AN ABSTRACT OF THE THESIS OF

<u>Orest E. M. Kawka</u> for the degree of <u>Doctor of Philosophy</u> in <u>Oceanography</u> presented on <u>May 11, 1990</u>.

 TITLE:
 Hydrothermal Alteration of Sedimentary Organic Matter in Guaymas

 Basin, Gulf of California

Redacted for privacy

Abstract Approved:

Bernd R. T. Simoneit

Guaymas Basin differs from most spreading centers in that the plate accretion occurs by dike and sill intrusions into an overlying thick cover of diatomaceous muds and turbidites. The associated hydrothermal activity results in a rapid metamorphism of the sediments at depth and a rapid transport of the pyrolysates to the seabed. These seabed hydrothermal oils are similar to normal reservoir petroleums in containing broad *n*-alkane distributions with no carbon-number-predominance and matured biomarker distributions but differ by often including high amounts of polar components. Their hydrocarbon compositions are consistent with variable entrainment and/or solubilization of less thermally mature bitumens during transport to the seabed. The hydrothermal oils also contain significantly higher concentrations of unalkylated PAH than normal crude oils, consistent with their higher generation temperatures. In the subsurface sediments, progressive hydrothermal alteration with depth, due to increasing temperatures and passage of fluids through the sediments, results in increased bitumen-based PAH concentrations. At the greatest depths, the bitumens are dominated by the unalkylated PAH, primarily dibenzothiophene and phenanthrene. Although the ranges of PAH concentrations in the seabed oils are comparable to those in bitumens downcore, the seabed distributions are more skewed towards the high molecular weight compounds (e.g. benzopyrenes, benzo(ghi)perylene, coronene). This is attributed to a selective solubilization and/or non-deposition of the more soluble/volatile aromatics at the seabed. The progressive change in hydrocarbon character with depth suggests that aliphatic and aromatic components can be transported to the seabed independently. Biomarker analysis and comparison with laboratory simulated maturations by hydrous pyrolysis

suggest that the mature signatures of many of the oils are caused by high pyrolytic temperatures (230 - 370°C) for short periods of time (< 10 days), which is reasonable in view of the dynamic nature of the hydrothermal process and the temperature ranges suggested by kerogen and mineralogy data. Diels' hydrocarbon and an apparently related series of C_{18} to C_{20} triaromatic steroid hydrocarbons are dominant components of the aromatic fractions of these petroleums. A number of indices, based on their occurrence, are suggested as possible tracers for hydrothermal and high-temperature processes of organic matter alteration.

HYDROTHERMAL ALTERATION OF SEDIMENTARY ORGANIC MATTER IN GUAYMAS BASIN, GULF OF CALIFORNIA

by

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A THESIS

submitted to

Oregon State University

in partial fulfillment of the requirements for the degree of

Doctor of Philosophy

Completed May 11, 1990 Commencement June 1991 APPROVED:

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Typed by Barbara McVicar for _____Orest E. M. Kawka

In memory of my father, Orest

ACKNOWLEDGEMENTS

I would like to thank my major advisor, Bernd R. T. Simoneit, for his guidance and financial support through the majority of my graduate education. I greatly appreciate him giving me the opportunity and the means to explore the various aspects of organic geochemistry. He has always tried to nurture the growth of new ideas and has, thereby, provided additional avenues of investigation for both my dissertation and future research. I am grateful to him for both his tutelage and patience over the years.

I also wish to thank the other members of my committee for their help. Fredrick G. Prahl has always been willing to give objective assessments of my research and has provided many helpful suggestions. I thank him for our "scientific" banter and both his technical and personal advice over the years. His special friendship and never-failing encouragement greatly contributed to the successful completion of this thesis. Special thanks go to Keith A. Kvenvolden, who served on my thesis defense committee and provided useful input, with relatively short notice. His comments and advice are greatfully acknowledged. Cyrus W. Field provided the geological facet of my committee, and his patience was appreciated. Although Bruce Brownawell was only on my committee a short time, our discussions and his suggestions proved invaluable. He also brewed some pretty good beer, and his friendship was always appreciated. My graduate council representative, Henry Van Dyke, was kind enough to return from retirement in order to serve on my defense committee.

I would also like to thank Philip A. Meyers, who gave me my first opportunity in the field of organic geochemistry and sparked my interest to continue in it, and Mary J. Leenheer, who first intoduced me to the practical aspects of this science and guided my initiation into research.

Over the years, many graduate students have helped me along the way with both their friendship and encouragement. Jeff Paduan has been a very good friend and longtime roommate of mine. I have always been able to count on him for both his good humor and support, both of which are of the utmost necessity in graduate school. I thank him for putting up with me and making my time in Oregon most memorable. Laurel Standley was a laboratory partner in the early stages of my research at OSU, and our scientific discussions were always interesting. I thank her for her friendship and companionship during the long and weird hours I used to spend with the mass spec at the Marine Science Center. Harry Beller, another former labmate, was also a very accommodating roommate during a part of my graduate days, and I thank him for both his friendship and introducing me to "life with composting". Jim Butler, Bruce Dubendorff, and Ahmed Rushdi were all additional classmates of mine whose friendship I valued greatly over the years.

Roald Leif has been a relatively recent but welcome adition to the organic geochemistry group for both his friendship and knowledge of chemistry. His encouragement and companionship and technical assistance in the last stages of my thesis are greatfully acknowledged. Luis Pinto, another organic geochemist and comrade in arms, has always been willing to discuss our research. I thank him for his help over the years and for continuing to be a friend of mine, even after long months at sea together. I also thank John O'Connor for both his friendship and the important "scientific consultations" at the Beanery. His encouragement to continue and finish my thesis will always be appreciated. I thank Jennifer Brophy (now Paduan) for making both Jeff happy and our house a more interesting place. I also thank Xiao Jing Chen, Sharon Roth, David Booth, Dana Desonie, Jim McManus, and Johnny Sharp, who have all, in one way or another, contributed to my sanity.

I thank Martine Brault for both her friendship and showing me the French version of organic geochemistry. She also tried unsuccessfully, through no fault of her own, to teach me to speak French without a Spanish accent. I would also like to thank the other members of the 3rd floor crowd, both new and old: Jacque Johnson, Margaret Sparrow, Celeste Correia, Joe Jennings, Bob Collier, and Lou Gordon and any I have failed to mention, who have all made my stay at OSU more pleasant and rewarding. Special thanks are due Barbara McVicar for not only "translating" my mostly illegible writing and typing a large portion of this thesis, but also for allowing me to use her office and computer.

During my graduate education in Oregon, I have made many additional friends. A special few have made my graduate years significantly more pleasureable and fulfilling. Susan Sparks has been my very special friend for a long time. I thank her for her love, encouragement, and moral support over the years. She has been the most important factor in my survival of graduate school, and I will always cherish our friendship. David Reinert has been a good and long-time friend, and I thank him for always providing the right amount of diversion from work to help me keep my sanity. David Madison was an always-willing sandball and fishing partner, whose friendship was a welcome connection with the "real" world. To all these people and those that I have not specifically mentioned, thanks for your help and support. Finally, but most of all, I thank my entire family, all the Kawkas and Brants: my mother and father, my sister Lydia, grandmother Vava (and Vectēvs), grandparents Babunia and Didyk, and aunt Oksana and family. Throughout my undergraduate and graduate years, they have all continually provided me with the love and unfaltering emotional and economic support I needed to accomplish my goals. They have always been willing to forego their own needs and comforts, so that I could succeed and attain my dreams. I especially want to thank my mother Benita for the very large sacrifice she made during the last few months of my thesis writing. I hope that I can someday show her how much it meant to me, and I will always love her the more for it. In all, I will never be able to repay my family for all they have done, except to say that this thesis is as much theirs as it is mine.

I thank the U. S. National Science Foundation and Deep Sea Drilling Project for access to the various samples used in this research and the crew and scientists aboard the *Atlantis II* and D.S.V. *Alvin* for their help and sample collection. Financial support for this thesis research from the National Science Foundation, Division of Ocean Sciences; Donors of the Petroleum Research Fund, administered by the American Chemical Society; and the Link Foundation Fellowship Program is gratefully acknowledged.

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HYDROTHERMAL ALTERATION OF SEDIMENTARY ORGANIC MATTER IN GUAYMAS BASIN, GULF OF CALIFORNIA

I. INTRODUCTION

This thesis is a compilation of papers that assess the hydrothermal pyrolysis of organic matter in Recent sediments at the Guaymas Basin spreading center in the Gulf of California. The samples described in this study were analyzed primarily for their hydrocarbon content and include both the surface expression of this hydrothermal process – seabed petroleums, recovered by the D.S.V. *Alvin*, and the inferred source of these oils – thermally altered downcore sediments, sampled by the Deep Sea Drilling Project (DSDP) Leg 64, Sites 477 and 478.

The overall goals of this study were to identify the processes controlling the composition of the organic pyrolysates accumulating at the seabed and to assess the overall significance of their occurrence in terms of the catagenesis of organic matter (petroleum-formation) and possible ecological effects. In attainment of these goals, the following objectives were identified: 1) to characterize the organic content of the seabed deposits of the hydrothermal process, 2) to compare these hydrothermal petroleums to normal reservoir petroleums and, consequently, this high-temperature, hydrothermal process of oil formation to that in basins with normal geothermal gradients, 3) to identify molecular constituents of these pyrolysates which could be used to identify such high-temperature maturation of organic matter, and 4) to delineate the processes and their effects that post-depositionally alter seabed deposits.

Each of the papers (chapters) of this thesis contributes to the accomplishment of these objectives. The first paper (Chapter II) is a survey of the general organic character of the seabed deposits of hydrothermal petroleums in the Guaymas Basin. In addition, a selection of these pyrolysates are compared to normal reservoir petroleums in terms of bitumen character and thermal maturity, as reflected by their molecular composition. Various chemical, physical, and biological processes that appear to influence their composition are discussed.

The second paper (Chapter III) is a more detailed characterization of the seabed petroleums in terms of their aromatic hydrocarbon contents. High-temperature pyrolysis of organic matter that should lead to an enhancement of polycyclic aromatic hydrocarbons (PAH) in these hydrothermal oils, and their contents are evaluated. The PAH content of Guaymas Basin petroleums are compared to those of normal reservoir petroleums. A further comparison of the sedimentary concentrations of these naturally formed PAH in the hydrothermal vent environments with anthropogenic PAH concentrations in various locations is used to assess the environmental significance of such a natural source of PAH in the ocean. Finally, possible toxicological effects on the benthic vent communities is evaluated by comparison of the PAH concentrations with those in a PAH-rich creosote-contaminated sediment of known toxicity.

The third paper (Chapter IV) describes the bitumen character of downcore sediments recovered from DSDP Sites 477 and 478. The samples from the former site have been altered by an overall high heat flow at depth, while the latter set contain examples of thermal products generated by the more localized sill-induced pyrolysis. The data obtained, primarily PAH, is used to further clarify the formation, transport, and deposition of the hydrothermal petroleums at the Guaymas Basin seabed.

The final paper (Chapter V) is an evaluation of the molecular (biomarker) signatures of this hydrothermal process. The extent of thermal maturation in these pyrolysates as reflected by the biomarker indices is compared with that which occurs during low-temperature petroleum generation. The significance of the results in terms of the kinetic evaluation of sterane and hopane transformations and application thereto of laboratory simulations is discussed. The triaromatic steroid hydrocarbon contents of the hydrothermal petroleums are found to be unique, and specific tracers of the hydrothermal process are suggested.

Chapters II and III have already been published in Organic Geochemistry (Kawka and Simoneit, 1987) and Applied Geochemistry (Kawka and Simoneit, 1990), respectively. Chapters IV and V will be submitted, after revision, as a set to either Applied Geochemistry or Organic Geochemistry. Additional collaboration in conjunction with this thesis research has resulted in coauthorship of other articles describing the hydrothermal effects on organic matter: volatile hydrocarbon distributions (Simoneit *et al.*, 1988), biomarker transformations (Simoneit *et al.*, in press, 1990), and oil inclusions in hydrothermal minerals (Peter *et al.*, 1990).

II. SURVEY OF HYDROTHERMALLY-GENERATED PETROLEUMS FROM THE GUAYMAS BASIN SPREADING CENTER

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ABSTRACT

The Guaymas Basin spreading center and hydrothermal system are generating an assortment of petroleum-like bitumens by pyrolysis of organic matter in the overlying unconsolidated sediments. Samples collected by D.S.V. Alvin from hydrothermal fields in the Southern Trough exhibit large variations in the quantities and character of the solvent-soluble organic materials. Various pyrolytic regimes combined with fluctuating thermal gradients and migration velocities may impart a compositional fractionation, possibly by differential gaseous solubilization and hydrodynamic alteration of the multicomponent fluids. The data suggest that differential condensation/solidification, biodegradation, and water-washing cause selective removal of components at the seabed. Many hydrothermal oils are unlike normal reservoir petroleums, because they contain significant concentrations of polar material, due to their rapid genesis and transport and probable solubilization or advection of polar, immature components. The biomarker distributions confirm high-temperature pyrolysis at depth with variable entrainment of less thermally-mature bitumens during transport. Data for shallow core samples from the Northern Trough indicate that those locations experienced variable influx (predominantly volatiles) of a low-temperature pyrolysate.

INTRODUCTION

The Guaymas Basin spreading center in the Gulf of California is part of the diverging plate boundary between the Pacific and North American plates and is composed of a set of offset spreading axes (Fig. II.1). The two rift valleys so formed, the Northern and Southern Troughs, are sites of significant hydrothermal activity associated with the formation of new oceanic crust. Such activity is common at spreading ridges throughout the world (Edmond and Von Damm, 1983), but a thick sediment cover of diatomaceous oozes and mud turbidites (Curray *et al.*, 1982) distinguishes the basin from other spreading ridges and provides source material for a unique type of hydrothermal alteration. The combination of plate accretion by dike and sill intrusions into the sediments at depth and leaching/transport of altered and unaltered matter by the hydrothermal fluids. Precipitation of sulfide- and sulfate-rich hydrothermal deposits and condensation/entrapment of organic pyrolysates occurs at the seabed where the fluids are quenched.

The initial discovery in 1972 of thermogenic C_2 to C_8 hydrocarbons in a core from the Northern Trough by the Hypogene Expedition (Scripps Institution of Oceanography) suggested possible thermal stress on organic matter at depth due to high heat flow in the basin (Simoneit *et al.*, 1979). Subsequent coring by Deep Sea Drilling Project (DSDP) Leg 64 (see Fig. II.1, sites 477, 478, and 481) confirmed that thermal alteration of immature organic matter was occurring by dike and sill intrusions into the soft, unconsolidated sediments (Galimov *et al.*, 1982; Galimov and Simoneit, 1982; Simoneit, 1982a,b,c; Simoneit and Philp, 1982; Simoneit and Galimov, 1984; Simoneit *et al.*, 1984).

The first observation of hydrothermal activity within the basin occurred during dives of the DSV-4 *Seacliff* in 1977 (Lonsdale, 1978). The geological structure of the basin (Lonsdale, 1978, 1985) and descriptions of the hydrothermally generated minerals (Lonsdale and Lawver, 1980; Lonsdale *et al.*, 1980) and organic exudates sampled by a subsequent dredge haul (Simoneit, 1982c; Simoneit and Lonsdale, 1982) have been reported. The geological setting and history of the Gulf and Basin have been summarized (Simoneit, 1984a; Simoneit and Kawka, 1987) and additional details are available elsewhere (Campbell and Gieskes, 1984; Lonsdale, 1985; Lonsdale and Becker, 1985; Merewether *et al.*, 1985).

Fig. II.1. Guaymas Basin geography and tectonics including site locations of study: (a) Map of the Guaymas Basin trough system with inset of the basin location in the Gulf of California. Contours are 10^2 m. Numbers refer to DSDP sites (see text). Shaded areas are the approximate locations of the detailed maps (after Lonsdale and Becker, 1985). (b) Detail map of the Southern Trough study area. Open circles are DSDP drill holes at Site 477. Four digit numbers refer to *Alvin* dive track sites and provide general locations of samples (listed in Table II.1). 7D is the location of the dredge haul. Contours are in meters. (c) Map of the Northern Trough study area indicating the La Paz piston core and 30G gravity core (Simoneit *et al.*, 1979) sites and DSDP Site 481.



Fig. II.1.

Rapid high-temperature pyrolysis of the underlying sediments with subsequent transport by hydrothermal fluids results in the accumulation of petroleum-like exudates at the Guaymas Basin seabed. Analyses of the pyrolysates should provide insight into the role of hydrothermal and/or high-temperature processes in petroleum formation and deposition and the role of the pyrolysates in the hydrothermal ecosystem. In January 1982, the Deep Submergence Vessel (D.S.V.) *Alvin* was used to sample hydrothermal deposits in the trough of the Southern Rift. A survey of the general characteristics of these hydrothermal organic pyrolysates is presented. Included herein are the *Alvin* and dredge (Simoneit and Lonsdale, 1982) samples from the Southern Trough and previously unreported core samples from the Northern Trough. Some pyrolysates are analyzed in terms of their similarity to reservoir petroleum. A discussion of various mechanisms of hydrothermal transport and post-depositional processes, as implied by the character of the exudates, is also included.

SAMPLING AND ANALYSES

These results are for samples from two cruises in the Gulf of California. Dredge (7D) and 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. Additional samples were collected in the Southern Trough (Fig. II.1) with the D.S.V. *Alvin* during January 1982.

Dredge 7D sampled one of several massive mineral mounds within the northern half of the Southern Trough (Fig. II.1). The subsampling and analysis of the dredge haul is described elsewhere (Simoneit and Lonsdale, 1982). Total lipid/bitumen contents of subsamples 7D-3B and 7D-5A were obtained from analysis of the freeze-dried residues after gasoline-range hydrocarbon determinations (Whelan *et al.*, 1987).

The core samples were collected from the Northern Trough (Fig. II.1) using a piston corer (18m barrel with a 2m gravity core trip weight). The composited core sections which were analyzed had a characteristic petroliferous odor and are as follows: Core 9P (15m total), section 12.86-14.38m; core 13P (15m total), section 10.5-12.4m; core 15P (13m total), section 11.2-11.9m. The sediments were extracted with 3:1 methylene chloride/methanol using a shaker-table apparatus. Extracts were separated using silica gel-coated plates with 9:1 hexane/diethyl ether as developing solvent. Visualization of bands was by ultraviolet light and iodine vapor.

General locations for the *Alvin* samples are indicated by their respective dive numbers in Fig. II.1. The hand-collected samples were subsampled at the surface and sealed in glass containers with methylene chloride to preserve the volatiles and minimize biodegradation. The larger samples were subsequently extracted by sonication with addition of methanol to remove water. The extracts were then washed with commercially available distilled-in-glass pure water (Burdick and Jackson) to remove the inorganics (salts). Aqueous layers were back-extracted with methylene chloride. A silver and mercury amalgam was used to remove sulfur from total extracts with low levels of organic matter. Total extract weights were obtained by weighing residues of aliquots removed from known volumes of extracts.

A selected number of organic extracts obtained from petroleum-rich samples were further separated into fractions. Aliquots of the organic extracts were dried under a prepurified N₂ stream at room temperature to constant mass (less than a 1% total change in a 20 minute period) and weighed. Asphaltenes were then precipitated overnight using hexane. Filtering and extensive hexane washing of the asphaltenes resulted in a C_{15} +

hexane-soluble fraction (HSF) and an asphaltene (ASPH) fraction. These fractions were dried to constant weight as before for quantitation and analysis. The HSF was further subdivided by liquid-solid column chromatography using neutral alumina (activity grade I) over silica (Woelm, 100-200 μ m, 70-150 mesh) activated at 425°C and 140°C, respectively, for 24 hours before use. Columns (1 x 30cm) were dry-packed using 3.8 g of each adsorbent giving a column length/width ratio of approximately 15/1. Up to 150 mg of each HSF was placed on the column with 5 ml hexane, after column preelution with 25 ml of hexane. Elution and fraction collection proceeded in the order: Aliphatic (F1), 25 ml (+ 5 ml for sample transfer) hexane; Aromatic (F2), 35 ml toluene; Polar NSO (F3), 35 ml methanol. The term aliphatic, as used here, includes the alicyclic hydrocarbons. Fractions were concentrated under reduced pressure, dried under a N₂ stream to constant weight, and quantitated. The % NSO (F3) was calculated by difference to correct for irreversible loss (17±5% of F3, n = 5) of highly polar compounds on the column. Residual sulfur was removed from the fractions using the copper column technique (Blumer, 1957).

Gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS) were conducted on various fractions. A Vista 44 gas chromatograph outfitted with a J & W Scientific DB-5 ($30m \ge 0.25mm$ i.d., $0.25 \ \mu m$ film) fused silica capillary column and He carrier was used. The conditions were: FID, 300° C; injector, 300° C; initial oven temperature 38° C, programmed to 290° C at 4° C/min, isothermal at 290° C ($60 \ min$). The GC-MS analyses were performed with a Finnigan 9610 gas chromatograph [identical column with initial temperature 50° C (isothermal 6 min), programmed at 4° C/min to 310° C (isothermal 60 min)] interfaced directly with a Finnigan 4021 quadrupole mass spectrometer (electron impact mode; emission current -0.45mA; electron energy + 70eV; scanned from 50 to 650 daltons). Data were processed with a Finnigan-Incos Model 2300 data system. Compound identifications are based on comparison with standards and previously characterized sediment extracts and petroleums.

RESULTS

General

A summary with sample and bulk mineralogical (where available) descriptions is given in Table II.1. Samples are grouped according to their general location: Northern or Southern Trough; sample type, hand-collected (Alvin), dredge/core (La Paz); and site or dive track (cf. Fig. II.1). For the Alvin samples each site number (e.g. 1168, 1170, etc.) identifies those samples collected during a specific dive and day. The sample numbers that follow the site numbers are an indication of the general order in which the samples were catalogued on ship after the dive. Spatial relationships amongst the samples cannot be inferred from these numbers. The subsample numbers, on the other hand, do depict close structural associations. The descriptions include both the character or physical structure of the samples (e.g. crustal fragments, wax, etc.) and the actual or inferred source of the material (e.g. chimney, mound, etc.). The physical structures of the hydrothermally deposited formations are described in Lonsdale and Becker (1985). The mineralogical characterizations, with approximate percentages, are restricted to general descriptions of the site locations or sample origins rather than detailed analyses of individual samples. Although not precise, the mineralogies and the physical descriptions are useful for overall sample classification and exemplify the broad variability exhibited by the assorted samples from these hydrothermal vent fields.

The Alvin specimens consist of seabed crust and mound fragments, rocks and chimney rubble characterized by differences in hardness, fragility and amounts of petroliferous matter. Furthermore, the observed physical qualities vary with both the ambient temperature and pressure. Organic exudates observed to be solid at the ambient water temperature (~ 2° C) and pressure (~ 200 bars) during collection liquefied at surface conditions (~ 25° C, ~ 1 bar). For example, at depth sample 1172-2A (red wax) was a crystalline substance in the vugs of a mound (passageways for hydrothermal fluid emanations) but became a viscous liquid upon warming. As a result, some samples rigidly cemented by organics at depth become friable at sea-surface conditions when the exudates soften.

Subsampling (e.g. 1170-1) was used to evaluate the impact of exposure to the environmental conditions at depth on both the organic and inorganic mineral assemblages. Sections from the interiors and exteriors of mound fragments were isolated and analyzed for comparison.

Table II.1. Summary of samples.

	7—	SAI	MPLE IDEN	TIFICATION	· · · ·	
		Site Sa	ample No.	Subsample No.	Description	Bulk Mineralogy
		1168	1	1	Mound material - Large rock	Major amounts diatom debris; minor/major amounts of clays; traces of Fe _x O _y , ISS, Pyr, Sph.
				2 3B	- Large rock - Small rock	
		1170	1	1 2 3	Mound rubble - Iridescent rock, total - Iridescent rock, inside - Leidescent rock, inside	70-85% AmS; 10% Prr; 3% Sph; traces of Anh, Bar, ChP, Gal, ISS, Pyr
			1A	3	Chips	Similar to 1170-1
			1B		Chips	Similar to 1170-1
			6		Crust fragments	Similar to 1170-1
ł			BC6		Box core	D. â.
			20		n.a.	•
				1	- Red wax	•
				2	- Red wax & microbes	•
				3	 Surface rock, tar 	•
8	_	1172	1		Mound fragments	n.a.
51 1	q		1A		Mound crust bulk, oily	n.a.
e i	51		1B		Mound crust	n.a.
₹I 6			2		Inactive chimney,	10-50% Cal; 10-20% AmS; 5-10% Prr; 5% Sph or Wur; 3-5%
2	5				Interior fragments	Anh; traces of ChP, Gal, ISS; (Exterior bacteria covered)
目子			2A		Red wax	•
313	3		3		Mound crust fragments	n.å.
∼ °			4		Fragments	n.a.
		1173	28		Chimney exterior crust	n.â.
			3		Fragments	n.a.
			8		Bottom of chimney Piece of eave from Pagoda- shaped chimney	n.a. 85% Cal; 5-7% Anh; 2-3% Prr; 2% Sph or Wur; trace of Gal, ISS
		1174	5		Exposed mound material	n a
		11/4	8		Inside tall chimney	40% Cal; 30% Bar; 10% Anh; 1-2% Prr; traces of Gal, ISS, Sph or Wur
		1175	1		Piece of extinct mound (lithified sediment)	Major amounts of AmS and clay; 30-45% diatom debris
		1176	4		Active chimney piece	n.a.
		1177	•		Mound material	Major amounts of Bar, 30% AmS; 2% Prr; 1% Sph or Wur, traces
			2C		Crust, oily	of Cal, ISS
			2D		Crust, oily	
			3		Crust, oily	
			3A		Fragments, misc.	
- H			_ <u>4B</u>		Crust interior, oily	
. F -	-	7D*	Dredge		Sinter deposits, mound	
ជាទ ា	24			2B	- Massive sulfide	Equal amounts of Bar, ChP, Prr, Sph
티코	5			38	- Claystone	n.a.
zjor	4			4A,B	- Claystone	n.a.
<u>الا</u>	4—			<u></u>	- Claystone	<u>n.a.</u>
	20	9P	Core	Sections (12.86-14.38m)	Firm, low-porosity mud and	n.a.
	5		_		crust	
귀양부	-1	13P	Core	(10.5-12.4m)	Firm petroliferous mud	n.a.
			~			

Munerals: Amorphous Silica (AmS), Anhydrite (Anh), Barite (Bar), Calcite (Cal), Chalcopyrite (ChP), Galena (Gal), Cu-Fe Intermediate Solid Solutions (ISS), Iron Oxides (Fe_xOy), Pyrite (Pyr), Pyrrhotite (Prr), Sphalerite (Sph), Wurtzite (Wur); (As determined by optical microscopy. Courtesy of Jan Peter, Univ. of Toronto). n.a. = data not available.
 * Descriptions and mineralogy from Simoneit and Lonsdale (1982)

The La Paz dredge sampled a mixture of mound material and claystones, while the cores sampled predominantly firm low porosity muds with some hydrothermal crusts and organic pyrolysates with a petroliferous odor.

The data (Table II.1)show that the specimen structural associations are many and that the bulk mineralogy percentages vary amongst the sample groupings. A common characteristic of most of the samples is that, in addition to diatom and clay debris incorporated into the hydrothermally-precipitated structures, the major mineral assemblages consist of nonmetallic minerals, such as calcite, barite, and amorphous silica. Sulfates and carbonates predominate, while sulfides, of which pyrrhotite is the most common, contribute less to the total compositions. This is consistent with the inferred hydrothermal circulation pattern in the basin and a direct result of the mixing and reaction of the hydrothermal fluid end member with the ~ 500 m of overlying sediments (Kastner and Siever, 1983; Scott, 1983, 1985; Von Damm *et al.*, 1985).

Southern Trough

Character of Total Extracts

Fig. II.2 is a summary of the general character of the organic extracts. The yields range from traces (elemental sulfur predominant component) for the barren samples 1174-5 and 1174-8 to a high 350 mg/g dry sediment (35% solvent soluble) for sample 1172-4 (mound fragments). The large spatial variability in concentrations probably results from competing input and removal processes at the seabed surface of such a hydrothermally active region.

The bitumen character in Fig. II.2, gives a qualitative overview of the original composition of the hydrothermal exudates before subsequent geochemical analyses with their concommitant loss of the more volatile components. Significant variations occur in both the types and molecular weight ranges of the hydrocarbons dominating the total extracts. Three types of extracts are evident.

N-Alkanes dominant. The most common are samples (labelled "ALK," Fig.
 II.2) in which a prominent series of n-alkanes is found. These samples may also contain a broad "hump" or unresolved complex mixture (UCM), consisting of both naphthenes (cycloalkanes) and unresolved more polar compounds.



Fig. II.2. Total extract summary with sample identifications used in the text and Table II.1. The prefixes are synonymous with site locations (i.e. dive tracks; Fig. II.1). Total extract yield: ND = not determined; TR = trace; yields for piston cores (refer to Table II.1) are 10x actual for clarity. Bitumen character determined by direct GC injection of extracts. Hydrocarbon patterns, dominant classes: UCM = uncharacterized complex mixture; ALK = *n*-alkanes; ARO = aromatics; OS = organo-sulfur compounds; OLF = olefins; "/" indicates dual patterns while lower-case identifies minor component. *n*-Alkane range: vertical bar is modal point of distribution.

Samples with *n*-alkanes dominant are further differentiated by the range and skewness or modality of the homolog distributions. In all, the *n*-alkanes range from C₅ to C₃₅ with the red wax (1172-A) exhibiting the broadest suite (C₁₀-C₃₅, maximum at C₂₅). Within the *n*-alkane dominated sample class, the lowest range (C₅-C₁₈, maximum at C₁₃) is exhibited by sample 1177-3 (oily crust), while the narrowest range (C₁₀-C₁₈, maximum at C₁₃) is found in sample 1172-1 (mound fragments). Regardless of the range or skewness, a smooth unimodal distribution of the *n*-alkanes is common to all samples from the Southern Trough. Measurements of the carbon number preferences, using a modified CPI (carbon preference index; Bray and Evans, 1961) to include all the *n*-alkanes present, of thermally-unaltered sediments from DSDP Site 477, Southern Trough (Galimov *et al.*, 1982; cf. Fig. II.1) are significantly greater than one and typical of those for Recent sediments and attest to their immaturity. On the other hand, the CPI values, over the *n*-alkane ranges present, are approximately one (smooth distribution) for virtually all the seabed petroleums from the Southern Trough, which is characteristic of typical reservoir petroleums.

Although unimodal, the *n*-alkane distributions of the *Alvin* samples (Southern Trough) exhibit large variations in both range and modal maximum. Sediments within the basin consist of diatomaceous oozes and mud turbidites (Curray *et al.*, 1982). Much of the source signatures, though, in terms of *n*-alkane distributions are lost during thermal maturation (hydrothermal pyrolysis) as CPI's approach unity and the *n*-alkane patterns become skewed towards low-carbon numbers (Tissot and Welte, 1984; Philp, 1985). Nevertheless, source variation may be partially responsible for the pattern differences between samples with long-chain > C_{25} *n*-alkane biases (terrestrial plant waxes) such as 1170-1A (crustal chips), 1170-6 (crust), 1170-20-1 (red wax) and those with short-chain < C_{25} biases (algal/bacterial) such as 1173-3 (fragments), 1177-2C (oily crust). The large degree of inter- and intra-site variability cannot be wholly attributed to source differences and must also be dependent on processes inherent to such hydrothermal systems.

2) UCM dominant. The second most common class evident is composed of samples (labelled "UCM," Fig. II.2) characterized by the absence of significant amounts of *n*-alkanes but the presence of large UCM's. One such sample 1170-1-3 (cf. Fig. II.2) was obtained from the exposed surface of an iridescent mound fragment. In contrast, an isolate 1170-1-2 (cf. Fig. II.2) from the interior of the same fragment is dominated by an entire suite of *n*-alkanes from C_{11} to C_{34} (maximum at C_{27}).

Biodegradation of the exposed pyrolysate is one possible explanation of the difference (Simoneit, 1985a).

Other UCM-dominated patterns are exhibited by samples from dive 1168 and some subsamples of dredge 7D (similar location, Fig. II.1). Once again, either biodegradation (Simoneit, 1985a), minimal inputs of hydrothermal pyrolysates or both is suggested. In-chain olefins, usually indicative of pyrolytic processes and rarely found in mature crude oils (Hoering, 1977; Hunt, 1979; Tissot and Welte, 1984), are present only in subsample 7D-4A,B (Simoneit and Lonsdale, 1982) and imply an input of open-system pyrolysis products. On the other hand, the presence of a large UCM and only minor amounts of *n*-alkanes, unlike other "hydrothermal oil" saturated samples, suggests biodegradation. The unique olefin content of this sample may also be a microbial artifact. The interpretation of the genetic relationship amongst these samples is difficult due to the heterogeneity of hydrothermal vent fields and the unspecificity of dredge hauls.

3) Aromatic/organo-sulfur dominant. The minor third class of samples in Fig. II.2, exhibits patterns dominated by aromatic compounds (ARO) and/or organo-sulfur, cyclic polysulfides (OS), or with variable amounts of n-alkanes. The extract from sample 1173-9, a fluorescing light green oil, exhibits a total extract pattern consisting of a complicated mixture of broad, unresolved peaks in the high molecular weight range with a trace of n-alkanes (C-16 to C-23 and no pristane or phytane). Thin-layer chromatography isolated an aromatic fraction dominated by various polynuclear aromatic hydrocarbons (PAH) such as pyrene, chrysene and/or triphenylene, benzofluoranthenes, benzo(e)pyrene, benzoperylene and coronene. The oil's character including a strong dominance of the PAH's suggests that it represents a high-temperature end-member of the hydrothermal petroleums. A series of cyclic polysulfides was also a major component of the oil. These compounds had compositions of CH₂S₄ (tetrathiolane), (CH₂)₂S₄ (tetrathianes, two unidentified isomers), CH₂S₅ (pentathiane), (CH₂)₂S₅ (pentathiepane, two unidentified isomers), and CH_2S_6 (hexathiepane). Although a red alga Chondria californica has been identified as a natural source of lenthionine (1,2,3,5,6-pentathiepane); 1,2,4,6-tetrathiepane; 1,2,4-trithiolane; and isomers of tetrathiane (Wratten and Faulkner, 1976), the presence of the additional polysulfide compounds and isomers in the hydrothermal oil and its overall character suggest a thermal source for the cyclic polysulfides.

Trace amounts of these cyclic polysulfides are the dominant organic compounds in samples 1174-5 and 1174-8 (chimney fragments), otherwise barren (no UCM or alkanes) except for relatively large amounts of sulfur. In sample 1177-3A (mound fragments) the dominant compounds are very low concentrations of both a homologous series of *n*-alkanes (C₁₅-C₃₅, maximum at C₁₉) and a distribution of PAH, not unlike that of 1173-9. A minor cyclic polysulfide component is also present. Sample 1176-4 (active chimney pieces) also contains a series of *n*-alkanes, but with a narrower distribution (C₂₁-C₂₇, maximum at C₂₄) and in much lower abundance than the dominant cyclic polysulfides. The aforementioned PAH are also present. This sample was obtained from an active chimney, venting hot hydrothermal waters (290-300°C; K. Von Damm, personal communication and Von Damm *et al.*, 1985). The temperature and the relatively barren nature of these samples, except for the presence of PAH and the cyclic polysulfides, suggests that they represent the high-temperature end member of this collection and result from a rapid passage of the hydrothermal water through conduits in the sediments with minimal mixing or leaching.

Character of the Oils

1) Gross composition (C_{15} +). A ternary diagram of the gross organic (C_{15} +) composition, as determined by bulk chromatographic separation, of a select number of these hydrothermal petroleums is represented in Fig. II.3. The distribution of a collection of 636 crude oils (Tissot and Welte, 1984) is included for comparison. Although many of the samples do not exhibit compositions typical of crude oils, some clustering is apparent. One group contains more aliphatic (paraffinic/naphthenic) oils, while the other includes oils relatively depleted in aliphatic components but enriched in the more polar components, NSO + asphaltenes. In most normal thermally mature oils, the aliphatic components are prevalent. The compositions of such normal oils can become more polar and aromatic during biodegradation (Tissot and Welte, 1984). The polar components may also be high in shallow, immature reservoir oils that have not undergone much cracking. Compared to mature oils, bitumens in immature and mature source rocks are enriched in polar components. The polar character of many of these seabed samples or hydrothermal petroleums may be a result of limited migration and/or post-depositional biodegradation.



Fig. II.3. Ternary diagram representing the gross $(C_{15}+)$ compositions of the petroleums as a percentage of each of three compound fractions (see experimental section for analytical details). Line is a 1% isofrequency contour (triangle unit 10:10:10) from the distribution of a collection of 636 reservoir crude oils (from Tissot and Welte, 1984).

2) n-Alkanes/triterpenoid hydrocarbons. Fig. II.4 shows the aliphatic fractions of some samples selected as representative of the compositional distributions of the oils. Also included are m/z 191 mass fragmentograms characteristic of triterpane structures and used in oil-source rock and thermal maturity correlations.

Sample 1172-4 (Fig. II.4a), the most aliphatic in this collection (cf. Fig. II.3) has the broadest distribution of *n*-alkanes and resembles mature reservoir petroleums. It also has the highest concentration of solvent-soluble matter, 35% (cf. Fig. II.2). The triterpane distribution (Fig. II.4b) is very much unlike that of shallow unaltered basin sediments which have significant concentrations of unsaturated analogues (Simoneit and Philp, 1982; Simoneit *et al.*, 1984). The hopanes with the thermally most stable $17\alpha(H),21\beta(H)$ configuration (Ensminger *et al.*, 1974; 1977; Seifert and Moldowan, 1978) are dominant and range from C₂₇ to C₃₂ (C₂₈ absent). The biologically-derived $17\beta(H),21\beta(H)$ -hopane series is absent while the intermediate $17\beta(H),21\alpha(H)$ -hopane configuration is present. The extended series of hopanes ($\geq C_{31}$), that occur as mixtures of two epimers 22S and 22R (biological precursor configuration is 22R), exhibit a ratio of 1.3 (22S/22R) which is very close to the reported equilibrium ratio of 1.5 (Ensminger *et al.*, 1977).

The *n*-alkane distribution of sample 1173-8 (Fig. II.4c), chosen to represent a cluster of less aliphatic oils (cf. Fig. II.3), is similar to 1172-4 (Fig. II.4a) but not as broad with *n*-C₂₄ being the highest homolog. The triterpane distribution (Fig. II.4d) is also nearly identical to that of 1172-4 (Fig. II.4b) except that it has a narrower range with no triterpanes above $C_{32}\alpha\beta$ (S,R). A difference in the vertical thermal gradients experienced by the pyrolysates during their transport to the seabed could impart a selective condensation/exsolution of the higher-molecular-weight-components before deposition and could effect such a variation.

The composition of sample 1173-3 is predominantly polar (cf. Fig. II.3). A homologous series of *n*-alkanes is present in the range of C₁₄-C₂₆ (Fig. II.4e). *n*-Alkanes above C₂₆ are minor and are overwhelmed by a series of polycyclic alkanes including various triterpanes and steranes. The triterpane trace (Fig. II.4f) shows an entire series of hopanes (C₂₇ to C₃₅, no C₂₈) of various configurations, including significant concentrations of the biologically-derived 17β ,21 β isomers. In addition to a much more prevalent 17β ,21 α (H) series compared with the other two samples, the S/R ratios are inverted with 0.97 and 0.63 for 17α (H),21 β (H)-homohopane and 17α (H),21 β (H)-bishomohopane epimer pairs, respectively. This distribution documents the thermal immaturity of the exudate and reflects a lower temperature of

Fig. II.4. Representative GC-MS data for samples: (a, b) 1172-4; (c, d) 1173-8; (e, f) 1173-3; (g, h) 1168-1-3B. Reconstructed Ion Current (RIC) plots (a, c, e, g) are analogous to FID traces: Numbers = *n*-alkane chain length; PR = Pristane, PH = Phytane; i = isoprenoid; IS = Internal Standard; S = Elemental Sulfur. Mass fragmentograms (b, d, f, h) for m/z 191, characteristic triterpane fingerprint: Numbers refer to carbon skeleton size while suffixes are their configuration; $\alpha = 17\alpha(H), 21\beta(H)$ -, and $\beta = 17\beta(H), 21\beta(H)$ - and $\beta\alpha = 17\beta(H), 21\alpha(H)$ -hopane series; T = triterpane of unknown structure; * = suspected gammacerane; $\Delta 17, 21(30) = hop-17, 21$ -ene. Scan number similar to retention time.



Fig. II.4.
pyrolysis, as compared with the other samples, and/or the entrainment of less mature bitumens during transport to the seabed. Such an admixture would not only add the $17\beta(H),21\beta(H)$ -hopane series to a thermally mature signature but would also alter the extended hopane epimer ratios by input of the biologically-derived 22R configuration. Further analyses are needed to differentiate the effects of these two processes.

The most polar composition of a hydrothermal oil is exhibited by sample 1168-1-3B. The total aliphatic trace (Fig. II.4g) shows no discernable *n*-alkanes and a large UCM. The resolved components are complicated mixtures of long-chain alkyl benzenes and probable substituted cycloalkanoaromatics based on GC/MS interpretation. However, the triterpenoid trace (Fig. II.4h) is dominated by hop-17(21)-ene, a microbial marker, and contains only a small amount of $17\beta(H),21\alpha(H)$ -hopane. No other saturated or unsaturated triterpanes are detectable. Although the lack of *n*-alkanes and other aliphatic components, in general, indicates severe biodegradation, the absence of the thermally more equilibrated hopanes could suggest that this exudate is also quite immature. Alternatively, this sample may represent a biodegraded condensate. Initial analyses of samples recently collected from Guaymas Basin (August, 1985) have identified several examples of condensates without any sterane or hopane biomarkers.

3) Steroid hydrocarbons. Steroid derivatives (Fig. II.5), useful for oil-source rock and maturity comparisons (Seifert, 1978; Seifert and Moldowan, 1978, 1979; Mackenzie *et al.*, 1982; Philp, 1985), also exhibit differences amongst these samples. Sample 1168-1-3B (not pictured) contains no steranes, diasteranes, or their unsaturated analogues. Sample 1173-3 (Fig. II.5c), on the other hand, contains significant concentrations of C₂₇ to C₂₉ steranes, primarily the 5α (H), 14α (H), 17α (H)-(2OR), with smaller amounts of the less thermally stable 5β (H) configuration (Philp, 1985). Since the 20S epimer of the 5α series is in very low concentration, epimerization at C-20, as occurs during thermal maturation (Seifert and Moldowan, 1978; Mackenzie *et al.*, 1980), has been minimal. The distribution is qualitatively identical to that found in sediments near a sill intrusion at DSDP Site 477 (Simoneit *et al.*, 1984) (see Fig. II.1b for location). Diasteranes are also present but in much lower concentrations. Sterenes are absent while diasterenes are minor components. Sample 1168-1-2 (cf. Fig. II.3) shows similar sterane (Fig. II.5d) and diasterene patterns, with traces of diasteranes and no sterenes.

Samples 1172-4 (Fig. II.5a) and 1173-8 (Fig. II.5b), contain much lower concentrations of the steranes and diasteranes relative to the triterpanes than sample





Fig. II.5. GC-MS mass fragmentograms of m/z 217 (characteristic sterane fingerprint) for samples: a) 1172-4, b) 1173-8, c) 1173-3, d) 1168-1-2. Numbers refer to carbon skeleton size while letters represent the structure: α or β = hydrogen configurations at C-5, C-14, C-17, respectively; R or S = epimer at C-20; D = rearranged sterane/diasterane (shaded).

1173-3, consistent with increased levels of thermal maturity (pyrolysis; Seifert, 1978). Furthermore, the relative amounts of diasteranes to steranes are also higher, with the rearranged analogs dominant in sample 1173-8. In both samples, additional epimerization to the $14\alpha(H)$, $17\alpha(H)(20S)$ and $14\beta(H)$, $17\beta(H)$ -(20R,S) configurations has occurred, also consistent with increased maturation. None of the unsaturated series are present.

4) Aromatic hydrocarbons. PAH and alkyl aromatic hydrocarbons are present in these hydrothermal petroleums, analogous to those reported for the dredge samples (Simoneit and Lonsdale, 1982). The PAH are comprised mainly of phenanthrene, pyrene, benzanthracene, chrysene (and/or triphenylene), benzo(e)pyrene, benzo(a)pyrene, perylene, benzoperylene and coronene, with minor amounts of naphthalene, acenaphthene, fluorene, methylene phenanthrene, 2,3-benzofluorene, fluoranthene, benzofluoranthenes, and 1,2,5,6-dibenzanthracene. The presence of the analogs with a five-membered alicyclic ring (e.g. acenaphthene, fluorene, fluoranthene, etc.) in relatively constant proportion to the other peri-condensed aromatic hydrocarbons confirms the pyrolytic origin of these PAH compounds (Blumer, 1975; Scott, 1982; Simoneit and Lonsdale, 1982). The only trend in PAH distributions observed from immature (e.g. 1168-1-3B, 1168-1-2) to mature (e.g. 1172-4) samples is the relative decrease of pervlene vs. benzofluoranthenes and benzopyrenes. Perylene occurs in the thermally unaltered lipids of Guaymas Basin sediments at depth (Baker and Louda, 1982; Simoneit and Philp, 1982; Simoneit et al., 1984), but not near the seabed (Simoneit et al., 1979). It appears to be generated by diagenetic processes at depth but is not stable at catagenetic temperatures (Louda and Baker, 1984).

The dominant alkyl aromatic hydrocarbons are of the naphthalene, phenanthrene and pyrene series with more abundant higher alkyl homologs (> C_2), similar to reservoir petroleums. The methylphenanthrene index (MPI; Radke and Welte, 1983), ranges from 0.43 for the immature sample 1168-1-2 to 1.08 for the most mature sample 1172-4. This maturity trend is consistent with the qualitative trends of other molecular indicators. Polyalkylnaphthalenes could not be utilized as indicators of thermal maturity (Alexander *et al.*, 1984, 1985), because of preferential loss of the more volatile components during compositional determinations by liquid-solid column chromatography.

Northern Trough

n-Alkane Distributions

For core samples 13P and 15P from the La Paz cruise, the *n*-alkanes have biomodal distributions and range from C_{17} through C_{35} with maxima at C_{24} , C_{29} and C_{23} , C_{29} , respectively. Core sample 9P contains unimodal *n*-alkanes ranging from C_{13} through C_{33} with a maximum at C_{18} . CPI values, over the *n*-alkanes present, are 1.7, 1.2 and 1.1 for samples 13P, 15P and 9P, respectively. The presence of bimodal *n*alkane distributions, usually characteristic of dual source inputs of algal/bacterial debris and terrestrial plant waxes (Simoneit, 1978; Cranwell, 1982; Philp, 1985), differentiates these samples from those of the Southern Trough.

Triterpenoid Hydrocarbons

The core sections from the Northern Trough (Fig. II.1c) exhibit differences in their molecular marker distributions indicative of variations in maturity. The dominant compound in the triterpane/triterpane series of all three samples is hop-17(21)-ene, identical to the major hopanoid in sample 1168-1-3B (cf. Fig. II.4h and Figs. II.6a,b,c). The samples differ in the relative amounts of other hopanes, hopenes and other triterpenes. Sample 15P (Fig. II.6b) has the greatest percentage of the $17\beta(H), 21\beta(H)$ hopane series as well as significant concentrations of $17\beta(H), 21\alpha(H)$ - and $17\alpha(H), 21\beta(H)$ -hopanes. The extended $\alpha\beta$ -hopane series ($\geq C_{31}$) occurs in epimeric ratios (S/R) of 0.32 attesting to a low degree of thermal maturation. Sample 13P (Fig. II.6a) also exhibits a similar triterpenoid distribution but in lower concentration relative to hop-17(21)-ene. Sample 9P (Fig. II.6c) contains the largest relative concentration of hop-17(21)-ene and very minor amounts of the other components. For comparison, Fig. II.6d is the triterpenoid fingerprint of another core sample (30G-II, 1.73-1.79m; Simoneit et al., 1979) from the Northern Trough (Fig. II.1c). This sample differs from the La Paz cores in that it contains various triterpenes and the $\beta\beta$ -hopanes but lacks the more thermally equilibrated $\alpha\beta$ - or $\beta\alpha$ -hopane series.



SCAN NUMBER

Fig. II.6. GC-MS mass fragmentograms of m/z 191 for samples: (a) 13P, (b) 15P, (c) 9P, (d) 30G-II (Simoneit *et al.*, 1979). Key as in Fig. II.4 with: numeral following colon = degree of unsaturation; $\Delta 13,18(i30) = isohop-13(18)$ -ene; $\Delta 22,29(30) = hop-22(29)$ -ene.

Steroid Hydrocarbons

Only section 15P shows a sterane pattern comparable to *Alvin* sample 1173-3 (cf. Fig. II.5c). Diasteranes are absent, but both diasterenes and sterenes occur. Sample 9P, on the other hand, is barren of steranes, diasteranes and diasterenes, but does contain some sterenes. Sample 13P is intermediate between the two extremes in terms of its content of steroid hydrocarbons.

DISCUSSION

Generation of Pyrolysates

Based on the chemistry of the pore waters and solids in DSDP drill cores of Guaymas Basin (Leg 64), Kastner (1982) suggests the presence of two types of hydrothermal systems in the basin. The first, driven by sill intrusions with concomitant expulsion of pore waters, appears to be the primary system at Site 481 (Fig. II.1a and II.1c) in the Northern Trough. The second type, a result of heating by a shallow magma chamber with recharge by passage of water through basalt, is dominant at Site 477 in the Southern Trough (Fig. II.1b). The sill-induced system may contribute, in part, to the hydrothermal circulation in the Southern Trough. Conductive heat flow calculations for Sites 477 and 481 gave values of 0.84 W m⁻² and 0.13 W m⁻², respectively (Curray *et al.*, 1982), confirming the presence of a higher thermal gradient in the Southern Trough and a deep-seated heat source (magma chamber).

The superimposition of the overall thermal gradient on the local sill-induced heating of sediments provides two sources of thermal energy for the alteration of organic matter in the Southern Trough. The lipid and kerogen character of sediments at Sites 477 and 481 (Simoneit and Philp, 1982; Simoneit *et al.*, 1984) support the existence of such a dual source of pyrolytic effects. The complexity of the thermal gradients in the Southern Trough is enhanced by convective heat loss through hydrothermal discharges at the seabed, the dominant process by which the accreted oceanic crust is cooled (Lonsdale and Becker, 1985).

Heat flow measurements made with the *Alvin* in the Southern Trough suggested a third type of hydrothermal circulation consisting of a recharged convection within the sediments driven by heating from the shallow sills (Lonsdale and Becker, 1985).

The interaction of these various thermal processes implies a complex system of pyrolytic regimes that generates the hydrothermal petroleums in the sediments. In contrast to the classical scheme of petroleum formation, these hydrothermal analogues are generated at high temperatures and virtually instantaneously. As such, they are more akin to pyrolysates generated during laboratory simulations of thermal maturation of organic matter.

Although source differences and variations in temperatures of genesis could explain some of the differences amongst the hydrothermal organic exudates described previously, they are insufficient to account for the large intra-site variability or the large concentrations of relatively polar and immature exudates at the seabed. Factors affecting the mode of transport must also play a role.

Transport of Pyrolsates

Thermal and Velocity Gradients

Lonsdale and Becker (1985) describe various forms of hydrothermal discharges at the seabed of the Southern Trough that differ in their associated mineral deposit and the temperature and velocity of the venting fluids. High-velocity discharges through chimneys on top of hydrothermal mounds displayed temperatures ranging from 270°C to 314°C with a maximum velocity of 2m/sec ($80cm^2$ orifice; 314°C). At the other extreme, low-temperature (<100°C) and slow ($\leq 0.12cm/sec$) fluids were observed to emanate through holes in the muds surrounding some hydrothermal mineral deposits. The most significant accumulations of hydrocarbons were associated with an intermediate type of discharge (80-130°C) through porous barite (BaSO₄) spires. Based on the inorganic composition of the fluids, their temperatures and character are inferred to arise from variable mixing and reaction of a hydrothermal end member (seawater reacted with basalt) with sediments (Bowers *et al.*, 1985; Von Damm *et al.*, 1985).

Such variations in discharges imply the existence of horizontal gradients as well. Conductive heat flows of 2 to 9 W m⁻² were measured near hydrothermal discharges (Lonsdale and Becker, 1985). The flux was found to decrease as the inverse of the horizontal distance (1.43 W m⁻² at 120m) away from an isolated vent site, near Hole 477 (cf. Fig. II.1b), characterized by barite spires with fluids emanating at 80-130°C (Lonsdale and Becker, 1985).

Horizontal transport of the fluids in the surface sediments and temporal variations in gradients are suggested by the inferred development of many Guaymas Basin chimneys, as described by Lonsdale and Becker (1985). Multi-level pagoda-like chimneys may develop from simple columnar chimneys. Rapid discharges become slow and diffuse emanations with the growth of a porous cap of anhydrite and pyrrhotite on the top of the chimney. Additional precipitation results in a horizontal impermeable cap which slows the flow further and directs it downward. As the cap continues to develop, the discharges can become negligible when mineral precipitation causes the entire cap to become virtually impermeable. Subsequent breakthrough of the fluids through the top of the cap continues the growth. Significant overpressuring of a high-temperature (270-300°C) fluid was observed to occur during the impermeable cap stage (Lonsdale and Becker, 1985). We suggest that this may lead to an increase in horizontal advection of the fluids which could contribute, in part, to the lower temperature discharges observed in the muds surrounding the mounds.

The previous measurements and observations support the existence of large spatial and temporal variations in thermal gradients and velocities of the hydrothermal discharges at the Guaymas Basin seabed.

Modes of Transport

The broad range of fluid temperatures and velocities provide various means by which the organic pyrolysates can reach the seabed. Primary migration of petroleum during the peak phase of oil generation is normally thought to be a pressure-driven hydrocarbon phase migration, with diffusion only important for gases (Welte and Leythaeuser, 1983; Tissot and Welte, 1984). Bulk transport by buoyant oil droplets and/or through aqueous fluid flow, induced by compaction, is thought to be minimal (Tissot and Welte, 1984). The massive advection of fluids in a hydrothermal system such as this, though, intensifies these processes by providing a transport medium and fracturing the unconsolidated sediments. The high temperatures facilitate the transport by lowering the viscosity of both the fluid and the petroleum. Droplets of oil were seen in the high-temperature hydrothermal discharges and were also observed rising slowly from the muds surrounding the hydrothermal mounds.

The temperatures, pressures, and gaseous contents of the hydrothermal discharges may also increase the transport of organic matter by molecular solution. Studies of aqueous hydrocarbon solubilities at elevated temperatures and pressures have shown that solubilities increase with increasing temperature and methane content (Price, 1976; 1981a,b; Price *et al.*, 1983). Above 100°C, a rapid increase in solubilities occurs with the greatest relative increase for the least-soluble high molecular weight compounds. Supercritical water (critical points: Tc = 374.2°C, Pc = 218.3 bars; Josephson, 1982) is reported to be an excellent solvent for hydrocarbons and polar organics (Deshpande *et al.*, 1984). Although the measured temperatures of hydrothermal fluids in the Southern Trough sediment are below the critical point for water, near-critical water also exhibits enhanced solvent properties for petroleum. Significant concentrations of methane and carbon dioxide are found in subsurface sediments (Galimov and Simoneit, 1982) and in the hydrothermal fluids venting at the seabed (unpublished results) of the Southern Trough. These gases can affect the aqueous solubilities of petroleum, with the extent dependent on the molecular weight range of the solute hydrocarbons and the fluid temperature (Price, 1981b).

The effects of the gases on aqueous solubilities of hydrocarbons may, in part, be due to the supercritical properties of the pure gases. For example, conditions in the hydrothermally-altered sediments of the Southern Trough are adequate for the formation of supercritical carbon dioxide (critical points: Tc = 31.06°C, Pc = 72.86 bars; Josephson, 1982). Supercritical carbon dioxide is an efficient solvent for organic matter from natural products and has been used for coal extraction (Josephson, 1982). The addition of gases such as carbon dioxide under supercritical conditions to water increases the solubilization of petroleum and thereby lowers the temperatures necessary to transport the hydrothermal petroleums by the migrating fluids. Such a process could provide a mechanism by which immature bitumens from sediments, exposed to subpyrolysis temperatures, may be entrained and transported to the seabed. Furthermore, the use of supercritical carbon dioxide in enhanced oil recoveries from reservoirs (Orr and Taber, 1984), attests to the ability of such a fluid to aid in the advection of petroleum or bitumen by hydrothermal fluids.

The conditions present in the Guaymas Basin support the transport to the seabed of both high-temperature pyrolysates and low-temperature leachates of organic matter. The evidence suggests that migration occurs by bulk transport and solubilization in a multicomponent mixture that is rapidly advected to the seabed during hydrothermal circulation. This type of migration is much more rapid than that which normally occurs during primary migration and the accumulation of petroleum in reservoirs. The effects of such rapid migration on the composition of the petroleums would also be expected to differ from those inferred from the classical interpretations of petroleum formation.

Compositional Fractionation During Transport

The broad variations in composition and molecular weight ranges of the components in the hydrothermal exudates (cf. Figs. II.2 and 3) suggest that physicochemical fractionation or selective extraction must be occurring during transport. The temporal and spatial variations in thermal gradients and transport velocities previously discussed can impart such an effect in various ways.

The temperature of the medium affects the character and quantities of pyrolysates and leachates by influencing the hydrodynamic factors, phase of transport and by inducing differential solubilization. Extensive mixing and cooling of migrating hydrothermal fluids at subbottom depths would selectively remove the heavier and less soluble components because of increased viscosity, solidification and exsolution. A comparison of *n*-alkane and triterpane distributions for samples 1172-4 (Fig. II.4a,b) and 1173-8 (Figs. II.4c,d), suggests such a selective removal of the heavier components from the latter.

Compositional fractionation by polarity is also possible during selective dissolution controlled by the temperature of the aqueous phase. Price (1981b) has observed that the composition of an aqueous hydrocarbon solute, equilibrated at 202°C with a C_{14} - C_{20} petroleum distillate, is primarily aromatic and polar. An irregular "hump" with minimal *n*-alkanes is the main feature of a gas chromatograph of the solute's extract. With increasing temperature, the solute becomes more aliphatic and less aromatic/polar, with *n*-alkanes becoming the prominent resolved constituents above a rounded hump (UCM).

In general, increasing gas contents of hydrothermal fluids results in enhanced aqueous solubilities of hydrocarbons. Compositional fractionation can also occur with changes in gas concentration. For example, the solute hydrocarbons in an aqueous system equilibrated at 290°C with a C_{19} - C_{25} distillate becomes less polar and more aliphatic with increasing CO₂ concentration (Price, 1981b). The gas chromatograms of the solute undergo changes analogous to those described above for increasing temperatures. Increasing methane concentrations cause similar effects (Price, 1981b).

Although most transport of the hydrothermal petroleum is probably due to massive advection of the pyrolysate in bulk, compositional fractionation during solubilization may be partially responsible for the high-polarity and UCM-dominated samples from site 1168 and dredge 7D (cf. Figs. II.2-3, II.4g). A low-temperature, low-gas solubilization of an immature bitumen could occur during slow seepage of cooler hydrothermal fluids.

Variations in the speed of transport may also result in fractionation. Rapid vertical migration limits lateral dispersion and the associated mixing and cooling. Slow transport results in more diffuse flow and additional cooling by the near-surface hydrothermal circulation (Lonsdale and Becker, 1985) postulated to occur as a result of localized heating from sills. In general, though, the migration encountered in Guaymas Basin is much more rapid than that expected in normal primary migration, induced by compaction, and shorter in distance than secondary migration. Studies of chemical fractionation during primary migration indicated that the lower molecular weight ($< C_{19}$)

hydrocarbons were preferentially expelled from organic-rich shales to interbedded sandstones during compaction (Mackenzie *et al.*, 1983). The lower carbon number *n*alkanes were expelled more easily than the rest of the soluble organic matter, although there was no selective expulsion of the total alkanes vs. the total aromatics. This was attributed to the lower *n*-alkanes being less adsorbed by the host material than the rest of the bitumen. On the other hand, Leythaeuser *et al.* (1983) observed that in an apparently diffusion-controlled process, the aromatics benzene and toluene had higher transportation rates comparable to those of propane and *n*-butane, respectively. This is in accord with the aqueous solubilities of the light hydrocarbons at 25°C. Benzene and toluene are greater than two orders of magnitude more soluble than their straight chain counterparts (Price, 1976). Aqueous solubilities may be most important for the very light hydrocarbons while adsorption phenomena may be more important for fractionation during migration of heavier components.

The rapid transport of the hydrothermal petroleums may diminish the adsorption effects by minimizing the time that the petroleum is in contact with the matrix during migration. This would explain, in part, the higher polar content of some of the hydrothermal petroleums. The high aliphatic content of some of the petroleums (cf. Fig. II.3) may be simply a function of high-temperature pyrolysis (thermal-cracking of kerogen) releasing sufficient aliphatic components to obscure the more polar components of the bitumen transported to the seabed.

Deposition of Pyrolysates

The high-temperature pyrolysates from depth and low-temperature leachates entrained and solubilized by the migrating hydrothermal fluids are transported to the seabed as a multicomponent fluid/bulk phase (Simoneit, 1984). Mixing of the heated hydrothermal fluids with cooler (~ 2° C) ambient and saline water at the seabed determines the condensation and solidification/precipitation of the transported organic matter. This rapid quenching should impart its own fractionation effect on the composition of the exudates similar to that postulated to occur during transport of the hydrothermal fluids at subbottom depths. The condensates/precipitates from the lowtemperature and diffuse seeps would tend to be concentrated on the seabed near their exits. On the other hand, high-temperature and rapid discharges would disperse their organic contents over larger areas as they are rapidly mixed with the ambient waters.

Since the aqueous solubilities of the volatile hydrocarbons are high relative to all hydrocarbons for the thermal conditions prevalent at the seabed, the fractionation effects due to quenching should be most evident for these gasoline-range hydrocarbons. The distributions of the hydrocarbons in the petroleums sampled (cf. Fig. II.2) support this. Except for 1173-3 (oily crust), all samples lack the gasoline range ($< C_{10}$) hydrocarbons. This is unlike normal reservoir petroleums in which entire suites of alkanes ($\geq C_1$) are usually present. Biodegradation or water-washing (selective removal of the more soluble components, Tissot and Welte, 1984) after deposition could conceivably contribute to this removal. Although some outgassing of the more volatile hydrocarbons occurs during transport of the samples to the seasurface, a lack of condensation of these components as the exudates reach the seabed is probably most important. The exiting vent waters are rapidly mixed with the ambient waters which apparently dilute and subsequently remove the more volatile/soluble components. Evidence supporting this hypothesis was obtained during recent return dives (August 1985) to the Southern Trough. Headspace and gas chromatographic analyses of collected vent waters identified high concentrations of an entire series of methane through gasoline-range hydrocarbons (Simoneit et al., 1988). Furthermore, Merewether et al. (1985) have detected strong acoustic reflecters rising as plumes above the Guaymas Basin seabed. Although methane was considered the major component, data was presented which suggested that other light hydrocarbons may also be important constituents of the bubbles or drops (Merewether et al., 1985).

Post-Depositional Alteration of Pyrolysates

Once deposited at the seabed, the hydrothermal petroleums may undergo waterwashing and biodegradation. The number of UCM-dominated samples (cf. Fig. II.2) in this collection of exudates would suggest a significant control by biodegradation. Such patterns, with little or no *n*-alkanes present, could occur by compositional fractionation through differential solubilization, as discussed previously. The comparison between the interior (1170-1-2) and exterior (1170-1-3) of a hydrothermal mound fragment (cf. Fig. II.2) suggests, however, that biodegradation can also be important. The GC traces of the total extracts for the interior and exterior of the sample (Figs. II.7a and II.7b, respectively) are strikingly different. The absence in Fig. II.7b of the broad distribution of *n*-alkanes found in the interior isolate in Fig. II.7a and the presence of identical



Fig. II.7. Gas chromatograms of total extracts for samples: (a) 1170-1-2, (b) 1170-1-3, (c) 1170-20-1, (d) 1172-2A. Key as in Fig. II.4.

thermally mature triterpane (compositionally similar to 1172-4, cf. Fig. II.4b) and sterane distributions in both strongly supports biodegradation.

Complete removal of *n*-alkanes, as in the previous discussion, is an extreme form of biodegradation. An intermediate stage of biodegradation may be exhibited by sample 1170-20-1 (red wax) in Fig. II.7c. *n*-Alkanes from C_{19} to C_{31} (maximum at C_{23}) dominate the pattern. Above C_{23} , the concentrations decrease smoothly while they disappear abruptly below C_{20} . Only a series of branched alkanes, with pristane and phytane the dominant isoprenoids, are present at chromatographic retention times less than C_{19} . Biodegradation, which selectively removes *n*-alkanes less than $\sim C_{25}$ and 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, 1985a). For comparison, Fig. II.7d is a chromatogram of an analogous red wax (1172-2A) from another location with a similar *n*-alkane pattern (C_{10} - C_{35} , max at C_{24}) which appears less affected by biodegradation.

In addition to specific examples as above, a general trend in the compositional distribution of hydrothermal petroleums (cf. Fig. II.3) is also consistent with biodegradation. 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).

Southern vs. Northern Troughs

The samples from the Southern Trough exhibit a great deal of variation in the organic character of the exudates. Most of the differences amongst samples is explainable in terms of variable mixing and reaction of a high-temperature hydrothermal fluid end member with the overlying sediments. Differential transport of the components is feasible in consideration of the gradients observed.

The compositional differences between the hydrothermal petroleums in Fig. II.3 are of particular interest. The low aliphatic content, with minimal *n*-alkanes, of the samples (site 1168 and dredge 7D) from the northeastern portion of the Southern Trough (Fig. II.1b) is more similar to that found in immature bitumens and unlike normal reservoir petroleums. Although the absence of *n*-alkanes in two of the most polar samples, 1168-1-2 and 1168-1-3B (cf. Figs. II.2-3 and II.4g) is consistent with

biodegradation, the broad distribution of *n*-alkanes in sample 1173-3 (Fig. II.4e), also quite polar and apparently unaltered, suggests that another process could be responsible. The triterpane and sterane distributions (Figs. II.4f and II.5c, respectively) indicate that the oil of sample 1173-3 is also less mature than the more aliphatic petroleums. Solubilization and entrainment of bitumens or low-temperature pyrolysates during migration could effect such a more polar C_{15} + composition without removing the *n*alkanes as in biodegradation. A rapid and limited migration of such a hydrothermal oil which would minimize the separation of the aliphatic from the polar components, as is thought to occur during primary migration of petroleums, could also increase a petroleum's polar constituents. The more immature character of the triterpane distribution of 1173-3 (Fig. II.4f) as compared to that of 1173-8 (Fig. II.4d) supports the hypothesis of the oil from 1173-3 being a lower temperature pyrolysate or an admixture containing entrained immature bitumen from a less thermally-altered sequence. The rapid and limited migration of the 1173-3 petroleum would not explain the difference between the two triterpane distributions, since the various hopanes are similar in polarity and the migration of the immature configurations would normally not be retarded. Transformation, after deposition or during transport, of the functionalized analogs, however, could result in the addition of the immature $\beta\beta$ -hopane series, with the 22R configuration for the extended homologs. The solubilization and/or entrainment of bitumens and/or low-temperature pyrolysates along with subsequent biodegradation probably contributes to the unusual character of the samples from the northeastern part of the Southern Trough.

The bitumens of the core samples from the Northern Trough (Fig. II.1c) are distinctly different from those from the Southern Trough. The triterpane, sterane, and total extract composition of the three Northern Trough samples suggest that their character results from an admixture, by hydrothermal circulation, of a low-temperature pyrolysate with the organic matter indigenous to those depths sampled. Based on biomarker distributions, 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 this 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. This evidence supports the hypothesis that the migration was primarily horizontal and resulted from a sill intrusion in the vicinity. Apparently, the character of the samples was not due to a high thermal gradient at the core location. The petroliferous odor appears to be a result of preferential migration of the more volatile products released during hydrothermal alteration.

The composition of the Guaymas Basin hydrothermal oils can be affected in a number of ways. Variations in the temperature and residence time of genesis will affect the maturity and aliphatic character of the oil. During the subsequent transport of the pyrolysate to the seabed, minor amounts of immature bitumens, containing relatively large proportions of polar compounds, may become entrained within the fluids. After deposition, biodegradation and water-washing may also change the compositions.

SUMMARY

The hydrothermal petroleums from the Southern Trough exhibit great variability in both their character and quantity of organic matter. Their petroleum-like n-alkane patterns 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 sediments, with subsequent transport by the hydrothermal fluids and thermal gradients. The upward migration of the pyrolysates and bitumens appears to occur by both bulk transport and a combination of high temperature/pressure aqueous and supercritical gaseous (e.g. CO₂, CH₄, etc.) solubilization in a multi-component fluid phase. Organic source material differences (terrigenous/bacterial/algal) are insufficient to explain the high variability of molecular weight ranges and qualitative distributions of the hydrocarbons. Observations of discharges and heat flow measurements suggest the presence of fluctuating pyrolysis temperatures, thermal gradients and transport velocities. These conditions impart a compositional fractionation effect on the exudates, possibly by varying solubilization and altering the physical aspects (hydrodynamics) of the resulting mixtures. At the seabed, differential condensation/solidification of the hydrothermal petroleums occurs during cooling (quenching) and mixing with ambient seawater. Subsequent biodegradation and water-washing cause selective removal of components from accessible and unconsolidated samples.

Compared to normal reservoir petroleum, hydrothermal petroleums are similar in having broad *n*-alkane distributions with no carbon-number-predominance but differ in that many show higher concentrations of polar compounds. Samples with the greatest aliphatic character contain biomarkers, triterpanes and steranes, in their thermally stable configurations comparable to those in mature oils. Some of the more polar petroleums show large amounts of biomarkers characteristic of immature bitumens. These changes are attributed to variable entrainment of thermally less mature and polar components in the hydrothermal fluids containing the high-temperature pyrolysates. In addition, the relatively instantaneous maturation and short transport/migration of these petroleums, as compared to "normal genesis" and migration of reservoir petroleums, may also enhance their polar character.

Site 1168 (NE Southern Trough) samples are very different from other exudates in having a predominantly polar (asphaltic) composition, with aliphatic hydrocarbons dominated by an UCM with either no or only minor *n*-alkanes. The predominant biomarker in sample 1168-1-3B is hop-17,21-ene indicating a strong microbial source

signature. Preliminary interpretation attributes this character to severe biodegradation and a hydrothermal input limited to entrained or solubilized bitumens with minimal thermal maturation.

The triterpanes of the core samples from the Northern Trough are also dominated by hop-17,21-ene with the addition of variable amounts of hopanes, ($\beta\beta$, $\alpha\beta$ and $\beta\alpha$) and other triterpenes. The organic character of these samples and their petroliferous odor, not detected in the rest of the cores, suggest that these sections experienced variable influx of pyrolysates (predominantly volatiles) by horizontal migration of hydrothermal fluids.

The Guaymas Basin hydrothermal system is an *in situ* laboratory, where an entire range of processes important to petroleum genesis, migration, and evolution occur instantaneously in geological terms and can be sampled. Further analyses will augment the existing petroleum geochemistry database, as well as provide valuable *in situ* information for the application of hydrothermal petroleum genesis (pyrolysis) in exploration.

ACKNOWLEDGEMENTS

We thank the National Science Foundation for access to the various samples, participation in D.S.V. *Alvin* cruises and for financial support (Division of Ocean Sciences, Grants OCE81-18897, OCE-8312036 and OCE-8512832) and the Link Foundation for a fellowship supporting O.E.K. We also thank Dr. Kenneth E. Peters whose comments greatly improved this manuscript.

III. POLYCYCLIC AROMATIC HYDROCARBONS IN HYDROTHERMAL PETROLEUMS FROM THE GUAYMAS BASIN SPREADING CENTER

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ABSTRACT

Hydrothermal petroleums from the Guaymas Basin spreading center have been analyzed for their polycyclic aromatic hydrocarbon (PAH) content. The PAH concentrations have been compared to those in crude oils from production reservoirs and in coastal sediments. Hydrothermal petroleums contain higher relative concentrations of unsubstituted PAH than crude oils. However, the alkylated homolog distributions of the tricyclic aromatic hydrocarbons suggest that the aromatic hydrocarbons of these oils contain both resynthesized and diagenetically produced PAH. The PAH concentrations in the hydrothermal petroleums are influenced by differing thermal, mixing and postdepositional alteration processes, resulting in considerable variability. Concentrations of the unsubstituted PAH in the hydrothermal mounds/sediments are comparable to those in sediments from highly polluted and industrial areas. The presence of large concentrations of toxic and carcinogenic PAH in these hydrothermal oils could have toxicological effects on the benthic ecosystems of such vent environments.

INTRODUCTION

The combination of crustal accretion and the associated hydrothermal process is generating petroleum from recent, immature sediments in the rift area of Guaymas Basin, a young spreading center in the Gulf of California (Fig. III.1a; Simoneit and Lonsdale, 1982; Simoneit, 1984; 1985b; Kawka and Simoneit, 1987). The inverse relation between time and temperature for petroleum formation requires that the rapid genesis in Guaymas Basin must be at temperatures well above those in the normal petroleum window, 60°-150°C (Hunt, 1979; Tissot and Welte, 1984). In fact, temperatures >300°C (Simoneit *et al.*, 1988) in venting fluids of the Guaymas hydrothermal system imply rapid high-temperature pyrolysis of organic matter at depth. The formation of polycyclic aromatic hydrocarbons (PAH) is also a temperature dependent process with the unsubstituted (parent) PAH dominating at high pyrolytic temperatures (Giger and Blumer, 1974; Blumer and Youngblood, 1975; Youngblood and Blumer, 1975; Blumer, 1976). Hydrothermal petroleums generated at high temperatures would therefore be expected to have an unique aromatic character.

We have analyzed seabed deposits of hydrothermal petroleums from the Southern Trough of Guaymas Basin (Fig. III.1b) for their unsubstituted PAH content and composition to test this hypothesis. The PAH distributions in the hydrothermal petroleums are contrasted with those in a selection of crude oils produced by catagenetic processes (non-hydrothermal), under normal geothermal gradients. In addition, the degree of alkylation of the tricyclic aromatic hydrocarbons in the oils is compared to combustion-produced signatures. These comparisons are used to investigate the thermal source of the PAH in the hydrothermal petroleums. The sediment concentrations of the hydrothermal PAH are compared to those in sedimentary sinks of both pristine and highly polluted or industrialized areas. The environmental significance of the PAH to the hydrothermal ecosystems and possible toxicological implications are subsequently discussed.



Fig. III.1. Maps of (a) Guaymas Basin with inset of basin location in the Gulf of California and (b) enlargement of the Southern Trough of Guaymas Basin with sampling sites indicated. Sample 7D is a dredge haul from 1980, while the other numbers refer to dive sites of the D.S.V. *Alvin* during 1982. More details of locations and sampling can be found in Kawka and Simoneit (1987) from which the figure is adapted.

SAMPLING AND ANALYSIS

The sampling of the hydrothermal oils from the Guaymas Basin seabed and the extraction and isolation of the aromatic compounds are described in Kawka and Simoneit (1987). The aromatic fractions of the Bradford, North Sea, and Jiang Han crude oils were isolated by thin-layer chromatography on silica gel plates developed with a mixture of hexane and diethyl ether. The conditions for analysis of the oils by gas chromatography-mass spectrometry (GC-MS) were identical to those in Kawka and Simoneit (1987) except as specified below.

Procedural recoveries of the PAH from the Guaymas Basin hydrothermal oils are considered to be comparable to those for PAH from crude oils or reservoir rocks. In the hydrothermal samples, near complete recoveries of PAH are envisioned due to the high total bitumen contents relative to the sediments. Similarly, evaporative loss, during sample work-up, of the lower molecular weight PAH of interest (volatilities less than or equal to that of phenanthrene) is thought to be minimal due to the matrix effects associated with the organic-rich phase (Socha and Carpenter, 1987). Near complete recoveries of perdeuterated anthracene added to downcore hydrothermally altered sediments from Guaymas Basin with similar bitumen contents (unpublished results) further attests to the absence of selective loss of the triaromatic PAH in these samples.

Multiple ion detection (MID) was used for quantitation of the PAH in the hydrothermal oils, unless stated otherwise. This method monitored the molecular ions (MW = molecular weight; see Table III.1) of each of the PAH. Selective scanning of the mass spectrometer was controlled with six MID descriptors, each containing six masses (1 amu wide) of interest. Dwell times of 210 ms per mass and total scan times of 1.5 s per descriptor were used. MID descriptors were time-programmed under computer control to coincide with expected GC elution times of components in each descriptor. The GC oven was temperature-programmed from 65° C (2.0 min) to 135° C at 15° C/min followed by 4° C/min to 310° C (40 min). Quantitation of the PAH used response factors from authentic standards calculated relative to an internal standard, perdeuterated anthracene. This standard was added to the aromatic fractions of the hydrothermal samples immediately before GC-MS. The relative response factor of benzo(g,h,i)perylene was used for indeno(c,d)pyrene.

RESULTS AND DISCUSSION

Comparison of PAH in hydrothermal and crude oils

A selection of 19 unsubstituted PAH present in the hydrothermal petroleums recovered at the seabed of the Southern Trough of Guaymas Basin have been quantified and are listed in Table III.1. Most of the tabulated PAH are primarily of a catagenetic or pyrolytic origin. Perylene is considered to be diagenetic in source and may be unstable at higher temperatures (Louda and Baker, 1984; Venkatesan and Kaplan, 1987; Venkatesan, 1988). Although some of the other unalkylated PAH listed, such as phenanthrene, may also be formed during low-temperature (diagenetic) reactions in sediments (Wakeham *et al.*, 1980), their proportion, relative to alkylated homologs, should increase at elevated temperatures due to catagenesis. This enhancement is expected to be most pronounced at high pyrolytic temperatures where resynthesis can occur.

For comparison, the concentration ranges of some of the PAH in various crude oils from production reservoirs have been compiled from literature sources in Table III.2. Three types of data are presented. First, concentration ranges in oils of different maturities from a single basin, Gifhorn Trough (northwest Germany), are summarized from Grimmer and Böhnke (1978). The second set of ranges is for oils of various origins (see Table III.2) and is summarized from Grimmer *et al.* (1983). Third, the data for the PAH concentrations in the two individual oils, Kuwait and S. Louisiana, is taken from Pancirov and Brown (1975). Although differences in the PAH concentrations in crude oils are apparent upon examination of Table III.2, the similarity in the ranges obtained from the different studies suggests that the data is quite representative of the overall composition of crude oils regardless of their maturity, origin, or the methods of analysis.

In the hydrothermal oils, pyrene and benzo(g,h,i)perylene are the two most prevalent unalkylated PAH, overall (see Table III.1). They are consistently among the four PAH in highest concentration in the hydrothermal oils, except for samples 1168-1-2 and 1168-1-3B, with quantities ranging from 91 to 1400 and 69 to 2200 ng/mgbitumen, respectively. The concentrations of pyrene and benzo(g,h,i)perylene in the crude oils from Gifhorn Trough, on the other hand, range from 2.3 to 11.4 and 1.7 to 5.2 ng/mg-oil, respectively (see Table III.2). The pyrene and benzo(g,h,i)perylene concentrations in the hydrothermal oils are between 8 to 120 and 13 to 420 times,

		Guaymas Basin (Southern Trough) Hydrothermal Oils													
MW	Compound	1172-4	1172-1A	<u>1177-2D</u>	1172-2	1172-3	1173-8	1177-2C	1177-4B	1172-1	7 <u>D-5</u> A	7D-3B	1 <u>1</u> 73-3	1168-1-2	<u>1168-1-3</u> B
166	Fluorene	20	53	100	20	73	9.3	56	15	100	5.4	6.1	6.2	0.28	1.4
184	Dibenzothiophene	59	100	180	37	140	1200	110	50	270	29	150	31	100	9.7
178	Phenanthrene	120	200	400	81	230	190	260	200	510	8.3	27	72	7.4	11
178	Anthracene	21	27	63	12	37	10	46	4.9	1 10	26	15	5.1	3.7	5.1
202	Fluoranthene	22	35	84	17	36	77	54	50	120	90	190	54	110	98
202	Pyrene	100	190	410	91	170	350	240	640	620	400	1400	260	380	430
216	2,3-Benzofluorene	26	47	100	27	46	57	57	34	160	80	190	13	41	67
228	Benz(a)anthracene	42	68	150	42	60	64	100	42	230	110	58	31	9.2	31
228	Chrysene/Triphenylene	84	150	210	79	130	200	160	120	470	240	340	94	53	83
252	Benzofluoranthenes	45	94	230	69	92	300	190	430	280	200	710	130	81	-86
252	Benzo(e)pyrene	68	110	210	83	110	340	190	560	370	230	740	210	140	110
252	Benzo(a)pyrene	52	77	180	62	71	150	170	190	250	130	320	69	43	31
252	Perylene	19	21	29	13	34	67	48	100	96	290	530	46	180	600
276	Indeno(c,d)pyrene	11	38	110	38	35	81	84	390	120	91	210	58	11	6.8
276	Benzo(g,h,i)perylene	130	170	390	160	160	530	400	2200	550	380	790	670	89	69
276	Anthanthrene	20	12	21	9.3	8.4	18	75	55	28	10	7.5	n.a.	11	0.77
278	Dibenz(a,h)anthracene	21	25	52	22	19	44	73	32	55	30	57	11	13	1.7
300	Coronene	110	110	200	110	83	220	320	1200	300	210	190	290	34	6
302	Dibenzo(a,e)pyrene	50	55	120	46	25	_75	190	28	78	42	56	13	20	1 <u>.6</u>
Tota	l PAH ug/mg-bitumen	1.0	1.6	3.2	1.0	1.6	<u>4</u> .0	2.8	6.3	4.7	2.6	6.0	2.1	1.3	<u>1.6</u>
Tota	l PAH ug/mg-aromatics	8.3	7.9	12	_ <u>5</u> .7	. 8.7	11 -	11	41	14	10	23	18	8.4	24
Oil c (mg-	concentration in sediment -bitumen/g-dry)	350	45	71	80	12	97	63	10	150	90	32	n.a.	81	19

TABLE III.1. Concentrations (ng/mg-bitumen) of selected polycyclic aromatic hydrocarbons (PAII) in the Guaymas Basin petroleums.*

* Sample numbers and descriptions are identical to those described in Kawka and Simoneit (1987). D.S.V. Alvin dive sites in Fig. III. 1b can be used for approximate locations. n.a.. = not analyzed.

		Gifhor	rough*	Assorte	ude oils†	Individual oils‡				
		(NW Germany)			(Vario	origins)	Kuwait S. Louisia			
MW	Compound	Range	1	Average ± s	Range	1	Average ± s	(ng/mg-oil)	1	(ng/mg-oil)
166	Fluorene	-	I		-	1		•	1	-
184	Dibenzothiophene	-	1		-	1		-	1	-
178	Phenanthrene	•	T		-	I		26	ł	70
178	Anthracene	-	I		-	ł	ł	· · -	I	
202	Fluoranthene	0.6 - 5.3	I	2.7 ± 1.3	•	1		2.9	ł	5
202	Pyrene	2.3 - 11.4	1	6.5 ± 2.6	1.6 - 10.7	1	4.7 ± 2.8	4.5	1	3.5
216	2,3-Benzofluorene	-	1		-	I		-	l	-
228	Benz(a)anthracene	-	ł		1.0 - 6.7	I	3.0 ± 2.0	2.3	ł	1.7
228	Chrysene/Triphenylene	11.9 - 42.9	1	24.1 ± 10.7	4.9 - 43.5	ſ	19.2 ± 12.2	9.7	ł	28
252	Benzofluoranthenes	-	ł		•	ł		<4.0	ι	<3.7
252	Benzo(e)pyrene	2.9 - 18.7	1	9.4 ± 5.3	1.2 - 28.9	ł	7.3 ± 8.9	0.5	1	2.5
252	Benzo(a)pyrene	<0.1 - 2.3	ł	1.2 ± 1.0	0.1 - 3.6	ł	1.0 ± 1.2	2.8	I	0.75
252	Perylene	0.2 - 7.6	1	2.5 ± 2.7	•	۱		<0.1	ł	34.8
276	Indeno(c,d)pyrene	0.6 - 1.9	ł	1.3 ± 0.5	•	1		-	ł	-
276	Benzo(g,h,i)perylene	1.7 - 5.2	ł	4.2 ± 1.1	0.6 - 5.0	I	1.9 ± 1.5	<1	ì	1.6
276	Anthanthrene	•	ł		-	I		-	ı	-
278	Dibenz(a,h)anthracene	-	١		-	1		-	1	-
300	Coronene/Dibenzo(fg,op)tetracene	0.7 - 7.9	I	3.2 ± 2.5	-	1		-	I	-
302	Dibenzo(a,e)pyrene		L			1		L	L	• •

TABLE III.2. Concentrations (ng/mg-oil) of selected polycyclic aromatic hydrocarbons (PAH) in crude oils of various origins and maturities.

= not reported

* Summary of data from Grimmer and Böhnke (1978) for 8 crude oils of different maturities in a single basin. Concentrations based on GC-MS analysis.

† Summary of data from Grimmer et al. (1983) for 8 crude oils (Agha Jari; Arab, Medium; Dubai; Gach Saran; Nigeria, Light; Qatar; Sahara; Sarir) of different origins (see ref.). Concentrations obtained by GC analysis.

‡ Concentrations for two individual oils from Pancirov and Brown (1975) and based on GC,GC/UV and MS analyses. Benzofluoranthene concentrations obtained by summation of maximal values for 4 isomers. repectively, greater than the highest concentration of each compound in the crude oils from the Gifhorn Trough. Assuming the crude oil from the Gifhorn Trough with the highest concentration of pyrene and benzo(g,h,i)perylene represents the highest maturity (greatest thermal stress) oil from that basin, the hydrothermal petroleums are enriched in these two compounds by at least one order of magnitude above the concentrations in crude oils produced by catagenesis under normal geothermal gradients. The concentrations of pyrene and benzo(g,h,i)perylene in normal crude oils of differing origins range from 1.6 to 10.7 and 0.6 to 5.0 ng/mg-oil, respectively (see Table III.2). These ranges do not differ significantly from those in the crude oils from the single location, Gifhorn Trough, and indicate that hydrothermal oils are distinctly enriched in these PAH, relative to crude oils in general.

Other unsubstituted PAH which are consistently enhanced in the hydrothermal petroleums relative to crude oils (cf. Tables III.1 and III.2) include fluoranthene, benz(a)anthracene, chrysene/triphenylene (enrichment factors between 1.2 and 320) and benzo(e)pyrene, benzo(a)pyrene (enrichment factors between 2.4 and 3200). [Enrichment factors are presented as the range between c_{min} (hydrothermal)/ c_{max} (crude) and c_{max} (hydrothermal)/ c_{min} (crude) where c_{min} and c_{max} are the minimum and maximum concentrations, respectively, of a compound in the hydrothermal or crude oils.] The compounds phenanthrene and perylene are occassionally depleted in the hydrothermal oils relative to crude oils. The ratios of the phenanthrene concentrations in the hydrothermal oils to those in the two crude oils, Kuwait and S. Louisiana (see Table III.2), range from 0.11 to 20. The ratios of the perylene concentrations in the hydrothermal oils to those in the tabulated crude oils range from 0.37 to 6000. The variability in perylene is likely due to its generation mostly during diagenesis (Louda and Baker, 1984; Venkatesan, 1988) and its alkylation or degradation at elevated temperatures, as suggested by some previous studies (Louda and Baker, 1984; Venkatesan and Kaplan, 1987). The relative depletion of phenanthrene in some of the hydrothermal oils may reflect post-depositional removal or loss (see later discussion) of the diagenetically and catagenetically produced compound in the sediments or oils.

Summing the concentrations of the PAH listed, results in values of 1.0 to 6.3 μ g PAH/mg-bitumen for the hydrothermal oils (see Table III.1). Transforming to a total aromatics (unsubstituted and substituted) basis, the totals of the tabulated PAH range in concentration from 5.7 to 41 μ g-PAH/mg-aromatics (total aromatics determined gravimetrically) in the hydrothermal oils, with the lowest (0.57%) and highest (4.1%) concentrations in samples 1172-1 and 1177-4B, respectively.

Degree of alkylation for tricyclic aromatics

The degree of alkylation of thermally generated aromatic hydrocarbons is a function of the temperatures encountered during formation (Giger and Blumer, 1974; Blumer and Youngblood, 1975; Youngblood and Blumer, 1975; Blumer, 1976). High-temperature pyrolysates are characterized by a dominance of the unsubstituted PAH, while normal crude oils generated at lower temperatures (60-150°C; Hunt, 1979; Tissot and Welte, 1984) contain larger proportions of the alkylated homologs. The relative proportions of the unsubstituted and substituted PAH have been used to distinguish between pyrolytic sources (anthropogenic and natural combustion) and fossil fuel or diagenetic sources in environmental samples (Blumer and Youngblood, 1975; Youngblood and Blumer, 1975; Hase and Hites, 1976).

The distribution of the tricyclic PAH (phenanthrene + anthracene) and their alkylated (substituted) homologs in the Guaymas Basin hydrothermal petroleums, crude oils from production reservoirs, and two surficial sediments near urban areas are presented in Fig. III.2. The Guaymas Basin oils exhibit a wide variation in the relative proportions of these unsubstituted and alkylated tricyclic PAH (Fig. III.2a). For most of the samples, the alkylated homologs (C2- and C3-) dominate. Differences in the proportions of the C_1 - and C_0 - (unsubstituted compound) are the greatest variable in most of the Guaymas Basin samples. The hydrothermal oils can be separated into two major groups by their alkylation pattern. The first group consists of oils with the Coand C1- tricyclic aromatics representing concentrations between 20 and 85% of the dominant homolog (C2- or C3-). The second group of hydrothermal oils (7D-5A, 7D-3B, 1168-1-2, 1168-1-3B) have much lower relative proportions of the C_0 - and C_1 triaromatics (0 to 35% of C₃-). This latter set of hydrothermal petroleums has aliphatic hydrocarbon compositions consistent with extensive biodegradation (Kawka and Simoneit, 1987). Such a process will preferentially remove the unsubstituted and monosubstituted triaromatics (Fedorak and Westlake, 1981; Rowland et al., 1986). In addition, water-washing (Tissot and Welte, 1984) at the seabed can also result in similar effects due to the higher aqueous solubility and enhanced aqueous partitioning of the lower molecular weight homologs (Yalkowsky and Valvani, 1979; May, 1980). The steep slopes of the alkylation patterns (less alkylation, greater relative depletion) of the second group of samples is consistent with such a process. Therefore, the most likely

Comparison of the distributions of phenanthrene + anthracene (C₀) and Fig. III.2. their alkylated homologs (C_1 through C_3) in: (a) hydrothermal oils of Guaymas Basin and (b) crude oils: Bradford, North Sea and Jiang Han (our study) and Kuwait and South Louisiana (replot of data from Youngblood and Blumer, 1975); surficial sediments from Buzzards Bay, West Falmouth, MA [replot of data for Station B from Youngblood and Blumer (1975); location as described in Giger and Blumer (1974), Youngblood and Blumer (1975)] and Charles River Basin, Boston, MA [replot of original data from Hites and Biemann (1975)]. The broken lines in (a) indicate samples that appeared to be extensively biodegraded as discussed in Kawka and Simoneit (1987). Data for (a) and for Bradford, Jiang Han and North Sea crude oils in (b) are based on summation of intensities of the molecular ions of each of the isomeric series (m/z 178, 192, 206, 220) obtained during gas chromatography-mass spectrometry and are uncorrected for response. Data for Charles River and Buzzards Bay sediments and for Kuwait and South Louisiana crude oils were similarly obtained but using probe distillation (isomers not chromatographically resolved) and high resolution mass spectrometry (HRMS).







Fig. III.2.

explanation of the general pattern for these oils is that they have been altered postdepositionally. Extensive biodegradation and water-washing of this group of hydrothermal oils (7D-5A, 7D-3B, 1168-1-2, 1168-1-3B) is supported by their lowest absolute concentrations of phenanthrene (see Table III.1) of all the hydrothermal oils.

A comparison of the triaromatic distributions of the hydrothermal oils (see Fig. III.2a) with those of the three crude oils, Bradford, North Sea, and Jiang Han (see Fig. III.2b) indicates that some of the hydrothermal oils (1172-4,1177-2D,1177-2C,1173-8, 1173-3) may be more enriched in the unsubstituted triaromatic hydrocarbons relative to the normal oils. The small number of crude oils used for comparison, though, limits the significance of this distinction. The two crude oils, Kuwait and South Louisiana, are relatively more depleted in Co- and C1- triaromatics than the other crude oils. They are,therefore, very different from the bulk of the hydrothermal oils and most similar to the few biodegraded hydrothermal oils. Although this distinction probably reflects an actual difference in the alkylation pattern of the crude oils, the fact that the Kuwait and S. Louisiana oil data were obtained by probe distillation/HRMS (Pancirov and Brown, 1975) rather than GC/MS may suggest an analytical artifact.

The surficial sediment from the Charles River Basin has a tricyclic aromatic distribution (Fig. III.2b) very different from the others described. The unsubstituted homolog dominates with the proportion of alkylated components rapidly decreasing with the higher degrees of alkylation. Such a distribution was interpreted as being consistent with a pyrolytic or combustion source (anthropogenic or natural) of the PAH (Hase and Hites, 1976). The sample of sediments from Buzzards Bay, New Bedford, Station B (Fig. III.2b) is also quite different from the oils but has a more equal distribution of the tricyclic aromatics than the Charles River Basin sediment. This distribution, somewhat intermediate between the oils and Charles River Basin sediment, was originally interpreted to be a result of inputs from natural fires (Youngblood and Blumer, 1975) with some fossil fuel contributions. Subsequent research by Hase and Hites (1976) compared the PAH compositions of air particles (unsubstituted PAH dominate), river water and sediments. The authors concluded that the distributions of PAH in the surficial sediment from Buzzards Bay may have resulted from preferential removal of the more soluble (less-alkylated) components from air particulate matter of anthropogenic (pyrolytic and combustion) sources during and after deposition in the aqueous environment (Hase and Hites, 1976; LaFlamme and Hites, 1978). A combination of such a process and mixing of combustion-derived inputs with sedimentary or fossil fuel inputs (oil spills) is most tenable, especially since Station B in Buzzards Bay is near the

entrance of polluted New Bedford Harbor (Giger and Blumer, 1974; Youngblood and Blumer, 1975).

Most of the Guaymas Basin oils contain distributions of tricyclic PAH homologs that are within the range of the normal crude oils and surficial sediments near urban areas (cf. Figs. III.2a and b). One exception is sample 1177-4B, a hydrothermal oil which contains the highest proportion of the parent PAH. This homolog distribution is even steeper than those of the urban surficial sediments (cf. Figs. III.2a and b). Based on this data, we interpret this sample as representing an effectively higher-temperature petroleum than the other hydrothermal oils or a lower-temperature petroleum that received an influx of a very high-temperature pyrolysate at a time after initial deposition at the seabed . This interpretation is corroborated by the 1177-4B oil also containing the highest concentrations (see Table III.1) of the higher molecular weight PAH of a pyrolytic origin (e.g. pyrene, benzofluoranthenes, benzopyrenes, indeno(c,d)pyrene, benzo(g,h,i)perylene, and coronene).

The aromatic hydrocarbons in normal petroleums generated under low temperatures are thought to result from defunctionalization and aromatization, through dehydrogenation and cracking/cyclization, of biologically derived compounds. Pyrolytic temperatures, on the other hand, increase alkyl-cracking and favor thermal resynthesis which enhances the unsubstituted PAH. The triaromatic distributions of most of the hydrothermal oils, other than 1177-4B, are not very different from those of crude oils (cf. Figs. III.2a and b). Although a few of the hydrothermal oils appear to be slightly enriched in the parent compound relative to the alkylated homologs, the limited number of crude oils used for comparison does not allow definitive conclusions. The general patterns and the unusual character of 1177-4B, though, suggest that the triaromatic distributions of hydrothermal petroleums, in general, result from a combination of processes. Variable temperatures of genesis and mixing of higher-temperature pyrolysates with the aromatic distributions produced by diagenesis and low-temperature catagenesis are probably the primary controls on the triaromatic distributions as well as total PAH contents of the hydrothermal oils. The mixing of components occurs during hydrothermal transport of the fluids and deposition of the petroleum at the seabed and includes both solubilization and advection of the bitumen in the sediments overlying the heat source (Kawka and Simoneit, 1987; Simoneit et al., 1988). The previously discussed post-depositional processes of biodegradation and water-washing also affect all of the hydrothermal petroleums to varying degrees and, thereby, impart an additional control on the PAH distributions.

Sedimentary concentrations

Concentrations of the PAH in the hydrothermal oils are presented on a $\mu g/g$ -dry sediment basis in order to illustrate the possible environmental significance of their occurrence at the seabed in hydrothermal vent areas. Such concentrations of individual or groups of PAH in the Guaymas Basin hydrothermal sediments are presented in Table III.3. For comparison, the selected sediment concentrations of these PAH in various polluted (urban) and pristine coastal areas are included.

PAH concentrations in the hydrothermal sediments of Guaymas Basin vary considerably -exemplified by wide ranges and large standard deviations from the average concentrations (see Table III.3). This variability results from two factors: (a) variation in concentrations of the hydrothermal oils in the seabed sediments and (b) differences in the PAH distributions in the individual oils. The first parameter (mg-bitumen/g-dry sediment; see Table III.1) exhibits values ranging from 1% to 35% soluble organic matter. The oils are associated inhomogeneously with fragments of crusty material containing the hydrothermally precipitated minerals (e.g. amorphous silica, calcite, barite, anhydrite, sulfides) intermixed with diatom debris and clay (Simoneit, 1985; Kawka and Simoneit, 1987). The heterogeneities in spatial distributions of these mineral crusts and of the hydrothermal fluid/oil discharges result in considerable variation in the petroleum/matrix associations at the seabed. The variability in PAH concentrations in the oils, evident in Table III.1 and discussed previously, is determined by the thermal influences of different pyrolytic regimes at depth in the sediments, mixing during hydrothermal transport, and post-depositional alterations by biodegradation and/or water-washing (aqueous solubilization).

The average concentrations of PAH in Guaymas Basin vary from 5.4 to $40\mu g/g$ sediment for fluoranthene and benzofluoranthenes + benzopyrenes, respectively (Table III.3). The highest variability in concentration, based on the standard deviation normalized to the mean, is exhibited by phenanthrene + anthracene. This pattern is probably a reflection of differential alteration by post-depositional processes because those compounds are more water-soluble (Yalkowsky and Valvani, 1979; May, 1980) and more susceptible to biodegradative effects (Dean-Raymond and Bartha, 1975; Fedorak and Westlake, 1981; Rowland *et al.*, 1986a) than the other PAH examined in this study.

Compounds	Ounds Guaymas Basin Hydrothermal Sedime Range Average		Washing <u>Coastal Se</u> Range	$\frac{1}{2}$ gion [†] diments Average ± s	Alaska H-24 [‡] , Hitchenbrook Island	New York‡ Bight	Charles [‡] River, Boston, MA
Phenanthrene + Anthracene	0.30 - 90	18±26	0.002 - 0.074	0.031 ± 0.022	0.0025	0.74	5.0
Fluoranthene	0.44 - 18	5.4 ± 4.8	0.004 - 0.220	0.043 ± 0.049	0.0006	1.2	15
Pyrene	2.1 - 89	27 ± 24	0.006 - 0.120	0.039 ± 0.030	0.0006	1.3	13
Benzanthracenes + Chrysene/Triphenylene	1.6 - 100	22 ± 27	0.006 - 0.120	0.043 ± 0.029	0.0014	0.89	21
Benzofluoranthenes + Benzopyrenes	3.2 - 130	40 ± 36	0.008 - 0.294	0.088 ± 0.069	0.006	1.7	33
Benzo(g,h,i)perylene	1.3 - 44	26 ± 26	0.003 - 0.058	0.027 ± 0.017	n.a.	n.a.	n.a.

Table III.3. Concentrations $(\mu g/g dry sediment)^*$ of various PAH in sediments of the Guaymas Basin hydrothermal vent areas and in various surficial sediments of coastal areas.

n.a. = not analyzed

* Values for Guaymas Basin sediments calculated using concentrations of PAH based on extractable organic matter (bitumen) and the concentrations of bitumen associated with the hydrothermal sediments (Table III.1). Concentrations within each entry of more than one compound or isomer have been summed.

[†] Summary of data from Prahl (1982)

[‡] Hites et al. (1980)
The concentrations of the selected PAH in Washington coastal sediments (Prahl, 1982) also exhibit a high degree of variability (see Table III.3), which is caused by processes unlike those controlling the distributions in the hydrothermal samples. The sediments sampled were located in transects perpendicular to the shoreline and separated by as much as 80 km, laterally. The spatially dependent concentrations were reported as resulting from differential transport by coastal processes of combustion-produced PAH associated with particles of specific hydrodynamic properties in the suspended sediment load of the Columbia River (Prahl, 1982). The average concentrations of the tabulated PAH in Guaymas Basin sediments are $10^2 - 10^3$ times higher than those calculated for the Washington coastal sediments. The Guaymas Basin concentrations are even more significant $(10^3 - 10^5 \text{ times higher})$ when compared with those in sediments of an intertidal zone (Alaska H-24, Table III.3) near Hitchinbrook Island, Alaska sampled as a location remote from contamination by anthropogenic sources or oil spills (Hites et al., 1980). The concentrations of PAH in the Guaymas Basin sediments are much higher than the background levels in coastal sediments, and such high values are a reflection of the accumulation of hydrothermal pyrolysates at the seabed. Thus the vent/mound areas are a point source of PAH, significantly above those from either anthropogenic or natural combustion sources.

Concentrations of PAH more comparable to the hydrothermal sediment contents are found in sediments near urbanized areas of high anthropogenic activity. A sediment sample from New York Bight, an area receiving high inputs of industrial wastes, sewage, and atmospheric deposition from metropolitan New York (Hites et al., 1980), contained concentrations of PAH which are in the range of, or within a factor of two of, the lowest concentrations found in Guaymas Basin (see Table III.3). The average concentrations in the hydrothermal sediments are 4-25 times greater than those reported for the one sample from the New York Bight area. The Charles River in Boston, MA is an extreme example of an highly polluted river (Hites and Biemann, 1975). The concentrations of the selected PAH in an anoxic sediment of this river are all within the ranges of those in the hydrothermal sediments (see Table III.3). Comparing the averages in the Guaymas Basin samples with those in the Charles River sediment, fluoranthene is the only PAH which has an average concentration lower (by a factor of 3) in the hydrothermal samples. While in the Guaymas samples the average concentrations of phenanthrene+anthracene and pyrene are approximately 4 times and 2 times greater, respectively, the average concentrations of benzanthracene+ chrysene/triphenylene and benzofluoranthenes+benzopyrenes are nearly identical to

those in the Charles River sediment. Moreover, the highest values in the PAH ranges for the Guaymas samples represent enrichments between 4 and 18 times (exclusive of fluoranthene) the concentrations in the polluted sediments of the Charles River Basin.

PAH associations and toxicological implications

The concentrations of PAH in the hydrothermal vent areas of Guaymas Basin are comparable and often much higher than those in highly industrialized and polluted coastal areas. The presence of high concentrations of carcinogenic compounds, such as benzo(a)pyrene and benzo(b+j+k)fluoranthenes (Dipple, 1980), can affect the abundant biota present at the Guaymas Basin seabed. Much of the toxic and carcinogenic PAH of anthropogenic sources is often associated with soot or creosote-coated particles (Neff, 1979). Socha and Carpenter (1987) compared the concentrations of PAH in pore waters from sites in Puget Sound, Washington contaminated to varying degrees by combustion and creosote sources. The data suggested that partitioning of PAH into pore-waters from creosote-contaminated sediments (Eagle Harbor) was significantly greater than that in sediments where the PAH were more combustion-derived and associated with soot or coal particles. PAH within soot particles appear more protected from equilibration with the aqueous phase (Socha and Carpenter, 1987). Toxicological studies have suggested that bioavailability of contaminants is more determined by the interstitial water concentrations and desorption rates from sediments than by bulk sediment concentrations (Adams et al., 1985; Swartz et al., 1986; 1989; Landrum, 1989). The PAH in Guaymas Basin are within a lipid-rich bitumen (petroleum) which saturates the hydrothermal mineral/sediment matrix. This type of an association has more similarity to PAH in creosote adsorbed onto particles rather than to PAH within soot particles. As such, the bioavailability of the PAH in the Guaymas Basin sediments may be significantly higher than that of combustion-derived PAH due to increased partitioning into interstitial waters and the lack of the protective matrix soot particles provide.

In order to assess their possible toxicological significance, the PAH concentrations in Guaymas Basin sediments can be compared with the PAH concentrations in sediments of known toxicity and contaminated by PAH-rich creosote. Swartz *et al.* (1989) studied the toxicity of such a sediment (station EH08 in Eagle Harbor, WA) to the amphipod *Rhepoxynius abronius*. By diluting this highly toxic sediment with uncontaminated sediment from Yaquina Bay, OR, they calculated the 4-day LC50 (concentration of sediment exhibiting 50% mortality rate of the species) of these EH08 sediments to be 666 mg/kg wet weight. The predicted concentrations of selected PAH were then calculated using their initial concentrations in the undiluted sediment.

The concentrations of PAH in the Guaymas Basin hydrothermal sediments are compared with the predicted PAH concentrations in the LC50 of EH08 sediment mixture in Table III.4. Using the ranges in Guaymas Basin for comparison, the hydrothermal sediments contain comparable to or higher concentrations of anthracene and fluoranthene than the EH08 sediment dilution mixture. Although some hydrothermal sediments exhibit concentrations approximately 70% of the predicted value for anthracene and fluoranthene, enrichments of up to 240 times are also present. Phenanthrene is richer in Guaymas Basin by up to 81 times but also shows the greatest relative depletion in one sample with concentration of only 20% of the predicted value in the EH08 dilution. Pyrene, benz(a)anthracene, benzo(b+k)fluoranthenes and benzo(a)pyrene are all consistently enriched in the Guaymas Basin sediments relative to the LC50 of EH08 sediment mixture. The lowest relative enrichment in this group of PAH is for pyrene (5.3) and the highest is for benzo(a)pyrene (1800).

Enrichment factors for the specific PAH based on the average concentrations in the hydrothermal sediments are also presented in Table III.4. The lowest average enrichment (9) is found for fluoranthene, while the highly carcinogenic benzo(a)pyrene exhibits the highest average enrichment of 1000. Enrichments appear to be greater for the higher molecular weight PAH. This is caused by the aromatic distribution in the creosote being skewed towards the lower molecular weight PAH.

This comparison suggests that the PAH concentrations in Guaymas Basin may be toxicologically significant. It is difficult, though, to link directly and unequivocably the high toxicity of a sediment such as Eagle Harbor EH08 with the presence of PAH. Swartz *et al.*, (1989) also reported that the concentrations of phenanthrene and fluoranthene (the dominant PAHs) in the 4-day LC50 of EH08 sediment were significantly less than the 4-day and 10-day LC50's for the individual chemicals spiked into pure sediment from Yaquina Bay. The authors invoked the presence of other compounds and/or additive effects (Swartz *et al.*, 1988) to explain the enhanced toxicity of the sediment. The enhanced concentrations of the higher molecular weight PAH in the Guaymas Basin relative to the concentrations in the LC50 of EH08 sediment may, therefore, increase the toxicity of the hydrothermal petroleums even more. Nevertheless, the complexity of chemical interactions and the uncertainties regarding aqueous/organic partitioning in hydrothermal systems preclude definitive assessments of

Table III.4.	Comparison of selected PAH concentrations (µg-g dry sediment) in sediments of the Guaymas
	Basin hydrothermal vent areas with the predicted PAH concentrations in a creosote-contaminated
	sediment from Eagle Harbor Station EH08*, WA diluted with uncontaminated sediment from
	Yaquina Bay, OR to a level exhibiting a 4-day $LC50^{\dagger}$ to the amphipod <i>Rhepoxynius abronius</i> .

	Guaymas Hydrothermal	Basin Sediments	Eagle Harbor Sta. EH08 sediment			
Compounds	Range Average ± s		in a 666 mg/kg wet weight dilution with Yaquina Bay sediments	Enrichment in Guaymas Basin sediments ^{††}		
Phenanthrene	0.21 - 77	16 ± 22	0.95	17		
Anthracene	0.049 - 17	2.9 ± 4.6	0.07	41		
Fluoranthene	0.44 - 18	5.4 ± 4.8	0.60	9		
Pyrene	2.1 - 89	27 ± 24	0.35	77		
Benz(a)anthracene	0.42 - 35	7.2 ± 9.4	0.08	90		
Benzo(b+k)fluoranthene	1.1 - 42	14 ± 12	0.04	350		
Benzo(a)pyrene	0.50 - 18	10 ± 10	0.01	1000		

* Swartz et al., (1989).

[†] The calculated concentration of Eagle Harbor Station EH08 sediments (666 mg/kg wet wt.) that would induce a 50% mortality rate for the amphipod after 4 days.

^{††}Ratio [Average in Guaymas Basin] [Diluted EH08 sediment]

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the potential toxicological effects of the PAH. However, lesions have been found in mollusks near the hydrothermal vents (J.C. Harshbarger, pers. commun.). Although no direct correlation can be made between the PAH concentrations and such lesions, their co-occurrence does suggest that this area of research should be pursued.

Various suites of PAH have been characterized in petroleums or trace pyrolysates from other active hydrothermal areas, as for example Escanaba Trough (Kvenvolden and Simoneit, 1990), the East Pacific Rise at 13°N and 21°N (Brault *et al.*, 1988; 1990), and the Mid-Atlantic Ridge at 26°N (Brault and Simoneit, 1989). Thus it appears that this hydrothermal process is ubiquitous along the global rift systems of the oceans, generating both low and high temperature components of petroleum-like products from immature organic matter (Simoneit, 1984; 1985; 1988). Such a natural point source of pyrolytic and biologically active PAH may have important implications for the ecology of the hydrothermal benthic communities.

CONCLUSIONS

Comparison of the hydrothermal petroleums from Guaymas Basin with crude oils from production reservoirs indicates that the hydrothermal oils contain higher relative concentrations of unalkylated PAH as expected. On the other hand, distributions of the parent and alkylated homologs of the tricyclic aromatic hydrocarbons suggest that the aromatic hydrocarbons in the hydrothermal oils are mixtures of both thermally resynthesized and diagenetically produced PAH. In general, the PAH concentrations in the hydrothermal oils are determined by thermal influences (different pyrolysis temperatures), mixing during hydrothermal transport, and post-depositional alteration by biodegradation and/or water-washing (aqueous solubilization).

The concentrations of the unsubstituted PAH in the seabed mounds/sediments of the Guaymas Basin are comparable to those in sedimentary sinks of highly polluted and industrialized areas. High concentrations of toxic and carcinogenic PAH are present in solution in the lipid-rich petroleum of the hydrothermal sediments rather than as particleassociated (e.g. soot) contaminants. The possible enhanced bioavailability of these hydrothermal PAH suggests that toxicological effects on the benthic communities of the hydrothermal vent areas could be significant. Future research needs to address these toxicological concerns and the evolution and persistence of the hydrothermal ecosystems under such potentially adverse conditions.

ACKNOWLEDGEMENTS

We thank the crews and pilots of the D.S.V. *Alvin*, R.V. *Lulu*, and R.V. *Atlantis II* for their skillful recoveries of hydrothermal samples. We are grateful to F.G. Prahl and B. Brownawell whose helpful comments and discussion greatly improved this manuscript. We also thank J.W. Farrington and an anonymous reviewer for their constructive and appreciated reviews. Support for this research from the National Science Foundation, Division of Ocean Sciences (Grants OCE-8312036, OCE-8512832 and OCE-8601316), and partial support by the Donors of the Petroleum Research Fund, administered by the American Chemical Society, are gratefully acknowledged.

IV. HYDROTHERMAL PYROLYSIS OF ORGANIC MATTER IN GUAYMAS BASIN: 1. COMPARISON OF HYDROCARBON DISTRIBUTIONS IN SUBSURFACE SEDIMENTS AND SEABED PETROLEUMS

ABSTRACT

The bitumens of a selection of subsurface sediments from Guaymas Basin, Gulf of California have been analyzed in order to assess the hydrothermal effects on the organic matter and to better delineate the processes influencing the generation, deposition, and alteration of the hydrothermal petroleums at the seabed. Although the thermally generated subsurface bitumens are generally rich in polar/asphaltic materials, as are the seabed oils, the hydrocarbon transformations parallel the extent of hydrothermal alteration as reflected in the downcore mineralogy at DSDP Sites 477 and 478. At Site 477, a progressive change from *n*-alkane- to aromatic hydrocarbon-dominated patterns in the high resolution gas chromatography (HRGC)-resolvable fractions of the bitumens accompanies decreases in organic carbon and bitumen yields with depth. These transformations are indicative of incremental hydrothermal alteration of the sediments with depth, due to increasing temperature and/or progressive passage of hydrothermal fluid through the sedimentary column. The PAH distributions undergo extensive transformations (e.g. dealkylation) consistent with hydrothermal alterations, are dominant at depth, and have the broadest range as thermal maturation indices. The aliphatic and aromatic components of the seabed oils can be transported to the seabed independently as a result of their generation under different depth regimes and sequentially over time during pyrolysis. The concentrations of the parent PAH in the thermally altered subsurface bitumens are comparable to those in the seabed oils. The differential solubilization of the more soluble aromatics and selective solidification/condensation of the higher molecular-weight PAH out of the hightemperature fluids exiting at the seabed (chimneys) results in aromatic distributions of the oils significantly skewed towards the larger components (e.g. benzo(ghi)perylene) relative to the subsurface bitumens. Comparison of the downcore hydrocarbon distributions with those in the seabed petroleums support the contention that the hydrothermal oils are mixtures of pyrolysates from different thermal regimes (depths) and are significantly altered by differential solubilization during transport and at the seabed.

INTRODUCTION

Hydrothermal activity associated with the formation of new oceanic crust is common at spreading ridges throughout the world (Edmond and Von Damm, 1983). Both sedimentary and suspended detrital organic matter associated with these rift areas is readily pyrolyzed by the hydrothermal process forming petroleums and petroleum-like products (Simoneit, 1990). These hydrothermal pyrolysates range from the trace levels encountered in sediment-starved locations, such as East Pacific Rise, 13°N and 21°N, (Brault et al., 1985, 1988, 1990); Mid-Atlantic Ridge, 26°N (Brault and Simoneit, 1990) to the seabed petroleums (condensates to asphalts) found in locations with a significant sedimentary cover, such as Guaymas Basin, Gulf of California (Simoneit 1982c, 1984a,b, 1985b; Simoneit and Lonsdale, 1982; Kawka and Simoneit, 1987, 1990; Simoneit and Kawka, 1987; Bazylinski et al., 1988; Simoneit et al., 1988) and Escanaba Trough, NE Pacific (Kvenvolden et al., 1986; Kvenvolden and Simoneit, 1990). The hydrothermal alteration of organic matter in subsurface sediments has also been investigated in Guaymas Basin (Curray et al., 1982; Galimov and Simoneit, 1982; Galimov et al., 1982; Simoneit, 1982a,b; Simoneit and Philp, 1982; Simoneit et al., 1984); Bransfield Strait, Antarctica (Whiticar et al., 1985; Brault and Simoneit, 1988; Suess et al., 1990); and Atlantis II Deep, Red Sea (Simoneit et al., 1987).

The hydrothermal petroleums found at the seabed of the Southern Trough, Guaymas Basin exhibit great variability in both character and quantity of organic matter (Simoneit and Lonsdale, 1982; Kawka and Simoneit, 1987). The initial survey of these petroleums (Chapter II) suggested that this variability results from fluctuating pyrolytic regimes (different origins - depths and temperatures); differential transport from depth, due to thermal gradients, gaseous solubilization, and hydrodynamic alteration of the multi-component fluids; and post-depositional alteration, such as biodegradation and water-washing. Detailed characterization of the polycyclic aromatic hydrocarbons (PAH) in these seabed oils revealed that they contain higher levels of the unsubstituted PAH than normal petroleums, consistent with their inferred production at higher pyrolytic temperatures (Chapter III). The rapid maturation of the biomarkers (steranes and hopanes) also supported this inference of high temperatures of genesis (Chapter II; Simoneit et al., 1990a). In general, the character of the seabed petroleums is consistent with the nature of the hydrothermally altered bitumens in the subsurface sediments, as described by Galimov and Simoneit (1982); Galimov et al. (1982); Simoneit (1982a,b); Simoneit and Philp (1982); Simoneit et al. (1984).

In order to obtain a better understanding of the processes forming and controlling the composition of the seabed petroleums, the hydrocarbon distributions in a selection of subsurface sediments from Guaymas Basin have been analyzed in more detail. The samples described herein are previously uncharacterized sediments, recovered by the Deep Sea Drilling Project, Leg 64, which have been thermally altered to differing degrees by the hydrothermal process. The results presented include the aliphatic and aromatic compositions, the sterane and hopane distributions, the unsubstituted PAH concentrations, and the relative compositions of the tricyclic aromatic hydrocarbons in the bitumens of these subsurface sediments. The detailed characterization of the PAH in these bitumens is of particular interest, as the aromatic content of the seabed petroleums is unique (Chapter III) and previous analyses of the aromatics in the subsurface sediments have been limited. The hydrocarbon contents of the thermally altered subsurface bitumens are compared to the analogous data obtained for the seabed petroleums. The probable sources (thermal end-members) of the seabed oils are identified; and the processes controlling their formation/deposition at the seabed are discussed.

The companion paper (Chapter V) compares the biomarker transformations in the seabed oils and downcore sediments in more detail and discusses the relevance of laboratory simulations to biomarker maturations in hydrothermal systems. In addition, the distributions of triaromatic steroid hydrocarbons in these oils and sediments are presented and discussed as possible tracers of high-temperature and/or hydrothermal processes.

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SAMPLING AND ANALYSES

Sample Selection

The downcore sediments from Guaymas Basin described herein were recovered in December, 1978 during Leg 64 of the Deep Sea Drilling Project (DSDP). Two groups of sediments have been analyzed (see Table IV.1): eight samples from DSDP Site 477 in the Southern Trough and three samples from Site 478 between the Northern and Southern Troughs of Guaymas Basin (see Fig. IV.1).

Hole 477 contains a massive 47.5 m thick dolerite sill between 58.0 and 105.5 meters below seafloor (mbsf) (Curray *et al.*, 1982) (see Fig. IV.2). The site is characterized by a high heat flow of 0.84 Wm⁻², which is primarily conductive and probably due to the proximity of the basement rather than the cooled sill (Curray *et al.*, 1982; Gieskes *et al.*, 1982). The geothermal gradient is high and extends well below the dolerite sill with temperatures of 50° and 87°C measured at 50 and 168 mbsf, respectively (Curray *et al.*, 1982). Downhole logging in Hole 477 registered a bottomhole (191 mbsf) temperature of 105°C (unpublished results, Leg 64). The samples from Hole 477 analyzed here were recovered from below the major sill at depths between approximately 107 and 145 m subbottom and consist of clays, claystones, sandy siltstones, and silty sandstones, representing hydrothermally altered turbidites and diatomaceous muds of Pleistocene age (Table IV.1, Fig. IV.2 and Curray *et al.*, 1982).

Hole 478 contains a 12 m thick basaltic sill (with an intercalated sediment layer) beginning at 221.0 mbsf; a 4.5 m thick basaltic sill at 254.5 mbsf; and a 121 m thick massive intrusion at 342.5 mbsf, consisting of dolerites and basalts (see Fig. IV.2). Site 478 is characterized by a heat flow of 0.15 Wm⁻², which is significantly lower than that of Site 477 (Curray *et al.*, 1982). The three samples from Hole 478 described here were recovered from between approximately 251 and 253 mbsf and were located in close proximity to (3.37 to 1.35 m above) the deeper, thin sill (see Fig. IV.2). These sediments are diatomaceous muds and dolomitic claystones of late Pleistocene age with the latter dominant and thermally baked near the sill (see Table IV.1, Fig. IV.2 and Curray *et al.*, 1982).

The samples from Hole 477 were chosen from a sequence of sediments containing hydrothermal mineral assemblages (Curray *et al.*, 1982) and showing progressive hydrothermal alteration with depth (Kastner, 1982; Kelts, 1982). The samples represent sediments continually altered over a relatively long period of time by an open, active

Sample*	Depth (mbsf) [†]	Distance from upper thick sill (m) [‡]	Distance from lower thin sill (m) [‡]	Description/ Lithology [§]
477-15-1 (120-125) ^a	106.73	1.23	-	Hydrothermally altered diatomaceous muds/ turbidites (clays, siltstones-claystones)
16-2 (140-145) ^b	117.93	12.43		
16-2 (145-150) ^c	117.98	12.48	-	n
16-4 (130-135) ^d	120.83	15.33	-	u
16-4 (135-140) ^e	120.88	15.38	_	'n
17-1 (145-150) ^f	125.98	20.48		.,
19-1 (130-135) ^g	144.83	39.33	-	1
19-1 (135-140) ^h	144.88	39.38	-	n
478-29-1 (60-65) ⁱ	251.13	17.63	-3.37	Diatomaceous mud
29-2 (38-43) ^j	252.41	18.91	-2.09	(Graded)
29-2 (112-117) ^k	253.15	19.65	-1.35	Dolomitic claystone

Table IV.1. Sample summary for Sites 477 and 478.

* Sample listings are according to DSDP convention with hole-core-section (depth interval in cm from top of section). Superscripts correspond to sample labels in Fig. IV.2.

[†] Depth (meters-below seafloor) of sample is given as the center of the interval. Depth is calculated according to DSDP convention (see Curray et al., 1982).

[‡] Distance from sills is determined using the middle of each interval, depth as listed in core log, and the top or bottom of the sill, depth as reflected by dowhole log (see Curray *et al.*, 1982). Positive denotes distance away from seafloor, and negative towards the seafloor.

Sediment descriptions are from DSDP core log descriptions (Curray et al., 1982).







Figure IV.2. Lithologic columns for DSDP Sites 477 and 478 (adapted from Simoneit, 1982a). Blackened areas indicate percent of core recovered. Lowercase alphabet (a,b,c, etc.) indicates locations of samples identified in Table IV.1 and discussed in this chapter.

hydrothermal system with recharge (Kastner, 1982) and a high conductive heat flow (Curray *et al.*, 1982). The thermal gradient in Hole 477 is ~ 475°C km⁻¹, based on measured downhole temperatures (Curray *et al.*, 1982). The thermal alteration of the sediment samples from Hole 478 is considered to be more temporally and spatially limited due to the thermal stress resulting from a presently inactive and sill-induced hydrothermal event with no recharge (Kastner, 1982) and the presence of a significantly lower thermal gradient of ~ 130°C km⁻¹ (Curray *et al.*, 1982), based on downhole temperatures. These latter samples (Hole 478) were chosen to contrast those of Hole 477. Although Hole 477 also contains a sill, the overall higher geothermal gradient and more extensive hydrothermal system at this site overwhelm any of the sill-induced effects. While the sediments from both sites contain hydrothermal mineral assemblages, the character and extent of organic matter pyrolysis might be considered to differ in the two types of hydrothermal systems, described by Kastner (1982), as the relationship between time and temperature is an important variable in the thermal maturation of organic matter (Simoneit *et al.*, 1990a).

Additional data presented here for comparison are for the hydrothermal oils recovered from the Guaymas Basin seabed, originally characterized in Chapters II and III; a total extract (1175-7) of hydrothermal chimney material, recovered similarly in 1982 from the Southern Trough of Guaymas Basin and described by Peter (1986); and a hydrous pyrolysis simulation using Recent Guaymas Basin sediment (Simoneit, 1990).

Extraction and Separations

The sediments were stored frozen after recovery by DSDP, then freeze-dried, pulverized with a mortar and pestle, homogenized by stirring, and subsampled for organic and inorganic carbon analysis. Between 35 and 45 g of each sediment were extracted in a Whatman glass mirofibre thimble (GF 30 x 100 mm; precombusted at 500° C for ≥ 24 hours) using a Soxhlet apparatus and an azeotropic mixture (87/13% by volume) of chloroform and methanol (B & JTM Brand High Purity Solvents, Burdick & Jackson/Baxter). Each sediment was exhaustively extracted for a total of 330-530 cycles of the Soxhlet apparatus with a change of solvent after ~ 40% of completion.

The two extracts of each sample (300 ml each) were combined and washed with 200 ml of water (B & J^{TM} Brand High Purity Solvent) to remove salts. The aqueous layer was acidified with pre-cleaned 6N HCl to pH ≤ 2 to aid separation and then back-extracted three additional times with 25 ml each of methylene chloride. The organic

extract was then concentrated on a rotary evaporator, under reduced pressure, just to dryness.

Total lipid (bitumen) yields were determined gravimetrically after sulfur removal (see following discussion) from the total extracts. The weights were obtained by weighing either the total residues, after drying under a pre-purified N_2 stream at room temperature, or aliquots removed from known volumes of extracts.

All glassware used in the extraction and separation procedures was cleaned overnight in a mixture of concentrated sulfuric acid and the commercially available Nochromix[®] (Godax) followed by rinsing with distilled water. Before use, the glassware was rinsed with copious amounts of methanol and methylene chloride.

A procedural blank was determined by adding standards to an empty precombusted Soxhlet thimble and extracting and treating the isolate identically to and concurrently with the sediment samples. Both the gravimetric (see later discussion) and analytical results were corrected as necessary.

Sulfur Removal

Sulfur was removed from the total organic extracts using "activated" copper. Approximately 4 g (1-1.5 ml) of Cu powder (~ 40-mesh, 99.5% pure, Aldrich brand) was placed in a Pasteur pipette on top of a glass wool plug. The copper was then activated using 3-5 ml of 6N HCl and washed, consecutively, with copious amounts of the high-purity distilled water, acetone, methanol and methylene chloride while avoiding exposure to air. Each total extract was placed on a separate copper column using 1 ml of methylene chloride followed by washing of the vial with ~ 5 ml. The sample was then eluted with an additional 10 ml of methylene chloride.

Adsorption Chromatography

A select number of samples were additionally separated to isolate the aliphatic and aromatic fractions for analysis. The samples were deasphalted using excess hexane (6-8 ml) added to the total extracts dissolved in 100-200 μ l of methylene chloride. The maltenes (hexane-soluble fraction) were isolated from the precipitated asphaltenes (ASPH) using centrifugation. Residual maltenes were removed from the ASPH by three additional hexane washings (6-8 ml each) followed by centrifugation. The maltenes were combined to form a C₁₅₊ hexane-soluble fraction (HSF). The HSF and ASPH fraction yields were then determined gravimetrically. The details of the liquid-solid column chromatography of the HSF are as described in Chapter II with the following differences. The columns were slurry-packed using toluene and then gradually equilibrated to 100% hexane by elution with increasing percentages of hexane in toluene. The volumes of solvent for collection of each fraction were increased for this set of samples to compensate for differences in adsorbent batches and an apparent increased retention on the columns of the higher molecular weight components, particularly the polycyclic aromatic hydrocarbons (PAH), possibly due to lower HSF loading. The following fractions were collected: Aliphatic (F1), 40 ml hexane; Aromatic (F2), 85 ml toluene; Polar NSO (F3), 40 ml toluene. The term "aliphatic hydrocarbons" as used here includes the alicyclic components of the saturated hydrocarbons.

HRGC and HRGC-MS

High resolution gas chromatography (HRGC) of the total bitumen extracts and fractions from adsorption chromatography was conducted on a Hewlett-Packard (HP) 5890A GC equipped with a split/splitless capillary injection system and flame ionization detector (FID). The conditions were: FID, 325°C; injector, 290°C; split purge, 50 ml/min (enacted at 1.0 min after injection); septum purge, 4 ml/min. The samples were analyzed in the splitless mode using a fused silica capillary column, 28-30 m x 0.25 mm i.d. DB-5 (J & W Scientific) with a 0.25- μ m film thickness, using helium as carrier gas. The sample (0.50-2.5 μ l) was injected 0.10 min after syringe needle insertion and the beginning of the GC oven temperature program: initial 65°C (1.0 min), programmed to 135°C at 25°C/min and then to 300°C at 4°C/min, isothermal at 300°C (30.0 mins). The analog signal was monitored and/or integrated with an HP 3392A or 3393A integrator.

High resolution gas chromatography-mass spectrometry (HRGC-MS) of the samples was performed with a Finnigan 9610 gas chromatograph interfaced directly with a Finnigan Model 4021 quadrupole mass spectrometer. The GC was equipped with a split/splitless injector; a 29-31 m x 0.25 mm i.d. DB-5 (J & W Scientific) fused silica capillary column with a 0.25- μ m film thickness; and helium as carrier gas. The conditions were: injector, 240°C; split purge, 50 ml/min (enacted at 1.0 min after injection); septum purge, 4 ml/min; separator oven and transfer line, 300-325°C. Sample injection was as for the HP GC (see above) but with the temperature program: initial 65°C (2.0 min), programmed to 135°C at 1.5°C/min and then to 310°C at

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4°C/min, isothermal at 310°C (60.0 mins). The MS conditions and data processing were as described in Chapter I.

Quantitation

Concentrations were determined using perdeuterated compounds (e.g. d_{10} -pyrene, d_{10} -anthracene, n- $C_{24}D_{50}$) as internal standards added to sample solutions (either total extracts or chromatographic fractions) immediately before analysis by HRGC or HRGC-MS. The PAH were quantitated using response factors, calculated relative to the internal standard, from the analysis of a standard mixture. For some compounds, standards were unavailable which necessitated either substituting a response factor or leaving the values uncorrected. Such instances are so noted in the results. Unless explicitly stated otherwise, quantitation of the PAH used the integrated areas of the most intense and characteristic ions or mass fragments, usually the molecular ions (nominally equivalent to the molecular weights), obtained during normal scanning (50-650 amu/2 secs) of the mass spectrometer. For the aliphatic compounds, such as n- $C_{24}D_{50}$, quantities based on the integrated areas of three of the stronger mass fragments (e.g. m/z 66, 82, 98) were averaged to determine their concentrations. Further details of the quantitation procedures are presented in Appendix A.

Standard Recoveries

A series of perdeuterated aliphatic and aromatic standards was added to additional subsamples of three sediments to determine extraction efficiencies. The samples (see Table IV.2) were chosen so as to obtain recovery data for a range of sediments containing variable amounts of extractable organic matter (see Results section). Enhanced evaporative loss of the low molecular weight components in lipid-poor sediments compared to more lipid-rich sediments, as reported by Socha and Carpenter (1987), was of particular concern.

The percent recoveries for the total bitumen extracts (TEXT) are listed in Table IV.2. The most lipid- or bitumen-rich sediment from sample 477-16-2 exhibits the highest recoveries of both the aliphatic and aromatic standards. Greater than 90% of all the aliphatic and of the d_{10} -pyrene and d_{12} -chrysene standards were recovered. Only ~ 50% of the d_{10} -anthracene was recovered from all three samples, while the other standard of greatest volatility, d_{40} -pristane, was 84% recovered in the lipid-poor

	477-16-2 (140-145) TEXT-Recov*	477-16-4 (135-140) TEXT-Recov $(n = 3)^{\dagger}$	477-19-1 (135-140) TEXT-Recov $(n = 2)^{\dagger}$
Aromatic standards [‡] d_{10} -anthracene d_{10} -pyrene d_{12} -chrysene d_{12} -perylene	49 107 99 18	52 ± 4 74 ± 1 80 ± 3 7.5 ± 0.6	46 ± 1 89 ± 2 95 ± 0.4 0.98 ± 0.06
Aliphatic standards [§] d_{40} -pristane \underline{n} -C ₂₄ D ₅₀ \underline{n} -C ₃₂ D ₆₆	91 96 106	67 ± 8 63 ± 1 53 ± 2	84 ± 4 99 ± 4 98 ± 7

Table IV.2. Percent recoveries of perdeuterated standards after extraction, water-washing, and sulfur removal.

* TEXT-Recov denotes total extracts of sediments initially spiked with perdeuterated standards and extracted specifically for recovery determinations. See text for further details.

[†] Averages and standard deviations given for samples determined using repetitive (n = 2 or 3) injections and analyses by HRGC-MS.

[‡] Quantitation of the aromatic recovery standards used the areas of the molecular ions of each perdeuterated compound (m/z 188, 212, 240, 264, respectively).

§ Quantitation of the aliphatic recovery standards used the average of the more intense ion fragments (m/z 66, 82, 98) of each compound.

sediment. The former value is comparable to that for d_{10} -phenanthrene reported by Socha and Carpenter (1987). The extraction recovery efficiencies from the sediment (477-16-4) with an intermediate lipid concentration exhibit overall the lowest recoveries, particularly for the aliphatic components. This sample did differ from the others in containing the largest quantity of elemental sulfur, as observed during the sulfur-removal procedure; but a single analysis precludes any inferences regarding causal factors.

Excluding the results for sample 16-4, the extraction recoveries for d_{10} -pyrene and d_{12} -chrysene, greater than 89 and 95%, respectively, are very good and comparable to that reported by Socha and Carpenter (1987) for d_{12} -chrysene (96%) added to Puget Sound sediments. The recovery of the higher molecular weight d_{12} -perylene ranges from 1 to 18% in this study and is the lowest among all of the standards. This result appears inconsistent with those of the other PAH and is quite significant in terms of adjustments of concentrations of perylene and other higher molecular weight PAH for extraction recoveries. On the other hand, correcting concentrations using recoveries assumes that the perdeuterated analog behaves similarly to the normal PAH in terms of both extraction efficiency and/or susceptibility to degradative effects (e.g. photooxidation) during laboratory work-ups. As a consequence of these results, a study is presently being conducted investigating the recoveries of both the deuterated and non-deuterated higher molecular weight PAH from sedimentary samples.

Recovery for the adsorption chromatography procedure was tested by comparing the concentrations of PAH in an extract 1173-9 (low bitumen) before and after separation. This sample, predominantly aromatic in character, contained high concentrations of benzo(ghi)perylene and coronene. Recoveries for the PAH were better than 90% for all observed.

The concentrations reported in this study have not been corrected for recoveries and the results must therefore be interpreted accordingly. Instances where variable recoveries may be important are so noted in the text.

Inorganic and Organic Carbon

Inorganic and organic carbon values of the sediments were determined using acidification and oxidation with phosphoric acid and concentrated dichromate/sulfuric acid, respectively. Detection of the evolved CO_2 utilized a modified LECO carbon analyzer with the methodology as described by Weliky *et al.* (1983).

RESULTS

Bulk Character

The downcore sediments from Site 477 described herein range in Corg from 1.06% for the shallowest sample 477-15-1 to 0.31% for the deepest sample 477-19-1 (see Table IV.3). The values are consistent with those initially reported for cores 477-15 through 477-19 (range 1.1 to 0.3 %Corg) by Simoneit and Bode (1982). This decrease in organic carbon with depth correlates well with the progressive degree of hydrothermal alteration (Kelts, 1982; Gieskes et al., 1982a,b) described for the sediments below the sill at this site. The downcore sediments from Site 478 contain higher Corg values ranging from 2.21% for the sample 3.37 m above the sill, 478-29-1 (60-65), to 1.57% for the sample 1.35 m above the sill, 478-29-2 (112-117), (see Tables IV.1, IV.3). A similar decrease in Corg from 2.2 to 1.4% for comparable intervals was report by Simoneit and Bode (1982). The higher C_{org} values, compared to Site 477, are typical of the diatomaceous muds in the basin (Curray et al., 1982). The gradual and slight decrease in organic carbon approaching the sill reflects a decrease in diatom abundance and consequent increase in carbonate (see Table IV.3), as dolomite (core logs, Curray et al., 1982). Part of the decrease in C_{org} is also due to the progressive effects of hydrothermal pyrolysis approaching the sill, as interpreted from the mineralogical evidence (Kastner, 1982 and discussed later).

The carbonate contents, calculated as calcium carbonate (%CaCO₃), are relatively low for the shallower interval (106.73 - 125.98 mbsf) from Site 477 and range from 0.12 to 0.25% for samples 477-15-1 through 477-17-1. The two deepest samples, 477-19-1 (130-135) and (135-140) contain slightly higher carbonate contents at 4.26 and 4.34 %CaCO₃, (see Table IV.3). The Site 478 samples contain between 8.78 and 12.00 %CaCO₃, with values increasing as the sill is approached (see Tables IV.1, IV.3). Simoneit and Bode (1982) determined comparable values for samples from the same overall depth ranges at the two sites using a carbonate bomb: 0 to 4% and 3 to 16 %CaCO₃ for the sediments from Hole 477 and 478, respectively.

The bitumen yields were determined gravimetrically after sulfur removal from the total organic extracts and are presented in Table IV.3 on the basis of g-dry sediment and mg- C_{org} . The bitumen yields for the Site 477 samples decrease with depth on both bases. The shallowest sample, 477-15-1 (120-125), contains 1600 and 151 µg-bitumen per g-sediment and mg- C_{org} , respectively; and the deepest sample, 477-19-1 (135-140)

			Bitumen Yield		- Bitumen % Bulk Composition*				Dominant Total Extract
Sample	%C _{ORG}	%CaCO ₃	g-sediments	mg-C _{ORG}	ALIPH	AROM	NSO	ASPH	Character [†]
477-15-1 (120-125)	1.06	0.12	1600	151	14	15	20	51	alkanes
477-16-2 (140-145)	0.76	0.17	417	55	_		-		alkanes
477-16-2 (145-150)	0.77	0.21	458	59	33	11	28	28	alkanes
477-16-4 (130-135)	0.76	0.25	85	11	_	_	-		aromatic
477-16-4 (135-140)	0.74	0.12	134‡	18‡	-	-	-	-	aromatic
477-17-1 (145-150)	0.78	0.25	47.8	6.1	-	_	-	-	aromatic
477-19-1 (130-135)	0.29	4.26	7.7±1.3§	2.7	-	-		_	aromatic
477-19-1 (135-140)	0.31	4.34	8.4	2.7	-	-	-	_	aromatic
478-29-1 (60-65)	2.21	8.78	5140	233	3	3	20	74	biomarkers/ no alkanes
478-29-2 (38-43)	2.04	9.68	6890	338	4	5	22	69	biomarkers/ no alkanes
478-29-2 (112-117)	1.57	12.00	319	20.3	13	16	39	32	alkanes/ aromatic

Table IV.3. Summary of bulk organic geochemical parameters.

* Determined gravimetrically after adsorption chromatography.

[†] Dominant character as determined by direct injection of total extract on GC. Summary of patterns presented in Figs. IV.3 and IV.4.

[‡] Values may be inflated due to incomplete removal of "elemental" sulfur.

§ For weighing of replicate (n = 2) bitumen aliquots.

contains 8.4 and 2.7 µg-bitumen per g-sediment and mg-Corg, respectively. The yields for adjacent samples (e.g. 477-16-2, 140-145 and 145-150 intervals) are very similar and differ by less than 5% of the averages, with the exception of the samples from core/section 477-16-4. The two bitumen yields differ by about 22% from the average of the two intervals. Compared to the other samples of this study, the second deeper interval, 135-140 cm, was observed to contain a much higher elemental sulfur content during the sulfur removal procedure. The higher bitumen yield, 134 μ g/g-sediment and 18 μ g/mg-C_{org} of this interval may be inflated due to incomplete removal of the sulfur. Exceptionally high total sulfur concentration in core-section 16-4 (7.56 %S reported for sample 477-16-4 (20-22)) have been attributed, in part, to a dominance of anhydrite in many samples (Niemitz, 1982); but the reduced form might also be relatively significant. Galimov et al. (1982) obtained a bitumen yield of 87 µg/g-sediment for a sample at 121.73 mbsf, within a meter of the two samples in this study, which agrees very well with the value 85 µg/g-sediment obtained for the upper interval 477-16-4 (130-135) (see Table IV.3). For three sediment samples between 128 and 185 mbsf, Simoneit and Philp (1982) obtained bitumen yields decreasing from 1000 to 20 µg/g-sediment. The higher value is at a depth approximately 2 m above an interval for which a yield of only 47.8 µg/g-sediment was obtained in this study. As Simoneit and Philp (1982) did not desulfurize the bitumen extracts, their higher yield (by a factor of 20) may be due to elemental sulfur. The value of ~ 8 μ g/g-sediment for the samples from core/section 19-1 (see Table IV.3) is also significantly lower than their reported values (720 to 20 μ g/gsediment) for sediments from 10 to 40 m deeper. Part of that enrichment may be due to contamination of sediments by pipe-joint grease during drilling, as reported by Curray et al. (1982). In that respect, we have observed the presence of what appears to be grease in some freeze-dried samples from cores below 477-19.

The two Site 478 samples, farthest from the sill, exhibit the highest bitumen yields of any of the samples in this study (see Table IV.3). For the sample 478-29-1 (60-65) and 29-2 (38-43), 3.37 and 2.09 m above the sill, respectively, the bitumen yields are 5140 and 6890 μ g/g-sediment, respectively. The high bitumen contents are also reflected on an organic carbon basis, with values of 233 and 338 μ g/mg-C_{org}, respectively. These values are significantly higher than the value of 81.8 μ g/mg-C_{org} reported by Galimov *et al.* (1982) for a sample 6.15 m above the sill and the value of 95 μ g/mg-C_{org} for combined samples from an interval between 3.42 and 2.75 m above the sill reported in Simoneit and Philp (1982). The reason for the discrepancies is not known at the present time. The sample 1.35 m above the sill, 29-2 (112-117), contains 319 and 20.3 μ g-bitumen per g-sediment and mg-C_{org}, respectively. These relatively low values are most likely due to heating by the sill; transformation of organic matter to bitumen, CO₂, and CH₄; and movement of the products away from the sill, as described for diabase intrusions in a Cretaceous black shale (Simoneit *et al.*, 1981). The difference in bitumen content between the two samples farthest from the sill (3.37 and 2.09 m above) could then result from such a migration of the pyrolysates away from the sill elevating the bitumen concentration indigenous to the intermediate interval (2.09 m above). Changes in source material (see above) must also be considered as an additional factor.

The bulk compositions of bitumen for the samples separated by adsorption chromatography were determined and are listed in Table IV.3. At Site 477, the bitumen of the shallowest sample 15-1 (120-125) is composed of 29% hydrocarbons, aliphatic and aromatic components equal; 20% polar NSO's; and 51% asphaltenes. The bitumen in the sample 11 m deeper, 16-2 (145-150), has an enhanced hydrocarbon content of 44% (aliphatic: aromatic ratio of 3), a slightly higher polar NSO (28%) content and an approximate 2-fold decrease in the asphaltene content (28%), relative to the sample above. Similar changes with depth/maturation are evident for Site 478. The two samples farthest away from the sill have virtually identical bitumen compositions (see Table IV.3) with the hydrocarbons constituting between 6 and 9%, the polar NSO's between 20 and 22%, and the asphaltenes between 69 and 72% of the bitumen. Relative to the two Site 477 samples, these Site 478 sediments are more enriched in the polar asphaltic components. On the other hand, the sample, 478-29-2 (112-117), nearest the sill exhibits a 3-fold increase, relative to the more distant samples, in the proportion of hydrocarbons, 29% (aliphatic: aromatic ratio of 0.80). As for the Site 477 samples, the thermal maturation associated with the sill decreases the proportion of asphaltenes (32%) by a factor of two. An increase in the proportion of NSO's (39%) is also observed.

The limited number of samples preclude any definitive conclusions regarding the changes in the composition of the bitumens. The general change, increase in hydrocarbon content with depth or proximity to a thermal source, is consistent with that observed during thermal maturation of organic matter in sedimentary basins (Tissot and Welte, 1984) and in pyrolysis studies (e.g. Huizinga *et al.*, 1987a,b).

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Character of Total Extracts

The general character of the bitumen from the downcore samples was obtained through direct analysis by HRGC and confirmation by HRGC-MS when necessary. Figs IV.3 and IV.4 contain representative gas chromatograms for samples from Sites 477 and 478, respectively; and a summary of the dominant character of the samples, as indicated by the chromatograms, is provided in Table IV.3. The intensity of each individual chromatogram has been adjusted for maximum visibility of the compound distributions, and approximate concentration scales are included in each for comparison.

Site 477

The HRGC-resolvable fractions of samples 477-15-1 (120-125) through 477-16-2 (145-150) (see Figs.IV.3a-c) are dominated by *n*-alkanes (n-C₁₂ to n-C₃₅) and various isoprenoids, including pristane and phytane. The two adjacent samples in core-section 16-2 (Figs. IV.3b,c) are almost identical in character, as would be expected by their close sampling. The only difference between these two intervals, (140-145) and (145-150), is evident in the alkane distribution below n-C₁₅. The upper interval contains a slight relative enhancement in these lower molecular weight *n*-alkanes. This apparent difference is not considered significant since these compounds are quite volatile and their recoveries are inconsistent in the analytical scheme of this study.

A significant difference is apparent between the two shallowest samples from Site 477 (see Figs. IV.3a,b). In the chromatogram for 15-1 (120-125) (Fig.IV.3a), the isoprenoid pristane is the dominant compound, with the other alkanes at most one-half its concentration. On the other hand, the *n*-alkanes are the dominant compounds in sample 16-2 (140-145) (Fig. IV.3b), which is approximately 11m deeper. There is also a slight odd-even predominance for the n-C₂₆ to n-C₃₄ alkanes in the shallower sample not apparent in the deeper sample (cf. Figs. IV.3a,b). Both of these differences are consistent with changes that occur during the thermal maturation of organic matter: increasing relative proportion of *n*-alkanes and loss of odd-even predominance (Tissot and Welte, 1984). Assuming the source of the organic matter remains the same, the changes observed are interpreted as resulting from increased thermal stress with depth.

The bitumen characters of the four deeper samples from Site 477, 16-4 (130-135) through 19-1 (135-140), are significantly different from those described above, as indicated by the representative gas chromatograms (cf. Figs. IV.3d-f with 3a,b). The *n*-

Figure IV.3. Representative gas chromatograms (HRGC) of the total extracts from Site 477 downcore sediment extracts: (a) 477-15-1 (120-125); (b) 477-16-2 (140-145); (c) 477-16-2 (145-150); (d) 477-16-4 (130-135), also essentially identical to 477-16-4 (135-140); (e) 477-17-1 (145-150); and (f) 477-19-1 (130-135), also essentially identical to 477-19-1 (135-140). Numbers = *n*-alkane chain length; Pr = pristane; Ph = phytane; IS = internal standard; DBT = dibenzothiophene; P = phenanthrene; MP = methylphenanthrene isomers (3 = 3-methylphenanthrene, 2 = 2-methylphenanthrene, etc.); DMP = dimethylphenanthrene isomers; Py = pyrene; BaA = benz(a)anthracene; Ch/Tr = chrysene/triphenylene; BF = benzofluoranthenes; BeP = benzo(e)pyrene; M⁺ = molecular ion (characteristic of PAH); Cn1-3 = contaminants (Cn1 is a diethyl phthalate; Cn2 = unknown shipboard contaminant, see text; Cn3 = dibutyl nonanedioate). Depths of samples given in meters below seafloor (mbsf). Approximate concentration scales (based on peak height) in µg-component/mg-bitumen are provided for comparison.

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RETENTION TIME

Figure IV.3.



RETENTION TIME

Figure IV.3. (cont.)

alkanes are no longer the dominant compounds in the HRGC-resolvable fractions. At these greater depths (120.88 through 144.83 mbsf), the aromatic compounds predominate. Important differences in the aromatic distributions are also apparent within this deeper series of samples. In the chromatograms of 16-4 (130-135) and 17-1 (145-150) (Figs. IV.3d,e), the aromatic distributions are more complicated, with relatively large percentages of the alkylated aromatics (e.g. methyl- and dimethylphenanthrenes). In the deepest samples from core-section 19-1, represented by the chromatogram for 19-1 (130-135), the compound distribution is much simpler with phenanthrene the predominant compound and the alkylated aromatics virtually absent. Dibenzothiophene, pyrene, chrysene/triphenylene, benzofluoranthenes, benzo(e)pyrene, and benzo(ghi)perylene are present in various amounts in all of these samples.

Some contaminants (Cn1-3 in Fig. IV.3f) are also evident in this deepest sample. The compounds are a diethyl phthalate (Cn1) and dibutyl nonanedioate (Cn3), which are common plasticizers and are also ubiquitous in low-level environmental samples. These probably originate, in part, from the butylcellulose in the core tubes. The identity of compound Cn2 is unknown (see Appendix B for mass spectrum). Initial interpretation suggests a phenyl-carbonyl moiety with the attached group unknown. This contaminant is most likely of shipboard origin, as it is not a significant component of the procedural blank.

The transition from aliphatic-dominated to aromatic-dominated character in the HRGC-resolvable fractions of the bitumens at Site 477 is considered a result of extensive maturation by increasing thermal stress at depth. Similarly, the increased dominance of parent PAH, especially phenanthrene, in the deepest samples from core/section 19-1 is also reflective of high thermal stress (see Chapter III) and suggests high pyrolytic temperatures have dominated.

The present results for Site 477 differ somewhat from previously published data on the hydrocarbon distributions in sediments from comparable depths at the site. Galimov *et al.* (1982) did not report a dominance of aromatic compounds in the hydrocarbon fraction of a sample from 121.73 mbsf. Instead, a series of *n*-alkanes (C_{16} - C_{30}) were identified in the gas chromatogram of the hydrocarbons (Galimov *et al.*, 1982). Inspection of the gas chromatogram, though, reveals that the *n*-alkanes are actually intermixed with a number of unidentified compounds, possibly aromatic hydrocarbons. As the analyses by Galimov et al. (1982) involved separation techniques not used for the samples analyzed herein, conclusions regarding the apparent differences are not warranted. Similarly, Simoneit and Philp (1982) reported the presence of low concentrations of a broad range of n-alkanes in a saturate fraction of a sample from 127.9 m sub-bottom; but as the aromatic contents were not measured, the relative abundances of the hydrocarbons cannot be assessed nor compared with the results herein.

Site 478

For the two samples farthest from the sill at Site 478, 29-1 (60-65) and 29-2 (38-43), n-alkanes are not apparent in the gas chromatograms of the HRGC-resolvable fractions of the bitumens (see Figs. IV.4a,b); and the patterns are dominated by the biomarkers (steranes and hopanes) and variable amounts of isoprenoids (e.g. pristane, phytane). Two long-chain isoprenoids are also observed in the extract of the sample 2.09 m above the sill, 29-2 (38-43), but not in the intervals above nor below. The biomarker distributions and the isoprenoid identities are presented in the following section and discussions. The composition of the HRGC-resolvable fraction of the bitumen from the sample only 1.35 m above the sill, 29-1 (112-117) (Fig IV.4c) is significantly different from the others in containing a narrow distribution of low molecular-weight *n*-alkanes (n-C₁₁ to n-C₂₄). Phenanthrene and the methylphenanthrene series are present in comparable concentration, and lesser amounts of other aromatic hydrocarbons are also observed in the chromatogram (cf. Fig. IV.4c and IV.8c). This change in character of the HRGC-resolvable fraction of bitumen next to the sill is consistent with increased thermal stress resulting in formation of n-alkanes. Such a relative increase in low-weight n-alkanes was also observed near the 'Bramsche Massiv' igneous intrusion in Lower Jurassic Shales of NW Germany (Leythaeuser et al., 1980; Altebäumer et al., 1983). As the level of thermal maturation increased, based on vitrinite reflectance, the n-alkane distributions shifted to shorter-chain homologs. A change in vitrinite reflectance from 0.56 to 1.74 %Ro [beginning of oil window and within gas zone, respectively (Hunt 1979)] resulted in a shift in the peak of the *n*-alkane distributions from $n-C_{27}$ to $n-C_8$; which was attributed to preferential cracking of the long-chain to the short-chain alkanes by the elevated thermal stress (Leythaeuser et al., 1980; Altebäumer et al., 1983). Simoneit et al. (1981) reported similar changes in Cretaceous black shales altered by diabase intrusions in the Eastern Atlantic. More importantly, they reported that the traces of bitumen in the immediate vicinity of the diabase intrusions were dominated by polycyclic aromatic hydrocarbons, particularly the low molecular-weight components. This correlates well with the simultaneous

Figure IV.4. Representative gas chromatograms (HRGC) of the total extracts from Site 478 downcore sediment extracts: (a) 478-29-1 (60-65); (b) 478-29-2 (38-43); (c) 478-29-2 (112-117). Key as in Fig. IV.3 with: Biomarkers = include steranes and hopanes; long-chain isoprenoids (see Fig. IV.5 and discussion for details). Sample locations relative to sill given in meters above sill (mas). Approximate concentration scales (based on peak height) in μ g-component/mg-bitumen are provided for comparison.



RETENTION TIME

Figure IV.4.

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occurrence of aromatic hydrocarbons and short-chain n-alkanes in the chromatogram for sample 478-29-2 (112-117) nearest the sill (see Fig. IV.4c).

Aliphatic Components

Site 477

The compound distributions in the gas chromatograms of the aliphatic fractions (F1) of Site 477 samples are essentially identical to the distributions in the HRGCresolvable fractions of the total extracts (bitumen) in Fig. IV.3. The chromatograms of the aliphatic fractions are, therefore, not presented; and the reader should refer to the previous section, "Character of Total Extracts," for the description of the alkane content of these samples.

Site 478

The gas chromatograms of the aliphatic fractions (F1) for the samples from Site 478 are presented in Fig. IV.5. The aliphatic distributions (Fig. IV.5a,b) of the two samples, 29-1 (60-65) and 29-2 (38-43), are very similar to the character of the total extracts in Fig. IV.4a,b. *n*-Alkanes are not detectable even in the purified aliphatic fraction in either of the samples. Phytane is the predominant compound in the sample, 29-1 (60-65) farthest from the sill. The pristane/phytane ratio of 0.61 is slightly higher than those previously reported for the sediments at or ~3 m above this subbottom depth [Pr/Ph values of 0.50 and 0.47, respectively; Galimov *et al.* (1982),Simoneit and Philp (1982)]. It is significantly lower than the ratios, 1.14 and 3.00, that Simoneit and Philp (1982) reported for samples nearest the sill, 29-2 (108-110) and (129-131), (1.41 m and 1.20 m above the sill, respectively). A correlation between higher Pr/Ph ratios with increasing thermal stress near sills in sediments has been suggested by Simoneit *et al.* (1981).

The other dominant compounds in the sample farthest from the sill (3.37 m above) are the C₂₇ through C₂₉ $5\alpha(H)$,14 $\alpha(H)$,17 $\alpha(H)$,20R-steranes with lesser amounts of the 5 $\beta(H)$ - configuration (see Fig. IV.5a). No sterenes, steradienes, or diasterenes are present; and additional details on the biomarker distributions are presented in the following section ("Biomarker Distributions"). In addition to these biomarkers, a

Figure IV.5. Gas chromatograms (HRGC) of the aliphatic fractions (F1) from the Site 478 downcore sediment extracts: (a) 478-29-1 (60-65); (b) 478-29-2 (38-43); (c) 478-29-2 (112-117). Numbers = *n*-alkane chain length; Pr = pristane; Ph = phytane; IS = internal standard; MT₁₉ = monoaromatic tricyclic C₁₉ terpane (14-methyl-13-methylpodocarpa-8,11,13-triene); BI₂₅ = branched C₂₅ isoprenoid (2,6,10,14-tetramethyl-7-(3-methylpentyl)pentadecane; TAT = trialkylated thiophene (see text); I₃₈-I₄₀ = long-chain head-to-head linked isoprenoids (C₃₈-C₄₀). Sterane identifications: 27-29 β = 5 β (H),14 α (H),17 α (H),20R- and α = 5 α (H),14 α (H),17 α (H),20R-stereochemistry for the C₂₇-C₂₉ steranes. Hopane identifications: H30 = 17 α (H),21 β (H)-hopane; H31 = 17 α (H),21 β (H)-homohopane (22S and 22R). Sample locations relative to sill given in meters above sill (mas).



RETENTION TIME

Figure IV.5.

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tricyclic terpane derivative of presumably algal origin is present in this sample (see Fig. IV.5a). This compound, tentatively identified as a monoaromatic tricyclic C_{19} hydrocarbon (14-methyl-13-methylpodocarpa-8,11,13-triene) by mass spectral comparison, has been found to be the predominant monoaromatic tricyclic terpane derivative in extracts of Permian Tasmanite algae (Azevedo et al., 1990; Simoneit et al., 1990b). A branched C₂₅ isoprenoid [2,6,10,14-tetramethyl-7-(3methylphenyl)pentadecane] is also present in this interval (see Fig. IV.5a) and has been reported to occur in various Recent, freshwater and marine, sediments (Robson and Rowland, 1986). Two compounds (labelled TAT in Fig. IV.5) have a mass spectrum identical to that initially reported by Rullkötter et al. (1982) for two isomeric compounds present in sediments from core-section 478-28-4. These compounds were tentatively identified by the authors as trialkylated thiophenes. Damstè et al. (1989) subsequently refined the assignment and identified the compounds as diastereomers of a highly branched isoprenoid thiophene [5-(1-(1,5-dimethylhexyl)-4,8-dimethylnonyl)-2,3dimethylthiophene] through comparison of the mass spectrum with that of an authentic standard.

The aliphatic fraction of the sample 2.09 m above the sill, 29-2 (38-43), is similar to the previous more distant sample in having no *n*-alkanes and a predominance of the sterane biomarkers (see Fig. IV.5b). Pristane and phytane are in slightly lesser abundance, with no significant change in their ratio. Both the monoaromatic tricyclic terpane derivative (see above) and the highly branched isoprenoid thiophenes have decreased somewhat in their relative abundance. Unlike the sample 3.37 m above the sill, the biomarker region of the sample 2.09 m above the sill contains significant abundances of $17\alpha(H)$, $21\beta(H)$ -hopane and the $17\alpha(H)$, $21\beta(H)$ -homohopane series (22S- and 22R-). This increase in hopanes relative to steranes is expected for sediments under increased thermal stress, as evidenced by pyrolysis studies (Seifert, 1978).

An interesting aspect of this sample, 29-2 (38-43), is the appearance of long-chain C_{38} - C_{40} head-to-head linked isoprenoids, which were not present in the sample more distant from the sill (cf. Figs. IV.5a,b). This series of head-to-head linked isoprenoids are probably detrital remains of methanogenic bacteria (Ourisson *et al.*, 1984) and have been observed as important components in a California Miocene crude (Moldowan and Seifert, 1979) and several other oils (Albaiges, 1980). More importantly, Tannenbaum *et al.* (1986a) reported the appearance of the C₄₀ isoprenoid in laboratory pyrolysates of the asphaltenes and kerogen of an organic-rich Monterey Formation diatomite but its absence in the original bitumen. Therefore the occurrence of these isoprenoids in the

aliphatic fraction of 478-29-2 (38-43) suggests that this sample has been exposed to a higher thermal stress than the sample farther away from the sill, 478-29-1 (60-65). On the other hand, Rullkötter et al. (1982) found a therein unidentified C_{40} isoprenoid in thermally immature sediments from Site 479 (oxygen-minimum zone of the Guaymas Basin Slope). The strong likelihood that this compound is the C_{40} head-to-head linked isoprenoid suggests that it may not only be indicative of thermal maturation but also possibly of specific depositional environments.

Recently, Rowland (1990) has reported an abundance of the C_{39} and C_{40} head-tohead isoprenoids in the hydrous pyrolysate of a pure culture of *Methanobacterium thermoautotrophicum* but their absence in a similar pyrolysate of *Methanosarcina barkeri*. Interestingly, Rowland also found that the dominant aliphatic hydrocarbons in the two pyrolysates were pristane and phytane, with Pr/Ph ratios of 1.4 and 2.0, respectively; while the extract of the unheated culture of the former bacterium contained phytane but no pristane. This generation of pristane during hydrous pyrolysis of bacteria could explain the increase in Pr/Ph ratios in the vicinity of sills as reported by Simoneit and Philp (1982) and attributed, therein, to the increased thermal stress.

The aliphatic fraction of the sample nearest the sill, 478-29-2 (112-117), is very different from the previous two samples farther above the sill (see discussion above) in containing an abundance of *n*-alkanes (C_{15} through C_{28}) maximizing at C_{17} with no odd-to-even carbon predominance and no pristane or phytane apparent (see Fig. IV.5c). As stated earlier, this change in character reflects an increased cracking of kerogen and hydrocarbons due to the thermal stress near the sill. Comparison of the gas chromatogram of the total extract (Fig. IV.4c) with the gas chromatogram of the aliphatic fraction (Fig. IV.5c) of this same sample reveals a significant difference in the n-alkane distributions. The former chromatogram contains n-alkanes ranging from $n-C_{11}$ through $n-C_{24}$ and maximizing at $n-C_{13}$, whereas the *n*-alkanes in the latter range between $n-C_{15}$ and $n-C_{28}$ and maximize at $n-C_{17}$. The difference is attributed to selective loss of the more volatile fraction of the hydrocarbons during subsequent sample work-up (e.g. adsorption chromatography and gravimetric analysis). This result attests to the importance of minimizing sample exposure to the atmosphere during these analyses and the utility of direct bitumen analyses by HRGC for preliminary assays of hydrocarbon content in samples when specific techniques for analysis of volatiles are not available.

Biomarker distributions

The mass fragmentograms of m/z 191, characteristic triterpane fingerprint, for the three Site 478 samples and the shallowest sample from Site 477, 15-1 (120-125) are presented in Fig. IV.6. Triterpanes were not detectable in the deeper samples at Site 477. The predominant component of all four triterpane distributions in Fig. IV.6 is the C₃₀ homolog in the thermally most stable $17\alpha(H)$, $21\beta(H)$ configuration (Ensminger *et al.*, 1974; 1977; Seifert and Moldowan, 1978). In the sample farthest from the sill, 478-29-1 (60-65), (Fig. IV.6a) the entire hopane series (C₂₇ to C₃₅, exclusive of C₂₈) is present in the $17\alpha(H)$, $21\beta(H)$ -configuration. The biologically-derived configuration, $17\beta(H)$, $21\beta(H)$ -, and the configuration of intermediate stability, $17\beta(H)$, $21\alpha(H)$ -, are also present. The C₃₁ and C₃₂ hopanes exhibit C-22 S/R ratios of 0.49 and 0.20, respectively; which are quite different from the equilibrium ratio of 1.5 (Ensminger *et al.*, 1977). Minor amounts of triterpenes in this sample include hop-17(21)-ene and isohop-13(18)-ene. The former compound is often the dominant triterpane in unaltered sediments in and around Guaymas Basin (Rullkötter *et al.*, 1982).

In the triterpane distribution of the sample nearer the sill, 478-29-2 (38-43), (Fig. IV.6b) changes consistent with increased thermal stress have occurred. While the overall range in the triterpanes (C_{27} - C_{35}) has remained relatively constant, the triterpanes and the 17 β (H),21 β (H)-hopanes have disappeared, and the relative abundance of the 17 α (H),21 β (H)-hopanes has increased. Increased epimerization at C-22 in the extended hopane series ($\geq C_{31}$) has increased the S/R ratios of the C₃₁ and C₃₂ hopanes to 0.85 and 0.54, respectively.

The sample nearest the sill, 478-29-2 (112-117), (Fig.IV.6c) contains the lowest amount of triterpanes relative to the rest of the compounds in the aliphatic fraction. This sample, only 1.35 m above the sill, exhibits the narrowest range of hopanes (C_{27} - C_{33}); this is possibly due to thermal cracking of the hopanes, with enhanced losses of the higher homologs in a manner similar to that which occurs for the *n*-alkanes (see previous discussion). No significant change in the C-22 S/R ratios of the C_{31} and C_{32} hopanes has occurred.

The triterpane distribution in the single sample from Site 477, 15-1 (120-125), (Fig. IV.6d) is similar to the pattern of sample 478-29-2 (38-43) at 2.09 m above the sill, (Fig. IV.6c) in having a full series (C_{27} - C_{35}) of hopanes with the 17 α (H),21 β (H) configuration dominant. The sample from Site 477, though has more mature S/R ratios for the C31 and C32 hopanes, 1.38 and 1.08, respectively.



Figure IV.6. HRGC-MS mass fragmentograms of m/z 191 (characteristic triterpane fingerprint) for Sites 478 and 477 samples: (a) 478-29-1 (60-65); (b) 478-29-2 (38-43); (c) 478-29-2 (112-117); (d) 477-15-1 (120-125). Numbers refer to carbon skeleton size while suffixes are their configuration: $\alpha = 17\alpha(H), 21\beta(H)$ - and $\beta = 17\beta(H), 21\beta(H)$ - and $\beta \alpha = 17\beta(H), 21\alpha(H)$ -hopane series; * = suspected gammacerane; $\Delta 17, 21(30) =$ hop-17,21-ene; $\Delta 13, 18(i30) =$ isohop-12(18)-ene. Site 478 sample locations relative to sill given in meters above sill (mas). Site 477 sample depth given in meters below seafloor (mbsf).

The changes in hopane configuration and stereochemistry near the sill are consistent with previously published data for intrusions in Guaymas Basin sediments (Simoneit and Philp, 1982; Simoneit *et al.*, 1984) and at other locations (Simoneit *et al.*, 1981; Gilbert *et al.*, 1985).

The mass fragmentograms of m/z 217, characteristic fingerprint of steranes, are presented in Fig. IV.7 for the same four samples. The dominant homologs in the three samples near the sill at Site 478 (Fig. IV.7a-c) are the $5\alpha(H)$,14 $\alpha(H)$,17 $\alpha(H)$ -(20R)- C_{27} to C_{29} steranes with lower concentrations of the less thermally stable $5\beta(H)$ configuration (Philp, 1985). Trace amounts of the 5 β - and 5α - C_{26} steranes are also visible in the sample farthest from the sill (see IV.7a). Neither steradienes nor sterenes were detectable in any of the samples. An increase in the relative amount of the 20S epimer of the $5\alpha(H)$ -series in the two samples nearest the sill (cf. Fig. IV.7a with IV.7b,c) results from the epimerization at C-20 associated with thermal maturation (Seifert and Moldowan, 1978; Mackenzie *et al.*, 1980). In addition, the relative increase in the diasteranes of sample 29-2 (112-117), next to the sill (Fig. IV.7c), is also a consequence of thermal maturation. The changes in sterane composition for the samples from Site 478 (Fig. IV.7a-c) result from the sill-induced maturation and are consistent with the transformations evident in the hopane series (see Fig. IV.6a-c).

The sterane distribution in sample 477-15-1 (120-125) (Fig. IV.7d) exhibits the greatest degree of thermal alteration of the samples presented. The S/R ratio at C-20 of the $5\alpha(H)$, $14\alpha(H)$, $17\alpha(H)$ -C₂₉ sterane is 0.52, which is significantly higher than the ratio of 0.20 for the sample nearest the sill at Site 478 but still less than the equilibrium value of 1.174 (Petrov, 1976; van Graas *et al.*, 1982). In the Site 477 sample (Fig. IV.7d), the thermal maturation has resulted in an increase in the relative abundance of the diasteranes and additional isomerization of the steranes to the more thermodynamically stable $14\beta(H)$, $17\beta(H)$ configuration.

The hopane and sterane distributions in these four samples compare well with the biomarker distributions in the seabed hydrothermal oils in the Southern Trough of Guaymas Basin (see Figs. II.4 and II.5). The ratios of the sterane and hopane diastereomeric pairs for the seabed oils and subsurface sediments with further discussion are presented in the companion paper (Chapter V).



Figure IV.7. HRGC-MS mass fragmentograms of m/z 217 (characteristic sterane fingerprint) for Sites 478 and 477 samples: (a) 478-29-1 (60-65); (b) 478-29-2 (38-43); (c) 478-29-2 (112-117); (d) 477-15-1 (120-125). Numbers refer to carbon skeleton size while letters represent the structures: α or β = hydrogen configurations at C-5, C-14, C-17, respectively; R or S = epimer at C-20; D = rearranged sterane/diasterane (shaded). Site 478 sample locations relative to sill given in meters above sill (mas). Site 477 sample depth given in meters below seafloor (mbsf).

Aromatic Components

The gas chromatograms for the aromatic fractions (F2) isolated from the three Site 478 samples and the two shallowest Site 477 samples are presented in Figs. IV.8 and IV.9, respectively. Concentrations, normalized to total bitumen, of individual PAH in these subsurface sediments and concentration ranges in the seabed hydrothermal petroleums, summarized from Chapter III, are tabulated in Table IV.4. The PAH concentrations in the subsurface sediments based on both total dry sediment and C_{org} are provided in Appendix C.

Site 478

At Site 478, the dominant aromatic hydrocarbon in the sample 3.37 m above the sill, 29-1 (60-65), is perylene, which is considered to be diagenetic in source (Louda and Baker, 1984; Venkatesan and Kaplan, 1987; Venkatesan, 1988). Other compounds in lower concentrations (see Fig. IV.8a) are a series of C32-C34 benzohopanes, with structures as identified by Hussler et al. (1984); two unknowns (U1,U2), which appear to be related to each other in structure; and a third unkown compound (U3) (see Appendix B for mass spectra). The compound labeled DT_{18} in Fig. IV.8a has a mass spectrum identical to that of tetrahydroretene, but coinjection of the authentic standard by HRGC disproved that. Further evaluation of the mass spectrum and the occurrence of an apparently related compound (monoaromatic tricyclic terpane derivative; see previous results) in the aliphatic fractions of the Site 478 samples suggest that the compound is a diaromatic C₁₈ tricyclic terpane derivative (1,1,7,8-tetramethyl-1,2,3,4tetrahydrophenanthrene). This compound has also been found in Tasmanian tasmanite of Permian age and has been suggested as one of a series of possible indicators for tasmanitids (Prasinophycean algae) (Azevedo et al., 1990; Simoneit et al., 1990b). No direct source correlation of tasmanitids with the Guaymas Basin samples is hereby intended, but present day analogs of such algae might be sources of the compound. Another possibility, based on mass spectral interpretation, is that the compound in the Site 478 sample is the 8-ethyl-1,7-dimethyl-1,2,3,4-tetrahydrophenanthrene; such a compound has not been reported in the tasmanite.

The aromatic distribution in sample 29-2 (38-43) nearer the sill (see Fig. IV.8b) is somewhat different from the previous sample. Perylene is no longer apparent and is replaced by a C_{26} triaromatic steroid hydrocarbon as the predominant component. While

Figure IV.8. Gas chromatograms (HRGC) of the aromatic fractions (F2) from the Site 478 downcore sediment extracts: (a) 478-29-1 (60-65); (b) 478-29-2 (38-43); (c) 478-29-2 (112-117). IS = internal standard; DT_{18} = diaromatic C_{18} tricyclic terpane derivative (1,1,7,8-tetramethyl-1,2,3,4-tetrahydrophenanthrene; TT_{17} = triaromatic C_{17} tricyclic terpane derivative (1,2,8-trimethylphenanthrene); U1-U3 = unknown compounds (see Appendix B for mass spectra); $BH_{32-34} = C_{32}$ - through C_{34} benzohopanes; TA_{26} = triaromatic C_{26} steroid hydrocarbon; P = phenanthrene; MP = methylphenanthrenes (3-methylphenanthrene, 2-methylphenanthrene isomers, etc.); DMP = dimethylphenanthrene; TMP = trimethylphenanthrenes; Py = pyrene; MPy = methylpyrenes; BaA = benz(a)anthracene; Ch/Tr = chrysene/triphenylene; M⁺ = molecular ion (characteristic of PAH); BeP = benzo(e)pyrene; BaP = benzo(a)pyrene; BPer = benzo(ghi)perylene. Sample locations relative to sill given in meters above sill (mas).



RETENTION TIME

Figure IV.8.

the diaromatic C_{18} tricyclic terpane derivative is still present, an additional compound, a trimethylphenanthrene isomer (TT_{17} in Fig. IV.8b) appears. Mass spectral interpretation and confirmation by coinjection of the authentic standard indicate that the compound is 1,2,8-trimethylphenanthrene and, possibly, a product of the complete aromatization of the diaromatic C_{18} tricyclic hydrocarbon. Perylene is thought to be unstable at elevated temperatures (Louda and Baker, 1984), and its apparent loss near the sill is consistent with the increased thermal stress as reflected by the maturation of the aliphatic components (e.g. biomarkers). This assumes, however, that the source of perylene was constant between the two intervals. A 10-fold decrease in perylene concentration, based on bitumen content (see Table IV.4) and similar, but not as large, decreases on both a sediment and an C_{org} basis (see Appendix C) supports the hypothesis of sill-induced thermal degradation of the perylene.

The aromatic fraction (F2) of the sample nearest the sill, 29-2 (112-117), is strikingly different from the samples more distant (cf. Fig. IV.8a,b and IV.8c) in that it contains abundant amounts of phenanthrene and its alkylated homologs, pyrene, chrysene/triphenylene, benzopyrenes, and benzo(ghi)perylene. This aromatic pattern is very similar to the total HRGC-resolvable fraction patterns of samples 16-4 (130-135) and 17-1 (145-150) in Hole 477 (cf. Figs. IV.8c with IV.3d,e). The individual PAH concentrations, based on bitumen, and exclusive of perylene, increase to levels between 13 and 4600 times higher than those in the sample 2.09 m above the sill (see Table IV.4 and following discussion). Such enrichments of pyrolytic PAH near sills were also suggested by data on intruded Cretaceous black shales (Simoneit *et al.*, 1981).

Site 477

The aromatic fractions (F2) from the two shallowest samples, 15-1 (120-125) and 16-2 (145-150), in Hole 477 are comparable and contain abundant PAH, including phenanthrene and its alkylated homologs, pyrene, chrysene/triphenylene, and benzo(ghi)perylene (see Fig. IV.9). Slight compositional differences between the two are also evident in the relative proportions of phenanthrene and the methylphenanthrene isomers (cf. Fig. IV. 9a,b), which are consistent with increased thermal maturation versus depth (see later discussion). Comparable decreases in the degree of pyrene and chrysene/triphenylene alkylation (m/z 216 and m/z 242 interpreted methyl homologs of the two, respectively) are also evident. The overall patterns are similar to the aromatic fraction of the sample nearest the sill at Site 478 (cf. Figs. IV.9a,b with IV.8c) and the



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Figure IV.9. Gas chromatograms (HRGC) of the aromatic fractions (F2) from the Site 477 downcore sediment extracts: (a) 477-15-1 (120-125); (b) 477-16-2 (145-150). Key as in Fig. IV.8 with TeMN = tetramethylnaphthalene (isomer unknown); numbers 35-37 refer to *n*-alkanes (bleed-over from F1 during adsorption column chromatography). Depths of samples given in meters below seafloor (mbsf).

HRGC-resolvable fractions of the total bitumens from the two deeper samples at Site 477 (cf. Figs. IV.9a,b with IV.3d,e). Although the compositions are similar, it must be remembered that the aromatic fraction (F2) patterns in Fig. IV.9 are for samples in which the *n*-alkanes actually dominate the HRGC-resolvable fractions of the bitumens (see Fig. IV.3a,c), while the similar PAH distributions in samples 477-16-4 (135-140) and 17-1 (145-150) are already apparent in the HRGC-resolvable fraction of the total extracts (see Fig. IV.3d,e). Apparently, the aliphatic components of the latter set have been extensively removed by transport and/or degraded by the higher temperatures encountered at greater depths.

PAH Concentrations in Downcore Sediments

The lowest individual PAH concentrations (bitumen-based) in the downcore sediments, exclusive of perylene, are found at Site 478 in the two intervals farthest from the sill, 29-1 (60-65) and 29-2 (38-43), (see Table IV.4). Perylene is highest in the former where it represents 86% of the PAH and rapidly decreases as the sill is approached. The other PAH are all at levels ≤ 6.2 ng/g-bitumen in these two samples, except for benzo(ghi)perylene, and probably represent background levels and/or crosscontamination between samples. The relatively high values, 24 and 12 ng/g-bitumen, for benzo(ghi)perylene in the two samples, 29-1 (60-65) and 29-2 (38-43) are more difficult to explain; and they suggest that the compound may have a structurally similar biological precursor that can be easily transformed to the PAH during diagenesis. The bitumen of sample 29-2 (112-117), nearest the sill, is highly enriched in PAH relative to the bitumens of the samples farther from the sill (see Table IV.4). The highest enrichments are for the lower molecular weight components (e.g. phenanthrene increases 3300- and 4600-fold); while the lowest 13-fold enrichment is exhibited by coronene. The three dominant parent PAH in the bitumen of 29-2 (112-117) are phenanthrene, pyrene, and chrysene/triphenylene (unresolvable by HRGC or HRGC-MS) (see Table IV.4).

The bitumen-based concentrations of PAH in the six samples from Site 477 increase consistently with depth. The highest concentrations of PAH, inclusive of Site 478, are found in sample 19-1 (130-140 comb) at ~145 mbsf. The three dominant PAH in this interval are dibenzothiophene, phenanthrene, and chrysene/triphenylene at 31, 77 and 10 μ g/g-bitumen, respectively. These concentrations represent 910-, 290-, and 17-fold enrichments, respectively, above the levels at ~118 mbsf, sample 15-1 (120-125).

	Downcore Sediments [§]											
	478-29-1	478-29-2	478-29-2	477-15-1	477-16-2	477-16-4	477-17-1	477-19-1*	Guaymas Basin [†]			
0	(60-65)	(38-43)	(112-117)	(120-125)	(145-150)	(130-135)	(145-150) 126 mbsf	(130-140 comb.)	Seabed Petroleums			
Compound	5.57 mas	2.09 mas	1.55 mas	107 mosi		121 111051	120 11051	145 111081	Kange		erage	<u>= = =</u>
Dibenzothiophene	0.23	0.34	310	34	62	4600	8600	31000	9.7 - 1200	180	±	300
Phenanthrene	0.80	0.57	2600	270	590	16000	31000	77000	7.4 - 510	170	±	150
Anthracene	0.15	n.d.	230	7.1	n.d.	n.d.	n.d.	n.d.	3.7 - 110	28	±	30
Fluoranthene	1.4	1.1	520	110	110	1800	2500	3200	17 - 190	74	±	46
Pyrene	3.1	3.3	1 500	280	290	3900	4800	4000	91 - 1400	410	±	330
Benz(a)anthracene	1.6	2.3	920	80	28		-	1200	9.2 - 230	74	±	58
Chrysene/Triphenylene	2.0	6.2	1600	550	790	9800	1 5000	10000	53 - 470	170	±	120
Benzofluoranthenes	3.5	1.5	310	200	360	3100	4800	4500	45 - 710	210	±	180
Benzo(e)pyrene	3.4	4.1	300	240	450	3300	4700	2500	68 - 740	250	±	200
Benzo(a)pyrene	2.5	1.8	130	24	n.d.	n.d.	n.d.	n.d.	31 - 250	130	±	86
Perylene	274	26	18	38	n.d.	n.d.	n.d.	n.d.	19 - 600	150	±	190
Indeno(cd)pyrene	2.6	n.d.	43	17	35	240	470	650	6.8 - 390	92	±	100
Benzo(ghi)perylene	24	12	180	110	280	1400	1800	880	69 - 2200	480	±	550
Anthanthrene	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.77 - 75	21	±	21
Dibenz(ah)anthracene	0.21	0.29	73	19	40	530	770	800	1.7 - 73	33	±	21
Coronene	2.2	1.4	28	23	74	260	400	500	6 - 1200	240	±	290
Dibenzo(ae)pyrene	1.1	0.49	47	21	110	420	620	650	1.6 - 190	57	Ŧ	49
Total PAH µg/mg-bitumen	0.32	0.061	8.8	2.0	3.2	45	75	140	0.97 - 6.3	2.7	'±	1.8

Table IV.4. Comparison of selected PAH concentrations (ng/mg-bitumen) in Guaymas Basin downcore sediments (Sites 477, 478) and in seabed oils.

n.d. = not detected

- = not detected
- = not resolved from Chrysene/Triphenylene by HRGC-MS.
* 477-19-1 (130-135) and 477-19-1 (135-140) combined before analysis by HRGC-MS.

[†] Summary of data from Chapter III (Kawka and Simoneit, 1990).

* Average of 14 seabed oils, except for anthanthrene where n = 13.

For Site 478, sample locations given as meters above sill (mas). For Site 477, sample depths given as meters below seafloor (mbsf).

Of the samples in Hole 477, the largest downcore change in PAH concentrations occurs between samples 16-2 (145-150) and 16-4 (130-135). These intervals are also characterized by a transition from *n*-alkane-dominated to PAH-dominated patterns in the HRGC-resolvable fractions of the bitumens (cf. Fig. IV.3c,d). Relative to the sample most distant from the sill at Site 478, the bitumen-based concentrations of the individual PAH (exclusive of perylene) in the deepest sample at Site 477, 19-1 (130-140 comb) are between 37 and 9600 times higher (see Table IV.4). The highest relative enrichment is for phenanthrene, while the lowest is exhibited by benzo(ghi)perylene. Perylene is present at 38 ng/mg-bitumen in the shallowest sample from Hole 477 and not detectable at greater depths (see Table IV.4), attesting to the suggested instability of the compound at elevated temperatures (Louda and Baker, 1984).

An interesting result of the PAH concentrations is the internal consistency between the samples from the two Sites 477 and 478. The sample nearest the sill, 478-29-2 (112-117) contains PAH concentrations (bitumen-based) intermediate between those of 477-16-2 (145-150) and 477-16-4 (130-135), (see Table IV.4). The character of the HRGC-resolvable bitumen fraction of this sample near the sill is dominated by *n*alkanes, but with a visible PAH component (see Fig. IV.4c and previous discussion). In character, it is intermediate between the pure *n*-alkane dominated sample 16-2 (145-150) and the PAH-dominated sample 16-4 (130-135) (cf. Figs. IV.4c with IV.3c,d); which is consistent with the intermediate character of its PAH concentrations.

The sums of the selected PAH concentrations range from a low of 0.061 μ g/mgbitumen in 478 29-2 (38-43) to a high of 140 μ g/mg-bitumen in the deepest sample from Site 477, 19-1 (130-140); the latter concentration representing 14% of the bitumen. The total PAH concentrations in the three deepest samples from Hole 477 are between 5 and 16 times higher than the sample nearest the sill at Site 478, even though the latter is ~110 to 130 m deeper. As previously discussed, Site 477 has a significantly higher overall geothermal gradient than Site 478. The PAH data supports the hypothesis that Site 477 sediments are more thermally altered than those at Site 478 because of the continuity of the hydrothermal system and the close proximity of the heat source at the former location, as discussed by Kastner (1982). The pyrolysis of the sediments at Site 478 is limited to sill-induced alteration and cannot be as extensive due to the short-lived nature of the associated hydrothermal process and the overall lower heat flow at the site.

Comparison with Seabed Oils

The gas chromatograms of the aromatic fractions (F2) of a selection of the seabed hydrothermal oils, initially described in Chapters II and III are presented in Fig. IV.10 for comparison with the downcore distributions of sediment bitumens. Hydrothermal oil 1172-4 is the most aliphatic-rich sample analyzed in the previous studies (see Fig. II.3). The aromatic fraction of 1172-4 is characterized by a broadly skewed hump which maximizes near the HRGC elution times of the benzopyrenes (see Fig. IV.10a). Various PAH are clearly visible on this hump and include phenanthrene, alkylphenanthrenes, pyrene, and benzo(ghi)perylene. The other PAH previously discussed in the downcore sediments are not easily resolvable from the multitude of coeluting peaks characterizing the broad hump in 1172-4, F2 (see Fig. IV. 10a). The most prominent compound in this sample is Diels' hydrocarbon (DHC in Fig. IV.10c), 1,2-(3'-methylcyclopenteno)phenanthrene, which is discussed in Chapter V.

The aromatic character of 1172-4 is very different from the PAH distributions in the downcore sediments at Site 477 (cf. Figs. IV.10a with IV.9 and IV.3d-f) in that it contains the broad hump which is not found in the latter distributions. This broad hump, maximizing in the high molecular weight range, appears to be more characteristic of the less thermally altered aromatic distributions distant from the sill at Site 478 (cf. Figs. IV.10a with IV.8a,b). If the latter are representative of the aromatic character of the more indigenous (non-thermally- or less-altered) bitumen at the seabed, the aromatic distribution of 1172-4 (Fig. IV.10a) could result from an admixture of a pyrolysate (e.g. 477-15-1 (120-125), see Fig. IV.9a) with an immature seabed bitumen (e.g. 478-29-1 (60-65), see Fig. IV.8a).

The second example for comparison is the hydrothermal oil 1177-4B which was reported as containing the highest concentration of unsubstituted (parent) PAH, representative of high temperatures of pyrolysis (see Chapter II). The aromatic distribution of 1177-4B (Fig. IV.10b) is similar to that of 1172-4 in containing an identical broad hump maximizing at high molecular weight. It differs significantly, though, in containing a much simpler distribution of resolved components on top of the hump which are dominated by the parent PAH (cf. Figs. IV.10a,b). The alkylkated homologs of the PAH are in very low concentration and not detectable on the chromatogram.

The final example of the seabed oils is sample 1168-1-2, which contains a predominance of polar/asphaltic components in the bitumen (see Fig. II.3) and is



Figure IV.10. Representative gas chromatograms (HRGC) of the aromatic fractions of a selection of seabed hydrothermal oils from Guaymas Basin: (a) 1172-4; (b) 1177-4B; (c) 1168-1-2. Key as in Fig. IV.8 with DHC =Diels' hydrocarbon (1,2-(3'-methylcyclopenteno)phenanthrene); Cor = coronene.

virtually devoid of *n*-alkanes (see discussion Chapter II and Fig. II.2). The absence of *n*-alkanes and a low maturity of the biomarker distributions [see Fig. II.5d and Chapter V] suggest that the oil is a biodegraded condensate intermixed with bitumen indigenous to the seabed and/or of lesser maturity. The aromatic distribution of this sample (Fig. IV.10c) confirms this hypothesis. The gas chromatogram is characterized by a narrow hump maximizing at the low-molecular weight range. The resolved components are dominated by the monoaromatic and diaromatic tricyclic terpane-derived hydrocarbons; perylene; and the pyrolytic PAH such as pyrene, benzofluoranthenes, benzopyrenes and benzo(ghi)perylene (see Fig. IV.10c). The relatively high concentrations of perylene and the aromatic terpane derivatives are also characteristic of the aromatic distributions of the two *n*-alkane deficient samples 478-29-1 (60-65) and 29-2 (38-43) most distant from the sill (see Figs. IV.5a and IV.8a,b).

The predominance of the unsubstituted PAH in sample 1177-4B (interior crust of mound material) is of particular interest. An aromatic distribution with such high relative (see Fig. IV.10b) and absolute concentrations (see Chapter III) of benzo(ghi)perylene and coronene is most similar to the character of the HRGC-resolvable fractions of the bitumens from two hydrothermal chimneys, 1173-9 and 1175-7 (see Fig. IV.11). In sample 1173-9, characterized as a light green oil, the predominant compound in the total extract is benzo(ghi)pervlene at a concentration of ~48 μ g/mg-bitumen or 4.8% of the total extract (see Fig. IV.11a). This level represents a 27-fold increase over the highest concentration of the compound in the downcore samples, 1.8 µg/mg-bitumen in 477-17-1 (145-150) (see Table IV.4). Sample 1175-7 (see Fig. IV.11b) is another example of such a bitumen with a large relative enhancement of the high molecular-weight PAH. The major difference between the seabed oil 1177-4B and chimney samples 1173-9 and 1175-7 is the presence of the hump in the first sample. The PAH distributions in the two latter samples are envisioned to result from the selective condensation/solidification of the higher molecular-weight PAH from a high-temperature fluid exiting the chimneys. The parent PAH-dominant pyrolysate would then have originated at great depth and may have had a character similar to that of 477-19-1 (130-140 comb) in Table IV.4. Similarly, the oil 1177-4B could be considered to be an admixture of such a hightemperature pyrolysate with an immature, PAH-deficient, bitumen at the seabed (cf. Figs. IV.10b with IV.11).

The ranges in individual PAH concentrations (bitumen-based) in the seabed hydrothermal oils (summarized from Table III.1) are provided in Table IV.4 for comparison with the downcore samples. A high degree of variability is evident in the



Figure IV.11. Gas chromatograms (HRGC) of the total extracts of seabed hydrothermal oils from Guaymas Basin: (a) 1173-9, light green oil; (b) 1175-7 (sample described in Peter, 1990). Key as in Fig. IV.8 with IPy = indeno(cd)pyrene; Cor = coronene. Unidentified peaks in (b) are various biologically-derived components indigenous to the seabed and plasticizer contaminants from sample-handling procedures.

large ranges and high standard deviations, relative to the averages, of the PAH concentrations. Comparing the total PAH concentrations (based on summation of tabulated compounds), the average value in the seabed oils, $2.7 \pm 1.8 \,\mu$ g/mg-bitumen, is within the range exemplified by samples 477-15-1 (120-125) and 16-4 (130-135), with concentrations of 2.0 and 45 μ g/mg-bitumen of PAH, respectively. These subsurface samples, at subbottom depths between ~ 107 and 121 m, also bracket the transition between *n*-alkane-dominated and PAH-dominated bitumens (see earlier discussion).

While most of the concentrations of individual PAH in the seabed oils are within the ranges of the levels in these three subsurface sediments: 477-15-1 (120-125), 16-2 (145-150), and 16-4 (130-135), the relative concentrations (low-molecular-weight vs. high-molecular weight constituents) of the PAH are different. The PAH in the subsurface sediments tend to be enriched in the lower molecular-weight compounds when compared to the seabed oils. This is especially evident if the PAH concentrations of the three deepest samples from Site 477 are compared to the seabed oils. For example, the concentrations of benzo(ghi)perylene in core-sections 16-4 through 19-1 range from 0.88 to $1.4 \mu g/mg$ -bitumen and are comparable to the high-end of the range in the seabed oils, but are between 1.8 and 3.8 times higher than the average. On the other hand, phenanthrene ranges between 16 and 77 $\mu g/mg$ -bitumen in the subsurface bitumens, which is much higher than the range and between 94 and 450 times greater than the average in the seabed oils.

These differences in the relative distributions of the PAH between the downcore sediments and the seabed petroleums can be seen best in histograms of the bitumenbased concentrations of the two sets. Appendix D contains the complete collection of PAH concentration (bitumen-based) histograms for the seabed oils and the downcore sediments from Guaymas Basin. A representative selection of these are found in Figs. IV.12 and IV.13. The predominance of perylene in sample 478-29-1 (60-65) at 3.37 m above the sill (Fig. IV.12a) is in contrast to the broad distribution of PAH, dominated by phenanthrene, in sample 29-2 (112-117) next to the sill (Fig. IV.12b). This latter pattern can be envisioned as being intermediate, in relative composition of PAH, between that of the shallowest, 15-1 (120-125), and the deepest sample, 19-1 (130-140 comb) in Hole 477 (cf. Figs. IV.12b with c,d).

The histograms for the three examples of seabed oils in Fig. IV.13a-c are quite different from those of the downcore samples (see Fig. IV.12). While the hydrothermal oil of 1172-4 (Fig. IV.13a) contains a broader, more even distribution of PAH than the previous downcore set, the pyrolysate 1177-4B (Fig. IV.13b) is significantly enriched



Figure IV.12. Histograms of selected PAH concentrations (ng/mg-bitumen) for a representative selection of downcore sediments from Guaymas Basin: (a) 478-29-1 (60-65); (b) 478-29-2 (112-117); (c) 477-15-1 (120-125); (d) 477-19-1 (130-140 comb.). Site 478 sample locations relative to sill given in meters above sill (mas). Site 477 sample depths given in meters below seafloor (mbsf).



Figure IV.13. Histograms of selected PAH concentrations (ng/mg-bitumen) for a representative selection of seabed hydrothermal oils from Guaymas Basin: (a) 1172-4; (b) 1177-4B; (c) 1168-1-3B; and a histogram of the relative concentrations of the PAH in a hydrous pyrolysate (d) simulation 1176-PC2. Histograms for entire collection of seabed oils and downcore sediments are given in Appendix D.

in the high-molecular-weight PAH. The distribution of PAH in sample 1168-1-3B (Fig. IV.13c) is significantly different from both of the other seabed oils (Fig. IV.13a,b) and the downcore samples (Fig. IV.12). It contains high relative concentrations of perylene and pyrene, with the other PAH in lower abundance. This sample can be characterized as a biodegraded condensate [based on the absence of *n*-alkanes, high polar/asphaltic content, and dominance of the low molecular weight components (see Chapter II)] which has invaded the surface sediments where a high concentration of perylene is present, as in sample 478-29-1 (60-65) (see Fig. IV.12a). The relative distribution of PAH generated during a laboratory simulation (hydrous pyrolysis of 1176-PC2; Simoneit, 1990) is presented in Fig. IV.13c. This pyrene-dominated distribution is very similar to that of seabed oil 1168-1-3B, except for the occurrence of perylene (cf. Figs. IV.13c,d).

Tricyclic Aromatic Hydrocarbon Indices

Degree of Alkylation

The degree of alkylation of thermally generated aromatic hydrocarbons is a function of the temperatures encountered during their formation: unsubstituted (parent) PAH dominate at higher temperatures (see Chapter III and references therein). Accordingly, the degree of alkylation of the tricyclic aromatic hydrocarbons (phenanthrene+anthracene skeletons) should decrease with the increasing thermal stress induced by a sill intrusion (Site 478 sample suite) and by increases in depth or extent of hydrothermal alteration (Site 477 sample suite). The distributions of the parent and alkylated tricyclic aromatic PAH in the downcore sediments and in the laboratory simulation (1176-PC2; Simoneit, 1990) are presented in Figs. IV. 14a,b. For comparison, a summary plot of the distributions in the seabed deposits (adapted from Chapter III) is presented in Fig. IV.14c.

The degree of alkylation of the tricyclic aromatics in samples from Site 477 decreases with increasing depth, as expected (see Fig. IV.14a). In the two shallowest samples at ~107 and ~118 mbsf, 15-1 (120-125) and 16-2 (145-150), respectively, the C₃- alkylated homologs dominate (see Fig. IV.14a). In the deeper intervals at ~121 and ~126 mbsf, samples 16-4 (130-135) and 17-1 (145-150), the dominant series becomes the C₂- alkylated homologs; while in the deepest sample at ~145 mbsf, 19-1 (130-140

Figure IV.14. Comparison of the distributions of phenanthrene + anthracene (C_0) and their alkylated homologs (C_1 through C_3): (a) Site 477; (b) Site 478 and the laboratory simulation (hydrous pyrolysis of 1176-PC2) (Simoneit, 1990); and (c) summary of data for hydrothermal seabed oils from Guaymas Basin (Chapter III; Kawka and Simoneit, 1990). Relative intensities were based on summations of intensities of the molecular ion of each series (m/z 178, 192, 206, 220) obtained by HRGC-MS, uncorrected for response. Site 478 sample locations relative to sill given in meters above sill (mas). Site 477 sample depths given in meters below seafloor (mbsf).





comb), only the unsubstituted (phenanthrene+anthracene) compounds remain at a significant level (see Fig. IV.14a).

The degree of alkylation plots for the samples near the sill at Site 478 (Fig. IV.14b) do not exhibit the same general trend as those from Site 477. The sample nearest the sill 29-2 (112-117) attains a level of "dealkylation" that is between that of the two shallowest samples and that of the two intermediate depth samples in Hole 477 (cf. Figs. IV.14a,b). This is consistent with all the previously discussed aliphatic and aromatic parameters, which indicated that the sample nearest the sill exhibited a character representative of a transition between the aliphatic-rich bitumen of 477-16-2 (145-150) and the aromatic-rich bitumen of 16-4 (130-135). On the other hand, the alkylation patterns of the two samples farthest from the sill at Site 478, 29-1 (60-65) and 29-2 (38-43), are the reverse of the expected order, with the latter indicating a higher degree of alkylation (see Fig. IV.14b). This apparent discrepancy may not be significant since the concentrations of phenanthrene and, consequently, the alkylated homologs are very low (see Table IV.4) and probably only represent background levels (see previous discussion). The degree of alkylation plot of the laboratory simulation at 330°C (1176-PC2) is comparable to those of the two shallowest samples at Site 477. Similarly, the simulation product also contained a broad distribution of *n*-alkanes (Simoneit, 1990), which is characteristic of the two Site 477 samples (cf. Figs. IV. 14a,b).

Comparison of the downcore alkylation patterns (Fig. IV.14a,b) with the pattern ranges in the hydrothermal seabed oils (Fig. IV.14c) reveals that the degree of tricyclic aromatic alkylation in many of the oils is comparable to the shallower samples from Site 477. The tricyclic aromatic homolog distribution in sample 1177-4B, which has the unusual predominance of the parent PAH, is most comparable to the pattern exhibited by the deepest sample from Site 477 (cf. Figs. IV.14a,c). This corroborates the previous evidence (see earlier discussion) which suggested that the aromatic content of oil 1177-4B was effected by an input of a high-temperature pyrolysate from greater depth which underwent selective condensation/solidification of the high-molecular-weight components. The tricyclic aromatic distributions in the two samples farthest from the sill at Site 478 bracket the range in patterns for the biodegraded (based on interpretations in Chapters II, III) seabed oils (cf. Figs. IV.14b,c). The concentrations of the pyrolytic PAH in these "biodegraded" seabed oils, though, far exceed the background levels in the Site 478 samples (cf. Tables III.1 and IV.4). This suggests that the tricyclic aromatic alkylation patterns alone cannot distinguish between immature bitumens and biodegraded or weathered oils.

Phenanthrene-methylphenanthrene Indices

Various ratios of the phenanthrene and methylphenanthrene isomers have been formulated as thermal maturation indices for bitumens in petroleum source rocks and coals (Radke et al., 1982a,b, 1986; Radke and Welte, 1983; Garrigues *et al.*, 1988). Some of these ratios for the downcore sediments at Sites 477, 478 and seabed petroleums of Guaymas Basin and in a pyrolysate generated during a laboratory simulation (1176-PC2; Simoneit, 1990) are summarized in Table IV.5.

Under normal maturation conditions in sedimentary basins (non-hydrothermal), the MP/P ratio increases with depth (temperature); which has been interpreted as indicating increased incidence of phenanthrene methylation (Radke *et al.*, 1982a). The range for the ratio in Western Canada Basin rock samples, containing Type III or terrestrial organic matter, has been reported as ~1 to 3.2 (Radke *et al.*, 1982a). The maximal value of the ratio coincided with the peak of the oil generation curve, based on hydrocarbon yields (Radke et al., 1982a), and near it, based on the vitrinite reflectance (R_0) of 0.77% reported by Radke *et al.* (1982) (% R_0 = 0.9 at peak in oil generation curve, Type III kerogen; Tissot and Welte, 1984). A decrease with depth following the peak in the ratio was interpreted as resulting from increased demethylation (Radke *et al.*, 1982a). In relatively immature Mahakam Delta coals from the Handil field, Garrigues *et al.* (1988) reported MP/P ratios of 0.9 to 2.6, with the maximum corresponding to a R_0 of 0.64%, at the approximate boundary between the immature stage and incipient oil generation for Type III kerogen (Tissot and Welte, 1984).

The methylphenanthrene isomer distributions also exhibit changes during thermal maturation, with the 3-methyl- and 2-methylphenanthrenes (3MP, 2MP, respectively) increasing relative to 9-methyl- and 1-methylphenathrenes (9MP, 1MP, respectively). This change has been attributed to a methyl shift (isomerization) of the 9MP, 1MP to the more thermodynamically stable 3MP, 2MP isomers (Radke *et al.*, 1982a; Garrigues *et al.*, 1988 and references therein). The MPI₁ as originally defined by Radke *et al.* (1982a, 1983) incorporates the changes in both the relative distribution of these methylphenanthrene isomers and the degree of phenanthrene methylation (see Table IV.5 footnotes). The MPI₃ as originally defined by Garrigues *et al.* (1988), on the other hand, monitors only the relative changes in the MP isomers (see Table IV.5 footnotes). For the Western Canada Basin rock samples, the MPI₁ increased with depth (maturation) from 0.58 to 1.57 (R_0 =1.3% at maximum), after which the index decreased

0 1		Phenanthrene a	nd Methylphena	nthrene Ratios*
Sample		MP/P	MPI ₁	MP13
Downcore				
478-29-1 (60-65)	3.37 mas	6.55	0.85	0.72
29-2 (38-43)	2.09 mas	3.73	0.92	0.93
29-2 (112-117)	1.35 mas	2.51	1.52	2.37
477-15-1 (120-125)	107 mbsf	5.18	0.80	0.71
16-2 (145-150)	118 mbsf	3.25	1.36	1.64
16-4 (130-135)	121 mbsf	1.98	1.25	2.17
17-1 (145-150)	126 mbsf	1.34	1.07	2.67
19-1 (130-140 con	1b.) 145 mbsf	0.06	0.06	2.04
Lab Simulation [§]		1.42	0.80	1.44
Seabed Oils				
1172-4		1.67	0.90	1.50
1172-1A		1.96	0.94	1.40
1177-2D**		1.24±0.08	0.78±0.00	1.65 ± 0.12
1172-2		2.10	1.01	1.46
1172-3**		1.82±0.11	0.84±0.05	1.25 ± 0.04
1173-8		1.15	0.68	1.40
1177-2C		1.12	0.72	1.59
1177-4B		0.20	0.23	3.80
1172-1		2.58	0.97	1.20
7D-5A		70.58	0.40	0.27
7D-3B		8.55	0.58	0.45
1173-3		1.04	0.61	1.30
1168-1-2§		1.5±0.04	0.45 ± 0.08	0.61 ± 0.13
1168-1-3B		8.55	0.54	0.42

Table IV.5. Phenanthrene and methylphenanthrene ratios as thermal maturity indicators for downcore sediments (Sites 477 and 478), Guaymas Basin seabed petroleums and a laboratory simulation.

*Ratios, as defined by Radke et al. $(1982a)^{\dagger}$ and Garrigues et al. $(1988)^{\ddagger}$, calculated using integrated areas of characteristic mass fragments (m/z 178, 192) uncorrected for response on HRGC-MS.

where

3MP refers to 3-methylphenanthrene

P refers to phenanthrene

2MP refers to 2-methylphenanthrene, etc.

<u>MP†</u>	_	<u>3MP+2MP+9MP+1MP</u>	
Р	=	Р	

 $MPI_1^{\dagger} = \frac{1.5(3MP+2MP)}{P+1MP+9MP}$

$MPI_3^{\ddagger} = \frac{3MP + 2MP}{1MP + 9MP}$

Note: 4MP is not resolved from 9MP by HRGC or HRGC-MS and is therefore integrated as part of 9MP in all parameters. Garrigues *et al.* (1988) isolated and quantitated 4MP separately using Schpolskii-fluorescence spectroscopy; and MPI₃, as originally defined, includes 4MP in the denominator

[§]Hydrous pyrolysis simulation of 1176-PC2 (Simoneit, 1990).

******Repetitive analysis (n = 2) by HRGC-MS.

(Radke *et al.*, 1982a). For the coal samples from the Mahakam Delta, Garrigues *et al.* (1988) reported MPI₁ and MPI₃ values ranging from 0.29 to 0.78 and 0.73 to 0.76, respectively.

In the downcore sediments from Site 478, the MP/P ratio decreases from 6.55 for the sample farthest from the sill, 29-1 (60-65), to 2.51 for the sample nearest the sill, 29-2 (112-117) (see Table IV.5). The sediments in Hole 477 also exhibit a consistent decrease in the ratio with depth (maturation), from a maximum of 5.18 for sample 15-1 (120-125) to 0.06 for sample 19-1 (130-140 comb.) (see Table IV.5). These decreases in the ratio indicate that the thermal maturation has reached a stage beyond that of the oil generation window. The relatively high initial MP/P ratios of 6.55 and 5.18 in samples 478-29-1 (60-65) and 477-15-1 (120-125), respectively, compared to the maximum values for the Western Canada Basin (see above), could be a result of the relatively high-temperatures of maturation in a hydrothermal system. On the other hand, source-dependent variation in the indices, as suggested by Radke *et al.* (1986), may be important, as the organic matter in the Guaymas Basin sediments is of both marine and terrestrial origin (Types II and III kerogen) (Simoneit *et al.*, 1982)) while the Western Canada Basin sediments contain primarily terrestrial (Type III kerogen) organic matter (Radke *et al.*, 1982a).

The MPI₁ does not change consistently with depth or proximity to the sill in the downcore sediments at Sites 477 and 478 of Guaymas Basin. The ratio increases approaching the sill at Site 478 and first passes through a maximum before decreasing with depth in Hole 477 (Table IV.5). On the other hand, the MPI₃ consistently increases with depth or maturation (proximity to the sill), except for the deepest sample of Hole 477 in which the value decreases slightly (Table IV.5). Apparently, MPI₁ is not very useful at these high levels of maturation in high-temperature hydrothermal systems, while the utility of MPI3 continues well past the oil-generation window. This discrepancy between the two very similar indices (see Table IV.5 footnote) is a direct result of the increased demethylation of alkylphenanthrenes at high temperatures, as indicated by MP/P ratio and suggested in Chapter III (and references therein). This dealkylation leads to an increase in the proportion of phenanthrene and affects the denominator in MPI₁ but not that in MPI₃ (see Table IV.5 footnotes). The slight decrease in MPI₃ in the deepest Hole 477 sample is not significant since the MP/P ratio can be easily used to identify such instances (see Table IV.5). Overall, the indices provided by MP/P and MPI₃ appear to be the most useful for monitoring the thermal alteration in such a hydrothermal system.

The values for the three indices in the simulation of hydrothermal alteration (1176-PC2 at 330°C; Simoneit, 1990) are within the ranges for the hydrothermally altered subsurface sediments in Guaymas Basin.

The MP/P ratios in the Guaymas Basin seabed oils range between 0.20 and 2.58, with the exception of three samples: 7D-5A, 7D-3B, and 1168-1-3B with values of 70.58, 8.55, and 8.55, respectively (Table IV.5). The exceptionally high values result from selective removal of phenanthrene by water-washing/biodegradation, as discussed in Chapter III (and references therein), since these oils exhibit characteristics consistent with extensive biodegradation (see Chapter II). The MP/P values for the bulk of the seabed oils fall within the range of the downcore sediments. The MPI₃ values in the seabed oils range from 0.42 to 3.80 and are, for the most part, within the range of the downcore sediments (Table IV.5). The highest value of 3.80 is found in oil 1177-4B and is higher than the maximum (2.67) in the next to deepest sample of Hole 477. Accordingly, the oil 1177-4B has the lowest MP/P ratio (0.20) of the seabed oils, which falls between the values (1.34 and 0.06) for the two deepest samples from Hole 477. As previously discussed, sample 1177-4B has the highest concentration of unsubstituted PAH of all the seabed oils (Chapter III); and the values of the two indices are consistent with the interpretation that 1177-4B is a condensate/precipitate of a high-temperature pyrolysate from deeper in the subsurface sediments.

DISCUSSION

General Trends and Maturation Levels

Site 477

In the downcore sediments at Site 477, the transition with increasing depth from the *n*-alkane-dominant to the PAH-dominant character of the HRGC-resolvable bitumen (Fig. IV.3) is coincident with the following: (1) an overall decrease in C_{org} (1.06 to 0.31%). (2) a 200-fold decrease in bitumen yield on a dry sediment basis and a 50-fold decrease on an organic carbon basis (Table IV.3), (3) a rapid loss of steranes and hopanes (see Results section), (4) a decrease in the degree of alkylation for the tricyclic aromatic hydrocarbons (Fig IV.14a), and (5) a progressive maturation of the phenanthrene-methylphenanthrene indices past the "oil window" (Table IV.5 and Results section). The qualitatively described increase in aromatic character with depth is confirmed by a consistent increase in almost all of the individual, bitumen-based PAH concentrations (Table IV.4). The totals of the tabulated PAH also become a larger proportion of the extractable organic matter as depth increases, with values increasing from 0.20% to 14% of the bitumen. The aforementioned trends are indicative of high pyrolytic temperatures and increasing levels of thermal maturation and fluid expulsion with depth.

The Site 477 samples can be divided into 4 general levels of thermal maturation based on the character of the bitumen and distributions of the PAH. The first stage, as exemplified by 477-15-1 (120-125), is characterized by the dominance, in the HRGC-resolvable portion of the bitumen, of a mixture of the isoprenoids pristane and phytane, particularly the latter, and *n*-alkanes (Fig. IV.3a) and the presence of steranes and hopanes in their thermally mature configurations (Figs. IV.6d and 7d). The two samples from core-section 477-16-2 represent a second stage in which the increase in the overall saturate character of the bitumen (Table IV.3) is concomitant with an increase in the amount of *n*-alkanes relative to the isoprenoids (Fig. IV.3b,c), and a disappearance of the steranes and hopanes (see Results section). A difference between the two stages is also evident in the absolute PAH concentrations, although the aromatic fraction changes very little in relative composition (cf. Fig. IV.9a,b). All of the PAH concentrations (normalized to bitumen) in the second stage either increase or remain constant relative to the first stage (Table IV.4). A slight decrease in the degree of

alkylation (see Fig. IV.14a) and significant changes in the phenanthrenemethylphenanthrene indices, consistent with higher levels of maturation (Table IV.5 and Results section), also characterize the transition between the first and second stages of maturation in this hydrothermal system. In both stages one and two, the dimethylphenanthrenes are the dominant series of tricyclic aromatic homologs.

The third stage is characterized by a disappearance of *n*-alkanes and the first instance of a dominance of the aromatic hydrocarbons in the HRGC-resolvable fraction of the bitumen. The samples from core-sections 477-16-4 and 477-17-1 are exemplary of this level of maturation (Fig. IV.3d,e). The PAH concentrations in these two samples increase, by an order of magnitude, above those of the previous stage (Table IV.4); and the methylphenanthrenes become the dominant tricyclic aromatic homolog (Fig. IV.14a). The phenanthrene-methylphenanthrene indices change in a manner consistent with increased levels of maturation. Increased thermal alteration is also evident between the two samples exemplary of this stage. The PAH concentrations and the degree of phenanthrene "dealkylation" in the two samples, 477-16-4 and 477-17-1, increase with depth (Tables IV.4 and 5).

The final stage is exemplified by samples 477-19-1 (130-135) and (135-140) in which the dominant component is phenanthrene (Fig. IV.3e), exclusive of a shipboard contaminant (see Results section). In the composite of these two samples, the concentrations of most of the PAH either stay the same or decrease slightly, relative to the samples of the previous stage, except for dibenzothiophene and phenanthrene. These two compounds increase in concentration 3.6 and 2.5-fold, respectively (Table IV.4). The degree of alkylation plot for this sample and stage is highly skewed towards the unalkylated compounds (phenanthrene+anthracene) and is very unlike the others (see Fig. IV.14a). Consequently, this highest stage of maturation is also reflected in this sample exhibiting the lowest MP/P and MPI₁ ratios (Table IV.5). The slight reversal in the MPI₃ index suggests its utility may be diminished at the highest levels of maturation when phenanthrene becomes the dominant compound in the HRGC-resolvable fraction of the bitumen. At this stage, dibenzothiophene and phenanthrene account for 11% of the total bitumen, compared with 4.0% in the previous stage.

Site 478

The assignment of thermal maturation levels to the three Site 478 samples near the sill is more difficult than for Site 477. The thermal alteration of the sample nearest the

sill, 478-29-2 (112-117), is easily recognized by the dominance therein of the low molecular weight *n*-alkanes (cf. Fig. IV.4c with 4a,b) and an aromatic distribution similar to the highly altered sections of Site 477 (cf. Fig. IV.8c with 3d,e). The aromatic character of this sample is significantly different from the samples farther away from the sill (cf. Fig. IV.8c with 8a,b). On the other hand, the two samples more distant from the sill, 478-29-1 (60-65) and 29-2 (38-43), are very comparable (Figs. IV.5a,b and 8a,b); and thermal maturation is recognized primarily by the increased sterane and hopane isomerizations found in the latter sediment (Figs. IV.6a,b and 7a,b). The absence of *n*-alkanes in these two samples, though, is difficult to account for given the difference in maturation of the biomarkers and the basic premise of alkane generation with increasing thermal maturation (Tissot and Welte, 1984).

Two processes could be responsible for the unusual aliphatic distribution of the Site 478 samples. Microbial degradation has been shown to preferentially remove the nalkanes from crude oils in both reservoirs and laboratory simulations (Bailey et al., 1973; Connan, 1984) and may have thus effected the observed character of the Site 478 samples. The absence of *n*-alkanes in some of the exposed deposits of hydrothermal oils at the Guaymas Basin seabed has been previously attributed to such a degradative process (see Chapter II). Similarly, Bazylinski et al. (1988) invoked microbial processes to account for the observed absence of *n*-alkanes and aliphatic components in cored surface sediments $(\leq 20 \text{ cm below seabed})$ of a Guaymas Basin hydrothermal area. In a characterization of several oils and source rocks from the Monterey Formation, California, Curiale et al. (1985) identified two source rock bitumens (Midway-Sunset Field, San Joaquin Basin), which were interpreted to be biodegraded, based on absence of *n*-alkanes and the presence of the 25-norhopane series (often observed in biodegraded reservoir oils). A predominance of pristane, phytane, and the sterane/hopane biomarkers in the aliphatic fraction of one of these source rocks is strikingly similar to the two Site 478 samples farthest from the sill, 29-1 (60-65) and 29-2 (38-43), (see Fig. IV.5a,b). Similarly, Tannenbaum et al. (1986a) described an organic-rich (18.2% total organic matter, TOM) Monterey Formation diatomite which consisted of an unusual abundance of bitumen (94% of TOM) and contained an aliphatic composition consisting only of the acyclic isoprenoids and the sterane and hopane biomarkers, with negligible amounts of *n*-alkanes. Tannenbaum et al. (1986a) attributed the very high bitumen content and unusual aliphatic character of this diatomite as arising from a migration of a deeper-sourced bitumen, with subsequent biodegradation, although an early release from an immature kerogen during diagenesis was also suggested. Biodegradation of the nalkanes is, therefore, one possible explanation of the n-alkane deficiency of the Site 478 samples next to the sill.

On the other hand, the prevalent association of the *n*-alkane deficient bitumens with diatomites or diatom-rich sediments, in the previous examples, suggests that the cause might actually be source-related. Accordingly, a second possible explanation is that the source matter of the samples at Site 478 is unique and that the *n*-alkane deficiency originates in the sedimented organic matter and continues through the initial stages of thermal maturation. Curiale *et al.* (1985) similarly suggested that the character of the San Joaquin extracts (see above) might actually be due to a change in source material rather than microbial degradation.

Rullkötter et al. (1982) described a single diatom-rich sample from Site 478 and a number of such samples from Site 479, on the Guaymas Basin slope, as being relatively deficient in n-alkanes. Algal liptinites (kerogen macerals derived from algae, usually lipid-rich) were consistently dominant in these samples (Rullkötter et al., 1982), which alludes to a commonality of source and/or controlling processes for these samples. The aliphatic character of the single sample 478-28-4 (120-140) at 248.3 mbsf, described by Rullkötter et al. (1982), contains very low n-alkanes and a predominance of the biomarkers and is very similar to the compositions of samples 478-29-1 (60-65) and 478-29-2 (38-43) analyzed and discussed herein. Unlike these two samples at 251.13 and 252.41 mbsf, respectively, the sample described by Rullkötter et al. (1982) contains a predominance of the unsaturated analogs of the steranes and hopanes and, consequently, appears very immature. Such a character has also been observed by Sturz et al. (1990) for some sediment intervals obtained from an 8 m piston core taken at the Guaymas Basin seabed. Therefore, the character of the two samples 478-29-1 (60-65) and 29-2 (38-43) can be envisioned as resulting from a progressive and sill-induced thermal maturation, which leads to a loss of the unsaturated components, an increase in both the saturated analogs and the thermodynamically more stable configurations of the hopanes and steranes, and epimerizations of the respective diastereomers (Figs. IV.6a,b and 7a,b and Results section). Slight additional maturation of the biomarker distributions (cf. Figs IV.6c with 6a,b; IV.7c with 7a,b) accompanies the generation of n-alkanes and PAH in the sample nearest the sill, 478-29-2 (112-117), (cf Figs. IV.5c with 5a,b; IV.8c with 8a,b; and Table IV.4).

The bitumen of the immature sample 478-28-4 (120-140) at 248.3 mbsf, as described by Rullkötter *et al.* (1982), contains 5.7% non-aromatic hydrocarbons, while the two Site 478 sediments at 3.37 and 2.09 m above the sill contain 3 and 4% aliphatic

components, respectively (Table IV.3). Although the compositions of the bitumens are very similar, the yields in the two samples near the sill are significantly different from that in the immature sample. While the immature sample 478-28-4 (120-140) contains bitumen at only 261 µg/g-sediment (Rullkötter et al., 1982), the two n-alkane deficient samples 478-29-1 (60-65) and 29-2 (38-43) near the sill contain bitumen at 5140 and $6890 \mu g/g$ -sediment, respectively (Table IV.3). These yields represent 20 and 26-fold enrichments of bitumen in the latter two samples relative to the immature sample 28-4 (120-140). The two samples near the sill also contain enhanced contents of bitumen on an Corg basis with 19 and 28-fold enrichments, respectively, relative to the shallower sample. On the other hand, Gilbert and Summerhayes (1982) obtained a bitumen yield of 3584 µg/g-sediment for a thermally unaltered and varved diatomite, 479-9-2 (130-135), on the Guaymas Basin Slope. Compared to this immature sample, the bitumen concentrations in the diatomaceous mud samples 478-29-1 (60-65) and 29-2 (38-43) near the sill are less than a factor of 2 higher. This suggests that although the higher bitumen yields in the two latter samples may reflect sill-induced bitumen generation and transport away from the sill, a source of the organic matter that is naturally rich in bitumen cannot be fully discounted.

This dominance of the non-aliphatic components in the two bitumens near the sill is consistent with results reported for early pyrolytic stages during laboratory simulations. Pyrolysis studies on kerogen from the diatomites of the Monterey Formation, California (Tannenbaum et al., 1986a,b,c; Huizinga et al., 1987a,b) might furnish thermal maturation trends comparable to those observed near the sill at Site 478. In a 300°C dry pyrolysis of Monterey kerogen, alone and mixed with various minerals, Huizinga et al. (1987a) obtained low yields of saturated hydrocarbons constituting <3% of the bitumen-1 (easily extractable and not adsorbed onto the mineral matrix, as defined by Huizinga et al., 1987a) after 2 hours, which increased to between 4.3 and 8% of the bitumen-1 released after 100 hours (excluding <1% yield for kerogen + montmorillonite). The pyrolysis data of Huizinga et al. (1987a) indicates that the sillinduced generation of bitumen from the kerogen at Site 478 can conceivably retain the high polar/asphaltic character of the indigenous and immature bitumen if the time of heating is relatively short. In addition, the presence of water during pyrolysis decreases the retention of the polar constituents on clays and can increase the polar content of the bitumen even more (Huizinga et al., 1987a). Such a water-induced enhancement of the polar component of the bitumens might be especially important during the *in situ* pyrolysis of the Recent and unlithified sediments in Guaymas Basin.

Huizinga *et al.* (1987b) provided evidence that the *n*-alkanes and acyclic isoprenoids generated during pyrolysis of Monterey and Green River kerogens are derived primarily through the thermal degradation of the polar/asphaltic bitumen released from the kerogen and only secondarily from the kerogen directly. Therefore, the inferred and hydrothermally facilitated movement of the initially polar- and asphaltenerich bitumen away from the zone of intense thermal alteration near the sill at Site 478 might then isolate the bitumen from further transformation and limit production of *n*-alkanes.

The previous discussions have centered upon the processes that occur during pyrolyses which might cause *n*-alkane deficiency in the hydrothermally generated bitumens near the sill at Site 478. Of equal viability and importance, though, is the contention that the organic matter of these intervals might be unique and thus be predisposed to contain and generate bitumen lacking in *n*-alkanes. As suggested earlier, the common dominance of algal liptinite in the Guaymas Basin samples lacking the *n*-alkanes is supportive of this hypothesis. Such a predisposition requires that the organic matter lacks *n*-alkane-like structures in the protokerogen and/or be very resistant to the diagenetic and thermal release of such components. With the limited data, the cause of the unusual aliphatic character of these samples, whether due to biodegradation or source, cannot be irrevocably determined. Hydrous pyrolysis of the kerogen and bitumen isolates from these intervals, 478-29-1 (60-65) and 29-2 (38-43), might be useful in this regard; and such simulations are presently planned in continuation of this study.

The overall similarities in the aliphatic and aromatic distributions between the two samples 478-29-1 (60-65) and 29-2 (38-43), exclusive of the increased biomarker maturation in the latter, suggests that the two were similarly sourced. Even so, the possibility cannot be discounted that the change in maturity of the biomarker distributions between the two may in itself reflect a minor change in source of the sedimentary organic matter or mineral content.

Comparison with Kerogen Maturation Indices

Site 477

Rueda-Gaxiola *et al.* (1982) and Gilbert and Summerhayes (1982) investigated the degree of maturation for DSDP Leg 64 sites using the coloration of organic matter (spores and pollen; and dinoflagellates, in the latter study) as an index of thermal maturation. For the depth interval (106-146 mbsf) of the Site 477 samples described in this paper, Rueda-Gaxiola *et al.* (1982) identified increasing levels of maturation equivalent to -3 through -4 on the thermal alteration index (TAI) scale (total scale ranges from 1-5 in the order: 1,+1,-2,2,+2, etc and is based on organic matter coloration). A TAI of -3 is approximately equivalent to a vitrinite reflectance of 1.0 %R₀ (Tissot and Welte, 1984) and corresponds to the upper portion of the oil window. The TAI of -4, on the other hand, is equivalent to a vitrinite reflectance of 2.6 %R₀, which is past the oil window and well within the stage of metagenesis where methane is considered the main hydrocarbon generated from Type II kerogen (Tissot and Welte, 1984).

Of particular interest is the sample from 120.83 mbsf, 477-16-4 (130-135) in which the predominance of aromatic components in the bitumen is first observed. The absence of aliphatic components would suggest a highly pyrolyzed sediment whose maturity has extended well beyond the oil window. For the sample 477-16-5 (58-62) at 121.60 mbsf, very near the interval described here, Gilbert and Summerhayes (1982) obtained a TAI of 3, approximately equivalent to a vitrinite reflectance of 1.5% (Tissot and Welte, 1984), representing maturation approaching an overmature stage and within the wet gas-prone stage for Type II kerogen. This high degree of maturation is wellreflected in the absence of *n*-alkanes and the dominance of the aromatics in the bitumen of this sample.

The high degree of thermal maturation (overmature) for the deepest samples from Site 477 is also reflected in the abundance of methane and carbon dioxide at those depths (Galimov and Simoneit, 1982).

Site 478

TAI or vitrinite reflectance values are presently not available for the Site 478 samples analyzed herein nor have they been determined for comparable samples described elsewhere. Curie-point pyrolysis/GC of combined kerogen concentrates from
samples at 3.42 m and 2.75 m above the sill, 478-29-1 (57-59) and 29-1 (124-126), revealed a dominant series of alkene/alkane doublets with a broad unresolved complex hump, indicative of a lack of thermal alteration (Simoneit and Philp, 1982) and a potential of alkane generation. This composite is comparable in distance from the sill to the sample analyzed herein at 3.37 m above the sill, 29-1 (60-65). The pyrolysis data suggests that this latter sediment has not been affected significantly by the sill, if at all. In comparison, the Curie-point pyrolysis (Cupy) of kerogen from sample 478-29-2 (108-110) at 1.41 m above the sill, comparable to sample 29-2 (112-117) of this study at 1.35 m above the sill, contained a simpler distribution of resolved components and a less pronounced hump, indicative of more extensive thermal alteration (Simoneit and Philp, 1982). In general, the Curie-point pyrolysis data confirms differential thermal alteration of the organic matter near the sill. In concept, comparison of bitumen character and Cupy results should provide sufficient evidence to resolve the extent of pyrolysate migration away from the sill. Although the lack of Cupy analyses of the samples specifically analyzed herein precludes such a definitive assessment of the migration effects, the bitumen yields and characters (Table IV.3 and earlier discussion) of the two samples farthest from the sill suggest that at least some of the bitumen in sample 29-2 (38-43) may have migrated into the interval nearer the sill after generation.

Associations with Mineralogical Zonations

Site 477

Changes in bitumen character and kerogen maturities with depth are also coincident with mineralogical changes associated with the high thermal gradient and hydrothermal alteration of the sediments at Site 477. Kastner (1982) and Kelts (1982) discussed mineral zonations with depth at Site 477 and concluded that the progressive metamorphism attains a level equivalent to lower greenschist facies. Based on their data, the samples analyzed herein correspond to the following roughly delineated mineral zones, which are differentiated by the extent of hydrothermal alteration.

The first two stages of organic matter maturation (see earlier discussion), as exemplified by the *n*-alkane-dominated bitumens of samples 477-15-1 (120-125) through 16-2 (145-150), are within the "anhydrite-dolomite claystone" zone between approximately 105 and 125 mbsf, as classified by Kelts (1982) based on a paragenetic

sequence. This zone is characterized by (1) the absence of opal-CT throughout with variable amounts of opal-A, (2) presence of both detrital and hydrothermal quartz, (3) some pyrite, gypsum, and anhydrite, (4) absence of calcite but increasing protodolomite with depth, (5) increased crystallinity of smectite but clay amount decreasing with depth, and (6) newly formed chlorite at the bottom (Kastner, 1982; Kelts, 1982).

The third stage of organic maturation (see earlier discussion) characterized by the dominance of the aromatic hydrocarbons in the HRGC-resolvable fraction of the bitumens, 477-16-4 (130-135) through 17-1 (145-150), is primarily within the second mineral paragenesis zone, between 125 and 140 mbsf, referred to as the "illite-chlorite-pyrite-quartz claystone" zone by Kelts (1982). Samples 16-4 (130-135) and (135-140) at 120.8 mbsf overlap the previous zone slightly in depth. This second zone is characterized by (1) a total absence of opal-A, (2) presence of both detrital and new quartz, (3) small amounts of detrital clays, (4) occurrence of new chlorite, (5) presence of calcite but no dolomite, and (6) small amounts of pyrite, gypsum, anhydrite, sphene and hydrothermal K-feldspar (Kastner, 1982; Kelts, 1982).

The final stage of organic matter maturation (see earlier discussion) characterized by a dominance of the parent PAH and exemplified by the samples from core-section 477-19-1 is within the paragenetic zone of "chlorite-pyrite-quartz-calcite-carbonaceous claystones with traces of K-feldspar, albite, and epidote" identified by Kelts (1982) and between 140 and 190 mbsf. This zone contains minor calcite and abundant pyrite but is primarily differentiated on the basis of the first appearance of epidote (Kelts, 1982).

Site 478

The mineralogical transformations in the sediments above the sill at Site 478 reflect the localized hydrothermal alteration induced by the thin 4.5 m sill. In the vicinity of the sill, opal-A decreases rapidly, and opal-CT and new well-crystallized smectite are formed (Kastner, 1982). Closer to the sill, opal-CT decreases significantly and quartz, including ~50% recrystallized, becomes dominant (Kastner, 1982). Although the transitions are rapid near the sill and the mineralogy of the exact intervals analyzed herein are not available, the mineralogical descriptions of comparable intervals as provided by Kastner (1982) allow inferences to be made regarding the extent of alteration in the sediments described here. At ~ 3.73 and 2.24 m above the sill, only opal-A and detrital quartz are present along with calcite, gypsum, pyrite, smectite, and a trace of illite (Kastner, 1982). These two intervals bracket sample 478-29-1 (60-65) analyzed here, and their mineralogies suggest that thermal alteration of the sample has been minimal, which is consistent with the interpretations of the bitumen and kerogen characterizations. At 2.01 m above the sill, only a trace of opal-A remains and opal-CT becomes abundant along with pyrite (Kastner, 1982). Hydrothermal alteration, as reflected by the transformation of opal-A to opal-CT, is evident in the increased bitumen yields and hydrocarbon (biomarkers) transformations in the sample at 2.09 m above the sill, 29-2 (38-43). Opal-A disappears completely at ~ 1.44 m above the sill; while at 1.16 m above the sill, opal-CT decreases, quartz becomes the dominant silica, calcite disappears, and smectite becomes well crystallized (Kastner, 1982). Sample 29-2 (112-117) at 1.35 m above the sill is within this transition zone, and the extensive alteration is similarly reflected in the organic matter by the decreased bitumen yield and an appearance of both *n*-alkanes and pyrolytic PAH in high concentrations (Tables IV.3,4 and Figs. IV.5,8).

Temperature Estimates

By comparing the mineralogical assemblages for the sediments below the major sill at Site 477 with those of an active and continental geothermal area, Cerro Prieto Field, Kelts (1982) assigned approximate and tentative temperatures of 200°C to the depth represented by core-section 477-16, (115.0-124.5 mbsf), and 270°C for the base of Hole 477A (270 mbsf), adjacent and comparable to Hole 477. The temperature interpretations are uncertain, as noted by Kelts (1982) due to the fact that the hydrothermal system of Guaymas Basin has a different fluid and sediment composition than the geothermal field. Kelts (1982) stated that the temperatures may be underestimated due to the cooling effects of drill fluids, as suggested by McDowell and Elders (1979). Using the appearance of greenschist facies rocks and δ ¹⁸O values, Kastner (1982) similarly estimated temperatures of 300±50°C for sediments below ~154 mbsf in Hole 477.

For sill-intruded sediments, such as those of Site 478 described in this report, Kastner (1982) suggested temperatures of 150 to 200°C at the sill contacts with possible excursions to a maximum between 230 and 250°C, based on mineralogies and δ^{18} O values of recrystallized calcite. The appearance of opal-CT near sample 478-29-2 (38-43) at 2.09 m above the sill would therefore indicate temperatures of < 150°C for this interval. The observation of sterane and hopane maturation in this sample, relative to 29-1 (60-65) at 3.37 m above the sill (see earlier discussion), is consistent with the lower temperature alteration suggested by the mineralogies.

Temperature estimates based on vitrinite reflectances (% R_0) in sediments can be highly variable and are dependent on the age (time of heating) of the sediment, as shown by Bostick (1979). The equivalent R_0 's of 1.0 through 2.6% (see earlier discussion) for the depth interval betwen 106-146 mbsf at Site 477 correspond to paleotemperatures of approximately 125 to >230°C based on data for the Salton geothermal field in California (Bostick, 1979). Using temperature estimates from hydrothermal bomb heatings of lignitic shales (Bostick, 1979), these same reflectances indicate temperatures of approximately 300 to 440°C. The R_0 of 1.5% at ~ 122 mbsf corresponds to temperatures of 175 and 350°C based on the two calibrations, respectively. The actual *in situ* temperatures of reaction are probably intermediate between these extremes and are within the range of estimates provided by the mineralogical evidence (see above).

Thermal Maturation of Bitumen in Subsurface Sediments

The results of the hydrothermal pyrolysis of organic matter in subsurface sediments at Sites 477 and 478 are comparable. In general, the hydrothermal maturation of sedimentary organic carbon results in the generation of polar/asphaltic bitumen sequentially dominated by *n*-alkanes, aromatic hydrocarbons, and unalkylated PAH, as presented by the conceptual diagram in Fig. IV.15. Two processes are envisioned in the production of these successive hydrocarbon distributions. In the first process, the higher temperatures encountered either at deep sub-bottom depths or in direct contact with a thermal source (e.g. sill) result in a dominant production of PAH and cracking of alkanes or alkyl-components. The production of the aliphatic compounds are then limited to the lower temperature regions more distant from the heat source (Fig. IV.15). The resulting changes apparent in the downcore bitumens are purely a result of different pyrolytic temperatures. The second process is time-dependent and is a direct result of the continued hydrothermal flow in the subsurface sediment sequence, as it occurs at Site 477. Within a specific depth interval, the aliphatic components produced at lower temperatures are transported away by the hydrothermal flow (Fig. IV.15). With continued heating, the pyrolysate becomes more aromatic in character until a point is reached at which only the PAH remain, predominantly the unalkylated components. Although such a sequence can occur in a geothermal system, the hydrothermal process



Figure IV.15. Conceptual schematic of the formation and transport of the aliphatic and aromatic components of the hydrothermal pyrolysates in the subsurface sediments and their deposition and alteration at the seabed in Guaymas Basin, Gulf of California.

accentuates the removal of the intermediate products away from the heat source at depth by providing a constant flow of transport medium (Fig. IV.15). Both of these mechanisms occur in Guaymas Basin, although the latter is probably less important at Site 478 due to the short-lived nature and limited vertical extent of the sill-induced hydrothermal process (Kastner, 1982). The effect of the hydrothermal fluid circulation is especially evident in the low-yield and PAH-dominated bitumens below 120 mbsf at Site 477.

All of the aliphatic and aromatic maturation indices (e.g. *n*-alkanes, biomarkers, bitumen-based parent PAH concentrations, and phenanthrene-methylphenanthrene indices) undergo comparable changes at Sites 477 and 478, although the overall extent of maturation is greater in the Site 477 samples. For example, the character of the sample nearest the sill, 478-29-2 (112-117), is what would be expected of a transition between the aliphatic and aromatic bitumens of the samples from core-section 477-16-2 and 16-4, respectively (see Results section and earlier discussions). The temperature estimate of 200°C for core 477-16, based on mineralogical evidence (Kelts, 1982) agrees well with the estimates of 150 to 200°C near the sill contact zone of 478-29-2, based on mineralogies and δ^{18} O values (Kastner, 1982). The temperatures in these instances may have been briefly higher, since the estimates are based on equilibrium considerations and present-day geothermal gradients in basins with comparable mineral sequences.

The extent of thermal alteration in bitumens generated within such a hydrothermal system is best monitored using the distributions of the aromatic hydrocarbons, as they have the broadest range in thermal stability. In particular, the concentrations of parent PAH in the bitumens, degree of the tricyclic aromatic hydrocarbon alkylation, and the methylphenanthrene indices (MP/P and MPI₃) are all of consistent utility; and the combination of these parameters may be additionally applicable in other non-hydrothermal but high-temperature geothermal systems.

Implications for Formation/Deposition of Seabed Petroleums

Two of the most pertinent observations of the hydrocarbon generation by hydrothermal pyrolysis in subsurface sediments are: (1) the aliphatic and aromatic components of the bitumens can be transported to the seabed independently as a result of their formation under different temperatures at increasing depths, respectively, and/or sequential generation during essentially "isothermal" pyrolysis (Fig. IV.15) and (2) the PAH distributions are consistently skewed towards the low molecular-weight and more soluble compounds, regardless of the overall concentrations of the PAH. The latter observation is particularly interesting in that the lower molecular weight components would be expected to be scavenged most efficiently by the hydrothermal fluids at depth leaving behind the higher molecular-weight components. These two observations are critical to the evaluation of the relationship between the seabed petroleums and the downcore pyrolysates that follows.

Comparison of Seabed Oils and Subsurface Pyrolysates

The comparison between the hydrocarbon contents of the thermally altered downcore sediments and the seabed hydrothermal petroleums (see Results and Discussion sections and Chapter V) has identified a number of similarities and differences between the bitumens of the two sets. Both can contain broad distributions of *n*-alkanes and biomarkers in their thermally mature or near-mature configurations and often contain a dominance of the more polar (NSO+ asphaltene), non-hydrocarbon fractions of the bitumen. The bitumen-based PAH concentrations in the subsurface sediments are within the ranges of those present in the seabed petroleums, although their relative distributions are significantly different from the seabed deposits (see later discussion). In addition, some of the bitumens from greater depths (>120 mbsf at Site 477) contain only the unalkylated analogs of the PAH, unlike most of the seabed oils. The character of the seabed deposits is consistent with their rapid generation at temperatures ranging from 125 to >300°C, based on mineralogical evidence, with instantaneous temperatures as high as 440°C possible, based on equivalent vitrinite reflectances. Transport within the hydrothermal medium quickly isolates the pyrolysates from the heat source and deposits the products at the seabed where they are quenched. High temperatures of the transport medium associated with the oils are also suggested by fluid-inclusion analyses. Trapping temperatures of 116 to 226°C were determined for aqueous inclusions, adjacent to hydrocarbon inclusions, in hydrothermally precipitated amorphous silica at the Guaymas Basin seabed (Peter et al., 1990a).

Chapters II and III suggested that the hydrothermal petroleums at the Guaymas Basin seabed are admixtures of pyrolysates from various thermal regimes (depths). The downcore data presented and the inference (see above) that the aliphatic and aromatic components can be transported essentially independently tend to support this contention. The significance of such a process can be seen in the following examples:

a) 1177-4B. The aliphatic fraction of this seabed petroleum is characterized by a broad distribution of *n*-alkanes, C_{14} - C_{31} with no odd-carbon predominance, (Chapter II) and biomarkers not fully isomerized (Chapter V). The PAH concentrations, particularly benzo(ghi)perylene, in this oil are the highest of any of the petroleums discussed in Chapter III, on both total aromatic and bitumen bases. The phenanthrenemethylphenanthrene indices (Table IV.5) and the plots of tricyclic aromatic alkylation (cf. Fig. IV.14a and 15a) for the seabed oil 1177-4B and the downcore sediments indicate that the PAH distribution in 1177-4B is most similar to the PAH-dominated bitumen from samples 477-17-1 (145-150) and 19-1 (130-140), (> 126 mbsf). The relative distribution of PAH in 1177-4B, though, is different from those in the Site 477 samples (cf. Figs. IV.12d and 13b; cf. Figs. IV.3e,f and 10b) in that the higher molecular weight PAH dominate in the seabed oil. As previously reported in the Results section, the PAH distribution in 1177-4B is most similar to the distribution of dominant compounds in the total extract of 1173-9 (light green oil) and 1175-7 (cf. Figs IV.10b and 11a,b) and could be effected by a preferential solidification/condensation of the higher molecular weight PAH entrained in a high-temperature fluid from a depth similar to 477-19-1 (130-140) (see Fig. IV.15). This observation of a high-temperature aromatic distribution in a bitumen dominated by aliphatic components more reminiscent of a lower-temperature (shallower depth) pyrolysate is evidence of the admixture of pyrolysates from different thermal regimes and the importance of differential solidification/condensation of compounds to the character of the hydrothermal petroleums at the seabed.

b) 1168-1-2. This sample is characterized by the absence of significant amounts of *n*-alkanes and a predominantly polar/asphaltic character of the bitumen (Chapter II). The biomarker distribution is one of the two most immature distributions in the seabed oils, based on hopane and sterane isomerizations, and is comparable to that of sample 478-29-1 (60-65) farthest from the sill (Chapter V). The aromatic fraction of this oil contains significant amounts of the monoaromatic and diaromatic tricyclic terpane derivatives also characteristic of the sample farthest from the sill (cf Fig. IV.8a with 10c). On the other hand, sample 1168-1-2 also contains the fully aromatic analog of the tricyclic terpane derivative (1,2,8-trimethylphenanthrene) and significantly higher concentrations of pyrolytic PAH and lower concentrations of perylene than 478-29-1 (60-65) (cf. Tables III.1 and IV.4). In addition, the aromatic distribution has a hump maximizing at the

lower molecular weight range (HRGC elution time of pyrene) as opposed to the high range (between HRGC elution times of perylene and benzo(ghi)perylene) in the latter (cf. Figs. IV.8a with 10c). The seabed oil appears to have resulted from the influx of a higher temperature pyrolysate (condensate), dominated by pyrolytic PAH, into a less mature *n*-alkane-deficient bitumen reminiscent of that associated with the sediments farther from the sill at Site 478.

Although the downcore evidence indicates that the seabed petroleums are mixtures of pyrolysates from different thermal regimes (depths), the bulk of the oils appear to originate near the seabed rather than at great depths. Carbon-14 dating of a collection of the seabed oils obtained ages of ~ 5kybp (present identified as 1950 AD), uncorrected for seabed offset of the oceanic carbon reservoir, which suggests that the organic carbon source of the bulk of the oils is located at depths of ≤ 30 mbsf (Peter *et al.*, 1990b). The sedimentation rate in the Southern Trough is rapid and has been estimated at 1-2m/1000y based on radiocarbon dating and biostratigraphy (Curray et al., 1982). The apparently shallow origin of at least some of the petroleums requires very high thermal gradients near the seabed. Such high gradients have been confirmed by Bazylinski et al. (1982), who reported temperatures as high as 150° C at ~40 cm below the surface in the southeastern portion of the Southern Trough of Guaymas Basin (Fig. IV.1). Whether the high gradient is due to sill-induced heating or an overall high heat flow from depth is not known. Regardless, the high trapping temperatures (116 to 226°C) for fluid inclusions in hydrothermal amorphous silica (see above) suggest that the entire process of generation, transport, and deposition can occur over very narrow depth intervals. Furthermore, the broad range of pyrolysis conditions as exemplified by the bitumen distributions between 106 and 145 mbsf at Site 477 can be effectively compressed into this narrow section of the sediment column at the seabed.

The inference that the seabed oils represent admixtures of pyrolysates from different thermal regimes (depths), particularly the parent PAH (see previous discussion), suggests that the components from greater depths (older carbon) may, in general, represent a relatively small proportion of most of the deposited petroleums. Future carbon-14 determinations will examine the ages (depths of origin) of the various fractions of the bitumens. Such analyses would aid in the resolution of the actual sources of the PAH in the seabed petroleums.

Formation and Deposition of PAH in Seabed Oils

The recognition that the PAH distributions in the seabed oils are skewed towards the high molecular-weight compounds (e.g. benzo(ghi)perylene) relative to the distributions in the subsurface sediments is tantamount to the understanding of the processes controlling the deposition of the seabed petroleums. Two suggested explanations are: a) the PAH distributions at the seabed are the result of an earlier stage of pyrolysis wherein the higher molecular weight components predominate (aromatizations of biologically-derived components) or that the source of these PAH originates at a greater depth (higher pyrolytic temperatures) not sampled in this study, where resynthesis could occur, and b) post-depositional removal of the more soluble low molecular weight components at the seabed or their non-deposition due to the higher temperatures of the venting fluids.

The latter explanation seems most reasonable in view of the prevalence of the water-washing of exposed oils and mounds at the Guaymas Basin seabed (see Chapters II and III; Bazylinski *et al.*, 1988), the low concentrations of C_1 through C_{10} hydrocarbons (aliphatic and aromatic components) in older mound samples, and their high concentrations in venting fluids and fresh deposits associated with chimneys (Simoneit et al., 1988; also see Fig. IV.15). Even in fresh hydrothermal deposits, the volatile concentrations probably represent minimum amounts since degassing due to decompression during retrieval of samples from the seabed was frequently observed (Simoneit et al., 1988). Partitioning of hydrocarbons between an organic phase (e.g. bitumen/oil) and seawater is dependent on their water solubilities and mole fractions and normally follows the same general trends as the solubilities. The more soluble components of the hydrothermal oils would then be preferentially removed by waterwashing at the seabed (Fig. IV.15). The enhanced removal of the low molecular weight PAH would result in aromatic distributions skewed towards the heavier components at the seabed even though the original distributions in the subsurface sediments are enriched in the lighter components. This preferential loss of the low molecular weight aromatic compounds would be most pronounced as a result of their significantly higher aqueous solubilities relative to the aliphatic components, as shown in McAuliffe (1980). In a compilation of alkane and aromatic solubilities in water at 25°C, McAuliffe (1980) reported phenanthrene as being approximately 100 to 200 times more soluble and pyrene 15 to 60 times more soluble than the $n-C_{12}$ through $n-C_{20}$ alkanes. Although the

overall solubilities in seawater are expected to be lower, the relative enhanced solubilization of the aromatic compounds should remain.

Such a removal of the lower molecular weight aromatics (e.g. naphthalene through pyrene) from the seabed oils during and after their deposition would thus result in the observed difference in the distributions of the aromatics in the seabed oils compared to the subsurface sediments (Figs. IV.12,13 and associated discussion). An extreme case of such preferential removal of the low molecular weight PAH is exemplified by the unalkylated PAH-rich pyrolysates (benzo(ghi)perylene and coronene dominant), 1173-9 and 1175-7 (see Fig. IV.11), associated with active chimneys. These distributions would thereby occur through a selective condensation/solidification of these higher molecular-weight PAH from a high-temperature fluid exiting the chimneys, which is dominated by the parent PAH and originally similar to that associated with the deeper sections of Site 477 (e.g. 19-1, 130-140 comb) (see Fig. IV.15).

Biodegradation versus Limited Maturation

The least thermally mature downcore sediments from Site 478, 29-1 (60-65) and 29-2 (38-43), have hydrocarbon distributions (no *n*-alkanes present) reminiscent of the hydrothermal petroleums initially interpreted as being extensively biodegraded, e.g. 1168-1-2 and 1168-1-3B, dredge samples 7D (see previous discussion and Chapters II and III). The biomarkers of the two Site 478 samples nearest the sill, though, have undergone transformations (isomerizations) consistent with more advanced degrees of maturation. The complete absence of *n*-alkanes in an otherwise bitumen-rich sediment containing extensively isomerized biomarkers does not necessarily require the invocation of microbial processes and may only be indicative of a specific type of source (e.g. liptinite-rich diatomite), mineral matrix, and/or unusual maturation trends induced by the hydrothermal process (see discussion of Site 478 results). On the other hand, the observation of hydrocarbon patterns characteristic of biodegraded oils on the surface of hydrothermal mounds but n-alkane-rich bitumens in the interior (see Chapter II) implies that microbial degradation of the petroleums can be pervasive at the seabed. Therefore, interpretations of the hydrocarbon distributions in exposed or near-surface sediments must take into account both possibilities.

It is apparent from the results of this and the previous studies (Chapters II, III) that *n*-alkane distributions, the degree of alkylation of the tricyclic aromatic hydrocarbons, and the phenanthrene-methylphenanthrene indices are insufficient parameters to assess the extent of maturation and biodegradation of the seabed petroleums in Guaymas Basin. They are inadequate because, as shown by the data of Site 478, sediments which have undergone either marginal or significant thermal maturation (based on biomarkers) may contain no *n*-alkanes nor significant concentrations of PAH other than the diagenetically-derived compounds (e.g. perylene). In addition, water-washing (see Chapters II-III), which is often concommitant with biodegradation, will preferentially remove the more volatile and water-soluble PAH, which highly limits the utility of the phenanthrene series as indicators of maturation and/or biodegradation. Biomarkers (hopanes, steranes, and their aromaticized analogues) cannot always be used as they are absent in highly mature bitumens (see Results for Site 477).

A better assessment of the degree of thermal maturation and, hence, biodegradation might be obtained by examining the concentrations and distributions of the higher-molecular-weight PAH produced by catagenesis and pyrolysis, such as pyrene, benzofluoranthenes, benzopyrenes, benzo(ghi)perylene, and Diels' hydrocarbon (Chapter V). These compounds are not as susceptible to water-washing and biodegradation and are present over a broader range of thermal maturity than the aliphatic components of petroleums. All of the hydrothermal petroleums from the Guaymas Basin seabed contain measurable amounts of pyrolytic PAH, although their concentrations are highly variable (Chapter III and Table IV.4). Even the samples (e.g. 1168-1-2, 1168-1-3B, Dredge 7D) which appear biodegraded, based on absence of *n*-alkanes, contain significant concentrations of the higher molecular weight PAH, particularly pyrene (also see Appendix D). On the other hand, the two alkane-deficient sediment samples from Site 478 contain predominantly perylene with other PAH in much lower concentrations than the levels encountered in the seabed deposits of the hydrothermal petroleums (c.f.Table IV.4 with Table III.1).

Limitations of These Geochemical Interpretations

The aforementioned examples of mixing and post-depositional alterations are a testament to an inherent problem in the analysis of hydrothermal effects on organic matter. Since the seabed petroleums are mixtures of pyrolysates from various thermal regimes at depth and immature seafloor organic matter, concentrations and ratios of compounds are dependent on the respective contributions of the sources. Discussions of the character of the hydrothermal petroleums at the seabed are limited to parameters based on amounts relative to the quantity of bitumen, a variable which itself is dependent

on the degree of mixing. No independent normalization factor (e.g. g-dry sediment) of the concentrations is viable since the seabed deposits are too heterogeneous in both bitumen and inorganic contents (fragments of hydrothermally precipitated minerals intermixed with diatom debris and clays). The concentration parameters available are, therefore, inadequate for completely deconvoluting the hydrothermal processes which generate, transport, and deposit the petroleums at the seabed.

Discussions of the thermal maturity of the seabed petroleums are similarly limited. The evidence presented indicates that the admixing of pyrolysates from different thermal regimes is an important process in the formation of the seabed petroleums. The PAH components of these petroleums appear to originate from greater depths or closer to sill intrusions (higher thermal stress) than the aliphatic components. This suggests that the two fractions of the petroleums should be evaluated separately in terms of thermal maturation or catagenesis. The broad range of thermal sources, differential transport effects, and the inability to externally normalize the component concentrations in the seabed bitumens (see previous discussion) preclude the assignment of a specific maturity level to any individual seabed petroleum. The hydrothermal system is an inherently complex and dynamic system, much less amenable to maturation studies than normal petroleum basins, and discussions of the thermal maturity of hydrothermal oils may not have any viable meaning except in the most general terms.

CONCLUSIONS

The hydrothermal alteration of subsurface sediments in Guaymas Basin results in the rapid pyrolysis of the organic matter and generation of petroleum-like bitumens, which are then scavenged and transported to the seabed by the circulating fluids. Increasing thermal stress with depth or proximity to a heat source (magma-chamber or sill intrusion) is reflected in the character of both the solvent-soluble and insoluble portions of the sedimentary organic matter. The thermal alteration indices based on organic matter complement the assessments of hydrothermal alteration based on the mineralogies of the subsurface sediments.

Below the major sill at DSDP Site 477, the HRGC-resolvable fractions of the bitumens exhibit a progressive transition from *n*-alkane- to aromatic hydrocarbon-dominated distributions, which accompanies the decreasing bitumen and organic carbon contents with depth. In the deepest and most altered sediments, the hydrocarbons are comprised of the unalkylated PAH, with dibenzothiophene and phenanthrene dominant. Although increased thermal stress with depth is essential for these transformations, the additional influence of hydrothermal fluid flow is also important. This process results in a continual removal of the initial and intermediate products (e.g. *n*-alkanes, alkylated PAH) of pyrolysis from the heated zone. Both processes, increased thermal stress with depth and temporal passage of hydrothermal fluid through the sediments, results in low-yield and parent PAH-dominated bitumens at the greatest depths of Site 477 (>120 mbsf). Similar thermal alterations are envisioned near sills, such as those of Site 478, but the extent of thermal alteration is more restricted due to the shorter-lived character and limited influence of such sill-induced hydrothermal systems.

The PAH have the broadest range of occurrence and/or stability in the hydrothermally altered sediments; and specific indices, such as parent PAH concentrations, degree of tricyclic aromatic hydrocarbon alkylation, and selected methylphenanthrene indices, appear to be good monitors of thermal alteration in such high-temperature regimes.

The altered and unaltered subsurface bitumens exemplify the entire character range of the seabed petroleums in containing broad distributions of n-alkanes and biomarkers in their thermally mature or near-mature configurations and a frequent dominance of the polar, non-hydrocarbon fractions. As a result of formation at different depths or under dissimilar thermal regimes, the aliphatic and aromatic components of the subsurface pyrolysates can be transported to the seabed independently. Even so, the parent PAH concentrations in the subsurface bitumens are within the ranges of those in the seabed petroleums. The seabed distributions of PAH, though, are consistently more skewed towards the high molecular-weight (e.g. benzo(ghi)perylene) and less soluble compounds than the subsurface bitumens. This is attributed to non-deposition and post-depositional removal of the more soluble PAH due to the higher temperatures of the venting fluids and water-washing of exposed deposits, respectively. The relative enhancement of the low-molecular weight PAH in the subsurface bitumens, though, is opposite of that expected if solubilization during hydrothermal transport is important. This latter observation suggests that the subsurface "pool" of PAH in the thermally altered sediments is continually being replenished by generation from the kerogen and/or differential transport by solubilization is not prevalent at the higher temperatures.

The absence of n-alkanes in sediments with high bitumen concentrations and thermally matured biomarkers next to a sill at Site 478 suggests that such a composition may be the result of an unusual source (liptinite-rich, possibly) with little n-alkane potential and/or limited thermal maturation. Similar n-alkane deficiencies in the exposed seabed petroleums appear due to their preferential removal by microbial degradation. Although other thermal maturity indicators, such as PAH distributions, can aid in distinguishing the two processes, hydrocarbon distributions in near-surface sediments must be interpreted with caution.

Estimates of the temperatures causing the rapid genesis of petroleums in the subsurface sediments of Guaymas Basin vary considerably: $125 \text{ to} > 300^{\circ}\text{C}$ and $125 \text{ to} 440^{\circ}\text{C}$ based on mineralogies and kerogen data, respectively. Part of this variability probably reflects the different thermal regimes prevalent in the subsurface and is responsible for the broad range in compositional character of the hydrothermal petroleums. The hydrocarbon data obtained in this study similarly suggests a broad range in pyrolytic temperatures. While the character of the bitumen in the subsurface sediments can be used to designate relative temperatures, absolute temperatures are difficult to assign without external calibrations (e.g. with respect to time). Hydrous pyrolysis simulations over large temperature ranges and using the sediments indigenous to Guaymas Basin are required. Analysis of the aromatic contents of these laboratory pyrolysates would be most useful in temperature assignments in view of their broad stabilities and occurrence. In addition, analyses of the biomarker and *n*-alkane distributions in these products may clarify the occurrence of *n*-alkane deficient bitumens in the subsurface sediments and seabed petroleums.

ACKNOWLEDGEMENTS

We thank the crews and pilots of the D.S.V. *Alvin*, R.V. *Lulu*, and R.V. *Atlantis II* for their skillful recoveries of hydrothermal samples and Kathryn Brooksforce for the carbon analyses . We thank R.N. Leif for both technical assistance and stimulating discussions of this research and F.G. Prahl for his helpful comments. Support for this research from the National Science Foundation, Division of Ocean Sciences (Grants OCE-8312036, OCE-8512832 and OCE-8601316), and partial support by the Donors of the Petroleum Research Fund, administered by the American Chemical Society, are gratefully acknowledged.

V. HYDROTHERMAL PYROLYSIS OF ORGANIC MATTER IN GUAYMAS BASIN: 2. BIOMARKER TRANSFORMATIONS AND IMPLICATIONS FOR HIGH-TEMPERATURE MATURATION

ABSTRACT

The pyrolysis of immature organic matter by the crustal accretion and hydrothermal activity at the Guaymas Basin spreading center results in a rapid maturation of the biomarkers. Most of the seabed deposits of the hydrothermal oils contain sterane and hopane distributions exhibiting extensive isomerizations, consistent with the high thermal gradients in the basin and the high temperatures of the hydrothermal fluids venting at the seabed. Comparison of the isomerization trends of this hydrothermal maturation with those in low-temperature regimes of other basins and those observed under the high-temperature and hydrous conditions of laboratory simulations suggests that they are more similar to the latter. Using the kinetic parameters of the sterane and hopane isomerization reactions so determined by Zumberge et al. (1984), estimates of the average to maximum temperatures of pyrolysis of 230 to 370°C with reaction times of 1 to 10 days were obtained for the hydrothermally generated petroleums. On the other hand, discrepancies between the model results and the actual conditions of a single laboratory pyrolysis of Guaymas Basin organic matter suggests that the character of the source matter may also be an important factor. Characterization of the triaromatic steroid hydrocarbons in hydrothermal oils and subsurface sediments and in a hydrous pyrolysis simulation has identified Diels hydrocarbon and an apparently related series of unusual C₁₈ to C₂₀ triaromatic steroid hydrocarbons that appear to be good tracers of hydrothermal processes. Several new maturation indices for high-temperature and hydrous processes have been formulated based on the occurrence of this unsual series of short-alkyl-chained triaromatic steroid hydrocarbons.

INTRODUCTION

Crustal accretion and hydrothermal activity at the Guaymas Basin spreading center, Gulf of California are generating petroleum at depth in the sediments through the pyrolysis of immature organic matter. Details of the process, its geological setting, and the history of its discovery have been summarized in the initial survey of the compositions of these hydrothermal petroleums (Chapter II and references therein).

The maturation of organic matter to petroleum is normally thought to occur at relatively low temperatures 60-150°C over periods of millions of years (Hunt, 1979; Tissot and Welte, 1984). The history of the formation of Guaymas Basin requires that the sediments in the rift areas be <200 ky old (Curray et al., 1982) and, therefore, the hydrothermal petroleums be significantly younger. In compensation for the relatively short maturation times, these petroleums must be formed at temperatures significantly higher than 150°C. Simulations of petroleum formation (thermal maturation) by pyrolysis in laboratories are also conducted at temperatures above those in sediments in order to compensate for the lack of maturation over geological time scales (Lewan, 1985). The hydrothermal system at the Guaymas Basin spreading center is of continuing interest to organic geochemists because it offers the opportunity to investigate these high-temperature and hydrous reactions of organic matter under *in situ* conditions.

Biological marker (biomarker) analysis, founded on the genetic relationship between chemical fossils (Eglinton and Calvin, 1967; Eglinton, 1973) in the geosphere and their biologically-derived precursors, is currently used by petroleum geochemists for both oil-oil and oil-source rock correlations (Philp, 1985). Monitoring of the diagenetic (biologically/chemically-induced) and catagenetic (thermally-induced) transformations of biomarkers in sediments and oils has led to the formulation of specific molecular indices of thermal maturation and the use of these indices in exploration (Philp, 1986; Philp and Lewis, 1987). The hydrothermal maturation of these biomarkers in the Guaymas Basin sediments is rapid (Chapter II); and the inferred high-temperatures of that process make it an important link between biomarker transformations during laboratory simulations, also conducted at high-temperature, and those in other basins with normal geothermal gradients.

Chapter IV described the hydrocarbon content of downcore sediments from DSDP Sites 477 and 478 and compared the hydrothermally altered organic matter with the Guaymas Basin seabed petroleums. This chapter addresses, in more detail, the effects of hydrothermal pyrolysis, a high-temperature and hydrous process, on the

biomarker transformations (isomerizations) normally used as indicators of thermal maturity in oils and sediments. Specifically, I compare the hydrothermal maturation of biomarkers as preserved in the Guaymas Basin seabed petroleums and downcore sediments with biomarker maturation under the high-temperature conditions of laboratory simulations and low-temperature regimes of other basins. Data is also presented on the distributions of triaromatic steroid hydrocarbons. The presence and significance of a newer series of these compounds, possibly unique to high-temperature hydrous processes, are discussed.

BACKGROUND

Biomarker Transformations

The biomarkers to be discussed herein are diagenetic and catagenetic derivatives of steroids and hopanoids. The product-precursor relationships and transformation pathways for the steroids in the biogeosphere have been reviewed by Mackenzie *et al.* (1982a). As summarized therein, the steroidal precursors are derived from various plankton and benthic organisms as well as higher plants (terrestrial). The hopanoids are derived primarily from cellular constituents of microorganisms and are ubiquitous indicators of such microbial activity (Ourisson *et al.*, 1979; 1982; 1984).

The thermal maturation of the hydrocarbon analogs of these biomarkers, steranes and hopanes, results in stereochemical transformations (changes in structural arrangement of atoms) and aromatizations (removal of hydrogen to form aromatic rings) of individual molecules. The stereochemical distributions of steranes and hopanes originally used in oil-source rock correlations (Leythaeuser *et al.*, 1977; Seifert, 1977), were found to change systematically with sediment depth (Ensminger et al., 1977) and upon laboratory heating (van Dorsselaer *et al.*, 1977; Seifert, 1978). Rapid developments in oil-oil and oil-source rock correlation studies followed (Seifert and Moldowan, 1978; 1981; Seifert *et al.*, 1979; Philp, 1985; Philp and Lewis, 1987;).

Three of the biomarker reactions to be discussed are presented in Fig.V.1. The thermally-induced epimerization of the biologically-derived 22R diastereomers of the extended ($\geq C_{31}$) 17 α (H), 21 β (H)-hopane series to mixtures of the 22S and 22R configuration,s depicted in Fig. V.1a, results in an equilibrium ratio for 22S/22R of 1.5 (Ensminger *et al.*, 1977). Analogous stereochemical changes in the distribution of the 5 α (H),14 α (H),17 α (H)-steranes (C₂₇-C₂₉), represented in Fig. V.1b, result in a 20S/20R ratio of 1.17 at equilibrium (Mackenzie and Maxwell, 1981; van Graas *et al.*, 1982). These specific isomerizations were originally observed in sedimentary basins by various researchers (Mackenzie *et al.*, 1980; Seifert and Moldowan, 1980). Laboratory pyrolysis of an immature Toarcian shale from the Paris Basin, France (Mackenzie *et al.*, 1981b) and hydrous pyrolyses of Phosphoria Retort Shale (Lewan *et al.*, 1984) caused epimerizations similar to those in the sediments of basins. A third reaction of interest is the aromatization (dehydrogenation) of the monoaromatic C₂₇-C₂₉ to the triaromatic C₂₆-C₂₈ steroid hydrocarbons (Fig. V.1c). This aromatization process, observed in



Figure V.1. Biomarker transformations monitored as thermal maturity indicators in the hydrothermal seabed oils and subsurface sediments of Guaymas Basin: (a) isomerization of the extended ($\geq C_{31}$) 17 α (H),21 β (H)-hopane series from the biologically-derived R- to a mixture of the R- and S- configurations at C-22; (b) isomerization of the 5 α (H),14 α (H),17 α (H)-steranes (C₂₇-C₂₉) from the biologically derived R- to S- configuration at C-20; and (c) aromatization of the monoaromatic 5 α (H)- and 5 β (H)20R monoaromatic C₂₇-C₂₉ to the triaromatic 20R C₂₇-C₂₉ steroid hydrocarbons. (The reaction is shown for the aromatization of the C₂₉ monoaromatic). The k_r and k_f refer to reverse and forward rate constants for the respective reactions in the reversible isomerizations. Note that the aromatization is irreversible. Further details on the rate constants are given in Appendix E. Toarcian shales of the Paris Basin (Mackenzie et al., 1981a), was subsequently simulated in the laboratory by Mackenzie et al. (1981b).

The triaromatic steroid hydrocarbons found in petroleums and source rocks occur in a number of structural forms that differ in the number of nuclear methyls they contain. The triaromatic steroid hydrocarbons with two, one, and no nuclear methyl groups attached to the polycyclic structure can be referred to as the m/z 245 (Fig. V.2c), 231 (Fig. V.2b), and 217 series (Fig. V.2a), respectively (so named for the dominant ions of each series during HRGC-MS). In a study of the Toarcian shales in Paris Basin, France, Mackenzie *et al.*, (1981a) observed that the m/z 231 and m/z 245 series of the triaromatic steroid hydrocarbons were dominant, while the m/z 217 series and a fourth type with three nuclear methyls (m/z 259 base peak) were relatively lower in concentration.

A second group of reactions that appears to monitor thermal maturation, depicted in Fig. V.2, is the thermal-cracking of the long-alkyl-chained to short-alkyl-chained components in the various series of triaromatic steroid hydrocarbons. The cleavage of the alkyl side-chains of steroid hydrocarbons, first suggested for the monoaromatics (see Fig. V.1c) by Seifert and Moldowan (1978), has been offered as an explanation of the observed increase in the m/z 231 series (Fig. V.2b) of short-alkyl-chain (C₂₀-C₂₁) relative to the long-alkyl-chain (C₂₆-C₂₈) triaromatic steroid hydrocarbons in the deeper parts of sedimentary basins (Mackenzie et al., 1981a). The ratio of $C_{20}/(C_{20}+C_{27})$ triaromatic steroid hydrocarbons, used as an index, was found to be correlated with thermal maturity only in instances where the aromatization (Fig. V.1c) of the monoaromatic to triaromatic steroid hydrocarbons had proceeded past 70% completion in a series of petroleums and shales from the Shengli oilfield (Ji-Yang et al., 1982). Cracking of the alkyl side-chains of the triaromatic steroid hydrocarbons was reported to be relatively minor during laboratory heating of Toarcian shales at temperatures up to 285°C (Mackenzie et al., 1981b). Hydrous pyrolysis of Phosphoria Retort Shale at temperatures between approximately 345 and 360°C resulted in only the $C_{20}+C_{21}$ analogs of the m/z 231 triaromatic steroid hydrocarbons remaining (Lewan et al., 1986). On the other hand, Lu and Kaplan (1989) observed an increase in the abundance of the C_{20} relative to the C_{28} m/z 231 triaromatic steroid hydrocarbons during anhydrous pyrolysis of Cretaceous black shale kerogen at 300°C and complete degradation of the triaromatic steroid hydrocarbons when the kerogen was mixed with montmorillonite.



 $R = H, CH_3, CH_2CH_3$

 $R = H, CH_3, CH_2CH_3, CH_2CH_2CH_3$

Figure V.2. The apparent thermally-induced cracking of long-alkyl-chained to shortalkyl-chained triaromatic steroid hydrocarbons in each of three series, which differ in the number of nuclear methyls: (a) m/z 217 series, (b) m/z 231 series, and (c) m/z 245 series.

Rates of Reaction and Kinetic Models

Mackenzie *et al.* (1981b) suggested that the relative degree of sterane isomerization and aromatization may be useful in distinguishing the thermal histories of different basins . Mackenzie *et al.* (1982b) confirmed this by comparing the extent of the two reactions in the Pannonian Basin (Pliocene in age), Mahakam Delta (Miocene), and Paris Basin (Toarcian). Within the young Pannonian Basin, with average heating rates 20 times greater than that of the Paris Basin, aromatization was enhanced relative to isomerization, apparently due to the former being a more temperature-dependent process. This enhancement of the aromatization, relative to isomerization, was also observed at the higher temperatures in laboratory simulations (Mackenzie *et al*, 1981b).

Kinetic models of the isomerizations and aromatizations of the steranes and hopanes followed (Mackenzie and McKenzie, 1983; McKenzie et al., 1983). By modelling the progress of the isomerizations of the C₃₂ hopane (Fig.V.1a) and C₂₉ sterane (Fig. V.1b) and the aromatization of the C₂₉ monoaromatic to the C₂₈ triaromatic steroid hydrocarbon (Fig. V1c) in various extensional basins, Mackenzie and McKenzie (1983) were able to obtain the kinetic parameters (activation energies and frequency factors) for the reactions, assuming first-order unimolecular mechanisms. Similar kinetic parameter values for the isomerization reactions were obtained for the Hód-I borehole (Pannonian Basin, Hungary) by Sajgó and Lefler (1986). Mackenzie and McKenzie (1983) concluded that the aromatization rate in basins was consistent with that reported for laboratory simulations (Mackenzie et al, 1981b) at high temperatures, but that the hopane isomerization rate was different. This suggested that different mechanisms may dominate under different thermal regimes; hence, laboratory simulations of biomarker maturation may not be extendable to basins with normal geothermal gradients. On the other hand, the laboratory simulations may be more pertinent in the case of the high-temperature maturation of biomarkers evident in the Guaymas Basin hydrothermal system.

The kinetic parameters of these three reactions have also been determined using laboratory simulations. The activation energies (E) and frequency factors (A) for the isomerizations and aromatizations as determined for basins (Mackenzie and McKenzie, 1983; Mackenzie *et al.*, 1984; Sajgó and Lefler, 1986) are summarized in Table V.1. Also included are laboratory simulation values of the isomerization parameters determined by hydrous pyrolysis of Monterey Formation outcrop samples (Zumberge *et al.*, 1984) and the aromatization parameters obtained by heating a mixture of

	C ₃₂ Hopane Isomerization at C-22		C ₂₉ Sterane Isomerization at C-20		Steroid Hydrocarbon Aromatization		Triaromatic Steroid Cracking (m/z 231)**	
	$A_{\rm H}(s^{-1})$	E _H (kJ mole ⁻¹)	$A_{S}(s^{-1})$	E _S (kJ mole ⁻¹)	$A_A(s^{-1})$	E _A (kJ mole ⁻¹)	A(s ⁻¹)	E(kJ mole ⁻¹)
Basin Studies Mackenzie & McKenzie (1983), Mackenzie <i>et al.</i> (1984) [†]	.025	91	.007	91	1.8 x 10 ¹⁴	200	_	-
Sajgó & Lefler (1986)	.035	87.8	.0024	91.6	-		-	-
Laboratory Simulation Abbott et al. (1984, 1985) [‡]	-	-	-	-	6.7 x 10 ¹²	145	-	-
Hydrous Pyrolysis Zumberge <i>et al.</i> (1984) [§]	.002	33	96	90	-	-	-	-
Hydrous Pyrolysis Lewan <i>et al.</i> (1986)	-	-	-	-	-	-	1.02 x 10 ¹⁷	176

Table V.1. Summary of the empirically determined frequency factors (A) and activation energies (E) for the forward reactions* of the hopane and sterane isomerizations, steroid hydrocarbon aromatization and "alkyl-cracking" (see Figs. V.1 & V.2).

* The temperature dependence of a rate constant "k" is given by the integrated form of the Arrhenius equation $k = Aexp\left(\frac{-E}{RT}\right)$ where R and T

are the gas constant and temperature (°K), respectively, and the other terms are as defined in the table. See Appendix É for details.

[†] Aromatization parameters for the transformation of the C₂₉ monoaromatic to the C₂₈ triaromatic steroid hydrocarbon.

 \ddagger Aromatization parameters for the transformation of the C₂₇ monoaromatic to the C₂₆ triaromatic steroid hydrocarbon.

S Hopane parameters for the C₃₁ hopane (homohopane) rather than the C₃₂ hopane (bishomohopane) isomerization.

** Side-chain cleavage of the C₂₆ - C₂₈ to form the C₂₀ - C₂₁ triaromatic steroid hydrocarbons (see Fig. V.2b).

monoaromatic C₂₇ steroid hydrocarbons with solvent extracted carbonate sediment (Cretaceous, Abu Dhabi) and elemental sulfur to form the C₂₆ triaromatic steroid hydrocarbon (Abbott *et al.*, 1984;1985). Kinetic parameters have also been determined for the cracking of the alkyl-chains on the C₂₆-C₂₈ triaromatic steroid hydrocarbons using data obtained during hydrous pyrolysis of Phosphoria Retort Shale (Lewan *et al.*, 1986) and are included in Table V.1 for comparison.

For the purposes of the following discussion, the kinetic constraints on the hopane and sterane isomerizations are of greatest interest. Comparison of the E and A values for the two isomerizations as determined for basins by Mackenzie and McKenzie (1983) and for hydrous pyrolysis by Zumberge et al. (1984) reveals some significant differences (see Table V.1). The activation energy (E_H) of 33 kJ mole⁻¹ for the laboratory simulated hopane isomerization (Zumberge et al., 1984) is approximately a third of that obtained empirically from downcore data in basins, 91 kJ mole-1 (Mackenzie and McKenzie, 1983; Mackenzie *et al.*, 1984). The frequency factor (A_H) of 0.002 s⁻¹ is also lower, but by an order of magnitude, approximately. For the sterane isomerization, the E_S values of 90 and 91 kJ mole⁻¹ determined from the basin studies and hydrous pyrolysis, respectively, are virtually identical; but the A_S of 96 s⁻¹ from the latter study is significantly higher than the 0.007 s⁻¹ determined from the basin. These differences confirm some of the previous hypotheses (Mackenzie and McKenzie, 1983) that the mechanism of isomerization, particularly of the hopanes, may depend on the thermal regimes (i.e. low geothermal gradients vs. laboratory pyrolyses) of the reactions.

The apparent rapid thermal maturation of biomarkers in the Guaymas Basin subsurface sediments (see Chapter IV; Simoneit and Philp, 1982; Simoneit *et al.*, 1984) and the seabed deposits of the hydrothermal oils (Chapter II) and the high temperatures (125 to 400°C) envisioned for the hydrothermal system (see Chapter IV) suggest that laboratory simulations conducted at high temperatures (e.g. >200°C) may best model the reactions. Application of the kinetic parameters from hydrous pyrolysis, as conducted by Zumberge *et al.* (1984) on Monterey Formation rocks, to the Guaymas Basin hydrothermal samples is also reasonable in view of the initial high water content (Curray *et al.*, 1982) in such Recent sediments and the very nature of the hydrothermal system. In addition, the similarity in organic matter source type of much of the Monterey Formation and the Guaymas Basin sediments (see Chapter IV) further supports such an application.

SAMPLING AND ANALYSES

The isolation, analysis and initial characterization of the hydrothermal seabed oils from the Southern Trough of Guaymas Basin, Gulf of California are described in Chapters II and III. The analyses and descriptions, including overall hydrocarbon contents, of the subsurface sediments from Deep Sea Drilling Project Sites 477 and 478 discussed here are presented in Chapter IV.

The high resolution gas chromatography-mass spectrometry (HRGC-MS) analysis of the steranes, hopanes, and aromatic steroid hydrocarbons in the seabed oils used the Multiple Ion Detection (MID) mode. The relative amounts of these compounds were obtained by integration and selective summation of the ions (base peaks) characteristic of each of the biomarker series. The ions m/z 191, 217, 253 were used to monitor the hopanes, steranes, and monoaromatic steroid hydrocarbons, respectively, while each of the three series of triaromatic steroid hydrocarbons (see Background section) was detected using its respective and characteristic ion: m/z 217, 231, 245. MS dwell times of either 105 or 210 msec per mass (1 amu wide) were used, with the ions monitored in descriptors of 6 to 10 masses each. The composition of these descriptors (total scan times of 1.5 to 2.0 sec each) were set to facilitate computer-controlled time-programming of the masses scanned so as to have them coincide with the expected HRGC elution times of the compounds of interest. Monitoring of the biomarker distributions in the aromatic fractions was concurrent with the quantitation of various polycyclic aromatic hydrocarbons, as described in Chapter III. The HRGC-MS conditions used were similar to those described in Chapter II.

HRGC-MS analysis of the biomarkers in the subsurface sediments of Guaymas Basin used the mass spectrometer in the normal scanning mode. The HRGC details are described in Chapter IV, whereas the MS conditions and data processing were given in Chapter II.

Determining the extent of aromatization of the monoaromatic (base peak m/z 253) to the triaromatic steroid (base peak m/z 231) hydrocarbons was made difficult by their separate elution in the saturated and aromatic hydrocarbon fractions, respectively, during liquid-solid chromatography. The proportions of the two series in each seabed oil or subsurface bitumen was obtained by quantitation of the integrated areas of their base peaks relative to that of an internal standard, perdeuterated anthracene or perdeuterated pyrene (base peaks m/z 188 and 212, respectively), added to each fraction before

HRGC-MS. Other details concerning the analysis and quantitation of various compounds are described in the text and figure/table captions, whenever necessary.

The kinetic equations, parameters, and terminology used for comparison of the biomarker reactions are outlined in Appendix E.

RESULTS AND DISCUSSION

Isomerization and Aromatization Trends

Sterane, Hopane Isomerizations and Steroid Hydrocarbon Aromatizations

The hopane- and sterane-based indices of thermal maturation (see Appendix E for definitions of indices) in a selection of the seabed hydrothermal oils and subsurface sediments from Guaymas Basin and the laboratory simulation at 330°C (Simoneit, 1990) are presented in Table V.2.

In the seabed oils, the extent of isomerization (S_H) at C-22 of the C₃₁ and of the C_{32} 17 α (H),21 β (H)-hopanes are comparable, for the most part, and range from 0.13 through 0.59 (see Table V.2). The hopane isomerization has reached 75% or more of completion [S/(S+R)=0.61 at equilibrium (Mackenzie and McKenzie, 1983)] in over 75% of the seabed oils. The degree of isomerization (S_S) at C-20 in the $5\alpha(H)$, $14\alpha(H)$, $17\alpha(H)$ -C₂₉ steranes in the oils is highly variable but, generally, not as extensive, ranging from 0.047 through 0.53 and the reaction is less than 50% complete [S/(S+R) = 0.54 at equilibrium (Petrov, 1976; van Graas *et al.*, 1982] for more than half of the oils (see Table V.2). The aromatization of the $5\alpha(H)$ and $5\beta(H)$, 20R-C₂₉ monoaromatic to the 20R-C₂₈ triaromatic steroid hydrocarbons has been considerable for most of these petroleums (see Table V.2), with the aromatization parameter (T_A) above 0.50 for all the oils ($T_A=1.0$ at completion). The effectively more advanced stage of steroid hydrocarbon aromatization relative to the sterane isomerization in most of the seabed oils is consistent with the inferred high heating rates in Guaymas Basin. A high heating rate would tend to enhance the aromatization rate, relative to sterane isomerization, since it is the more temperature-dependent reaction according to the estimates of the kinetic parameters, E and A (see Table V.1 and Mackenzie and McKenzie, 1983; Mackenzie et al., 1982b; 1984).

In the subsurface sediments at Sites 477 and 478, the S_H values for the C_{31} and C_{32} hopanes are within the range displayed by the seabed oils (see Table V.2). Unlike for the oils, though, the dissimilarity in S_H values between the C_{31} and C_{32} hopanes appear more significant, with the ratio in the latter always lower. This difference is particularly evident for the sample farthest from the sill, 478-29-1 (60-65), in which the ratios of 0.33 and 0.17, respectively, are also the most immature of the set. Although differences in the rate of isomerization of the two homologs might be responsible, a

Sample	C ₃₁ -Hopane S _H *	C ₃₂ -Hopane S _H *	C ₂₉ -Sterane S _S *	$C_{29} MA \rightarrow C_{28} TA^{\dagger}$
<u>Seabed Oils</u> [‡] 1172-4 1172-1A 1177-2D 1172-2 1172-3 1173-8 1177-2C 1177-4B 1172-1 7D-5A 7D-3B 1173-3 1168-1-2	0.52 0.52 0.50 0.56 0.56 0.52 0.49 0.49 0.49 n.d. 0.43 0.47 0.47 0.31	0.54 0.59 0.45 0.53 0.56 0.54 0.49 0.48 n.d. n.d 0.48 0.40 0.23	0.29 0.53 0.11 0.43 0.40 0.45 0.12 0.15 n.d. 0.059 0.057 0.071 0.047	0.69 0.85 0.59 0.90 0.59 0.85 0.53 0.87 0.98 0.99 0.92 0.56
1168-1-3B	0.13	n.d.	n.d.	-
<u>Downcore</u> § 477-15-1 (120-125) 478-29-1 (60-65) 29-2 (38-43) 29-2 (112-117)	0.58 0.33 0.46 0.46	0.52 0.17 0.35 0.39	0.34 0.048 0.12 0.17	0.92 0.24 0.65 0.54
Lab Simulation**	0.25	0.19	0.061	-

Table V.2. Hopane and sterane isomerization and steroid hydrocarbon aromatization data for seabed oils and downcore sediments (Sites 477, 478) from Guaymas Basin and a laboratory simulation.

n.d. = not detected

- = value not determined due to absence of one compound and/or analytical difficulties.

- * Percentage isomerization calculated using integrated areas of ion intensities of m/z191 and ion intensity heights of m/z 217, for hopanes and steranes, respectively, and $s_{I} = \frac{S}{S + R}$.
- [†] Degree of aromatization calculated using $T_A = \frac{TA}{MA + TA}$ and the areas of the ion intensities *m/z* 253, 231 for the C₂₉ monoaromatic and C₂₈ triaromatic steroid hydrocarbons, respectively.
- [‡] Character of petroleums originally discussed in Chapters II and III.
- [§] Character of downcore sediments detailed in Chapter IV.
- ** Hydrous pyrolysis simulation of 1176-PC2 (Simoneit, 1990) with additional description in Chapter IV.

more reasonable cause is that the coelution of other compounds, such as other triterpanes or triterpanes, might be affecting the ratio. Unsaturated hopenes and other triterpanes have been observed coeluting with the first epimer, 22S of C_{31} (see Chapter II). As a result of such interferences, the S_H ratio of the C_{32} -hopanes is normally preferred for comparisons and will, therefore, be used for the isomerization plots and calculations later in this report.

The T_A values for the downcore sediments range from 0.24 to 0.92 with the highest for 477-15-1 (120-125) and the lowest for the sample farthest from the sill 478-29-1 (60-65), which is consistent with the thermal maturities as reflected by the sterane and hopane isomerizations (Table V.2). The extent of steroid hydrocarbon aromatization in the samples nearer the sill, 478-29-2 (38-43) and (112-117), is intermediate with values of 0.65 and 0.54. The slight decrease in T_A for the sample nearest the sill is not expected, and possible causes are suggested in the following section.

Sterane versus Hopane Plots: Time and Temperature Estimates

Mackenzie *et al.* (1984) used the relationship between extent of steroid hydrocarbon aromatization and hopane and sterane isomerization in sediments to assess maximum temperatures and timing of uplift in basins. While the use of steroid aromatization in their calculations was reasonable, this parameter is most likely unreliable in the case of analysis of pyrolysates produced by hydrothermal systems for a number of reasons. Lewan *et al.*, (1986) reported that the degree of aromatization T_A was different in the expelled oils and bitumen extracts of a hydrous pyrolysate of Phosphoria Retort Shale, and this discrepancy was attributed to the preferential release of the monoaromatic steroid hydrocarbons. Since the hydrothermal seabed oils have been moved to the seabed by both bulk transport and in solution with the hydrothermal fluids (Chapter II), such migrational effects might have affected the index adversely. In addition, the decreased precision and accuracy of the aromatization parameter resulting from the separation of the monoaromatic and triaromatic steroid hydrocarbons into different chromatographic fractions (see Sampling and Analyses section) suggest that the isomerization indices are probably more reliable and, therefore, of greater utility.

The hopane and sterane isomerizations alone cannot be used to estimate the maximum temperatures of reaction if the activation energies (E_I) for the reactions are identical, as is the case for the determinations made by Mackenzie and McKenzie (1983)

(Table V.1). Additionally, the application of their kinetic parameters to high-temperature systems, such as Guaymas Basin is not warranted because of the apparent difference in isomerization mechanisms in low and high-temperature systems, as discussed previously. As a result, the approach taken here is to use the kinetic parameters of the isomerization reactions determined by hydrous pyrolysis of Monterey Formation sediments (Zumberge *et al.*, 1984). The large difference between the determined activation energies for the two reactions (Table V.1) indicates that the relative rates will vary, and the magnitude of the difference will be a function of the temperature. This property will enable the assignment of approximate temperatures to the biomarker distributions formed under the high temperature conditions of Guaymas Basin.

The hopane and sterane isomerization data for the samples listed in Table V.2 and the path that the indices S_S and S_H would follow if the reactions obeyed the kinetic parameters determined by Mackenzie and McKenzie (1983) for non-hydrothermal basins are plotted in Fig. V.3. Although some of the samples do fall near the line, two separate groups appear evident. In one group, the hopane isomerization appears to be faster, relative to the sterane isomerization, than that predicted by the kinetic model; while in the other, the reverse is true. Some of the scatter might be due to the admixture of immature bitumens with the pyrolysates during transport to the seabed. On the other hand, if the mechanisms of the isomerization reactions in the hydrothermal system are modeled better by hydrous pyrolysis, as herein suggested, then the discrepancies are not surprising.

The same data set is presented in Fig. V.4, but the isomerization trends as predicted using the kinetic parameters determined by Zumberge *et al.* (1984) for hydrous pyrolysis are plotted. As these activation energies for the sterane and hopane isomerizations are significantly different (Table V.1), the single trend of isomerization presented in Fig. V.3 is replaced by multiple lines, isotherms (constant temperature, variable time) and isochrons (constant time, variable temperature), obtained using the equations detailed in Appendix E. These lines represent different paths that the isomerizations would follow under various thermal and temporal conditions.

The effective time and temperature estimates for the samples obtainable from the isotherms and isochrons in Fig. V.4 were determined mathematically using the equations provided in Appendix E. The pairs of values so calculated for the various seabed oils, subsurface sediments, and the laboratory simulation are presented in Table V.3. The temperature estimates for the seabed oils range from 270 to 350°C with associated reaction times ranging between 1 and 10 days. These values are not unreasonable in consideration of the temperatures estimated by kerogen data and mineralogies (Chapter



Figure V.3. Sterane versus hopane isomerization (S_S and S_H) trends in the hydrothermal seabed oils (•), subsurface sediments from Sites 477 and 478 (+), and a laboratory simulation (•), SIM) (1176-PC2 Simoneit, 1990). The seabed oils were originally described in Chapters II and III and subsurface sediment characterizations and identifications are found in Chapter IV. The solid line is the path that the isomerizations would follow if the reactions were governed by the kinetic parameters (E_I and A_I) determined by Mackenzie and McKenzie (1983) (see Table V.1). The line was obtained using sterane and hopane equilibrium ratios of $\gamma_S = 1.174$ and $\gamma_H = 1.564$, respectively, and the rate equations as described in Appendix E. The dashed line connects the three samples near the sill at Site 478.



Figure V.4. Sterane and hopane isomerization (S_S and S_H) trends for samples as in Fig. V.3. Single line in previous figure replaced by families of isotherms (-) and isochrons (----) depicting progress of isomerizations expected using kinetic parameters determined by Zumberge *et al.* (1984) for hydrous pyrolysis of Monterey Formation outcrop samples(see Table V.1). The isotherms, in °C, and isochrons, in hours, were plotted using equations detailed in Appendix E and equilibrium ratios of $\gamma_S = 1.174$ and $\gamma_H = 1.564$.

Sample	Temperature (°C)	Time (days)	
<u>Seabed Oils</u> 1172-4 1172-1A 1177-2D 1172-2 1172-3	300 370 270 340 320	7.7 6.1 7.3 4.6 7.0	
1173-8 1177-2C 1177-4B 7D-5A 7D-3B 1173-3 1168-1-2	350 260 280 240 230 260 270	4.7 9.3 7.4 9.3 1.4 6.7 2.4	
Downcore 477-15-1 (120-125) 478-29-1 (60-65) 29-2 (38-43) 29-2 (112-117)	320 291 293 303	5.4 1.3 3.4 3.5	
Lab Simulation	297	1.4	

Table V.3. Temperature (T) and time (t) estimates* for Guaymas Basin seabed oils and subsurface sediments and a laboratory simulation using extent of hopane and sterane isomerizations.

Solutions for T and t determined by solving simultaneously the equations for S_S and S_H as detailed in Appendix E. The kinetic parameters used were those determined by hydrous pyrolysis (see Table V.1), Zumberge *et al.*, 1984). Equilibrium ratios of $\gamma_S = 1.174$ and $\gamma_H = 1.564$ were used. Values for S_S and S_H are given in Table V.2.
IV) and the high temperatures of the venting fluids (occasionally> 330° C, unpublished results). The young C-14 ages of some of the seabed oils (~ 5000 ybp, present identified as 1950 AD; Peter *et al.*, 1990b) further supports a very rapid pyrolysis of shallow sediments. Even though such heating times of < 10 days are reasonable in consideration of the dynamic nature of the hydrothermal system and the inherent rapid advection of pyrolysates away from the heat source, these oils probably also contain biomarker components from lower temperature regimes which have been heated over longer periods of time. In a sense, the calculated temperatures probably represent average to maximum temperatures of reaction for these pyrolysates. Such an interpretation is supported by the data obtained for the subsurface sediments, as discussed below.

Kvenvolden *et. al.* (1988) similarly analyzed the extent of hopane and sterane isomerizations in a hydrothermal petroleum from Escanaba Trough. They were unable to determine a unique time-temperature solution since the kinetic parameters used were determined from sedimentary basins with normal geothermal gradients (Mackenzie and McKenzie, 1983) and are characterized by equal activation energies for the two isomerizations (see Table V.1 and previous discussion). Nevertheless, their analysis did constrain a temperature window of 300-350°C for heating times as short as 100 years. In comparison, the heating times for the Guaymas Basin hydrothermal oils,calculated using kinetic parameters determined through hydrous pyrolysis (Zumberge *et al.*, 1984), were on the order of days for temperatures of <300°C (Table V.3).

The temperature estimates for the four downcore samples range between 291 and 320 °C (Table V.3). The isomerization data for the three samples from Site 478 near the sill suggests that they were exposed to very similar temperatures, increasing from ~290 to 300°C as the sill is approached. Based on bitumen, PAH, and kerogen data (see Chapter IV), the sample farthest from the sill, 29-1 (60-65) was heated very little, if at all, while the sample nearest the sill appeared to have been heated to much higher temperatures. Furthermore, the short time (5.4 days) of heating at a high temperature (320°C), envisioned for sample 477-15-1 (120-125), would seem to contradict the contention in Chapter IV that the sediment interval has been exposed to elevated temperatures (>125°C) and hydrothermal fluid flow for extended periods of time. On the other hand, this lower temperature process does not discount the possibility that the sediment was briefly exposed to a much higher temperature during its history, which might then be preserved in its biomarker signature.

While the previous analysis represents an oversimplification of the thermal maturation of biomarkers in Guaymas Basin, it does provide another means with which to characterize the hydrothermal pyrolysates. Further assessments or interpretations of data with such mathematical methods require that the kinetic parameters be determined through hydrous pyrolysis of organic matter, specifically from Guaymas Basin, to minimize any potential differences in reaction rates resulting from source and/or catalytic effects. Such effects are reasonable in view of the difference between the estimated temperature and reaction times of heating (297°C and 1.4 days; see Table V.3) and the actual conditions (330°C, 1.0 hour) for the laboratory simulation (Simoneit, 1990).

Triaromatic Steroid Hydrocarbons

Distributions in oils and subsurface sediments

The distributions of two series of triaromatic steroid hydrocarbons (m/z 217 and 231) in two seabed hydrothermal oils, 1173-3 and 1172-4, from Guaymas Basin and two crude oils, Jiang Han and North Sea, are given in Fig. V.5. The usual dominance of the m/z 231 series in sediments and oils (Mackenzie *et al.*, 1981a) is exemplified by the latter two oils (see Fig.V.5b,c). The triaromatic steroid hydrocarbons (C26-C28) with long alkyl side-chains are the major components in both of the oils and occur in diastereomer pairs (C-20S and R). The short-alkyl-chain triaromatic steroid hydrocarbons (C20 and C21) also occur but their abundance relative to the long-alkyl-chain counterparts differs in the two oils, possibly as a result of the catagenetically induced cleavage of the alkyl side-chain of the steroid hydrocarbons (see Background section, this chapter).

Unlike the crude oils just discussed, the hydrothermal oils 1173-3 and 1172-4 contain major amounts of triaromatic steroid hydrocarbons with no nuclear methyls (m/z 217), particularly the short-chained components (Fig. V.5a,b). The most prominent compound (DHC) in the m/z 217 series of the 1173-3 oil (Fig. V.5a) is identified as the C₁₈H₁₆ compound, Diels' hydrocarbon [1,2-(3'-methylcyclopenteno)phenanthrene], by comparison of its mass spectrum and retention time with that of the major product derived from laboratory pyrolysis of cholesteryl chloride and selenium (Simoneit *et al.*, 1990a). Other minor components in this m/z 217 series of oil 1173-3 are a second C₁₈ compound, possibly an isomer (methyl position on cyclopenteno-ring unknown) of

Figure V.5. HRGC-MS mass fragmentograms of m/z 217 and m/z 231 depicting the relative distributions of the two series of triaromatic steroid hydrocarbons in two hydrothermal seabed oils: (a) 1173-3 and (b) 1172-4; and two crude oils: (c) Jiang Han and (d) North Sea. The pairs of fragmentograms are normalized within each sample. Compounds characteristic of hydrothermal oils are shaded. Structures are provided for the C₁₇, DHC (Diels' hydrocarbon, C₁₈) and a C₁₈* isomer, and C_{19a}* in the m/z 217 series. Superscript * identifies the unusual series of compounds found in the hydrothermal pyrolysates, while subscripts identify the various isomers. Spectra for these compounds given in Figure V.7. Non-subscripted arabic numerals in m/z 231 series are for the triaromatic steroid hydrocarbons normally dominant in oils (S and R denote configurations at C-20). The long-alkyl-chained-triaromatic steroid hydrocarbons based on mass spectral interpretation).



Figure V.5.

DHC; a homologous $C_{19}H_{18}$ compound; and 1,2-cyclopentenophenanthrene, $C_{17}H_{14}$ (indicated on Fig. V.5 as C_{18}^* , C_{19a}^* , and C_{17} , respectively), with assignments based on preliminary interpretations of the mass spectra. These components have also been found as byproducts of the laboratory synthesis of DHC (heating cholesteryl chloride and selenium; Simoneit *et al.*, 1990a). This suggests that these compounds found in the hydrothermal environment may be commonly sourced through the thermal degradation of steroids. Mass spectra of DHC and C_{19a}^* are provided in Fig. V.7.

In oil 1172-4, the proportion of DHC and the associated hydrocarbons relative to all of the triaromatic steroid hydrocarbons is greater than in oil 1173-3 (cf. Fig. V.5a and b). This former oil is more mature in terms of its sterane and hopane distributions (Table V.2), which suggests that thermal maturation may lead to an increased generation of DHC, C_{18}^* , and C_{19a}^* .

The generation of DHC in large quantities during hydrous pyrolysis has been reported (Rowland *et al.*, 1986b), wherein its proportion increased with increasing pyrolysis temperature at the expense of the other triaromatic steroid hydrocarbons. Hydrous pyrolysis of immature seabed sediments from Guaymas Basin (1176-PC2, Simoneit, 1990) also generated Diels hydrocarbon in an amount similar in quantity to the other triaromatic steroid hydrocarbons (m/z 231), even though the extent of hopane and sterane isomerization in the pyrolysate (see Laboratory Simulation in Table V.2) was less than that in most of the hydrothermal oils.

It is therefore proposed that the formation of triaromatic steroid hydrocarbons at the high temperatures encountered during hydrothermal pyrolysis proceeds with a preferential loss of all nuclear methyls during aromatization and/or an enhanced thermal degradation of the more highly methylated (e.g. m/z 231) series (i.e. m/z 217 series more stable). Increased demethylation during aromatization at high temperatures was previously offered as an explanation for changes in the relative abundances of the m/z245 and 231 series with increasing burial depth in the Paris Basin (Mackenzie *et al.*, 1981a). Increased thermal stability of the m/z 217 series and/or methyl loss from the more alkylated series of triaromatic steroid hydrocarbons were also suggested by Lu and Kaplan (1989) in explanation of the observed increase in relative abundance, and eventual dominance (after 1000 hours), of the former during anhydrous pyrolysis of Cretaceous Black Shale kerogen at 300°C.

The crude and hydrothermal oils also differ in the presence of an unusual series of short-alkyl-chain triaromatic steroid hydrocarbons of the m/z 231 type in the latter, which predominate over the 20- and 21-carbon (marked as 20 and 21 in Fig. V.5)

compounds normally found in oils. These unusual compounds, indicated as C_{19b-d}^* and C_{20}^{*} in Fig V.5, have mass spectra similar to those of the other compounds with base peak m/z 231. The spectra of these unusual compounds (Fig. V.7e-h) can be compared with the spectra of the 20- and 21-carbon triaromatic steroid hydrocarbons (Fig. V.7a,b) normally found dominant in oils, but relatively less abundant in the hydrothermal deposits (cf. Figs V.5a,b with c,d). The various isomers of the C_{19}^* compounds (m/z 231 series) may differ in the position of the nuclear methyl group, perhaps on ring-A or ring-C rather than at position C-3' on the cyclopenteno-ring (C-17 on the steroid skeleton). The HRGC elution pattern of the multiple isomers of these unusual C_{19}^* compounds and the single isomer of the unknown C_{20}^* compound in the m/z 231 series is strikingly similar to that of the short-alkyl-chain compounds in the m/z 217 series (Fig.V.5). This suggests that the C_{18}^* (Diels hydrocarbon), and C_{19a}^* in the m/z 217 series and the C_{19b-d}^* and C_{20}^* compounds in the m/z 231 series may be related structurally and were possibly generated in a similar manner. As already noted, these compounds of possible similar origin and, apparently, characteristic of the hydrothermal process at the seabed are all marked with a superscript asterisk in the figures and following tables and text.

The distributions of the two series of triaromatic steroid hydrocarbons (m/z 217) and 231) in the subsurface sediments from DSDP Sites 477 and 478 (see Chapter IV) in Guaymas Basin are presented in Fig. V.6. The distributions in the two samples farthest from the sill, 29-1 (60-65) and 29-2 (38-43), at Site 478 (see Fig. V.6 a,b) are dominated by the long-alkyl-chained compounds (C_{26} - C_{28}) of the m/z 231 series. DHC and the 20- and 21-carbon compounds are observed as only traces compared with the previous series. In the sample nearest the sill, 29-2 (112-117), the dominant triaromatic steroid hydrocarbon is DHC (Fig. V.6c). This is consistent with the greater thermal maturation next to the sill as suggested by the PAH data and the biomarker distributions (see Chapter IV and Table V.2). The other compounds not identified in the m/z 217 mass fragmentogram of this sample are various methyl pyrenes/fluoranthenes and/or benzofluorenes (base peak m/z 216). The triaromatic steroid hydrocarbon distribution in sample 15-1 (120-125) from Site 477 (see Fig. V.6d) is once again dominated by the C_{26} - C_{28} components of the m/z 231 series but also contains significant concentrations of the 20- and 21-carbon analogs and some DHC. Triaromatic steroid hydrocarbons were not detected in samples from greater depths at Site 477.

The prevalence of DHC and the unusual series of C_{19a-d}^* and C_{20}^* compounds in the hydrothermal seabed oils, but their relative absence in the downcore bitumens is

Figure V.6. HRGC-MS mass fragmentograms of m/z 217 and m/z 231 depicting the relative distributions of the two series of triaromatic steroid hydrocarbons in subsurface sediments (see Chapter IV): (a) 478-29-1 (60-65), (b) 478-29-2 (38-43), (c) 478-29-2 (112-117), and (d) 477-15-1 (120-125). Key as in Fig. V.5. Site 478 sample locations relative to sill given in meters above sill (mas). Site 477 sample depth given in meters below seafloor (mbsf).



Figure V.7. HRGC-MS mass spectra (electron-impact mode) of selected triaromatic steroid hydrocarbons including the 20- and 21-carbon compounds normally found in crude oils (a), (b), respectively, and the unusual series of compounds found in the hydrothermal oils (c) Diels' hydrocarbon, DHC*; (d) C_{19a}^* ; (e) C_{19b}^* ; (f) C_{19c}^* ; (g) C_{19d}^* ; and (h) C_{20}^* . Compound elution order as in Fig. V.5.



Figure V.7.

difficult to explain. Possible explanations are: a) their formation and persistence are within a time-temperature window not sampled during this study; b) the hydrothermal process leads to a concentration of these compounds at the seabed; and c) the precursor of these compounds is limited to near-surface sediments. The last reason may be process-oriented in that the inferred formation of these compounds from steroid precursors might require the unsaturated or functionalized analogs (e.g. steradienes, sterols) more prevalent at the seabed than at greater depths in the seabed. Hydrothermal pyrolysis of such compounds could then lead to a preferential complete removal of the nuclear methyls akin to that observed during the pyrolysis of cholesteryl chloride and selenium (Simoneit *et al.*, 1990a). Alternatively, the actual source of these compounds may be algal in origin but unrelated to the C_{27} - C_{29} steroids and only present in specific sediments of Guaymas Basin. In this respect, DHC is a relatively minor component of the triaromatic steroid hydrocarbons in hydrothermal petroleum from Escanaba Trough (Kvenvolden and Simoneit, 1990).

Triaromatic Steroid Hydrocarbon Indices

Various indices of thermal maturation, based on the relative distributions of the triaromatic steroid hydrocarbons, of the hydrothermal seabed oils and subsurface sediments from Guaymas Basin, a lab simulation (Simoneit, 1990), and the two crude oils are presented in Table V.4. The alkyl-cracking index (ACI), as defined, is a measure of the relative percentage of the short-alkyl-chain (C₂₀ and C₂₁) in the total m/z231 series of compounds normally found in crude oils. This index increases from 0.04to 0.36 as the sill is approached at Site 478 consistent with the inferred cracking of the alkyl-chain at high thermal maturity. The level attained in sample 477-15-1 (120-125) is 0.16 and is intermediate between the two extremes. In the hydrous pyrolysis of Phosphoria Retort Shale for 72 hours, Lewan et al. (1986) observed this index to be \leq ~0.40 at temperatures $\leq 310^{\circ}$ C. Such temperatures for the sample nearest the sill are not inconsistent with the general range estimated by mineralogies (see Chapter IV) or that from the degree of sterane and hopane isomerizations (see Table V.3). The ACI values in the seabed oils are highly variable ranging from 0.05 to 0.68 with "infinity" obtained for 1168-1-3B (only short alkyl-chained components were evident), which was interpreted as possibly being a biodegraded condensate (see Chapters II,III;). The high variability might be the result of preferential transport of the C₂₀ and C₂₁ components by the hydrothermal fluids in addition to pyrolytic effects of different thermal regimes. On

Sample	ACI† 20+21 20+21+26+27+28	$\frac{\text{TSI}_1^{\ddagger}}{\frac{m/z}{m/z}\frac{217}{231}}$	$\frac{\text{TSI}_{2}^{\$}}{\frac{C_{19}^{*}+C_{20}^{*}}{20+21}}$	DHI ₁ †† <u>DHC</u> * 20+21	DHI ₂ ^{§§} DHC*+C* 20+21	DHC* <u>µg</u> mg-arom	DHC* <u>µg</u> mg-bitumen	DHC* <u>µg</u> g-sed	DHC* ng mg-Corg
Seabed Oils									
1172-4	0.19	0.82	3.29	4.70	8.70	1.2	0.15	-	-
1172-1A	0.48	1.17	3.07	4.71	8.53	2.0	0.40	-	· _
1177-2D	0.24	0.76	2.64	3.19	6.45	0.66	0.18	-	-
1172-2	0.29	0.77	2.82	3.23	6.69	1.1	0.19	-	-
1172-3	0.56	1.26	3.34	5.24	9.42	3.0	0.53	-	-
1173-8	0.24	0.75	2.92	3.66	7.16	1.9	0.46	· _	-
1177-2C	0.16	0.59	2.44	2.52	5.52	0.47	0.12	-	-
1177-4B	0.05	0.44	3.10	2.59	6.34	0.29	0.045	·	-
1172-1	0.68	1.16	3.38	4.66	8.80	4.1	1.4	-	-
7D-5A	0.36	0.84	2.99	3,80	7.38	4.0	1.0	-	-
1173-3	0.10	0.48	2.86	2.98	6.35	0.95	0.11	-	-
1168-1-2	0.26	0.30	1.56	0.32	2.19	0.23	0.036	-	-
1168-1-3B	~~	0.70	1.41	1.30	3.09	0.057	0.004	-	-
Downcore									
477-15-1 (120-125)	0.16	0.17	0.06	0.37	4.41	0.14	0.021	0.033	3.1
478-29-1 (60-65)	0.04	0.24	0.11	0.17	0.40	0.039	0.001	0.007	0.31
29-2 (38-43)	0.08	0.21	0.22	0.33	0.67	0.14	0.008	0.055	2.7
29-2 (112-117)	0.36	2.78	0.00	6.86	7.52	0.62	0.10	0.037	2.4
Lab Simulation	0.17	0.33	1.95	2.28	4.41	-	-	-	-
Crude Oils						-			
Jiang Han	0.06	0.21	0.00	0.34	0.45	-	-	-	-
North Sea	0.26	0.29	0.12	0.54	0.84	-	-	-	-
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Table V.4. Triaromatic steroid hydrocarbon data and maturation indices for seabed oils and downcore sediments (Sites 477, 478) from Guaymas Basin, a laboratory simulation, and two crude oils.

DHC = Diels' hydrocarbon (for these numbers, the C_{18}^* isomer is included); also identifies triaromatic steroid hydrocarbons (C_{19}^* and C_{20}^*) in both m/z 217 and m/z 231 series of apparently similar origin to Diels' hydrocarbon.

ŧ ACI = Alkyl-cracking index of the triaromatic steroid hydrocarbons. Arabic numerals refer to carbon skeleton size in the m/z 231 series normally found in oils.

ł $TSI_1 = Triaromatic Steroid Index 1$. Ratio of total m/z 217 series to m/z 231 series.

 $ISI_1 = Instrumento Staront Index 1.$ Ratio of the sum of the unusual C_{19}^{*} and C_{20}^{*} triaromatic compounds in the *m/z* 231 to the sum of the unusual C_{19}^{*} and C_{20}^{*} triaromatic compounds in the *m/z* 231 to the sum of the two 20- and 21-carbon triaromatic steroid hydrocarbons normally found in oils. DHI₁ = Diels' Hydrocarbon Index 1. Ratio of the sum of the two Diels' HC isomers to the 20- and 21-carbon triaromatic steroid hydrocarbons in the *m/z* 231 series. 5

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^{\$§} DHI₂ = Diels' Hydrocarbon Index 2. Ratio of the sum of Diels' HC (+ isomer) and the C₁₉*-C₂₀* components of m/z 217 and 231 series to the sum of the 20- and 21-carbon compounds of the m/z 231 series.

NOTE: Calculation of indices used integrated areas of the base peaks (e.g. m/z 217, 231) for each compound. Determination of DHC concentrations used area of m/z 217 for DHC and the response factors for the internal standards d₁₀-pyrene or d₁₀-anthracene based on the areas of their molecular ions (m/z 212 and 188, respectively).

the other hand, Lewan *et al.* (1986) found no difference in this index between the expelled oils and extracted bitumens of the hydrous pyrolysate even though significant differences were found in the degree of aromatization (see earlier discussion) in the two types. This suggests that a preferred migration of the short-alkyl-chained components paralleling that invoked as an explanation of the latter results may not be as important.

Finally, the inference (see earlier discussion) that changes in ACI are due to formation of the C₂₀ and C₂₁ from the C₂₆ - C₂₈ homologs by cracking of the alkyl chain on the latter might be in error. Recently, Beach *et al.* (1989) studied the thermal alteration of the C₂₀ and C₂₈ compounds by heating the compounds, together and separately, on bentonite at 200°C. They did not observe any formation of the C₂₀ and C₂₁ compounds from the C₂₈ homolog, but, rather, a more rapid thermal degradation (loss) of the long-chain compound relative to the short-chain homolog. Applied to sediments, this suggests that no conversion of the long-chain to the short-chain triaromatic steroid hydrocarbons occurs during maturation. This inference does not diminish the utility of indices such as ACI, since the changes in relative amounts of these compounds are still indicative of thermal effects.

The index based on the ratio of the m/z 217 to the m/z 231 series of triaromatic steroid hydrocarbons is highest (TSI₁=2.78) in the sample next to the sill, 478-29-2 (112-117) (see Table V.4), consistent with the suggested greater stability of the former compounds at high temperatures (see earlier discussion). The values of 0.21 and 0.24 for the two samples farther from the sill, 29-1 (38-43) and 29-2 (112-117), are much lower and not different from the values for the two crude oils, Jiang Han and North Sea, 0.21 and 0.29, respectively. The even lower value of 0.17 for the sample from Site 477, 15-1 (120-125), is puzzling. This sample has a more mature biomarker distribution than the sample nearest the sill (see Table V.2). On the other hand, it has lower concentrations of PAH and is less thermally altered based on the phenanthrene indices (see Chapter IV). This discrepancy cannot be explained presently and questions the utility of this index. The values in the seabed oils range from 0.33 to 1.17, thus never exhibiting either of the two extremes found in the subsurface sediments.

 TSI_2 is a measure of the ratio of the unusual series of C_{19b-d}^* and C_{20}^* to the C_{20} and C_{21} triaromatic steroid hydrocarbons of the m/z 231 series (see Figs. V.5,6). The index values range from 1.41 to 3.38 in the seabed oils and 0 to 0.22 in the subsurface sediments (see Table V.4). The lowest ratios, 0 and 0.06, in the latter set are for the two most thermally altered samples 477-15-1 (120-125) and 478-29-2 (112-117), respectively, and are not distinguishable from the values for the two crude oils Jiang

Han and North Sea, 0 and 0.12, respectively. The seabed oils are very enriched in the unusual series of the short-chained m/z 231 triaromatic steroid hydrocarbons relative to the two oils and to the hydrothermally altered subsurface sediments. TSI₂ does not account for the compounds of the m/z 217 series (DHC and C_{19a}^*) which are inferred to be related to the C_{19b-d}^* and C_{20}^* compounds of the m/z 231 series (see earlier discussion). The apparent inconsistencies of this index might, therefore, be due to a genetic relationship between these unusual compounds in the two series, which is excluded from the index as it is defined. This is supported by the examination of the last two indices, DHI₁ and DHI₂.

 DHI_1 and DHI_2 are the ratios of DHC (including the $\text{C}_{18}{}^*)$ and the sum of all the unusual compounds (DHC, C_{18}^* , C_{19a-d}^* , C_{20}^*) to the 20- and 21-carbon m/z 231 triaromatic steroid hydrocarbons normally found in crude oils, respectively (see Figs. V.5,6). The DHI₁ and DHI₂ values are consistently high in almost all of the seabed oils, with ranges of 0.32 - 5.24 and 3.09 - 9.42, respectively. These values are significantly higher than those for the Jiang Han and North Sea crude oils (see Table V.4). At Site 478, DHI₁ and DHI₂ increase from 0.17 to 0.686 and 0.40 to 7.52, respectively, as the sill is approached, consistent with the thermal stress envisioned near the sill (see Chapter IV). Both indices appear to be good indicators of hydrothermal alteration, except for sample 477-15-1 (120-125). Its DHI_2 value of 4.41 is within the range of the seabed oils and very different from the two crude oils (see Table V.4). On the other hand, the DHI_1 value of 0.37 for this sample is almost identical to the values of 0.34 and 0.54 for the two crude oils. As discussed earlier, the thermal maturity of this sample based on biomarker distributions and PAH concentrations is significantly different in comparison to the maturation found for the sample nearest the sill at Site 478. As such, the difference between DHI_1 and DHI_2 for other cases similar to this sample may serve as a "flag" of such occurrences. Although the actual cause cannot as yet be determined, possible differences in heating rate or migrational effects are suggested.

Overall, DHI₂ which includes all of the unusual triaromatic steroid hydrocarbons identified in this report (see Figs. V.5-7), displays the most consistent trends with hydrothermal maturation and may be a useful indicator of such processes. In addition, maturation indices based on only the short-alkyl-chained homologs would be superior to those based on the total distributions of the triaromatic steroid hydrocarbons as the short-alkyl-chained components are more persistent over a broader range of alteration (not as susceptible as the long-alkyl-chained homologs to thermal degradation, see earlier

discussion). Also, such indices would be less affected by migrational influences since the components of these indices should have similar properties and be transported equally.

DHC concentrations (both aromatic- and bitumen-based) in the hydrothermal petroleums at the seabed and in subsurface sediments are also presented in Table V.4. The seabed oils contain between 0.057 and 4.1 μ g of DHC/mg-aromatics, and the compound is often the dominant resolved aromatic hydrocarbon in the samples with the higher concentrations. The concentrations in the subsurface sediments range between 0.039 and 0.62 μ g/mg-aromatics and are in the lower range of the seabed concentrations. Approximately, half of the seabed oils are more enriched in DHC than the subsurface sample with the highest concentration, 478-29-2 (112-117) closest to the sill (see Table V.4). On a total bitumen basis, an increasing number of the seabed oils are enriched in DHC relative to the subsurface sediments, with ranges of 0.004 to 1.4 and 0.001 to 0.10 µg/mg-bitumen in the two sets, respectively. These higher concentrations of DHC in the seabed hydrothermal oils confirm the earlier qualitative observation that the triaromatic steroid hydrocarbon distributions of the seabed oils contain higher proportions of DHC and the unusual series of C_{19a-d}^* and C_{20}^* compounds than the subsurface sediments (see Figs. V.5,6 and associated discussion). Although Hoffman (1984) reported that DHC is generally considered to be low in reservoir oils, actual concentrations for comparison with the hydrothermal oils are presently not available.

Concentrations of DHC on a dry sediment and C_{org} basis are limited to the four subsurface samples (see Table V.4). The lowest concentration of 7 ng/g-sediment is found in the least mature sample, 478-29-1 (60-65), farthest from the sill. The two samples closest to the sill 29-2 (38-43) and (112-117) and the sample 15-1 (120-125) have significantly higher concentrations comparable to each other, 55, 37 and 33 ng/gsediment, respectively. The concentrations on a C_{org} basis mirror those based on dry sediment, with the least mature sample containing 0.31 and the other three samples averaging 2.7 ± 0.4 ng/mg-C_{org} of DHC. The results do not appear to contradict the previous interpretations, but the limited data precludes any definitive assessments.

Although the combination of DHI_1 and DHI_2 appears to monitor the hydrothermal alteration (maturation) of organic matter best, the possibility of a source-dependent factor (see earlier discussion) cannot be ruled out. Future research should include a comprehensive assessment of these indices and the concentrations of DHC in both crude oils and source rocks of different origins. Additionally, monitoring of these indices and

DHC production during hydrous pyrolysis simulations is required. Such data would further our understanding of the time-temperature relationships constraining the formation of this unusual series of triaromatic steroid hydrocarbons and, thereby, better assess the utility of maturation indices based on the occurrence of these compounds.

CONCLUSIONS

The hydrothermal pyrolysis of immature organic matter in Guaymas Basin results in a rapid maturation of the biomarkers. Most of the seabed deposits of the hydrothermal oils contain sterane and hopane distributions exhibiting extensive isomerizations, consistent with the high thermal gradients in the basin and the high temperatures of the hydrothermal fluids venting at the seabed.

This hydrothermal maturation of biomarkers is suggested to be similar to that produced by hydrous pyrolysis of organic matter during laboratory simulations. Using the kinetic parameters of the sterane and hopane isomerization reactions so determined by Zumberge *et al.* (1984), estimates of the average to maximum temperatures of pyrolysis were obtained for the hydrothermally generated petroleums. The calculated temperature range of 230 to 370°C with reaction times of 1 to 10 days is reasonable in view of the dynamic nature of the hydrothermal process and the temperature estimates based on mineralogies and kerogen (see Chapter IV). On the other hand, the calculated time of reaction for a single laboratory pyrolysis of Guaymas Basin organic matter was significantly longer than the actual time (1.4 days versus 1 hour) even though the temperatures were not too different (297 versus 330°C, actual). Such a difference suggests that the character of the source matter may also be an important factor.

Characterization of the triaromatic steroid hydrocarbons in the hydrothermal oils and subsurface sediments has identified Diels hydrocarbon and an apparently related series of unusual C_{18} to C_{20} triaromatic steroid hydrocarbons. The reported similar occurrence of Diels hydrocarbon in a hydrous pyrolysis experiment and its high concentration in the hydrothermal oils suggests that it may be a good tracer of hydrothermal processes. Several maturation indices for high temperature and hydrous processes, based on the occurrence of this unsual series of short-alkyl-chained triaromatic steroid hydrocarbons, have been formulated. Their applicability on a wider basis than Guaymas Basin is uncertain since source matter may also be an important variable. A comprehensive assessment of the occurrence of DHC and the related compounds in sediments and crude oils is required before their true significance can be ascertained.

VI. SUMMARY OF CONCLUSIONS

The organic geochemical characterization of the seabed deposits of hydrothermal petroleums in the Southern Trough of Guaymas Basin, Gulf of California and the bitumens of hydrothermally altered subsurface sediments has resulted in the following observations and conclusions:

- -The hydrothermal petroleum deposits exhibit great variability in both their character and quantity of organic matter, which is attributed to variable pyrolysis temperatures; compositional fractionation during transport due to fluctuating thermal gradients and migration velocities, differential gaseous solubilization, and hydrodynamic alteration of the fluids; and selective solubilization, condensation, and solidification during quenching at the seabed.
- -The pyrolysates are similar to reservoir petroleums in often having broad *n*-alkane distributions with no carbon-number-predominance and biomarkers in their thermally stable configurations.
- -Many samples differ from normal oils in containing higher concentrations of polar compounds, variable amounts of the immature biomarkers (e.g. unsaturated triterpenes), and possibly residual seabed bitumens.
- -These seabed oils contain variable amounts of both diagenetic and catagenetic (pyrolytic) PAH. They contain higher concentrations of unalkylated PAH than normal oils, particularly the heavier components (pyrene, benzo(ghi)perylene, coronene), which is consistent with them being formed at higher temperatures.
- -The high sedimentary concentrations of these parent PAH are comparable to those in highly polluted and industrialized areas. The possible enhanced bioavailability of the toxic and carcinogenic PAH associated with the hydrothermal petroleums suggests that toxicological effects on the benthic communities might be significant.
- -Exposed deposits of these petroleums can be heavily altered by water-washing and biodegradation which result in the loss of the more soluble/volatile components and selective degradation of *n*-alkanes, respectively.
- -Increased hydrothermal alteration with depth at DSDP Site 477 results in a progressive change in the HRGC-resolvable fractions of the bitumens from *n*-alkane- to PAH-dominated distributions with the deepest fractions containing only unalkylated PAH (dibenzothiophene and phenanthrene dominant).
- -Both increased thermal stress with depth and the passage of hydrothermal fluids through these subsurface sediments are important for establishing the observed patterns.

- -The aliphatic and aromatic components of the seabed petroleums can be transported to the seabed independently as a result of their formation at different depths or within dissimilar thermal regimes.
- -The PAH contents of the seabed petroleums are consistently more depleted in the low molecular-weight (e.g. phenanthrene) and more soluble compounds than the subsurface bitumens. This observation is attributed to non-deposition during venting of high temperature fluids and post-depositional removal by waterwashing of the lower molecular weight PAH.
- -The biomarker maturation in the hydrothermal system is thought to be most similar to that observed during laboratory hydrous pyrolyses. Estimated temperatures of pyrolysis based on the kinetic parameters so determined range between 230 and 370°C with times of reaction of ~1 to 10 days, which is not unreasonable based on the nature of the hydrothermal system.
- -Diels' hydrocarbon and an apparently related series of C_{18} through C_{20} triaromatic steroid hydrocarbons are important constituents of the hydrothermal petroleums, and it is hereby suggested that they may be good tracers of such hightemperature and hydrous organic matter alterations. Several new maturation indices for high-temperature and hydrous processes have been formulated based on the occurrence of this unsual series of short-alkyl-chained triaromatic steroid hydrocarbons.

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APPENDICES
APPENDIX A

Quantitation Methodology

Calculation of Concentrations

The concentration of a component X in a sample is calculated by first determining the total amount of X and then normalizing to a specific aspect of the sample (e.g. dry sediment weight, total bitumen, mg- C_{org}). The amount of X is given by the equation:

$$Amount_{X} = \frac{Amount_{IS}}{Area_{IS}} \times Area_{X} \times RRF_{X}$$

where	Amount _{IS} =	the amount by weight of internal standard (e.g. perdeuterated anthracene, pyrene) added to the solution immediately before sample analysis by either HRGC or HRGC-MS.							
	Area _{IS} =	integrated area of detector response to the internal standard. This can be either a total ion signal as measured by the flame ionization detector (FID) during HRGC or the intensity of a specific and characteristic mass fragment (e.g. m/z 188, 212) of the compound as detected by the electron multiplier during HRGC-MS.							
	Area _X =	integrated area for the compound of interest with the signal source as described above.							

 RRF_{X} = relative response factor for the compound X as defined below.

The relative response factor (RRF_X) for a compound X is determined by analyzing a standard mixture containing known concentrations of that compound X and the other compounds to be used as internal standards added to the samples before analysis. The concentration of internal standard in the standard mixture does not have to be identical to that in the samples; although the more similar the two are, the more accurate the results will be. Accuracy is also improved if the amount of internal standard added and the compounds to be quantitated in the samples are similar. In the standard mixture, the critical factor is the amounts of the standards relative to the internal standard and not the absolute concentrations. The RRF_X is calculated using the following equation:

$$RRF_X = \frac{RF_{IS}}{RF_X}$$

where the response factors for the internal standard (RF_{IS}) and component of interest (RF_X) are as defined below:

$$RF_{IS} = \left(\frac{Area_{IS}}{Amount_{IS}}\right)_{STD} =$$

$$RF_{X} = \left(\frac{Area_{X}}{Amount_{X}}\right)_{STD} =$$

the integrated area divided by the amount of internal standard in the standard mixture, with area as defined earlier.

the integrated area divided by the amount of component of interest in the standard mixture.

Area vs. Height

Calculations of concentrations can use either integrated peak areas or peak heights of detector response, and both methods are currently in use. In order to compare the results of the two methods, a suite of *n*-alkanes (n-C₁₈-C₃₂) in a mature hydrothermal petroleum (smooth distribution with no odd-to-even carbon number predominance) was analyzed using both HRGC and HRGC-MS. The relative concentrations of the compounds were determined using the response of a flame ionization detector (FID), common in HRGC analyses, and the reconstructed ion current (RIC) and mass fragment (m/z 99) intensities obtained by HRGC-MS. Figure A.1 contains the results of this comparison.

The FID response from HRGC is considered to be the most reliable measure of the amount of a compound (gC). The FID response curve (relative intensity) for this suite of *n*-alkanes (see Fig. A.1a) is very smooth and continuous. The distribution of the relative intensities for this same suite of compounds determined using the integrated areas of the RIC signal (See Fig. A.1a) from HRGC-MS is also quite smooth and compares very well with that for the FID response. On the other hand, the curve generated using the RIC heights, rather than areas, is quite different, which results in an apparent predominance of *n*-alkanes with an odd-carbon chain length between *n*-C₂₀ and *n*-C₂₄. This difference between area-determined and height-determined concentrations is even more pronounced when the detector response of a specific ion (m/z 99) is used. Figure A.1b contains the area and height responses for m/z 99, characteristic mass



Figure A.1. Comparison of FID (HRGC) and HRGC-MS detector responses to a suite of *n*-alkanes (n-C₁₈ to n-C₃₂): (a) FID area and RIC area and height responses; (b) mass fragment m/z 99 area and height responses.

fragment of *n*-alkanes, for the same suite of compounds. The response curve generated with the integrated m/z 99 areas is not quite as smooth as either the curve for the areadetermined FID responses or the area-determined RIC response (cf. Fig. A.1a and A.1b). It is, though, a more comparable measure than that generated using the m/z 99 heights (see Fig. A.1b), which gives the most pronounced deviations from the smooth curve of relative intensities as measured by the FID (Fig. A.1a).

The apparent discrepancy between the FID and HRGC-MS and area- and heightdetermined results is due to the analog/digital sampling differences between the two systems. While the FID provides a virtually continuous monitor of the ion signal, the HRGC-MS detection and monitoring are constrained by the scan rate and mass range over which detection of the ions is desired. For example, during HRGC-MS, a mass range of 50-650 amu and total scan rate of 2.0 s per cycle limits the monitoring of the mass fragment m/z 99 to 3.33 ms once every 2.0 s cycle. On the other hand, the analog signal from the FID during HRGC is continuously sampled and converted to digital format using 12.5 ms time slices, which are then summed to produce continuous 50 ms wide "area" slices. These may then be further bunched or processed depending on integrator settings. The FID gives a much more continuous monitoring of the total ion signal than that possible with HRGC-MS and typical scanning modes. It is possible, therefore, that the analyses by HRGC-MS may "miss" critical aspects (e.g. apex, shoulder) of a chromatographic peak due to insufficient sampling, which would result in poor accuracy and precision. Both area-determined and height-determined responses from HRGC-MS are susceptible to these sampling errors, but the errors are less pronounced for the former. The height-method uses the ion(s) intensity of a single scan which appears to be the apex of a chromatographic peak but may not be, due to too infrequent sampling of the signal. In the area-method, the individual "height" measurements of a number of scan samples over the temporal extent of the chromatographic peak are summed; this minimizes the error inherent in using a single scan height measurement. The area-method is also superior for comparing concentrations of compounds whose chromatographic peak-widths differ. In addition, the previous discussion was based on quantitation of a single HRGC-MS run, as is often the case in organic geochemistry. The errors associated with the sampling rates would probably be reduced if repetitive HRGC-MS runs were completed, and the signal (compound distributions and/or concentrations) was averaged.

The accuracy and precision of the calculations using the area-method with HRGC-MS improves with increasing width of the chromatographic peaks (i.e. more samples per peak). Analogously, increasing the scan rate (e.g. 50-650 amu in 1.0 s) also improves the results since more samples of the ion(s) signal will be taken from each chromatographic peak. Unfortunately, this change also results in decreased sensitivity for a specific ion, which can only be compensated for by decreasing the range of masses scanned. The chromatographic peak width is dependent on the nature of the compound (polar vs. apolar), GC oven temperature program, carrier gas flow rate, and the type of capillary column. The scan rate and mass range should be chosen to provide data for the ions of interest and optimize the sampling frequency for a given set of chromatographic conditions. This will ensure the best possible accuracy and precision in quantitation.

Almost all of the concentrations presented in this thesis were determined using the area-method and specific mass fragment intensities from HRGC-MS. Occasionally, peak heights were used to determine relative contributions of two peaks not fully resolvable by the integration methods in the HRGC-MS data system.

APPENDIX B

Mass Spectra of Unknowns

The spectra of a number of unknown compounds (U1-U3) found in the aromatic fraction of the sample farthest from the sill, 478-29-1 (60-65) (see Fig. IV.8a) are given in (a) through (c), respectively The compounds a) U1 and b) U2 seem to be related. The minor series of ions m/z 57, 71, 85 etc. in (b) appear to be from a trace of a coeluting *n*-alkane that has bled over from the aliphatic fraction during adsorption chromatography. The spectra of an unknown compound (Cn2) found in the total extract of sample 477-19-1 (130-135) (see Fig. IV.3f) is presented in (d). Initial interpretation suggests that the coumpound contains a phenyl-carbonyl moiety with the attached group unknown. This compound is most likely a contaminant of shipboard origin, since it was not a significant component of the procedural blank.



APPENDIX C

PAH Concentrations in Subsurface Sediments

A tabulation of the concentrations of selected parent PAH in the downcore sediments at DSDP Site 477 and 478 is presented. The concentrations are given on both a dry sediment and C_{org} basis.

		470		- 478.20.2 1 478.20-2		8-29-2	477-15-1		477-16-2		477-16-4		477-17-1		477-19-1*		
		4/8-29-1		4/8-29-2		(112-117)		(120-125)		(145-150)		(130-135)		(145-150)		(130-140 comb)	
		ng	ng	ng	ng	ng	ng	ng	ng	ng	ng	ng	ng	ng	ng	ng	ng
мw	COMPOUND	g-sed	mg-CORG	g-sed	mg-C _{ORG}	g-sed	mg-C _{ORG}	g-sed	mg-C _{ORG}	g-sed	mg-C _{ORG}	g-sed	mg-C _{ORG}	g-sed	mg-C _{ORG}	g-sed	mg-CORG
184	Dibenzothiophene	1.2	0.053	2.5	0.12	98	6.3	55	5.2	28	3.7	400	52	410	52	250	83
178	Phenanthrene	4.1	0.190	4.1	0.20	830	53	420	40	270	35	1400	180	1500	190	620	210
178	Anthracene	0.75	0.034	n.d.	n.d.	73	4.6	11	1.1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
202	Fluoranthene	7.0	0.32	8.2	0.40	160	10	180	17	49	6.4	160	20	120	15	26	8.7
202	Pyrene	16	0.72	24	1.2	480	31	450	43	130	17	330	44	230	29	32	11
228	Benz(a)anthracene	8.4	0.38	17	0.82	290	19	130	12	13	1.7	-	-	-	-	9.5	3.2
228	Chrysene/Triphenylene	10	0.48	45	2.2	500	32	880	83	360	47	830	110	700	90	83	28
252	Benzofluoranthenes	18	0.81	11	0.54	100	6.4	320	31	170	22	260	35	230	30	36	12
252	Benzo(e)pyrene	17	0.78	30	1.50	96	6.1	390	36	210	27	280	37	220	29	20	8.0 L
252	Benzo(a)pyrene	13	0.58	13	0.63	43	2.7	38	3.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.
252	Perylene	1400	64	190	9.2	5.9	0.37	61	5.8	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.
276	Indeno(c,d)pyrene	13	0.61	n.d.	n.d.	14	0.88	27	2.6	16	2.1	20	2.7	22	2.9	3.2	1.7
276	Benzo(g,h,i)perylene	130	5.70	89	4.4	56	3.6	180	17	130	16	120	16	88	- 1	1.0	2.5
276	Anthanthrene	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.a.	n.a.	n.a.	n.u. 0.1
278	Dibenz(a,h)anthracene	1.1	0.049	2.1	0.10	23	1.5	30	2.8	18	2.4	45	5.9	3/	4./	0.4	2.1
300	Coronene	11	0.51	10	0.51	8.8	0.56	37	3.5	34	4.4	22	2.9	19	2.4	4.0	1.5
302	Dibenzo(a,e)pyrene	5.9	0.27	3.6	0.18	15	0.96	34	3.2	52	6.8	36	4.7	29	3.8	5.5	1.8

Concentrations of selected PAH in downcore sediments at DSDP Sites 477 and 478.

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n.d. = not detected - = not resolvable from Chrysene/Triphenylene by HRGC-MS. * = 477-19-1 (130-135) and 477-19-1 (135-140) combined before analysis by HRGC-MS.

APPENDIX D

Histograms of PAH Concentrations in Bitumens of Subsurface Sediments and Seabed Petroleums

Histograms of the concentrations (ng/mg-bitumen) of PAH in the seabed hydrothermal petroleums (a-m,o), bitumens of the subsurface sediments from DSDP Sites 478 (n,p-q) and Site 477 (r-u,w). The histogram (v) for the laboratory similation (hydrous pyrolysis 1176-PC2; Simoneit, 1990) is based on relative concentration only. Symbol * indicates that the compound was not measured, while ‡ identifies instances in which benz(a)anthracene was not resolvable from chrysene/triphenylene.









APPENDIX E

Derivtations of Kinetic Equations and Solutions

The application of kinetic and equilibrium principles to the biomarker reactions during thermal maturation in sedimentary basins was developed and outlined in Mackenzie and McKenzie (1983). The equations used in the mathematical analyses of this thesis are extensions and modifications of those originally developed therein. Additional background on the general mathematical basis for kinetic treatments of isomerizaton reactions can be found in Starzak (1989).

ISOMERIZATIONS

The extent of isomerization of the 5α -C₂₉ steranes (S_S) and the C₃₁- or C₃₂-extended hopanes (S_H) is calculated by

$$S_{I} = \frac{[S]}{[S] + [R]}$$

where [S] and [R] are the concentrations of the two diastereomers at C-22 of the hopanes and at C-20 of the steranes. The R configuration of each is the biologically-derived component.

The interconversion of each pair of diastereomers has been modeled using a simple unimolecular and first-order approximations, where

$$R \xleftarrow{k_{f}}{S} \qquad k_{f}, k_{r} = \text{forward and reverse rate constants, respectively}$$

and
$$\frac{d[R]}{dt} = k_{r}[S] - k_{f}[R]$$
$$\frac{d[S]}{dt} = k_{f}[R] - k_{r}[S]$$

Assuming no other sinks or sources are active for the two diastereomers, i.e. ([S] + [R]) is constant, the percentage of each isomer (e.g. S_I) can be substituted into the solution for the concentration of [S]. This results in the equation:

$$S_{I} = \frac{1}{k_{f} + k_{r}} \left\{ k_{f} + (k_{r}S_{o} - k_{f}R_{o}) \exp \left[- (k_{f} + k_{r})t \right] \right\}$$

where S_0 is the initial condition of the extent of isomerization (S_I); R_0 is the analogous parameter for the R diastereomer, equivalent to (1 - S_0); and t is the time of reaction.

At equilibrium:

$$\frac{d[S]}{dt} = \frac{d[R]}{dt} = 0$$
$$k_r[S] = k_f[R]$$
$$K_{eq} = \frac{[S]}{[R]} = \frac{k_f}{k_r} = \gamma_I$$

This assumes that the dependence of the equilibrium constant γ_I is small compared to the dependence of k_f and k_r and defines the rate constant of isomerization (k_I) as the rate constant for the forward reaction (k_f). Substituting in the solution for S_I results in:

$$S_{I} = \frac{\gamma_{I}}{1 + \gamma_{I}} \left\{ 1 + \left(\frac{S_{O}}{\gamma_{I}} - R_{O} \right) \exp \left[- \left(1 + \gamma_{I} \right) \frac{k_{I}}{\gamma_{I}} t \right] \right\}$$

where γ_{I} is the equilibrium constant for the sterane (γ_{S}) and hopane (γ_{H}) isomerizations. The values for γ_{S} and γ_{H} used in these formulations are 1.174 (Petrov, 1976; van Graas *et al.*, 1982) and 1.564 (Mackenzie and McKenzie, 1983), respectively.

The temperature dependence of the rate constants is modeled by the Arrhenius equation:

$$\frac{\mathrm{dlnk}_{\mathrm{I}}}{\mathrm{dT}} = \frac{\mathrm{E}_{\mathrm{I}}}{\mathrm{RT}^2}$$

If the assumptions of elementary reactions and minor temperature dependence of the preexponential term A_I and the activation energy E_I over the temperature range of interest are used, the integrated form of the Arrhenius equation becomes:

$$k_{I} = A_{I} \exp\left(\frac{-E_{I}}{RT}\right)$$

where $A_I =$ frequency factor for the sterane (A_S) and hopane (A_H) isomerizations.

$$E_{I}$$
 = activation energy for the sterane (E_{S}) and hopane (E_{H}) isomerizations.

R,T = gas constant and absolute temperature, respectively.

The extent of isomerization after reaction at a known constant temperature T can then be calculated using:

$$\left[S_{I} = \frac{\gamma_{I}}{1 + \gamma_{I}} \left\{1 + \left(\frac{S_{o}}{\gamma_{I}} - R_{o}\right) \exp\left[-\frac{(1 + \gamma_{I})}{\gamma_{I}} \left\{A_{I} \exp\left(\frac{-E_{I}}{RT}\right)\right\} t\right]\right\}$$

If the initial conditions of the isomerization are such that only the biologicallyderived diastereomer (R) is present, as is the case in the real environment, $S_0 = 0$ and $R_0 = 1$ and the equation simplifies to:

$$\left[S_{I} = \frac{\gamma_{I}}{1 + \gamma_{I}} \left\{1 - \exp\left[-\frac{(1 + \gamma_{I})}{\gamma_{I}} \left\{A_{I} \exp\left(\frac{-E_{I}}{RT}\right)\right\} t\right]\right\}$$

AROMATIZATION

The extent of aromatization of the C_{29} monoaromatic steroid (MA) to the C_{28} triaromatic steroid hydrocarbon (TA) is given by

$$T_{A} = \frac{[TA]}{[MA] + [TA]}$$

where [TA] and [MA] are the concentrations of the C_{28} triaromatic and the C_{29} monoaromatic steroid hydrocarbons, respectively.

The conversion of the MA to the TA is irreversible, unlike that of the isomerizations, with

$$MA \xrightarrow{k_A} TA$$

A similar mathematical treatment of the kinetics for this reaction results in the solution:

$$T_A = 1 - M_0 \exp(-k_A t)$$

where $k_A =$ rate of aromatization

 $T_A =$ as defined above

 M_0 = initial percentage of the monoaromatic MA, equivalent to (1 - T_A)

with $k_A = A_A \exp\left(\frac{-E_A}{RT}\right)$

where $A_A =$ frequency factor for the aromatization reaction

 E_A = activation energy for the aromatization reaction.

Combining the two equations results in the following formulation for the extent of aromatization:

$$T_{A} = 1 - M_{o} \exp\left[-A_{A} \exp\left(\frac{-E_{A}}{RT}\right)t\right]$$

ISOTHERMS AND ISOCHRONS

The lines of constant temperature (isotherms) on the plots of sterane isomerization versus hopane isomerization are for the equation:

$$1 - \frac{(1 + \gamma_{\rm S})}{\gamma_{\rm S}} S_{\rm S} = \left[1 - \frac{(1 + \gamma_{\rm H})}{\gamma_{\rm H}} S_{\rm H}\right]^{\rm Q}$$
 F.1

where Q =
$$\frac{(1 + \gamma_S)}{(1 + \gamma_H)} \frac{\gamma_H}{\gamma_S} \frac{A_S}{A_H} \exp\left(\frac{E_H - E_S}{RT}\right)$$

The terms are as defined in Appendix E and the kinetic parameters used in each diagram are given in the figure captions. Various temperatures were used, with the range dependent on the kinetic parameters.

The lines of constant time (isochrons) on the plots of sterane isomerization versus hopane isomerization are for the equation:

$$1 - \frac{(1 + \gamma_{\rm S})}{\gamma_{\rm S}} S_{\rm S} = \exp\left[\frac{-(1 + \gamma_{\rm S})}{\gamma_{\rm S}} A_{\rm S} t z^{(E_{\rm S}/E_{\rm H})}\right]$$
F.2

where
$$z = \frac{-\gamma_H}{A_H(1 + \gamma_H)t} \ln \left\{ 1 - \frac{S_H(1 + \gamma_H)}{\gamma_H} \right\}$$

The equations for the isotherms (F.1) and isochrons (F.2) are derived from the following equations:

$$S_{S} = \frac{\gamma_{S}}{1 + \gamma_{S}} \left\{ 1 - \exp\left[\frac{-(1 + \gamma_{S})}{\gamma_{S}} A_{H} \exp\left(\frac{-E_{S}}{RT}\right) t\right] \right\}$$
F.3

$$S_{H} = \frac{\gamma_{H}}{1 + \gamma_{H}} \left\{ 1 - \exp\left[\frac{-(1 + \gamma_{H})}{\gamma_{H}} A_{H} \exp\left(\frac{-E_{H}}{RT}\right) t\right] \right\}$$
 F.4

The actual isotherms and isochrons were generated by using equations F.3 and F.4 and keeping temperature and time constant, respectively.

SOLUTIONS FOR TIME AND TEMPERATURE

The time and temperature represented by a specific degree of sterane (S_S) and hopane isomerization (S_H) were obtained by solving for temperature (T) in equation F.1 and then obtaining the time (t) by using the derived temperature in equation F.3 or F.4.