatic hydrocarbon, and polar compound fractions, respectively. To aromatic hydrocarbon fractions were added the perdeuterated pyrene (C16D10) internal standard in dichloromethane at 5.0 ng/µL (98% purity, Cambridge Isotope Laboratories, Andover, MA, USA). The aromatic hydrocarbon fractions were analysed on a Pegasus 4D GC×GC−TOFMS system (Leco Corporation, St. Joseph, MI, USA) using non polar/mid-polar column configuration (DB5-ms/BPX-50, 1D/2D). Aryl isoprenoids and aromatic carotenoids (m/z 119, 120, 134 and 237) were identified based on extracted ion chromatogram (EIC), retention time on first and second dimensions, elution order and comparison with literature mass spectra.

C40 isorenieratane and C32 and C33 diagenetic compounds, including β-carotene derivatives, were detected in the crude oils from Sergipe-Alagoas Basin, based on EIC m/z 134 and mass spectra. EIC m/z 237 shows the C18-C40 pseudo-homologous series (BP18−BP40) of biphenyl isoprenoids (molecular formula CnH2n+14) with unsaturation index 8, which were identified as 2,3,5',6-tetramethyl-2'-alkylbiphenyls derivatives (BP40), as shown the Fig. 1A. In addition, EIC m/z 237 shows the diagenetic compounds BPA32, BPA33, BPI40, BP40 and BPBP40.

However, EIC m/z 237 showed double peaks on isothermal 1D-GC separation, which were previously attributed to atropisomers related to petroleum biphenyls (Koomans et al., 1996; van Duin et al., 1996). Two diastereoisomers were detected on multi-ramps 2DGC (Fig. 1C) when compared to single-ramp (Fig. 1B). These molecules have an axial chirality and a high rotational barrier due to the hinderance caused by the ortho-methyl groups of 2,3,6-trimethylbenzenes (Koopmans et al., 1996). The structured chromatographic plane suggests that BP40 may have a similar pattern to BP4. Thus, the presence of chlorobactane (C40 2,3,6-trimethyl isoprenoid) and the diagenetic biphenyl chlorobactane (BP40) in Sergipe-Alagoas oils (BSO1 and BOS3) may indicate the contribution of green-pigmented GSB (Chlorobiaceae) in the nearshore, shallow-water (< 20 m depth) stratified paleoenvironment (cf. modern environment) (Brocks and Schaeffer, 2008 and references therein).
Figure 1 (A) EIC m/z 237 - distribution of pseudo-homologous of 2,3,5',6-tetramethyl-2'-alkylbiphenyls ($BP_{18}$ – $BP_{40}$) and diagenetic biphenyls ($BPn$, $BP_{40}$, $BPBP_{40}$, $BPI_{40}$) in aromatic fraction of BSO3 crude oil, Sergipe-Alagoas Basin, (B) single-ramp and (C) multi-ramps 2DGC for separation of atropisomeric biphenyls. Diagenetic structures: $BPA_{32}$, $BPA_{33}$, $BPI_{40}$, $BP_{40}$ and $BPBP_{40}$

References

Brocks, J.J., Schaeffer, P., 2008. Okenane, a biomarker for purple sulfur bacteria (Chromatiaceae), and other new carotenoid derivatives from the 1640 Ma Barney Creek Formation. Geochimica et Cosmochimica Acta 72, 1396–1414.


