

Purge and trap GC-MS analysis of volatile organic compounds from the Guaymas Basin hydrothermal site (gulf of California)

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(Received July 1993; revision received 28 March 1994; accepted 31 March 1994)

Summary – During the French-Mexican cruise 'Guaynaut', carried out in November 1991 in the southern depression of the Guaymas Basin (gulf of California), an actively spreading oceanic basin, various samples were collected by means of the submersible 'Nautile'. The on-line coupling of purge and trap to capillary gas chromatography-mass spectrometry (P/T-GC-MS) has been applied to the analysis of volatile organic compounds (VOC) in water, sediments and hydrothermal deposit samples in order to contribute to the characterization of the bacterial microflora activity which is developed on this particular hydrothermal site. The results obtained for alkanes, monoaromatic hydrocarbons and organosulfur compounds lead to successful interpretation in terms of bacterial activity.

Résumé – Analyse par chromatographie en phase gazeuse/spectrométrie de masse de substances organiques volatiles provenant du bassin de Guaymas (golfe de Californie). Durant la campagne franco-mexicaine « Guaynaut », effectuée en novembre 1991, dans la dépression sud du bassin de Guaymas (golfe de Californie), zone hydrothermale active, divers échantillons ont été prélevés à l'aide du sous-marin Nautile. Le couplage direct du système extraction gazeux/préconcentration sur adsorbant solide, avec l'ensemble chromatographie en phase gazeuse à haute résolution/spectrométrie de masse a été utilisé pour l'analyse des substances organiques volatiles dans des échantillons d'eau, de sédiments et dépôts minéraux hydrothermaux. Les résultats obtenus concernent les alcanes, les hydrocarbures mono-aromatiques et les composés organiques soufrés. Ils sont discutés afin de pouvoir caractériser notamment l'activité bactérienne qui se développe dans ce système hydrothermal sous-marin très particulier.

volatile organic compounds (VOC) / hydrothermalism / guaymas Basin

Introduction

The Guaymas Basin, located in the central part of the gulf of California, is an actively spreading oceanic basin which belongs to the system that extends from the East Pacific Rise to the San Andreas fault (fig 1). The basin floors, at about 2000 m depth, are covered with a thick layer of pelagic sediments which accumulate at a rate of about 1–2 mm/year⁻¹ [1]. The thickness of the sediment varies between 300 to 500 m. The very low concentrations of dissolved oxygen in the bottom waters (0.6–0.8 ml/l) and reducing conditions explain the high content of organic carbon in sediments. The temperature of deep-sea waters ranges from 2 to 3°C. Hydrothermal fluids generally discharge through porous sediments at about 50–150°C and through chimneys at 270–325°C ([2]; personal observations).

The Guaymas Basin is unique compared to other hydrothermal sites located along the East Pacific Rise. At 21°N, the hydrothermal fluid chemistry is controlled by the reactions of seawater with basalt at elevated temperature and high pressure. At Guaymas, other reactions occur between the basalt-derived hydrothermal solutions and the sediment at elevated temperatures. Differences in chemical composition of vent fluids are therefore explained by these additional reactions in sediment [3]. The main specific characteristic of Guaymas hydrothermal fluids, compared to the 21°N ones, are: pH values more important (pH 5.9), strong alkalinity (3–11 meq l⁻¹), high ammonium content (10–16 mM), lower concentrations of metal sulfides and formation of hydrothermal petroleum.

The thermal alteration of recent sedimentary organic matter in the Guaymas Basin was found to generate

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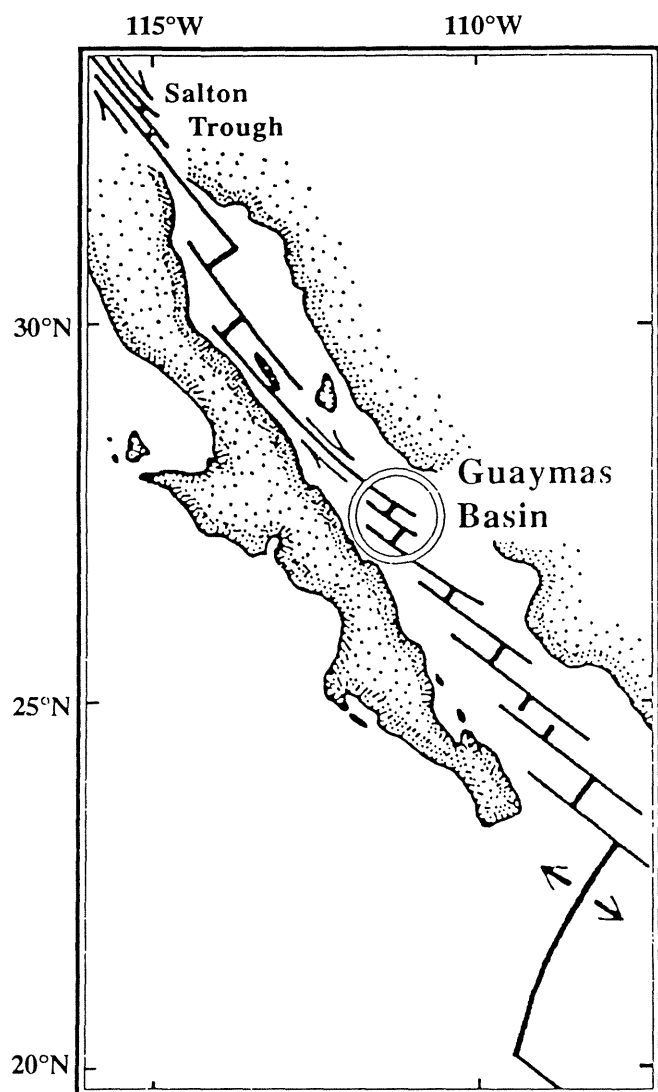


Fig 1. Location map of the Guaymas hydrothermal site in the gulf of California.

hydrothermal hydrocarbons. Hydrothermal fluids may carry large amounts of petroleum during hydrothermal circulation. Many sediment samples and hydrothermal mineral deposit samples are stained with oil and have a strong odour similar to diesel fuel. It is now established that the more volatile water-soluble petroleum components discharge or diffuse into the ambient seawater, and the heavier hydrocarbons condensate in the chimneys and mounds. Many observations and research studies on the formation and characteristics of hydrothermal petroleum have been published in recent articles [4–14].

Microbiological studies carried out in the Guaymas Basin show important and various bacterial communities: sulphur-oxidizing bacteria (*Beggiatoa* sp) [15] mats, thermophilic sulfate-reducing bacteria [16], thermophilic methanogenic archaeobacteria of the genus *Methanococcus* sp [17] or sulphur-dependent bacteria of the genus *Desulfurococcus* [18]. Several observations show that where the condensed petroleum is exposed on exterior surface mounds or surface sedi-

ments, it is easily degraded, which appears to be a result of microbial degradation [6]. Thus, microbiological alteration and utilization of hydrothermal petroleum fractions can provide a major biogenic carbon source in this peculiar hydrothermal ecosystem.

In November 1991, a French-Mexican cruise 'Guaynaut' was carried out in the Guaymas Basin with the R/V Nadir. Among the different scientific objectives of this campaign was the examination of the potential for hydrocarbon degradation by microbiota in the Guaymas Basin. A study has been undertaken to describe chemical characteristics of collected samples and more specifically several sediment cores which are also used for the screening of bacterial populations involved in oil degradation. The present study provides a description of volatile organic compounds (VOC) identified in various samples collected during this campaign.

Materials and methods

Sampling

The field investigations were conducted in the South Trough of the Guaymas Basin around four hydrothermal sites. All sample collections were taken using the French deep-sea submersible Nautile. A total of 37 samples was collected for VOC analysis. Various water samples were collected using a peristaltic pump system specially designed for the collection of seawater or hydrothermal vent fluids. Using the data of ionic major elements (Na^+ , Mg^{2+} , Ca^{2+} , K^+ , Cl^- , SO_4^{2-} [19] and NH_4^+ content (unpublished results) analyzed in the water samples, it was possible to define four groups of samples according to their composition: four seawater samples, three seawater samples with some traces of hydrothermal fluids (0.5–4.0%), five hydrothermal vent fluid samples (the content ranges from 16 to 87%) and three surface water samples sampled above the sediment with various contents of hydrothermal fluid (0–28%). A petroleum emulsion was also collected. All water samples were stored at 4°C in hermetically closed 25 ml vials, but without being poisoned with HgCl_2 . In addition, four sediment cores were sampled and they were cut in slices of 5 cm thick. These samples were characterized by a high organic carbon content (1.0–5.7%) and a high reduced sulfur content (3.0–19.6%). Three hydrothermal deposit samples were also sampled (OC: 2.6–4.6%; S: 14.3–25.8%) (unpublished results). All solid samples were stored frozen until VOC analysis.

Instruments

The purge and trap system, P/T (Tekmar LSC2000, equipped with a sorption trap packed with Carboxpack B and Carboxieve SIII) was directly coupled to the capillary gas chromatograph, CGC (Carlo Erba Mega 5300) by means of a cryofocusing cold trap (Carlo Erba MFA515) operated with liquid nitrogen. The CGC was directly coupled to the mass spectrometer (Carlo Erba QMD1000). The P/T-CGC-MS analysis was automated by means of the MS data station, equipped with LABBASE 2 software (VG MassLab).

Products

Blank laboratory was obtained by purging mineral water purchased in glass bottles by a stream of helium during 12 min with a flow of 40 ml/min. The system was optimized using calibration standards purchased from Supelco (VOC calibra-

tion kit # 4-8804. Toluene-d8 was obtained from Aldrich and methanol from Burdik and Jackson (P/T grade). Helium (Air Liquide, N60) was used as carrier and purging gas.

Purge and trap

A 5 ml sample aliquot of water, spiked with 1 ng of internal standard (toluene-d8) was either directly transferred to the purging vessel by means of a 25 ml syringe (Hamilton 1025 TLL), equipped with a gas tight valve (Hamilton HV 1-1) or after appropriate dilution with laboratory water. 1 g of fresh sediment was submitted to methanol extraction (ultrasonication, 5 min). After centrifugation, an aliquot (usually 10 μ l of the methanol solution) was added to 5 ml of laboratory water which was submitted to P/T. The working conditions were: trap temperature during purgin $9 < 30^{\circ}\text{C}$; purge flow, 40 ml/min; purge time, 12 min; desorption temperature, 240°C ; desorption time, 5 min; desorption flow, 10 ml/min; baking temperature, 260°C ; baking time, 10 min; valve oven temperature, 100°C ; transfer line temperature, 220°C ; cryofocusing temperature during desorption (cold trap), -150°C ; cold trap temperature during injection, 200°C ; cold trap base temperature, 200°C .

Chromatography

Column, DB 624 (60 m \times 0.32 mm \times 1.8 μm , from J/W Scientific), oven program, from 35°C to 245°C at $5^{\circ}\text{C}/\text{min}$; final hold, 5 min, carrier gas inlet pressure, 150 kPa.

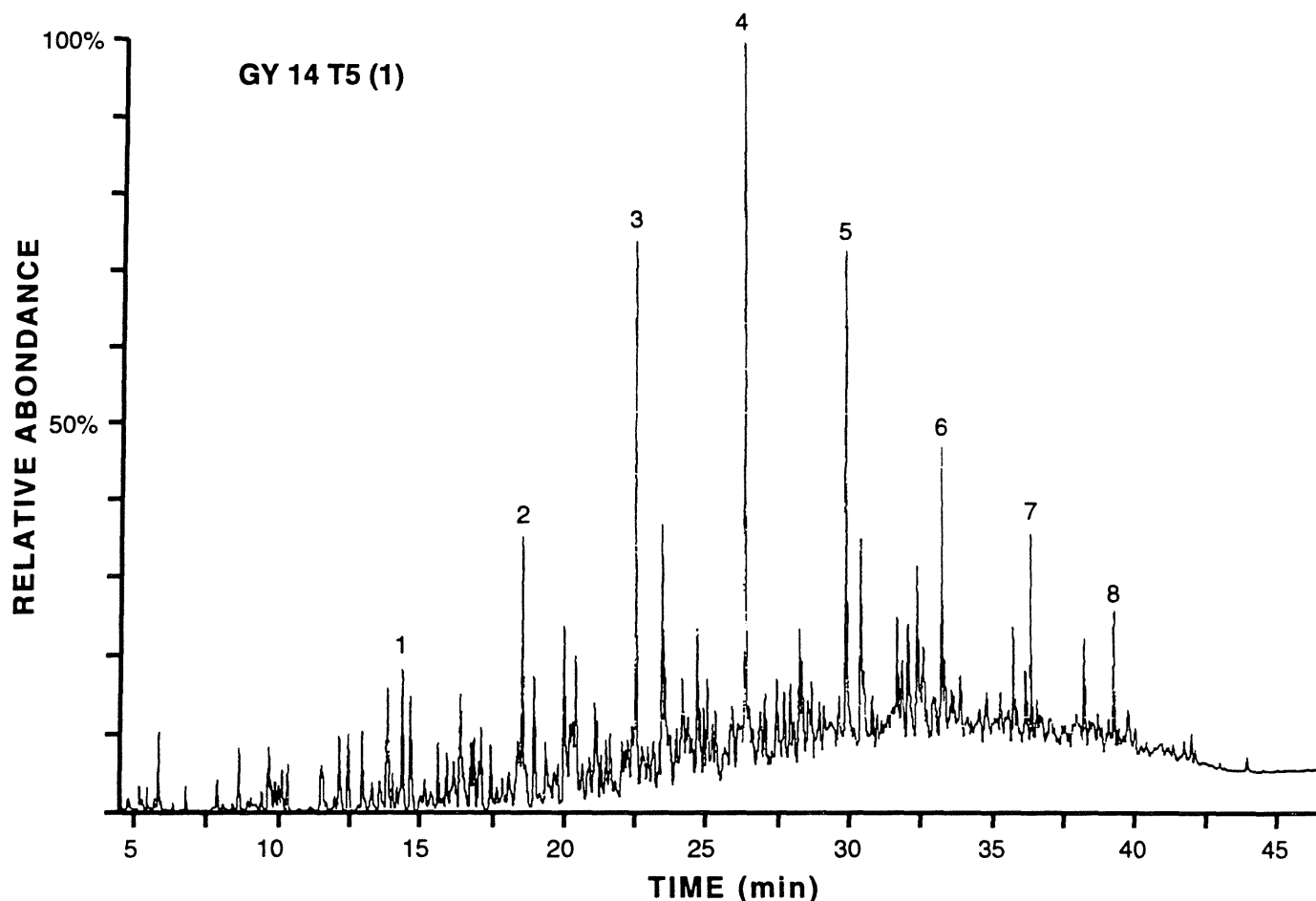


Fig 2. Purge and trap CGC-MS analysis of a sediment sample. 1, n-octane; 2, n-nonane; 3, n-decane; 4, n-undecane; 5, n-dodecane; 6, n-tridecane; 7, n-tetradecane; 8, n-pentadecane. Other conditions see text.

Mass spectrometry

GC-MS interface temperature, 250°C ; ionization mode, electron impact, ionisation energy, 70 eV, ion source temperature, 170°C ; scanning functions, m/z 35 to m/z 350 in 0.75 s (sediments) and m/z 10 to 350 in 0.75 s (waters). The identification of the eluting compounds was based on the comparison of the sample mass spectrum with those of the NIST mass spectral library and the chromatographic retention time of pure reference compounds. The comparisons were automatically performed by the data system. A typical chromatogram obtained for the analysis of a sediment samples is illustrated in figure 2.

Results and discussion

Aliphatic hydrocarbons

According to the analytical procedure used in this study, aliphatic hydrocarbons were identified from propane to hexadecane. The results are summarized in table I. The petroleum emulsion (GY09E) has a high content of aliphatic hydrocarbons (82%) and two-thirds of this fraction are n-alkanes, identified from C_3 to C_{16} . The aliphatics however were not detected in the water samples (vent fluids, seawater and sediment surface waters). Previous work [8, 9] showed that vent fluids are rich in volatile aliphatic hydrocarbons. Methane con-

Table I. Volatile aliphatic hydrocarbons measured in samples collected in Basin Guaymas hydrothermal sites.

Samples	Code	(n)	Total concentration (ppm)	n-alkane fraction (%)	Cycloalkane fraction (%)
Petroleum emulsion	GY9E	1	27	67	5
Hydrothermal deposit	GY14R	1	953	34	25
Sediment cores	GY14B1	2	100-178	41-42	25-32
	GY14T2	3	15-168	38-60	12-31
	GY14T5	4	7-69	43-62	12-28
	GY12T4	8	9-436	1-32	38-89

n, number of analysed samples.

concentrations are between 270 and 370 cm³ (STP) kg⁻¹ when the measured values range from 1 to 2 cm³ (STP) kg⁻¹ at the 21°N hydrothermal site. The general distribution of volatile alkanes, containing from 1 to 10 carbon atoms, is composed of n-alkanes, branched alkanes and cycloalkanes, especially of alkylcyclopentane compounds. It is probable that the absence of volatile alkanes in our water samples is the consequence of a microbial alteration during the storage period before VOC analysis (note that the samples were not poisoned).

Among the three deposit mound samples analyzed, only one (GY14R) had a high content of volatile aliphatic hydrocarbons (953 mg/kg), with significant fractions of n-alkanes (34%) and cycloalkanes (25%). Identical profiles were also observed in sediment core samples at the same hydrothermal sampling site (GY14B1, GY14T2, GY14T5). The distribution of n-alkanes, from C₆ to C₁₆, was found in different 5 cm thick layers, from surface to deep layers of the sediments which corresponded on average to 49% of the total volatile aliphatics. A significant fraction of cycloalkane compounds (on average 22%) was also found, identified from C₅ to C₁₃, with some specificities. Alkylcyclopentanes and alkylcyclohexanes (dimethyl- and trimethyl-derived compounds) are the predominant compounds of the cyclic constituents. No C₈ cyclic derived alkanes have been detected in analyzed samples.

One of the sediment cores (GY12T4), sampled in another hydrothermal site, had a different profile of volatile aliphatic hydrocarbons. In spite of high concentrations of total volatile aliphatic hydrocarbons in upper layers (the first 30 cm), of 70 to more than 400 mg/kg, n-alkanes are strongly modified. The n-alkane fraction represents only 1% to 8% of the total volatile aliphatics and any n-alkane compounds from n-C₈ to n-C₁₃ are detected in the analyzed samples. This distribution can be attributed to a biodegradation of volatile hydrocarbons by microbiota of the hydrothermal ecosystem. In addition, the cycloalkane fraction, which represents a class of compounds recognized as more refractory to the biodegradation process, is predominant in 74-89% of the total volatile aliphatics. In the deepest layer (30-40 cm), the distribution is reversed (fig 3). This kind of observation has already been described in the Guaymas Basin [8] and in a biodegraded reservoir condensate, where alkylcyclopentanes and alkylcyclohexanes predominate [20].

Aromatic hydrocarbons

Volatile aromatic hydrocarbons are detected in most of the various samples analyzed (table II). Among identified monoaromatic compounds in water samples which contain vent fluids, high concentrations of benzene and toluene are found, with minor amounts of ethylbenzene, xylenes and other C₃ to C₆ alkylbenzenes. Knowing ionic major elements (Mg²⁺, SO₄²⁻ and NH₄⁺) concentrations in water samples, it was possible to determine the percentages of vent fluids in eight water samples (3-87%) and thus to have an estimation of volatile aromatic hydrocarbon levels in end-member Guaymas vent fluids for benzene (2960 ± 1090 µg/l), toluene (552 ± 207 µg/l), ethylbenzene (28 ± 20 µg/l), xylenes (128 ± 58 µg/l) and naphthalene (109 ± 59 µg/l). These results compare favourably with those already published [8]. Generally speaking, it is well known that benzene and toluene are of a thermogenic origin and can be produced by thermal degradation of many organic materials such as amino acid phenylalanine [21] or β-carotene [22].

Table II. Volatile aromatic hydrocarbons identified in samples collected in Guaymas Basin hydrothermal sites (concentrations in ppb).

Samples	n	Benzene	Toluene	Ethyl benzene	Xylenes	C ₃ , C ₆ benzenes
Petroleum emulsion (GY9E)	1	592	418	152	494	2635
Vent fluids	5	582-2375	98-589	2-11	27-65	11-50
Sediment surface water	3	45-465	3-71	nd-10	2-26	3-29
Seawater	5	nd-9	nd-34	nd-2	nd-9	nd-13
Hydrothermal deposit (GY14R)	1	5300	3760	4300	5500	48 230
Sediment cores						
GY14B1 (0-10 cm)	2	739-1168	498-551	nd	nd	2364-3871
GY14T2 (0-15 cm)	3	629-1574	nd-663	nd	nd	nd-1388
GY14T5 (0-20 cm)	4	nd	nd	nd-129	nd-452	nd-1257
GY12T4 (0-40 cm)	8	nd	nd	nd-1064	nd-743	2360-64 675

n, number of analysed samples; nd not detected.

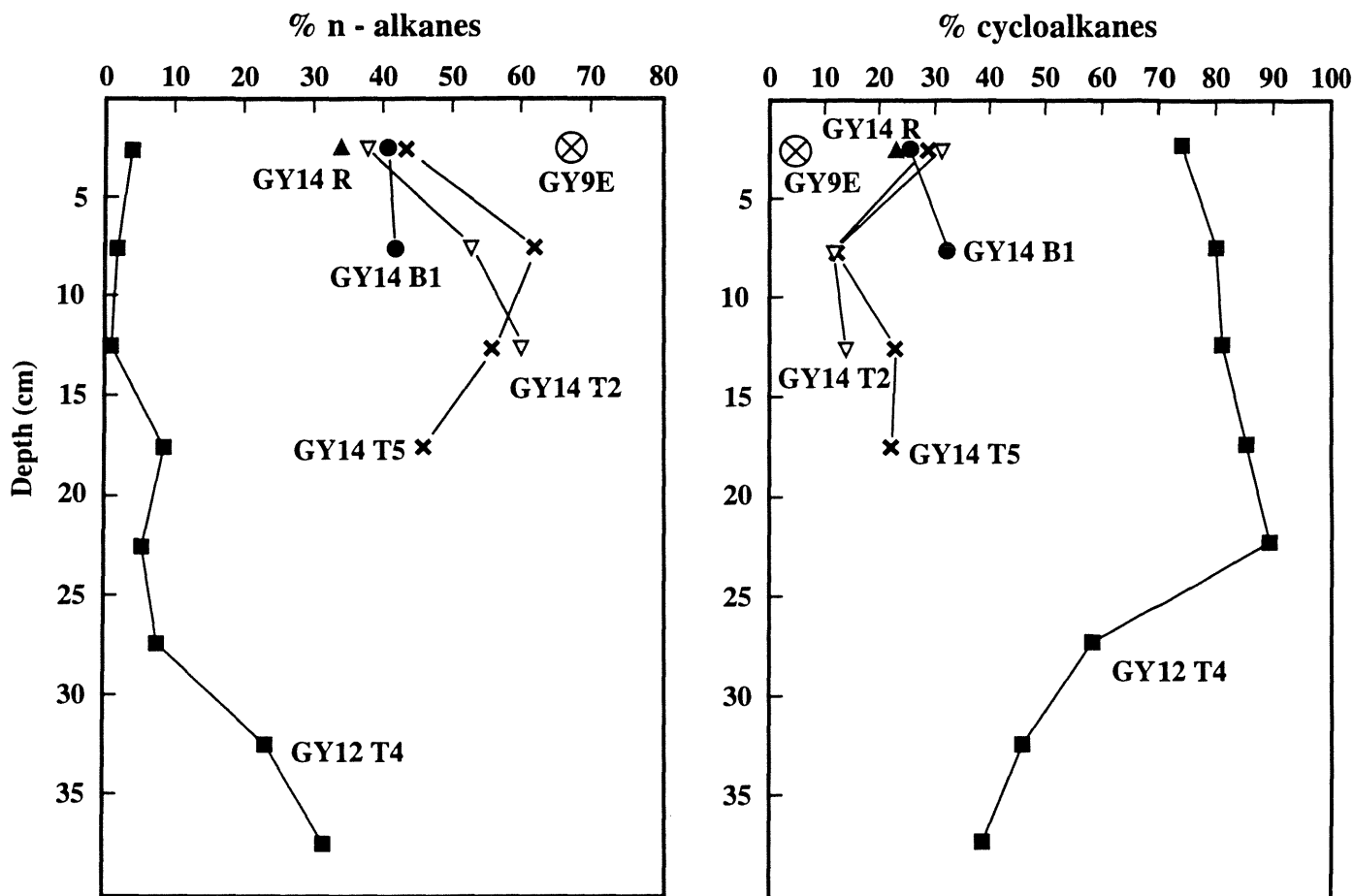


Fig 3. n-Alkane and cycloalkane content of total volatile aliphatic fraction in different samples from the Guaymas Basin hydrothermal site.

In one hydrothermal mineral deposit (GY14R), distribution of volatile aromatic hydrocarbons was slightly different. We could observe similar concentrations of ethylbenzene and xylenes related to benzene and toluene (3700–5500 $\mu\text{g}/\text{kg}$) and higher concentrations of other C_3 – C_6 alkylbenzenes (48 200 $\mu\text{g}/\text{kg}$). These differences could be a direct consequence of basic physical properties, such as different aqueous solubilities of aromatic compounds which contribute to a fractionation of condensates on solid materials.

The distribution of aromatic hydrocarbons in sediment cores is also dependent on collected samples. Generally, a high content of C_3 – C_6 alkylbenzenes is found compared with light volatile aromatics (collectively known as BTEX). In two sediment cores (GY12T4, GY14T5), the most volatile aromatic fraction (benzene to xylenes) was not detected. In other respects, there was no correlation between aromatic fraction and aliphatic fraction, as has already been observed [23]. Several potential causes can explain these differences. First of all, the volatile aromatic hydrocarbons are 10^4 – 10^5 times more water-soluble than similar alkanes [24] and vent fluid circulation preferentially moves the more soluble and volatile hydrocarbons and thus could affect the initial aromatic/alkane ratio. The lack of detection of some volatile aromatics in some subsurface sediment samples could also be attributed to a biodegradation effect.

Volatile sulfur compounds

Several volatile sulfur compounds were detected in some water samples, especially in vent fluids and sediment surface waters (GY14B1, GY14T2) and in one sediment core (GY12T4). The positive results are summarized in table III. The contents of these compounds are not homogeneous in the collected samples. The highest concentrations are found in vent fluid samples and range from 2 to 200 $\mu\text{g}/\text{l}$ according to the sulfur compounds detected: SO_2 (200 $\mu\text{g}/\text{l}$), H_2S (167 $\mu\text{g}/\text{l}$), CS_2 (70 $\mu\text{g}/\text{l}$), COS (26 $\mu\text{g}/\text{l}$), thiophene compounds (6.3 $\mu\text{g}/\text{l}$) and thioether compounds, DMS, DMDS, (2.6 $\mu\text{g}/\text{l}$). In one vent fluid sample (GY06A5), aliphatic thiols (from C_1 to C_3) were also detected, especially methylthiol (10 $\mu\text{g}/\text{l}$). In two sediment surface waters (GY14B1, GY14T2), these volatile sulfur compounds were identified, except for the thioether and alkanethiol compounds. The high productivity of H_2S is mainly attributed to a thermochemical origin in a deep-sea hydrothermal system. The presence of other sulfur compounds including thioethers (DMS, DMDS), thiophene, methylthiophene, carbon disulfide is given as a characteristic of the environment which contains or has contained a community of sulfate-reducing microorganisms [25]. These sulfur compounds have been seen in surface sediments at Walvis Bay [26] and in sediment cores collected with the Deep Sea Drilling

Table III. Volatile sulfur compounds identified in some samples collected in Guaymas Basin hydrothermal sites (concentrations in ppb).

Samples	Vent fluids	Sediment surface waters (GY14B1, GY14T2)	Sediment core (GY12T4)
(n)	5	2	8
SO ₂	nd-200	218-232	nd
H ₂ S	nd-167	58-93	nd
CS ₂	1-67	34-45	nd
COS	nd-26	17-18	nd
DMS	nd-2.2	nd	nd
DMDS	nd-0.4	nd	nd
Thiophenes	0.1-6.3	9-16	nd-4788*
Alkyl thiols	nd-11.6	nd	nd

n, number of analysed samples; nd, not detected. DMS, dimethylsulfide; DMDS, dimethyldisulfide. Thiophenes, thiophene and alkyl substitutes (CH₃, C₂H₅, C₃H₇). Alkyl thiols (C₁-C₃): methyl, ethyl, propyl thiol; *, only ethylthiophene.

Project [27]. Volatile sulfur compounds however were not identified in hydrothermal deposits and sediment cores. The absence of these sulfur compounds in hot sediments can be explained by a water movement of vent fluid through sedimentary materials. However, an exception is observed in one sediment core sample (GY12T4) where a high content of ethylthiophene is measured, up to 5000 µg/kg. Thiophene compounds have a relatively good thermal stability and are well known in ancient sediments such as shales and petroleum source rocks. Most data indicate the presence of thiophene and methyl-thiophenes and only the presence of ethyl-thiophene in this sediment sample cannot be explained.

Conclusion

This study has shown that the on-line coupling of purge and trap to capillary gas chromatography-mass spectrometry offers great possibilities in the analysis of volatile organic compounds in water, sediments and other solid samples collected in hydrothermal sites from the Guaymas Basin. The results obtained for aliphatic hydrocarbons, monoaromatic hydrocarbons and organosulfur compounds lead to an interpretation of the origin and geochemical distribution of some volatile compounds in this particular marine ecosystem and allow for some indications of bacterial activity, especially in terms of biodegradation of hydrocarbons.

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