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Articles

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 rifts occurs by both bulk transport and high temperature/pressure aqueous and supercritical gaseous (*e.g.* CO_2, CH_4) 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, overprinted 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.

Keywords: Hydrothermal petroleum, weathering, biodegradation, north rift, Guaymas Basin.

Resumen:

La cuenca oceánica de Guaymas del Golfo de California es una cuenca de extensión activa que pertenece al sistema de ejes y fallas transformantes que se extiende desde la dorsal Este del Pacifico hasta la Falla de San Andrés. En ella se produce la migración ascendente del petróleo hidrotermal hacia los sedimentos más superficiales del fondo marino a través de las brechas de la cuenca impulsado por fases fluidas de agua a temperatura y presión altas, así como gases en condiciones supercríticas (ej. CO_2, CH_4). Los montículos formados resultantes contienen el petróleo hidrotermal más joven que se conoce hasta el momento. El sistema hidrotermal de la brecha norte ha estado inactivo en los últimos ~3,000 años. Los análisis orgánico-geoquímicos de sedimento recogido mediante testigos manuales, de pistón y operaciones de dragado en el Golfo de California muestran que el material orgánico está compuesto principalmente de lípidos característicos de la biota marina sobrecargada con petróleo hidrotermal.

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Los biomarcadores alifáticos, aromáticos, esteroides y hopanoides presentes en el petróleo indican una degradación severa de las muestras expuestas a los procesos de meteorización. Dicho petróleo biodegradado está enriquecido en lípidos que contienen compuestos de azufre. En resumen, los procesos oxidativos y microbianos han meteorizado tanto los minerales hidrotermales como petróleo de los montículos de las brechas del lecho marino norte.

Palabras clave: Petróleo hidrotermal, Meteorización, Biodegradación, Brecha norte, Cuenca de Guaymas..

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; Nunez-Useche *et al.*, 2018).

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.

GEOLOGICAL 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 $W \cdot m^{-2}$; 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 unconsolidated sediments producing organically-derived thermal alteration products dominated by CH_4, CO_2, 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).

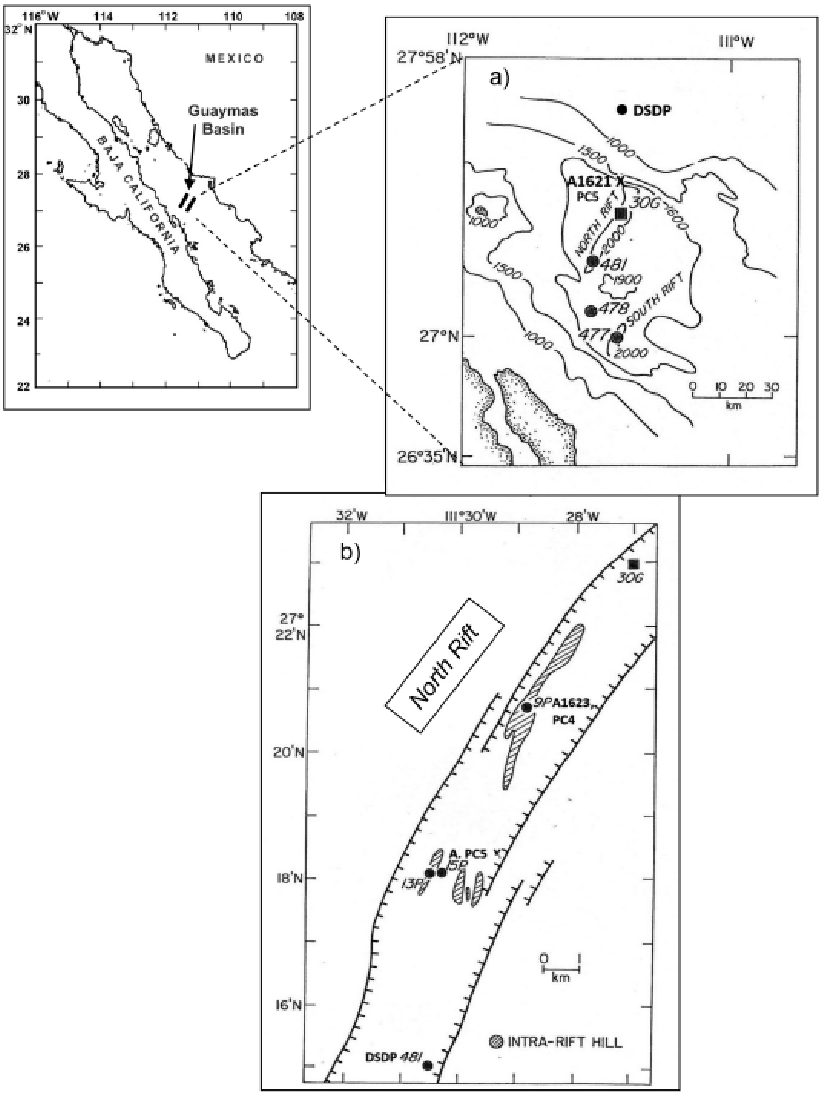

FIGURE 1

Location maps of sampling sites (adapted from Simoneit et al., 1983b): (a) Guaymas Basin showing the rifts and DSDP Holes, and (b) expanded view of the north rift.

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; 1985; 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 submergence 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 coring recovered gas-charged, stiff mud and strong petroliferous 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 C15+ 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).

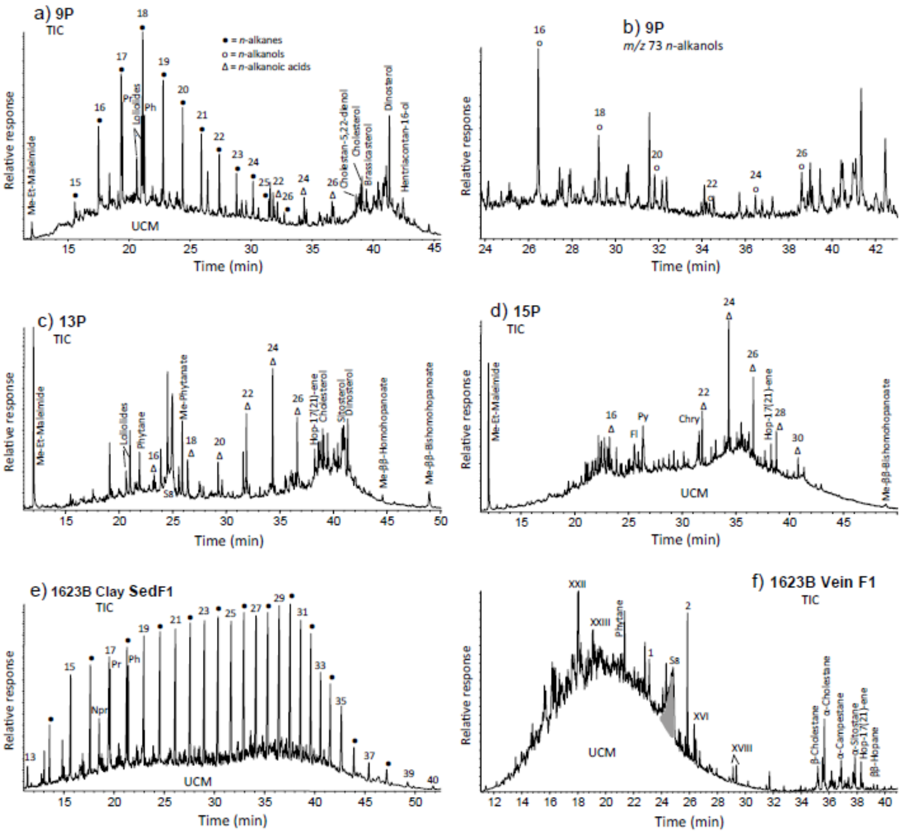

FIGURE 2

Annotated GC-MS data from shallow core and seabed samples

(a) Total ion current (TIC) trace for core 9P total extract as TMS, (b) *m/z* 73, key ion for n-alkanols as TMS of core 9P total extract, (c) TIC trace for core 13P total extract as TMS, (d) TIC trace for core 15P total extract as TMS, (e) TIC trace for total hydrocarbons of sediment sample 1623B, and (f) TIC trace for total hydrocarbons of oil vein sample 1623B (Roman numerals refer to structures in Appendix SM1).

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).

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

Samples (cf. Fig. 1)	**Total Bitumen Yield** ($\mu g \cdot g^{-1}$ dry wt.)	**Total Hydrocarbon Yield** ($\mu g \cdot g^{-1}$ dry wt.)	**CPI**[1] Range
30G (-3 m)	1600 – 28000	1 - 24	1.4 – 3.0
DSDP Leg 64			
481A-8-7, 0-5	1410	36	2.5
481A-12-1, 107-109	2700	74	4.1
481A-14-3, 50-52	1010	60	3.2
481A-20-1, 60-62	1740	64	2.8
481A-25-cc	560	26	3.4
Piston Cores			
9P (12.9 – 14.4 m)	2110	41	1.1
13P (10.5 – 12.4 m)	3040	17	1.7
15P (11.2 – 11.9 m)	5000	16	1.2
DSV *Alvin*			
1621-PC5	1170	26	1.1
1623-B vein	76000	28000	1.2
1623-B sediment	34200	680	1.1
1623-C1 interior	27000	1990	1.1
1623-C1 exterior	4800	72	0.9
1623-PC4	2660	21	1.1

1CPI - Carbon Preference Index summed for n-alkanes from C13 to C35.

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, H_2S and CO_2 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 12CH4 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 % (Simoneit 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 (Rullkotter *et al.*, 1982; Simoneit 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 C33 with a carbon number maximum (Cmax)=18 (Figure 2a). For core samples 13P and 15P the n-alkanes had bimodal distributions and ranged from C14 to C35 with Cmax at 24, 29 and 23, 29, respectively (Figure 2c, 2d). Carbon preference index (CPI) values for these nalkanes 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 from mainly marine algal/bacterial debris and minor terrestrial plant waxes (Simoneit, 1978; Philp, 1985), whereas for unimodal n-alkanes the source is marine detritus.

The lipids of the Pleistocene sediments drilled in Hole 481 had hydrocarbon distributions analogous to those described above, supporting the dual natural sources of marine productivity and terrigenous influx (Galimov *et al.*, 1982; Rullkotter *et al.*, 1982; Simoneit and Philp, 1982; Thomson *et al.*, 1982). The sedimentology was assessed as typical diatomaceous ooze with mud turbidites (Curray *et al.*, 1982).

The lipids of the samples analyzed from dive 1623 were completely overprinted with hydrothermal petroleum. The hydrocarbon fraction of one example comprised the full range of n-alkanes from C13-C40, with isoprenoids and UCM (unresolved complex mixture), whereas another was composed of only UCM with minor resolved alkylthiophenes and biomarkers as discussed below (Figure 2e, 2f).

The n-alkanoic acids were dominant components of cores 9P, 13P and 15P, and ranged from C14 to C30 with Cmax=24 and a strong biogenic even carbon number predominance (CPI=8-10) (e.g. Figure 2c, 2d). These alkanoic acids are interpreted to derive from degradation of wax esters from planktonic sources. A minor series of n-2-hydroxyalkanoic acids, also ranging from C14 to C28, an even carbon number predominance, but with Cmax=16, supports an algal source or a bacterial alteration component (Matsumoto et al., 1984). Minor n-alkanols from C16 to C26 with an even carbon number predominance and Cmax=16 were present (e.g. Figure 2b), supporting a primary marine origin.

Polar lipids were reported for one sample from Hole 481 and consisted of mainly dinosterol (I, all chemical structures are shown in Appendix SM1 of the Supplementary Material), related sterols, n-alkanols, n-alkanoic acids and triterpenoids (Thomson et al., 1982). The dominant inferred lipid contributors were diatoms and bacteria, including methanogens, reflecting marine bioproductivity. The extracts of the samples from dive 1623 contained minor amounts of stigmastanol and dinosterol from dinoflagellates, with a significant amount of α-tocopherol and hentriacontanol (Figure 3e) possibly from terrestrial plant waxes.

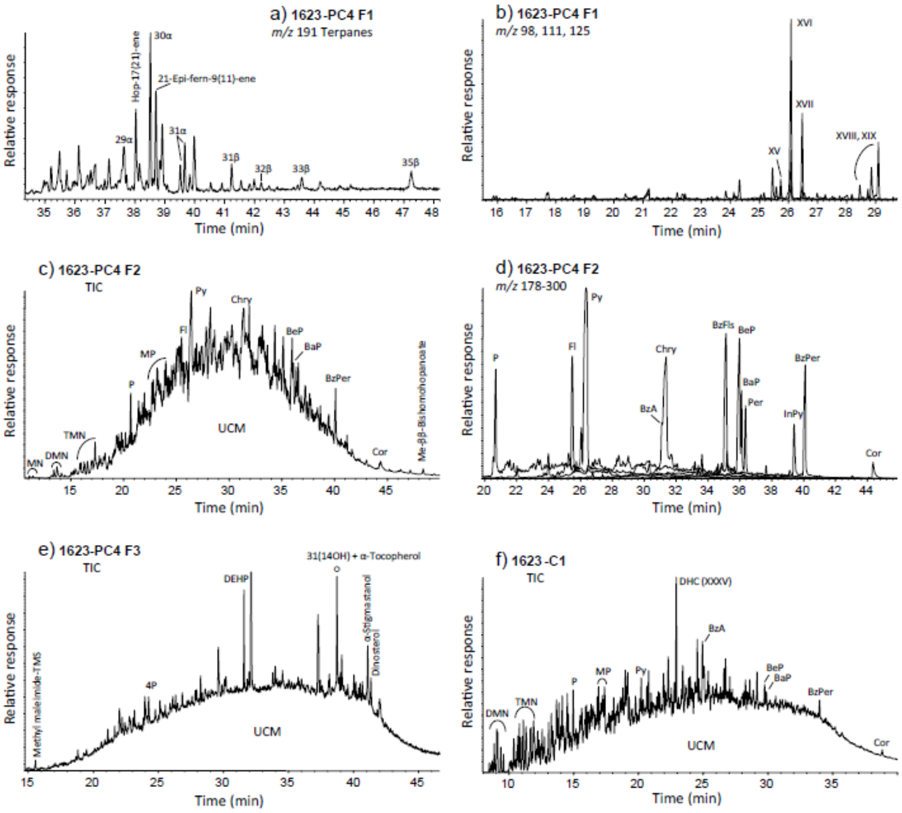

FIGURE 3

Annotated GC-MS data for samples from Alvin dive 1623: (a) *m/z* 191, key ion for the triterpenoids in push core sample 1623-PC4 (α = 17α(H), 21β(H)- and β = 17β(H), 21β(H)-hopane configurations), (b) *m/z* 98, 111+125, key ions for alkylthiophenes for sample 1623-PC4 (cf. Fig. 4d), (c) TIC trace of the total aromatic fraction of sample 1623-PC4 (abbreviations as in text), (d) m/z 178, 202, 228, 252, 276, + 300 key ions for the PAH molecular ions in the data as Figure 3c, (e) TIC trace of the polar fraction of sample 1623-PC4 (DEHP = diethylhexyl phthalate, 4P = butyl phthalate), and (f) TIC trace for the total extract of chimney fragment 1623-C1 (exterior).

Lipid natural products and their oxidative and diagenetic derivatives

The natural products in the lipids preserved in the sediments, especially in samples 9P, 13P and 1623-PC4, were dinosterol (I, *e.g.* Figures 2, 3, SM 2a, and SM 2b), 5-dehydrodinosterol (II, Figure SM 2c), 4α,24-dimethylcholestan-3β-ol (III, Figure SM 2d), and traces of steran-3-ones (IV, R=H,C_2H_5). These are a primary and diagenetic input from dinoflagellates (Boon *et al.*, 1979; Robinson *et al.*, 1984; Volkman *et al.*, 1993, 1998). Dinosterane 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= C_2H_5). 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 Simoneit, 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).

Various diagenetic derivative compound groups were detected. Methyl ethyl maleimide (3-methyl-4-ethyl-7-H-pyrrole-2,5-dione, IX, R=C2H5, e.g. Figure SM 2h) and minor dimethyl maleimide (IX, R=CH3) were significant components in core samples 9P, 13P and 15P (e.g. Figure 2a, 2c, 2d). Their presence is interpreted as diagenetic or oxidative products from remineralization of planktonic chlorophyll (Naeher et al., 2013). The samples with high levels of maleimides also contained phytanic acid (X, Figure SM 2i) and phytone (6,10,14-trimethylpentadecan-2-one, XI, Figure SM 2j), an inferred product from phytol of chlorophyll (e.g. Ikan et al., 1973).

Significant loliolide (XII, Figure SM 2k) and *iso*-loliolide (XIII) were detectable in core samples 9P and 13P (Figure 2a, 2c). 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.* C_{25}:1 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 H_2S and sulfur in these sediments resulted in diagenetic sulfurization of both isoprenoids and HBIs to series of alkylthiophenes (Sinninghe Damste *et al.*, 1986, 1989; Kohnen *et al.*, 1990; Rowland *et al.*, 1993). These were evident in extracts of the biodegraded/weathered surface sediments sampled by DSV *Alvin* dive 1623 (*e.g.* Figures 2f, 3b and, 4d). One group is comprised of the thiophene derivatives from phytol by sulfurization of phytadienes ($C_{20}H_{36}S$, XV-XVII, Figure SM 2m – SM 2o), 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, $C_{25}H_{46}S$], XVIII, Figure SM 2p), and 2-(1'-methylpropyl)-4-(1',5'-dimethylhexyl)- 5-(2',6'-dimethylheptyl) thiophene (C_{25}H46S, XIX, Figure SM 2q). The C_{25}:1 HBI precursors are indicators for input from diatoms (*e.g.* Rowland and Robson, 1990; Jaffe *et al.*, 2001). A single compound, $C_{15}H_{26}S$, MW=230, fits for 2,3-dimethyl-5-(2',6'-dimethylheptyl)thiophene (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 ($C_{12}H1_4S_2$, XXI, Figure SM 2s), 1,3-*bis*-methylthiophenylpropane ($C_{13}H_{16}S_2$, XXII, Figure SM 2t), and 1,2-*bis*-dimethylthiophenylethane ($C_{14}H_{18}S_2$, 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).

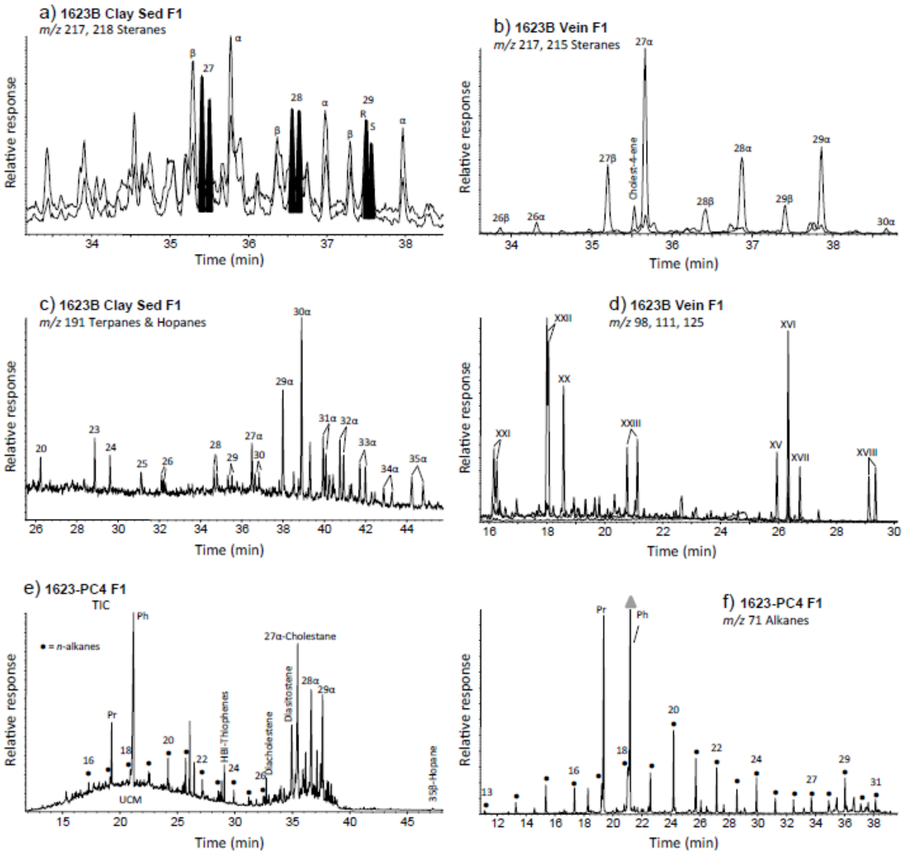

FIGURE 4

Annotated GC-MS data for samples from Alvin dive 1623: (a) m/z 217+218, key ions for steranes (β and α = βαα and ααα R epimers at C-20, solid peaks = αββ isomers with 20R eluting prior to 20S in F1 of clay sediment 1623B), (b) m/z 217+215, respective key ions for steranes and sterenes of oil vein sample 1623B, (c) m/z 191, key ion trace for tricyclic terpanes (C20-C30) and hopanes (all αβ) in F1 of clay sediment 1623B, (d) m/z 98, 111+125, key ions for alkylthiophenesin oil vein sample 1623B (Roman numerals refer to structures in Appendix SM1), (e) TIC trace for the total hydrocarbons of push core sample 1623-PC4, and (f) m/z 71, key ion plot showing the n-alkane distribution in push core sample 1623-PC4, Ph (phytane) is plotted off scale.

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), 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-hopane series (XXVI) from C27 to C35 (no C28), with an immature 22S to 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 C27 to C35 (no C28), a minor series of 17β(H),21α(H)-hopanes (moretanes, XXIX) from C29 to C33, and a series of tricyclic terpanes from C20 to C26 (no C21, XXX) (Figure 4c). Both the weathered chimney sample 1623-C1 and the 1623-B vein sample had only a trace of the C27 and C29-C31 αβ-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-steranes (XXXI) and 5β,14α,17α-steranes (XXXII) via the ster-4-enes (XXXIII) and diasterenes (XXXIV) in the unaltered sediments (Mackenzie *et al.*, 1982). Samples 9P and 13P were barren of steranes, diasteranes and diasterenes, but contained traces of ster-4-enes. Sample 15P had a mature sterane pattern comparable to sample 1623-B clay and samples from the south rift, with minor diasterenes and sterenes. Both samples 1623-B vein and 1623-PC4 had primarily the immature ααα- and βαα-steranes ranging from C26 to C30 with Cmax=27, and minor ster- 4-enes and diasterenes (Figure 4b). The occurrence of the C26 and C30 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 south 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 C26 to C29 with a dominance of C27>C28=C29 (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).

Polycyclic aromatic h ydrocarbons

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 traces of phenanthrene (P), fluoranthene (Fl) and pyrene (Py). PAHs were not detectable in sample 1623-B clay, but the oxidized crust from sample 1623-B vein had trace amounts of fluoranthene and pyrene. The weathered chimney, 1623-C1 (exterior), had a dominant amount of Diels' hydrocarbon (DHC, Simoneit *et al.*, 1992b, XXXV, Figure SM 2x), with minor amounts of di- to pentamethylnaphthalenes on a major UCM (Figure 3f). Whereas, sample 1623-PC4 had the typical full suite of PAHs as methyl- to pentamethylnaphthalenes, phenanthrene with methyl- to pentamethylphenanthrenes, and the higher molecular weight parent PAHs from fluoranthene, pyrene, benz[a]anthracene (BzA), chrysene (Chry), benzofluoranthenes (BzFl), benzo[e]pyrene (BeP), benzo[a]pyrene (BaP), perylene (Per), indeno[c,d]pyrene (InPy), benzo[g,h,i]perylene (BzPer), to coronene (Cor), all on a major UCM (Figure 3c, 3d). This PAH distribution is as reported for the initial dredge sample (7D) and for numerous other samples recovered with DSV *Alvin* in the south rift (Simoneit and Lonsdale, 1982; Kawka and Simoneit, 1990; Pikovskii *et al.*, 1996).

Post-depositional alteration of hydrothermal petroleum

During transport and deposition near the seabed, the hydrothermal petroleums can undergo water-washing and biodegradation. The number of UCM-dominated samples suggests a significant control by biodegradation (Simoneit, 1985; Simoneit and Kawka, 1987; Pearson et al., 2005). Such patterns, with little or no n-alkanes present, could occur by compositional fractionation through differential solubilization, as discussed previously. However, the comparison between the extracts of the interior (1170-1-2) and exterior (1170-1-3) of a hydrothermal mound fragment (Kawka and Simoneit, 1987; Simoneit and Kawka, 1987) suggested that biodegradation is important due to their striking difference. The absence of the broad distribution of n-alkanes found in the exterior, and the presence of identical thermally mature biomarker distributions in both, strongly supported biodegradation.

Complete removal of n-alkanes, as in the previous example, is an extreme form of biodegradation. An intermediate stage of biodegradation was observed for sample 1170-20-1 (red wax, Simoneit and Kawka, 1987), where the n-alkanes from C19 to C31 (Cmax=23) dominated the pattern. Above C23, the concentrations decreased smoothly, but disappear abruptly n-alkanes less than ~C25 or the n-alkanes as an entire group before affecting the isoprenoids of whole crudes, could have caused such a pattern (Bailey et al., 1973; Simoneit, 1985). Thus, during biodegradation, normal (aliphatic) oils can become more 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 extract compositions of the core samples from the north rift (9P, 13P, 15P) were not affected by biodegradation (Figure 2a– 2c). They are varying admixtures of syngenetic lipids undergoing accelerated diagenesis due to higher heat flow, with superimposed volatile and water soluble components from migrated hydrothermal petroleum.

The hydrothermal mound area visited by DSV *Alvin* (dive 1623, August 1985) appeared as a weathered talus of rubble blanketed with unconsolidated, fine grained, rusty sediment. Obviously, the hydrothermal minerals had oxidized and the residual mud was enriched in metal (especially iron) oxide-hydroxides, sulfates, silicates, and carbonates. No vent biota, or remnant tube worm casts were evident, and no warm fluid discharge was found. The samples recovered were: (1) a massive chimney fragment, with intact interior sulfides and matrix saturated with oil (sample 1623-C1); (2) a large brown claystone with veins containing oil (sample 1623-B), and (3) a short push core (PC4) (Table 1).

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 2f 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 pyrolysate 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 .-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) 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.* CO_2, CH_4) 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.

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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