

PETROLEUM GENERATION IN SUBMARINE HYDROTHERMAL SYSTEMS: AN UPDATE

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ABSTRACT

The conversion of organic matter to petroleum by hydrothermal activity is a process which occurs in many types of natural environments. Geologically immature organic matter in marine sediments is being altered by this process in the Guaymas Basin, Escanaba Trough, and Atlantis II Deep. In Guaymas Basin the sedimentary organic matter is derived primarily from algal and microbial detritus, with a minor influx of terrestrial higher plant components. It is easily cracked to petroleum and migrates in hydrothermal fluids. Emanations at the seabed result in dispersal of the more volatile components (C_1 - C_{10} hydrocarbons) and solidification of the heavier (C_{10} - C_{40+}) petroleum within the mineral matrix of the hydrothermal mounds. The petroleum compositions vary from condensates (C_1 - C_{15}) to naphthenic (probably extensively biodegraded residues, the most common surface samples) to waxy, all with significant amounts of asphaltenes and toxic polynuclear aromatic hydrocarbons (PAH). Contemporary organic detritus and living microorganisms are also converted in part to petroleum-like products when they become entrained by turbulent mixing into the vent waters, resulting in "instantaneous" hydrous pyrolysis. The latter process occurs in all hydrothermal vents, but is most clearly evident in vents which emanate from sediment-free oceanic ridges, as for example on the East Pacific Rise at 13° and 21°N and on the Mid-Atlantic Ridge at 26°N. The hydrocarbon products generated in the various areas are compared in terms of composition, organic matter sources and analogy to reservoir petroleum.

Keywords: hydrothermal petroleum, Guaymas Basin, Escanaba Trough, East Pacific Rise, Atlantis II Deep, Mid-Atlantic Ridge, *n*-alkanes, polynuclear aromatic hydrocarbons, petroleum migration.

SOMMAIRE

La transformation de la matière organique en pétrole par activité hydrothermale est un processus qui se produit dans divers milieux naturels. La matière organique géologiquement immature des sédiments marins est altérée par cette voie dans le Bassin de Guaymas, la Fosse d'Escanaba, et Atlantis II Deep. La matière organique sédimentaire du Bassin de Guaymas provient essentiellement de débris microbiens et algaires avec un faible apport de composés issus des végétaux supérieurs terrestres. Cette matière organique forme facilement par craquage des produits pétroliers qui migrent avec le fluide hydrothermal. Les émanations de fluides chauds au fond de l'océan entraînent une dispersion des composés plus volatiles (hydrocarbures C_1 - C_{10}) et une solidification des pétroles plus lourds (C_{10} - C_{40+}) dans la matrice minérale des monticules hydrothermaux. La composition des pétroles varie des condensats (C_1 - C_{15}) aux naphthènes (probablement des résidus considérablement biogénés rencontrés dans la plupart des échantillons de sur-

face) et cires, avec des quantités importantes d'asphaltènes et d'hydrocarbures aromatiques polycycliques (HAP). Les débris organiques contemporains et les microorganismes vivants sont aussi convertis partiellement en produits proches du pétrole par une pyrolyse acquise instantanée lorsqu'ils sont entraînés par les turbulences dans les eaux des événements. Ce dernier phénomène apparaît dans les champs hydrothermaux qui ne possèdent pas une couverture sédimentaire issue directement des rides océaniques telles que la ride du Pacifique Est à 13 et 21°N et la ride Médio-Atlantique à 26°N. Les composés hydrocarbonés produits dans ces sites ont été comparés en termes de composition, de sources de matière organique et d'analogie au pétrole de réservoir.

Mots-clés: pétrole hydrothermal, Bassin de Guaymas, Fosse d'Escanaba, Ride du Pacifique Est, Atlantis II Deep, Ride Médio-Atlantique, *n*-alcane, hydrocarbures aromatiques polycycliques, migration du pétrole.

INTRODUCTION

Organic matter of marine sedimentary basins is derived from the syngenetic residues of biogenic debris that originates from both autochthonous (marine) and allochthonous (continental) sources (e.g., Simoneit 1978, 1982a). The preservation of organic matter in sediments depends on the initial diagenetic processes, which involve microbial degradation and chemical conversions, together with the acidity and redox potential of the environment (e.g., Diddy *et al.* 1978, Demaison & Moore 1980). Subsequent sediment maturation and lithification causes metamorphism of the organic matter, ultimately yielding petroleum products through the effects of temperature, pressure and petrology (Hunt 1979, Tissot & Welte 1984). However, the action of hydrothermal processes on such sedimentary organic matter was found to generate petroleum-like products in Guaymas Basin almost "instantaneously" in geological time (Simoneit & Lonsdale 1982). The present paper reviews this process using examples from the extensively studied Guaymas Basin and other areas of hydrothermal activity at both sedimented and bare-rock spreading centers.

The analytical techniques of organic geochemistry have been used extensively to examine the character of organic matter in the geologic record in terms of its structural and compositional makeup (e.g., Simoneit 1978, van de Meent *et al.* 1980, Johns 1986). The sources, diagenetic and catagenetic histories, and migration mechanisms of this organic matter can be evaluated from such data. In the fol-

TABLE 1. ORGANIC MATTER OF SEDIMENTS AND PETROLEUM

SEDIMENTS

Recent (generally biogenic components, approx. age range 10^0 - 10^4 yr):

Gas	Lipids	Humic and Fulvic substances	Carbonaceous detritus (humin, pseudokerogen)
CH ₄ , CO ₂ , H ₂ S	C ₈ -C ₄₀ ⁺	macromolecular M.W. ~10 ³ to >10 ⁶ variable amount	macromolecular >humates major amount
minor amount of total C _{org}	minor amount (max. ~10%)		

Ancient (generally geogenic components, approx. age range 10^4 - 10^8 yr):

Gas	Bitumen	Asphaltenes (some humates)	Kerogen
CH ₄ -C ₈ , CO ₂ , H ₂ S	C ₈ -C ₄₀ ⁺	macromolecular, M.W. ~10 ⁴ to >10 ⁶ variable amount	macromolecular, >asphaltenes major amount
minor amount of total C _{org}	minor amount (max. ~10%)		

PETROLEUM

Composition (liquid products derived from mature sedimentary organic matter; also derived from immature organic matter in hydrothermal systems):

Gas (and gasoline range)	Bitumen	Asphaltenes	Kerogen
CH ₄ -C ₈ ⁺ , CO ₂ , H ₂ S, N ₂ minor amount of total C _{org}	C ₈ -C ₄₀ ⁺ major amount	macromolecular, M.W. ~10 ⁴ to >10 ⁶ major amount	absent spent kerogen remains in source rocks

lowing discussion, organic matter is classified as gas, lipids (bitumen), humic substances (with fulvic substances, or asphaltenes) and kerogen (with "pseudokerogen"). The characteristics of this organic matter are outlined in Table 1, which summarizes the equivalent organic fractions in recent and ancient sediments.

Various basic organic geochemical fractionation procedures have been routinely applied, with only minor modifications, prior to instrumental analyses. They are described in detail elsewhere (*e.g.*, Reed 1977, Boon *et al.* 1977, Simoneit *et al.* 1978, 1979, 1980, 1981, Simoneit 1978, 1981, 1982a,b, Stuermer *et al.* 1978, Philip *et al.* 1978, van de Meent *et al.* 1980).

Nature of organic matter in maturing basins

Immature organic matter in recent sediments is comprised of minor amounts (based on total organic carbon content) of biogenic gas (CH₄ and CO₂, sometimes H₂S), significant lipid residues of terrigenous or marine origins (or both), and a major

macromolecular fraction consisting of fulvic and humic acids and particulate detritus (*e.g.*, biopolymer fragments, cell membranes and miscellaneous carbonaceous matter; Table 1). The lipids and macromolecular material undergo alteration and diagenesis (including microbiological) according to the environmental conditions during transport and in the depositional sinks, *i.e.*, oxidative degradation in high-energy, oxygenated environments and reductive changes in low-energy anaerobic environments (Didyk *et al.* 1978, Demaison & Moore 1980, Simoneit 1983).

Following completion of early diagenesis, maturation of organic matter commences with increasing burial and concomitant rise in the geothermal gradient. This produces from kerogen (macromolecular organic matter) some low-temperature cracking products, such as natural gas (CH₄-C₈⁺), and bitumen C₈-C₄₀⁺, including a large envelope of an unresolved complex mixture of compounds or UCM), which are added to the endogenous biogenic gas and lipid residues (Table 1). Maturation of pseudokerogen occurs via molecular rearrangements and

addition of geomonomers by copolymerization. Further heating during catagenesis generates additional bitumen and gas, which far exceed the original concentrations of endogenous lipids and gas, thus erasing their compositional signatures and resulting in the characteristic distributions of petroleum compounds (Simoneit 1983). The spent kerogen remains as amorphous carbon. Late stages of catagenesis and the subsequent high-temperature phase called meta-genesis (very deep burial) primarily generate methane from both bitumen and kerogen; H_2S can also be formed, especially in carbonate sequences.

Nature of organic matter in hydrothermal systems

Hydrothermal systems can also act on sedimentary organic matter and on entrained ambient organic detritus in water; these processes result in "instantaneous" diagenesis and catagenesis, and thus produce petroleum products analogous to those from slower acting geothermal changes (Simoneit & Lonsdale 1982, Simoneit 1983, 1984a,b, 1985). Gas (CH_4 - C_{8+} , CO_2 and H_2S) and bitumen (C_8 - C_{40+} , with a large UCM) are cracked from the pseudokerogen and biopolymers, and are added to the endogenous gas and lipids. The bitumen additionally contains products characteristic of elevated thermal processes (e.g., olefins, polynuclear aromatic hydrocarbons or PAH, stabilized molecular markers, etc.). The spent kerogen remains as amorphous "activated" carbon.

The effects of pressure, temperature and time on the chemistry of the organic matter are all inter-related. Temperature and time, which primarily effect petroleum generation, control mineralogical interactions and the elemental composition of kerogens. Migration processes are understood least. In sedimentary basins, migration of petroleum seems to occur by diffusion and in solution ($H_2O/CH_4/CO_2$ solvent), whereas in hydrothermal areas migration proceeds by thermally driven diffusion, in solution, and by advection and mass transport as oil or emulsions (or both). Despite these differences, the overall result may be the same for both regimes. Pressure in both cases aids mainly the solubility of the petroleum in the $H_2O/CH_4/CO_2$ fluids.

SEAFLOOR SPREADING CENTERS AND HYDROTHERMAL PETROLEUM GENERATION

Although this review focuses on the occurrence of petroleum products in six geographic locations of hydrothermal activity, it is the author's opinion that petroleum generation and migration is a ubiquitous process associated with hydrothermalism and metallic-mineral formation in ocean-ridge systems. It should also be noted that the quantities of petroleum associated directly with submarine hydrothermal systems are negligible in terms of eco-

nomic interest because of the lack of structural traps and generally poor source-rock potential (i.e., low organic carbon content). These systems do, however, provide a "natural laboratory" for studying the processes of petroleum generation and the behavior of petroleum in high-temperature fluids. The following data illustrate the diverse suite of hydrothermal samples from different environments, and the wide ranges of organic-carbon source material.

Guaymas Basin, Gulf of California

Guaymas Basin is an actively spreading oceanic basin which is part of the system of spreading axes and transform faults that extends from the East Pacific Rise to the San Andreas fault (Curry *et al.* 1982, Lonsdale 1985). Ocean-plate accretion occurs through dyke and sill intrusions into the unconsolidated sediments, leading to high conductive heat flow (Einsele *et al.* 1980, Curry *et al.* 1982, Einsele 1985, Lonsdale & Becker 1985). Sediments accumulate rapidly (>2 m/1000 yr) and have covered the rift floors to a depth of ~400 m (Curry *et al.* 1982). The organic matter of these recent sediments is derived primarily from diatomaceous and microbial detritus, and averages about 2% organic carbon. Influx of terrigenous organic matter is low because deserts border the Gulf. Thermal stress causes rapid maturation with concomitant petroleum generation; the "oil window" seems to migrate upward as the magmatic heat front rises in the sedimentary column (Simoneit 1984a, Simoneit *et al.* 1984). Petroleum products have been characterized in samples obtained by shallow gravity coring in both rifts (Simoneit *et al.* 1979), piston coring in the North Rift (Simoneit 1983) and deep coring by Leg 64 of the Deep Sea Drilling Project (DSDP) (Curry *et al.* 1982). Petroleum-bearing samples have also been recovered from the seafloor by dredging operations (Simoneit & Lonsdale 1982) and submersible sampling with the ALVIN in 1982 and 1985 (Fig. 1; Simoneit 1984a,b, 1985, Kawka & Simoneit 1987, Simoneit & Kawka 1987).

Leg 64 of the DSDP encountered sills and hydrothermal alteration at depth in all holes drilled in the basin (Fig. 1). Thermogenic hydrocarbon gas, H_2S , and CO_2 were identified at all sites. Lipids (bitumen) were thermally altered close to and below the sills, especially at Site 477 in the South Rift (Simoneit & Philp 1982, Simoneit *et al.* 1984). This alteration is indicated by: i) loss of the odd-carbon-number predominance of the *n*-alkanes (CPI approaches 1.0*); ii) appearance of a broad hump

* CPI-Carbon Preference Index: for hydrocarbons it is expressed as a summation of the odd carbon number homologs over a range, divided by a summation of the even carbon number homologs over the same range (Cooper & Bray 1963, Simoneit 1978).

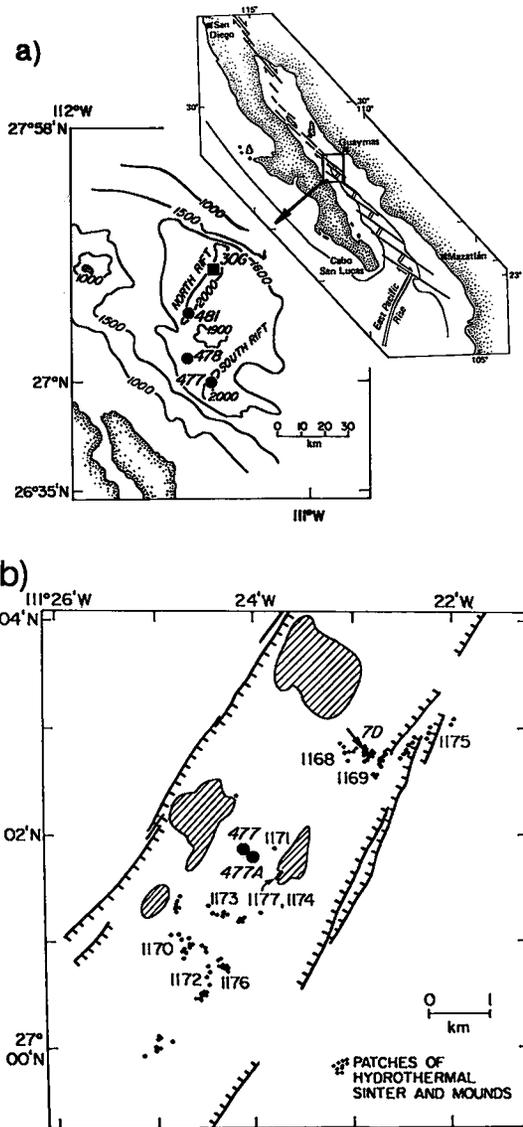


FIG. 1. (a) Location map of Guaymas Basin showing the North and South Rifts, and positions of the DSDP and gravity core (30G) sites; index map shows the location of Guaymas Basin in the Gulf of California. (b) Map of the South Rift showing the ALVIN dive areas by dive number (also dredge 7D and DSDP Site 477); the hachured areas are hills and high areas above the rift floor.

of UCM (naphthenes); iii) isomerization of various biomarkers; iv) presence of large amounts of terminal olefins (alk-1-enes), isoprenoid hydrocarbons, and elemental sulfur; and v) appearance of PAH.

The petroleum products have migrated away from

heat sources (e.g., sills or magma at depth) by advection, diffusion, distillation, and especially by cosolution in hydrothermal fluids (Simoneit & Philp 1982, Simoneit 1982b, Simoneit *et al.* 1984). Cosolution in this context refers to the solution in any proportion of petroleum (bitumen), itself a solution of a large number of compounds, in hydrothermal water, *i.e.*, the stage before emulsion. The kerogens (*i.e.*, insoluble detrital organic matter in sediments) of the shallow DSDP core samples are typical of unaltered marine organic matter (Simoneit & Philp 1982, Simoneit *et al.* 1984). In deeper sections (> ~180 m depth at Sites 477 and 478), the kerogens reflect complete expulsion of pyrolysate; in these zones of high thermal stress (entering greenschist facies) the kerogen residues resemble activated amorphous carbon (Simoneit 1982b).

Numerous hydrothermal mounds rise to 20–30 m above the South Rift floor (water depth about 2000 m) and most are actively discharging vent fluids with water temperatures of 315°C at ~200 bars (Lonsdale 1985, Lonsdale & Becker 1985, Merewether *et al.* 1985). Typical samples from these mounds are stained and cemented with petroleum; the samples have a strong odor reminiscent of diesel fuel (Simoneit & Lonsdale 1982). Samples have very diverse petroleum contents and hydrocarbon distributions (Figs. 2, 3; Simoneit 1984a,b, 1985, Kawka & Simoneit 1987, Simoneit & Kawka 1987), but are analogous to those described for bitumens at depth in the DSDP holes (Simoneit 1983, 1984b). The *n*-alkanes range from methane to greater than *n*-C₄₀, with usual maxima in the mid *n*-C₂₀ region and no carbon-number predominance (CPI = 1.0, Table 2). These data and the kinetic parameters of the biomarkers indicate that the petroleum products were generated by rapid and intense heating.

An example of a gas chromatographic (GC) trace of an aromatic/naphthenic fraction (F2) of a sample is shown in Figure 3b. The major resolved peaks are PAH, a group of compounds uncommon in petroleum products but ubiquitous in higher temperature pyrolysis residues (Geismann *et al.* 1967, Blumer 1975, Hunt 1979). The dominant analogs are the pericondensed aromatic series, for example, phenanthrene, pyrene, benzopyrenes, perylene, benzoperylene and coronene. A pyrolytic origin is also supported by the presence of five-membered alicyclic rings (e.g., acenaphthene, methylenephenanthrene, fluorene, fluoranthene, *etc.*). These are found in all pyrolysates from organic matter; once formed, they do not easily revert to pericondensed aromatic hydrocarbons (Blumer 1975, 1976, Scott 1982). These fractions also contain significant amounts of toxic PAH, e.g., the benzopyrenes. In addition, perylene is present; it is the predominant PAH of unaltered lipids in sediments deposited under oxygen-minimum environments in the Gulf (Simoneit & Philp 1982,

Simoneit 1982a,b). Thus, the chemical composition of the aromatic fractions indicates derivation through high-temperature pyrolysis and rapid quenching, presumably by hydrothermal fluids.

Hydrothermal petroleum migration in Guaymas Basin seems to occur as bulk-phase (pure petroleum), cosolute fluid and aqueous solution (high-temperature solution of predominantly *n*-alkanes only) upward to the seabed, where the petroleum condenses (solidifies) and collects in the conduits and vugs of hydrothermal mineral mounds in response to ambient temperatures. PAH and sulfur accumulate in the hot vents; waxes crystallize in intermediate-temperature regions (20–80°C), and volatile petroleum partly collects in cold areas (3°C) and emanates into the seawater with plume discharges (Simoneit 1984a,b, 1985, Merewether *et al.* 1985). Both the extensive maturation of organic matter to bitumen in the DSDP holes, and the significant accumulations of petroliferous exudate at the rift floor, confirm the importance of hydrothermal metamorphism (pyrolysis) as a feasible mechanism for the formation of petroleum.

Escanaba Trough, northeastern Pacific

The Escanaba Trough represents the southern extension of the Gorda Ridge, an active oceanic spreading center about 300 km long, bounded on the north and south by the Blanco and Mendocino fracture zones, respectively (McManus *et al.* 1970). The Trough is filled with up to 500 m of Quaternary turbidite sediments (McManus *et al.* 1970).

Petroleum cements the sediments and sulfide deposits that blanket the ridge axis and is derived from hydrothermal alteration of sedimentary organic matter (Kvenvolden *et al.* 1986). Typical GC traces of the saturated and aromatic hydrocarbon fractions are shown in Figure 4. The organic source material for these petroleum is terrigenous, on the basis of CPI, carbon-number range (Table 2), biomarker composition, and sedimentological considerations (Kvenvolden & Simoneit 1987).

In the aliphatic hydrocarbon fraction, the *n*-alkanes range from C₁₄ to C₄₀, with a carbon-number maximum at *n*-C₂₇. A predominance of odd carbon numbers >*n*-C₂₅ (CPI = 1.25, Fig. 4a) is typical of a terrestrial, higher plant origin. Homologs of a marine origin (<*n*-C₂₅) are less concentrated. This petroleum was probably generated by intense heating of short duration, as indicated by kinetic parameters of the biomarkers and by the high concentrations of unsubstituted PAH (Fig. 4b; Kvenvolden & Simoneit 1987).

East Pacific Rise, 13°N and 21°N

Hydrothermal activity and associated massive sulfide deposits are found on the unsedimented axis of the East Pacific Rise (EPR) in the region of 13°N;

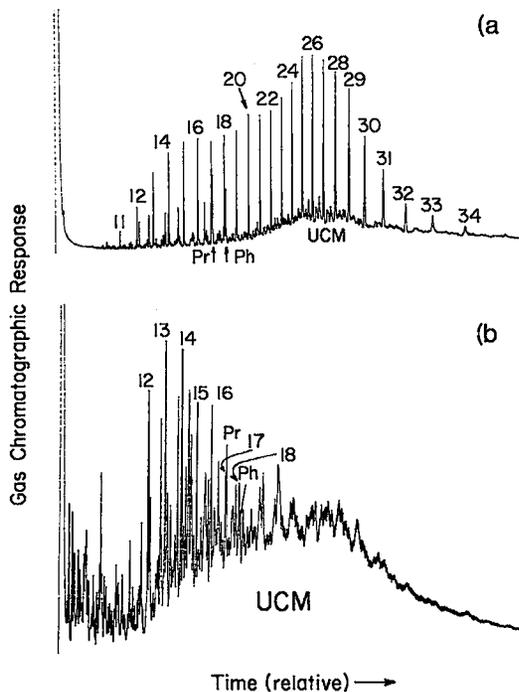


FIG. 2. Representative gas chromatograms of total oils extracted from samples recovered by DSV ALVIN in the South Rift: (a) 1170-1 interior of large chimney base; (b) 1177-3 oily crust on rock. Numbers on all GC traces are carbon chain length of *n*-alkanes. Pr = pristane, Ph = phytane; gas chromatographic conditions given in Simoneit (1984a).

abundant faunal communities are also associated with this activity (Hékinian *et al.* 1983). Aliphatic hydrocarbons have been analyzed in hydrothermal plumes and in metalliferous sediments near the active vents and at the base of an inactive chimney (Brault *et al.* 1985, 1988). Hydrocarbons from metalliferous sediments have characteristics of immature organic matter, which was recently biosynthesized and microbiologically degraded, as indicated by the abundance of low-molecular-weight (>C₂₅) *n*-alkanes and phytane; a contribution of continental higher plant material is shown by the presence of high-molecular-weight *n*-alkanes with an odd-carbon-number predominance (Fig. 5a, Table 2). The immature character of the organic matter is also indicated by the presence of biomarker hydrocarbons derived from steroids and triterpenoids, which are the result of low temperatures, as might be expected in the talus of an extinct vent system. The contents of a sediment trap deployed in the area within ~20 m of the vents are characterized by biologically derived material and also by biomarker compounds affected by thermal alteration (Brault *et al.* 1985).

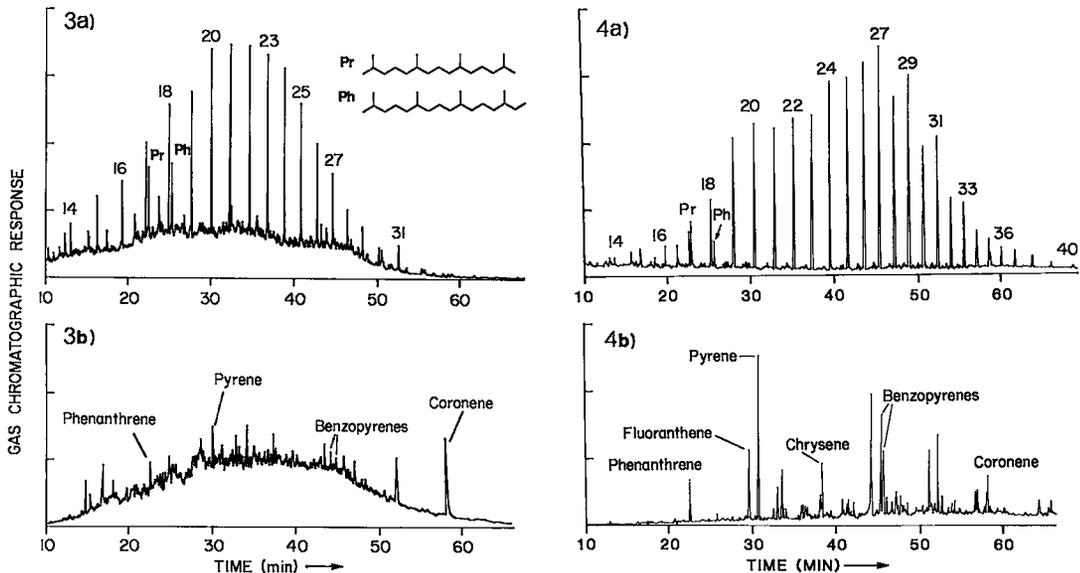


FIG. 3. Gas chromatograms of the (a) aliphatic and (b) aromatic hydrocarbons from dredge sample 7D-2B in Guaymas Basin (Simoneit & Lonsdale 1982). The structures of pristane and phytane are represented by the inset in (a).

FIG. 4. Gas chromatograms of the (a) aliphatic and (b) aromatic hydrocarbons in a petroleum sample from the Escanaba Trough (Kvenvolden *et al.* 1986).

TABLE 2. SUMMARY OF THE CHARACTERISTICS OF HYDROTHERMAL PETROLEUMS FROM SEVERAL SEAFLOOR SPREADING CENTERS.

Location	Total organic carbon of sed. (average %)	Petroleum Fractions (wt.%)			η -Alkane range	CPI ¹	Pristane: Phytane	References
		Aliphatic hydrocarbons	Aromatic hydrocarbons	NSO cpds & asphalt				
Guaymas Basin, Gulf of California	2	3	23	74	13-35	1.03	1.1	Simoneit & Lonsdale 1982, Simoneit & Kawka 1987
		65	15	20	1-40	1.02		
Escanaba Trough, Gorda Ridge	0.4	2	44	54	14-40	1.25	1.7	Kvenvolden <i>et al.</i> 1986
Atlantis II Deep, Red Sea	0.14	n.d. (230 ng/g) ²	n.d.	n.d.	15-40	1.1	0.8	Simoneit <i>et al.</i> 1987a
East Pacific Rise, 13°N	0.4	n.d. (1.0 µg/g) ²	n.d.	n.d.	15-34	1.1	1.2	Brault <i>et al.</i> 1985
East Pacific Rise, 21°N	n.d.	n.d. (0.2-6 ng/g) ²	n.d.	n.d.	14-40 ⁺	0.9-1.03	0.5-1.0	Brault <i>et al.</i> (unpublished data)
Mid-Atlantic Ridge, TAG Area 26°N	n.d.	n.d.	n.d.	n.d.	10-25	1.01	0.9-1.3	Brault & Simoneit 1988

¹ CPI - carbon preference index, calculated here over the range C₂₄ to C₃₄.

² Values in parentheses are total yield per gram dry sample.
n.d. = not determined

This indicates that higher temperature degradation of entrained organic detritus is an important process near hydrothermal discharge sites. Thermally matured compounds (Fig. 5b) are also present at

trace levels in waters collected within ~ 1 km above the hydrothermal vents. The hydrocarbon pattern of these waters is indicative in many cases of pyrolysis of bacterial matter in entrained ocean water during

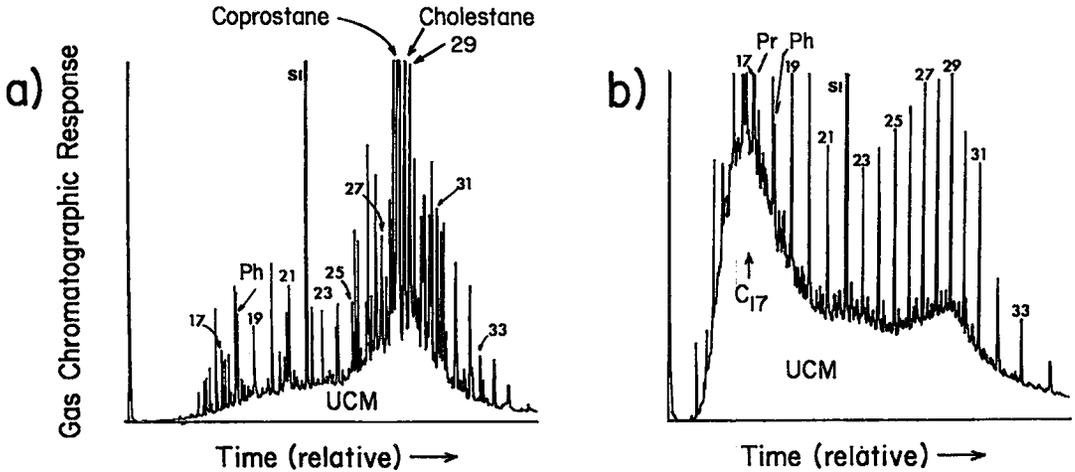


FIG. 5. Gas chromatograms of aliphatic hydrocarbons from extracts of: (a) hydrothermal metalliferous sediment and (b) surrounding water above the vents from the EPR at 13°N (Brault *et al.* 1985). SI = internal standard (*n*-C₂₂); Pr = pristane; Ph = phytane.

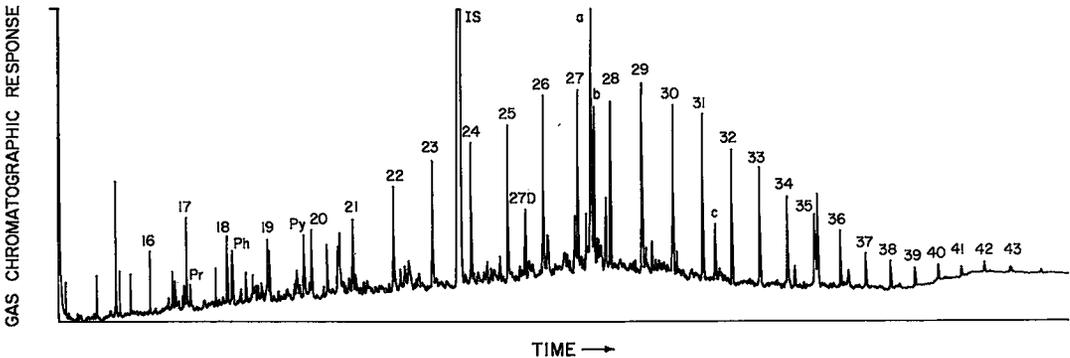


FIG. 6. Gas chromatogram of the total hydrocarbon fraction from an extract of a pyritized tube worm in sulfide matrix from the EPR at 21°N (Pr pristane; Ph phytane; Py pyrene; a, b cholestenes; c diploptene) (Brault *et al.* submitted).

cooling of discharging fluids (Brault *et al.* 1988).

Extensive hydrothermal activity and associated sulfide deposits have also been described at 21°N on the EPR where the crust is unsedimented (Spiess *et al.* 1980, Ballard *et al.* 1981). The hydrocarbon contents of massive sulfides from vent chimneys are extremely low but definitely thermogenic (Table 2). A GC trace for total hydrocarbons is shown in Figure 6 (Brault *et al.* submitted). The *n*-alkanes in massive sulfides range from C₁₄ to greater than C₄₀, with no carbon-number predominance; a pyritized tube worm from a chimney has a slight odd-carbon-number predominance. All samples contain PAH, providing evidence for hydrothermal activity. Coupled with the carbon-number maxima at *n*-C₂₇ or higher, this indicates that the hydrocarbons were entrapped/condensed in a high-temperature regime

such as an active chimney. The sample with pyritized tube worm residues (Fig. 6) also contains hydrothermally altered derivatives of biomarkers (e.g., cholestenes, hopenes) from the vent biota, *i.e.*, probably mainly tube worms and bacteria.

Atlantis II Deep, Red Sea

The Atlantis II Deep contains stratified brine layers, the deepest of which is at a temperature of 62°C (Hartmann 1980, 1985). Bulk organic matter and hydrocarbons have been analyzed in two sediment cores (No. 84 and 126, CHAIN 61 cruise) from the Deep (Simoneit *et al.* 1987). Although the brine overlying the coring areas is reported to be sterile, sedimentary organic material derived from autochthonous marine planktonic and microbial inputs and minor terrestrial sources is present. The

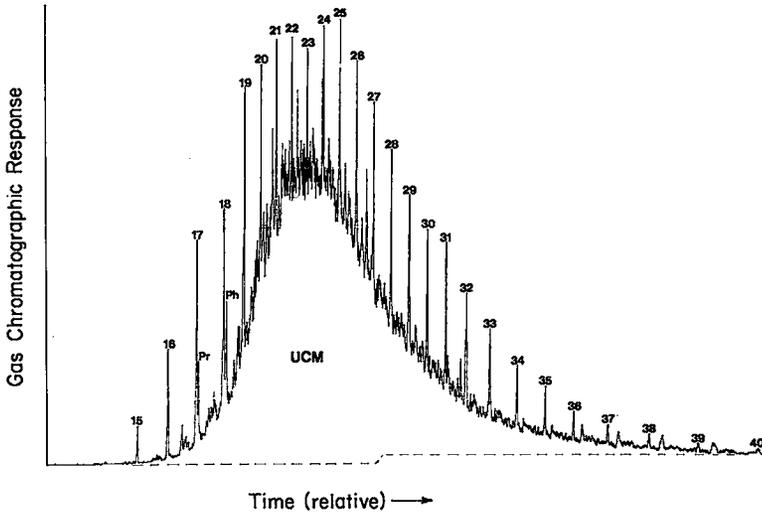


FIG. 7. Gas chromatogram of the total hydrocarbon fraction extracted from the Atlantis II Deep core sample 84, 443-453 cm (Simoneit *et al.* 1987).

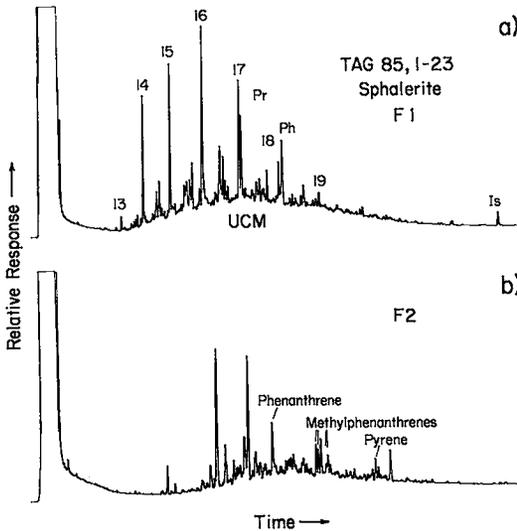


FIG. 8. Gas chromatograms of (a) aliphatic and (b) aromatic hydrocarbons from an extract of a massive sphalerite sample from the Mid-Atlantic Ridge (Brault & Simoneit 1988).

organic input derived from the water column above the brine is further metabolized by microorganisms, and the reworked compounds with organic detritus are apparently then incorporated into the sediments under the brine by sinking as material adsorbed or attached to particles of metallic oxide precipitates.

Low-temperature maturation in the sediments results in petroleum generation, even from low amounts of organic matter (average 0.05%). Both steroid and triterpenoid hydrocarbons (biomarkers) show that extensive acid-catalyzed reactions are occurring in the sediments. In comparison with other hydrothermal systems driven by intrusions (*e.g.*, Guaymas Basin; Cape Verde Rise, Simoneit *et al.* 1981), sediments in the Atlantis II Deep exhibit a lower degree of thermal maturation, as is clearly shown by the elemental composition of the kerogens and the absence of pyrolytic PAH in the bitumen.

The lack of carbon-number preference among the *n*-alkanes (CPI = 1.0) suggests, especially in the case of the long-chain homologs (*e.g.*, Fig. 7, Table 2), that the organic matter has been affected by catagenesis. However, the yields of hydrocarbons with respect to sediment weight are much lower than those observed in other hydrothermal areas. The low temperature and low organic-carbon content of the sediments in the Atlantis II Deep seem to be responsible for this difference.

Mid-Atlantic Ridge, TAG area 26°N

The Trans-Atlantic Geotraverse (TAG) hydrothermal field on the Mid-Atlantic Ridge crest at 26°N is one of two active vent systems known from slow-spreading oceanic ridges (Rona *et al.* 1984, Thompson *et al.* 1988). Hydrothermal deposits lying directly on oceanic crust have been dredged from the area (TAG 1985-1). Three sulfide-rich samples, consisting mainly of anhydrite, sphalerite, and chalcopyrite, respectively, contained minor amounts of the more volatile (C₁₀-C₂₂) hydrothermal petroleum (Brault

TABLE 3. FEATURES OF HYDROTHERMAL PETROLEUM COMPARED TO RESERVOIR PETROLEUM

Hydrothermal and Reservoir Petroleum:

1. Natural gas and gasoline-range hydrocarbons
2. Full range of *n*-alkanes, no carbon-number-predominance (CPI = 1.0-1.2)
3. Naphthenic components (major hump of UCM)
4. Isoprenoid hydrocarbons (including significant pristane and phytane)
5. Biomarkers (e.g. mature 17 α (H)-hopanes and steranes)
6. Alkylaromatic hydrocarbons and asphaltenes

Hydrothermal Petroleum only:

1. Polynuclear aromatic hydrocarbons (PAH) > alkyl aromatic hydrocarbons
2. Residual immature biomarkers and intermediates (e.g. 17 β (H)-hopanes, hopenes, sterenes)
3. Significant aromatic sulfur hetero compounds
4. High sulfur content
5. Alkene content near "source rock"

& Simoneit 1988). The saturated and aromatic hydrocarbon fractions separated from the extract of the sphalerite sample are shown in Figure 8. The *n*-alkanes range from C₁₁ to C₂₂ with a CPI = 1.0; pristane and phytane are present, and the UCM maximizes at the GC retention time for *n*-C₁₇. This pattern is analogous to that observed for samples from the EPR at 13°N and from the Atlantis II Deep. The aromatic fraction, which contains naphthalene, phenanthrene, their alkyl homologs and sulfur aromatic compounds, supports a hydrothermal origin.

DISCUSSION

Petroleum generation

The principal zone of petroleum formation in sedimentary sequences under normal geothermal gradients extends from about 1 km to 3 km depth (e.g., Hunt 1979, Tissot & Welte 1984). This depth corresponds to a temperature range of 50°–120°C. The effect of pressure on this process is significant, although it has not been quantified (Tissot & Welte 1984). The cracking of organic matter to natural gas is thought to take place at high temperatures of 150°–250°C (e.g., Kartsev *et al.* 1971, Vassoevich *et al.* 1974, Hunt 1979). These proposed temperature regimes for the oil and gas "windows" may need some adjustment in light of more recent data on hydrothermal systems and ultra-deep wells.

The "instantaneous" petroleum generation in hydrothermal systems is a facile process which occurs at temperatures approaching a maximum of 400°C. At such high temperatures, organic matter is only partly destroyed, probably because the thermogenic products are rapidly removed from the hot zone. Formation of hydrothermal petroleum seems to com-

mence in low-temperature areas, generating products from weaker bonds (e.g., ether, sulfide, carbonyl, tertiary carbon linkages). As the temperature regime rises, products are derived from more refractory organic matter and even "resynthesized" (e.g., PAH compounds). The major similarities and differences between hydrothermal petroleum and reservoir petroleum are summarized in Table 3. Most hydrocarbon products occur in both types of petroleum; the major difference is the enhanced content of PAH and sulfur in the hydrothermal products.

Organic matter associated with deeper hydrothermal systems (e.g., epithermal ores in volcanic terranes) is typically more asphaltic and has a high PAH content. Such organic matter is widely distributed (e.g., California mercury deposits: Geissman *et al.* 1967, Blumer 1975; other hydrothermal sulfides: Germanov & Bannikova 1972). Deep well drilling (>7000 m) has intersected Cretaceous shales which were at *in situ* temperatures of about 260°–300°C (e.g., Price *et al.* 1981, Price 1982). These samples were rich in bitumen components and their kerogens still had significant hydrocarbon-generation potential. This indicates that *in situ* petroleum is stable at much higher temperatures and pressures than those discussed above, and over long geologic time periods.

During mineral diagenesis and metamorphism under non-oxidizing conditions, the organic-matter composition changes progressively to more aromatic and asphaltic residues by the expulsion of volatile components (e.g., CO₂, CH₄, H₂O, *etc.*). The carbonaceous residues are often associated with heavy-metal enrichments, as for example uranium (e.g., Schidlowski 1981) or Carlin-type gold and silver ores

(*e.g.*, Radtke & Scheiner 1970). Heavy aromatic hydrocarbons (PAH), present in all the hydrothermal sites described here, are a product of high-temperature alteration and thus may be good indicators of such alteration peripheral to sulfide orebodies (*e.g.*, Germanov & Bannikova 1972, Blumer 1975).

Organic-matter type

The constitution of the initial organic matter determines the types of petroleum products that form in basins with a normal geothermal gradient, and in hydrothermal systems. The major source of petroleum compounds is kerogen, the sedimentary macromolecular organic detritus which generally constitutes the bulk of the total organic carbon content (Tissot & Welte 1984, Table 1). In general, terrestrial detritus from mainly vascular plants yields an aromatic kerogen (*e.g.*, coal) which has a natural-gas potential, whereas marine/lacustrine organic matter from primarily microbial and planktonic residues yields an aliphatic kerogen (*e.g.*, sapropel) which has a paraffinic petroleum potential (Hunt 1979, Tissot & Welte 1984). Kerogens in sedimentary basins are always mixtures of these inferred end members.

Syngenetic sedimentary lipid matter undergoes

alteration during diagenetic and early catagenetic processes; this changes the hydrocarbon signature (Fig. 9). During oil generation, however, large amounts of additional hydrocarbons are superimposed on the syngenetic lipids, thus obscuring the earlier signature (*e.g.*, loss or reduction of the odd-carbon-number predominance $>C_{25}$, *cf.* Fig. 9 *versus* Figs. 3, 4). Syngenetic lipids of sediments can usually be utilized to elucidate the various sources of the total organic matter (*e.g.*, Simoneit 1978, 1981, 1982a). For example, lipid hydrocarbons of normal sediment in Guaymas Basin (Fig. 9a) contain *n*-alkanes mostly $<C_{21}$, and a minor series of homologs $>C_{23}$ with a strong odd-carbon-number predominance. This composition is typical of a predominantly marine planktonic and microbial origin, and a minor influx of terrigenous vascular plant wax ($>C_{25}$). By contrast, lipid hydrocarbons of sediment in the Escanaba Trough (Fig. 9b) contain *n*-alkanes, mostly $>C_{23}$ with a strong odd-carbon-number predominance. This signature is derived mainly from terrigenous vascular plant wax, with a minor microbial component (Kvenvolden *et al.* 1986). In both the Guaymas and Escanaba samples, the compositions of the kerogens support the interpretations based on the nature of the lipid hydrocarbons (Simoneit 1978, Simoneit *et al.* 1979).

Migration processes

The aqueous solubility of petroleum and various hydrocarbon fractions has been determined experimentally (Price 1976). Petroleum solubility increases exponentially from 100 to 180°C and solubilities are high enough to account for the formation of petroleum reservoirs by migration of molecular or co-solutions. Increased salinities of 150‰ NaCl cause drastic exsolution of the petroleum and at 350‰ almost total "salt-out" occurs (Price 1976). This finding is consistent with the requirement for the separation of petroleum from migrating solutions in the salty waters of reservoir sands. It has been demonstrated that methane in the presence of water is an even better carrier for petroleum than water or methane alone (Price *et al.* 1983). Both increases in pressure (to about 1800 bar, 1.8×10^8 Pa) and temperature (to 250°C) raised the solubility of petroleum. Cosolubility was found at rather moderate conditions (*e.g.*, 100°C at 10^8 Pa, 200°C at 0.5×10^8 Pa). The addition of other gases such as CO₂ and ethane to this mixture also increases the solubility of petroleum. Under these experimental conditions, CH₄, C₂H₂ and CO₂ are all supercritical and H₂O approaches its near-critical state; thus, the gases and H₂O are all mutually soluble by the reduced hydrogen bonding in water, and are a good cosolvent for petroleum. Therefore, primary migration seems to proceed as gas/fluid and aqueous solution (see also Hunt 1979).

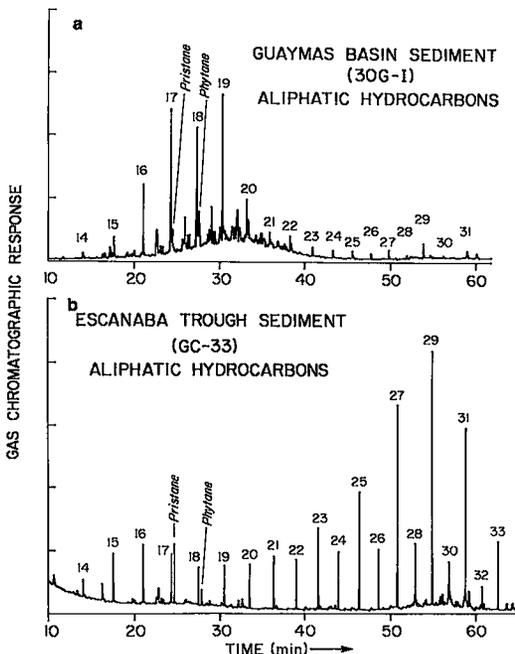


FIG. 9. Gas chromatograms of total hydrocarbons in extracts from surface sediments of (a) Guaymas Basin, Site 30G (Simoneit *et al.* 1979), and (b) Escanaba Trough (Kvenvolden *et al.* 1986).

CONCLUSIONS

Recent immature sediments receive biogenic detritus which, upon deposition, undergoes diagenetic and additional microbial alteration. Increasing burial in sedimentary basins results in the onset of organic-matter maturation, which generates some volatile products from the kerogen (easily cracked moieties) that become added to the endogenous lipid residues. This is the beginning of petroleum formation. As the depth of burial (*i.e.*, temperature) increases, catagenesis commences and major petroleum generation takes place. At still greater depths of burial the metagenetic stage is envisaged, where extensive cracking, disproportionation, and reforming of the organic matter (both petroleum and kerogen residues) occur to yield primarily gases and residual amorphous carbon.

In the case of hydrothermal systems, these processes are compressed into an "instantaneous" geological time frame. At seafloor spreading axes, hydrothermal systems operating below a sediment blanket (*e.g.*, Guaymas Basin and Escanaba Trough) generate petroleum from generally immature organic matter in the sediments. This petroleum then migrates upward, leaving behind a spent carbonaceous residue. The Guaymas petroleums are comprised of: 1) gasoline-range hydrocarbons (C_1 - C_{12}); 2) a broad distribution of *n*-alkanes (C_{12} - C_{40+}) with no carbon-number predominance; 3) a naphthenic hump, UCM; 4) pristane and phytane at significant concentrations; 5) mature biomarkers (*e.g.* α -hopanes); and 6) significant concentrations of PAH and sulfur. Exterior exposed petroleum, and petroleums in unconsolidated surface sediments, are microbially degraded and leached, whereas interior samples are chiefly unaltered.

Hydrothermal systems operating in unconsolidated rift areas (*e.g.*, EPR at 13°N and 21°N, Mid-Atlantic Ridge at 26°N) generate trace amounts of petroleum and emit methane. Low amounts of petroleum are generated by pyrolysis of suspended and dissolved biogenic organic detritus (including bacteria and algae) entrained during the turbulent cooling of the vents both for sedimented and bare-rock systems. However, this type of petroleum is swamped in the former case by the large quantity of petroleum generated from the sedimentary organic matter. In addition, low-level maturation is observed in the surrounding area at vent sites, probably due to warming of ambient detritus. Pyrolysis of organic matter and petroleum migration also appear to have occurred in geothermal regions characterized by epithermal ore deposits.

Gases, bitumen (lipids) and kerogen complement each other in providing information about the sources and thermal history of sedimentary organic matter. Kerogen is a sensitive *in situ* indicator of temperature, and petroleum (bitumen including asphalt

and gas) represents the product mixture of high-temperature stress. These products may have migrated or remained *in situ*.

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