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1. DATA REPORT: CARBON ISOTOPIC COMPOSITION OF INORGANIC CARBON AND METHANE DISSOLVED IN PORE WATERS AT SITES 1071, 1072, AND 1073[1]

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INTRODUCTION

Microbially mediated redox diagenetic processes in marine sediments are reflected in the amount and carbon isotopic composition of dissolved CO_2 and CH_4 (Claypool and Kaplan, 1974). Oxidation of organic matter gives rise to dissolved CO_2 with about the same $^{13}C/^{12}C$ ratio as the starting organic matter. Subsequent reduction of CO_2 to form CH_4 involves a large (~70‰) kinetic isotopic effect, resulting in significant ^{13}C depletion in the CH_4, and ^{13}C enrichment in the residual CO_2. Ocean Drilling Program Leg 174A (offshore New Jersey) presented an opportunity to study these processes in shelf and upper slope sediments. Holes 1071A–1071D, 1071F, and 1072A were drilled on the shelf in water depths of 88.0–98.1 m. Hole 1073A was drilled on the slope in 639.4 m of water. Pore-water samples were collected for analysis at all three sites, whereas gas samples could only be obtained from Hole 1073A on the slope.

SAMPLING AND ANALYTICAL PROCEDURES

Sampling procedures for pore waters and gases are described in the "Explanatory Notes" chapter of the Leg 174 *Initial Reports* volume (Austin, Christie-Blick, Malone, et al., 1998). Water samples (5-cm^3 aliquots) squeezed from whole-round core sections were stored in heat-sealed

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plastic tubes. Upon arrival (after a 2-month shipping delay caused by a United Parcel Service strike) the samples were stored frozen until analysis. After cutting off the ends of the plastic tubes, the frozen plugs of pore water were transferred under N_2 conditions to carbonate reaction flasks with side arms filled with concentrated phosphoric or 2N hydrochloric acid. The reaction flasks were evacuated, the side arms tipped to acidify the pore waters, and the solutions reacted overnight in a water bath at 25°C. The CO_2 produced was purified and collected by cryogenic transfer, and the volumes were measured according to procedures and in an apparatus similar to that described by Presley and Claypool (1971). Stable isotope ratios ($^{13}C/^{12}C$ expressed as $\delta^{13}C$ vs. Peedee belemnite [PDB]) of CO_2 were measured on a Finnigan MAT 251, 90°-sector isotope ratio mass spectrometer at the U.S. Geological Survey Organic Geochemistry Facility (Building 80, Federal Center, Lakewood, Colorado).

Gas samples were collected from visible core voids by puncturing the core liners, withdrawing gas in a 50-cm^3 syringe, and transferring it to 20-cm^3 vacutainers for shipping and storage. The CH_4 was separated from the gas, combusted to CO_2, and analyzed for $^{13}C/^{12}C$ ratio in an on-line gas chromatograph, combustion furnace, isotope ratio mass spectrometer (Hewlett-Packard 6890/Finnigan MAT Delta plus) at the Mobil Exploration and Producing Technology Center, in Farmers Branch, Texas.

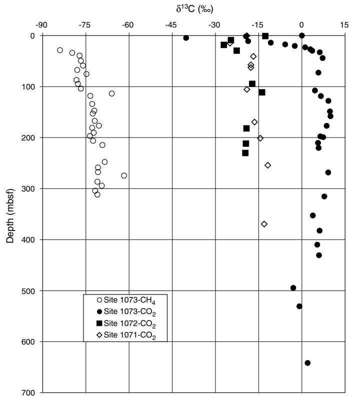
RESULTS

Table **T1** lists the measured yields and $\delta^{13}C$ values for dissolved total CO_2 (ΣCO_2) in selected pore-water samples from Holes 1071A–1071D, 1071F, 1072A, and 1073A, along with sample identification (hole, core, section, centimeter interval), depth in meters below seafloor (mbsf), and shipboard-measured alkalinity. Alkalinity is included for comparison with ΣCO_2 yields, with the difference possibly indicating the extent of CO_2 loss from the pore water prior to analysis for ΣCO_2. Table **T2** lists the $\delta^{13}C$ values of CH_4 from gas expansion pockets in cores from Hole 1073A, along with sample identification and depth. The $\delta^{13}C$ values of ΣCO_2 and CH_4 are plotted vs. depth in Figure **F1**.

T1. Alkalinity, concentration, and $\delta^{13}C$ of dissolved inorganic carbon, p. 6.

T2. Carbon isotopic composition of methane, p. 7.

F1. Carbon isotopic composition of dissolved ΣCO_2 and CH_4, p. 5.



Sites 1071 and 1072

Pore-water samples from these shallow-water shelf sites (water depths of 88.0–98.1 m) were analyzed only for $\delta^{13}C$ of ΣCO_2 because there was insufficient CH_4 in the sediments for sampling and analysis. The trends of $\delta^{13}C$ of ΣCO_2 with depth are similar at both sites, with negative $\delta^{13}C$ values (–13‰ to –27‰) throughout the depth intervals sampled. The most negative $\delta^{13}C$ values (–25‰ and –27‰) are found at shallow depths (10–30 mbsf) where salinity minima are observed, and sulfate reduction is indicated by changes in the pore-water chemistry (Shipboard Scientific Party, 1998a, 1998b). The salinity minimum at each site is believed to be the result of freshwater recharge during lowered sea level at the time of the last glacial maximum (Shipboard Scientific Party, 1998a, 1998b).

Beneath the shallow salinity minima, the remaining ΣCO_2 samples have $\delta^{13}C$ values ranging from –12‰ to –19‰. Incipient microbial methanogenesis was detected in Hole 1071F at depths of 369–405 mbsf, and in Hole 1072A at depths of 17–36 mbsf, where sulfate decreases to levels of 1–2 mM (Shipboard Scientific Party, 1998a, 1998b).

Hole 1073A

Gas expansion voids formed in cores from Hole 1073A at depths beneath ~25 mbsf, providing sufficient gas to measure $\delta^{13}C$ of CH_4 in addition to the $\delta^{13}C$ of ΣCO_2. Dissolved sulfate is depleted in Hole 1073A at a depth of ~5 to 6 mbsf. The depth of the sulfate/methane interface is constrained by the deepest pore-water sample with significant measurable sulfate content (7.34 mM) at 4.4 mbsf, and the shallowest sample with significant headspace methane content (2.6%) at 6.6 mbsf. The $\delta^{13}C$ value for ΣCO_2 at 4.4 mbsf is –40.2‰, suggesting that a significant amount (30%–40%) of the pore-water CO_2 at this depth is derived from the oxidation of CH_4.

With onset of microbial methanogenesis in Hole 1073A sediments deeper than ~6 mbsf, the $\delta^{13}C$ values of ΣCO_2 are shifted rapidly to positive values. Below a depth of ~25 mbsf, the $\delta^{13}C$ trends of CH_4 and ΣCO_2 are subparallel, consistent with the $\delta^{13}C$ of CH_4 being controlled by that of the ΣCO_2 at about the same depth. The maxima and minima in the $\delta^{13}C$ curves approximately match those for alkalinity and phosphate in Hole 1073A (Shipboard Scientific Party, 1998c).

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Figure F1. Carbon isotopic composition of dissolved ΣCO_2 and CH_4 as a function of sediment depth for Holes 1071A–1071D, 1071F, 1072A, and 1073A.

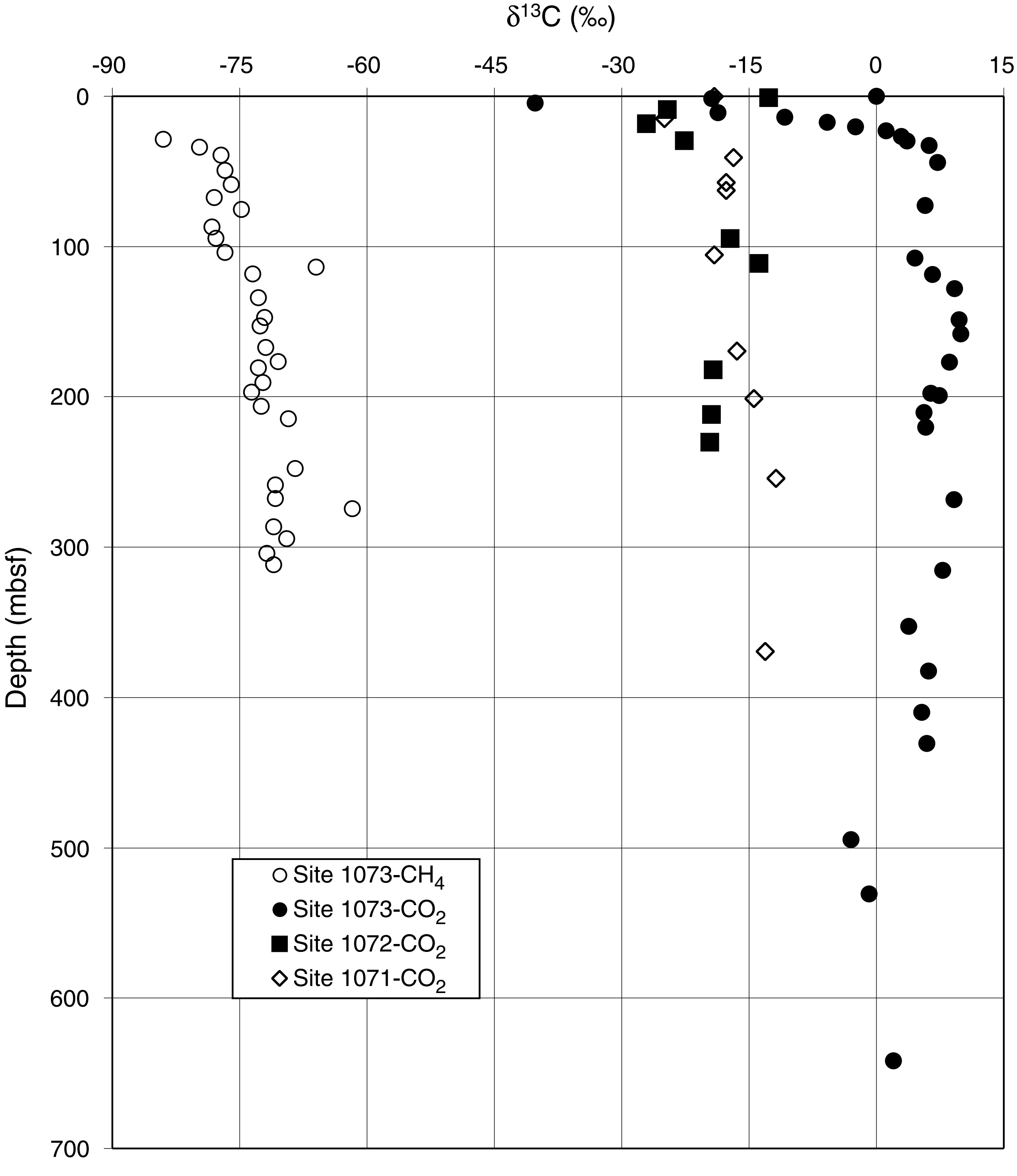

Table T1. Alkalinity, concentration, and δ^{13}C of dissolved inorganic carbon in pore-water samples, Sites 1071–1073.

Core, section, interval (cm)	Depth (mbsf)	Alkalinity (mM)	ΣCO_2 (mM)	δ^{13}C (‰)
174A-				
1071D-1R-1, 52-62	0.5	4.1	2.5	–19.1
1071A-4H-2, 145-150	14.9	6.9	3.5	–24.9
1071B-2X-1, 140-150	41.2	8.2	4.9	–16.8
1071D-7R-1, 33-43	57.7	5.9	2.3	–17.74
1071B-5X-3, 140-150	62.8	6.5	2.8	–17.72
1071C-7X-CC, 13-23	105.7	4.1	2.5	–19.1
1071C-15X-5, 140-150	169.8	5.9	5.3	–16.4
1071C-19X-CC, 0-16	201.2	18.8	5.9	–14.4
1071C-25X-2, 140-150	254.5	13.9	5.2	–11.8
1071F-11R-2, 58-68	369.5	26.9	13.0	–13.1
174A-1072A-				
1R-1, 134-144	1.3	4.5	2.3	–12.7
2R-1, 140-150	8.9	6.1	3.9	–24.6
3R-1, 140-150	18.4	7.2	4.6	–27.1
4R-2, 140-150	29.6	8.3	3.2	–22.6
16R-1, 104-114	95.0	4.3	3.0	–17.2
19R-2, 140-150	111.3	3.5	1.7	–13.8
33R-1, 140-150	182.2	9.9	3.8	–19.2
39R-3, 140-150	211.7	15.6	8.6	–19.4
43R-1, 140-150	230.5	19.8	11.0	–19.6
174A-1073A-				
1H-1, 140-150	1.4	7.8	4.7	–19.43
1H-3, 140-150	4.4	11.7	7.9	–40.2
2H-3, 140-150	11.0	8.9	5.9	–18.73
2H-5, 140-150	14.0	7.9	5.3	–10.83
3H-1, 130-140	17.4	6.1	3.9	–5.76
3H-3, 130-140	20.2	6.0	5.7	–2.54
3H-5, 130-140	23.0	8.6	4.3	1.1
4H-1, 130-140	26.9	8.3	6.1	2.9
4H-3, 130-140	29.8	9.4	7.1	3.6
4H-5, 130-140	32.7	9.5	7.0	6.2
5H-6, 140-150	44.1	12.3	9.5	7.2
8H-6, 140-150	72.5	10.2	7.6	5.7
12H-4, 140-150	107.5	6.3	4.6	4.5
13H-5, 140-150	118.5	9.2	6.6	6.6
14H-5, 140-150	128.0	11.8	6.4	9.2
16H-6, 140-150	148.5	19.1	13.6	9.7
17H-6, 140-150	158.0	17.0	13.3	9.9
19H-6, 140-150	176.9	12.5	8.7	8.6
22H-2, 140-150	197.5	9.8	7.3	6.4
22H-3, 140-150	199.0	10.4	8.7	7.4
23H-5, 140-150	210.2	9.4	8.2	5.6
25X-3, 135-150	220.1	8.3	5.6	5.8
30X-3, 135-150	268.4	19.0	13.3	9.1
35X-4, 135-150	315.4	11.2	8.8	7.8
39X-4, 135-150	352.5	5.4	3.6	3.8
42X-5, 135-150	382.2	7.3	4.1	6.1
45X-5, 135-150	409.9	10.4	5.6	5.3
47X-6, 135-150	430.4	10.0	6.3	5.9
54X-5, 135-150	494.6	11.4	8.2	–2.95
58X-4, 135-150	530.7	20.9	14.7	–0.93
70X-4, 135-150	641.7	15.3	4.8	2.0

Table T2. Carbon isotopic composition of methane, Hole 1073A.

Core, section	Depth (mbsf)	$\delta^{13}C$ (‰)
174A-1073A-		
4H-3	28.7	–84
4H-6	34.0	–79.7
5H-3	39.3	–77.2
6H-4	49.4	–76.7
7H-4	58.8	–76
8H-3	67.3	–78
9H-2	75.3	–74.8
10H-3	86.8	–78.3
11H-2	94.6	–77.8
12H-2	103.7	–76.7
13H-2	113.5	–66
13H-5	118.3	–73.5
15H-3	133.8	–72.8
16H-6	147.3	–72.1
17H-3	152.7	–72.6
18H-6	167.1	–71.9
19H-6	176.4	–70.5
20H-3	180.8	–72.8
21H-4	190.6	–72.3
22H-2	197.0	–73.6
23H-3	206.2	–72.5
24H-2	214.5	–69.3
28X-3	247.8	–68.5
29X-4	258.6	–70.8
30X-4	267.5	–70.8
31X-2	274.5	–61.7
32X-4	286.3	–71
33X-3	294.2	–69.5
34X-3	304.2	–71.8
35X-2	311.5	–71