25. CARBON ISOTOPE COMPOSITION OF CH_4 AND CO_2 IN SEDIMENTS OF THE MIDDLE AMERICAN TRENCH[1]

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Interstitial gases were collected from Holes 565, 566, 567A, 568, 569A, and 570 drilled during Deep Sea Drilling Project Leg 84 on the *Glomar Challenger*. The samples were provided at our request by the Organic Geochemistry Advisory Panel of JOIDES.

Stable carbon isotope analyses of CH_4 and CO_2 were carried out on these samples according to the procedure described by Galimov and Simoneit (1982). The precision of the analysis, including Mat-230 mass-spectrometric measurements, is $\pm 0.1‰$. The $\delta^{13}C$ values are presented versus PDB standard (Table 1).

The measured $\delta^{13}C$ values for methane in the upper parts of the various holes range from about -80 to $-70‰$, which is known to be characteristic of biogenic methane. The fact that methane with this biogenic isotope composition is found in Hole 567A (drilled near the basement of the Trench in a water depth of 5500 m) suggests that biochemical processes can proceed at pressures attaining very high values and at low temperatures.

A general trend consists of a gradual depletion of the light carbon isotope of methane observed for all sites with depth. The $\delta^{13}C$ values increase linearly up to -60 to $-50‰$, in the absence of such complicating phenomena as migration, high heat flows, and so on.

As was observed previously for analogous environmental conditions (Galimov and Kvenvolden, 1983), the change in CH_4 carbon isotope composition with depth is clearly paralleled by that of CO_2. This observation is in agreement with the concept of methane generation in oceanic sediments by the microbial reduction of CO_2.

The gradients with depth of the $\delta^{13}C$ values for CH_4 and CO_2 appear to be lower in the deepest parts of the ocean. In fact in Hole 567A (Table 1) the $\delta^{13}C_{CH_4}$ and $\delta^{13}C_{CO_2}$ data are almost constant over the interval from 200 to 450 m. This is obviously due to a lower microbial activity and thus slower production of CH_4 with concommitant CO_2 consumption at greater depths.

In Hole 570 methane is markedly depleted in the light carbon isotope ($\delta^{13}C_{CH_4}$ -35 to -42 ‰) between about 400 and 270 m sub-bottom, respectively. These values are characteristic of methane generated during the mature stage of organic matter transformation. The most probable cause of the phenomenon is the migration of catagenic gas from deeper sediments. The depletion in the light carbon isotope of methane is accompanied by the appearance of carbon dioxide relatively enriched in ^{12}C. The light CO_2 may be the result of a partial oxidation of hydrocarbons in the migrating fluids.

It should be emphasized that gas with the isotopic composition just described is characteristic of the gas hydrate zone at Sites 568 and 570. The higher gas concentration in these zones is obviously the result of entrapment of the migrating gas and its accumulation in the hydrate form.

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REFERENCES

Galimov, E. M., and Kvenvolden, K. A., 1983. Concentrations and carbon isotopic compositions of CH_4 and CO_2 in gas from sediments of the Blake Outer Ridge, Deep Sea Drilling Project, Leg 76. *In* Sheridan, R. E., Gradstein, F. M., et al., *Init. Repts. DSDP*, 76: Washington (U.S. Govt. Printing Office), 403–417.

Galimov, E. M., and Simoneit, B. R. T., 1982. Geochemistry of interstitial gases in sedimentary deposits of the Gulf of California, Deep Sea Drilling Project Leg 84. *In* Curray, J. R., Moore, D. G., et al., *Init. Repts. DSDP*, 64: Washington (U.S. Govt. Printing Office), 781–788.

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Table 1. Stable carbon isotopic composition of CH_4 and CO_2 in sediments of the Middle America Trench, DSDP Leg 84.

Section (site-core-section)	Sub-bottom depth (m)	$\delta^{13}C$ (‰ vs. PDB)		$\delta^{13}C_{CO_2} - CH_4$ [a]
		CH_4	CO_2	
565-19-4	177.0	−64.34	−17.19	47.15
565-21-3	195.3	−64.83	−16.49	48.34
565-22-3	204.4	−64.62	−19.12	45.50
565-22-6	208.1	−64.13	−19.17	44.96
565-23-5	216.9	−64.33	−18.05	46.28
565-24-3	223.1	−63.62	−19.26	44.36
565-25-5	235.2	−63.17	−19.73	43.44
565-26-4	243.1	−63.74	−19.71	44.03
565-27-2	250.7	−63.62	−18.27	45.35
565-31-5	293.0	—	−17.28	—
565-34-1	319.7	−62.24	−19.31	42.93
566C-7-1	127.8	−58.86	—	—
567A-1-6	203.2	—	−16.43	—
567A-2-5	211.8	−71.19	−18.30	52.89
567A-3-3	218.8	−71.83	−17.80	54.01
567A-4-1	225.9	−72.37	−19.83	52.44
567A-6-5	249.8	−71.88	—	—
567A-9-5	278.9	−72.64	−18.97	53.67
567A-10-1	281.0	—	−19.92	—
567A-11-2	291.3	−71.21	−19.01	52.20
567A-12-2	301.0	−68.26	−20.95	47.31
567A-14-2	319.0	−73.91	−21.40	52.51
567A-17-2	345.6	−70.20	−21.05	49.15
567A-23-1	411.8	−69.88	−20.75	49.13

[1] von Huene, R., Aubouin, J., et al., *Init. Repts. DSDP*, 84: Washington (U.S. Govt. Printing Office).

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Table 1. (Continued).

Section (site-core--section)	Sub-bottom depth (m)	$\delta^{13}C$ (‰ vs. PDB) CH_4	CO_2	$\delta^{13}C_{CO_2 - CH_4}$[a]
567A-24-1	421.2	−69.00	−19.71	49.29
567A-25-1	430.4	—	−20.78	—
567A-26-1	439.3	—	−19.66	—
567A-27-1	446.4	−73.44	−19.73	53.75
567A-29-2	486.4	—	−18.84	—
568-3-5	19.3	−70.24	−13.36	56.88
568-4-4	27.6	−69.74	−17.24	52.50
568-5-5	39.2	−66.78	−13.33	53.45
568-6-4	46.8	−66.28	− 7.71	58.57
568-7-3	55.8	−64.05	−10.91	53.14
568-8-5	68.1	−64.95	− 9.21	55.74
568-10-4	85.4	−64.46	−10.25	54.21
568-12-4	104.3	−62.86	− 9.83	53.03
568-13-4	114.1	−60.73	−11.83	48.90
568-15-6	135.4	−61.46	—	—
568-16-4	143.0	−59.92	−19.37	40.55
568-17-4	152.7	−57.79	−16.83	40.96
568-18-3	159.9	−54.67	−17.11	37.56
568-20-6	184.1	−55.05	−20.85	34.20
568-22-5	202.5	−50.69	—	—
568-23-2	207.5	−49.27	−18.57	30.70
568-24-4	219.5	−48.76	−19.20	29.56
568-25-6	232.0	−47.12	−18.82	28.30
568-27-3	247.4	—	−19.74	—
568-28-4	258.9	−49.19	−20.11	26.08
568-29-5	270.0	−45.98	−20.18	25.80
568-30-6	281.4	−45.60	−21.97	23.63
568-32-6	300.4	−46.00	−20.44	25.56
568-33-6	310.1	−45.75	−21.40	24.35
568-34-6	319.2	−44.68	−20.61	24.07
568-35-4	326.8	−47.28	−19.96	27.32
568-36-6	339.4	−45.03	−21.39	23.64
568-37-4	345.5	−44.17	−17.40	26.77
568-38-6	358.4	−42.07	−22.27	19.80
568-39-3	363.2	−45.03	−21.37	23.76
568-40-3	373.5	−46.69	−20.88	25.81
568-41-5	386.5	−43.21	−15.84	27.37
568-42-6	397.7	−43.64	−18.50	25.14
568-43-4	403.6	−43.87	−19.59	24.28
568-44-4	413.9	−42.90	−18.92	23.98
569-5-4	35.7	—	−20.87	—
569-5-6	48.7	—	−21.06	—
569-7-7	59.2	−81.62	−20.52	61.10
569-8-3	62.9	−85.79	−20.24	65.55
569-9-1	69.0	−83.92	—	—
569-10-1	78.6	−83.09	−20.39	62.70
569-11-2	89.6	−82.29	−18.42	63.87
569-12-6	104.8	−80.78	−21.88	58.90
569-13-3	110.2	−79.11	−20.51	58.60
569-14-1	117.3	−78.94	−19.45	59.49
569-15-3	129.4	−75.67	−20.22	55.45
569-16-1	136.0	−76.62	−20.41	56.21

Table 1. (Continued).

Section (site-core--section)	Sub-bottom depth (m)	$\delta^{13}C$ (‰ vs. PDB) CH_4	CO_2	$\delta^{13}C_{CO_2 - CH_4}$[a]
569-17-6	152.7	−76.37	−18.79	57.58
569-18-2	156.1	−76.20	−22.93	53.27
569-20-1	175.1	−75.32	—	—
569-21-2	185.7	−75.56	−20.52	55.04
569-22-2	195.0	−73.27	−19.86	53.41
569-23-3	206.6	−72.42	—	—
569-24-5	218.9	−70.34	−21.21	49.13
569-26-5	237.6	−68.54	−21.50	47.04
569-27-3	244.3	−67.86	−19.13	48.73
569A-1-2	248.1	−79.63	−19.96	59.67
569A-2-2	257.8	−75.19	−20.96	54.23
569A-4-1	275.2	−74.38	−20.63	53.75
569A-6-1	294.1	−68.79	−18.17	50.62
569A-9-1	333.2	−64.57	−19.49	45.08
570-1-4	4.7	—	−18.13	—
570-2-5	11.4	—	−20.03	—
570-3-6	26.3	−77.27	−17.66	59.61
570-4-2	29.9	−75.64	−15.15	60.49
570-5-3	41.3	−75.52	−13.95	61.57
570-6-5	52.9	−72.66	−11.38	61.28
570-7-4	60.6	—	−12.30	—
570-8-3	69.3	−68.52	− 8.27	60.25
570-9-2	77.8	−68.12	−15.24	52.78
570-10-2	88.0	−69.37	−15.35	54.02
570-11-1	96.2	−67.18	− 9.13	58.05
570-14-5	129.8	−67.83	−15.78	52.05
570-15-2	135.9	−68.32	−15.01	53.31
570-16-6	150.6	−66.45	− 9.93	66.52
570-17-3	152.7	—	−11.97	—
570-18-1	162.4	−66.69	− 8.90	57.79
570-19-3	175.6	−64.22	−12.18	52.04
570-20-1	182.9	−63.31	− 4.82	58.49
570-21-2	193.2	—	− 2.17	—
570-22-3	205.0	−61.64	− 6.82	54.82
570-23-2	212.9	−57.37	− 7.00	50.37
570-25-5	234.5	−55.99	+ 0.46	56.45
570-26-4	245.4	−53.70	−14.22	39.48
570-28-6	267.1	—	−11.48	—
570-29-4	274.1	−42.14	−14.28	27.86
570-30-4	283.9	−42.28	−16.90	25.38
570-31-1	288.8	−41.58	−10.98	30.60
570-32-4	302.3	−42.39	−15.46	26.93
570-34-1	317.6	−40.99	−19.69	21.30
570-35-2	328.6	−41.37	−20.72	20.65
570-36-1	336.5	−41.68	−22.40	19.28
570-37-1	346.6	−41.01	−22.55	18.46
570-41-2	386.3	—	−20.11	—
570-42-1	393.5	−35.92	−20.97	14.95

Note: Water depths at holes are as follows: Hole 565, 3099 m; Hole 566C, 3661 m; Hole 567A, 5500 m; Hole 568, 2010 m; Hole 569, 2744 m; Hole 569A, 2795 m; Hole 570, 1698 m. — indicates not determined.

[a] $\Delta = (\delta^{13}C_{CO_2} - \delta^{13}C_{CH_4})$ in ‰.