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## HYDROTHERMAL FLUIDS AND PETROLEUM IN SURFACE SEDIMENTS OF GUAYMAS BASIN, GULF OF CALIFORNIA: A CASE STUDY

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### ABSTRACT

Surface sediments in hydrothermally active zones of the Guaymas Basin, Gulf of California, have been analyzed for the inorganic chemical composition of sediments and their interstitial waters, as well as for their organic chemistry. Analysis of the inorganic constituents of vent fluids establishes end-member concentrations of hydrothermal fluids and also indicates that little change in chemical composition has occurred between 1981 and 1988. Special attention is given to short surface cores collected with DSV ALVIN in areas characterized by upward advection of fluids of hydrothermal origin, both in areas of strong advective flow as well as seepage through large bacterial mats of *Beggiatoa*. Interstitial-water compositions suggest that fluids consisting of hydrothermal and seawater components rise to the surface, often carrying a supply of sulfide of shallow origin; this in turn may serve as an energy source for the growth of sulfide-oxidizing bacteria. Studies of the composition of hydrothermally generated petroleum show that it is a condensate ( $C_1$ - $C_{20}$  hydrocarbons and polynuclear aromatic hydrocarbons), and much of this material has migrated with the upward-advecting fluids from short depths below the sediment-water interface. The petroleum in the sediments is found mainly in fractures in siliceous cemented clasts and it is biodegraded. In the vent/mound, the petroleum is an unaltered condensate, indicating active migration that exceeds biodegradation.

**Keywords:** *Beggiatoa* mats, condensate, diffuse flow, gas, Gulf of California, Guaymas Basin, hydrothermal fluid composition, hydrothermal petroleum, interstitial-water composition, organic carbon, polynuclear aromatic hydrocarbons, sulfide generation.

### SOMMAIRE

Les sédiments de surface des zones à manifestations hydrothermales dans le bassin de Guaymas, dans le golfe de Californie, ont été analysés afin de déterminer la composition chimique (fractions inorganique et organique) des sédiments et de l'eau interstitielle. L'analyse de la fraction inorganique de l'eau des évents définit la concentration des éléments dans les fluides hydrothermaux avant leur dilution, et montre que très peu de changements sont surve-

nus entre 1981 et 1988. Nous avons porté une attention toute spéciale aux courtes carottes prélevées dans la couche de surface au moyen du submersible DSV ALVIN; les prélèvements ont été faits dans des régions d'advection verticale des fluides d'origine hydrothermale, aussi bien dans des zones à fort écoulement advectif que près des écoulements diffus à travers les épaisses accumulations de la bactérie *Beggiatoa*. La composition des eaux interstitielles montre que les fluides qui contiennent une composante hydrothermale ainsi que l'eau de mer atteignent la surface, et sont généralement munis de sulfure d'origine peu profonde; ce milieu peut donc fournir une source d'énergie pour assurer la croissance de bactéries qui catalysent l'oxydation de sulfure. Nos études sur la composition du pétrole d'origine hydrothermale montrent qu'il s'agit d'un condensé (hydrocarbures  $C_1$ - $C_{20}$  et hydrocarbures polynucléaires aromatiques); en grande partie, cette fraction a migré avec les fluides transportés par advection verticale à partir d'une faible profondeur en dessous de l'interface eau-sédiment. Le pétrole des sédiments se trouve surtout dans les fissures des fragments à ciment siliceux, et est transformé par biodégradation. Près de l'évent, le pétrole est un condensé non altéré, ce qui indique que le taux de migration active dans ce milieu surpasse le taux de biodégradation.

(Traduit par la Rédaction)

**Mots-clés:** accumulations de *Beggiatoa*, condensé, écoulement diffus, gaz, golfe de la Californie, bassin de Guaymas, composition du fluide hydrothermal, pétrole hydrothermal, composition de l'eau interstitielle, carbone organique, hydrocarbures polynucléaires aromatiques, formation de sulfures.

### INTRODUCTION

The hydrothermal system in Guaymas Basin of the Gulf of California (Fig. 1) is of special interest in the study of hydrothermal ore deposition, especially because here newly formed oceanic basement consists either of sill intrusions in rapidly deposited, organic carbon-rich sediments, or of massive intrusions at greater depths (Moore 1973, Williams *et al.* 1979, Einsele *et al.* 1980, Gieskes *et al.* 1982a,b, 1988). Hydrothermal interactions involve both the alteration of basaltic rocks and of sediments, the lat-

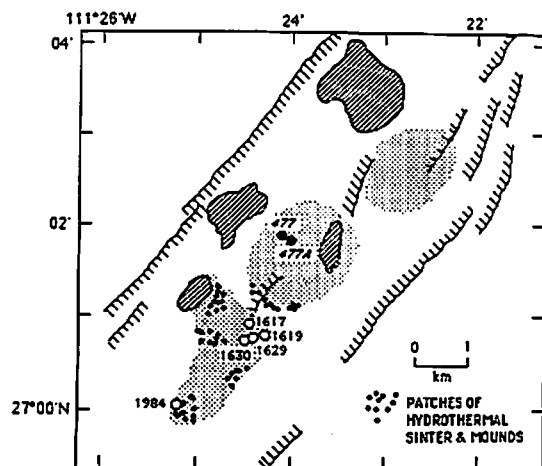


FIG. 1. Map of study area - note cores 1617-AC1, 1619-AC2, 1629-AC2, 1630-AC1, and 1984-AC1, all in the southern hydrothermal field. Shaded areas represent extent of sill complexes (Lonsdale & Becker 1985).

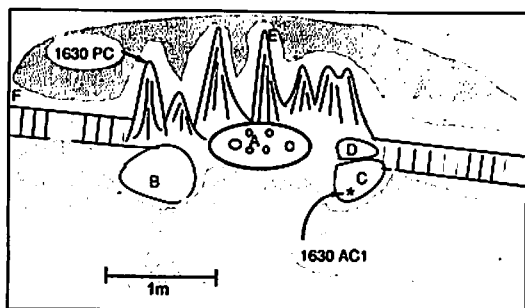


FIG. 2. Cartoon version of hydrothermal deposit - ALVIN dive 1630. A: diffuse flow, temperature  $< 206^{\circ}\text{C}$ ; B: yellow bacterial mat; C: yellow bacterial mat, sampled for core 1630-AC1; D: orange bacterial mat; E: hydrothermal spires (1-1.5 m tall); F: fault zone ( $< 30$  cm).

ter also providing a medium for the thermal generation of hydrocarbons (Einsele *et al.* 1980, Kastner 1982, Simoneit 1983, 1984a,b, 1985a,b, Simoneit & Lonsdale 1982, Kawka & Simoneit 1987, Simoneit *et al.* 1984).

Studies of Deep Sea Drilling Project (DSDP) cores obtained from Sites 477, 478, and 481 involved interstitial-water chemistry (Gieskes *et al.* 1982a), solid-phase geochemistry and mineralogy (Kastner 1982, Kelts 1982, Niemitz 1982), and physical properties of the sediments (Einsele *et al.* 1980, Einsele 1982). The results led Kastner (1982) and Gieskes *et al.* (1982b) to conclude that two major hydrothermal systems could be distinguished in Guaymas Basin:

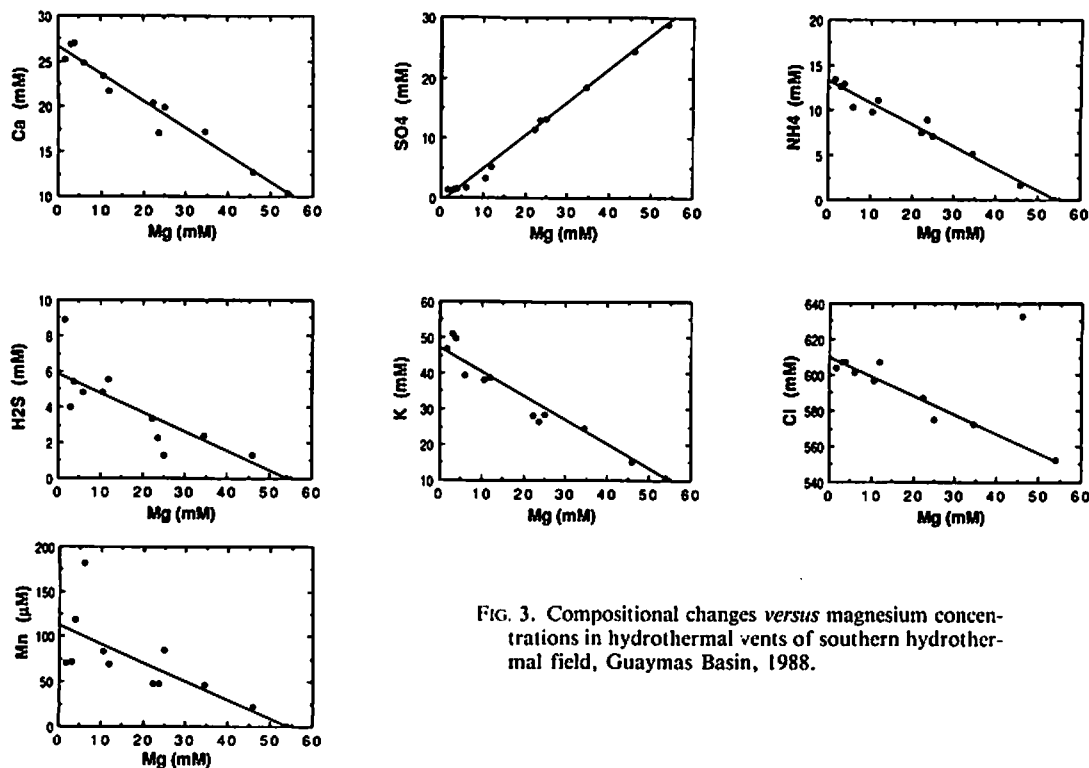


FIG. 3. Compositional changes versus magnesium concentrations in hydrothermal vents of southern hydrothermal field, Guaymas Basin, 1988.

(1) Hydrothermal activity associated with relatively thin, shallow basaltic sill intrusions in highly porous sediments. This activity is usually of short duration and is associated with temperatures  $< 200^{\circ}\text{C}$  in the vicinity of the sills. Decreased porosities indicate that expulsion of pore waters accompanies the sill emplacement.

(2) Hydrothermal activity associated with large magmatic intrusions at greater depths; this activity occurs in a deep-seated, recharging, circulation system. Hydrothermally altered waters, after reaction with underlying basalts, interact with overlying sediments and lead to greenschist formation at temperatures of  $> 300^{\circ}\text{C}$  (Kastner 1982, Kelts 1982). Mass-balance considerations of oxygen isotopes (Kastner 1982) indicated that open-system conditions prevailed during greenschist formation.

Lonsdale & Becker (1985) suggested the presence of an additional hydrothermal system in which slow recharging convection occurs within the sediments overlying the sills. However, this type of system appears to be part of the first type described above.

Hydrothermal fluids have been observed to exit the sediment column in several ways (Lonsdale & Becker 1985). Fluids emanate from hydrothermal mounds and chimneys at temperatures up to  $315^{\circ}\text{C}$  (Von Damm *et al.* 1985). They seem to have their origin at greater depths, and must have flowed rapidly along fissures and faults in the sedimentary column. Hydrothermal deposits typically occur along fault zones in the sediments. Fluids also emanate diffusely through the sediments. Areas of diffuse flow are typically characterized by shimmering water just above the sediments, or by bacterial mats of giant *Beggiatoa* on top of the sediments.

High-temperature vent fluids emanating from hydrothermal mounds and chimneys have been studied by Von Damm *et al.* (1985) and Campbell *et al.* (1988). Their chemical composition is similar to that of the fluids in the deeper parts of DSDP Hole 477A (Gieskes *et al.* 1982a). Together with the often extensive size of the hydrothermal deposits, this suggests that these fluids are associated chiefly with deeper-seated systems, which should operate on a longer basis than sill-induced systems.

In the present study we investigated the chemistry of sediments and interstitial waters associated with diffuse flow through the sediments. Of importance is the question with regard to the origin of hydrothermal fluids in this type of system. Diffuse flow has been observed both in the vicinity of large hydrothermal deposits, and in zones removed from such deposits. It is of interest to determine whether fluids in this type of system are associated mainly with a sill-induced hydrothermal system, with a deeper-seated system, or with both.

During DSV ALVIN operations in Guaymas Basin in 1982 and 1985 (Gieskes *et al.* 1988), a series of

short push cores was obtained in zones of diffuse flow or below *Beggiatoa* bacterial mats. In the present study we concentrate on one ALVIN dive area in particular, but discuss the results in a broader context.

## STUDY AREA

In August 1985 several dives were made in the southern vent field of the southern trough of Guaymas Basin (Fig. 1). In particular, core 1630-AC1 was obtained in an area where hydrothermal deposits indicated only very recent growth along a

TABLE 1. COMPARISON OF HYDROTHERMAL ENDMEMBER CONCENTRATIONS OF VENT FLUIDS IN SOUTHERN VENT FIELD

	Campbell <i>et al.</i> (1988)	This work
$\text{Cl}^-$ (mM)	597-617	610
$\text{Mg}^{2+}$ (mM)	0	0
$\text{SO}_4^{2-}$ (mM)	0	0
$\text{Ca}^{2+}$ (mM)	28	27
$\text{NH}_4^+$ (mM)	15	13
$\text{H}_2\text{S}$ (mM)	6	6
$\text{K}^+$ (mM)	43	47
Mn ( $\mu\text{M}$ )	140	110

TABLE 2. VISUAL OBSERVATIONS OF "ALVIN" CORE 1630-AC1

Sample	Interval (cm)	General Description	Smear Slide	
			Dominant Material	Color
1	0-1.5	Homogeneous marine mud	Diatoms $>70\%$	Green-brown
2	1.5-3	Marine mud with disseminated particles	Diatoms $>70\%$	Green-brown
3	3-4.5	Homogeneous marine mud	Diatoms $>70\%$	Green-brown
4	4.5-6	Petroliferous marine mud with disseminations of sandy diatom rich clasts	$>70\%$	Green-brown
5	6-7.5	Black, petroliferous mud with one tube like and one platy diatom rich clast impregnated with bitumen	$>70\%$	Green-brown
6	7.5-9	Very petroliferous green mud; numerous clasts of globular and platy nature, impregnated with bitumen	$>70\%$	Green-brown
7	9-10.5	Very petroliferous mud with numerous globular clasts and one platy clast with bitumen	Diatoms $>60\%$	Green-brown
8	10.5-12	Petroliferous green mud with very porous clasts with little bitumen	Diatoms $>60\%$	Green-brown
9	12-13.5	Petroliferous green mud, fewer clasts, one being large and porous but without bitumen	Diatoms $>60\%$	Green-brown
10	13.5-15	Petroliferous "clayey" mud with smaller clasts	Diatoms	Green-brown
11	15-16.5	Petroliferous "clayey" mud with few small clasts	Diatoms $>50\%$	Grey
12	16.5-18	Petroliferous "clayey" mud with few small clasts	Diatoms	Grey

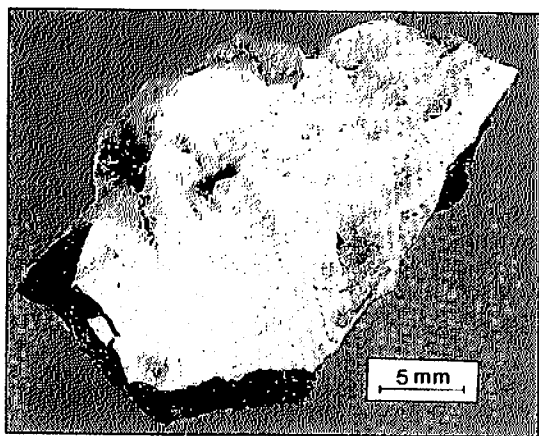


FIG. 4. Detail of "oil shale" piece, Core 1630-AC1, section 7.

fault zone, at least 30 m away from larger hydrothermal mounds. A cartoon of the area is presented in Figure 2. One push core (1630-AC1) was obtained in a yellow *Beggiatoa* bacterial mat, and another push core (1630-PC) sampled the top of one of the hydrothermal spires. The material of this hydrothermal spire consists mainly of barite and precipitated amorphous silica, saturated with petroleum condensate. Upon rising through the thermocline, several chimney pieces jumped out of the collection basket as a result of the release of pressurized gas and oil, which rose ahead of the ALVIN, thus causing the submarine to surface in a large oil slick. Core 1630-PC, of about 25 cm length, was half-filled with chimney material and the liquid phase above this was about one half water and one half oil. Below we discuss the nature of this oil compared to that found trapped between cemented pieces of silica in core 1630-AC1. Interstitial water samples were obtained from push core 1630-AC1, and these were analyzed for major ionic constituents (hydrogen sulfide onboard ship; major constituents in home laboratory). Solids analyses were carried out using wet-chemical techniques (Donnelly 1980, Brown, M.S. thesis in prep.).

Also studied were core 1617-AC1, obtained from an area of strong diffusive flow, and cores 1619-AC2, 1629-AC2, and 1984-AC1 from areas of bacterial mats. Interstitial-water data obtained from these cores are compared with results from core 1630-AC1 and hydrothermal fluids obtained from hydrothermal vents in the southern vent field in 1988.

## RESULTS

### Inorganic chemistry

**Vent fluids.** During February 1988 two of us (BRTS and AM) obtained hydrothermal fluids from

vents in the southern vent field (Fig. 1). End-member concentrations of hydrothermal fluids are obtained from extrapolation of correlation plots of concentrations of various constituents *versus* those of magnesium (Von Damm *et al.* 1985, Campbell *et al.* 1988; Fig. 3). The common assumption is that the end-member fluids contain no  $Mg^{2+}$  or  $SO_4^{2-}$ . Extrapolated hydrothermal fluid concentrations are compared with those presented by Campbell *et al.* (1988) and, in agreement with the latter authors' observations, no significant change has occurred over the last seven years (Table 1). This attests to the longevity of the hydrothermal system associated with mound formation in the southern hydrothermal field.

**Core 1630-AC1 – solids.** In Table 2 we present visual observations of centrifuged materials obtained during the extraction of the interstitial fluids from the sediments. The petroliferous nature of the sediments is most apparent below a depth of ~8 cm, coinciding with the depth at which most cementation has occurred in this core (see below). Numerous silica-cemented clasts occur in the sediments, particularly in section 6 (7.5–9 cm). Figure 4 presents a closeup of one clast demonstrating the "reservoir rock" nature of these clasts, *i.e.*, it appears to sandwich bitumen-like material. X-ray diffraction analysis of this clast revealed the presence of mostly amorphous silica with minor amounts of clay ( $SiO_2$  ~89.1%;  $Al_2O_3$  ~1.83%; Ca ~1.94%). Scanning electron microscope (SEM) observations have revealed that the clasts consist mainly of cemented diatoms, the cement appearing to be amorphous silica. The cement may have formed by the precipitation of silica from dissolved silica-rich hydrothermal fluids. In part this silica enrichment of the fluids can have been the result of diatom dissolution at depth.

The bulk chemical composition of the sediments is presented in Figure 5. The concentration of Al is given in wt.% (salt-corrected), whereas the other elements are presented as mole ratios with respect to Al. Such mole ratios are often indicators of chemical change in the sediments. Ti/Al ratios, and especially Fe/Al ratios, are quite variable in the upper 10 cm of the core. Si/Al ratios are high in the upper 12 cm of the core representing a substantial biogenic silica component; lower ratios at greater depths may signify dissolution of diatoms. The increase in K/Al below 10 cm is significant and probably represents uptake of  $K^+$  in clay minerals.

**Core 1630-AC1 – interstitial water.** The depth distributions of all components (Fig. 6) with the exception of sulfide show a change of slope at a depth of ~8 cm, *i.e.*, in the zone where the largest amounts of clasts have been observed. Sulfide concentrations reach a maximum at ~7 cm depth. We suggest that the silica cement in this layer is laterally continuous and that it represents a barrier to upward flow of hydrothermal fluids which, judging from the chem-

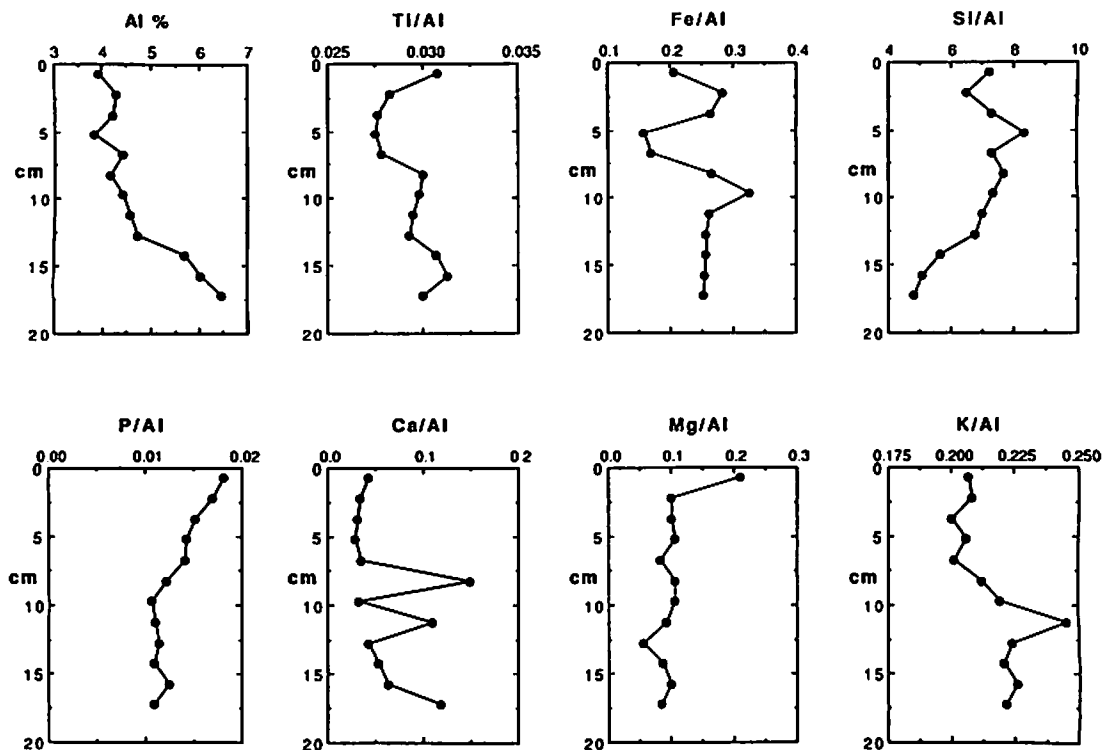


FIG. 5. Chemical composition of bulk sediments, core 1630-AC1.

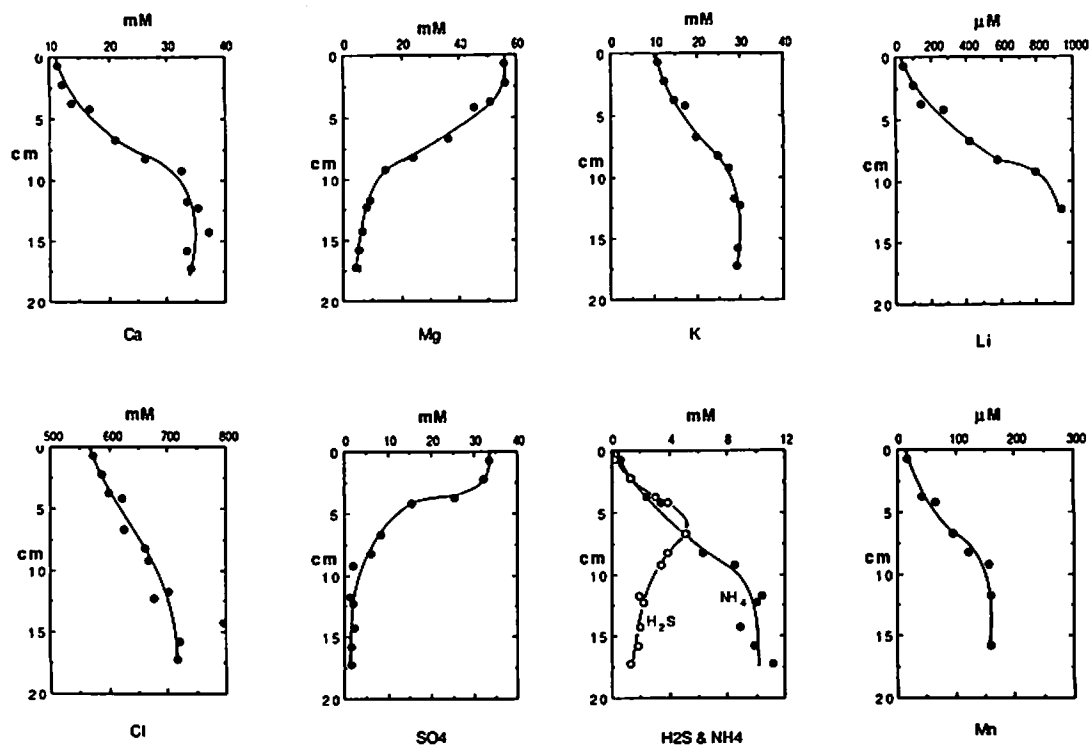


FIG. 6. Interstitial water chemistry, core 1630-AC1.

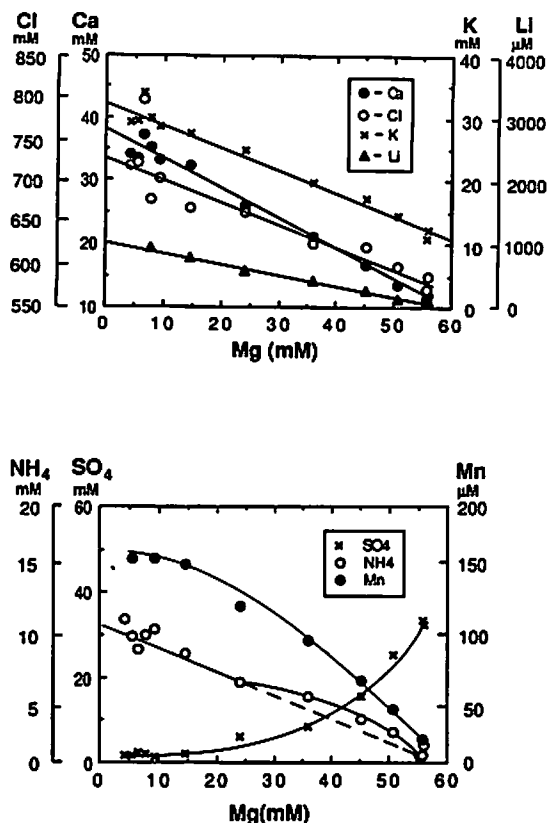


FIG. 7. Correlation between interstitial water components and magnesium in core 1630-AC1.

ical changes below this depth, appear to dominate the interstitial fluids. Silica cements might allow upward diffusion of dissolved constituents, but not actual fluid flow.

Of particular interest is the dissolved  $\text{H}_2\text{S}$  profile, which shows a distinct maximum at a depth of  $\sim 7$  cm. To investigate the problem of whether significant reactions have affected the concentration-depth profiles within the coring interval, we have assumed  $\text{Mg}^{2+}$  to be conservative, *i.e.* the concentration changes represent mixing between seawater and a modified hydrothermal fluid. Figure 7 presents correlation plots of several constituents *versus* magnesium concentrations. It is evident that for  $\text{K}^+$ ,  $\text{Li}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Cl}^-$ , conservative behavior can be inferred, but not for  $\text{SO}_4^{2-}$  or, to some extent,  $\text{NH}_4^+$ . The  $\text{Mn}^{2+}$  concentration variations indicate production of  $\text{Mn}^{2+}$  within the sampling interval.

The sulfate trend implies removal of  $\text{SO}_4^{2-}$ , presumably as a result of sulfate reduction in the upper 8 cm. This would be consistent with rapid increase in sulfide in this interval (Fig. 6). In addition, a slight production of ammonia is evident in

the upper 8 cm, presumably as a result of ammonification processes associated with the sulfate reduction process. It does appear, however, that the high dissolved  $\text{NH}_4^+$  and the low  $\text{SO}_4^{2-}$  at greater depths are primarily due to a hydrothermal component.

#### Comparison to other ALVIN cores

Figure 8 illustrates interstitial water profiles for cores 1617-AC1, 1619-AC2, 1629-AC2, 1630-AC1 and 1984-AC1. All these cores come from dives in the southern vent field (Fig. 1). Core 1617-AC1 was obtained in a zone characterized by strong upwelling of hydrothermal fluids (evident from flow through holes in the sediment); cores 1619-AC2, 1629-AC2 and 1984-AC1 were taken in bacterial mats. The concentration profiles of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  suggest that the interstitial waters, although showing typical upward curvature, usually associated with upward migration of fluids (Maris & Bender 1982, Sayles & Jenkins 1982), do appear to be characterized by mixtures of seawater and hydrothermal fluids in different proportions. Estimates of the hydrothermal contribution are based chiefly on the  $\text{Mg}^{2+}$  concentration, which should be vanishingly low in hydrothermal fluids (Table 1). Cores 1617-AC1 and 1630-AC1 contain at least a 90% hydrothermal component in their deeper parts, whereas core 1619-AC2 shows the least hydrothermal component.

Of interest are the profiles of dissolved sulfate. Though in core 1617-AC1 changes in  $\text{Mg}^{2+}$  and  $\text{SO}_4^{2-}$  are linearly correlated, this is not the case in cores 1629-AC2, 1630-AC1, 1984-AC1 and perhaps in 1619-AC2. This strong sulfate depletion can be understood in terms of sulfate reduction processes taking place in the upper 10 cm of the sediments, leading to the production of significant amounts of sulfides (Fig. 5). Upward transport of this sulfide would then provide the necessary sulfide to the bacterial mats for continued growth. Sulfate reduction processes are probably enhanced as a result of higher prevailing temperatures in these sediments. Thus, it is likely that the added transport of sulfide towards the surface of the sediments as a result of upward convection of highly diluted hydrothermal fluids creates the appropriate conditions for the growth of bacterial mats on top of the sediments in many areas of the Guaymas Basin.

Figure 9 is a correlation diagram for the various "end-member" compositions of the ALVIN cores, *i.e.*, the compositions at which the concentrations of most of the constituents become constant with depth. The data are plotted *versus* changes in concentration from that in seawater using  $\text{Mg}^{2+}$  as a reference on the assumption that this constituent shows conservative behavior. For comparison the data of the lowermost part of DSDP Hole 477A (Gieskes *et al.* 1982a) and those of the average vent-fluid composition of the southern hydrothermal field



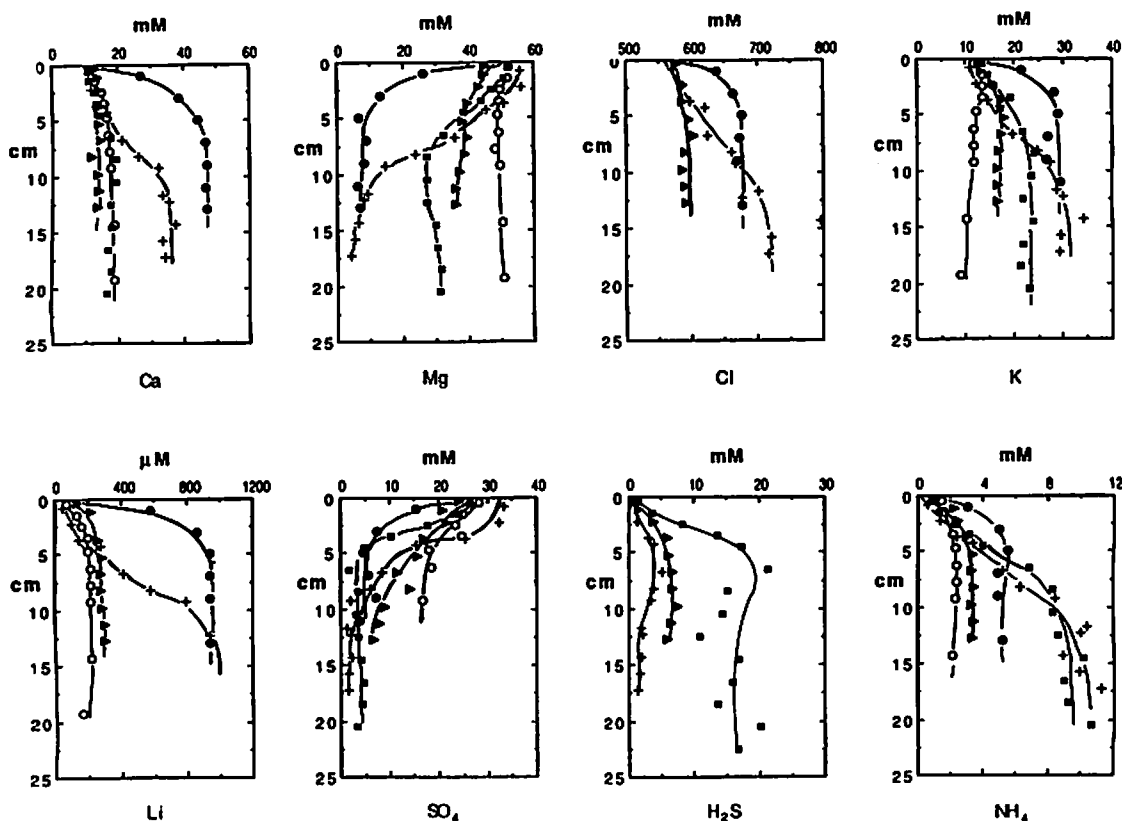


FIG. 8. Interstitial water chemistry in cores 1617-AC1, 1619-AC2, 1629-AC2, 1630-AC1, and 1984-AC1.

(Von Damm *et al.* 1985, Campbell *et al.* 1988; Table 1) are also plotted. Changes in  $\text{Li}^+$  are very similar to those expected from a mixture of seawater and of the end-member hydrothermal fluid. Though  $\text{K}^+$  concentration changes appear to follow a well-defined mixing line, the change in  $\text{K}^+$  calculated for the hydrothermal end-member ( $\Delta\text{K}^+ \sim 23 \text{ mM}$ ) is much smaller than that observed in the vent fluids ( $\Delta\text{K}^+ \sim 37 \text{ mM}$ ). For changes of  $\text{Cl}^-$  concentration, the observations suggest higher concentrations than expected from vent fluids. For  $\text{SO}_4^{2-}$ ,  $\text{NH}_4^+$ , and  $\text{Ca}^{2+}$ , considerable scatter occurs, indicating that reactions in the sediments may strongly affect the data. This, especially for  $\text{Ca}^{2+}$ , is also evident from Figure 8, in which  $\text{Ca}^{2+}$  changes do not necessarily reflect changes in  $\text{Mg}^{2+}$ . Smaller changes in  $\text{Ca}^{2+}$  in some cores may be the result of  $\text{CaSO}_4$  precipitation at greater depth (Stout & Campbell 1983, Gieskes *et al.* 1988).

Two processes must be considered to explain differences between observed changes in composition and those expected from simple end-member mixing. The first possibility is that potential artifacts

in the data may occur as a result of the interstitial-water retrieval process. Core samples are extracted at room temperature ( $\sim 25^\circ\text{C}$ ), whereas *in situ* temperatures may have been as high as  $100^\circ\text{C}$ . For  $\text{K}^+$  this could lead to lower  $\text{K}^+$  concentrations, *i.e.*, artifacts would be opposite to those found in DSDP sediments (Sayles & Manheim 1974, Gieskes 1974). On the other hand,  $\text{K}^+$  concentration changes of DSDP Site 477 are in close agreement with those of vent fluids. The other process involves reactions in the sediments during relatively slow percolation of hydrothermal fluids through the sediments. Uptake of  $\text{K}^+$  at temperatures below  $\sim 200^\circ\text{C}$  into authigenic feldspars was noted in Site 477 (Kastner 1982), and solids data on core 1630-AC1 (Fig. 5) also indicate  $\text{K}^+$  uptake. Changes in  $\text{SO}_4^{2-}$  and  $\text{NH}_4^+$  different from those expected from simple mixing of hydrothermal end-member fluid and seawater can be understood in terms of enhanced bacterial activity. In addition, possible precipitation of  $\text{CaSO}_4$  at depth (Stout & Campbell 1983, Gieskes *et al.* 1988), as well as possible dissolution of calcium carbonate (Von Damm *et al.* 1985) will affect con-

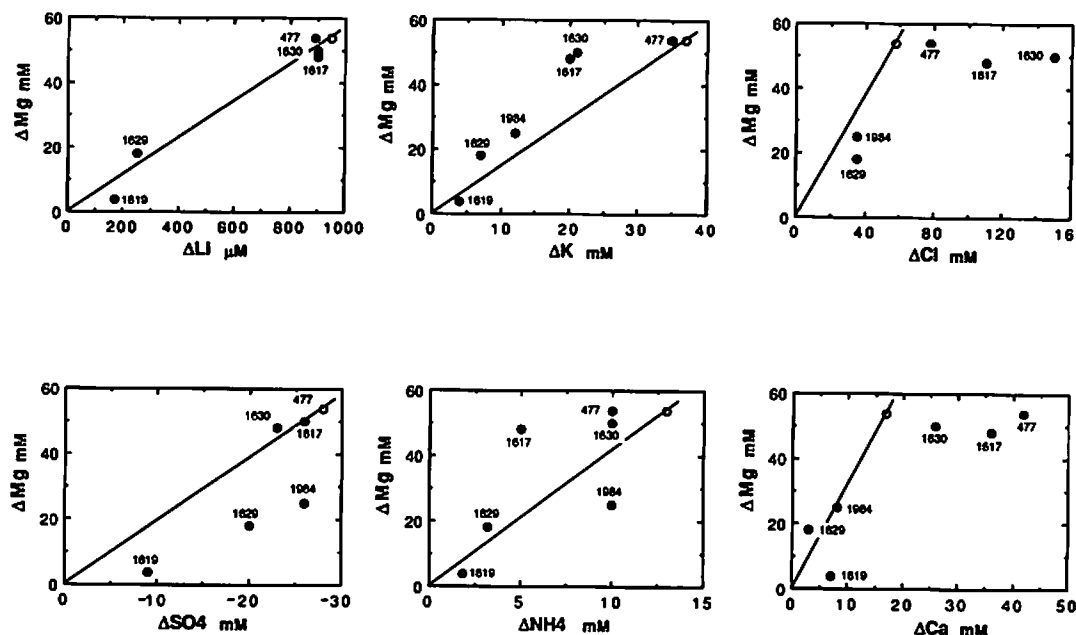


FIG. 9. Correlation plots for hydrothermal end-member composition of ALVIN cores, Hole 477A (Gieskes *et al.* 1982a), and average vent fluids (o) in southern field (Von Damm *et al.* 1985, Campbell *et al.* 1988; Table 1). Data in terms of changes from seawater concentrations.

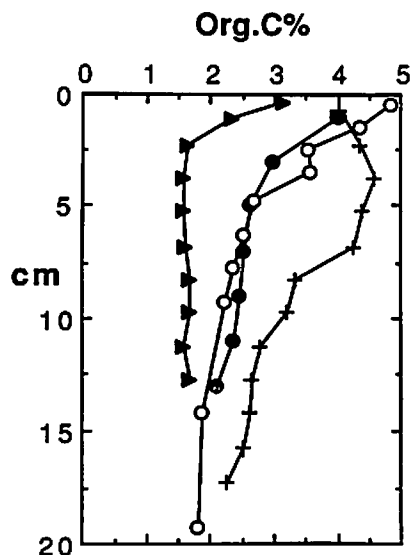


FIG. 10. Total organic carbon in ALVIN cores 1617-AC1, 1619-AC2, 1629-AC2 and 1630-AC1. Solid circles: 1617-AC1; open circles: 1619-AC2; triangles: 1629-AC2; crosses: 1630-AC1.

centration changes in  $\text{Ca}^{2+}$ . Similarly, higher-than-expected changes in  $\text{Cl}^-$  concentration may be the result of hydration reactions in the sediments.

The end-member hydrothermal fluid composition used in the above comparison is derived from vent fluids. Because of the constancy of this composition over a long period of time, we interpret the end-member to be a result of a deep-seated hydrothermal system (Kastner 1982, Gieskes *et al.* 1982b). Unfortunately, because of the possibility of modifications due to reactions during the slow ascent of the fluids through the sediment column, we are not able to judge whether the differences from the simple mixing line are due to a different hydrothermal end-member, *i.e.*, associated with a sill-induced system. However, there is little doubt that subsurface mixing of seawater and hydrothermal fluids does occur, and that local chemical reactions near the surface (*e.g.*, silica dissolution, gypsum precipitation, sulfate reduction) can act as important modifiers to the chemical composition of the interstitial waters. Below we show evidence also that important modifications of organic matter occur in the sediments when compared to organic materials obtained from hydrothermal vents.

#### ORGANIC GEOCHEMISTRY

##### Organic carbon

Determinations of organic carbon contents were carried out on dried, ground, bulk samples using a coulometric method. In all cores, organic carbon contents decrease with depth from surface values of

about 4% organic C to 1.5–2.5% at 10 cm sub-bottom (Fig. 10). In core 1630-AC1, a distinct decrease occurs below the clast-rich layer. Organic matter diagenesis may have been more extensive in cores 1619-AC2 and 1629-AC2, possibly because of a longer period of exposure to enhanced temperature conditions and hence a more advanced stage of organic carbon catagenesis. Temperature gradients in such sediments have been measured during ALVIN dives in 1988, and typical values in mat areas are: 5 cm  $-5^{\circ}\text{C}$ ; 10 cm  $-25^{\circ}\text{C}$ ; 15 cm  $-50^{\circ}\text{C}$ ; 50 cm  $-90^{\circ}\text{C}$ ; 1 m  $-110^{\circ}\text{C}$  (Sayles unpub. data, Simoneit unpub. data).

### Petroleum

The occurrence of petroleum in the sediments of Guaymas Basin is one of the chief characteristics of hydrothermal processes in this area (Simoneit 1983, 1984a,b, 1985a,b, Simoneit & Lonsdale 1982, Simoneit *et al.* 1984). The hydrothermal spire sample (1630-PC) contained abundant oil, and bitumen residues were found in clasts and mud of core 1630-AC1 (Fig. 2). Lighter normal hydrocarbons from the latter had vanished mostly due to the effects of biodegradation, and to some extent due to recovery, storage, and drying. However, the remaining bitumen portion is of particular interest as it contains the heavier non-biodegraded remnants.

The total *n*-heptane extracts of mud (sediment) and clasts from core 1630-AC1 were analyzed by gas chromatography (GC, operating conditions as in Simoneit 1984a) and the representative traces are shown in Figures 11 and 12, respectively. Sediment samples 6, 7 and 10 (Figs. 11b,c,d,) are identical in that their extracts consist primarily of aromatic hydrocarbons, and the same is the case for clasts 6 and 7 (Figs. 12a,b,c.). Three samples from section 7 (namely sediment, "shale" 7, and another clast 7) are all identical (Fig. 11c, Figs. 12b,c). "Shale" 7 was analyzed by gas chromatography – mass spectrometry (GC-MS) and details are given below. The clasts from sections 8 and 9 are, however, different. Their extracts are comprised primarily of low amounts of unidentified compounds. Also, the sediment from section 2 contains a different suite of compounds as discussed below.

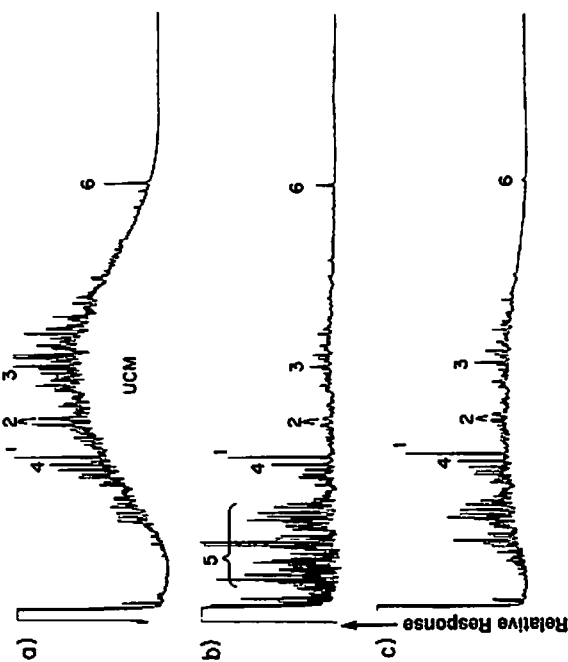
Sample 1630-AC1,7 from one of the "oil shale" clasts in section 7 (Fig. 4) was analyzed by GC-MS. The total hydrocarbons are comprised mainly of unresolved branched and cyclic components (also termed unresolved complex mixture, UCM); the major resolved chromatographic peaks are polynuclear aromatic hydrocarbons (PAH), thio-PAH and alkyl-PAH (Fig. 13a). The major PAH consist of phenanthrene (Fig. 14a), anthracene, fluoranthene, pyrene, benzanthrane, chrysene, benzfluoranthene, benzpyrenes and perylene. A high-temperature component ( $> \sim 300^{\circ}\text{C}$ ) reflecting

hydrothermal activity is indicated by this PAH distribution coupled with the presence of peri-condensed alicyclic PAH (e.g., methylenephenthrene, Fig. 14b; Simoneit 1983, 1984a,b). Biomarkers used as petroleum maturity indicators, such as triterpanes, steranes and extended tricyclic terpanes, are not detectable in this sample. Their absence, coupled with the resolved compound and UCM distributions, support an origin from a biodegraded condensate. However, various maturity indices can be calculated for the dimethylnaphthalenes (DNR) and methylphenanthrenes (MPI) (Fig. 14; Radke & Welte 1983, Radke *et al.* 1982, Alexander *et al.* 1984, 1985). These indices (Table 3) are within the range typical of immature petroleum. The immaturity, coupled with the high thermal gradient and observed oil discharges, are consistent with the interpretation of a short migration distance, for petroleum in this sample, from source sediment to the seabed (Kawka & Simoneit 1987); the immaturity also indicates that sediment samples 6, 7 and 10, and clast sample 6, can be interpreted analogously. Long distance ( $> 1$  km) migration at low temperature would be expected to deplete the high molecular weight PAH in the petroleum.

The GC-MS data for the total extract of the sediment from section 2 (Fig. 11a) indicate it to be a mixture of thermogenic and natural products. The dominant peak is phenanthrene, and the clusters are various series of alkyl PAH with mainly  $\text{C}_2$  and  $\text{C}_3$  alkyl substitution. These compounds are of a thermogenic origin and probably represent the water-soluble fraction of the condensates encountered deeper in the core. The cluster of peaks at longer GC retention time consists of various natural product derivatives such as mainly hopenes with exocyclic double bonds, stanols and other unknown  $\text{C}_{28}$  and  $\text{C}_{30}$  triterpenoids. Normal and isoprenoidal alkanes are not detectable, and their absence compared to other shallow sediments from the basin (e.g., Simoneit *et al.* 1979) indicates that this sample has been biodegraded. The presence of the labile hopenes indicates that the sediment has not been heated  $> \sim 50^{\circ}\text{C}$ , and thus the aromatic compounds probably have migrated as a cold aqueous phase.

Sample 1630-PC, from the vent spire (Fig. 2), was subsampled and sealed immediately upon arrival onboard. The distribution of the volatile hydrocarbons is shown in the GC trace (Fig. 15); they range from methane to *n*-decane, a typical condensate petroleum. It should be noted that homologs  $< n\text{-C}_5$  are depleted relative to typical reservoir condensates due to volatile loss during transit of the submersible through the thermocline and during recovery. Minor amounts of benzene and toluene are also present, as is the case for vent fluids analyzed from Guaymas Basin (Simoneit *et al.* unpub. data). These aromatic hydrocarbons are derived from high-

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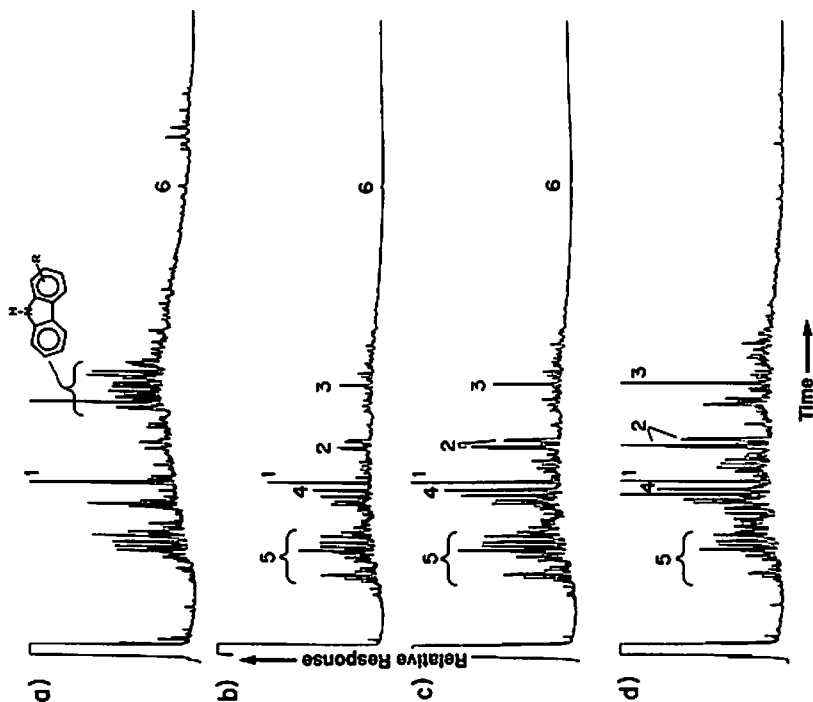


FIG. 11. Gas chromatograms for total extracts (*n*-heptane) of sediment (mud) samples from core 1630-AC1: (a) Section 2; (b) Section 6; (c) Section 7; (d) Section 10. [1 = phenanthrene, 2 = methylphenanthrenes, 3 = pyrene, 4 = dibenzothiophenes, 5 = alkylphenanthrenes, 6 = perylene. In (a) alkylcarbazoles are mainly trimethyl.]

FIG. 12. Gas chromatograms for total extracts (*n*-heptane) of clasts (oil veins) from core 1630-AC1: (a) Section 6; (b) Section 7, "shale" piece; (c) Section 7, other clasts; (d) Section 9. Peak identification numbers are same as in Figure 11.

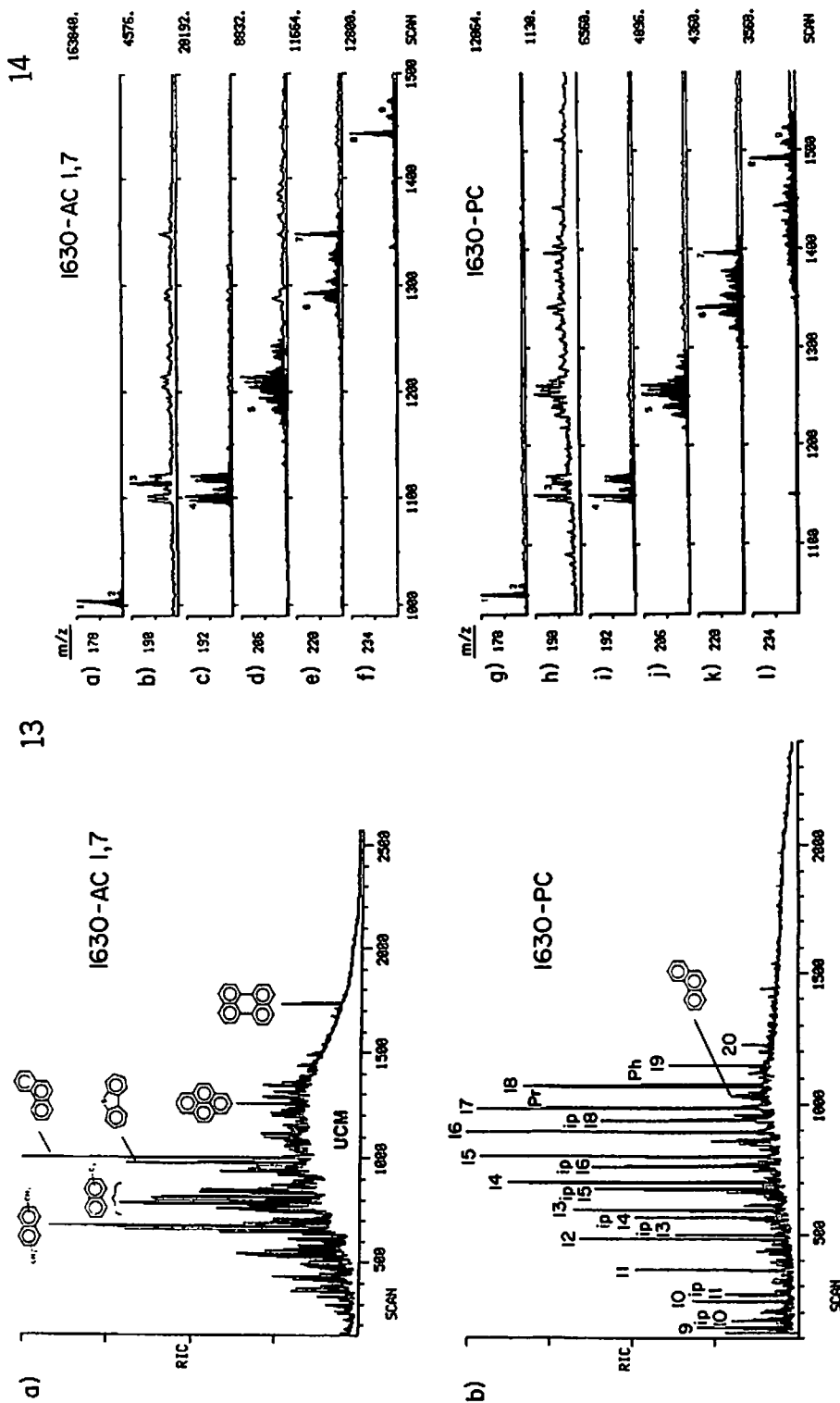


Fig. 13. Total ion current traces for total hydrocarbon fractions : (a) sample 1630-AC1,7; (b) sample 1630-PC [numbers refer to carbon chain length of *n*-alkanes, ip are isoprenoid alkanes, Pr pristane, Ph phytane; in (a) the dominant resolved peaks are homologous series of alkylbenzenes, alkylindanes, alkylnaphthalenes, alkybenzothiophenes and alkyphenanthrenes, all with a carbon substituent range of 1-3, with the parent PAH as phenanthrene, dibenzothiophene, pyrene and perylene].

Fig. 14. Selected mass fragmentograms (*m/z* versus scan number) for the phenanthrene series of sample 1630-AC1,7 (a-f) and sample 1630-PC (g-l): (a,g) *m/z* 178 (1 = phenanthrene, 2 = anthracene); (b,h) *m/z* 190 (3 = methylphenanthrene); (c,i) *m/z* 192 (4 = methylphenanthrene); (d,j) *m/z* 206 (5 = *C*<sub>2</sub> phenanthrenes); (e,k) *m/z* 220 (6 = *C*<sub>3</sub> phenanthrenes, 7 = unidentified); (f,l) *m/z* 234 (8 = benzo(b)naphthothiophene, 9 = *C*<sub>4</sub> phenanthrenes).

TABLE 3. MATURITY INDICES CALCULATED FOR THE ALKYL-PAH SERIES IN SAMPLES FROM ALVIN DIVE 1630

Index	1630-AC-1-7	1630-PC	Reference
MPI 1	0.30	0.79	Radke and Welte (1983)
MPI 2	0.31	0.93	Radke and Welte (1983)
DNR-1	4.4	1.9	Radke <i>et al.</i> (1982)
DNR-2	55	38	Alexander <i>et al.</i> (1985)
DNR-3	60	40	Alexander <i>et al.</i> (1985)
DNR-4	70	50	Alexander <i>et al.</i> (1985)
DNR-5	90	61	Alexander <i>et al.</i> (1985)

MPI = methylphenanthrene index; DNR = dimethylnaphthalene ratio

temperature catagenetic processes (Whelan *et al.* 1988). The ratios of the *iso*- to the normal alkanes ( $C_4$  and  $C_5$ ) are in the range of 3.3 to 1.0 and can be interpreted as immature to mature (Thompson 1979, Whelan *et al.* 1988). Solvent extracts of the bulk sample 1630-PC exhibit identical GC traces for interior (in contrast with vent fluid) and exterior sub-samples. GC-MS fingerprinting (*e.g.*, Fig. 13b) indicates that samples 1630-PC and 1630-AC1 have different compositions, partly as a result of losses of the normal and isoprenoidal alkanes from the latter. The dominant *n*-alkanes range from  $<C_9$  to  $C_{20}$ , with major amounts of isoprenoid hydrocarbons ( $C_{10}$  to  $C_{20}$ , no  $C_{12}$  or  $C_{17}$ ; Fig. 13b). Again, polycyclic biomarkers are not detectable, which, coupled with the resolved hydrocarbon range to  $C_{20}$ , is consistent with a condensate petroleum composition.

The major PAHs in sample 1630-PC consist of phenanthrene, anthracene, fluoranthene, pyrene, benzantracene, chrysene, benzfluoranthene, benzpyrenes, and perylene, with lesser amounts of thio-, oxo- and alkyl-PAH. The PAH distribution and the presence of peri-condensed alicyclic PAH (*e.g.*, methylenepheneanthrene, Fig. 14h) also indicate a

high-temperature component reflecting hydrothermal activity. However, the distribution of these compounds in 1630-PC is not identical to that sample 1630-AC1,7 (*cf.* Fig. 14h-l *versus* Fig. 14b-f) and is due to unknown influences.

The dimethylnaphthalene (DNR) and methylphenanthrene (MPI) indices for the chimney sample (Table 2) fall in the immature and oil or condensate range window (Radke & Welte 1983). This is also consistent with a short migration distance from source to seabed, and the alkane distribution suggests no biodegradation occurred en route.

In summary, the petroleum in dive area 1630 consists of immature condensates containing hydrocarbons from methane to about  $n-C_{20}$ , with admixed PAH components from high-temperature ( $> \sim 300^\circ\text{C}$ ) hydrothermal alteration of organic matter. In the mound/chimney system (Fig. 2) this condensate is present as unaltered oil (*i.e.*, non-biodegraded, Simoneit 1985a), even at the exterior surface of the chimney/mound matrix (sample 1630-PC). This indicates that active petroleum migration exceeds microbial degradation. Condensate migration seems to be from shallow depth (*i.e.*, few meters sub-bottom, consisting of the early petroleum-generation products moving over a short distance) and by bulk-phase movement, completely saturating the young mound/vent system. Based on visual observation, most of these condensates are lost in such areas to the seawater and rise as plumes (Merewether *et al.* 1985, Simoneit *et al.* in prep.). On the other hand, the petroleum in the sediment surrounding the mound/vent system (core 1630-AC1) is a completely biodegraded condensate, where only the UCM and the PAH remain. Making an oil-oil correlation, *i.e.*, matching biomarker and PAH compositions, this material is the same as the unaltered petroleum in the mound/vent area. Most of the petroleum in the core is present as vein fill-

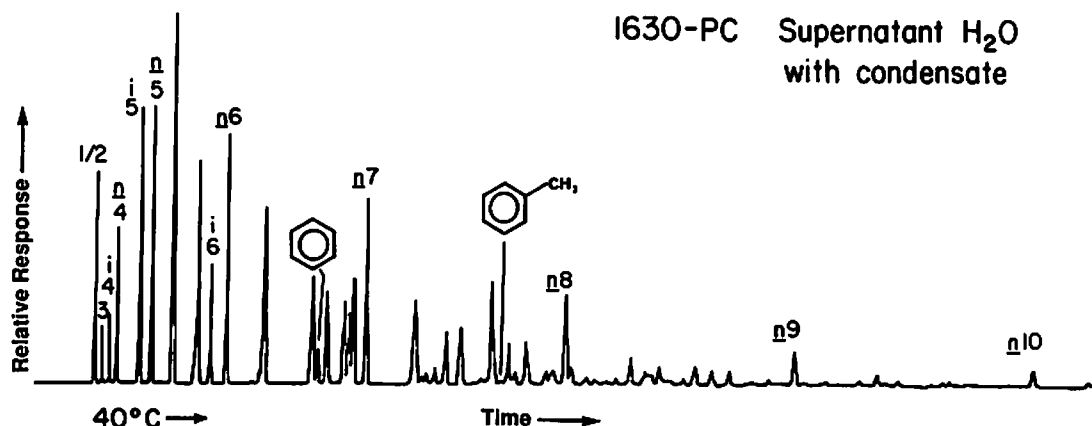


FIG. 15. Gas chromatogram for head space analysis of oil on water in sample 1630-PC (*i.e.*, the volatile components; numbers refer to alkanes, *n* = normal, *i* = iso).

ings in silica clasts (Fig. 4). Because the wallrock is porous silica and not carbonate, it is concluded that the oil filled fractures by bulk-phase migration and was biodegraded during deposition *in situ*. Additional and variable degradation and loss of volatiles occurred after recovery. Carbonate precipitation of the respiratory carbon dioxide from microbial petroleum degradation was not obvious in the core.

### CONCLUSIONS

Studies of the composition of interstitial waters and petroleums obtained from short ALVIN push cores in an area of upwelling fluids in Guaymas Basin have revealed the following:

1. Water samples taken in 1988 from hydrothermal vents indicate a hydrothermal fluid end-member chemistry very similar to those observed in 1982 and 1985, thus indicating a long-term stability of the hydrothermal system active in this area.
2. In regions characterized by shimmering waters overlying the sediments, "diffuse" flow occurs through the high-porosity sediments as well as through small holes. Core 1617-AC1, taken in an area of diffuse flow, contains porewaters with a substantial hydrothermal component (low  $Mg^{2+}$ ,  $SO_4^{2-}$ , high  $Ca^{2+}$ ,  $Li^+$ ,  $K^+$ ,  $Cl^-$ ), which becomes constant below a depth of 4 cm into the sediment.
3. In areas characterized by the formation of *Beggiatoa* bacterial mats, upward-moving porewaters have a much more diluted hydrothermal component (e.g., cores 1619-AC2, 1629-AC2). A strong depletion of sulfate in the upper 10 cm of the sediment leads to a large flux of sulfide to the sediment-water interface. This sulfide is then in turn consumed by the *Beggiatoa*. We postulate that bacterial sulfate reduction is enhanced both as a result of higher temperatures in these sediments, and increased nutrients in the rising porewaters.
4. In layers enriched in diatoms, cementation of sediments by silica precipitation can lead to the blockage of upward-flowing hydrothermal fluids. This results in channelling of migrating hydrothermal fluids to fractures associated with faults, and thereby focuses the location of hydrothermal deposits on the seafloor. Core 1630-AC1 is representative of such cementation.
5. A comparison of interstitial-water compositional changes in cores 1617-AC1, 1619-AC2, 1629-AC2, 1630-AC1 and 1984-AC1 indicates that they represent mixtures of seawater and hydrothermal fluids; *in situ* chemical reactions have caused overprints on these changes, so that the data cannot be used to distinguish whether the hydrothermal end-member is typically associated with a deep-seated hydrothermal system or with a sill-induced hydrothermal system.
6. In dive area 1630 large amounts of petroleum (both oil and gas) are associated both with hydrother-

mal spires/mounds (1630-PC) and nearby sediments (1630-AC1). In the sediments, the petroleum occupies mainly fractures in silica-cemented diatomaceous mudstone clasts. Geochemical analyses of the petroleum at both sites have shown that it consists of immature condensates with a hydrothermal PAH component. In core 1630-AC1 the petroleum is biodegraded.

7. Petroleum has and is actively migrating in bulk as a condensate ( $CH_4$  to  $\sim n-C_{20}$ , the early petroleum-generation products) over relatively short distances (less than a few meters). The steep thermal gradient, reaching  $\sim 100^\circ C$  at 1 m sub-bottom, provides the drive for this migration; most of the oil emanates to the seawater rising as plumes.

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