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18. PURGE-TRAP ADSORPTION GAS ANALYSIS OF SEDIMENTS OF THE WESTERN WOODLARK BASIN, SITES 1109 AND 1115[1]

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ABSTRACT

Low molecular weight hydrocarbon (LMWH) distributions were examined in sediments from Sites 1109 and 1115 in the western Woodlark Basin using purge-trap thermal adsorption/desorption gas analysis. A number of different hydrocarbon components $>C_1$, which were not detected during shipboard gas analysis, were detected at both sites using the purge-trap procedure. Concentrations of ethane, propane, and butane remained relatively low (<100 pmol/g) throughout Site 1109 and had no consistent trend with depth. In contrast, the longer-chain components increased in concentration with depth. Hexane concentrations rose to 716 pmol/g at the base of the site with a concomitant increase in both 2-methyl- and 3-methylpentane. At Site 1115, concentrations of ethane, propane, butane, and isobutylene + 1-butene remained low (<60 pmol/g) throughout the site and again had no consistent trend with depth. 2-Methylpentane, 3-methylpentane, and hexane concentrations had a subsurface maximum that coincided with sediments containing abundant plant-rich material. The LMWH downhole profiles plus low in situ temperatures suggest that the LMWH components were formed in situ by low-temperature biological processes. Purge-trap analysis has indicated the presence of some unexpected deep low-temperature bacterial reactions, which demonstrates that further analysis of LMWH may provide valuable information at future Ocean Drilling Program sites.

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[1] Mather, I.D., Wellsbury, P., Parkes, R.J., and Maxwell, J.R., 2001. Purge-trap analysis of sediments of the western Woodlark Basin, Sites 1109 and 1115. *In* Huchon, P., Taylor, B., and Klaus, A. (Eds.), *Proc. ODP, Sci. Results,* 180, 1–14 [Online]. Available from World Wide Web: <http://www-odp. tamu.edu/publications/180_SR/VOLUME/CHAPTERS/171.PDF>. [Cited YYYY-MM-DD]

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INTRODUCTION

Analysis of sedimentary hydrocarbon gases in Ocean Drilling Program (ODP) sediments is carried out routinely on board ship for safety and pollution prevention. Low molecular weight hydrocarbon (LMWH) gases (methane, ethane, and propane) are monitored in each core following a standardized headspace sampling method (Kvenvolden and McDonald, 1986). In this method, a sediment sample is placed in a glass serum vial and sealed and heated to 60°C for 30 min. A 5-cm^3 subsample of the headspace gas is then analyzed by gas chromatography (GC). When heavier molecular weight hydrocarbons (C_3 and above) are detected, the sample is analyzed by a natural gas analyzer (NGA) used to quantify hydrocarbons up to C_6 and also nitrogen, oxygen, and carbon dioxide. This technique provides consistent order-of-magnitude data on both methane and ethane and a meaningful C_1/C_{2+} gas ratio utilized for safety monitoring. However, it suffers from the disadvantage that in routine analytical procedures, compounds $>C_3$ will be missed if propane is not initially detected in the gas sample.

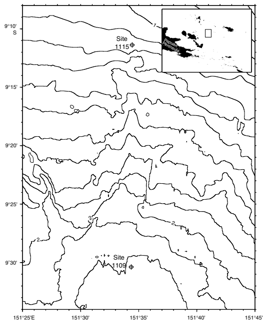
This study examined the LMWH distributions in sediments from two sites (Sites 1109 and 1115) in the western Woodlark Basin using purge-trap thermal adsorption/desorption gas analysis. The advantage of this method over normal shipboard headspace analysis is that all the hydrocarbons from the sediment sample are flushed from the vial headspace and concentrated on an absorbent trap, reducing the detection limit of volatile sedimentary hydrocarbons and also giving a complete analysis of C_2–C_6 hydrocarbon components.

METHODS AND PROCEDURES

Site Description

The western Woodlark Basin is an active extension spreading center to the east of the Papuan Peninsula of Papua New Guinea (Fig. F1). Sites 1109 and 1115 are located just ahead of the spreading tip north of Moresby Seamount. Site 1109 is located on the Woodlark Rise and was cored to a depth of 802.5 meters below seafloor (mbsf). The sedimentary succession at Site 1109 shows a progressive subsidence (from subaerial to lagoonal followed by shallow marine and deep water). At the base of the section, a massive dolerite is present (~773–802 mbsf). Site 1115 is located ~35 km north of Site 1109 and was cored to 802 mbsf. The thick dolerite layer is not present at the base of this site, and the sediments are far older (~15 Ma at base). Organic carbon contents were low throughout both sites, averaging ~0.42 and 0.34 wt% at Sites 1109 and 1115, respectively. The thermal gradients were also similar at both sites, 31°C/km at Site 1109 and 28°C/km at Site 1115 (Taylor, Huchon, Klaus, et al., 1999).

F1. Location of Leg 180 sites, p. 9.



Shipboard Handling

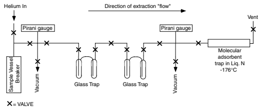
Samples for sediment gas analysis were taken onboard ship as 5-cm whole-round cores (WRC) sampled using a specially designed core cutting rig (Cragg et al., 1992b). The cut ends were capped under a flow of oxygen-free nitrogen (OFN), sealed in OFN-flushed, gas-tight "wine" bags (Cragg et al., 1992a), and immediately frozen. The samples were transported back to the laboratory by air in insulated trunks containing dry ice. The samples remained frozen throughout transportation.

Laboratory Measurement of Sediment Gases

Sedimentary Gas Desorption

Sediment gases were analyzed using a specially designed purge-trap gas apparatus (Fig. F2). A frozen WRC sediment sample was subsampled using a metal corer (~2.5 cm diameter × 5 cm). This subcore was then extruded into a glass vessel that had been preflushed with helium. The vessel was attached to the apparatus, sealed, and the sample allowed to defrost for ≥1 hr at room temperature. After this time, the glass vessel headspace was flushed with helium for 15 min (flow rate = 60 mL/min). The eluent was passed through a mixed bed adsorbent trap containing, sequentially, 75 mg Porapak Q, 75 mg Carboxen 1001, and 150 mg molecular sieve 5 Å, externally cooled with liquid nitrogen. The adsorbent trap was then removed and immediately analyzed (see "GC Analysis," p. 3). The apparatus was then sealed and the sample vessel heated (60°C) for 1 hr. After this time, a new adsorbent trap was installed in the apparatus and the sample vessel flushed with helium as before. The results from both these procedures were then summed. In general, hydrocarbon distributions were similar between the two analyses, although increased concentrations of the higher molecular weight components were usually found at 60°C (typically between 50% and 100% more). Methane could not be quantified reliably using this technique because it was not quantitatively adsorbed onto the adsorbent trap.

F2. Diagram of purge-trap apparatus, p. 10.



GC Analysis

Samples were desorbed (at 200°C for 15 min) from the molecular adsorbant using an SGE concentrated headspace injector (SGE P/N 0932208) installed in a Perkin Elmer 8500 series gas chromatograph fitted with a 23% SP-1700 on Chromosorb P AW (acid-washed support) stainless steel packed chromatography column (30 ft × 1/8 in, by Supelco). The column temperature was held at 70°C for 35 min and then ramped to 110°C at 5°C/min. Detection was by flame ionization (FID), and peak areas were recorded with a Hewlett Packard 3392A integrator using backward horizontal baseline correction. Compounds were identified by their retention positions, and concentrations were calculated by comparison to areas of a C_1 to C_6 *n*-alkane standard (100 ppm, by Supelco) analyzed prior to the samples. Analysis of C_1 to C_6 *n*-alkane standards showed an average error of <13% and linear correlation coefficients of >0.98. Detection limits were calculated to be <3.3 pmol for C_2 and <2.5 pmol for C_3–C_6 *n*-alkanes. Analysis of two samples from the same WRC gave an average error of 23%; however, these samples were not true replicates. The compounds isobutylene and 1-butene were found to coelute using the above conditions and are quoted as a single value below.

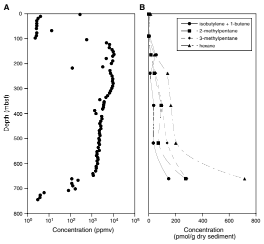
RESULTS AND DISCUSSION

Site 1109

Hydrocarbons $>C_1$ were found in all sediments analyzed from Site 1109 (Table T1). The shallowest sample (1.4 mbsf) contained small quantities of ethane and propane (<30 pmol/g). Low levels of isobutylene + 1-butene, 3-methylpentane, and hexane were also detected. The concentrations of ethane, propane, and butane remained relatively low (<100 pmol/g) throughout Site 1109 and had no consistent trend with depth. In contrast, the longer-chain components increased in concentration with depth. The concentration of hexane increased from 15 pmol/g at the surface to 716 pmol/g at 660.7 mbsf with a concomitant increase in both 2-methyl- and 3-methylpentane (Table T1; Fig. F3). The highest concentrations of these compounds were present at the base of the hole where low levels of trans-2-butene and isopentane were present for the first time. Shipboard headspace methane concentrations had a typical downhole profile with initially low methane concentrations (~2–4 ppmv) increasing (1000–10,000 ppmv) once sulfate had been removed from the pore water at ~100 mbsf (Taylor, Huchon, Klaus, et al., 1999) (Fig. 3A). Methane concentrations remained relatively constant until ~640 mbsf, after which concentrations decreased to 3–6 ppmv at the bottom of the hole. The high C_1/C_2 ratio throughout the hole (>1000) indicated that the methane was of biogenic origin (Taylor, Huchon, Klaus, et al., 1999). Unusually, the entire sedimentary sequence was sampled at this site, down to an older (50 Ma) basement (massive dolerite) (**Monteleone et al.,** this volume), and methane concentrations decrease towards this basement. Decreases in deep methane concentrations have been observed at other ODP sites; however, these decreases were coincident with increases in pore water sulfate (Mather and Parkes, 2000; Cragg et al., 1990), indicating methane oxidation via anaerobic sulfate reduction (e.g., Hoehler et al., 1994). In contrast, at this site there was no sulfate increase and therefore some other mechanism must be responsible for the decrease in methane.

T1. Hydrocarbon gases, Site 1109, p. 13.

F3. Depth distribution of Site 1109 sediment hydrocarbons, p. 11.

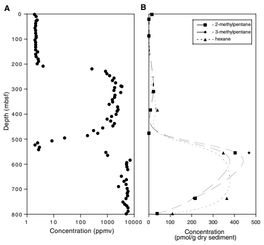


Site 1115

All sediments analyzed from Site 1115 contained hydrocarbons $>C_1$ (Table T2). Low concentrations (<20 pmol/g) of ethane, propane, 2-methyl- and 3-methylpropane, and hexane were present in the surface sample (1.5 mbsf). The concentrations of ethane, propane, butane, and isobutylene + 1-butene remained low (<60 pmol/g) throughout Site 1115, and as with Site 1109, had no consistent trend with depth. 2-Methylpentane and 3-methylpentane concentrations had a broad subsurface peak maximizing at 554.8 mbsf. Hexane was also elevated at this depth but continued at similar concentrations until 736.2 mbsf (Table T2; Fig. F4). Small amounts of cis-2-butene, 1,3-butadiene, and pentane were detected in the lower part of the core. 2,2-Dimethylbutane occurred for the first time at the base of the hole at a concentration of 102 pmol/g. As found at Site 1109, shipboard headspace methane began to increase in concentration below 210 mbsf coincident with the removal of pore water sulfate (Fig. F4A) (Taylor, Huchon, Klaus, et al., 1999). Concentrations remained between ~1000 and 10,000 ppmv throughout the rest of the hole except for a narrow zone around ~550 mbsf, coinciding with the regional unconformity and hiatus resulting

T2. Hydrocarbon gases, Site 1115, p. 14.

F4. Depth distribution of Site 1115 sediment hydrocarbons, p. 12.



from the emergence of the forearc sequence (Taylor, Huchon, Klaus, et al., 1999). The C_1/C_2 ratio indicates a biological source for methane at this site (Taylor, Huchon, Klaus, et al., 1999).

General

Low molecular weight hydrocarbons (C_1–C_7) have been detected in a number of Holocene sediments at part-per-billion concentrations (e.g., Hunt, 1975; Hunt and Whelan, 1979; Hunt et al., 1980; Rowe and Muehlenbachs, 1999; Simoneit et al., 1988; Whelan et al., 1980) and also in numerous ODP sediments (e.g., Berner and Faber, 1993; Froelich et al., 1995; Ingle, Suyehiro, von Breymann, et al., 1990; Kastens, Mascle, Auroux, et al., 1987; Mountain, Miller, Blum, et al., 1994; Westbrook, Carson, Musgrave, et al., 1994; Whelan, 1979; Whiticar and Suess, 1990; Whiticar et al., 1994). The thermal generation of LMWH is generally thought to be a high-temperature, ~>50°C process (Hunt, 1996), although the exact formation mechanism for these components in thermally immature sediments is still unknown (Mango, 1997). As the thermal gradients at both Site 1109 and 1115 are low, with extrapolated sediment temperature reaching only ~25° and ~22°C at the base of Site 1109 and 1115, respectively (Taylor, Huchon, Klaus, et al., 1999), this would appear to exclude thermogenic origin of these LMWH. However, low-temperature thermal generation of nonmethane components is also considered to be possible at temperatures below 62° and even down to 20°C (Rowe and Muehlenbachs, 1999). Hence, at these sites, both biological and thermogenic mechanisms may be responsible for LMWH generation.

Low-temperature bacterial production of a range of low molecular weight branched hydrocarbons including 2- and 3-methylpentane from farnesol, ß-carotene, and α-2-pinene has been demonstrated in laboratory experiments (Hunt et al., 1980). As sterile controls showed no formation of LMWH, it was concluded that their production was a result of low-temperature bacterial processes. Therefore, it seems reasonable to assume the same is true at these sites. The reason for the much higher concentrations of 2-methyl- and 3-methylpentane at depth at these sites, however, is unclear. It may, however, reflect the more terrigenous nature of organic matter at depth, which was deposited during continental rifting. These sites became increasingly marine during subsequent seafloor spreading where terrigenous input would decline. Terrigenous plant material would contain potentially more isoprene biopolymers than marine-derived organic matter (Harwood and Russell, 1984). Hence, there would be greater potential for generation of branched-chain LMWH within the deeper terrestrial sections. An additional aspect may be that even the small increases in temperature at these sites may enhance bacterial degradation of sedimentary organic carbon, as shown by Wellsbury et al. (1997), thus contributing to the formation of branched LMWH compounds at depth (Figs. F3, F4).

The elevated LMWH concentrations at both sites appear to coincide with a minimum in methane (Figs. F3, F4). This is surprising and may indicate a different origin for LMWH to methane, as has been previously suggested (Rowe and Muehlenbachs, 1999) or by preferential consumption of methane by bacteria compared to the other LMWH components. Further investigation of the LMWH distributions in ODP sediments may help resolve this issue.

SUMMARY

A number of different hydrocarbon components were detected in sediments from Sites 1109 and 1115 using the purge-trap procedure, which were not detected during shipboard gas analysis. Considerable concentrations of volatile hydrocarbon components >C_5 were also measured in the presence of very low concentrations of propane and, more importantly, where no propane was detected during routine shipboard headspace analysis. The LMWH downhole profiles plus low in situ temperatures suggest that these components are formed in situ by low-temperature biological processes rather than high-temperature thermogenic processes, which are usually thought to be involved. Purge-trap analysis has indicated the presence of some unexpected deep low-temperature bacterial reactions, which demonstrates that further analysis of LMWH may provide valuable information at future ODP sites.

ACKNOWLEDGMENTS

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Figure F1. Locations of Leg 180 Sites 1109 and 1115 with 100-m bathymetric contours (thicker contours are labeled every kilometer).

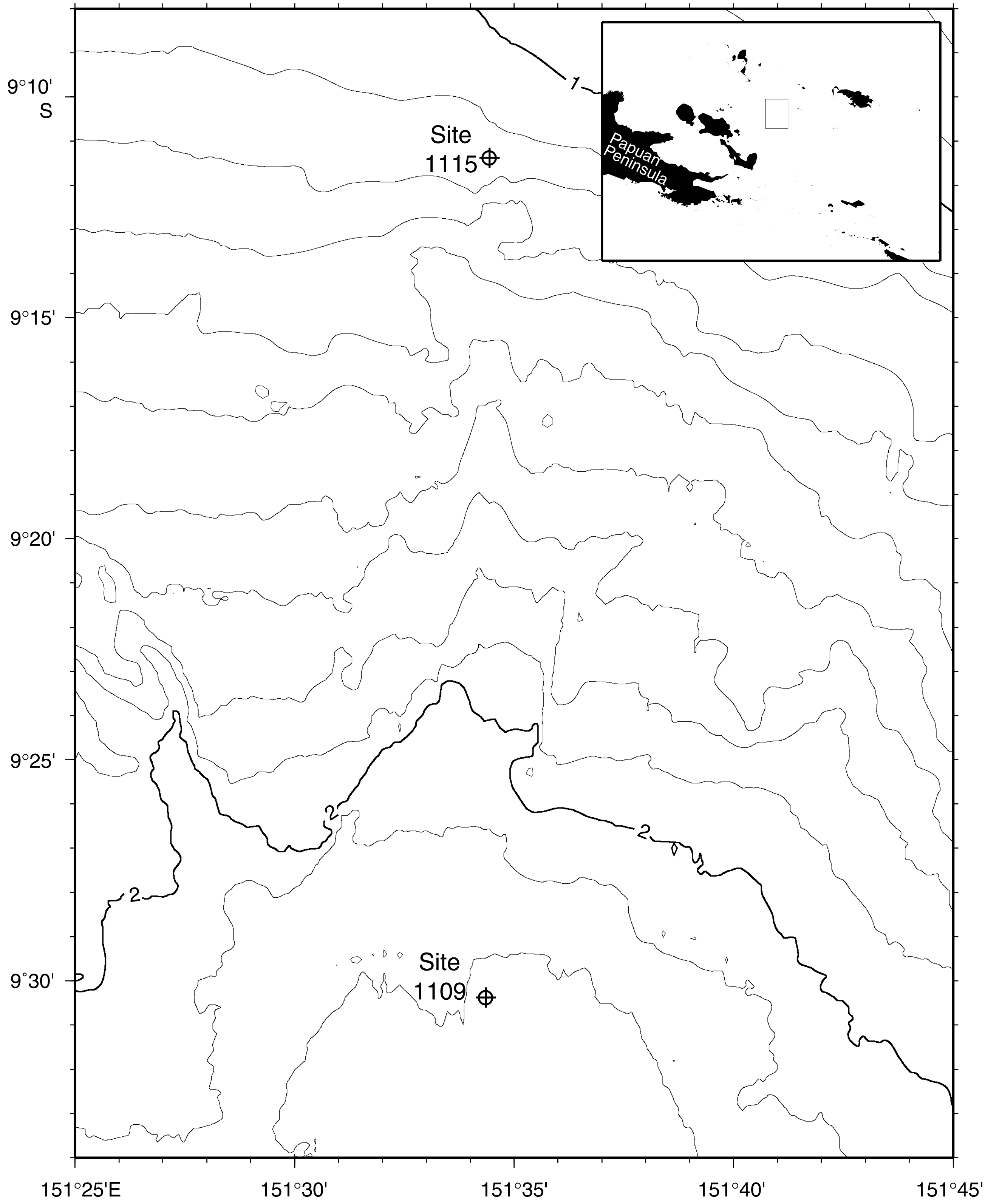

Figure F2. Schematic diagram of purge-trap apparatus used for analysis of sedimentary volatile hydrocarbon gases.

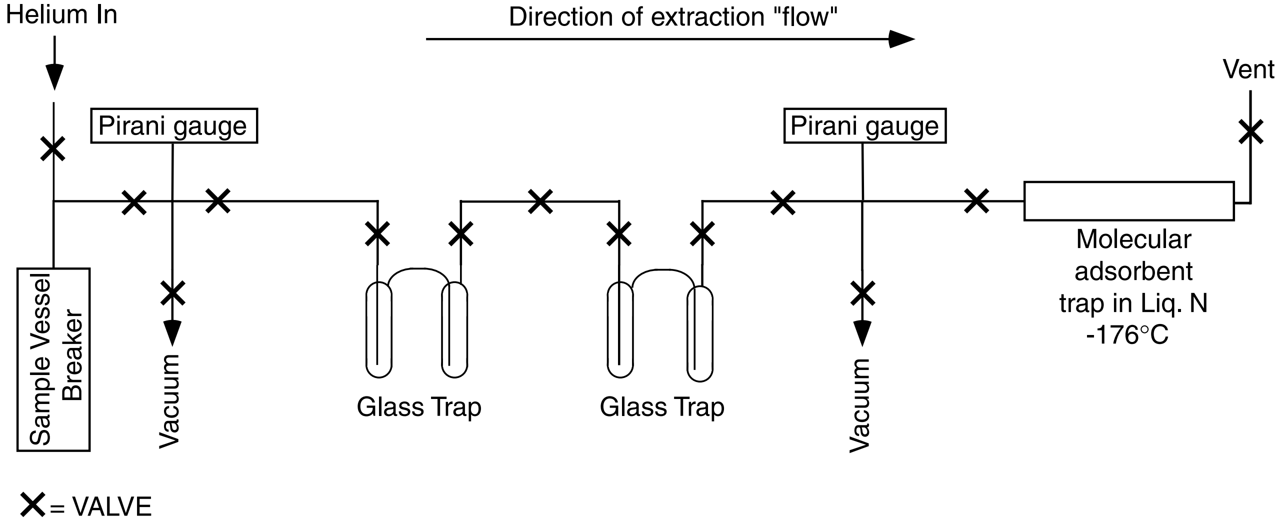

Figure F3. Depth distribution of hydrocarbons of sediments from Site 1109. **A.** Shipboard methane concentrations (from Taylor, Huchon, Klaus, et al., 1999). **B.** Selected hydrocarbon gas concentrations detected by shore-based purge-trap analysis.

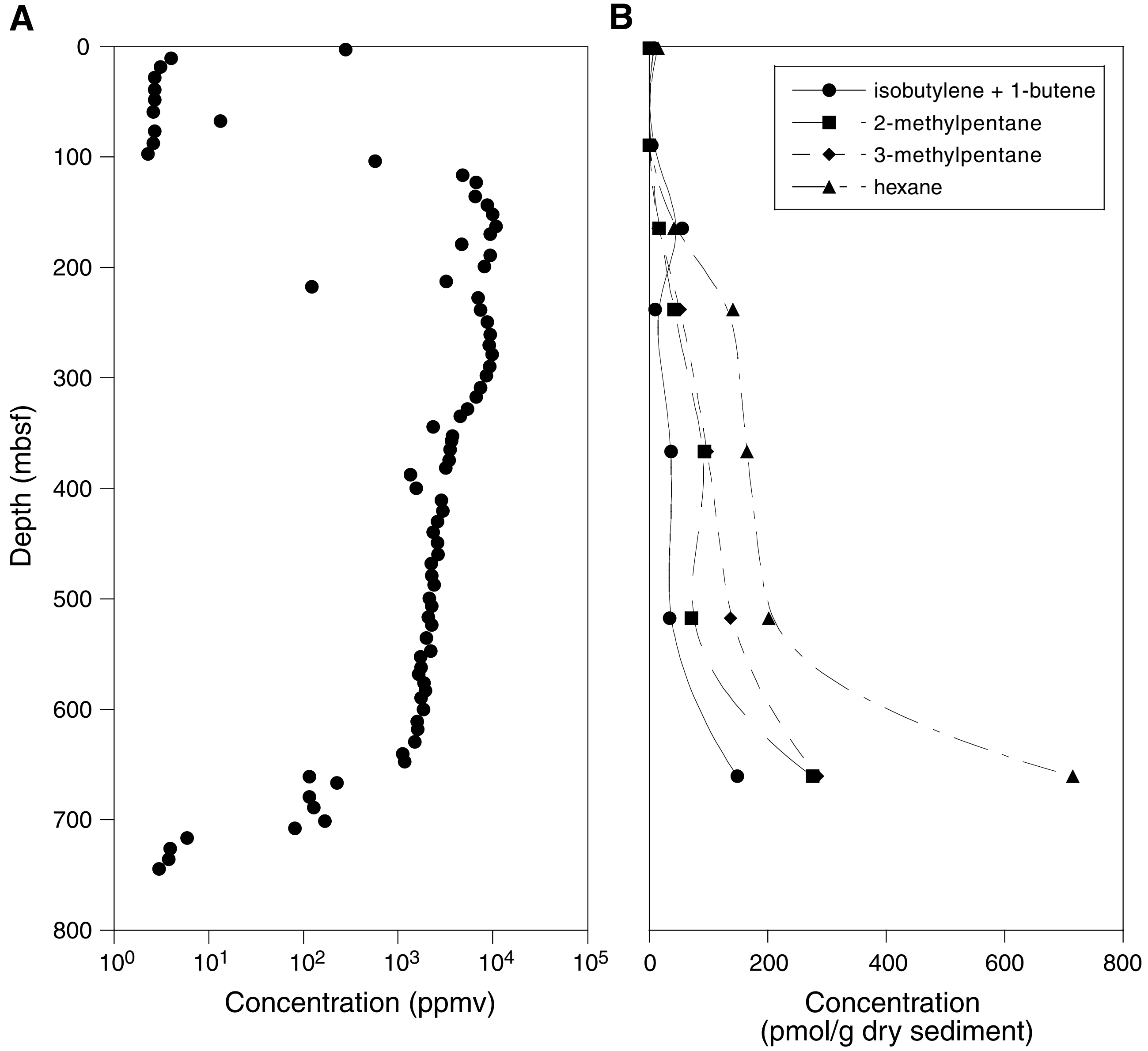

Figure F4. Depth distribution of hydrocarbons of sediments from Site 1115. **A.** Shipboard methane concentrations (from Taylor, Huchon, Klaus, et al., 1999). **B.** Selected hydrocarbon gas concentrations detected by shore-based purge-trap analysis.

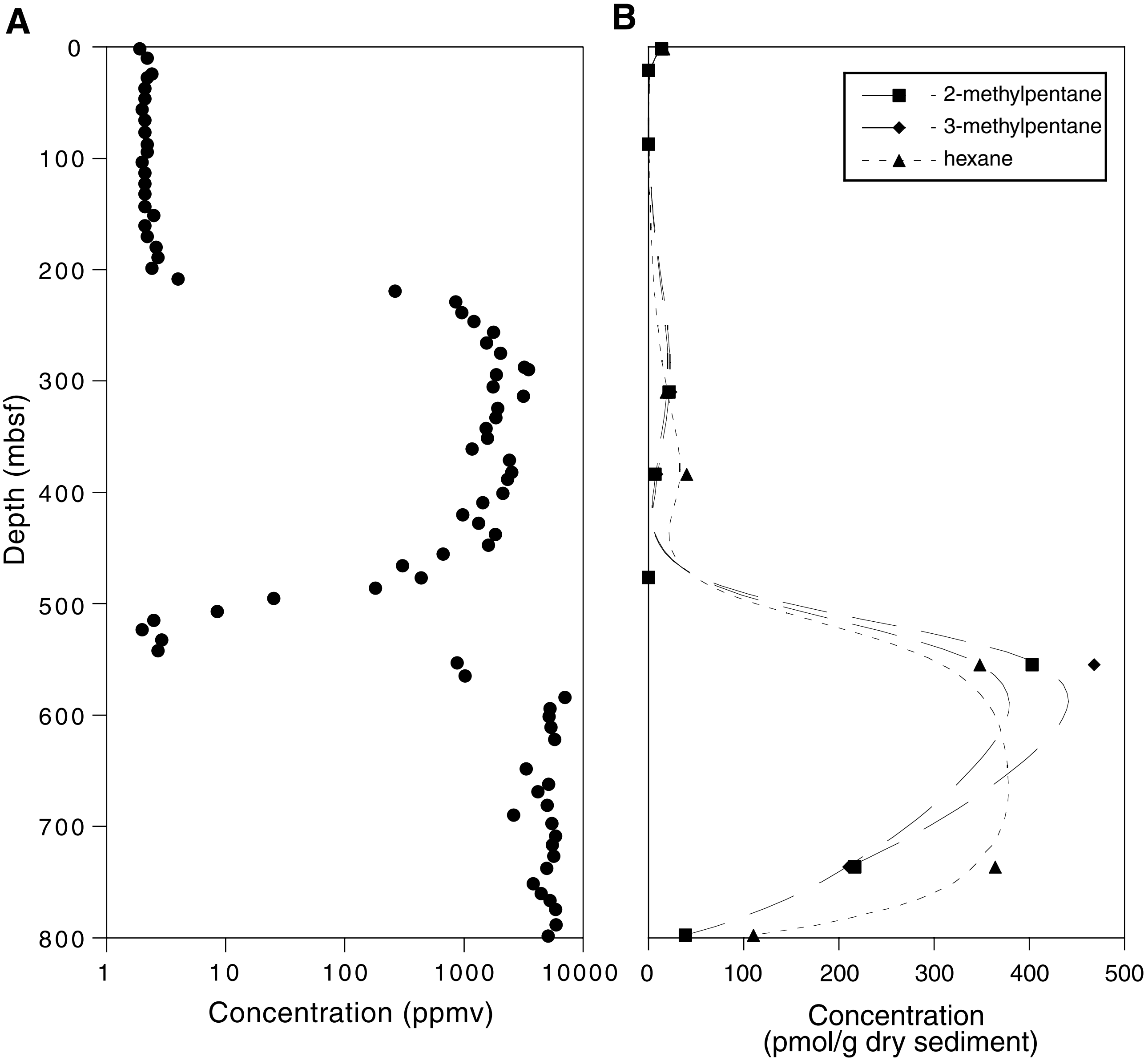

Table T1. Concentration of C_2–C_6 hydrocarbon gases detected by purge-trap analysis in sediments, Site 1109.

Core, section, interval (cm)	Depth (mbsf)	Concentration (pmol/g dry sediment)									
		Ethane	Propane	Isobutane	Butane	Isobutylene + 1 butane	trans-2-Butene	Isopentane	2-Methylpentane	3-Methylpentane	Hexane
180-1109B-											
1H-1, 140–145	1.40	25	13		8	9				8	15
180-1109C-											
10H-4, 145–150	89.35	41	28		3	4					
18X-3, 145–150	164.55	54	67	2	7	56			17	15	42
26X-1, 110–115	238.10	8	2	1	1	10			42	52	142
40X-3, 145–150	366.65	27	2		5	37			93	98	165
18R-4, 90–95	517.42	78	34	3		35			71	137	202
34R-3, 93–98	660.74	36	6		3	149	12	12	276	285	716

Table T2. Concentrations of C_2–C_6 hydrocarbon gases detected by purge-trap analysis in sediments, Site 1115.

Core, section, interval (cm)	Depth (mbsf)	Concentration (pmol/g dry sediment)											
		Ethane	Propane	Isobutane	Butane	Isobutylene + 1-butene	cis-2-Butene	1,3-Butadiene	Pentane	2,2-Dimethylbutane	2-Methylpentane	3-Methylpentane	Hexane
180-1115A-													
1H-2, 117–122	1.45	8	5								14	13	17
180-1115B-													
3H-3, 115–120	20.85	0	3										
10H-3, 115–120	87.35	11	19		7	7							
180-1115C-													
3R-5, 145–150	309.95	57	4		5	12					22	24	19
11R-4, 0–5	383.42	22	1		6	13					7	9	40
21R-2, 56–61	476.28	10	8	1	3	12							
29R-3, 48–53	554.77	13	8		3	7					403	468	348
48R-1, 113–118	736.23	29	9			6	11				217	211	364
54R-4, 110–115	797.84	29	14		2	9		4	4	102	39		110