26. DATA REPORT: CARBONATE RECORDS FROM SITES 1012, 1013, 1017, AND 1019 AND ALKENONE-BASED SEA-SURFACE TEMPERATURES FROM SITE 1017¹

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INTRODUCTION

One of the expected scientific results of Ocean Drilling Program Leg 167 was to reconstruct the Neogene history of biogenic calcium carbonate accumulation in the northeastern Pacific along the California margin (Lyle, Koizumi, Richter, et al., 1997). This aims to constrain inorganic carbon burial rates, deep-water hydrography in the North Pacific, and linkages between deep Atlantic and Pacific circulation and carbonate accumulation or dissolution patterns.

Data are presented for four sites. Two of them are located in the California bight—East Cortez Basin (Site 1012: 32°16.970'N, 118°23.024'W, 1773 m) and San Nicholas Basin (Site 1013: 32°48.040'N, 118°53.992'W, 1564 m). The others are the dedicated Hole 1017E at Site 1017 (34°32.099'N, 121°6.430'W, 955 m) and Site 1019 in the Eel River Basin (41°40.972'N, 124°55.975'W, 977 m).

Reconstruction of paleo-sea-surface temperatures (SST) by determining the alkenone unsaturation index of the extractable organic matter is an independent technique and helps to verify oxygenisotope-based estimates. Results from the uppermost 600 cm of the dedicated Hole 1017E are expected to reveal the local temperature history of the last 30 k.y.

METHODS

Carbonate carbon contents were determined using a Coulometrics 5011 carbon dioxide coulometer as in shipboard measurements. Depending on carbonate contents of the samples, 20–200 mg of freezedried, ground sediment was reacted with 10% HCl. The liberated CO₂ was back titrated to a colorimetric endpoint, yielding the inorganic carbon content (IC [wt%]). By X-ray diffraction measurements of each sample, the bulk mineralogy was determined and calcite verified as the carbonate phase. Therefore, the percentage of carbonate is calculated as CaCO₃ (wt%) = IC (wt%) × 8.333. By measuring shipboard samples, replicates of samples, and calcite and calcite-quartz mixture standards, it was ensured that there is no offset compared to shipboard CaCO₃ data. The accuracy of the IC (wt%) determination is 0.05%, and the relative standard derivation of CaCO₃ contents of replicates is 0.6%.

Quantification of long-chain alkenone concentrations for the determination of the U_{37}^{s7} used the following method. Total extractable organic matter of 2-g freeze-dried sediment with added recovery standards was obtained by ultrasonic extraction for 15 min with 12.5 mL of methanol, then with 12.5 mL methanol:dichloromethane (1:1), and finally with 12.5 mL dichloromethane. After each extraction step, samples were centrifuged, and the solvent was collected by pipette. The three lipid extracts were combined, and salts were removed from the dichloromethane layer by addition of 10 mL H_2O_{bidest} . After concentration by rotary evaporation and removal of remaining solvent under a gentle stream of nitrogen, the total extract was redissolved in hexane and separated on a silica gel column in three compound classes by elution with 4-mL hexane (fraction 1), 4-mL ethylacetate:hexane (3:97) (fraction 2 containing alkenones), and 3-mL dichloromethane followed by 2-mL methanol (fraction 3). After saponification of the second fraction, lipids were redissolved in 100-µL hexane containing an injection standard. The sample (1-4 µL) was injected in solvent vent mode onto an HP 6890 gas chromatograph fitted with a 50-m glass capillary column (Ultra 2, ID 0.2 mm, film thickness = $0.11 \,\mu\text{m}$) coupled to an HP 5973 mass selective detector. Helium was used as carrier gas (2 bar constant). The temperature program was 50° for 2.5 min, 250° at 20°/min, 290° at 3°/min, 310° at 0.5°/min, 320° at 10°/min, and isothermal at 320°C for 10 min. Quantification was performed on total ion current signals. Results of duplicate analyses (N = 20) indicate that the standard deviation of the measurements is 0.005 $U_{37}^{k'}$ units. Replicate extractions (N = 4) of a pooled homogenized sample resulted in standard deviations up to 0.015 $U_{37}^{k'}$ units. The $U_{37}^{k'}$ is calculated according to the equation $U_{37}^{k'}$ = (37:2)/(37:2 + 37:3) and converted into sea-surface temperatures according to Prahl et al. (1988) as SST (°C) = $(U_{37}^{k'} - 0.039)/0.034$.

RESULTS

Carbonate contents decrease along the California margin transect to the north. At Site 1012, carbonate contents vary between 2 and 69 wt% and increase with depth with strong fluctuations (Fig. 1; Table 1). Similar CaCO₃ percentages at Site 1013 (Fig. 2; Table 2) range from 2 to 61 wt% and show a decrease towards shallower depth. Sediments from the dedicated core from Hole 1017E contain 2–16 wt% carbonate (Table 3). Remarkably smooth variations characterize the uppermost 180 cm, culminating in a maximum of 15.8 wt% at 220 cm. Concentrations vary between 2.3 and 10.8 wt% in the deeper part of the core (Fig. 3). At the northernmost Site 1019, CaCO₃ percentages are extremely low and vary from 0.1 to 8.8 wt%. Distinct changes of intervals characterized by very low or elevated carbonate contents occur throughout the core (Fig. 4; Table 4).

The reconstructed sea-surface temperatures at Site 1017 vary from 14.6° to 16.2° C in the uppermost 170 cm, show a distinct maximum of 16.8° C at 200 cm, and decrease to 12.5° – 14.0° C below 220 cm (Fig. 5; Table 5).

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Figure 1. CaCO $_3$ contents in sediments from Site 1012. Shipboard measurements are also shown.

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Table 1. CaCO₃ data from Site 1012.

Leg	Site	Hole	Core	Туре	Section	Top (cm)	Bottom (cm)	CaCO ₃ (wt%)
167	1012	А	1	Н	1	40	42	30.3
167	1012	Α	1	Н	2	40	42	24.1
167	1012	Α	1	Н	2	60	62	24.9
167	1012	Α	1	Н	3	40	42	16.0
167	1012	Α	2	Н	1	40	42	16.0
167	1012	Α	2	Н	2	40	42	11.3
167	1012	Α	2	Н	3	40	42	10.0
167	1012	Α	2	Н	4	40	42	10.6
167	1012	Α	2	Н	5	40	42	21.4
167	1012	А	2	Н	5	60	62	20.5

This is a sample of the table that appears on the volume CD-ROM.



Figure 2. CaCO₃ contents in sediments from Site 1013. Shipboard measurements are also shown.

Table 2. CaCO₃ data from Site 1013.

Leg	Site	Hole	Core	Туре	Section	Top (cm)	Bottom (cm)	CaCO ₃ (wt%)
167	1013	А	1	н	1	50	52	21.0
167	1013	Α	1	н	3	35	37	13.8
167	1013	Α	1	Н	3	60	62	14.2
167	1013	A	1	Н	4	25	27	18.7
167	1013	A	2	H	2	35	37	14.3
167	1013	A	2	H	4	35	37	14.8
167	1013	A	23	п	1	40	42	21.1
167	1013	A	3	н	3	35	37	11.2
167	1013	A	3	Ĥ	4	35	37	5.9
167	1013	Α	3	Н	6	35	37	22.1
167	1013	Α	3	Н	7	35	37	12.0
167	1013	A	4	н	2	35	37	16.2
167	1013	A	4	H	3	35	3/	22.8
167	1013	A	4	н	4	50 60	58 62	4.9
167	1013	A	4	Ĥ	6	35	37	22.7
167	1013	Α	5	Н	1	35	37	25.9
167	1013	Α	5	Н	3	35	37	14.7
167	1013	A	5	Н	4	35	37	33.3
167	1013	A	5	H	6	35	37	17.7
167	1013	A	6	п	2	35	37	25.0
167	1013	A	6	н	2	70	72	27.2
167	1013	A	ĕ	Ĥ	4	35	37	44.6
167	1013	Α	6	н	6	35	37	20.3
167	1013	A	7	Н	1	35	37	32.9
167	1013	A	7	H	2	35	37	37.5
167	1013	A	7	H	5	35 60	57	42.6
167	1013	A	7	н	6	35	37	19.1
167	1013	A	8	Ĥ	1	35	37	31.6
167	1013	Α	8	Н	2	35	37	11.7
167	1013	Α	8	Н	4	35	37	45.2
167	1013	A	8	H	6	35	37	10.1
167	1013	A	9	H	1	35	37	35.3
167	1013	A	9	н	5	35	37	20.0
167	1013	A	9	Ĥ	6	35	37	20.4
167	1013	Α	10	Н	1	35	37	18.9
167	1013	Α	10	Н	3	35	37	43.8
167	1013	A	10	H	4	35	37	32.4
167	1013	A	10	H V	6	35	37	10.6
167	1013	A	11	Ĥ	3	35	37	34.0
167	1013	A	12	x	1	35	37	42.9
167	1013	Α	12	Х	2	54	56	15.5
167	1013	Α	12	Х	4	10	12	43.6
167	1013	A	13	X	1	35	37	45.3
167	1013	A	13	X	2	35	37	22.1
167	1013	A	13	X	4	35	37	35.0
167	1013	A	14	x	1	35	37	34.3
167	1013	A	14	X	2	35	37	36.4
167	1013	Α	14	Х	4	35	37	40.1
167	1013	A	14	X	6	35	37	54.0
167	1013	A	15	X	1	35	37	48.6
167	1013	A	15	л Х	2 4	35	37	40.7
167	1013	A	15	X	6	35	37	47.9
167	1013	A	16	X	ĭ	35	37	57.6
167	1013	Α	16	Х	2	35	37	35.4
167	1013	A	16	X	4	35	37	57.0
167	1013	A	16	X	5	35	37	41.2
10/	1013	A	16	X Y	5	35	03 37	33.3 56.4
107	1015	A	10	л	0	33	51	50.4

This table also appears on the volume CD-ROM.

Table 3. CaCO₃ data from Site 1017.

Leg	Site	Hole	Core	Туре	Section	Top (cm)	Bottom (cm)	CaCO ₃ (wt%)
167	1017	Е	1	Н	1	0	3	7.1
167	1017	E	1	Н	1	3	6	7.2
167	1017	Е	1	Н	1	6	9	7.4
167	1017	Е	1	Н	1	9	12	7.5
167	1017	E	1	Н	1	12	15	7.5
167	1017	E	1	Н	1	15	18	7.8
167	1017	E	1	Н	1	18	21	7.6
167	1017	E	1	Н	1	21	24	7.6
167	1017	E	1	Н	1	24	27	7.4
167	1017	Е	1	Н	1	27	30	7.8

This is a sample of the table that appears on the volume CD-ROM.



Figure 3. CaCO₃ contents in sediments from Hole 1017E.



Figure 4. CaCO $_3$ contents in sediments from Site 1019. Shipboard measurements are also shown.

 Table 4. CaCO₃ data from Site 1019.

Leg	Site	Hole	Core	Туре	Section	Top (cm)	Bottom (cm)	CaCO ₃ (wt%)
167	1019	С	1	н	1	90	92	1.5
167	1019	С	1	Н	3	90	92	3.7
167	1019	С	1	Н	5	90	92	5.1
167	1019	С	2	Н	2	90	92	5.1
167	1019	С	2	Н	4	90	92	5.4
167	1019	C	2	H	6	90	92	4.2
167	1019	C	3	H	1	90	92	4.4
167	1019	C	3	H	3	90	92	8.7
167	1019	Č	4	H	1	90	92	0.1
167	1019	č	4	п	5	90	92	0.9
167	1019	č	5	н	1	90	92	1.8
167	1019	č	5	Ĥ	3	90	92	1.0
167	1019	č	5	Ĥ	5	90	92	1.6
167	1019	Č	6	H	1	90	92	1.4
167	1019	Ċ	6	Н	3	90	92	3.4
167	1019	С	6	Н	5	90	92	4.3
167	1019	С	7	Н	2	90	92	3.6
167	1019	С	7	Н	4	90	92	1.1
167	1019	C	7	Н	6	90	92	3.6
167	1019	ç	8	H	2	93	95	8.4
167	1019	Č	8	H	4	90	92	7.1
167	1019	č	ô	п v	1	90	92	1.0
167	1019	č	9	X	3	90	92	4.0
167	1019	č	ó	x	5	90	92	41
167	1019	č	10	x	3	90	92	6.5
167	1019	č	10	x	5	<u>90</u>	<u>92</u>	2.7
167	1019	Ċ	11	Х	1	90	92	1.5
167	1019	С	11	Х	3	90	92	2.0
167	1019	С	11	Х	5	90	92	0.7
167	1019	С	12	Х	1	90	92	0.5
167	1019	C	12	X	3	90	92	1.5
167	1019	Č	12	X	2	90	92	3.8
167	1019	č	13	A V	2	90	92	4.5
167	1019	č	14	X	3	90	92	3.1
167	1019	č	15	x	2	90	92	44
167	1019	č	15	x	4	90	92	4.3
167	1019	Č	15	X	6	90	92	7.2
167	1019	С	16	Х	2	90	92	0.5
167	1019	С	16	Х	4	90	92	0.5
167	1019	С	17	Х	1	90	92	1.7
167	1019	C	17	X	3	90	92	2.4
167	1019	C	18	X	2	90	92	2.0
167	1019	č	10	A V	4	90	92	2.0
167	1019	č	19	X X	3	92	02	3.2
167	1019	č	20	X	1	90	92	43
167	1019	č	20	x	3	92	94	1.0
167	1019	Č	21	X	1	89	91	0.3
167	1019	С	21	Х	3	89	91	0.5
167	1019	С	21	Х	5	90	92	0.3
167	1019	С	21	Х	7	73	75	0.6
167	1019	C	22	X	3	90	92	3.0
167	1019	C	22	X	5	90	92	5.9
167	1019	C	22	X	2	90	92	4.1
167	1019	č	23 23	X	2 4	90	92	3.0
167	1019	č	24	x	3	90	92	3.8
167	1019	č	25	x	2	90	<u>92</u>	1.3
167	1019	Č	25	x	4	90	92	0.3
167	1019	С	25	Х	6	90	92	1.1
167	1019	С	26	Х	3	91	93	4.1
167	1019	С	26	Х	5	92	94	2.3

This table also appears on the volume CD-ROM.



Figure 5. Variations of sea-surface temperatures (SST) at Hole 1017E. Cmbsf = centimeters below seafloor.

Leg	Site	Hole	Core	Туре	Section	Top (cm)	Bottom (cm)	$U_{37}^{\mathbf{k}'}$	SST (°C)
167	1017	Е	1	Н	1	0	3	0.586	16.1
167	1017	E	1	Н	1	3	6	0.569	15.6
167	1017	Е	1	Н	1	9	12	0.536	14.6
167	1017	E	1	Н	1	12	15	0.537	14.6
167	1017	E	1	Н	1	18	21	0.574	15.7
167	1017	E	1	H	1	24	27	0.579	15.9
167	1017	E	1	H	1	30	39	0.568	15.5
167	1017	E	1	H	1	42	45	0.591	16.2
167	1017	E	1	H U	1	60	60	0.580	16.0
167	1017	E	1	н	1	72	75	0.564	15.0
167	1017	E	1	н	1	84	87	0.579	15.5
167	1017	Ē	1	Ĥ	1	90	93	0.532	14.5
167	1017	Ē	1	Ĥ	1	96	99	0.551	15.0
167	1017	Ē	1	Н	1	102	105	0.551	15.1
167	1017	E	1	Н	1	108	111	0.566	15.5
167	1017	E	1	Н	1	120	123	0.551	15.0
167	1017	E	1	Н	1	132	135	0.564	15.5
167	1017	E	1	Н	1	144	147	0.542	14.8
167	1017	E	1	Н	2	6	9	0.566	15.5
167	1017	E	1	H	2	18	21	0.598	16.4
167	1017	E	1	H	2	30	33	0.604	16.6
167	1017	E	1	H	2	30	59	0.611	10.8
167	1017	E	1	H	2	48	51	0.535	14.0
167	1017	E	1	п	2	54	62	0.504	13.4
167	1017	E	1	н	2	72	75	0.522	14.2
167	1017	Ē	1	Ĥ	$\frac{2}{2}$	84	87	0.489	13.2
167	1017	Ē	1	Ĥ	$\overline{2}$	96	99	0.515	14.0
167	1017	Ē	1	Н	2	120	123	0.511	13.9
167	1017	E	1	Н	2	132	135	0.527	14.4
167	1017	E	1	Н	2	144	147	0.480	13.0
167	1017	E	1	Н	3	6	9	0.492	13.3
167	1017	E	1	Н	3	18	21	0.505	13.7
167	1017	E	1	Н	3	30	33	0.463	12.5
167	1017	E	1	H	3	42	45	0.464	12.5
167	1017	E	1	H	3	66	69	0.497	13.5
167	1017	E	1	H	3	90	93	0.478	12.9
167	1017	E	1	H H	3	102	105	0.403	12.5
167	1017	E	1	п	3	126	120	0.402	13.0
167	1017	E	1	н	3	138	141	0.490	12.5
167	1017	Ē	1	Ĥ	4	138	3	0.480	13.0
167	1017	Ē	1	Ĥ	4	12	15	0.429	11.5
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Table 5. $U_{37}^{\,k^\prime}$ and sea-surface temperature (SST) data from selected samples at Site 1017.

This table also appears on the volume CD-ROM.