

5. INTERSTITIAL WATER STUDIES, LEG 15 – ISOTOPIC MEASUREMENTS ON CO₂ GAS FROM GAS POCKETS IN DEEP-SEA CORES, SITE 147¹

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INTRODUCTION

Cores taken on Leg 15 of the DSDP at Site 147, off the coast of Venezuela, were found to contain many gas pockets between 47 and 175 meters. These gas samples were collected on board ship by a technique described by Horowitz et al. (this volume) and returned to Lamont-Doherty Geological Observatory where aliquots were taken for gas chromatographic analysis (Hammond et al., this volume) and for mass spectrometric analysis of CO₂. An additional aliquot was sent to New Zealand (Lyon, this volume) for isotopic analysis. The time lapse between the gas sampling and the time the samples were under in situ conditions was about 1 hour maximum.

PROCEDURE

For the isotopic analyses, the gas samples were frozen into liquid air and noncondensable gases were removed. The frozen gas (CO₂ + H₂O) was then allowed to warm up and was passed through two dry ice traps in order to remove any water. The isotopic measurements were made with a Nuclide double collector mass spectrometer, and the results are expressed in per mil deviation from the P.D.B. standard.

DISCUSSION OF RESULTS

The isotopic results and abundance of CO₂ are given in Table 1. It may be seen that the δC^{13} values gradually increase with depth in the upper 150 meters and appear to be related to the general increase in percent CO₂, with the exception of the 83 meter sample (Figure 1). The reason for this apparent relationship is not clear, but the same situation was observed by Nissenbaum et al. (1972) in a reducing fjord in British Columbia. They found evidence that CO₂ is used up to produce methane under the influence of bacteria breaking down the organic matter. This would explain the δC^{13} increase of the CO₂ with depth in the cores, because more methane is produced deeper down in the cores. Since this methane is greatly depleted, the remaining CO₂ will become more enriched in C¹³.

When the δC^{13} results on the CO₂ gas are compared with the values for dissolved bicarbonate in the interstitial water near gas pockets (Presley et al., this volume), it is seen that the fractionation between bicarbonate and CO₂ gas [$\delta_{HCO_3^-} - CO_2(g)$] is about 6.4‰ in three out of four samples. If this represents equilibrium between the CO₂

TABLE 1
Isotopic Results and Abundance
of CO₂ from Ten Gas Pocket
Samples

Sample	% CO ₂ ^a	% CO ₂ ^b	δC^{13} vs. PDB	δO^{18} vs. PDB
147-6-4	2.6	1.0	—	—
147B-6-2	4.6	2.4	-3.18	-0.33
147B-7-4	5.4	2.7	—	—
147-10-3	6.9	3.0	-1.65	+0.08
147B-9-4	13.4	3.7	-0.89	+0.06
147B-11-3	12.2	12.4	+0.08	-0.30
147-14-3	11.8	4.7	+0.09	-1.08
147C-2-2	12.7	13.2	+0.23	-0.10
147C-4-4	10.7	11.1	+0.09	-1.18
147C-7-3	6.7	7.5	-1.11	-1.54

^aHammond et al., this volume.

^bLyon, this volume.

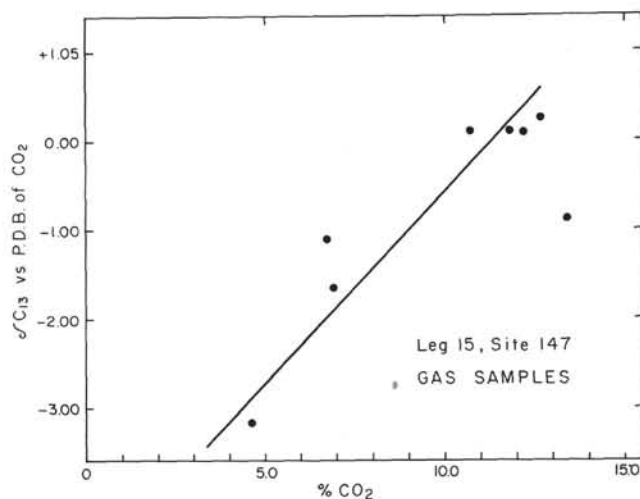


Figure 1. δC^{13} of CO₂ gas from gas pockets plotted as a function of the CO₂ concentration.

and the remaining bicarbonate at the time of shipboard sampling of the gas pocket, it corresponds to a temperature of about 40°C (Emrich et al., 1970). The expected core temperature should lie between 17 and 25°C on the basis of the deep-water temperature and the shipboard air temperature.

If the oxygen isotopic results on CO₂ represent equilibrium with the interstitial waters under sampling

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conditions (assuming the interstitial waters to have isotopic compositions close to SMOW), they would give us calculated temperatures of between 24 and 33°C (Bottinga and Craig, 1969), with the higher temperatures (lower δO^{18} values) in the deeper parts of the cores.

It is clear that both the carbon and oxygen isotopic compositions of the CO_2 gases indicate that equilibrium under sampling conditions had not been reached. It should be noted that the oxygen isotopic compositions are closer to equilibrium than the carbon isotopic compositions. This indicates that the kinetics of oxygen isotopic exchange between CO_2 and water is faster than that of carbon isotopic exchange between CO_2 and HCO_3^- .

There are significant discrepancies in the isotopic results presented here and those of Lyon (this volume) (Table 2). The reason for this is not clear, but in all cases where there are large discrepancies in the isotopic results, there are also large discrepancies in the percent CO_2 data obtained by Lyon (this volume) and those obtained at Lamont-Doherty Geological Observatory (Hammond et al., this volume). In cases where the percent CO_2 data agree, the isotopic results show a reasonably good agreement between the two laboratories. Since more sample material is still available, some of the analyses will be repeated.

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TABLE 2
Comparison of Isotopic Results on Gas Pocket Samples

Sample	Depth (m)	δC^{13} (‰ PDB)				δO^{18} (‰ PDB)	
		CO_2^a	CO_2^b	HCO_3^{-c}	CH_4^b	CO_2^a	CO_2^b
147-6-4	47	—	—		-76.3	—	—
147B-6-2	51	-3.2	-2.9		-67.6	-0.3	—
147B-7-4	63	—	-4.2	+8.41	-65.7	—	—
147-10-3	82	-1.7	-2.9		-64.6	+0.1	-2.9
147B-9-4	83	-0.9	-2.2	+5.44	-60.8	+0.1	-2.2
147B-11-3	100	+0.1	0.0	+8.09	-65.8	-0.3	-0.3
147-14-3	118	+0.1	-1.5		-59.6	-1.1	-3.4
147C-2-2	128	+0.2	+0.2	+6.54	-65.1	-0.1	+0.4
147C-4-4	148	+0.1	+0.5	+6.44	-64.4	-1.2	-0.3
147C-7-3	175	-1.1	-0.5		-64.6	-1.5	-0.4

^aThis report.

^bLyon, this volume.

^cPresley et al., this volume.

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