

Hydrothermal petroleum in sedimented rifts

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Hydrothermal systems associated with oceanic spreading centers are now commonly known and the morphology, mineralogy, sedimentology, and fluid chemistry of the active systems in oceanic rifts have been amply reviewed. The geochemistry of the alteration of sedimentary organic matter to hydrothermal petroleum (bitumen) and the associated fluid interactions have also been described extensively (e.g., [Gieskes *et al.*, 1988; Simoneit, 1985, 1990; Simoneit *et al.*, 1984, 1992; Welhan and Lupton, 1987]). Only one sedimented hydrothermal system, i.e., the Guaymas Basin, Gulf of California, had been drilled by the Deep Sea Drilling Project prior to 1991 [Curry *et al.*, 1982].

ODP drilled the hydrothermal systems in Middle Valley during Legs 139 and 169 and the Escanaba Trough during Leg 169, both active sediment covered rifts in the northeastern Pacific Ocean [Shipboard Scientific Party, 1992, 1997; Mottl *et al.*, 1994]. Hydrothermal petroleum is produced in both of these systems from sedimentary organic matter by contact alteration with hydrothermal fluids. It consists of compounds generated over a greater temperature window (100°-400°C) than observed for conventional petroleum and proceeds from the biological

precursors that have not undergone diagenesis [Simoneit, 1994]. Fluid extraction and migration of hydrothermal petroleum from the source sediment is also highly efficient.

The organic matter in sediments at Site 139-857, for example, has experienced *in situ* accelerated diagenesis (natural maturation) and catagenesis (thermal maturation), yielding fully mature bitumen at depth. One interval appears to contain a minor amount of migrated bitumen, based on elevated yield (oil horizon). The biomarkers (molecular tracers) indicate a significant input of terrestrial components with the predominant material derived from marine autochthonous sources. Maturation has proceeded to yield *n*-alkanes with a strong even carbon number predominance. Due to the low organic carbon content these sediments do not generate high amounts of hydrocarbons from kerogen, as is the case in Guaymas Basin, thus revealing the unique even-to-odd preference of the *n*-alkanes in the mature samples.

The sedimentary organic matter at Site 139-858 for example has also been converted to hydrothermal petroleum. Relatively immature bitumen is encountered only in the upper few meters

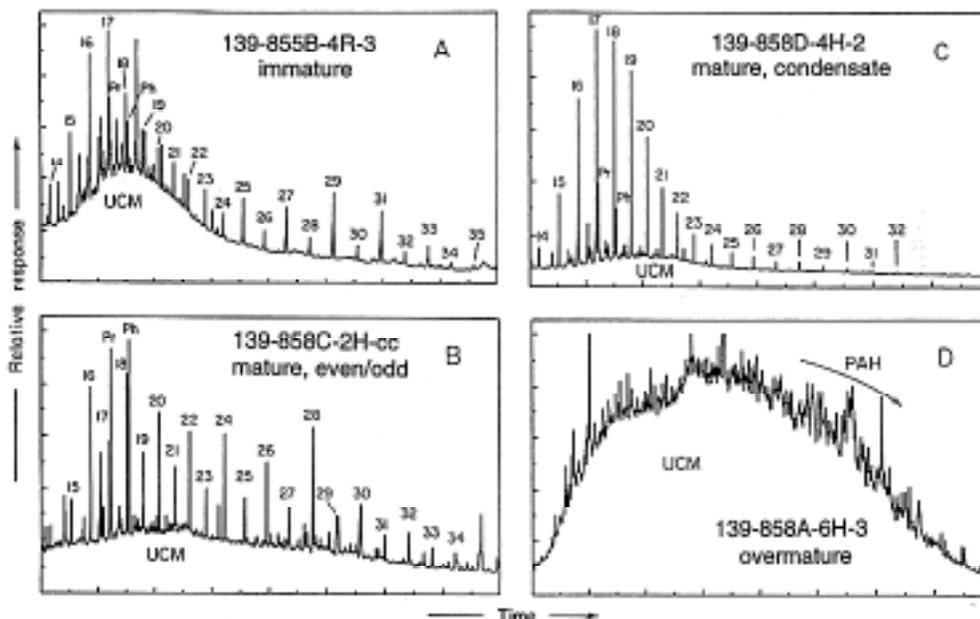


Fig. 1: Gas chromatograms of total extracts of representative samples of sediment lipids and hydrothermal petroleum. A) Immature lipids. B) Hydrothermal bitumen (mature). C) Condensate petroleum (mature). D) Overmature PAH and UCM. Numbers over peaks refer to *n*-alkanes, Pr = pristane, Ph = phytane, UCM = unresolved complex mixture of branched and cyclic compounds, PAH = polycyclic aromatic

of the holes (Fig. 1). The biomarkers in the upper sections show a moderate input of terrestrial components, with products derived predominantly from autochthonous marine sources. Maturation has progressed to form *n*-alkanes with a strong even carbon number predominance at depth. There is an over-mature bitumen interval in Hole 858A at about 50 mbsf (Fig. 1d). The different hydrothermal petroleum intervals (zones with high bitumen concentrations) have many compositions (condensates to asphalts) and maturities, reflecting formation in various temperature windows followed by lateral migration into the sediment sections sampled.

The biomarkers are present as precursors, intermediates, and fully mature products. The steroids are altered to stenones, stanones, and then steranes; the terrigenous triterpenols proceed to triterpenones, triterpenes, and then triterpanes; and the bacterial hopenes and hopanols are converted to hopanes. Maturation of the biomarkers begins here with the biogenic precursors and results in their interconversion to the thermodynamically most stable configurations as known in conventional sedimentary basins with mature organic matter. Cracking reactions degrade higher molecular weight compounds to smaller molecules (e.g., waxy oil to condensate, C₃₅ hopanes to the C₂₉ and C₂₇ nor compounds).

The high-temperature components in these bitumens are PAHs, as is the case for most hydrothermal petroleum studied to date. These samples contain only traces of low molecular weight PAHs and alkyl PAHs (e.g., phenanthrene/alkylphenanthrenes) and high concentrations of heavy PAHs. This is interpreted to result from the high solubility of the smaller PAHs in warm water and consequent removal from the sediments by pore-fluid flow. Such a process would then concentrate the high molecular weight PAHs in these sediment associated bitumens.

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