Weathering and biodegradation of hydrothermal petroleum in the north rift of Guaymas Basin, Gulf of California

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ABSTRACT

The Guaymas Basin, Gulf of California, is an actively spreading ocean basin, part of the system of spreading axes and transform faults extending from the East Pacific Rise to the San Andreas fault. Upward migration of hydrothermal petroleum in the basin occurs by both bulk transport and high temperature/pressure aqueous and supercritical gaseous (e.g. CO₂, CH₄) fluid phases into the seabed sediments. The resulting mounds are laden with the youngest hydrothermal petroleum known to date. The north rift hydrothermal system has been dormant for ~3000 years, and organic geochemical analyses of sediment samples collected by both piston and push corers and by dredging operations from various cruises to the Gulf of California show that the organic matter is composed primarily of autochthonous lipids from marine biota, overlain by hydrothermal petroleum. The chemical composition of this petroleum indicates severe biodegradation for exposed samples, based on the contents of aliphatic, aromatic, steroid, and hopanoid biomarkers. Sulfurized lipids are enriched in the biodegraded oils. Both hydrothermal minerals and petroleum in the mounds of the north rift seabed have been weathered by oxidative/microbial processes.

Key words: hydrothermal petroleum; weathering; biodegradation; north rift; Guaymas Basin.

INTRODUCTION

The discovery and exploration of submarine hydrothermal systems (Corliss et al., 1979), with their associated chemistry and chemosynthetic biota have had a great impact on the geosciences, biosciences and chemistry (Simoneit and Lonsdale, 1982; Rona, 1984; Barrett and Fox, 1988; Childress, 1988; Simoneit, 1990, 2018; Humphris et al., 1995; Bock and Goode, 1996). The sedimentary organic matter in and around such vent systems is usually marine, derived from bioproductivity of an immature Recent origin (Simoneit, 1982a). The gas/bitumen products generated by the rapid thermal alteration in high fluid flow systems (high water to rock ratio) of generally immature organic matter in such sediments is defined as hydrothermal petroleum (Simoneit, 1999).

The Guaymas Basin in the Gulf of California (a.k.a. Sea of Cortez) is a young marginal rift basin characterized by active seafloor spreading and rapid deposition of organic-rich, diatomaceous sediments from highly productive overlying waters (Calvert, 1966). The northern and southern axial troughs of Guaymas Basin are bounded by extensive systems of axial-parallel fault lines on both sides (Lonsdale, 1985; Lonsdale and Becker, 1985). Different geochemical and temperature settings form a complex hydrothermal landscape on the seafloor. Their hydrothermal reactions generate and mobilize volatile hydrocarbons that migrate to the sediment surface (Kastner, 1982; Peter et al., 1991), limiting or favoring biological oxidation and assimilation (Teske et al., 2002, 2014; Pearson et al., 2005; Biddle et al., 2012; McKay et al., 2016). This subsurface processing system and flow pathways that ultimately reach the sediment surface are evident in hydrothermal edifices and mineral deposits, venting orifices emitting hot hydrothermal fluids, and hydrothermally altered sediments (Simoneit et al., 1990; Teske et al., 2016; Nuñez-Usoche et al., 2018).

DOI: http://dx.doi.org/10.22201/cgeo.20072902e.2019.2.1054
The initial exploration of Guaymas Basin started in the north rift, but after heat flow surveying it centered on the active south rift, where the hydrothermal sediments, mounds and chimneys form a complex hydrothermal landscape on the seafloor (Lonsdale, 1985; Lonsdale and Becker, 1985). Subsequently, the Deep Sea Drilling Project (DSDP) carried out coring on Leg 64 in the Guaymas Basin area. Hydrothermal petroleum was encountered at depth in both rifts and extensively in seabed mounds of the south rift. No data has been reported for the weathered mounds of the north rift. The aim of this study is to characterize the hydrothermal petroleum on a seabed mound and shallow sediment cores from the north rift of Guaymas Basin. It provides an overview of the organic biomarker compositions, diagenetic transformations, biodegradation, weathering/oxidation effects, and the dominant contributing biogenic sources of the extractable bitumen. Furthermore, this report provides comparative analytical results to those from the southern, active rift of the basin.

GEOLICAL SETTING

Guaymas Basin is an actively spreading ocean basin, which is part of the system of spreading axes and transform faults that extend from the East Pacific Rise to the San Andreas fault (Curray et al., 1982; Lonsdale, 1985). It is comprised of two grabens, the northern and southern rifts, connected by a transform fault zone (Figure 1). The process of ocean plate accretion results in high conductive heat flow (locally exceeding 1.2 W·m⁻²; Einsele et al., 1980). Organic-rich sediments of several hundred meters thickness overlie the spreading centers of Guaymas Basin and alternate with shallow intrusions of magmatic sills into the unsedimented sediments producing organically-derived thermal alteration products dominated by CH₄, CO₂, and hydrocarbons (Simoneit and Lonsdale, 1982; Simoneit, 1985; Bazylinski et al., 1988; Gieskes et al., 1988; Whelan et al., 1988) that are released into sedimentary pore fluids and the ocean (Teske et al., 2016). The north rift had no obvious high heat flow signals and appeared hydrothermally dormant for ~3000 years (Williams et al., 1979). Sediments accumulate at a rate of more than 1 m/1000 years and have covered the rift floors to a depth of up to 400 m (Curray et al., 1982).

The organic matter of these recent hemipelagic sediments is derived primarily from planktonic and microbial detritus, which is highly sensitive to thermal stress and thus easily pyrolyzed (cracked) to petroleum-like products. The maximum of the oil generation "window" appears to migrate upward as the magmatic heat front moves up in the sedimentary column of the southern rift (Simoneit, 1984; Simoneit et al., 1984). Petroleum products have been described in samples from the north rift taken by shallow gravity coring (30G, Simoneit et al., 1979), piston coring (LaPaz cruise) (Simoneit, 1983a, 1983b), and deep coring (DSDP Leg 64 Hole 481; Curray et al., 1982). Seabed manifestations of petroleum were recovered by dredging operations (7D, Simoneit and Lonsdale, 1982), as well as samples taken with the deep submersive vehicle (DSV) Alvin (Simoneit, 1984, 1985; Simoneit and Kawka, 1987). These sample extracts from the north rift have been reanalyzed and their molecular compositions are discussed here in an overview.

EXPERIMENTAL METHODS

Samples and extraction

This study describes samples taken in the north rift of Guaymas Basin on various cruises in the Gulf of California. Core samples were obtained during a deep-tow and heat flow survey cruise (La Paz, Leg 2) by the R/V Melville (Scripps Institution of Oceanography) during July-August 1980, using a piston corer (10 m barrel with a 2 m gravity core trip weight). Three composited samples (six intervals of 2 cm each per sample) were analyzed from cores 9P (15 m total), 13P (15 m total) and 15P (13 m total) (Figure 1b). Site 9P is located on a large intra-rift hill and the core lithology consists of stiff, low-porosity mud, with possible pieces of hydrothermal crust. Sites 13P and 15P are located on a narrow ridge and cores recovered gas-charged, stiff mud and strong petrolierous odor. The core sections selected for composite analysis had a strong petroleum odor and comprised the following depth intervals: Core 9P (section 12.9–14.4 m), core 13P (section 10.5–12.4 m), and core 15P (section 11.2–11.9 m).

Additional samples were collected in the north rift with the DSV Alvin (dives 1621, along the continental margin fault, and 1623) in 1985 (Figure 1). Bulk samples (1623-B and 1623-C1) were a weathered sediment with oil saturated veins, and a weathered chimney with talus, respectively, from the base at the dormant mound to the west. Sample 1623-PC4 was a push-core into sediment on the rift floor near mounds. The manipulator-collected and push-core samples were subsampled at the surface and sealed in glass containers with dichloromethane (DCM) to preserve the volatiles and minimize biodegradation. The larger samples were subsequently extracted by sonication with addition of methanol (MeOH) to remove water. The extracts were then washed with distilled-in-glass pure water to remove the inorganics. Aqueous layers were back-extracted with DCM. Aliquots of the organic extracts were dried under a pre-purified N₂ stream at room temperature to constant mass (less than 1 % total change in a 20 min period) and weighed. A selected number of organic extracts obtained from petroleum-rich samples were further separated into fractions. First, asphaltenes were precipitated overnight using hexane. Filtering and extensive hexane washing of the asphaltenes yielded the soluble Cₜ₊ compounds. These fractions were dried to constant weight as before for quantitation and analysis. The de-asphalted extracts were further separated by liquid-solid column chromatography on neutral alumina over silica or by thin layer chromatography (TLC) on silica to isolate the following fractions: saturated (F₁), aromatic (F₂), and polar (NSO, F₃) compounds (Simoneit et al., 1981).

Instrumental analysis

The analyses of both total extracts and separated fractions were carried out by gas chromatography-mass spectrometry (GC-MS). Aliquots of the total extracts were silylated with N,O-bis(trimethylsilyl) trifluoroacetamide (BSTFA) containing 1 % trimethylchlorosilane (TMCS) and pyridine (Pierce) for 3 h at 70 °C prior to GC-MS analysis. A Hewlett-Packard 6890 GC coupled to a 5973 Mass Selective Detector was used with a DB-5MS (Agilent) fused silica capillary column (30 m x 0.25 mm i.d., 0.25 μm film thickness), and He as carrier gas. The GC was temperature programmed from 65 °C (2 min initial time) to 300 °C at 6 °C min⁻¹ (isothermal for 20 min final time). The MS was operated in the electron impact mode at 70 eV ion source energy. Data were acquired and processed with a Hewlett-Packard ChemStation. Compounds were identified by GC retention index and comparison of mass spectra with those of authentic standards, literature and library data, and characterized mixtures. Unknown compounds were characterized by interpretation of the fragmentation pattern of their mass spectra. Compounds were quantified using the total ion current (TIC) peak area, and converted to compound mass using calibration curves of external standards. A procedural blank was run in sequence to sediment samples, presenting no significant background interferences. The mass spectra of the unknown and uncommon compounds are presented in the Supplementary Material (Figure SM 2).
RESULTS AND DISCUSSION

Nature of organic matter in the Guaymas Basin hydrothermal system

Table 1 shows the total hydrocarbon and bitumen yields of north rift samples. The first indication of diffusion of thermogenic products to the seabed from depth was found in a gravity core taken at Site 30G in the north rift (Figure 1) (Simoneit et al., 1979). The bulk of the extractable organic matter was of an autochthonous marine origin derived from planktonic/microbial detritus. The lower section of the core contained significant concentrations of gasoline range hydrocarbons (Whelan et al., 1988). Similar migration of hydrocarbons was observed in other shallow (9P, 13P and 15P) cores or in seabed samples from this rift (Simoneit, 1983a, 1983b; Merchand et al., 1994).

DSDP Leg 64 encountered intrusives and hydrothermal alteration at depth in Holes 477, 478, and 481 (Figure 1) (Curray et al., 1982). Thermogenic hydrocarbon gas, H2S and CO2 were identified for all sites based on composition and stable carbon isotope data (Simoneit, 1982b; Galimov and Simoneit, 1982a, 1982b; Whelan and Hunt, 1982; Simoneit and Galimov, 1984; Simoneit et al., 1988). At shallow depths, the gas data indicated a typically biogenic pattern (DSDP Sites 481 and 478, and also 30G, cf. Simoneit et al., 1979). With increasing depth,
the δ13C values became heavier indicating the removal (by diffusion and/or solution) of the lighter 14CH4 due to the thermal stress from intrusive and conductive heat sources. The CH4 at Site 477 was heaviest, reflecting the highest temperature effects, and the data for Site 481 between the sill intrusions indicated various less severe thermal effects.

The organic carbon contents of the thermally unaltered sediments in the north rift varied from 1–3 % (Simonet and Bode, 1982). The source of the organic matter was primarily from marine input based on its δ13C values (Galimov et al., 1982; Jenden et al., 1982). However, the contemporary lipids were dominated by terrigenous input superimposed on the autochthonous marine components (Rullkötter et al., 1982; Simonet and Philp, 1982).

A sediment sample was also taken with a push core (Alvin dive 1621-PC5, Figure 1a) on the transform fault along the continental slope of the Sonoran margin. No evidence for hydrothermal activity was observed along the fault, but hydrocarbon seeps were documented there by Deep Tow survey (Lonsdale, 1985). The interstitial water of PC5 contained wet hydrocarbon gas (methane to pentane), and the solvent extract of the sediment had a low amount of mature hydrothermal petroleum superimposed on the autochthonous lipids (Simoneit et al., 1990). Thus, the hydrothermal petroleum migrated into the shallow sediments in fluids with hydrocarbon gas advecting due to regional high heat flow.

North rift

Aliphatic lipid series

Core sample 9P contained unimodal n-alkanes ranging from C13 to C35 with a carbon number maximum (Cmax)=18 (Figure 2a). For core samples 13P and 15P the n-alkanes had bimodal distributions and ranged from C16 to C40 with Cmax at 24, 29 and 23, 29, respectively (Figure 2c, 2d). Carbon preference index (CPI) values for these n-alkanes were 1.1, 1.7 and 1.2 for samples 9P, 13P and 15P, respectively (Table 1). Bimodal distributions are characteristic of dual source inputs all higher organisms and is oxidized in the depositional environment to the lactone derivative (VIII) (Green et al., 1959).

Various diagenetic derivative compound groups were detected. Methyl ethyl maleimide (3-methyl-4-ethyl-7H-pyrrole-2,5-dione, IX, R=C4H9, e.g. Figure SM 2h) and minor dimethyl maleimide were composed of dominantly cholesterol (V, R=H), with lesser amounts of brassicasterol (VI, Figure SM 2e) and sitosterol (V, R=C17H35). Note the ethyl configuration at C-24 of sitosterol vs. clionasterol cannot be easily distinguished by GC-MS. Thus, the sterol distribution is interpreted to derive from marine microbiota (Goad, 1978), and subsequent early diagenesis altered them to steran-3-ones and sterenes (Brault and Volkman, 1993, 1998). Dinosterol was not detectable in these samples, but the fate of dinosterol under hydrothermal conditions is not known. The sterols present in the shallow sediments were comprised of dominantly cholesterol (V, R=H), with lesser amounts of brassicasterol (VI, Figure SM 2e) and sitosterol (V, R=C17H35). Note the ethyl configuration at C-24 of sitosterol vs. clionasterol cannot be easily distinguished by GC-MS. Thus, the sterol distribution is interpreted to derive from marine microbiota (Goad, 1978), and subsequent early diagenesis altered them to steran-3-ones and sterenes (Brault and Simonet, 1988).

α-Tocopherol (VII, Figure SM 2f) and its oxidation product 4,8,12,16-tetramethylheptadecan-4-olide (or homophytanic acid γ-lactone, VIII, Figure SM 2g) were present in sample 1623-PC4 (e.g. Figure 3e). α-Tocopherol (vitamin E) is an antioxidant in the lipids of all higher organisms and is oxidized in the depositional environment to the lactone derivative (VIII) (Green et al., 1959).

Table 1. Summary of total bitumen and hydrocarbon yields from typical samples in the north rift of Guaymas Basin.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Total Bitumen Yield (µg.g⁻¹ dry wt.)</th>
<th>Total Hydrocarbon Yield (µg.g⁻¹ dry wt.)</th>
<th>CPI¹</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>30G (-3 m)</td>
<td>1600 – 28000</td>
<td>1 - 24</td>
<td>1.4 – 3.0</td>
<td></td>
</tr>
<tr>
<td>DSDP Leg 64</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>481A-8-7, 0-5</td>
<td>1410</td>
<td>36</td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td>481A-12-1, 107-109</td>
<td>2700</td>
<td>74</td>
<td>4.1</td>
<td></td>
</tr>
<tr>
<td>481A-14-3, 50-52</td>
<td>1010</td>
<td>60</td>
<td>3.2</td>
<td></td>
</tr>
<tr>
<td>481A-20-1, 60-62</td>
<td>1740</td>
<td>64</td>
<td>2.8</td>
<td></td>
</tr>
<tr>
<td>481A-25-cc</td>
<td>560</td>
<td>26</td>
<td>3.4</td>
<td></td>
</tr>
<tr>
<td>Piston Cores</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9P (12.9 – 14.4 m)</td>
<td>2110</td>
<td>41</td>
<td>1.1</td>
<td></td>
</tr>
<tr>
<td>13P (10.5 – 12.4 m)</td>
<td>3040</td>
<td>17</td>
<td>1.7</td>
<td></td>
</tr>
<tr>
<td>15P (11.2 – 11.9 m)</td>
<td>5000</td>
<td>16</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td>DSV Alvin</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1621-PC5</td>
<td>1170</td>
<td>26</td>
<td>1.1</td>
<td></td>
</tr>
<tr>
<td>1623-B vein</td>
<td>76000</td>
<td>28000</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td>1623-B sediment</td>
<td>34200</td>
<td>680</td>
<td>1.1</td>
<td></td>
</tr>
<tr>
<td>1623-C1 interior</td>
<td>27000</td>
<td>1990</td>
<td>1.1</td>
<td></td>
</tr>
<tr>
<td>1623-C1 exterior</td>
<td>4800</td>
<td>72</td>
<td>0.9</td>
<td></td>
</tr>
<tr>
<td>1623-PC4</td>
<td>2660</td>
<td>36</td>
<td>1.1</td>
<td></td>
</tr>
</tbody>
</table>

¹CPI - Carbon Preference Index summed for n-alkanes from C15 to C35.
maleimides also contained phytanic acid (X, chlorophyll (Naeher et al., 2013). The samples with high levels of diagenetic or oxidative products from remineralization of planktonic and 15P (Figure 2a, 2c, 2d). Their presence is interpreted as e.g. (Isoe et al., 1973).

rapid photochemical alteration in senescent phytoplankton detritus has been interpreted as input from carotenoid pigments undergoing product from phytol of chlorophyll (6,10,14-trimethylpentadecan-2-one, XI, \( R = \text{CH}_3 \)) were significant components in core samples 9P, 13P and 15P (e.g. Figure 2a, 2c, 2d). Their origin has been interpreted as input from carotenoid pigments undergoing rapid photochemical alteration in senescent phytoplankton detritus (Isoe et al., 1969, 1972; Klok et al., 1984; Rontani et al., 1998). The loliolide presence in sediments has also been attributed to anaerobic microbial alteration of carotenoids during diagenesis (Repeta, 1989).

Highly branched isoprenoid hydrocarbons, e.g. \( \text{C}_{23} \) HBI [i.e., 2, 6, 10, 14-tetramethyl-7-(4’-methylpentyl)pentadecane, XIV, Figure SM 2l] were not detectable in these samples, but the high levels of \( \text{H}_2\text{S} \) and sulfur in these sediments resulted in diagenetic sulfurization of both isoprenoids and HBIs to series of alkylthiophenes (Sinninghe Damsté et al., 1986, 1989; Kohnen et al., 1993). These were evident in extracts of the biodegraded/weathered surface sediments sampled by DSV \textit{Alvin} dive 1623 (e.g. Figures 2f, 3b and, 4d). One group is comprised of the thiophene derivatives from phytol by sulfuration of phytofenes (\( \text{C}_{29}\text{H}_{50}\text{S}, \text{XV}-\text{XVII}, \text{Figure SM 2m} - \text{SM 2o})
and the 7R and 7S epimers of sulfurred C_{25:1} HBIs as ([2,3-dimethyl-5-(2,6,10,14-tetramethyl-7'-pentadecyl)thiophene, C_{39}H_{38}S], XVIII, Figure SM 2p), and 2-(1'-methylpropyl)-4-(1',5'-dimethylhexyl)-5-(2',6'-dimethylthiophene) (C_{30}H_{38}S, XIX, Figure SM 2q). The C_{25:1} HBIs are indicators for input from diatoms (e.g. Rowland and Robson, 1990; Jaffé et al., 2001). A single compound, C_{35}H_{54}S, MW=230, fits for 2,3-dimethyl-5-(2,6'-dimethylthiophene) (XX, Figure SM 2r), as a possible product from farnesol by sulfurization of farnesene. The other group, apparent recombination products from thermal cracking of alkylthiophene precursors, consists of compounds: 1,2-bis-methylthiophenylethane (C_{35}H_{54}S, XXI, Figure SM 2s), 1,3-bis-methylthiophenylpropane (C_{36}H_{56}S, XXII, Figure SM 2t), and 1,2-bis-dimethylthiophenylethane (C_{36}H_{56}S, XXIII). This group seems to be concentrated in the biodegraded surface sediments probably due to their recalcitrance to microbial alteration. They were also found in shallow sediments of the south rift (Simoneit et al., 1992a).

**Biomarker hydrocarbons**

The core sections from the north rift exhibit differences in their biomarker hydrocarbon distributions indicative of overprinting by hydrothermal petroleum or variations in maturity (Kawka and Simoneit, 1987). The dominant triterpenoid compound of samples 9P, 13P and 15P was hop-17(21)-ene (XXIV, Figure SM 2u), and they had different amounts of 17β(H),21β(H)-homohopanoic acids (XXV, Figure SM 2v), and the 7R and 7S epimers of sulfurized C_{25:1} HBIs as ([2,3-dimethyl-5-(2,6,10,14-tetramethyl-7'-pentadecyl)thiophene, C_{39}H_{38}S], XVIII, Figure SM 2p), and 2-(1'-methylpropyl)-4-(1',5'-dimethylhexyl)-5-(2',6'-dimethylthiophene) (C_{30}H_{38}S, XIX, Figure SM 2q). The C_{25:1} HBIs are indicators for input from diatoms (e.g. Rowland and Robson, 1990; Jaffé et al., 2001). A single compound, C_{35}H_{54}S, MW=230, fits for 2,3-dimethyl-5-(2,6'-dimethylthiophene) (XX, Figure SM 2r), as a possible product from farnesol by sulfurization of farnesene. The other group, apparent recombination products from thermal cracking of alkylthiophene precursors, consists of compounds: 1,2-bis-methylthiophenylethane (C_{35}H_{54}S, XXI, Figure SM 2s), 1,3-bis-methylthiophenylpropane (C_{36}H_{56}S, XXII, Figure SM 2t), and 1,2-bis-dimethylthiophenylethane (C_{36}H_{56}S, XXIII). This group seems to be concentrated in the biodegraded surface sediments probably due to their recalcitrance to microbial alteration. They were also found in shallow sediments of the south rift (Simoneit et al., 1992a).
but only traces of 17β(H),21β(H)-hopanes (XXVI). Sample 1623-PC4 exhibited a mixture of diagenetic and minor migrated mature hopanes (Figure 3b). The immature compounds consisted of hop-17(21)-ene, 21-epi-fern-9(11)-ene (XXVII, Figure SM 2w), and the ββ- and ααα-hopanes series (XXVII) from C_{25} to C_{33} (no C_{27}), with a minor immature 22R epimer ratio for homohopane, 22S(22S+22R) = 0.3 (Peters and Moldowan, 1993). Sample 1623-B clay had mainly the fully mature 17α(H),21β(H)-hopanes (XXVIII) ranging from C_{25} to C_{33} (no C_{27}), a minor series of 17β(H),21α(H)-hopanes (moretanes, XXIX) from C_{25} to C_{33}, and a series of tricyclic terpanes from C_{20} to C_{28} (no C_{27}, XXX) (Figure 4c). Both the weathered chimney sample 1623-C1 and the 1623-B vein sample had only a trace of the C_{27} and C_{29}-C_{31} αββ-hopanes, indicating high thermal stress that destroys biomarkers.

The steroid hydrocarbon patterns for these samples reflect their diagenetic origin from the steroid precursors to the 5α,14α,17α-stereanes (XXXI) and 5β,14α,17α-stereanes (XXXII) via the ster-4-enes (XXXIII) indicating high thermal stress that destroys biomarkers. The steroid hydrocarbon patterns for these samples reflect their diagenetic origin from the steroid precursors to the 5α,14α,17α-stereanes (XXXI) and 5β,14α,17α-stereanes (XXXII) via the ster-4-enes (XXXIII) indicating high thermal stress that destroys biomarkers.

Polycyclic aromatic hydrocarbons
The polycyclic aromatic hydrocarbon (PAH) contents of the background shallow sediments were low. For samples 9P, 13P, and 15P the PAH consisted mainly of the more volatile and water soluble compounds such as naphthalene (N) to trimethylnaphthalenes (TMN), with minor amounts of di- to pentamethylnaphthalenes on a smooth, but disappearing pattern <C_{20}, with only a series of isoprenoid terpanes (C_{20} to C_{28}, XXX) (Figure SM 2w), and the ββ-hopanes (Figure 4b). The occurrence of the C_{21} and C_{29} homologues with the dominance of cholestanes (XXXI and XXXII, R=H) support the marine plankton origin of the precursor organic matter (Volkman, 1986). These sterane distributions are the same as reported for shallow sediments in the north rift (Simoneit et al., 1992b) and deeper samples from DSDP Hole 478 in the transform fault zone between the north and south rifts (Kawka and Simoneit, 1994). The oil saturated sample 1623-B clay had a fully mature suite of steranes and diasteranes, ranging from C_{25} to C_{33} with a dominance of C_{27}>C_{28}=C_{29} (Figure 4a). This pattern is typical as reported for hydrothermal petroleum generated in the south rift of Guaymas Basin (e.g. Simoneit, 1990; Simoneit et al., 1992a, 1992b).

Post-depositional alteration of hydrothermal petroleum
During transport and deposition near the seabed, the hydrothermal petroleum may alter significantly before reaching the bottom sediments, both biologically (through biodegradation) and chemically (through diagenesis). This alteration can be complex and depend on factors such as temperature, sedimentation rate, and the presence of bacteria. The hydrothermal petroleum in the North rift of Guaymas Basin, Gulf of California, has undergone significant alteration since its deposition on the seabed. The petroleum is characterized by the presence of diagenetic and minor biodegraded compounds, which can be identified through the analysis of biomarkers and other organic compounds.

The presence of alkylthiophenes and high amounts of aromatics, including PAH (Figure 3b, 3c, 3d), support the overwhelming influx of hydrothermal petroleum into these sediments. The polar and aromatic by both a relative increase in the non-aliphatic components due to microbial removal of n-alkanes and an absolute increase in the polar components as a result of this metabolism (Bailey et al., 1973; Price, 1980). The only unaltered hydrothermal petroleum was extracted from the bulk matrix of the brown claystone (Figures 2e and 4a, 4c). Whereas, the oil in the veins of the same sample was a biodegraded petroleum residue of UCM, biomarkers and alkylthiophenes (Figures 2a and 4b, 4d), which may reflect heat driven emplacement of bulk biodegraded oil. The presence of alkylthiophenes indicated that this sample had experienced sulfurization reactions. The petroleum in the chimney fragment (1623-C1) is comprised of a major UCM with superimposed PAH and alkyl-PAH, including Diels’ hydrocarbon (Figure 3f). It is a typical aromatic residue of hydrothermal petroleum pyrolysed that permeated and solidified in the chimney when active. The extracts of the push cores adjacent to the weathered mound reflect similarities to the core samples (9P, 13P, 15P above) in that the n-alkanes are mostly biodegraded, leaving a dominance of phytane and pristane (e.g. Figure 4e, 4f), with immature biomarkers (e.g. Figure 3a, 3e). The presence of alkylthiophenes and high amounts of aromatics, including PAH (Figure 3b, 3c, 3d), support the overwhelming influx of biodegraded hydrothermal petroleum into these sediments. The polar fractions of the mound samples (e.g. Figure 3e) contained residual
stanols, dinosterol, tocopherol and alkylmaleimides, reflecting the contemporary lipid input analogous as described for the core samples.

**South versus north rift**

The samples from the south rift exhibited a great deal of variation in the organic character of the extracts. Most of the differences amongst these samples were explainable in terms of variable mixing, differential transport, and reaction of a high-temperature hydrothermal fluid end member with the overlying sediments.

The bitumens of the core samples and push core (1623-PC4) from the north rift are distinctly different. The biomarker and total extract compositions of the three shallow samples resulted from an admixture, by hydrothermal circulation, of a low-temperature pyrolysate with the organic matter indigenous to those depths sampled. Thus, sample 15P exhibits the most "mature" character and 9P the most immature/bacterial character. The sediments of sample 13P have apparently received a smaller input of pyrolysate compared to 15P. It was observed that the sections of the cores above and below those reported (composited)
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here did not have the characteristic petroliferous odor, which is due to the presence of benzene, toluene and xylenes in the interstitial fluids (Simoneit et al., 1988). This evidence indicates migration was primarily horizontal, resulting from a sill intrusion in the vicinity, but not due to a high thermal gradient at the core location. Migration in pore fluids or diffusion is supported by the analogous observation of no obvious oil droplets visible throughout the cores (cf. Sayles and Jenkins, 1982).

The dive 1623 mound consists of hydrothermal petroleum in veins, disseminated in the semi-lithified matrix, and saturating the remnant chimney fragments. This oil has varying compositions depending on thermal history during formation and subsequent alteration during migration/deposition among the hydrothermal minerals. The oils biodegraded further where accessible as the mound weathered. The push core contains biodegraded oil in talus deposited with the minor autochthonous components from the background sedimentation in the basin. Thus, biodegradation and water-washing severely changed the oil compositions after deposition as the area visited by DSV Alvin dive 1623 weathers and oxidizes.

CONCLUSIONS

The hydrothermal petroleums from the north rift of Guaymas Basin are variable in both character and quantity, but generally fully biodegraded. Their petroleum-like hydrocarbon patterns with high PAH contents are due to pyrolysis of organic matter by overall high heat flow at depth, and localized heating due to dike and sill intrusions into the sediment, with subsequent transport to shallow depth and seabed sediments by the hydrothermal fluids and thermal gradients. The upward migration of the hydrothermal petroleum appears to have occurred by both bulk transport and a combination of high temperature/pressure aqueous and supercritical gaseous (e.g., CO₂, CH₄) solubilization in a multi-component fluid phase. The Guaymas north rift is currently dormant and the hydrothermal mounds with minerals and petroleum have weathered and biodegraded, resulting in a distinctively different composition compared to the south rift.

ACKNOWLEDGEMENTS

We thank the officers and crew of the research vessels Melville and Atlantis for the highly successful operations onboard. We also thank T.A.T. Aboul-Kassim for technical assistance and O.E. Kawka for valuable discussions of the data. The two reviewers are acknowledged for their constructive suggestions, which led to an improved manuscript. This research was supported by the National Science Foundation, Division of Ocean Sciences (OCE-8118897, OCE-8312036, OCE-8512832, OCE-8601316, and OCE-9002366).

SUPPLEMENTARY MATERIAL

Appendix SM1 and Figure SM2 can be found at the journal web site <http://rmcg.unam.mx/>, in the table of contents of this issue.

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