Shinohara, M., Salisbury, M.H., and Richter, C. (Eds.)
Proceedings of the Ocean Drilling Program, Scientific Results Volume 195

7. DATA REPORT: STABLE ISOTOPE COMPOSITIONS OF DISSOLVED INORGANIC CARBON, METHANE, SULFATE, AND SULFIDE IN PORE WATER FROM THE SOUTH CHAMORRO SERPENTINITE MUD VOLCANO, MARIANA SUBDUCTION COMPLEX[1]

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ABSTRACT

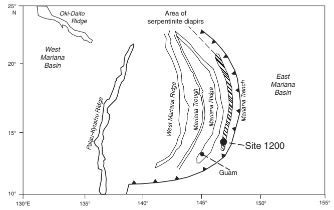
The South Chamorro Seamount is a serpentinite mud volcano near the southern end of the Mariana forearc. The mud volcano was sampled by drilling during Ocean Drilling Program Leg 195. Samples of pore water squeezed from serpentinite mud were analyzed for stable isotope compositions of carbon in dissolved inorganic carbon and methane, sulfur in sulfate and sulfide, and oxygen in sulfate.

INTRODUCTION

Serpentinite mud volcanoes are formed on the ocean floor in a curvilinear belt along the outer forearc of the Mariana subduction complex in the western Pacific Ocean (Fig. F1). After more than a decade of study, numerous individual mud volcanoes with distinct geochemical and geomorphic features have been recognized (Fryer et al., 2000). This paper concerns the South Chamorro Seamount, which is near the southern terminus of the belt.

The mud volcanoes are derived by serpentinization of peridotite in the mantle wedge in the hanging wall of the subduction zone. Water released by dehydration of hydrous minerals in the décollement fluxes

F1. Study area schematic map, p. 5.



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[1] Komor, S.C., and Mottl, M.J., 2005. Data report: Stable isotope compositions of dissolved inorganic carbon, methane, sulfate, and sulfide in pore water from the South Chamorro serpentinite mud volcano, Mariana subduction complex. *In* Shinohara, M., Salisbury, M.H., and Richter, C. (Eds.), *Proc. ODP, Sci. Results,* 195, 1–12 [Online]. Available from World Wide Web: <http://www-odp.tamu.edu/publications/195_SR/VOLUME/CHAPTERS/109.PDF>. [Cited YYYY-MM-DD]

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Initial receipt: 8 June 2004
Acceptance: 14 September 2005
Web publication: 20 December 2005
Ms 195SR-109

these rocks, which converts harzburgites near water flow paths to serpentinite mud with entrained blocks of partially serpentinized harzburgite. The serpentinite mud rises along fractures in the mantle wedge and protrudes to the seafloor through normal faults in the outer forearc.

In this data report, we summarize the stable isotope geochemistry of pore fluids in South Chamorro Seamount. An overview of the complete geochemistry of pore water is given by Mottl et al. (2003).

SAMPLING AND ANALYTICAL PROCEDURES

Cores recovered by drilling were brought on deck in plastic liners and sliced into sections with pipe cutters and a spatula. Duplicate plugs of sediment (~5 cm^3) were collected from the ends of core sections immediately upon cutting and placed in duplicate sets of glass vials that were flushed with helium and sealed with a rubber septum and metal crimp top. One set was used to determine the concentrations of light hydrocarbons by shipboard gas chromatography, and the other set, poisoned with HgCl, was returned to shore for carbon isotope analyses of methane at the University of Hawaii.

Cores chosen for pore water extraction were refrigerated to ~1°–3°C, the in situ pore water temperature, and then slowly squeezed in a hydraulic ram that reached maximum pressures of 0.28 GPa (40,000 psi). Extracted water was forced through 0.45-µm cellulose filters and aliquoted for various measurements. Alkalinity was measured by automated titration with HCl at 25°C, sulfate by ion chromatography, and dissolved reduced sulfur by iodometric titration. Dissolved inorganic carbon (DIC) was calculated from pH and alkalinity, as measured at 25°C, with the PHREEQC computer program (Parkhurst and Appelo, 1999). Headspace gas analyses results were converted to concentrations in millimoles per liter by use of the measured porosity of the wet unconsolidated serpentinite. Reported methane concentrations are minima because degassing occurred during retrieval and processing of the cores.

Samples of pore water for carbon and sulfur isotopic analyses were processed in a nitrogen-filled glove bag as soon as they were squeezed from the cores. The samples were treated with mercuric chloride to arrest bacterial activity. Aliquots were collected for stable isotope analyses of carbon in methane and DIC (Table T1) and for oxygen and sulfur in sulfate (Tables T2, T3). Other pore water aliquots were treated with $AgNO_3$ or zinc acetate for isotopic analysis of dissolved reduced sulfur. Isotopic analyses of sulfate, dissolved reduced sulfur, and DIC were conducted at the Environmental Isotope Laboratory at the University of Waterloo in Canada.

T1. Methane $\delta^{13}C$ compositions, p. 10.

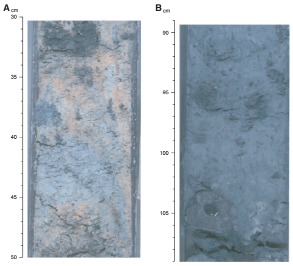
T2. Stable isotope compositions, p. 11.

T3. Sulfur isotope compositions, p. 12.

LITHOLOGY

X-ray diffraction analyses and light microscopy identified the muds as fibrous chrysotile with accessory aragonite, lizardite, calcite, magnetite, brucite, talc, and mixed-layer smectite/illite clays. Many samples contain relict grains of forsterite (Fo_{92}), enstatite, and clinopyroxene. Many samples also contain xenocrysts and gravel-sized xenoliths of metabasalt and calcic to sodic amphibolites (Fryer et al., 1999). Oxidized muds contain blue-green serpentinite and yellowish orange calcareous ooze (Fig. F2A). The surfaces of core sections that emit strong odors of hydrogen sulfide are gray to black and contain various unidentified opaque sulfide minerals (Fig. F2B). Particulate organic material is virtually absent (Mottl et al., 2003).

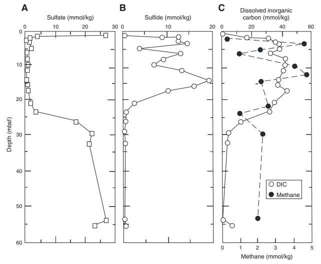
F2. Core sections, p. 6.



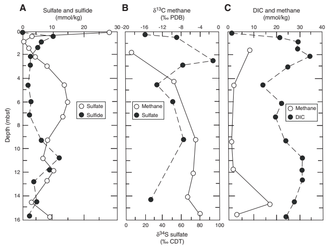
CARBON AND SULFUR CHEMISTRY

Sulfate concentrations in Hole 1200E decrease sharply with depth to ~0 over the interval 0.45–2.15 meters below seafloor (mbsf) (Fig. F3A). In Hole 1200E, sulfate concentrations average 1.2 mmol/kg in the upper 20 mbsf of core, exclusive of the shallowest sample, then increase to between 25 and 30 mmol/kg at greater depths. In contrast, sulfide concentrations are near zero at the seafloor, reach their largest concentrations at 2.85 mbsf, and then decrease to near zero at depths greater than ~14 mbsf (Fig. F3B). A similar pattern occurs in Hole 1200F, where sulfate concentrations decrease rapidly to a minimum at ~1 mbsf (Fig. F4A). In Hole 1200F, however, sulfate concentrations recover to values of 10–15 mmol/kg below ~5 mbsf. Values of $\delta^{34}S$ in sulfate peak in the upper 2.2 mbsf in Holes 1200E and 1200F (Figs. F4B, F5B). The peaks correspond to large DIC concentrations and small sulfate concentrations.

F3. Pore water concentrations, Hole 1200E, p. 7.

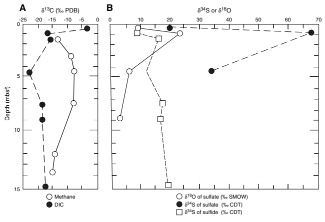


F4. Pore water concentrations, Hole 1200F, p. 8.



Concentrations of DIC in Holes 1200D and 1200F are dominated by CO_3^- and $NaCO_3$, instead of HCO_3, because pH values of samples unaffected by mixing with seawater average 12.2 ± 0.3 mmol/kg. Concentrations of DIC in Hole 1200E are rather constant at ~35–40 mmol/kg between ~3 and 17 mbsf but decrease rapidly above and below those depths (Fig. F3C). All the analyses of $\delta^{13}C_{DIC}$ are from Hole 1200E (Fig. F5A). The $\delta^{13}C_{DIC}$ value at 0.45 mbsf is –2.4‰, a typical value for marine HCO_3. Deeper samples have much lower $\delta^{13}C_{DIC}$ values in the range of –16.6‰ to –22.6‰. Concentrations of DIC in Hole 1200F reach 34.8 mmol/kg at 2.15 mbsf and then decrease to 20–30 mmol/kg in most of the remaining cored section (Fig. F4C). The DIC peak is near the depths where sulfate is at a minimum (Fig. F4A) and $\delta^{34}S$ is at a maximum (Fig. F4B).

F5. Isotope values, p. 9.



Methane and ethane were detected in all 28 of the analyzed samples, with an average concentration of 2.9 mmol/L. Values of $\delta^{13}C$ in methane, which were measured for 22 samples, range from –4‰ to –19‰, except for the sample nearest the seafloor in Hole 1200D, in which $\delta^{13}C$ = –73.7‰ (Table T1). Methane concentrations in Hole 1200E range from 0.98 mmol/L at 1.50 mbsf to 4.82 mmol/L at 3.0 mbsf (Fig. F3C). Methane concentrations in Hole 1200F are 1.70–17.79 mmol/kg (Fig. F4C). The $\delta^{13}C_{CH4}$ values in Holes 1200E and 1200F are from –7.5‰ to –13.3‰ (Fig. F5A) and –3.5‰ to –18.7‰, respectively. (Fig. F4B).

ACKNOWLEDGMENTS

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 Institutions (JOI), Inc. Funding for this research was provided by the U.S. NSF.

REFERENCES

Fryer, P., Lockwood, J.P., Becker, N., Phipps, S., and Todd, C.S., 2000. Significance of serpentine mud volcanism in convergent margins. *Spec. Pap.—Geol. Soc. Am.,* 349:35–51.

Fryer, P., Wheat, C.G., and Mottl, M.J., 1999. Mariana blueschist mud volcanism: implications for conditions within the subduction zone. *Geology,* 27:103–106.

Mottl, M.J., Komor, S.C., Fryer, P., and Moyer, C.L., 2003. Deep-slab fluids fuel extremophilic *Archaea* on a Mariana forearc serpentinite mud volcano: Ocean Drilling Program Leg 195. *Geochem., Geophys., Geosyst.,* 4. **doi:10.1029/2003GC000588**

Parkhurst, D.L., and Appelo, C.A.J., 1999. Users guide to PHREEQC (version 2)—Water-Resources Investigations Report 99–4259, Denver.

Figure F1. Schematic map of the study area in the western Pacific Ocean.

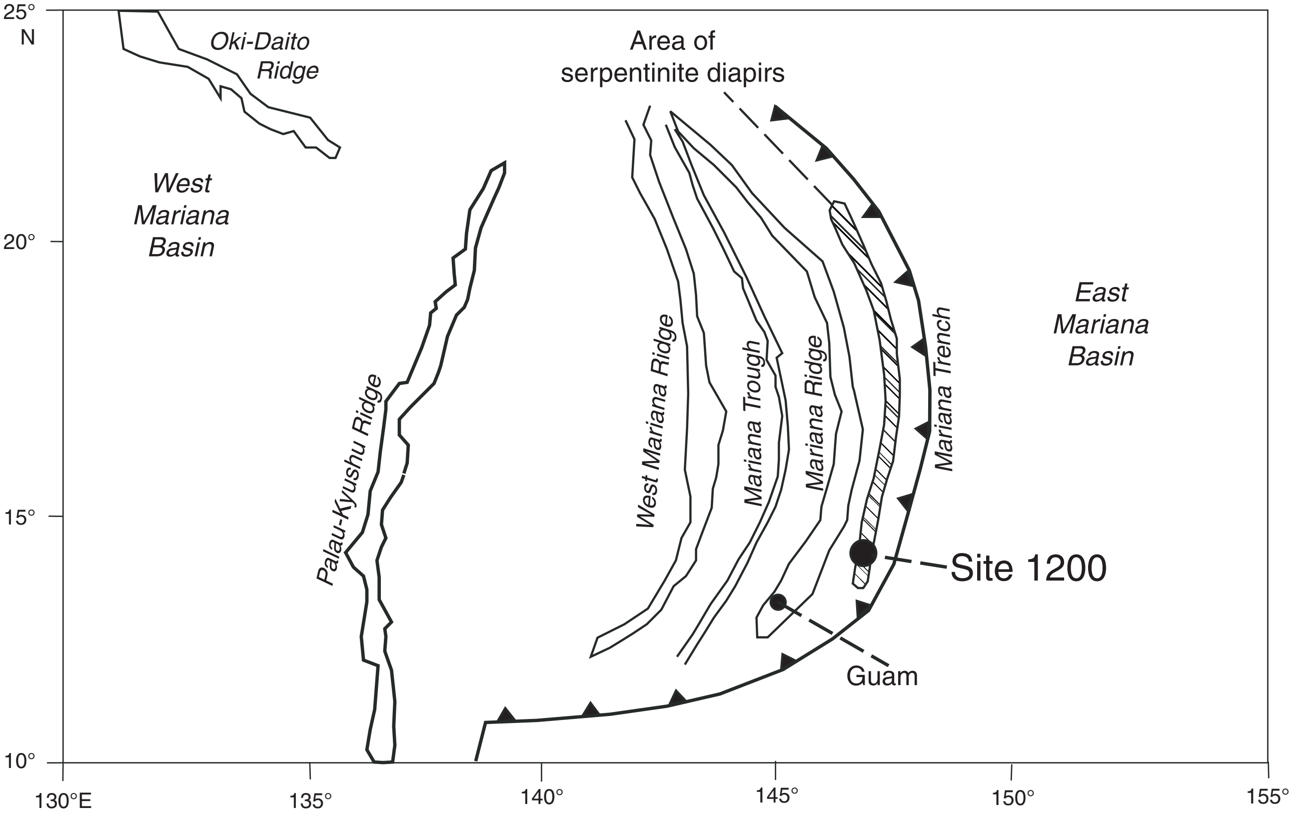


Figure F2. Core sections. Note the color contrasts between (**A**) the oxidized core, distinguished by the orange color, particularly between 35 and 40 cm, and (**B**) the more reduced core with dark gray or black intervals between 93 and 97 cm and between 104 and 108 cm, which are rich in sulfides.

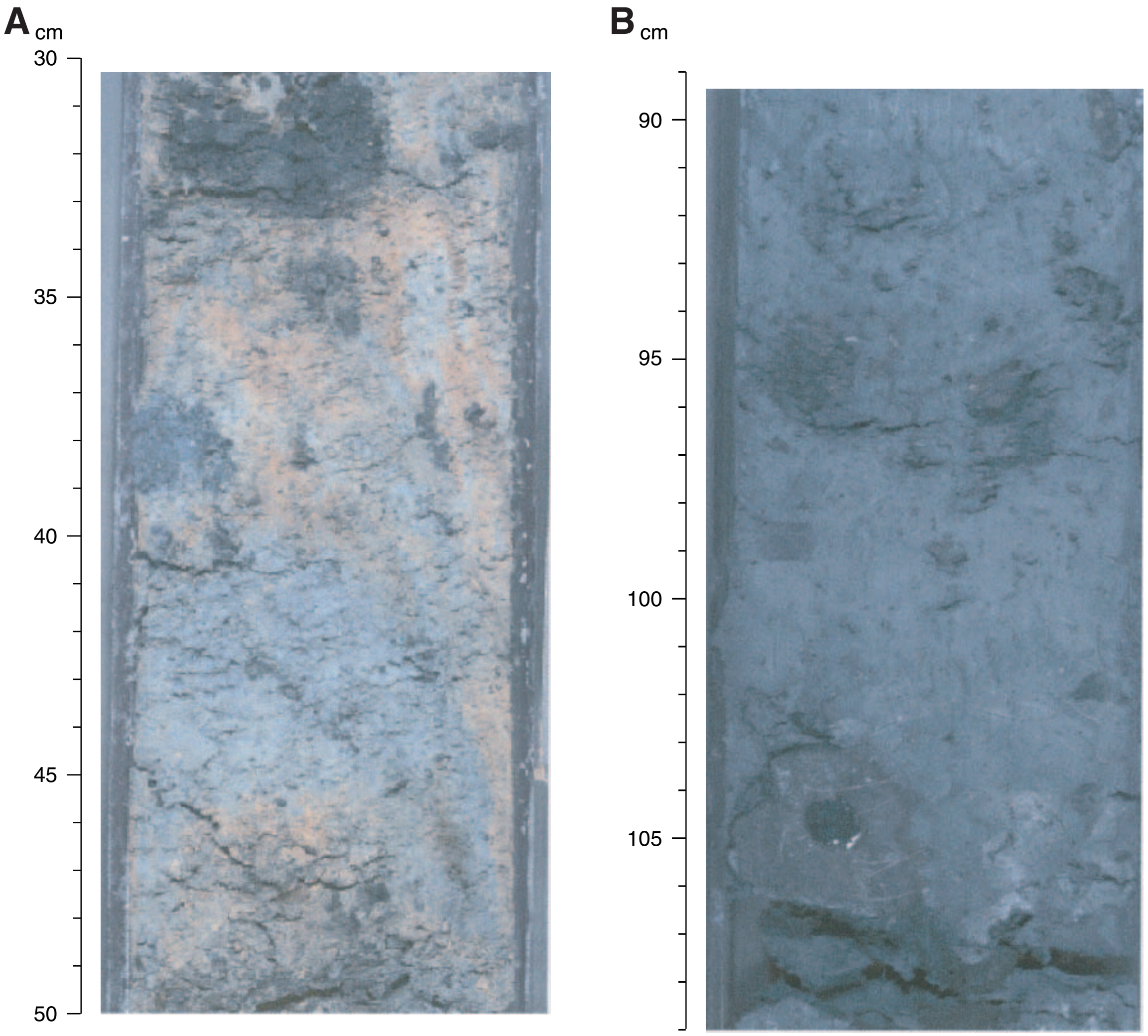


Figure F3. Hole 1200E. **A.** Sulfate concentration vs. depth. **B.** Sulfide concentration vs. depth. **C.** Methane and dissolved inorganic carbon (DIC) vs. depth, as determined by the pH and alkalinity calculated from the PHREEQC computer program (Parkhurst and Appelo, 1999).

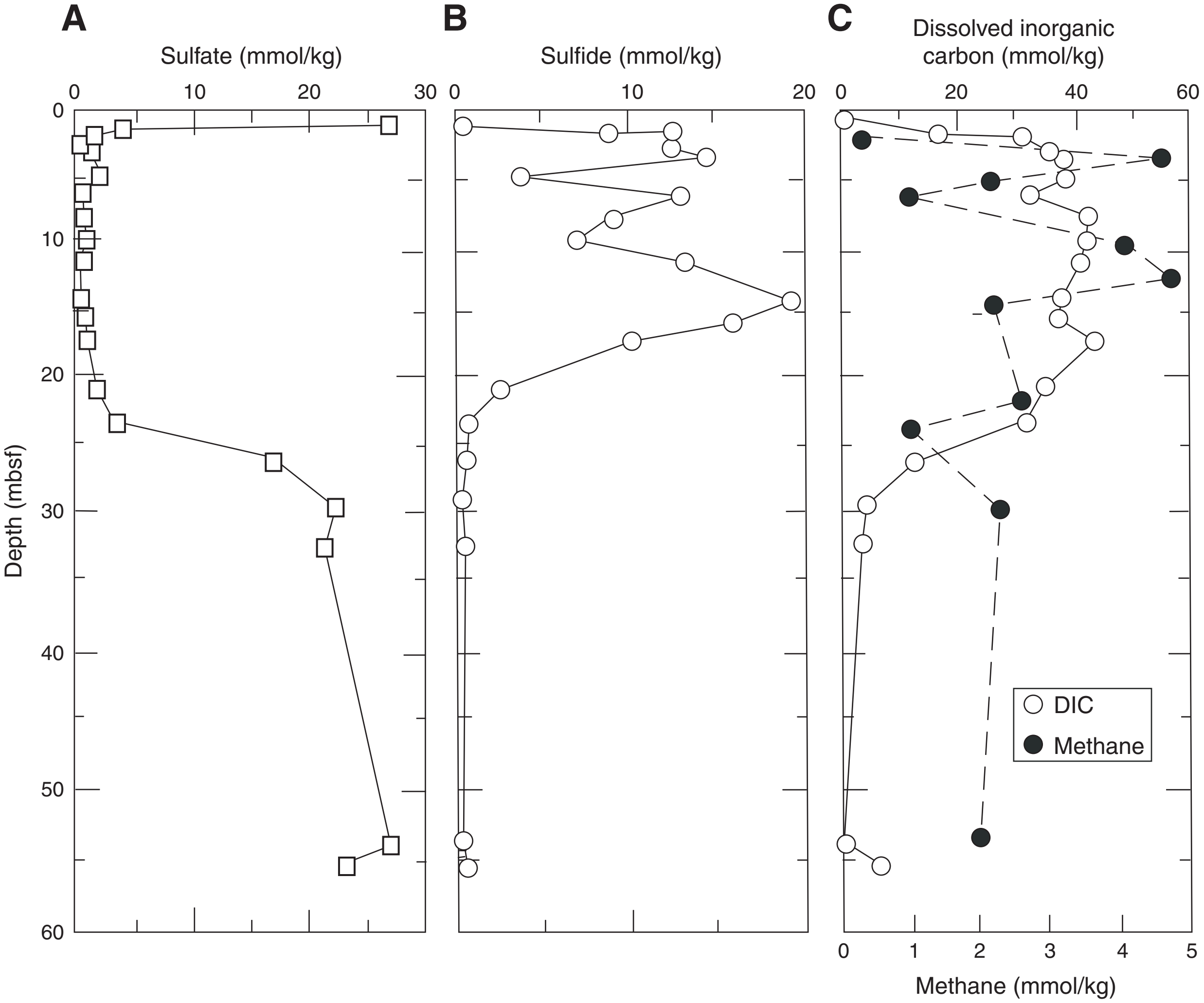


Figure F4. Hole 1200F. **A.** Sulfate and sulfide concentration vs. depth. **B.** Values of δ^{13}C in methane and δ^{34}S in sulfate. PDB = Peedee belemnite, CDT = Canyon Diablo troilite. **C.** Dissolved inorganic carbon (DIC) and methane vs. depth.

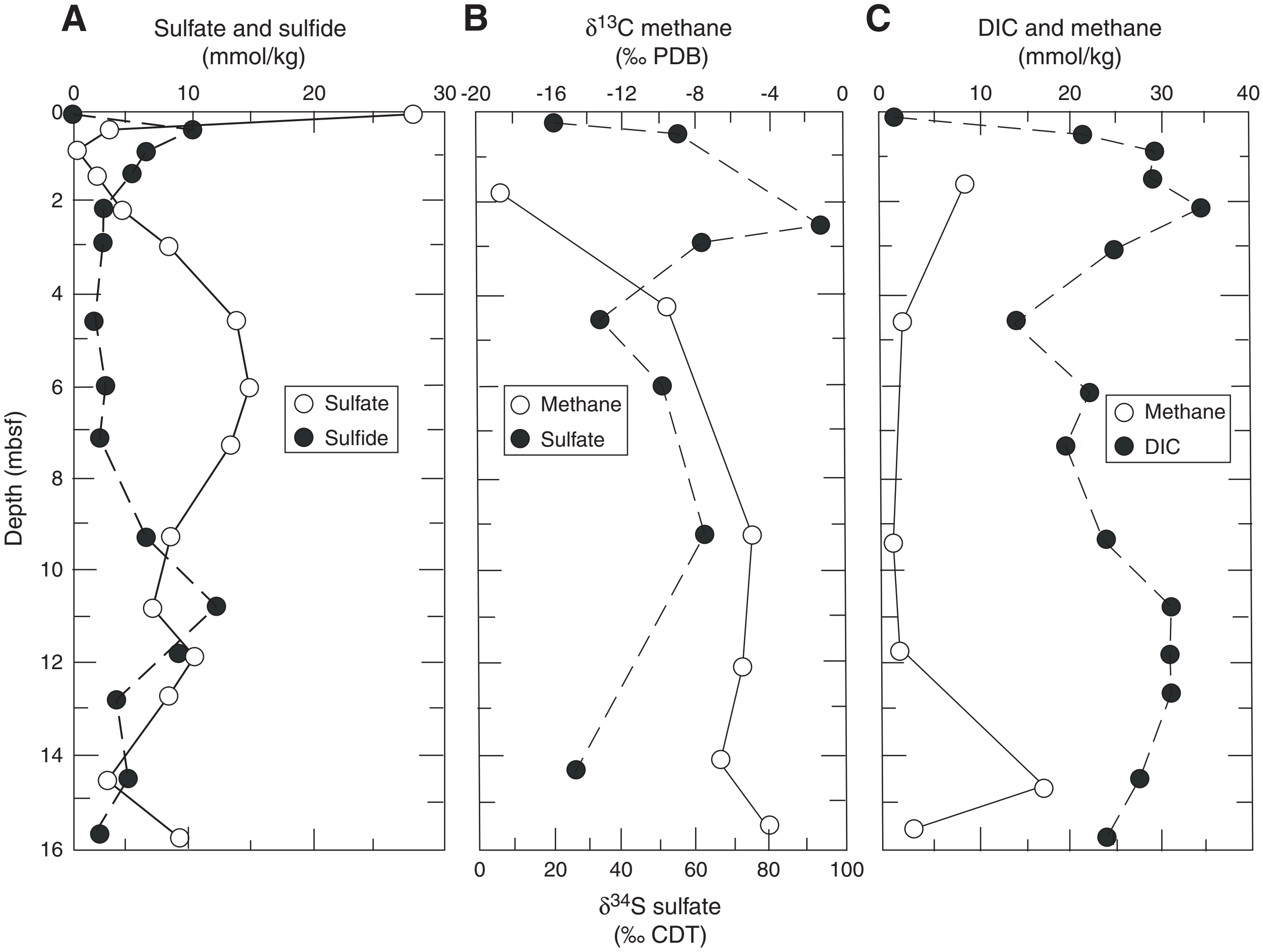


Figure F5. Hole 1200F. **A.** Values of $\delta^{13}C$ in dissolved inorganic carbon (DIC) and methane. PDB = Peedee belemnite. **B.** Values of $\delta^{34}S$ in sulfate and sulfide and values of $\delta^{18}O$ in sulfate. SMOW = standard mean ocean water, CDT = Canyon Diablo troilite.

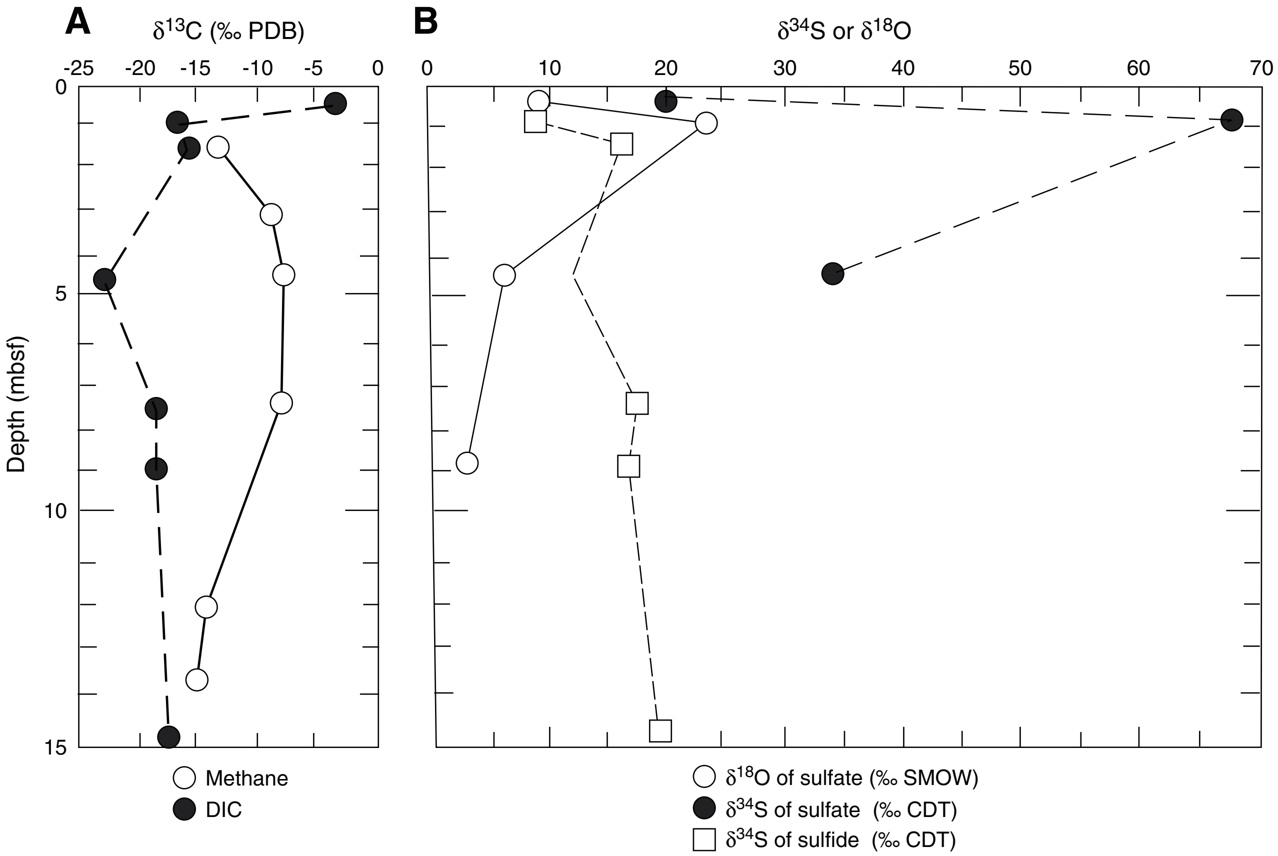


Table T1. Methane carbon isotope compositions.

Core, section, interval (cm)	Depth (mbsf)	$\delta^{13}C_{CH4}$ (‰ PDB)
195-1200D-		
1H-2, 70–75	2.23	–73.7
2H-2, 0–5	8.43	–16.5
3H-1, 0–2	11.43	–13.8
5H-1, 30–40	14.05	–15.9
6H-1, 115–126	22.71	–14.6
7H-1, 120–130	24.75	–14.0
195-1200E-		
1H-2, 0–5	1.53	–13.3
1H-3, 0–5	3.03	–8.4
2H-2, 0–5	4.63	–7.6
2H-3, 0–5	9.13	–7.8
3H-1, 0–5	11.03	–14.2
4H-2, 0–5	13.53	–15.0
5H-3, 0–5	20.63	–14.9
6H-2, 0–5	22.73	–7.4
7H-3, 0–5	28.93	–16.6
l0X-2, 0–5	51.93	–12.5
195-1200F-		
1H-2, 120–130	1.53	–18.7
1H-4, 0–5	4.53	–9.4
2H-2, 0–5	9.23	–4.8
2H-4, 0–5	12.23	–5.4
3H-2, 0–5	14.23	–6.5
3H-2, 121–126	15.64	–4.0

Note: PDB = Peedee belemnite.

Table T2. Stable isotope compositions of carbon in dissolved inorganic carbon, oxygen in sulfate, and sulfur in sulfide, Hole 1200E.

Core, section, interval (cm)	Depth (mbsf)	$\delta^{13}C_{DIC}$ (‰ PDB)	$\delta^{18}O$ in sulfate (% SMOW)	$\delta^{34}S$ in sulfide (‰ CDT)
195-1200E-				
1H-1, 40–50	0.45	–2.4	9.5	NES
1H-1, 90–100	0.95	–16.6	23.5	9.2
1H-1, 130–140	1.35	–15.6	NES	16.8
1H-3, 130–140	4.35	–22.6	6.6	12.1
2H-1, 130–140	7.45	–18.6	NES	17.5
2H-2, 130–140	8.95	–19.4	3.2	17.1
4H-2, 130–140	14.85	–16.4	NES	19.1

Notes: DIC = dissolved inorganic carbon, PDB = Peedee belemnite, SMOW = standard mean ocean water, CDT = Canyon Diablo troilite. NES = not enough sample to analyze.

Table T3. Sulfur isotope compositions of sulfur in sulfate, Holes 1200E and 1200F.

Core, section, interval (cm)	Depth (mbsf)	δ^{34}S in sulfate (‰ CDT)
195-1200E-		
1H-1, 40–50	0.45	20.0
1H-1, 90–100	0.95	67.9
1H-3, 130–140	4.35	34.3
195-1200F-		
1H-1, 0–10	0.05	21.7
1H-1, 40–50	0.45	54.5
1H-2, 60–70	2.15	93.9
1H-2, 140–150	2.95	60.8
1H-3, 140–150	4.45	32.8
1H-4, 140–150	5.95	50.6
2H-1, 140–150	9.15	61.5
3H-1, 140–150	14.35	27.3

Note: CDT = Canyon Diablo troilite.