SOURCE AND FATE OF HEAVY OIL AT DEEPWATER ASPHALT SEEPS IN THE SOUTHERN GULF OF MEXICO

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Environmental catastrophes such as the recent Deepwater Horizon oil spill in the Gulf of Mexico have spurred the need to better understand transformations of pollutants that may harm marine and coastal ecosystems (Joye et al., 2014). Of particular interest hereby is the role that microorganisms play in the aerobic and anaerobic degradation of petroleum and other toxins in the marine environment (Hazen et al., 2010). Deepwater asphalt volcanoes, discovered in 2003 in the southern Gulf of Mexico, are an ideal site to study such processes as they represent unique cold seep habitats that are nurtured by the seepage of hydrocarbon-rich gases and heavy oil. Previous studies have investigated aerobic and anaerobic chemosynthetic biological processes associated with asphalt seepage, including authigenic carbonate formation (Nähr et al., 2009), bacterial symbionts in mussels (Raggi et al., 2013) and the anaerobic oxidation of methane and other hydrocarbon compounds in oil-rich sediments (Schubotz et al., 2011a, b). However, none of these studies have targeted the geochemical alteration and transformation of the oil at the sediment-water interface. We revisited the Campeche Knolls in the southern Gulf of Mexico in 2015 to further explore microbial transformations of petroleum compounds at the seafloor and in the water column. During this expedition, multiple asphalt fields and oil seeps were targeted in water depths up to 3400 m in order to also assess the quantitative relevance of heavy oil and asphalt seepage in the Gulf of Mexico.

This study addresses fundamental questions related to the source and fate of deepwater asphalt deposits by using a comprehensive organic geochemical approach. Source and maturity-related biomarkers were investigated to understand processes involved in asphalt formation. Our results indicate that no substantial biodegradation has occurred within the asphalts and instead suggest that the high amounts of asphaltenes in these samples may have resulted from early generation of the oils. Post-depositional alterations of asphalts were investigated by two-dimensional gas chromatography coupled to mass spectrometry (GC×GC-MS). A sequential loss of aliphatic and aromatic compounds, including sulfur-containing hydrocarbons indicate that the asphalts are substrates for aerobic and anaerobic hydrocarbon degraders after deposition on the seafloor. To track the transfer of oxidized hydrocarbon species into the water column, we investigated both the molecular composition of the asphalt resins and compared it to the dissolved organic matter (DOM) of the overlying water column using ultrahigh-resolution mass spectrometry (FT-ICR-MS). Asphalt resin-derived molecular formulae were only partly found in the DOM pool, indicating only minor contributions to the polar petroleum-derived compounds in the overlying water. It is likely that either most of the oil is transformed and incorporated into microbial biomass *in situ* or that the oil-derived DOM pool is rapidly diluted and dispersed by bottom-water currents. Our field-based investigations will be amended by long-time (up to 10 year) asphalt incubation experiments that were designed to obtain both qualitative and quantitative information on the

types and amounts of hydrocarbon compounds that may be leached out of the asphalt by both biotic and abiotic processes.

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