SEARCHING FOR A DEEP BIOSPHERE, HYDROCARBON FINGERPRINT IN HYDROTHERMAL VENT SEDIMENTS AT GUAYMAS BASIN

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Conventional petroleum producing basins evolve over millions of years with sediment accumulations reaching thousands of meters thick. These systems involve a mixed input of sedimentary organic matter, making their diagenetic and catagenetic evolution difficult to disentangle. Many, if not all, of these basins also contain a deeply buried subsurface microbiome. As these microbes die their remains are recycled, or added to the existing pool of buried sedimentary organic matter. It is unknown to what degree, if any; these post depositional overprints affect the primary signature of solvent-extractable hydrocarbons.

At sedimented, mid-ocean spreading ridges, the circulation of hydrothermal fluids near the seafloor generates vent temperatures up to 350°C, which almost instantly pyrolyzes organic matter resulting in the rapid acceleration of petroleum hydrocarbons in shallow sediments (i.e. Simoneit, 1988). These environments are also home to a subsurface microbial biosphere (i.e. Amend and Teske, 2004). We therefore hypothesize that the conditions in these systems will 1) improve our understanding of how mixed-source inputs of organic matter are naturally transformed into petroleum and 2) resolve to what extent the molecular constituents added by the subsurface microfauna can be detected.

Guaymas Basin is a submarine depression at the northern end of the East Pacific Rise, mid-oceanic spreading ridge in the Gulf of California. Various hydrothermal vent complexes occur along this margin. One of which is Cathedral Hill, a cluster of white smokers encrusted with giant tube worms (*Riftia pachyptila*) and surrounded by a *Beggiatoa* sulfur oxidizing microbial mat. Cathedral Hill receives high inputs of organic matter from elevated productivity in the overlying surface waters and runoff from the surrounding continent. The high sedimentation rate produces near-uniform compositions of sedimentary organic matter that is further mixed with the benthic and subsurface micro- and macro-fauna.

Four push cores (ranging from 16-23 cm deep) were collected along a transect line running from the center sulfide chimney complex to the outside of the microbial mat using HOV *Alvin*. Thermal-probe measurements yielded dramatic increases with depth. By 7-9 cm pore-fluid temperatures were 200°C indicating, the active microbiome necessarily resides in the upper 6 cm (from 18-105°C) of sediment. Upon collection, push cores were immediately sectioned into 2 cm-thick blocks. The resulting samples were frozen in pre-backed glass vials at -70°C and lyophilized prior to solvent extraction. Polar and maltene abundances peak at 5-14 cm depth (Figure 1a and b) suggesting that this range marks the zone of catagenesis, with core 4462-3 located just exterior the mat having a much broader polar lipid profile (Figure 1a).

The maltene and polar fractions were further analyzed by comprehensive two-dimensional gas chromatography (GC×GC) and Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) in electrospray ionization mode, respectively. The maltene fractions of these sediments contain up to 6200 compounds with abundant bacterial, archaeal, and eukaryote biomarkers (Figure 1c). Future studies using difference chromatograms and multi-way principle components analysis of GC×GC-FID chromatograms will measure the mass loss/gain of all GC-amenable hydrocarbons as a function of depth and distance from the center of the chimney complex and track the rates and alteration pathways resulting in membrane lipids becoming mature biomarkers. The polar fractions contain an abundant array of acid and neutral compounds. Semiquantitative analysis of Z class ($Z_{number}=C_nH_{2n+z}+H_n$) and molecular weight distributions display systematic depth and distance changes, with acid and diacid functional groups being most resilient in these hydrothermal settings.

These functionalized and hydrocarbon fingerprints will be further compared with data on the microbial community composition collected from the same transect site. We expect that by using these multi-molecular techniques in conjunction with the data mining power of chemometrics we will be able to detect and quantify the pyrolyzed remains of the subsurface microbiota. If successful, this approach may eventually lead to similar detection schemes for conventional petroleum forming basins.

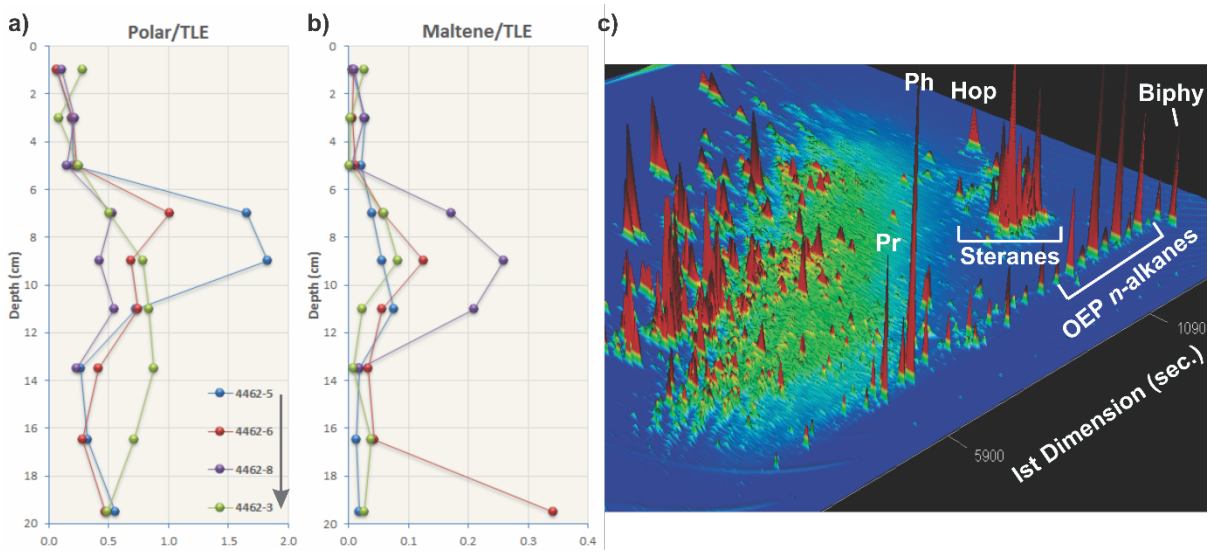

Figure 1 *Depth profiles of a) polar/total lipid extract (TLE) and b) maltene/TLE (arrow points from interior to the exterior of the vent field). GC×GC-FID chromatogram c) of the maltene fraction from core 4462-8 core, located near the perimeter of the microbial mat, at 6-8cm depth displaying pronounced bacterial (Hop=hopene), archaeal (Byph=biphytane), and eukaryote (Pr= and Ph=, pristane and phytane, respectively; steranes; and terrestrial plant wax (C_{25} to C_{33} odd-over-even preference (OEP) n-alkanes) inputs.*

References

Simoneit, B., 1988. Petroleum Generation in Submarine Hydrothermal Systems: An Update. *Canadian Mineralogist*, 26, 827-840.

Amend, J., Teske, A., 2004. Expanding frontiers in deep subsurface microbiology. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 219,131– 155.