Tiedemann, R., Mix, A.C., Blum, P., and Ruddiman, W.F. (Eds.) Proceedings of the Ocean Drilling Program, Scientific Results Volume 202

7. DATA REPORT: ORGANIC CARBON AND BIOMARKER VARIATIONS, SITES 1237 AND 1239¹

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INTRODUCTION

We generated preliminary downcore records of total organic carbon content, calcium carbonate, long-chain *n*-alkane concentration, total alkenone concentration, and alkenone-based sea-surface temperature for samples from the easternmost flank of Nazca Ridge (Site 1237) and the eastern crest of Carnegie Ridge (Site 1239). Total organic carbon and long-chain *n*-alkane concentrations will be used to evaluate terrestrial sediment sources. Downcore records of alkenone sea-surface temperature will benefit studies of paleoceanography of the southeastern Pacific. Since these sites are located under the influence of major tectonic events, such as the uplift of the Andes Mountains and the closure of the Isthmus of Panama, the records will help us to examine the effects of the tectonic events on the oceanic environment.

SAMPLES AND METHODS

Samples

Two sites were sampled on the Nazca and Carnegie Ridges: Sites 1237 and 1239, respectively (Fig. F1) (Mix, Tiedemann, Blum, et al., 2003). Site 1237 is located at 16°0.42′S, 76°22.69′W, at 3212 m water depth. Samples were taken from 0.01 to 180.04 meters composite depth (mcd). According to the age model of this site (Shipboard Scientific Party, 2003a), the ages of the samples range from 0 to 10.4 Ma. The sediments of the uppermost 41 mcd consist mostly of olive and olive-gray

F1. Site 1237 and 1239 locations, p. 6.



¹Abe, C., Yamamoto, M., and Irino, T., 2006. Data report: organic carbon and biomarker variations, Sites 1237 and 1239. *In* Tiedemann, R., Mix, A.C., Blum, P., and Ruddiman, W.F. (Eds.), *Proc. ODP, Sci. Results*, 202: College Station, TX (Ocean Drilling Program), 1–14. doi:10.2973/odp.proc.sr.202.203.2006 ²Graduate School of Environmental Earth Science, Hokkaido University, Kita-10, Nishi-5, Kita-Ku, Sapporo 060-0810, Japan. Correspondence author: **myama@ees.hokudai.ac.jp**

Initial receipt: 15 September 2004 Acceptance: 13 September 2005 Web publication: 29 March 2006 Ms 202SR-203

nannofossil-bearing silty clay. The sediments from 41 to 100 mcd consist mostly of light greenish gray clayey nannofossil ooze (Shipboard Scientific Party, 2003a). Site 1239 is located at 0°40.32'S, 82°4.86'W, in 1414 m water depth. Samples were taken from 0.01 to 489.40 mcd. According to the age model for this site (Shipboard Scientific Party, 2003b), the ages of the samples range from 0 to 6.56 Ma. Sediments are dominated by light to dark olive-gray foraminifer-nannofossil ooze with varying amounts of diatoms, clay, and micrite (Shipboard Scientific Party, 2003b).

Analytical Method

A total of 135 freeze-dried sediment samples were analyzed for total carbon (TC) and total organic carbon (TOC) using a LECO WR-112 carbon analyzer, following the method of Yamamoto (2004). The analyzer was attached to a halogen trap (antimony and potassium iodide). To remove carbonate carbon, the sample was acidified according to the following procedure. The sample (~0.1–0.5 g) was soaked in a 1-mol/L HCl solution in a ceramic crucible overnight and was heated at 150°C for 3 hr after adding more 1-mol/L HCl solution. The sample was rinsed twice to remove chlorides by adding pure water and then was heated again at 150°C for 3 hr. The precision of measurement for TC and TOC was better than 0.01 wt%. Inorganic carbon (IC) and calcium carbonate (CaCO₃) contents were calculated according to the following equations:

$$IC = TC - TOC$$

and

$$CaCO_3 = IC \times 8.33.$$

A total of 43 freeze-dried sediment samples (1 g) were extracted by a Dionex ASE-200 accelerated solvent extractor (two times at 100°C and 1000 psi for 5 min) with a mixture of dichloromethane:methanol (6:4 v:v). The lipid extract was separated into four fractions (Fraction 1: 3 mL of hexane, Fraction 2: 3 mL of hexane/toluene [3:1 v:v], Fraction 3: 4 mL of toluene, and Fraction 4: 3 mL of toluene/methanol [3:1 v:v]) by column chromatography (SiO₂ with 5% distilled water, 5.5-mm internal diameter [ID] × 45-mm long). n-C₂₄H₅₀ was added as an internal standard to Fraction 1 (*n*-alkanes). n-C₃₆H₇₄ was added as an internal standard to Fraction 3 (alkenones and alkenoates).

Gas chromatography for Fractions 1 and 3 was conducted using a Hewlett Packard 6890 gas chromatograph (GC) with on-column injection and electronic pressure control inlet systems and a flame ionization detector. The column used was a capillary column coated with Chrompack CP-Sil5CB (60 m long \times 0.25 mm ID, 0.25 mm coating). The GC oven temperature for analysis of Fraction 1 was programmed from 70° to 130°C at 20°C/min, from 130° to 310°C at 20°C/min, and then was held at 310°C for 30 min. The GC oven temperature for analysis of Fraction 3 was programmed from 70° to 290°C at 20°C/min, from 290° to 310°C at 0.5°C/min, and then was held at 310°C for 30 min. Helium was used as a carrier gas, and flow velocity was maintained at 30 cm/s.

The odd/even carbon number preference index (CPI) of long-chain *n*-alkanes (LNAs) was calculated using the following equation (Bray and Evans, 1961):

$$CPI = [\Sigma(C_{25} - C_{33})_{odd} / \Sigma(C_{24} - C_{32})_{even} + \Sigma(C_{25} - C_{33})_{odd} / \Sigma(C_{26} - C_{34})_{even}] / 2.$$

The average chain length (ACL) of LNAs was calculated using the following equation (Poynter and Eglinton, 1990):

ACL =
$$(27 \times C_{27} + 29 \times C_{29} + 31 \times C_{31})/(C_{27} + C_{29} + C_{31})$$
.

The alkenone unsaturation index $U_{37}^{k'}$ was calculated from the concentrations of di- and triunsaturated C_{37} alkenones (C_{37} MK) using the following equation (Brassell et al., 1986; Prahl et al., 1998):

$$U_{37}^{k'} = (C_{37:2}MK) / [(C_{37:2}MK) + (C_{37:3}MK)].$$

The calculation of temperature was conducted according to the following equation:

$$U^{k'}_{37} = 0.034T + 0.039,$$

where T = temperature (°C), based on an experimental result for cultured Strain 55a of *Emiliania huxleyi* (Prahl et al., 1988) with an estimated accuracy of 0.5°C (Prahl and Wakeham, 1987).

RESULTS

Total Organic Carbon and Calcium Carbonate

TOC varied between 0 and 1.27 wt% of dry sediment, with an average of 0.20 wt% at Site 1237 (Fig. F2; Table T1). CaCO₃ varied between 0.3 and 94.9 wt% of dry sediment, with an average of 67.2 wt%. Below ~110 mcd, TOC contents were very low and CaCO₃ values were higher than 89 wt% with an exception at 160.08 mcd (ash layer). Above ~110 mcd, TOC gradually increased and CaCO₃ gradually decreased with decreasing depth. The increase of TOC and the decrease of CaCO₃ were marked above ~41 mcd.

In Site 1239 samples, TOC varied between 0.21 and 3.35 wt%, with an average of 1.22 wt% (Fig. F3; Table T2). $CaCO_3$ varied between 18.9 and 82.4 wt%, with an average of 60.0 wt%. Below ~90 mcd, TOC gradually increased and $CaCO_3$ gradually decreased upward. TOC maximized at 89.71 mcd, and $CaCO_3$ minimized at 84.51 mcd. TOC abruptly decreased at 84.51 mcd, and $CaCO_3$ was almost constant in the uppermost 84.51 mcd.

Total *n*-Alkanes, CPI, and ACL

Normal alkanes were analyzed for Site 1237 sediments. The concentration of LNAs (n-C₂₅-C₃₃) varied between 0.18 and 5.18 µg/g of sediment, with an average of 1.46 µg/g (Fig. F4; Table T1). LNAs were below detection limit in the sediments below 125.51 mcd. CPI varied between 2.4 and 5.9, with an average of 4.1. ACL varied between 29.0 and 30.0,

F2. TOC and $CaCO_3$ depth profiles, Site 1237, p. 7.





F3. TOC and $CaCO_3$ depth profiles, Site 1239, p. 8.



T2. Site 1239 sediment data, p. 12.

F4. *n*-alkane, CPI, and ACL depth profiles, p. 9.



with an average of 29.8. The concentration of LNAs and CPI gradually increased uphole, and they maximized at 15.02 mcd. Above ~15 mcd, the concentration of LNAs and CPI decreased. ACL was almost constant throughout the range of the site.

The increase of LNAs uphole is associated with the increase of TOC and the decrease of calcium carbonate, which is attributed to the increasing contribution of terrestrial organic matter together with Aeolian dusts. The variation of CPI presumably reflects the changes of terrestrial organic matter compositions such as mixing ratio of the fresh higher plants with high CPI and the diagenetic products with low CPI in weathered sedimentary rocks.

Total Alkenones and Alkenone-Based Temperature

Total alkenone (C_{37} – C_{39} alkenones) concentrations in dry sediment varied between 0.14 and 18.03 µg/g, with an average of 3.54 µg/g in Site 1237 samples (Fig. F5; Table T1). The alkenones were below detection limit in the sediments below 118.56 mcd. Total alkenones increased uphole and maximized at 15.02 mcd. Alkenone-based paleotemperature varied from 17.3° to 25.4°C. The temperature decreased uphole and minimized at 15.02 mcd. The temperature decreased uphole above 15.02 mcd. The core-top temperature (0.01 mcd) was 20.3°C, which agrees with the present mean annual sea-surface temperature (~20°C) (Levitus and Boyer, 1994).

In Site 1239 samples, total alkenone concentration varied between 1.41 and 22.28 μ g/g, with an average of 11.17 μ g/g (Fig. F6; Table T2). The alkenones were below detection limit in the sediments below 450.59 mcd. Below ~300 mcd, total alkenones increased uphole and maximized at 300.62 mcd. The total alkenone content decreased gradually above ~300 mcd with a single peak at 100.31 mcd. The paleotemperature varied from 24.2° to 27.9°C. The temperature gradually decreased uphole. The core-top temperature (0.01 mcd) was 25.3°C, which is ~1°C higher than the present mean annual sea-surface temperature (~24°C) at Site 1239 (Levitus and Boyer, 1994).

ACKNOWLEDGMENTS

We thank Noriko Edasawa and Masao Minagawa (Hokkaido University) for assistance in experiments. We also thank the shipboard scientists for valuable discussions. This research used samples and/or data provided by the Ocean Drilling Program (ODP). ODP is sponsored by the U.S. National Science Foundation (NSF) and participating countries under management of Joint Oceanographic Institution (JOI), Inc.





F6. Alkenone and temperature depth profiles, Site 1239, p. 11.



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Figure F1. Map showing the locations of Sites 1237 and 1239 (Mix, Tiedemann, Blum, et al., 2003).

В Α 0 1 Ma 2 Ma 50 3 Ma 4 Ma Depth (mcd) 5 Ma 100 6 Ma 7 Ma 150 8 Ma 9 Ma 10 Ma 11 Ma 200 1.2 1.4 20 100 0.2 80 0 0.4 0.6 0.8 0 40 60 1 CaCO₃ (wt%) TOC (wt%)

Figure F2. Depth profiles of (A) total organic carbon (TOC) and (B) CaCO₃ contents of Site 1237 sediments.



Figure F3. Depth profiles of (A) total organic carbon (TOC) and (B) CaCO₃ contents of Site 1239 sediments.

Figure F4. Depth profiles of (A) total C_{25} - C_{33} *n*-alkane concentrations, (B) odd/even carbon number preference index (CPI), and (C) average chain length (ACL) of long chain *n*-alkanes in Site 1237 sediments.



Figure F5. Depth profiles of (A) total alkenone concentrations and (B) $U^{k'}_{37}$ -based temperature in Site 1237 sediments.



Figure F6. Depth profiles of (A) total alkenone concentrations and (B) U_{37}^{k} -based temperature in Site 1239 sediments.



Table T1. TOC and CaCO₃ contents, C_{25} - C_{33} LNA concentration, odd/even CPI, ACL, alkenone concentrations, $U^{k'}_{37}$, and the $U^{k'}_{37}$ -based temperatures at Site 1237.

Core, section, interval (cm)	Depth (mcd)	TOC (wt%)	CaCO ₃ (wt%)	LNA (µg/g)	CPI	ACL	Alkenone (µg/g)	U ^{k′} ₃₇	Temperature (°C)
202-									
1237B-1H-1, 1–1	0.01	1.27	1.17	0.23	3.1	29.5	1.98	0.730	20.3
1237D-1H-2, 120–121	5.01	0.79	19.47	0.45	3.5	29.5	7.00	0.677	18.8
1237D-1H-6, 18–19	10.01	0.99	8.34	0.36	5.6	29.7	15.71	0.691	19.2
1237C-2H-5, 81-82	15.02	0.99	0.98	0.77	5.9	29.6	18.03	0.627	17.3
1237D-2H-5, 111–113	20.63	0.68	9.04	0.63	4.9	29.6	8.14	0.684	19.0
1237D-3H-4, 111–113	29.99	0.40	17.35	0.39	4.9	29.6	5.25	0.778	21.7
1237C-4H-4, 111–113	35.38	0.75	0.31				4.73	0.720	20.0
1237D-4H-5, 111–113	40.71	0.42	15.53	0.39	5.4	29.7	4.53	0.711	19.8
1237C-5H-3, 111-113	44.80	0.16	65.10				2.13	0.775	21.6
1237C-5H-6, 111-113	49.33	0.18	61.40	0.11	5.3	29.7	1.86	0.850	23.8
1237B-6H-4, 112–114	54.86	0.09	65.95	0.11	5.4	29.6	0.64	0.868	24.4
1237C-6H-6, 111–113	60.43	0.04	59.88	0.19	3.5	29.7	6.00	0.746	20.8
1237B-7H-5, 111–113	65.69	0.08	74.48	0.09	5.1	29.7	0.96	0.842	23.6
1237C-7H-6, 111–113	70.40	0.04	83.01	0.08	3.2	29.7	0.28	0.871	24.5
1237C-8H-3, 29–31	75.29	0.05	85.75	0.07	3.6	29.7	0.33	0.831	23.3
1237D-5H-4, 32–34	80.32	0.08	88.96	0.05	3.3	29.6	0.55	0.856	24.0
1237C-9H-3, 32–34	85.31	0.04	73.34	0.06	4.4	29.7	0.61	0.830	23.3
1237D-6H-3, 32–34	90.71	0.03	91.40	0.04	2.4	29.6	0.18	0.902	25.4
1237D-6H-6, 32–34	95.24	0.02	87.52	0.05	3.1	29.6	0.14	0.848	23.8
1237C-10H-6, 17–19	100.23	0.03	90.01	0.04	2.9	29.5	0.28	0.868	24.4
1237D-7H-6, 17–19	105.53	0.03	87.17				0.26	0.825	23.1
1237C-11H-5, 17–19	109.19	0.07	90.61				1.42	0.832	23.3
1237D-8H-6, 43–45	115.34	0.01	94.04	0.04	2.4	29.5	0.42	0.793	22.2
1237C-12H-4, 112–114	118.56	0.01	94.26	0.03	3.7	29.4	BDL		
1237B-13H-3, 112–114	125.21	0.01	92.15	BDL			BDL		
1237C-13H-4, 112–114	130.65	0.01	94.08	BDL			BDL		
1237B-14H-3, 112–114	135.39	0.00	94.86	BDL			BDL		
1237C-14H-3, 102–104	140.39	0.00	94.36	BDL			BDL		
1237B-15H-3, 112–114	145.69	0.01	94.12	BDL			BDL		
1237C-15H-3, 112–114	149.99	0.01	94.14	BDL			BDL		
1237B-16H-3, 112–114	155.33	0.01	88.85	BDL			BDL		
1237B-16H-6, 134–136	160.08	0.01	32.15	BDL			BDL		
1237B-17H-2, 112–114	165.43	0.00	93.58	BDL			BDL		
1237B-17H-5, 112–114	169.95	0.00	94.07	BDL			BDL		
1237C-17H-5, 112–114	174.81	0.01	91.31	BDL			BDL		
1237B-18H-5, 112–114	180.04	0.00	89.36	BDL			BDL		

Notes: TOC = total organic carbon, LNA = long-chain *n*-alkanes, CPI = carbon number preference index, ACL = average chain length. BDL = below detection limit.

Table T2. TOC and CaCO₃ contents, alkenone concentrations, $U^{k'}_{37}$, and the $U^{k'}_{37}$ -based temperatures at Site 1239. (See table notes. Continued on next page.)

Core, section,	Depth	тос	CaCO ₃	Alkenone		Temperature
interval (cm)	(mcd)	(wt%)	(wt%)	(µg/g)	U ^ĸ 37	(°C)
202-						
1239A-1H-1, 1–3	0.01	1.09	36.52	2.72	0.900	25.3
1239C-1H-4, 11–13	4.99	0.66	53.81			
1239B-2H-2, 71–73	10.02	1.44	48.54			
1239C-2H-4, 21-23	15.03	0.75	67.99 42.36			
1239R-311-4, 121-123	20.03	0.98	52 70			
1239B-4H-1, 91–93	30.01	0.90	56.74			
1239C-4H-3, 111-113	35.03	0.90	54.55			
1239B-5H-1, 31-33	40.01	0.80	58.84			
1239B-5H-4, 81–83	45.04	0.85	62.10			
1239C-5H-4, 141–143	49.91	0.99	53.48	5.12	0.888	25.0
1239B-6H-4, 66–68	54.59	1.36	50.85			
1239A-7H-3, 100–102	60.15	0.89	49.37			
1239A-/H-6, 100-102	64.66 70.02	1.04	51.91			
1239C-7H-3, 00-00 1239A-8H-6 100 102	70.02	1.10	JZ.9Z			
1239A-9H-2 100-102	79 71	1.50	43 97			
1239A-9H-5, 126–128	84.51	0.84	18.88			
1239A-10H-2, 100–102	89.71	3.35	39.83			
1239A-10H-5, 100–102	94.24	2.76	46.00			
1239A-11H-2, 100–102	100.31	3.14	33.82	17.59	0.861	24.2
1239A-11H-5, 100–102	104.84	2.69	38.82			
1239A-12H-2, 100–102	110.71	2.95	42.50			
1239A-12H-5, 100–102	115.25	2.12	43.10			
1239A-13H-1, 100–102	119.70	2.35	53.05			
1239A-13H-4, 100–102	124.25	2.00	53./5			
1239A-14H-1, 100-102 1220A 14H 5 72 74	129.75	1.32	44.85			
1239A-1411-3, 72-74 1239A-15H-1 102-104	140.07	2.56	40.00			
1239A-15H-4, 102–104	144.61	1.16	60.40			
1239A-16H-1, 100–102	150.20	1.35	54.29	11.11	0.961	27.1
1239A-16H-4, 102–104	154.76	1.84	48.56			
1239A-17H-1, 100–102	159.95	1.34	50.96			
1239A-17H-4, 102–104	164.51	1.25	55.43			
1239A-18H-1, 100–102	171.40	2.20	43.67			
1239A-18H-3, 102–104	174.44	1.56	51.18			
1239A-19H-1, 100–102	180.20	2.04	43.3/			
1239A-19H-4, 102-104	184.//	1.19	55.14 40.20			
1239A-20X-1, 102-104 1239A-20X-4 102-104	190.36	1.01	49.20			
1239A-21X-4, 102–104	200.78	2.09	48.57	15.98	0.937	26.4
1239A-22X-1, 102–104	206.80	1.85	50.25	13.70	0.757	20.1
1239A-22X-3, 102–104	209.82	1.84	43.79			
1239A-22X-6, 102–104	214.35	2.23	49.98			
1239A-23X-3, 102–104	220.39	1.77	49.11			
1239A-23X-6, 102–104	224.92	1.41	59.76			
1239A-24X-2, 102–104	229.42	1.28	57.61			
1239A-24X-6, 102–104	235.42	1.77	48.76			
1239A-25X-2, 102–104	239.48	1.97	51.00			
1239A-25X-6, 102-104	245.50	1.05	55.94	1 (7)	0.052	26.0
1239A-20A-2, 102-104 1220A 268 5 102 104	250.04	1.30	55.20 62.04	10.72	0.955	20.9
1239A-20A-3, 102-104 1239A-27X-2 102-104	254.50	1.07	60.65			
1239A-27X-5, 102–104	264.71	1.14	62.19			
1239A-28X-2, 102–104	270.66	1.23	65.49			
1239A-28X-5, 102–104	275.18	1.56	60.16			
1239A-29X-1, 102–104	279.62	1.45	67.31			
1239A-29X-5, 102–104	285.64	0.88	71.81			
1239A-30X-1, 100–102	290.06	0.82	58.84			
1239A-30X-4, 100–102	294.56	1.26	61.55		<u>.</u>	_
1239A-31X-1, 100–102	300.62	1.39	62.43	22.28	0.983	27.8
1239A-31X-4, 100–102	305.12	0.80	/0.95			
1239A-32X-1, 100-102	311.08	0.61	65.13 57.44			
1239A-32A-4, 100-102 1239A-32X-5 100 102	313.00	0.79	57.40 66.23			
12377732773, 100-102	517.10	0.02	00.25			

Table T2 (continued).

Core, section, interval (cm)	Depth (mcd)	TOC (wt%)	CaCO ₃ (wt%)	Alkenone (µg/g)	U ^K 37	Temperature (°C)
1239A-33X-3, 100–102	324.65	0.53	72.91			
1239A-33X-6, 100–102	329.15	0.78	70.56			
1239A-34X-3, 100–102	335.11	1.02	70.40			
1239A-34X-6, 100–102	339.62	0.74	69.59			
1239A-35X-3, 100–102	345.58	1.16	67.29			
1239A-36X-1, 100–102	353.12	0.99	73.97	7.56	0.989	27.9
1239A-36X-3, 100–102	356.14	0.58	77.13			
1239A-36X-6, 100–102	360.67	0.63	77.55			
1239A-37X-2, 100–102	365.10	0.70	74.27			
1239A-37X-5, 100–102	369.61	1.02	62.68			
1239A-38X-2, 100–102	375.55	0.67	78.75			
1239A-38X-5, 100–102	380.05	0.67	80.01			
1239A-39X-1, 100–102	384.50	0.65	75.08			
1239A-39X-5, 99–101	390.51	0.48	78.08			
1239A-40X-1, 100–102	395.06	0.57	73.35			
1239A-40X-4, 100–102	399.59	0.62	75.80	1.41	0.988	27.9
1239A-41X-1, 100–102	405.52	1.00	73.50			
1239A-41X-4, 100–102	410.05	0.71	77.38			
1239A-42X-1, 99–102	416.07	0.54	75.48			
1239A-42X-4, 99–102	420.59	0.61	66.98			
1239A-43X-1, 99–102	426.53	0.80	70.43			
1239A-43X-3, 99–102	429.54	0.48	81.35			
1239A-43X-6, 99–102	434.05	0.53	73.83			
1239A-44X-3, 99–102	440.01	1.04	74.08			
1239A-44X-6, 99–102	444.53	0.79	77.74			
1239A-45X-3, 100–103	450.59	1.01	78.84	BDL		
1239A-45X-6, 104–107	455.17	0.97	70.25			
1239A-46X-2, 100–103	459.43	1.01	77.93			
1239A-46X-6, 100–103	465.44	0.58	57.69			
1239A-47X-2, 100–103	469.89	0.65	74.95			
1239A-47X-5, 100–103	474.41	0.44	77.68			
1239A-48X-2, 98–101	480.43	0.21	82.27			
1239A-48X-5, 100–103	484.98	0.60	76.55			
1239A-49X-1, 100–103	489.40	0.36	82.40	BDL		

Notes: TOC = total organic carbon. BDL = below detection limit.