Data report: geochemical and microbial biomarker investigations of sedimentary successions from the Belgica carbonate mound province in the Porcupine Basin, offshore Ireland[1]

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Chapter contents

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Abstract

This report contains a compilation of geochemical (long-chain *n*-alkanes) and microbial biomarkers (hopanoids and phospholipids), elemental parameters (total organic carbon [TOC] content and bulk carbon isotope data), gas composition data (methane, ethane, propane, *n*-butane, and *iso*-butane), and methane carbon and hydrogen isotope data from sediment samples of Sites U1316, U1317, and U1318 drilled during Integrated Ocean Drilling Program Expedition 307 in the Belgica carbonate mound province (Porcupine Basin, offshore Ireland). At the mound site (U1317), we detected the highest concentrations of microbial biomarkers in the sediments below the mound base. At the upslope site (U1318), microbial biomarkers show high abundances in lithostratigraphic Subunits 1B and 1C, which are also characterized by high TOC contents. Methane, ethane, and propane concentrations are low in the sediments of the mound section (Site U1317) but increase with increasing depth below the mound base. Methane carbon isotope data range between –63.9‰ and –64.5‰ and hydrogen isotope data range between –148‰ and –163‰. Gas wetness data plot in the mixed gas zone between thermogenic and biogenic gas.

Introduction

The investigation of the extent and dynamics of deep microbial ecosystems in sedimentary basins is a new and intriguing topic in today's geoscience research (Horsfield et al., 2007). With sedimentary organic matter becoming more recalcitrant with depth, microbial communities have to endure a decrease in the available carbon and energy sources in addition to increasing temperature and pressure conditions (Parkes et al., 2000). Therefore, the search for and characterization of deep microbial ecosystems are closely connected with the investigation of potential carbon and energy sources for these microorganisms.

Hydrocarbon leakage can form a food source for deep microbial communities by liberating a wide range of biologically utilizable compounds. In a previous study (the Geomound project) computer simulations of the basin history, undertaken at GeoForschungsZentrum (GFZ) Potsdam (Naeth et al., 2005), revealed

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that below the carbonate mounds in the Belgica mound province specific sandstones from Cretaceous and Tertiary sequences represent important migration pathways for natural gases to the surface. Thus, hydrocarbon gases could have migrated to the mound base stimulating microbial activity at this interval. Concomitantly, microorganisms oxidizing methane in near-seafloor sediments (anaerobic oxidation of methane) might have precipitated carbonate crusts, forming potential hardgrounds for coral colonization (Henriet et al., 2002).

In this report, data on molecular microbial indicators are presented for the three sites (U1316, U1317, and U1318) drilled during Integrated Ocean Drilling Program Expedition 307, (April–May 2005) in the Porcupine Basin area offshore Ireland. Additionally, gas composition and gas isotope data are shown for the sediments from Challenger Mound Site U1317. To investigate the microbial ecosystem, phospholipids and defunctionalized hopanoids were selected. Phospholipid esters represent microbial biomass from living organisms because these bacterial cell membrane components are only stable in intact cells over geological times (White et al., 1979). Defunctionalized hopanoids are already partly degraded. Thus, they are more likely remains from past microbial populations. Furthermore, the steric configuration of hopanoids can be used to identify the occurrence of fossil hydrocarbons, because oils usually contain a series of hopanoids in the "geological" 17α(H),21β(H)-configuration. Concentrations of long-chain *n*-alkanes were determined to assess the supply of terrestrial organic matter into the sediments of the study area (Eglinton and Hamilton, 1967).

Methods

Sampling

Sediment material from three sites on Challenger Mound (Holes U1317A and U1317D), downslope of Challenger Mound (Holes U1316B and U1316C), and upslope of Challenger Mound (Holes U1318A and U1318B) in the Belgica carbonate mound province was drilled and gathered taking strict precautions to avoid any microbial contamination. For details on contamination control, see the **"Methods"** chapter. For biomarker analysis, 12 cm whole-round cores (WRCs) were taken, capped, and packed into a gas-tight aluminium bag in a nitrogen atmosphere with an oxygen scrubber sachet (Merck "Aerocult A"). Approximately 5 cm WRCs were sampled from the mound site (U1317) for gas analysis. The sample material was removed from the liner and sealed in a tin after addition of 20 mL of a 1% sodium azide Milli-Q water solution to prevent subsequent microbial activity. All samples were stored at 4°C until finally sent to GFZ Potsdam in a cool box. Samples for biomarker analysis were subsampled using the inner coring technique (Kallmeyer et al., 2006).

Biomarker analysis

Intact phospholipids were analyzed using an extraction method modified after Bligh and Dyer (1954). Approximately 80–90 g of freeze-dried and ground sample aliquots were extracted using a flow blending system with a mixture of methanol/dichloromethane/ammonium acetate buffer (pH 7.6), 2:1:0.8 (v/v) for 5 min. For compound quantification an internal phospholipid standard (1-palmitoyl(D_{31})-2-hydroxy-glycero-3-phosphocholine) was added prior to extraction. The solvent extract was separated from the residual sediment by centrifugation. After removal of the supernatant the sediment residue was reextracted ultrasonically twice using the same solvent mixture. The combined solvent extracts were then collected in a separation funnel and dichloromethane and water were added to achieve a ratio of 1:1:0.9 (v/v). After phase separation the organic phase was removed and the water phase was reextracted twice with 20 mL dichloromethane. The combined organic phases were evaporated to dryness For details of this method see Zink and Mangelsdorf (2004). The obtained sediment extract was separated into fractions of different polarity (low polar lipids, free fatty acids, glycolipids, and phospholipids) using a pure silica column and a Florisil column in sequence as well as solvents of different polarity (Zink and Mangelsdorf, 2004). Finally, the phospholipid fraction was measured using a liquid chromatography–mass spectrometry system (Shimadzu SCL-10a VP high performance liquid chromatography and a Finnigan MAT TSQ 7000 mass spectrometer). For details see Zink and Mangelsdorf (2004). Phospholipid concentrations were determined relative to the internal standard taking into account different response factors of the different phospholipid classes (Mangelsdorf et al., 2005; Zink et al., 2008).

For hopanoids and long-chain *n*-alkanes the low–polar lipid fraction was separated on a medium-pressure liquid chromatography (MPLC) system into fractions of different polarity (aliphatic, aromatic, and hetero component fractions). The aliphatic hydrocarbon fraction was analyzed for hopanoids and long-chain *n*-alkanes using a gas chromatographic–mass spectrometry system (Agilent 6890 Series GC and a Finnigan MAT 95 XL mass spectrometer). Compounds were quantified relative to an internal

standard (5α-androstane) added prior to extraction. For details on the analytical method see Mangelsdorf et al. (2000).

Elemental parameters

Total organic carbon (TOC) was measured using an elemental analyzer (euro EA 3000, Hekatech). Bulk $\delta^{13}C$ measurements of TOC were performed after dissolution of carbonates with 0.1 N HCl and subsequent drying of the samples overnight using an elemental analyzer coupled with an isotope ratio mass spectrometer (ThermoQuest delta plus XL).

Gas analysis

The gas-tight tins were sent to a laboratory in Norway (Applied Petroleum Technology AS) for headspace gas analysis to determine the gas compositions and carbon and hydrogen isotope data of the indigenous methane. The total tin volume was 470 cm^3. Approximately 176 cm^3 of wet sediment and ~215.5 cm^3 Milli-Q water containing 20 mL of a 1% sodium azide solution were placed into the tins, resulting in a headspace volume of ~78.5 cm^3. A volume of 176 cm^3 of wet sediment corresponds on average to ~125 g dry sediment.

A septum was attached to each tin with a hose clip (metal band with a hole). The tins were shaken at a stirring board for 2 h. A headspace sample was taken with a syringe penetrating the tin through the septum. Aliquots of 0.1–1 mL were sampled with the syringe for gas chromatographic analysis on a Carlo Erba HRGC 5300 equipped with a Porabond Q column. The detection limit for the hydrocarbon gas components is 0.001 µL/mL using a flame ionization detector. The detection limit for CO_2 is 0.05 µL/mL using a thermal conductivity detector (TCD/HWD).

The carbon isotopic composition of the hydrocarbon gas components was determined by gas chromatography–isotope ratio–mass spectrometry (GC-C-IRMS) system. Aliquots were sampled with a syringe and analyzed on a Trace GC2000, equipped with a Poraplot Q column, connected to a Delta plus XP IRMS. The components were burnt to CO_2 and water in a 1000°C furnace over Cu/Ni/Pt. The water was removed by Nafion membrane separation. Repeated analyses of standards indicate that the reproducibility of $\delta^{13}C$ values is better than 1‰ Peedee belemnite (PDB).

The hydrogen isotopic composition of methane was also determined by GC-C-IRMS. Aliquots were sampled with a syringe and analyzed on a Trace GC2000, equipped with a Poraplot Q column, connected to a Delta plus XP IRMS. The components were decomposed to H_2 and coke in a 1400°C furnace. The international standard National Geologic Society (NGS)-2 and an in-house standard (Std A) were used for testing accuracy and precision. The "true" value of NGS-2 is given as –172.5‰ (Vienna standard mean ocean water). Repeated analyses of standards indicate that the reproducibility of δD values is better than 10‰ PDB.

Results

Site U1316, downslope site

TOC content in the sediments of Site U1316 varies between 0.24% and 0.97% (Fig. **F1A;** Table **T1**) and seems to be more variable above (Hole U1316B) the coral intersection (flank of Challenger Mound, lithostratigraphic Unit 2) than below (Hole U1316C). The $\delta^{13}C$ signal of the TOC above the coral intersection has values between–24.9‰ and –26.0‰, on average ~2.1‰ lighter than values below the coral layer, which vary between –22.3‰ and –23.8‰ (Fig. **F1A;** Table **T1**). This shift in the bulk carbon isotope data of the organic matter coincides with the *n*-alkane distribution in Figure **F1B,** indicating a higher supply of long-chain cuticular wax *n*-alkanes from higher land plants (Eglinton and Hamilton, 1967) in the sediments above the coral intersection (Hole U1316B).

Phospholipids were not detected in the sediments of Site U1316. In contrast, a series of hopanoids (17β(H),21β(H)-hopanes, 17α(H),21β(H)-hopanes, and hopenes) were detected in all samples investigated (Fig. **F2;** Table **T1**). With one exception (Sample 307-U1316C-8R-2, 28–40 cm) showing a relatively high hopanoid content, the hopanoid distribution related to the TOC content is relatively similar, ranging ~43.1 µg/g TOC. The conformity in the distributions of the hopanoids with the β,β-configuration, being characteristic for immature microbial biomass, and those with the α,β-configuration indicates that the α,β-hopanes are also from an immature microbial source rather than representing oil-derived mature hydrocarbons (Fig. **F2B; F2C**). This is corroborated by the lack of the typical α,β-hopane distribution with S- and R-epimer pairs in the carbon-number range between C_{31} and C_{35}, as usually observed in oils. Thus, oil-derived hydrocarbons were not detected in sediments of Site U1316.

Site U1317, mound site

Although there are some samples with a relatively high TOC content in the sediments of the carbonate mound, the TOC content ~0.46%, in general, is higher in the Miocene sediments below the mound

base (Fig. F3A; Table T2). The $\delta^{13}C$ data of the total organic matter in the samples from below the mound base range from –23.6‰ to –22.4‰ (Fig. F3A; Table T2) and are comparable to those of the sediments below the coral intersection at Site U1316. With exception of two samples (307-U1317A-2H-3, 58–70 cm, and 12H-3, 68–80 cm) the bulk carbon isotope signal shows a gradual increase from the mound base to the top to a value of –20.6‰. This might resemble a slightly increasing proportion of marine organic matter in the mound section.

Related to the sediment extracted, a higher content of terrestrial organic matter is indicated below the mound base by the amount of long-chain *n*-alkanes (Fig. F3B) being somewhat higher than in the mound section. In general, the *n*-alkane concentrations from below the mound base correspond to the *n*-alkane concentrations below the coral intersection at Site U1316. However, because of the higher TOC contents below the mound section, the higher amounts of terrestrial organic matter are not recognizable if related to the TOC contents. Thus, there seems to be not much difference in the *n*-alkane proportions related to TOC between the mound section and the sediments below, which might explain the small difference in the carbon isotope signal of the organic matter above and below the carbonate mound base. The exceptionally low $\delta^{13}C$ signal of Sample 307-U1317A-12H-3, 68–80 cm (–26.7‰), from within the mound section, might be explained by a higher proportion of terrestrial organic matter, as indicated by a very high *n*-alkane concentration (also related to the TOC content) in this sample (Fig. F3B; Table T2).

Traces of phospholipids, just above the detection limit of the applied method, were detected in only one sample ~10 m below the mound base (Sample 307-U1317D-6R-3, 5–17 cm). Surprisingly, microbial biomarker proportions such as the hopanoids (Fig. F4; Table T2) are distinctly lower in the mound section than below the mound base. The lower hopanoid concentrations in the mound section related to the amount of sediment extracted does not derive from a dilution effect by the coral carbonate in the mound sequence, because almost the same distribution can be observed when the sediments are corrected for carbonate contents (carbonate-free basis). Again, there is no indication for migrated oil-derived organic compounds.

Headspace gas analysis reveals low methane concentrations above the mound base (Fig. F5A; Table T3). However, below the mound base (130.1 meters below seafloor [mbsf] in Hole U1317A and 146.1 mbsf in Hole U1317D) the methane concentrations increase with increasing depth (Table T3). The same can be observed for the ethane and propane concentrations. The gas wetness data $[C_1/(C_2 + C_3)]$ plot in the mixed gas zone between thermogenic and biogenic gas with a higher tendency to a biogenic gas source. The same trend can be observed when considering the carbon isotope data of the indigenous methane showing values around –64.3‰ (Fig. F5B; Table T3).

Site U1318, upslope site

The highest TOC values (average = 1.06%) are observed in the sediments of the lithostratigraphic Subunits 1B and 1C (Fig. F6A; Table T4). Above and below these lithologic units the TOC values range between 0.25% and 0.36%. TOC values of sediments from the lower part of this site (Hole U1318B) show slightly higher values ranging from 0.50% to 0.70%. The $\delta^{13}C$ data of the sediments below Subunits 1B and 1C are characterized by values of –23.2‰ to –22.3‰ (Fig. F6A; Table T4). In Subunits 1B and 1C there is a clear shift (average = 2.6‰) to lighter carbon isotope data ranging from –25.8‰ to –24.8‰. Above these lithologic units the values are again slightly heavier (–24.4‰).

A higher supply of terrestrial organic matter during sedimentation of Subunits 1B and 1C is indicated by higher proportions of long-chain *n*-alkanes (Fig. F6B; Table T4), which coincides with the lighter $\delta^{13}C$ data for this section. However, the high concentrations of *n*-alkanes in the uppermost samples are not recognizable in the carbon isotope data.

Hopanoid biomarkers are highest in Subunits 1B and 1C and in the sample nearest to the seafloor (Fig. F7; Table T4). Again, there is no indication of oil-derived hydrocarbons. In contrast to the other sites, in the samples of Hole U1318A microbial phospholipids were detected in significant amounts (phosphatidylglycerol and phosphatidylethanolamine esters) (Fig. F8; Table T5). In general, there is a decrease of the phospholipid concentrations from the top to the bottom of Hole U1318A. However, there is a small increase of these microbial life markers in the section of Subunits 1B and 1C, which corresponds to the higher amount of hopanoid biomarkers and higher TOC contents. In Hole U1318B, phospholipids were not detected.

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Figure F1. A. Distribution of total organic carbon (TOC) data and carbon isotope data of the total organic matter of sediment samples from Holes U1316B and U1316C. Shaded area = coral intersection (flank of Challenger Mound). **B.** Distribution of long-chain *n*-alkanes (C_{23}–C_{35}) in sediment samples from Holes U1316B and U1316C related to the amount of dry sediment (g Sed) extracted, g Sed corrected for its carbonate content (carbonate-free basis [CFB]), and TOC content.

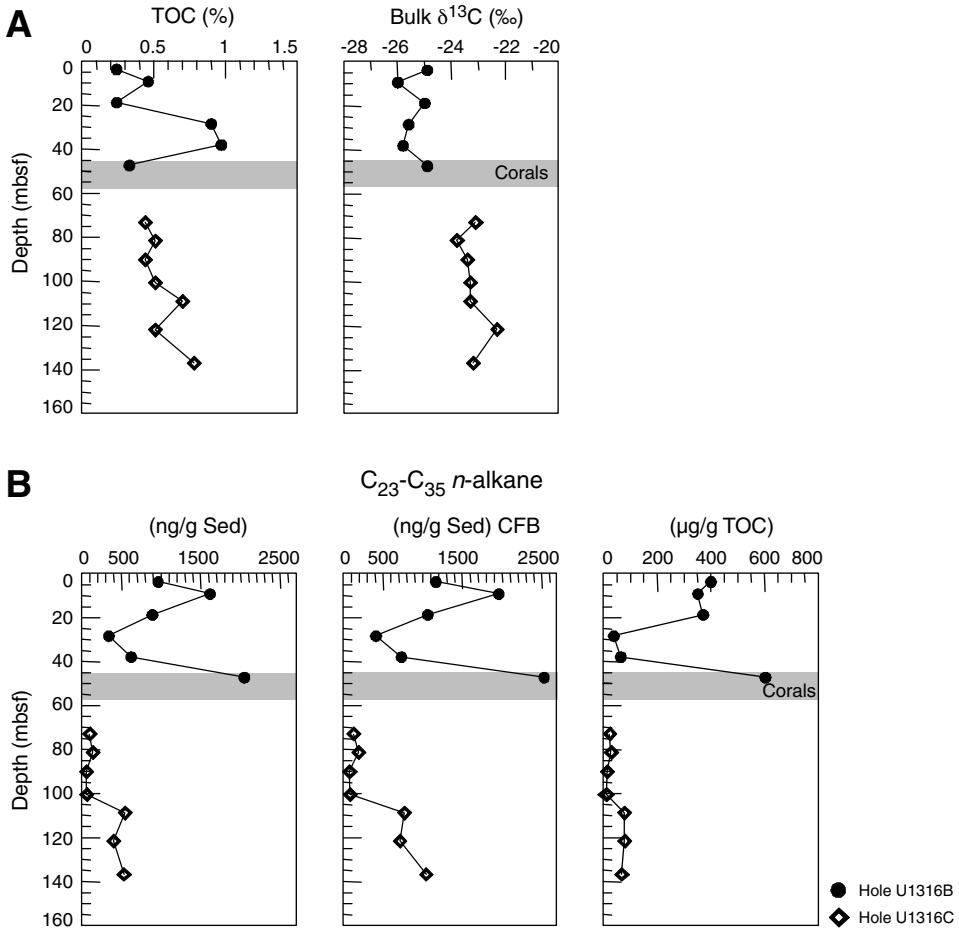

Figure F2. Distribution of (**A**) total hopanoids (sum of all hopanes and hopenes detected), (**B**) α,β-hopanes, and (**C**) β,β-hopanes in sediment samples from downslope Site U1316 related to the amount of dry sediment (g Sed) extracted, g Sed corrected for its carbonate content (carbonate-free basis [CFB]), and total organic carbon (TOC) content. Shaded area = coral intersection (flank of Challenger Mound).

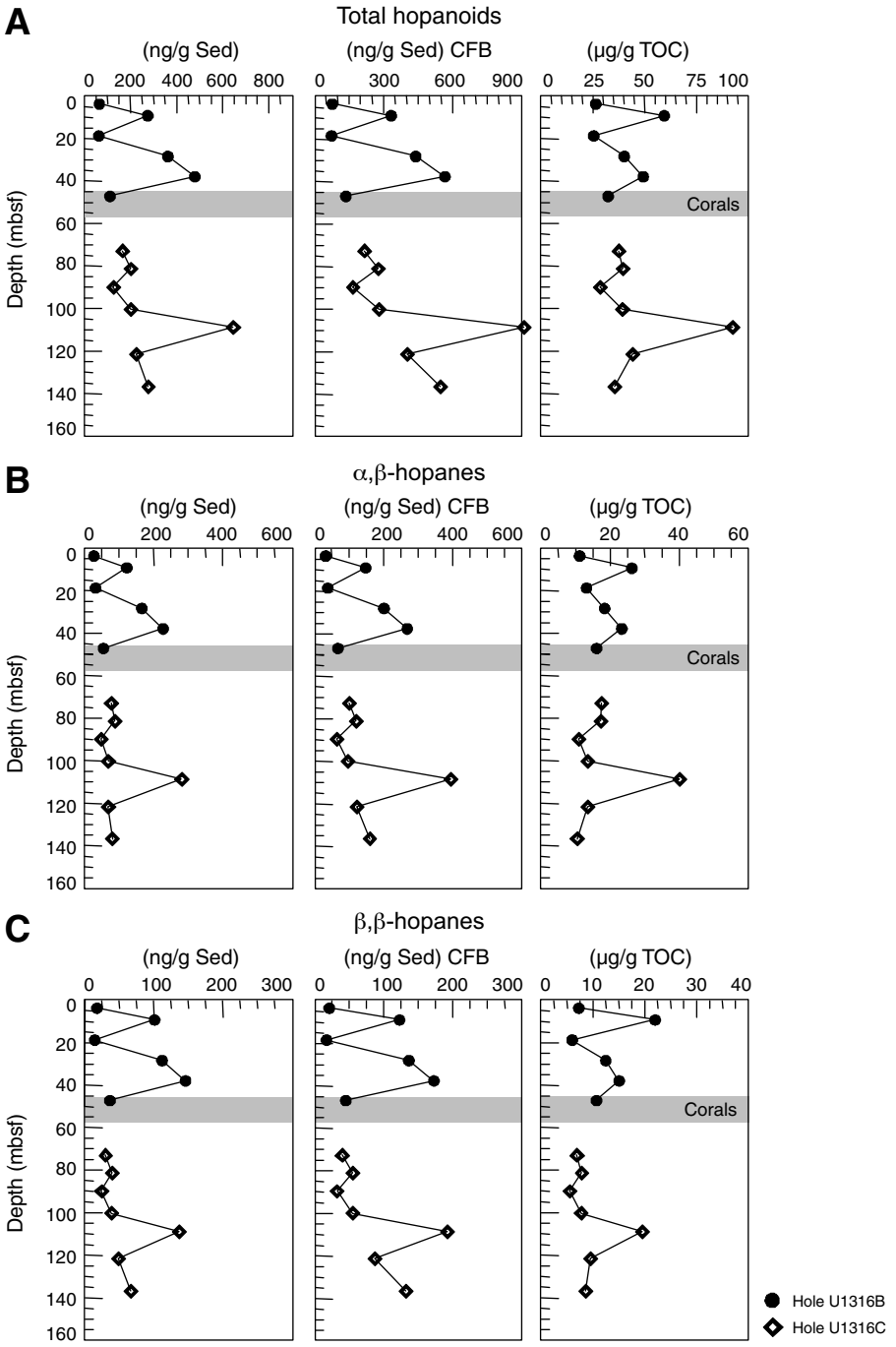

Figure F3. A. Distribution of total organic carbon (TOC) data and carbon isotope data of the total organic matter of sediment samples from Holes U1317A and U1317D. Shaded area = coral mound section of Challenger Mound. **B.** Distribution of long chain *n*-alkanes (C_{23}–C_{35}) in sediment samples from Holes U1317A and U1317D related to the amount of dry sediment (g Sed) extracted, g Sed corrected for its carbonate content (carbonate-free basis [CFB]), and TOC content. Note that the depth scales of Hole U1317A and U1317D appear mismatched. The two holes were aligned at the depth of the carbonate mound base.

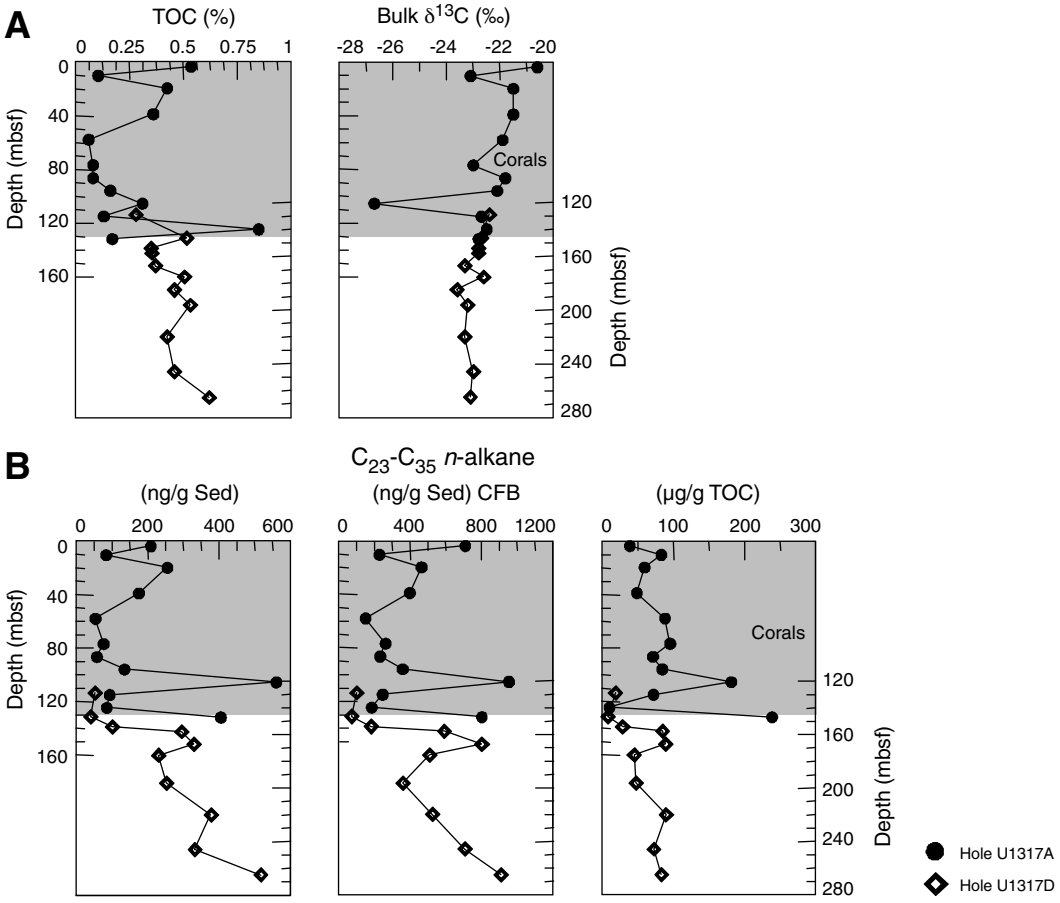

Figure F4. Distribution of (**A**) total hopanoids (sum of all hopanes and hopenes detected), (**B**) α,β-hopanes, and (**C**) β,β-hopanes in sediment samples from mound Site U1317 related to the amount of dry sediment (g Sed) extracted, g Sed corrected for its carbonate content (carbonate-free basis [CFB]), and total organic carbon (TOC) content. Shaded area = coral mound sequence at mound Site U1317. Note that the depth scales of Hole U1317A and U1317D appear mismatched. The two holes were aligned at the depth of the carbonate mound base.

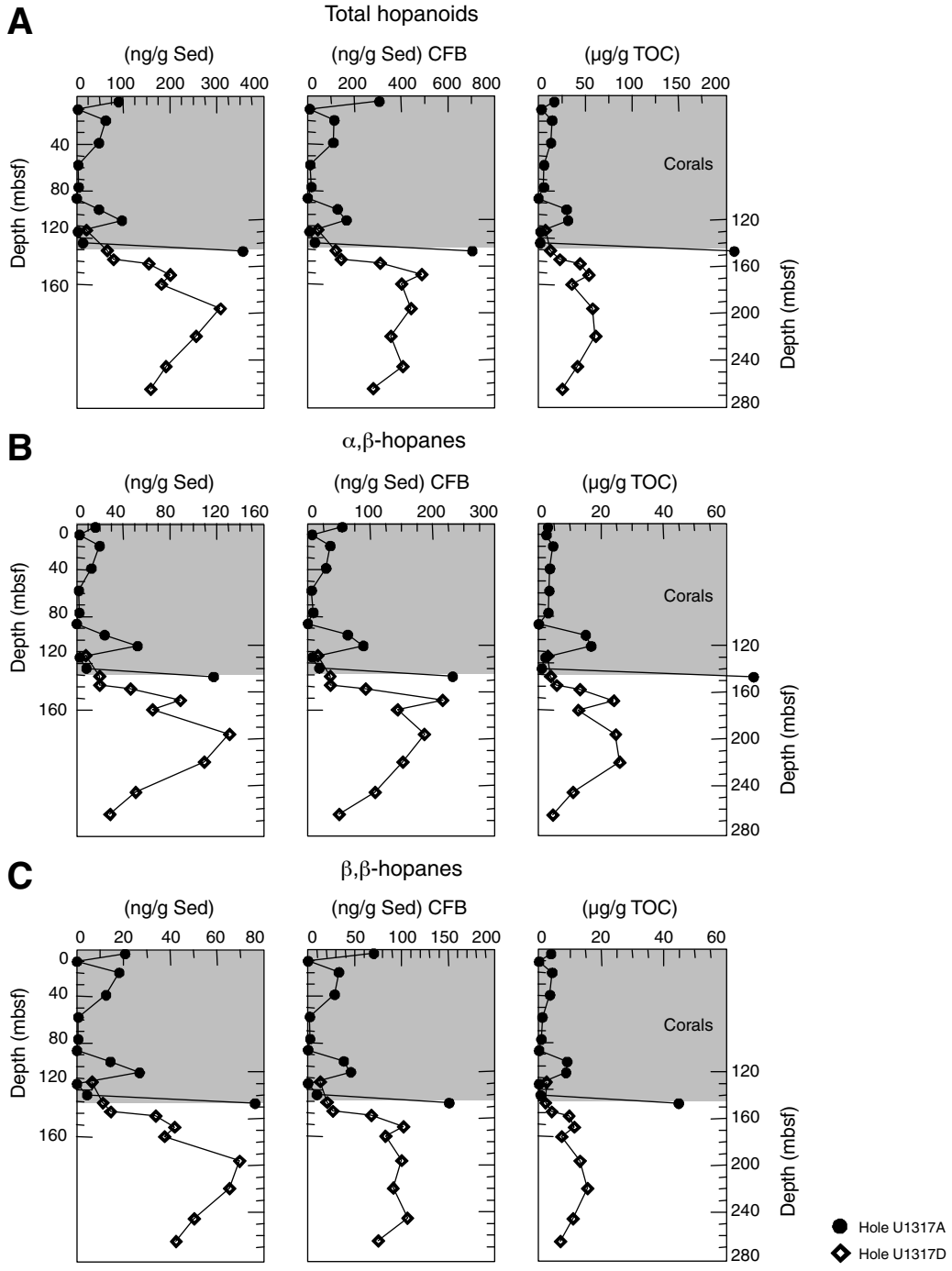

Figure F5. A. Methane, ethane, and propane concentrations in the headspace samples from the sediments at and below the mound base of Challenger Mound (Site U1317) as well as the gas wetness data calculated from these concentrations. **B.** Carbon isotope data of methane plotted against gas wetness data (Site U1317). Note that the depth scales of Hole U1317A and U1317D appear mismatched. The two holes were aligned at the depth of the carbonate mound base. PDB = Peedee belemnite.

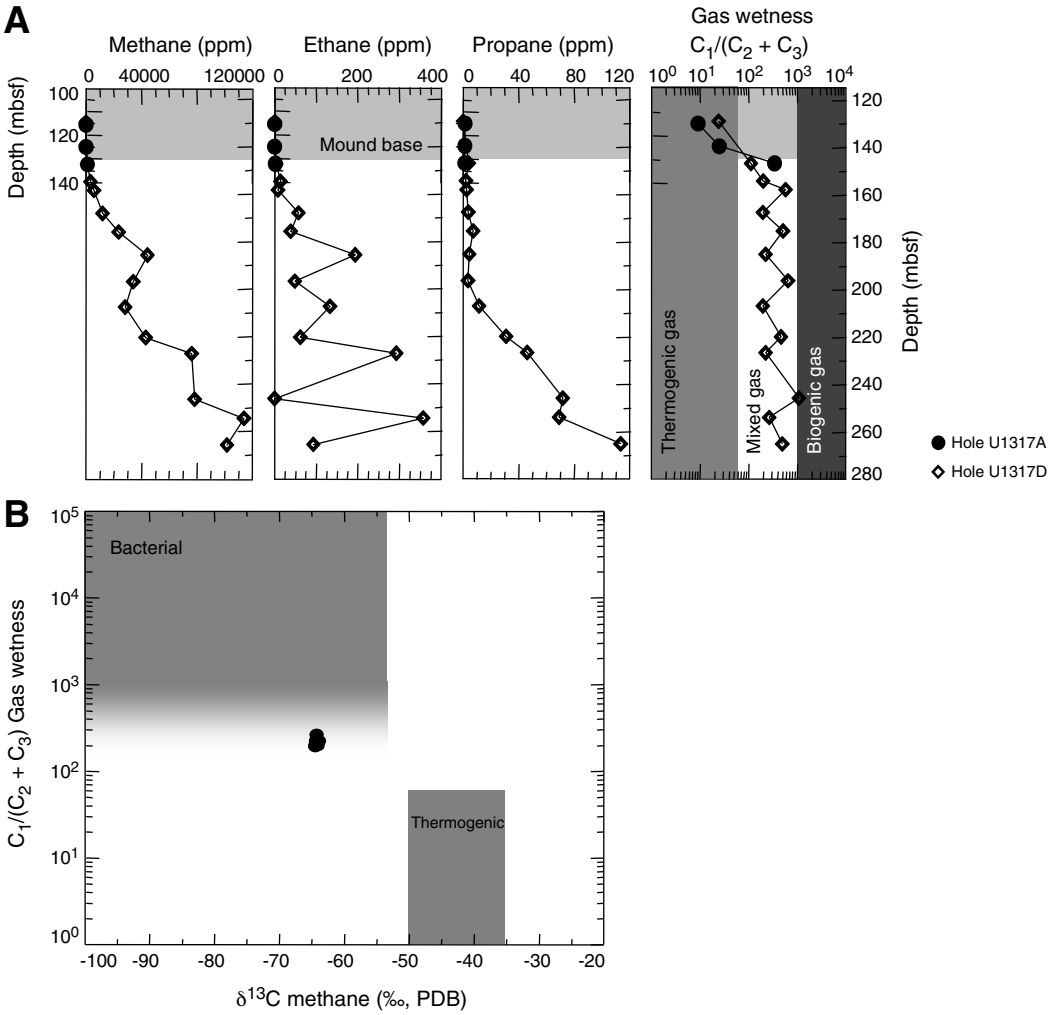

Figure F6. A. Distribution of total organic carbon (TOC) data and carbon isotope data of the total organic matter of sediment samples from Holes U1318A and U1318B. Hatched area = lithostratigraphic Subunits 1B and 1C. **B.** Distribution of long chain *n*-alkanes (C_{23}–C_{35}) in sediment samples from Holes U1318A and U1318B related to the amount of dry sediment (g Sed) extracted, g Sed corrected for its carbonate content (carbonate-free basis [CFB]), and TOC content.

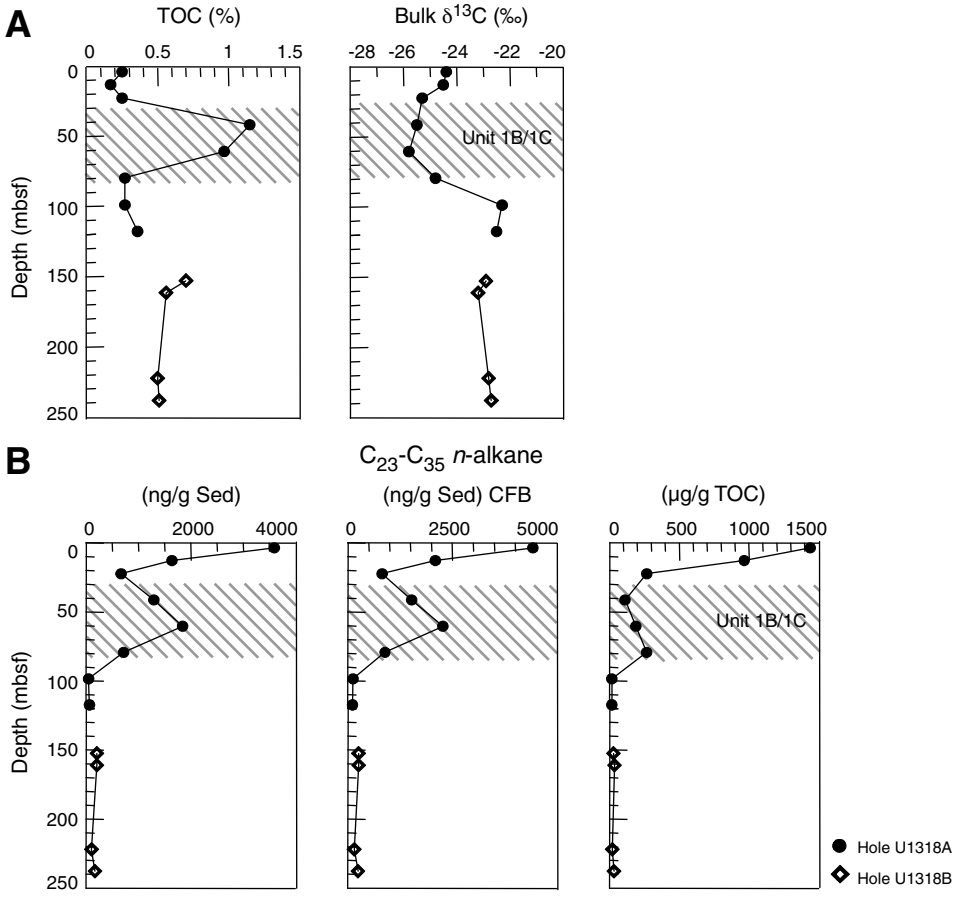

Figure F7. Distribution of (**A**) total hopanoids (sum of all hopanes and hopenes detected), (**B**) α,β-hopanes, and (**C**) β,β-hopanes in sediment samples from upslope Site U1318 related to the amount of dry sediment (g Sed) extracted, g Sed corrected for its carbonate content (carbonate-free basis [CFB]), and total organic carbon (TOC) content. Hatched area = lithostratigraphic Subunits 1B and 1C.

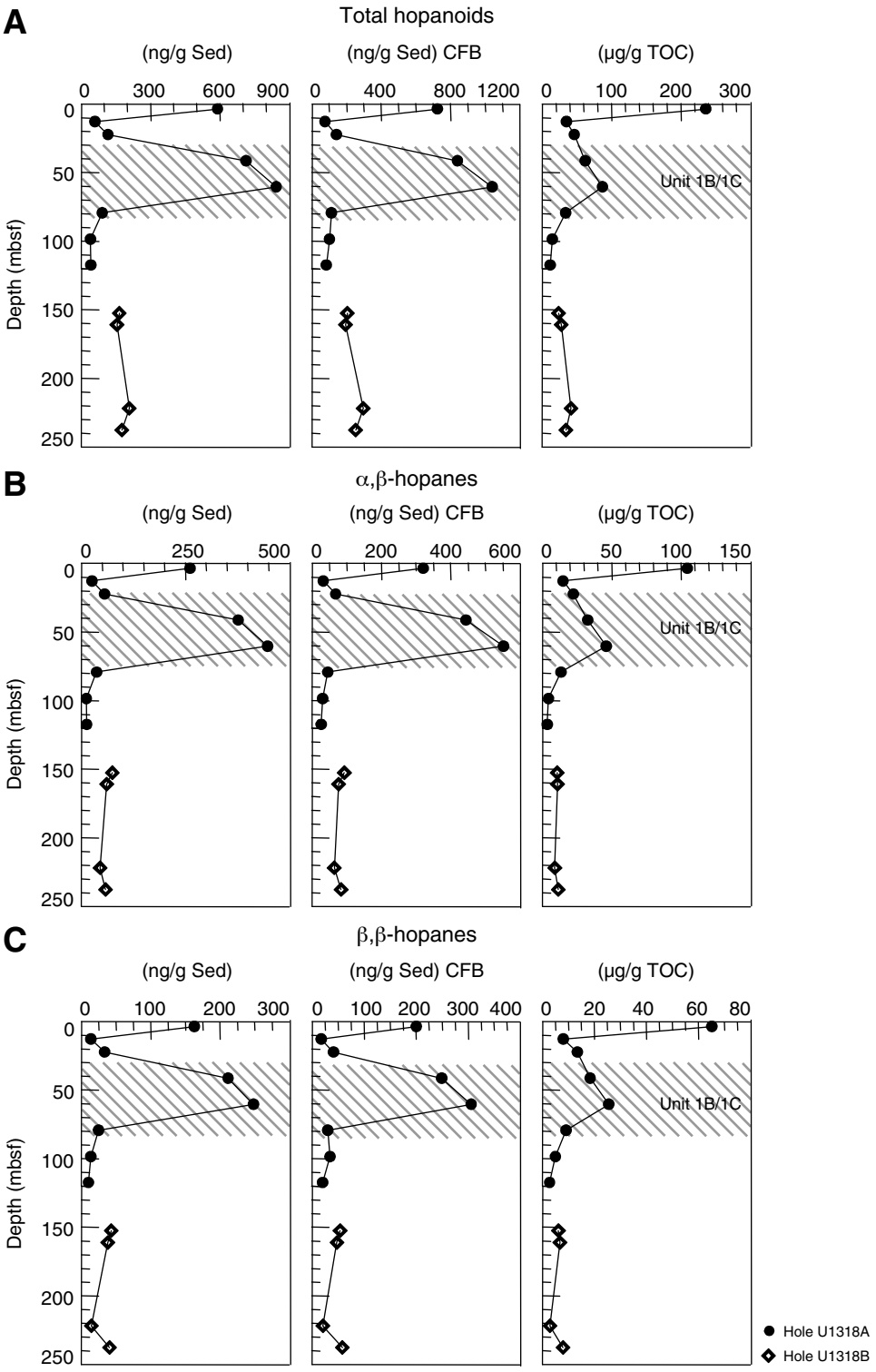

Figure F8. Distribution of phospholipid esters in sediment samples from the upslope Site U1318 related to the amount of sediment (g Sed) extracted, g Sed corrected for its carbonate content (carbonate-free basis [CFB]), and total organic carbon (TOC) content. Hatched area = lithostratigraphic Subunits 1B and 1C.

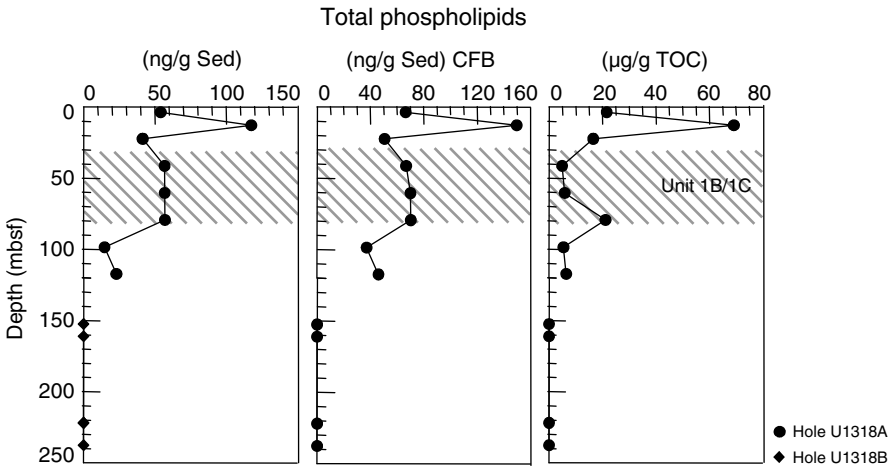

Table T1. Carbon, isotope, and biomarker data, Site U1316. (See table notes.)

Core, section, interval (cm)	Depth (mbsf)	TOC (%)	$\delta^{13}C$ (‰)	C_{23}–C_{35} *n*-alkanes			Total hopanoids			α,β-hopanes			β,β-hopanes		
				Dry sed. (ng/g)	Dry sed.* (ng/g)	TOC (µg/g)	Dry sed. (ng/g)	Dry sed.* (ng/g)	TOC (µg/g)	Dry sed. (ng/g)	Dry sed.* (ng/g)	TOC (µg/g)	Dry sed. (ng/g)	Dry sed.* (ng/g)	TOC (µg/g)
307-U1316B-															
1H-3, 56–68	3.62	0.24	–24.9	959.3	1165.0	399.7	63.3	76.8	26.4	26.6	32.3	11.1	17.3	21.0	7.2
2H-3, 58–70	9.14	0.46	–26.0	1612.3	1958.0	350.5	273.0	331.6	59.4	122.1	148.3	26.5	101.0	122.7	22.0
3H-3, 58–70	18.64	0.24	–25.0	888.2	1063.6	370.1	60.9	72.9	25.4	31.4	37.6	13.1	14.2	17.0	5.9
4H-3, 73–85	28.29	0.90	–25.6	337.3	410.4	37.5	360.6	438.9	40.1	165.2	201.0	18.4	111.8	136.1	12.4
5H-3, 73–85	37.79	0.97	–25.8	619.3	732.8	63.8	478.2	565.9	49.3	226.6	268.1	23.4	145.5	172.2	15.0
6H-3, 53–65	47.09	0.33	–24.9	2046.1	2528.4	601.8	109.6	135.4	32.2	54.5	67.3	16.0	36.2	44.7	10.6
307-U1316C-															
4R-4, 0–15	72.98	0.44	–23.1	100.6	132.1	22.9	165.4	217.2	37.6	77.0	101.1	17.5	30.3	39.8	6.9
5R-3, 26–36	81.31	0.51	–23.8	140.1	192.1	27.5	201.7	276.6	39.6	88.1	120.8	17.3	39.9	54.7	7.8
6R-2, 75–87	89.91	0.44	–23.4	61.4	82.4	14.0	125.3	167.9	28.5	48.1	64.5	10.9	24.2	32.5	5.5
7R-3, 0–12	100.26	0.51	–23.3	63.1	88.3	12.4	200.4	280.5	39.3	68.9	96.5	13.5	39.3	55.0	7.7
8R-2, 28–40	108.74	0.70	–23.3	547.3	769.9	78.2	646.4	909.2	92.3	281.0	395.2	40.1	136.6	192.2	19.5
9R-4, 37–49	121.53	0.51	–22.3	399.1	714.6	78.3	225.4	403.5	44.2	68.8	123.1	13.5	48.6	87.1	9.5
11R-3, 20–32	136.66	0.78	–23.2	530.9	1045.8	68.1	277.6	546.8	35.6	81.2	159.9	10.4	67.0	131.9	8.6

Notes: TOC = total organic carbon. Dry sed. = dry sediment, * = carbonate-free basis (corrected for carbonate content).

Table T2. Carbon, isotope, and biomarker data, Site U1317. (**See table notes.**)

Core, section, interval (cm)	Depth (mbsf)	TOC (%)	$\delta^{13}C$ (‰)	C_{23}–C_{35} *n*-alkane			Total hopanoids			α,β-hopanes			β,β-hopanes		
				Dry sed. (ng/g)	Dry sed.* (ng/g)	TOC (µg/g)	Dry sed. (ng/g)	Dry sed.* (ng/g)	TOC (µg/g)	Dry sed. (ng/g)	Dry sed.* (ng/g)	TOC (µg/g)	Dry sed. (ng/g)	Dry sed.* (ng/g)	TOC (µg/g)
307-U1317A-															
1H-3, 53–65	3.59	0.54	–20.6	208.2	709.1	38.6	89.9	306.3	16.7	16.1	54.8	3.0	20.6	70.2	3.8
2H-3, 58–70	10.14	0.10	–23.1	82.8	226.7	82.8	3.0	8.2	3.0	2.5	6.8	2.5	BD	BD	BD
3H-3, 58–70	19.64	0.43	–21.5	254.5	462.6	59.2	62.3	113.2	14.5	19.8	35.9	4.6	18.1	32.9	4.2
5H-3, 73–85	38.79	0.36	–21.5	175.2	398.0	48.7	47.9	108.9	13.3	12.8	29.0	3.6	12.5	28.4	3.5
7H-3, 73–85	57.79	0.06	–21.9	52.8	149.4	88.0	3.5	9.9	5.9	2.0	5.7	3.4	0.6	1.8	1.1
9H-3, 63–75	76.69	0.08	–23.0	76.1	262.0	95.1	4.5	15.4	5.6	2.5	8.5	3.1	0.6	2.1	0.7
10H-3, 75–85	86.3	0.08	–21.8	56.8	230.7	71.0	BD	BD	BD	BD	BD	BD	BD	BD	BD
11H-3, 73–85	95.79	0.16	–22.1	134.6	357.2	84.1	47.9	127.0	29.9	24.1	63.9	15.1	14.4	38.1	9.0
12H-3, 68–80	105.24	0.31	–26.7	560.2	953.3	180.7	97.1	165.3	31.3	52.2	88.8	16.8	26.8	45.6	8.6
13H-3, 78–90	114.84	0.13	–22.7	93.4	245.0	71.8	2.8	7.3	2.1	2.8	7.3	2.1	BD	BD	BD
14H-3, 83–95	124.39	0.85	–22.5	84.5	183.0	9.9	13.8	29.9	1.6	8.3	18.1	1.0	4.4	9.4	0.5
17X-1, 70–82	131.56	0.17	–22.8	405.0	801.7	238.2	355.8	704.3	209.3	117.2	232.1	67.0	76.2	150.9	44.8
307-U1317D-															
3R-2, 60–72	128.76	0.28	–22.4	51.8	101.5	18.5	21.5	42.1	7.7	8.2	16.0	2.9	6.6	12.9	2.4
5R-1, 60–72	146.46	0.52	–22.7	40.4	72.9	7.8	66.2	119.4	12.7	19.8	35.7	3.8	11.2	20.2	2.2
6R-3, 5–17	154.01	0.35	–22.8	100.8	182.8	28.8	79.3	143.9	22.7	19.8	36.0	5.7	14.5	26.3	4.1
7R-2, 55–67	157.51	0.35	–22.8	296.0	592.8	84.6	154.2	308.7	44.1	46.2	92.5	13.2	33.7	67.6	9.6
8R-2, 45–57	167.11	0.37	–23.3	329.1	802.2	88.9	200.4	488.4	54.1	88.9	216.6	24.0	41.8	102.0	11.3
9R-1, 48–60	175.24	0.51	–22.6	230.4	508.9	45.2	182.1	402.2	35.7	65.0	143.7	12.8	37.5	82.9	7.4
10R-1, 50–62	184.86	0.46	–23.6	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
11R-2, 68–80	196.14	0.53	–23.2	252.0	360.8	47.5	307.8	440.7	58.1	130.8	187.2	24.7	69.7	99.8	13.2
13R-5, 63–75	219.79	0.42	–23.3	377.1	524.9	89.8	255.6	355.8	60.9	109.5	152.4	26.1	65.3	90.9	15.5
16R-3, 70–82	245.66	0.46	–23.0	332.5	705.9	72.3	191.9	407.3	41.7	50.8	107.9	11.1	50.1	106.4	10.9
18R-3, 49–61	264.76	0.62	–23.1	516.7	910.2	83.3	159.1	280.3	25.7	28.6	50.3	4.6	42.5	74.9	6.9

Notes: TOC = total organic carbon. Dry sed. = dry sediment, * = carbonate free base (corrected for carbonate content). ND = not determined, BD = below detection limit. The detection limit of the gas chromatography–mass spectrometry system used for *n*-alkanes is 250 ng/mL (1 µL injection volume = 50 pg of target substance).

Table T3. Gas data, Site U1317. (See table note.)

Core, section, interval (cm)	Depth (cm)	C_1 (ppm)	C_2 (ppm)	C_3 (ppm)	*i*-C_4 (ppm)	*n*-C_4 (ppm)	CO_2 (ppm)	$C_1/(C_2 + C_3)$	*i*-C_4/*n*-C_4	$\delta^{13}C_1$ (‰)	$\delta D\ C_1$ (‰)
307-U1317A-											
13H-3, 115–120	115.18	13.8	0.1	1.4	0.1	0.1	1,242.6	9.2	1.0	ND	ND
14H-3, 115–120	124.68	35.0	0.2	1.2	BD	3.5	2,291.0	25.0	—	ND	ND
17X-1, 112–117	131.95	1,116.6	2.2	1.1	0.5	0.4	680.8	344.4	1.5	ND	ND
307-U1317D-											
3R-2, 112–117	129.25	14.4	0.6	BD	0.1	0.1	1,470.6	24.3	1.0	ND	ND
5R-1, 117–122	147.00	848.5	3.4	4.2	1.1	1.0	750.3	112.1	1.2	ND	ND
6R-3, 42–47	154.35	3,310.6	14.7	1.9	1.1	0.8	432.6	200.0	1.5	–64.1	ND
7R-2, 112–117	158.05	5,928.4	7.7	2.6	2.6	0.6	468.4	577.5	4.0	ND	ND
8R-2, 104–109	167.67	11,997.7	57.1	3.7	3.7	1.2	360.2	197.1	3.0	–64.5	–148
9R-1, 81–87	175.54	23,533.0	38.7	7.3	7.3	2.4	604.7	512.1	3.0	ND	ND
10R-1, 104–109	185.37	44,398.9	193.8	4.5	4.5	BD	450.8	223.9	—	–64.4	–146
11R-2, 107–112	196.50	34,043.2	48.7	3.5	BD	BD	696.2	652.0	—	ND	ND
12R-2, 109–114	207.20	28,321.5	133.1	11.6	5.8	2.9	347.1	195.8	2.0	–64.5	–150
13R-5, 95–100	220.08	42,955.6	61.7	30.8	22.0	8.8	969.3	464.3	2.5	ND	ND
14R-3, 107–112	226.80	76,077.8	292.3	46.2	38.5	15.4	384.6	224.,8	2.5	–63.9	–156
16R-3, 107–112	246.00	78,305.4	BD	71.8	55.9	23.9	1,277.2	1,090.0	2.3	ND	ND
17R-2, 107–112	254.10	113,812.7	357.1	69.1	57.6	23.0	760.3	267.0	2.5	–64.3	–163
18R-3, 107–112	265.31	101,566.3	92.8	113.4	82.5	41.3	1,031.1	492.5	2.0	ND	ND

Note: ND = not determined, BD = below detection limit, — = not applicable.

Table T4. Carbon, isotope, and biomarker data, Site U1318. (**See table notes.**)

Core, section, interval (cm)	Depth (mbsf)	TOC (%)	$\delta^{13}C$ (‰)	C_{23}–C_{35} *n*-alkanes			Total hopanoids			α,β-hopanes			β,β-hopanes		
				Dry sed. (ng/g)	Dry sed.* (ng/g)	TOC (µg/g)	Dry sed. (ng/g)	Dry sed.* (ng/g)	TOC (µg/g)	Dry sed. (ng/g)	Dry sed.* (ng/g)	TOC (µg/g)	Dry sed. (ng/g)	Dry sed.* (ng/g)	TOC (µg/g)
307-U1318A-															
1H-3, 57–69	3.63	0.25	–24.4	3,598.3	4,419.2	1,439.3	589.9	724.4	235.9	261.2	320.8	104.5	163.0	200.2	65.2
2H-3, 57–-69	12.83	0.17	–24.5	1,642.7	2,090.2	966.3	59.3	75.5	34.9	25.4	32.3	14.9	13.7	17.4	8.1
3H-3, 57–69	22.33	0.25	–25.3	669.7	818.3	267.9	115.9	141.6	46.4	55.7	68.1	22.3	33.7	41.1	13.5
5H-3, 58–70	41.34	1.15	–25.5	1,295.7	1,525.7	112.7	713.0	839.6	62.0	377.0	443.9	32.8	211.6	249.2	18.4
7H-3, 63–75	60.39	0.97	–25.8	1,844.5	2,274.6	190.2	843.7	1,040.5	87.0	447.6	551.9	46.1	248.2	306.1	25.6
9H-3, 53–65	79.29	0.27	–24.8	720.5	888.5	266.9	91.3	112.5	33.8	36.6	45.1	13.6	24.6	30.3	9.1
11H-3, 78–90	98.54	0.27	–22.3	48.6	123.8	18.0	39.8	101.4	14.8	12.1	30.8	4.5	13.6	34.5	5.0
13H-3, 58–70	117.34	0.36	–22.5	63.7	113.1	17.7	41.8	83.5	11.6	13.0	26.0	3.6	10.2	20.4	2.8
307-U1318B-															
17X-4, 23–35	152.49	0.70	–22.9	207.0	257.4	29.6	165.1	205.2	23.6	74.9	93.1	10.7	43.3	53.8	6.2
18X-3, 68–80	161.04	0.56	–23.2	206.9	259.1	36.9	154.6	193.7	27.6	61.1	76.5	10.9	38.3	47.9	6.8
24X-5, 115–127	221.91	0.50	–22.8	105.5	150.7	21.1	207.7	296.7	41.5	45.1	64.4	9.0	14.6	20.9	2.9
27X-2, 115–127	237.66	0.51	–22.7	170.1	244.7	33.4	175.9	253.0	34.5	58.4	84.0	11.5	40.6	58.4	8.0

Notes: TOC = total organic carbon. Dry sed. = dry sediment, * = carbonate-free basis (corrected for carbonate content).

Table T5. Phospholipid ester concentrations, Site U1318. (See table notes.)

Core, section, interval (cm)	Depth (mbsf)	Total phospholipids		Phosphatidylglycerol		Phosphatidylethanolamine	
		Sed. (ng/g)	TOC (µg/g)	Sed. (ng/g)	TOC (µg/g)	Sed. (ng/g)	TOC (µg/g)
307-U1318A-							
1H-3, 57–69	3.63	54.0	21.6	27.2	10.9	26.8	10.7
2H-3, 57–69	12.83	117.6	69.2	27.9	16.4	89.8	52.8
3H-3, 57–69	22.33	41.4	16.6	8.9	3.6	32.5	13.0
5H-3, 58–70	41.34	56.8	4.9	23.1	2.0	33.7	2.9
7H-3, 63–75	60.39	56.9	5.9	11.5	1.2	45.4	4.7
9H-3, 53–65	79.29	57.0	21.1	14.1	5.2	43.0	15.9
11H-3, 78–90	98.54	14.6	5.4	14.6	5.4	BD	BD
13H-3, 58–70	117.34	23.1	6.4	7.8	2.2	15.2	4.2
307-U1318B-							
17X-4, 23–35	152.49	BD	BD	BD	BD	BD	BD
18X-3, 68–80	161.04	BD	BD	BD	BD	BD	BD
24X-5, 115–127	221.91	BD	BD	BD	BD	BD	BD
27X-2, 115–127	237.66	BD	BD	BD	BD	BD	BD

Notes: Sed. = dry sediment extracted, TOC = total organic carbon. BD = below detection limit. Detection limit for phospholipids is difficult to determine because it can vary depending on the phospholipid class and the different sediment matrixes. For a phosphatidylglycerol standard, detection limit of the liquid chromatography–mass spectrometry system used is ~250 ng/mL (5 µL injection volume = ~1.3 ng of target substance).