posed to one-half to one-fifth of these levels (*15*).

Our very limited survey has shown that NMOR (and in some cases NDMA) was present in the highest amounts at the chemical plant in the compounding and mixing areas and at the tire factory in the curing, extrusion, mixing, and cooling areas. A much more comprehensive survey is needed to firmly establish that these are indeed the most contaminated areas (*16*). However, several recent studies show increased rates of lung and gastrointestinal (including colorectal) cancers among workers in several of these areas (*1*). In addition, an increased risk of several other types of cancer has been reported for rubber workers (*1*). However, it would be premature to speculate further on the possible involvement of *N*-nitroso compounds in the etiology of the cancer of rubber workers until more extensive workplace monitoring has been carried out.

J. M. Fajen, G. A. Carson
Division of Surveillance, Hazard Evaluation and Field Studies, National Institute for Occupational Safety and Health, Cincinnati, Ohio 45226
D. P. Rounbehler, T. Y. Fan
R. Vita, U. E. Goff, M. H. Wolf
G. S. Edwards, D. H. Fine
New England Institute for Life Sciences, Waltham, Massachusetts 02154
V. Reinhold, K. Biemann
Chemistry Department, Massachusetts Institute of Technology Cambridge 02139

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6. Bulk aqueous samples were prepared for analysis by exhaustively extracting with DCM and then concentrating the DCM in a Kuderna-Danish evaporator, using 0.1 ml of isooctane as a "keeper." Solids, chemicals, and soil samples were extracted with DCM in the presence of excess sulfamic acid, dried over sodium sulfate, and then concentrated. Samples were analyzed by both GC-TEA and HPLC-TEA.
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11. A 1-ml portion of the 1*N* KOH air-trapping solution was acidified to *p*H 3 with H_2SO_4 and then nitrosated at 53°C with sodium nitrite. The reaction mix was extracted with 6 ml of DCM and analyzed for NMOR by GC-TEA and HPLC-TEA. The increase in NMOR compared to that in an unnitrosated sample was assumed to be due to MOR (or a MOR-generating substance) in the trap. Calibration curves for standard MOR solutions were used for quantitation.
12. In separate experiments, not reported here, we demonstrated that airborne MOR and NDPhA levels had to be above 600 and 6000 μg/m^3, respectively, for detectable transnitrosation to occur.
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14. We assume a 70-kg man breathing 20 liter/min for 8 hours per day. Because NMOR is relatively nonvolatile (boiling point, 225°C) and soluble in both water and lipids, we assume most of it is removed from inspired air.
15. To put this in perspective, eating 100 g (approximately five strips) of cooked bacon containing nitrosamines at the U.S. Department of Agriculture limit of 10 parts per billion would mean exposure to 1.0 μg.
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Submarine Seep of Carbon Dioxide in Norton Sound, Alaska

Abstract. *Earlier workers have described a submarine gas seep in Norton Sound having an unusual mixture of petroleum-like, low-molecular-weight hydrocarbons. Actually, only about 0.04 percent of the seeping gas is hydrocarbons and 98 percent is carbon dioxide. The isotopic compositions of carbon dioxide ($\delta^{13}C_{PDB} = -2.7$ per mil) and methane ($\delta^{13}C_{PDB} = -36$ per mil, where PDB is the Peedee belemnite standard) indicate that geothermal processes are active here.*

During the summer of 1976 Cline and Holmes (*1*) discovered anomalous concentrations of hydrocarbon gases, particularly ethane (C_2), propane (C_3), *n*-butane (*n*-C_4), and isobutane (i-C_4), in the waters of Norton Sound, south of the Seward Peninsula of Alaska. The hydrocarbon plume appeared to be emanating from a point source on the sea floor south of Nome (Fig. 1) and moving to the north and northwest, following current movements in the sound. The relative molecular composition of these hydrocarbons indicated that they could have a deep-seated thermal origin and could possibly be related to a liquid petroleum deposit (*1, 2*). In the summer of 1977 a geochemical investigation of bottom sediment beneath the hydrocarbon-rich plume showed that near-surface sediment at a site approximately 50 km south of Nome and at a water depth of 19 m also contains unusually high concentrations of hydrocarbons heavier than methane (C_1), including gasoline-range (C_{5+}) hydrocarbons (*3, 4*). Although geophysical surveys over this area showed near-surface acoustic anomalies apparently caused by gas-saturated sediment, the measured concentrations of hydrocarbon gases in the sediment were unusually high but well below saturation (*4*). The contradiction between the geophysical and geochemical evidence led to a further investigation of the seep site during the summer of 1978 when we discovered that hydrocarbons are only a minor component of the seep gas and that, in fact, CO_2 is the principal gas bubbling from the sea floor. This report is the first to describe both the molecular and carbon isotopic composition of a submarine seep off the shore of Alaska.

Detailed geophysical, geological, and geochemical measurements made during 1978 clearly indicate the presence of an active gas seep (*5*). Acoustic anomalies from geophysical records at the seep site have characteristics similar to those observed elsewhere by Schubel (*6*), who attributed the anomalous acoustic responses to the presence of gas bubbles in the sediment. Further geophysical evidence for an active gas seep comes from high-resolution geophysical records that show trains of gas bubbles rising from

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the sea floor and traversing the water column.

Geological observations support the geophysical evidence. Remote television videotapes and photographs of the sea floor show small pits, many of which are actively venting gas bubbles. A core 4.5 m long and 8.5 cm in diameter, recovered by means of a vibracorer driven by compressed air, contained disruptions, pockets, and cracks due to the expansion of gas when the pressure was reduced upon recovery of the core. A second acoustic anomaly about 12 km northwest of the seep site was cored (Fig. 1). The recovered sediment showed gas expansion features with no significant gas pockets; high-resolution geophysical records showed no evidence of gas bubbles in the water column.

Geochemical analyses of gases were carried out both on board ship and in shore-based laboratories. In a core from the seep site, a gas pocket about 10 cm long in the core liner at a depth of about 178 cm was sampled (*7*) for analysis by gas chromatography (*4*) to obtain an in situ gas-phase composition. Also analyzed was gas that had been extracted from canned sediment sampled about every meter from cores obtained at both the seep and nonseep areas (*5*). In addition, carbon isotopic compositions were determined for C_1 and CO_2 (*8*).

Molecular and isotopic compositions of the sediment gas provide a basis for evaluating the possible origins of the seep. The most abundant compound is CO_2, which constitutes 98 percent (by volume) of the gas mixture and has a carbon isotopic composition $\delta^{13}C$ of −2.7 per mil (Table 1). The concentrations of N_2 (1.9 percent), O_2 (0.05 percent), and Ar (0.03 percent) indicate that contamination by air is minimal. Our results suggest that the CO_2 was derived from thermal processes. For example, in thermal waters from both Yellowstone National Park (*8, 9*) and North Island, New Zealand (*10*), CO_2 is also the most abundant dissolved gas and has $\delta^{13}C$ values between +2 and −10 per mil. Possibly the CO_2 in the Norton Sound seep comes from thermal decarbonation of deeply buried marine carbonates, which are thought to underlie the area (*11*). The isotopic composition of the seep CO_2 falls within the range of compositions observed from marine limestones (*8, 12*). Decarbonation of limestone at elevated temperatures (700°C) produces CO_2 that is enriched in ^{13}C relative to the limestone by 1 or 2 per mil (*13*). As this CO_2 migrates toward the sediment surface, its ^{13}C content could be lowered slightly either by isotopic equilibration with shallower carbonates (*9*) or by the addition of ^{13}C-depleted CO_2 produced from the thermocatalytic breakdown of sedimentary organic matter.

The idea of a thermal origin for the seep is supported by the hydrocarbon gas data (Table 1). Bernard *et al.* (*14*) used two parameters, $C_1/(C_2 + C_3)$ ratios and $\delta^{13}C$ values of C_1, to determine the origin of natural hydrocarbon gases in marine seeps. The sedimentary microbial activity of methanogenic bacteria produces hydrocarbon gases with $C_1/(C_2 + C_3)$ ratios exceeding 1000 and $\delta^{13}C_1$ values lighter than −60 per mil (*15*). On the other hand, thermal degra-

Table 1. Chemical and isotopic composition of gas at seep and nonseep sites.

Component	Percent (by volume)*		$\delta^{13}C$ (per mil)†	
	Seep‡	Nonseep§	Seep‡	Nonseep§
CO_2	98	25	− 2.7 ± 0.1	−14.2 ± 0.2
N_2	1.9			
O_2	0.05			
Ar	0.03			
H_2	0.01			
He	< 0.01			
H_2O	Trace			
Methane (C_1)	0.0360	75	−36 ± 2	−80.5 ± 0.2
Ethane (C_2)	0.0039	0.0019		
Ethene		0.0001		
Propane (C_3)	0.0018	0.0013		
Propene		0.0001		
n-Butane (*n*-C_4)	0.0004	0.0004		
Isobutane (i-C_4)	0.0020	0.0009		

*Analyzed by W. C. Evans and G. D. Redden, U.S. Geological Survey, Menlo Park, Calif. †Measurements were made at the NASA Ames Research Center, Moffett Field, Calif. Results given are the average of replicate analyses. ‡Gas analyses on samples recovered from a gas pocket in the core liner at a depth of 178 to 187 cm. §Gas analyses from the headspace of the canned sediment sample (depth, 190 to 199 cm). Concentrations are calculated on the basis that the total gas mixture is composed only of CO_2 and gaseous hydrocarbons.

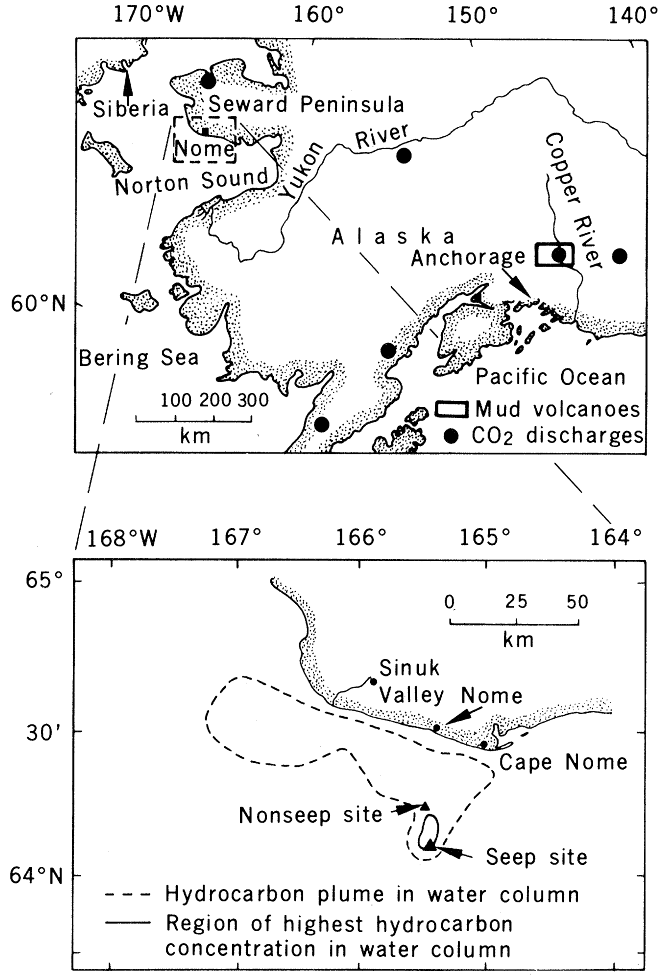

Fig. 1. Location maps showing the onshore areas of CO_2 discharges, mud volcanoes, the submarine seep with the associated hydrocarbon-rich water column anomaly, and the nonseep site.

dation of sedimentary organic matter produces hydrocarbons with $C_1/(C_2 + C_3)$ ratios between 0 and 50 and $\delta^{13}C_1$ values generally heavier than −50 per mil (*16, 17*). The seep gas of Norton Sound has a $C_1/(C_2 + C_3)$ ratio of 6.4 and a $\delta^{13}C_1$ value of about −36 per mil. These data clearly indicate that the seep hydrocarbons originated from thermal sources.

We know of only three other reported examples of submarine seeps where molecular and isotopic compositions of hydrocarbons suggest thermogenic sources (*18*). These seeps in the Gulf of Mexico and offshore southern California are in areas of active petroleum provinces.

Thermally produced hydrocarbons generally can be related to the sedimentary organic matter from which they are derived by means of an examination of their molecular and isotopic compositions. The hydrocarbons of the Norton Sound seep may have at least three sources (geothermal activity, alteration of terrestrial coaly deposits, and alteration of marine sapropelic organic matter) that have given rise to a mixture having a $\delta^{13}C_1$ value of −36 per mil and a $C_1/(C_2 + C_3)$ ratio of less than 10. The relative contribution from each of these sources cannot be firmly established. Geothermally derived C_1 generally has a $\delta^{13}C$ value in the range of −20 to −30 per mil (*8-10*), but accompanying C_2, C_3, and C_4 hydrocarbons in one example of a geothermal discharge from Yellowstone National Park (*19*) are in very low concentration relative to C_1. At the stage of thermal maturation when coaly organic matter produces appreciable amounts of C_2 and C_3 (*20*), the $\delta^{13}C$ is usually in the range of −25 to −40 per mil (*21*). At the stage where marine sapropelic organic matter produces abundant C_2, C_3, and higher hydrocarbons, the $\delta^{13}C$ values are typically in the range −40 to −50 per mil (*17*). In addition to these possible thermal sources, minor contributions to the final mixture may come from microbial decomposition of near-surface organic matter (*22*). In view of these possible sources, we believe that the hydrocarbons in the Norton Sound seep are best described as a combination of some C_1 and possibly some heavier hydrocarbons from geothermal sources and gas- and gasoline-range hydrocarbons derived from the thermal alteration of marine sapropelic organic matter deeply buried within the sediments of Norton Basin (*23*).

In contrast to the case at the seep site, sediment at the nonseep site (Fig. 1) contains C_1, at or near saturation, as the dominant gas, with CO_2 subordinate by a factor of 3 (Table 1). The gases accumulated here undoubtedly derive from microbial decomposition of organic matter (*22*), evidenced by a $C_1/(C_2 + C_3)$ ratio of 24,000 and a $\delta^{13}C_1$ value of −80 per mil. The lower abundance of CO_2 with a $\delta^{13}C$ value of −14 per mil is also consistent with a bacterial sedimentary source for this gas. The carbon isotopic compositions here are similar to the compositions in anoxic marine sediments (*15*). At the seep site, organic matter (*22*) is also present but its microbial decomposition is not evident in the molecular and isotopic compositions of the hydrocarbons. It is probable that the high flux of geothermal CO_2 through the sediment there rapidly sweeps away the CO_2 and hydrocarbons slowly formed by the microbial decomposition of organic matter.

Both CO_2 and hydrocarbon seeps are found onshore in Alaska (Fig. 1). Where seep gases are mainly hydrocarbons, C_1 is the dominant constituent and only traces of heavier hydrocarbons occur (*24*). Barnes *et al.* (*25*) have identified six areas with CO_2 discharges. One locality on the Alaska Peninsula produces gas with 98 percent CO_2 ($\delta^{13}C = -6.36$ per mil). Reitsema (*26*) analyzed gases from several mud volcanoes in the Copper River Basin (Fig. 1). The western volcanoes in the basin produce mainly CO_2 ($\delta^{13}C = -6.5$ and -8.3 per mil). Volcanoes to the east release a mixture of C_1, N_2, and very little CO_2. Some 55 to 71 percent of the gas in three volcanoes is C_1, and $\delta^{13}C_1$ values range from −22.3 to −33.9 per mil. The seep gases from Norton Sound differ from the gases from onshore seeps both in their isotopic content and in their abundant amounts of heavier hydrocarbons.

In summary, the Norton Sound seep is probably a geothermal discharge producing large quantities of CO_2. This CO_2 assimilates thermally produced hydrocarbons as it percolates through shallower organic-containing sediment. The gas becomes saturated in the sediment, as indicated by the acoustic anomalies, and enters the water column through discrete vents. Although the composition of the hydrocarbon gases is consistent with the generation of petroleum hydrocarbons at depth in Norton Basin, our data do not establish that there are economically significant petroleum accumulations there.

KEITH A. KVENVOLDEN
KAREN WELIKY
HANS NELSON
U.S. Geological Survey,
Menlo Park, California 94025
DAVID J. DES MARAIS
NASA Ames Research Center,
Moffett Field, California 94035

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$$\delta^{13}C = \left(\frac{{}^{13}C/{}^{12}C_{\text{sample}} - {}^{13}C/{}^{12}C_{\text{standard}}}{{}^{13}C/{}^{12}C_{\text{standard}}} \right) \times 1000$$

where the standard is Peedee belemnite (PDB).
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23. Because geothermally derived C_1 is probably mixed with isotopically lighter C_1 from organic sources, an equilibrium temperature of about 200°C, estimated from the isotopic compositions of C_1 and CO_2 [Y. Bottinga, *Geochim. Cosmochim. Acta* **33**, 49 (1969)], represents a minimum temperature for the postulated geothermal production of C_1 and CO_2.
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