Thermochemical oil formation in hydrothermal vent sediments at Guaymas Basin, Gulf of California, USA, and the search for a deep biosphere hydrocarbon fingerprint

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Accelerated petroleum production is occurring naturally at Cathedral Hill, a hydrothermal vent complex in Guaymas Basin, Gulf of California. At this site, high temperature vent fluids, projected to reach 155°C within only 21 cm sediment depths, are not only capable of pyrolyzing in situ organic matter to produce petroleum, but may equally begin to thermochemically break down these newly-cracked petroleum-forming compounds. In this study, we aim to elucidate how the hydrocarbon matrix is attenuated or added to by biodegradation, thermochemical degradation, in situ hydrocarbon production, and migration. To this end, a multi-molecular, chemometric survey using comprehensive two-dimensional gas chromatography (GC×GC) has been conducted on 34 samples collected from a four push-core transect extending from the center of the vent complex to the exterior of an overlying *Beggiatoa* microbial mat. Preliminary extract data and matrix compositional patterns resolved by hierarchical cluster analysis, and multi-way principal components analysis of stacked whole GC×GC chromatograms of the entire sample set, indicates a patchy distribution of elevated oil signatures. One of these is a thin horizon uniformly extending across the transect at ~6–10cm sediment depth. Subtracted GC×GC chromatograms also reveal elevated levels of high-temperature pyrolytic hydrocarbons, including relatively high abundances of higher molecular weight PAHs (pyrenes-coronene) and equivalent perhydro-PAHs, at ~6–10 cm depth consistently across-transect. This band corresponds to a wide range of sediment temperatures spanning 18 to 125°C, which for the outer perimeter of the vent is too low for active in situ pyrolysis. Furthermore, the presence of abundant archaeal *glycerol dialkyl glycerol tetraether* (GDGT) core lipids and a lack of significant biphytanes in the apolar fractions of solvent extracts, suggests sediment temperatures are too low to promote cleavage of isoprenoid skeleton ether bonded to glycerol of the core lipid. Collectively, these data indicate the oil derives from multiple charge events deeper within the basin. Lastly, ratios of low to intermediate molecular weight *n*-alkanes and acyclic isoprenoids show increasing levels of biodegradation (reaching 2–3 on the Wegner *et al.* 2002 biomarker biodegradation scale) down-core across the transect. An unknown pseudohomologous series of tetracyclic compounds, along with decoupled ratios of bacterial-sourced lipids C_{30} hopene and C_{30} hopane (indicating the hopene biomarker is not being thermally altered to hopane) implies that a living microbial community is hosted by the vent complex shallow sediments.

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