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14. Data Report: *n*-Alkanes, Fatty Acids, and Hopanoids for ODP Leg 190 Site 1178[1]

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INTRODUCTION

Ocean Drilling Program (ODP) Leg 190 was programmed to investigate deformational, diagenetic, and hydrologic processes and their interactions in the Nankai Trough accretionary prism. Site 1178 is the northernmost site in the Muroto Transect. Slope sediments and the underlying landward-dipping reflector zone were successfully cored. Temperature measurements and Cl concentrations in pore water indirectly indicate the presence of gas hydrate between 120 and 400 meters below seafloor (mbsf) at Site 1178, with the highest concentrations between 150 and 200 mbsf (Shipboard Scientific Party, 2001). Sedimentary structures show a broad range of deformation structures rich in fractures, suggesting active fluid circulation in the Nankai Trough prism.

One of the objectives of Leg 190 was to clarify the interplay of various fundamental processes taking place in the Nankai Trough accretionary prism. Bacteria or prokaryotes in deep subsurface sediment play an important role for material transformation and circulation in an accretionary prism. Significant amounts of bacteria are detected in many of the samples examined (Shipboard Scientific Party, 2001). The type of organic matter in sediments is an important factor related to bacterial activity. To assist investigations on material circulation in deep subsurface sediments, the samples from Site 1178 were analyzed for geolipids (extractable organic matter). The basic data set is preliminarily compiled in the present report to show the types of organic matter and their concentrations in sediments from Site 1178.

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METHODS

The samples were freeze-dried and pulverized to <250 mesh. Geolipids were extracted using an ultrasonic cell crusher (BIORUPTOR BD-1, Cosmo Bio Co.) with a mixed solution of dichloromethane (DCM) and methanol (MeOH) as follows. Solvent extraction was performed a total of six times; DCM:MeOH (1:3) twice, DCM:MeOH (1:1) twice, and DCM twice. All extracts were combined and subjected to saponification under a reflux of 0.5-N KOH/MeOH for 3 hr. After saponification, the KOH/MeOH solution was transferred into a separatory funnel and neutral lipids were extracted four times with a mixed solution of hexane:diethylether (9:1). Organic acids were extracted four times with DCM after acidification by 1-N HCl.

Column chromatography for neutral lipids was performed using silica gel 60N (Kanto Chemical Co.). Saturated hydrocarbons, unsaturated hydrocarbons, and alcohols in neutral lipids were fractionated with hexane (30 mL), hexane:ethyl acetate (9:1) (25 mL), and ethyl acetate:MeOH (1:1) (30 mL), respectively. Alcohols were trimethylsilylified (TMS) using BSTFA (Wako Co.) at 60°C. Esterification of organic acids was carried out with 12% BF_3/MeOH (Acros Organics Co.). Hydrocarbons, TMS alcohols, and organic acid methyl esters were analyzed by gas chromatography (GC) and gas chromatography/mass spectrometry (GC/MS).

GC was performed using a Hewlett-Packard HP6890 GC equipped with a fused silica capillary column (HP-5, 30 m × 0.25 mm; Hewlett Packard Co.). The oven temperature was programmed isothermally at 60°C for 2 min, from 60°C to 250°C at 10°C/min, from 250°C to 320°C at 3°C/min, and held at 320°C for 20 min. GC/MS was performed using a Hewlett-Packard HP6890 GC and HP5973 mass selective detector (MSD) equipped with a fused silica capillary column (DB-5, 30 m × 0.25 mm; J&W Co.). The same oven temperature program was applied to the GC/MS analysis. The mass spectrometer was operated at electron energy of 70 eV and an ion source temperature of 250°C. The interface temperature between the GC and MSD was held at 320°C. Identification of hopanes, hopenes, and hopanoic acids was based on the mass spectra library and published literature (e.g., Ishiwatari et al., 2000; Farrimond et al., 2002).

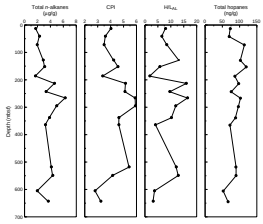
RESULTS

The results of hydrocarbon analyses are shown in Table T1 and Figure F1 with composite core depth. Concentrations of total *n*-alkanes are comparatively high in depths from 200 to 400 mbsf (Subunit IIA), which is characterized by abundant sand and silt turbidites with carbonate-poor mudstones (Shipboard Scientific Party, 2001). Total *n*-alkane concentration (C_{15}–C_{37}) ranges from 1.63 to 6.23 µg/g. Variation of total *n*-alkane concentration corresponds well with the change of carbon preference index (CPI) and terrigenous to aquatic *n*-alkane ratio (H/L_{AL}) (Fig. F1). Total hopane concentrations are in the range from 50 to 120 ng/g (Table T1; Fig. F1).

Concentration of total fatty acids (C_{12}–C_{34}), terrigenous to aquatic fatty acids ratio (H/L_{FA}), and concentration of regular hopanoic acids (C_{30}–C_{32}) are shown in Table T2 and Figure F2. Concentrations of fatty acids range from 0.62 to 4.85 µg/g. Relative abundance of terrigenous

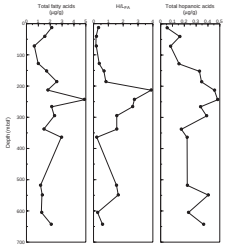
T1. *n*-Alkanes, CPI, H/L_{AL}, and hopanes, p. 8.

F1. *n*-Alkanes, CPI, H/L_{AL}, and hopanoic acids, p. 5.



T2. Fatty acids, H/L_{FA}, and hopanoic acids, p. 9.

F2. Fatty acids, H/L_{FA}, and hopanoic acids, p. 6.



fatty acids tends to be significantly high in Subunit IIA, showing high terrigenous organic matter contribution as indicated by terrigenous to aquatic *n*-alkane ratio (H/L_{AL}) (Fig. **F1**). Concentrations of hopanoic acids are also high in Subunit IIA, suggesting a terrestrial origin.

Concentrations of diploptene (Hop-22(29)-ene) and diploptene-related hopenes such as hop-21-ene, hop-17(21)-ene, and neohop-13(18)-ene are shown in Table **T3** and Figure **F3.** Diploptene is present in various types of bacteria and occurs in diverse environments (Rohmer et al., 1984; Ourrisson et al., 1987). Concentrations of diploptene and hop-21-ene decrease quickly with depth. Diploptene and hop-21-ene were not detected in the samples below 200 mbsf. Concentration of hop-17(21)-ene tends to increase from 21.1 to 276.4 ng/g with increasing depth, whereas concentrations of neohop-13(18)-ene are in the range from 7.3 to 20.4 ng/g. Diagenetic transformation of diploptene to form hop-21-ene, hop-17(21)-ene, and neohop-13(18)-ene has been proposed by Brassell et al. (1980).

T3. Diploptene, hop-21-ene, hop-17(21)-ene, and neohop-13(18)-ene, p. 10.

F3. Diploptene, hop-21-ene, hop-17(21)-ene, and neohop-13(18)-ene, p. 7.

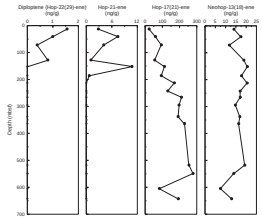


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Figure F1. Total *n*-alkane concentrations, *n*-alkane carbon preference index (CPI), terrigenous to aquatic *n*-alkane ratio (H/L_{AL}), and total hopane concentrations vs. depth for Site 1178.

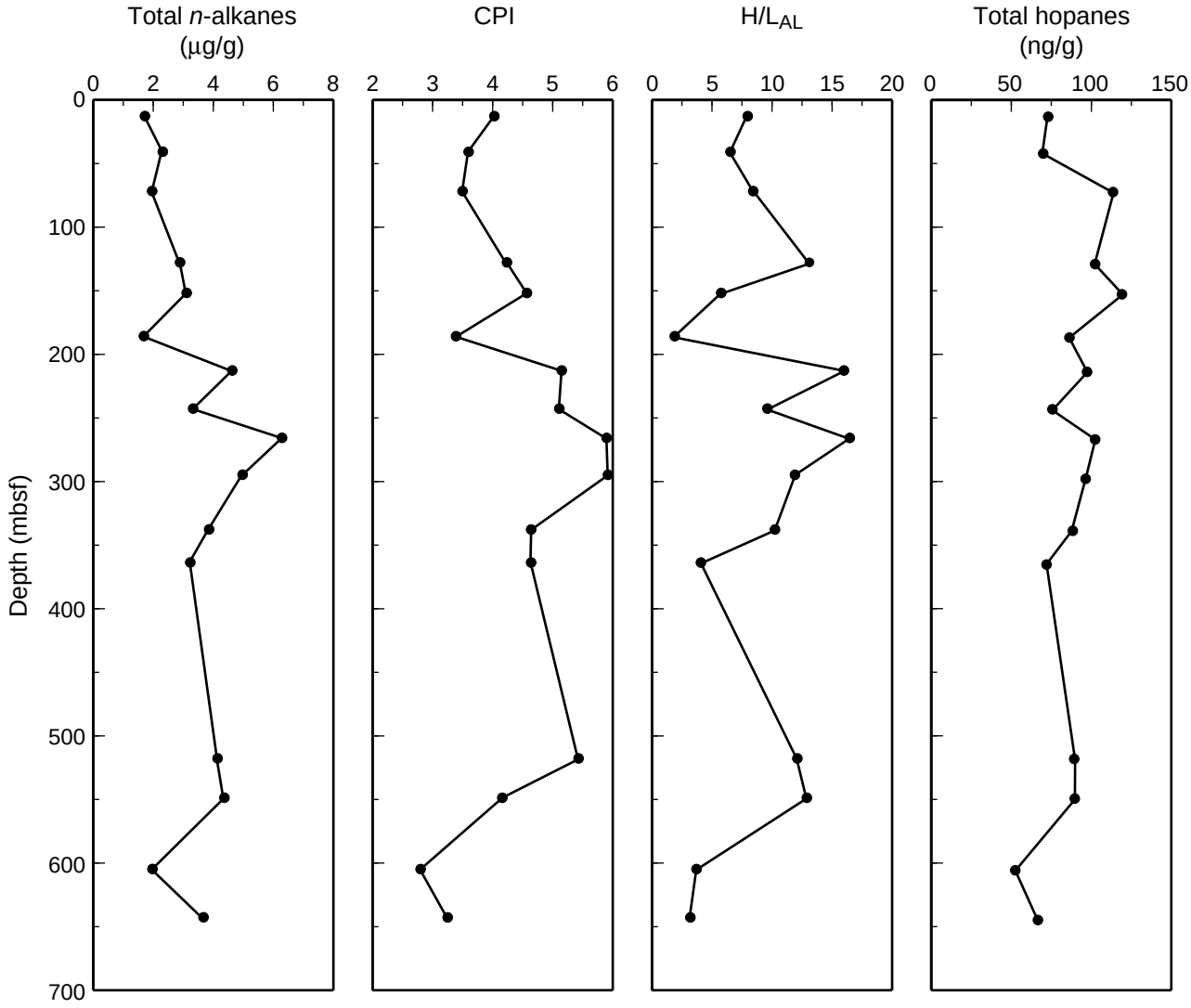

Figure F2. Total fatty acid concentrations, terrigenous to aquatic fatty acids ratio (H/L_{FA}), and total hopanoic acid concentrations vs. depth for Site 1178.

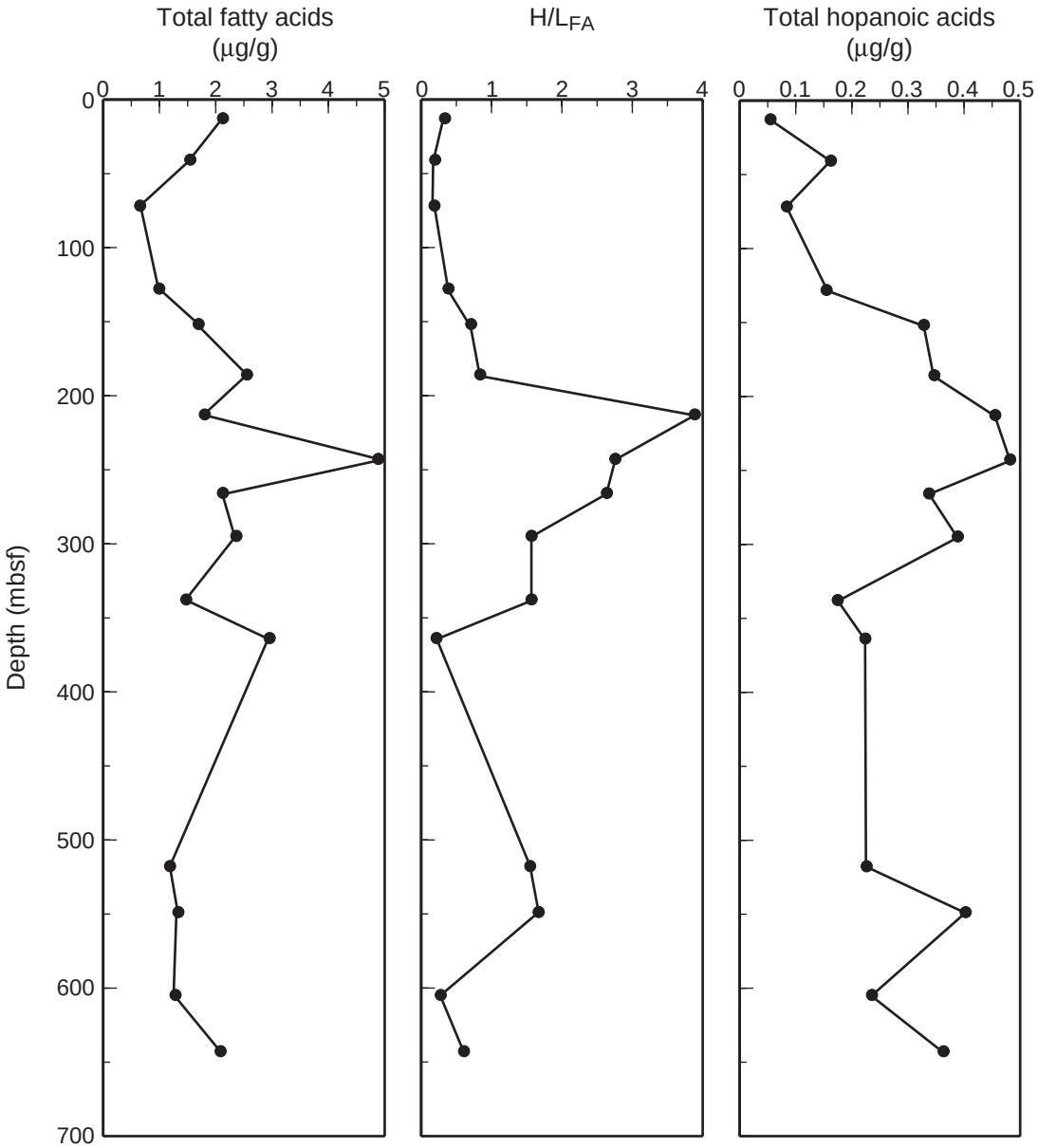

Figure F3. Diploptene (hop-22(29)-ene), hop-21-ene, hop-17(21)-ene, and neohop-13(18)-ene concentrations vs. depth for Site 1178.

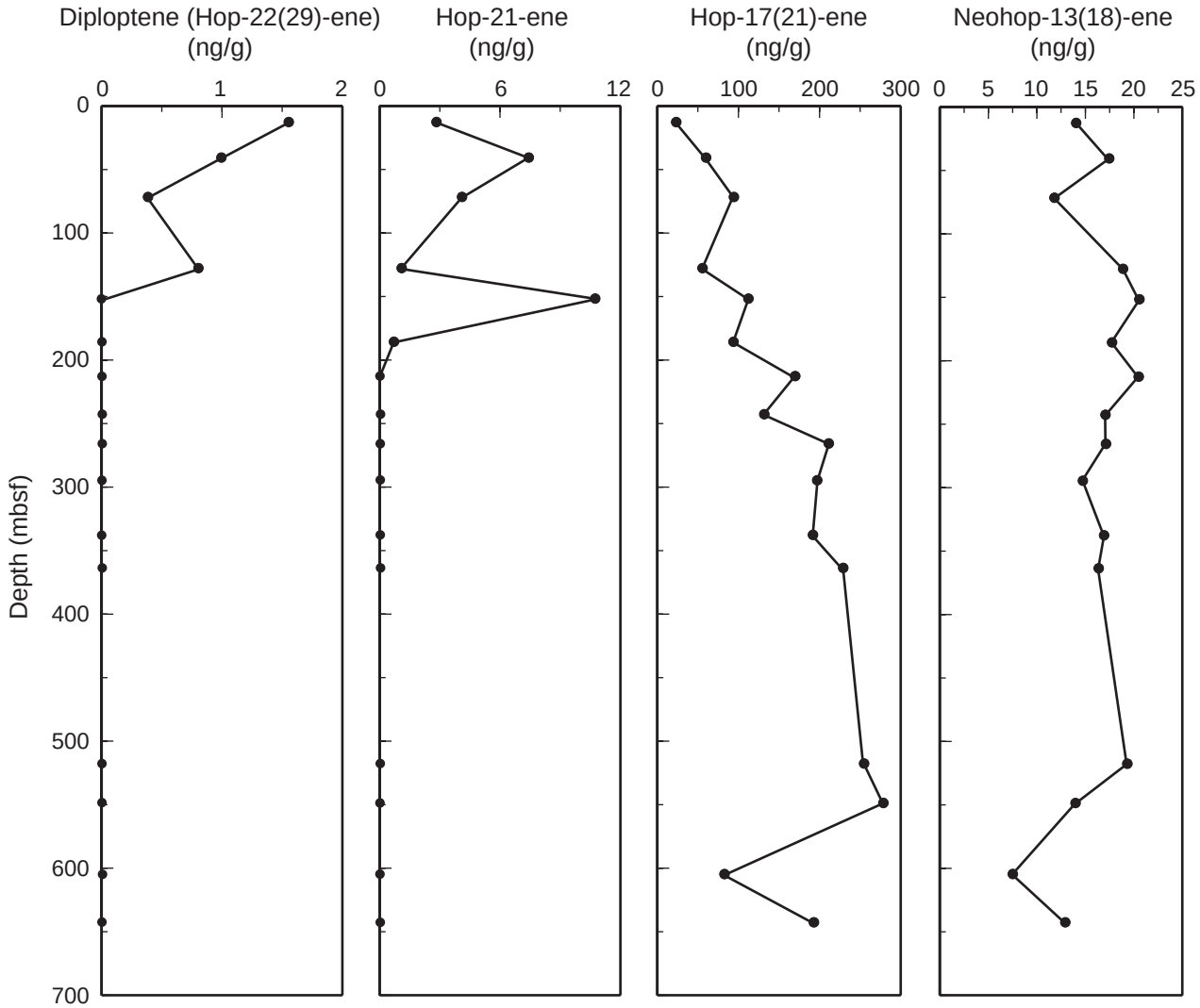

Table T1. Total *n*-alkane concentrations, *n*-alkane CPI, H/L_{AL}, and total hopane concentrations, Site 1178.

Core, section, interval (cm)	Depth (mbsf)	Total *n*-alkanes (µg/g)	CPI	H/L_{AL}	Hopanes (µg/g)
190-1178A-					
3H-2, 100–115	13.9–15.4	1.66	4.00	7.8	43.1
6H-2, 115–130	42.4–43.9	2.26	3.57	6.4	71.5
9X-7, 91–106	73.6–74.8	1.90	3.47	8.3	49.4
15X-5, 115–130	129.2–130.7	2.83	4.21	12.7	67.4
18X-2, 6–22	152.8–153.7	3.05	4.54	5.6	69.8
21X-5, 29–44	186.4–187.9	1.63	3.36	1.8	46.9
24X-4, 120–135	213.2–214.7	4.57	5.12	15.8	94.0
27X-5, 10–25	243.8–245.3	3.27	5.08	9.5	68.0
30X-1, 70–86	266.6–268.1	6.23	5.87	16.3	85.5
33X-1, 75–90	295.5–297.0	4.92	5.89	11.8	83.0
37X-4, 75–90	338.5–340.0	3.80	4.61	10.1	67.2
40X-2, 34–51	364.4–365.9	3.17	4.61	3.9	64.9
190-1178B-					
15R-3, 20–35	518.6–520.1	4.08	5.40	12.0	71.7
18R-5, 25–38	550.4–550.8	4.31	4.13	12.8	70.7
24R-3, 76–91	605.1–606.6	1.91	2.77	3.6	36.5
28R-3, 66–81	643.7–645.0	3.61	3.22	3.1	45.4

Notes: *n*-alkanes = ΣC_{15}–C_{37} *n*-alkanes/g dry sediment. CPI (carbon preference index) = $1/2 \times [(C_{25} + C_{27} + C_{29} + C_{31} + C_{33})/(C_{24} + C_{26} + C_{28} + C_{30} + C_{32}) + (C_{25} + C_{27} + C_{29} + C_{31} + C_{33})/(C_{26} + C_{28} + C_{30} + C_{32} + C_{34})]$. $H/L_{AL} = (C_{27} + C_{29} + C_{31})/(C_{15} + C_{17} + C_{19})$. Total hopanes = Σ[17α-22,29,30-trisnorhopane + 17β-22,29,30-trisnorhopane + 17α,21β-30-norhopane + 17β,21β-30-norhopane + 17α,21β-hopane + 17β,21β-hopane + 17α,21β-homohopane (22S + 22R) + bishomohopane (22S + 22R)]/g dry sediment.

Table T2. Total fatty acid concentrations, H/L_{FA}, and total hopanoic acid concentrations, Site 1178.

Core, section, interval (cm)	Total fatty acids (µg/g)	H/L_{FA}	Total hopanoic acids (µg/g)
190-1178A-			
3H-2, 100–115	2.09	0.31	0.05
6H-2, 115–130	1.51	0.17	0.16
9X-7, 91–106	0.62	0.16	0.08
15X-5, 115–130	0.96	0.36	0.14
18X-2, 6–22	1.61	0.68	0.33
21X-5, 29–44	2.52	0.81	0.34
24X-4, 120–135	1.77	3.86	0.45
27X-5, 10–25	4.85	2.73	0.48
30X-1, 70–86	2.09	2.61	0.33
33X-1, 75–90	2.33	1.54	0.39
37X-4, 75–90	1.44	1.54	0.17
40X-2, 34–51	2.86	0.19	0.22
190-1178B-			
15R-3, 20–35	1.15	1.52	0.22
18R-5, 25–38	1.30	1.64	0.40
24R-3, 76–91	1.25	0.25	0.23
28R-3, 66–81	2.05	0.58	0.36

Notes: Total fatty acids = ΣC_{12}–C_{34} fatty acids/g dry sediment. $H/L_{FA} = (C_{24} + C_{26} + C_{28})/(C_{14} + C_{16} + C_{18})$. Total hopanoic acids = Σ[17α,21β-hopanoic acid (22S + 22R) + 17β,21β-hopanoic acid (22S + 22R) + 17α,21β-homohopanoic acid (22S + 22R) + 17α,21β-bishomohopane acid (22S) + 17β,21β-1bishomohopanoic acid (22R) + 17β,21β-trishomohopanoic acid (22R)]/g dry sediment.

Table T3. Diploptene (Hop-22(29)-ene), hop-21-ene, hop-17(21)-ene, and neohop-13(18)-ene concentrations, Site 1178.

Core, section, interval (cm)	Diploptene* (ng/g)	Hop-21-ene (ng/g)	Hop-17(21)-ene (ng/g)	Neohop-13(18)-ene (ng/g)
190-1178A-				
3H-2, 100–115	1.5	2.8	21.1	13.9
6H-2, 115–130	1.0	7.4	57.9	17.3
9X-7, 91–106	0.4	4.0	92.2	11.6
15X-5, 115–130	0.8	1.0	53.6	18.7
18X-2, 6–22	0	10.7	110.2	20.4
21X-5, 29–44	0	0.6	91.7	17.6
24X-4, 120–135	0	0	167.8	20.3
27X-5, 10–25	0	0	129.7	16.9
30X-1, 70–86	0	0	209.1	17.0
33X-1, 75–90	0	0	195.0	14.6
37X-4, 75–90	0	0	189.6	16.8
40X-2, 34–51	0	0	227.0	16.2
190-1178B-				
15R-3, 20–35	0	0	252.7	19.1
18R-5, 25–38	0	0	276.4	13.8
24R-3, 76–91	0	0	80.6	7.3

Note: * = hop-22(29)-ene.