Seep Oil and Gas in Gulf of Mexico Slope Sediment

Abstract. *Concentrations in Gulf of Mexico slope sediment of material soluble in methanol and benzene as high as 4.5 percent are shown to be attributable to biodegraded petroleum. Associated carbonate deposits and organic sulfur are the products of the microbial oxidation of petroleum and sulfate reduction. The results of chemical and carbon isotope analyses indicate that high concentrations of hydrocarbon gases, from methane to pentane, are petroleum rather than microbiologically derived. These hydrocarbons, believed to have been produced thermally at depth, probably reached the surface through faults and fractures associated with salt diapirs.*

Although the northern Gulf of Mexico shelf is a region of bountiful oil and gas production, liquid petroleum seeps have not been directly sampled and characterized. The indirect evidence for oil seeps, mostly beach tar and floating oil, was reviewed recently (*1*). Natural gas seeps in the Gulf of Mexico have been reported and classified as biogenic, that is, recently produced by bacteria, or as petrogenic, formed at depth by the same thermal process that generates petroleum (*2*). We report here chemical and isotopic characteristics and the geological setting for liquid petroleum and natural gas discovered in cores from the upper slope of the northern Gulf of Mexico. The finding of this material, in cores taken as part of a geophysical and geochemical survey of the slope, was unexpected. Core IG-46-5, the 99th of 109 cores, was the discovery core (Fig. 1). This discovery led to a second field effort to determine if indeed the organic matter was natural and widespread (as opposed to whether the site was a highly localized dump). The second study included a dense bathymetric and high-resolution (3.5 kHz) reflection profiling survey of 1500 km^2 and the taking of 15 additional piston cores.

In all, 9 of the 16 cores taken in the study area contained trace to abundant quantities of liquid hydrocarbons. These were located in a a narrow (2 km) east-west band 10 km long in water depths of 550 to 615 m. The band is just upslope of a steeply inclined zone and has complex bathymetry with several fault scarps, some as high as 100 m.

East-west seismic profiles just to the north of the oil-bearing cores show a slightly uplifted area, the center of which is downfaulted in a graben-like manner. North-south profiles show a slope with three gradients. The northernmost portion has the lowest gradient with associated small-scale faulting. The central portion with a steeper gradient has an abundance of complex, generally small-scale faults. The lowest portion (basinward) has the steepest gradient, often too steep to permit a good bottom echo. It generally has little or no faulting. These structures are typical of areas overlying diapirs whose upward movements create radial tensional stresses relieved by roughly concentric graben faulting.

A single, deeply penetrating, multichannel, seismic line through the area confirms that a diapir occurs within the region with crestal, shallow structures. No strongly reflecting cap rock is apparent in the seismic section, but downward-increasing interstitial water salinity in a nearby core indicates that it is a salt rather than a shale diapir. On the flanks of the diapir, the 3.5-kHz reflection profiles commonly show many parallel subbottom reflectors. These often disappear, being replaced by weak to moderately strong, prolonged bottom echoes with no subbottoms. These "wipeouts" occur almost exclusively within the tensionally rifted zone over the diapir crest. Oil-bearing cores come from areas where the high-resolution seismic profiles exhibit the wipeout pattern. This pattern has been shown to be most commonly associated with gas in the sediment (*3*). In this case it is also clearly associated with faulting over a diapir crest.

Table 1. Chemical and isotopic characteristics of oil, oil fractions, carbonate, and organic residue from three cores from the upper slope of the northern Gulf of Mexico.

Interval (cm)	Bitumen*	Hexane†	Benzene†	Methanol†	Carbonate $\delta^{13}C$	Residue‡ $\delta^{13}C$
			Core IG-46-5			
10 to 15	4.0	22.4	51.3	27.1	−12.4	
	−26.5	−26.8		−26.3		
40 to 45	4.4	25.7	44.7	20.3	−27.5	−36.7
	−26.7	−26.6	−26.4	−27.1		
70 to 75	4.3	36.4	38.6	17.4	−22.7	−30.6
	−26.3	−26.2	−26.3	−26.6		
100 to 115	4.5	34.8	42.3	17.6	−9.6	
	−26.4	−26.3	−26.2	−26.6		
130 to 135	1.6	34.8	44.3	13.4		
		−26.3	−26.4	−26.3	−3.9	−24.5
160 to 165	2.3	44.1	45.0	11.5	−0.2	−25.2
	−26.2	−26.2	−26.2	−26.2		
190 to 195	0.91	40.0	38.0	14.0	+0.6	−24.2
	−26.3	−26.4	−26.2	−26.6		
280 to 285	0.79	33.9	42.0	13.9	−5.0	−26.0
	−26.3	−26.4	−26.6	−26.6		
410 to 415	0.14	13.7	23.0	18.9	−1.6	−25.7
	−26.7	−26.7		−27.0		
			Core IG-47-2-7			
10 to 40	0.21	14.8	35.0	23.8		
	−26.4	−27.1	−26.4	−26.3	−0.4	−21.8
80 to 120	0.18	12.7	21.1	17.0		
	−25.2	−27.2	−26.8	−26.9	−3.5	−25.2
180 to 210	0.08	21.2	18.5	27.8		
	−28.6	−29.1	−28.7	−29.2	−16.1	−26.9
250 to 310	0.09	29.1	25.4	30.4		
	−26.8	−27.1	−26.8	−28.2	−12.2	−26.1
450 to 470	0.06	13.2	15.8	60.2		
	−28.6	−29.6	−28.4	−28.8	−3.0	−26.5
530 to 550	0.06	22.1	22.2	23.6		
	−27.4	−27.3	−27.2	−28.3	−1.4	−26.0
570 to 600	0.12	24.0	20.8	23.3		
	−27.2	−26.9	−26.8	−28.2	−1.3	−25.7
750 to 780	0.10	21.8	16.9	16.9		
	−27.6	−26.8	−26.9	−29.4	−0.2	−25.7
880 to 905	0.06	19.6	15.0	24.7		
	−27.9	−28.1	−28.0	−28.8	−0.5	−26.3
			Core IG-47-2-12			
30 to 330	1.5	23.3	40.1	16.2		
	−26.7	−26.3	−26.7	−27.0		

*The upper value is the percentage total of material soluble in methanol-benzene, based on the dry weight of extracted sediment; the lower number is the $\delta^{13}C$ value. †Saturated compounds were eluted from silica gel with hexane; unsaturated compounds were eluted with benzene; polar compounds were eluted with methanol; all were calculated on the basis of weight of bitumen put on the column; asphaltic material not eluted accounts for the balance. The upper value is the percentage, the lower one is the $\delta^{13}C$ value. ‡Residue is the organic matter remaining in the bitumen- and carbonate-free sediment.

We analyzed the cores chemically and

isotopically, using standard organic geochemical techniques. Examination of the discovery core revealed that the oil was highly fluorescent under ultraviolet light and often highly localized in fracture planes. The presence of intense fluorescence was used to select cores for immediate processing (*4*). The piston cores were kept in their plastic liners while at sea, a period of up to 6 days. On shore, the cores were stored at 4°C until subsampled and were then stored at −20°C until analyzed. The total bitumen, material soluble in methanol and benzene, was separated into three fractions, corresponding to saturated hydrocarbons, unsaturated (aromatic) hydrocarbons, and polar molecules, by silica-gel chromatography (*5*). The saturated and unsaturated fractions were analyzed by high-resolution gas-liquid chromatography (GLC), and portions were subjected to mass spectrometry for stable isotope analysis (*5, 6*).

The bitumen concentration ranged between 0.06 and 4.5 percent (Table 1). The higher values are remarkable for Gulf sediments, which generally contain about 1 percent total organic matter and less than 0.05 percent bitumen (*7*). Even highly reduced Orca Basin sediments have values of 2 and 0.25 percent, respectively, for these parameters. The GLC analysis of the saturated fraction showed that the relative concentrations of normal alkanes were low, compared to Gulf coast oils, often lost within the unresolved, complex mixture. Bacterial degradation is the likely mechanism for this depletion. Further evidence for bacterial activity is the zero SO_4^{2-} concentration below 300 cm in core IG-47-2-7. The unsaturated fraction showed a similar depression of major aromatic hydrocarbon peaks, probably resulting from bacterial action plus water washing. For many of the GLC patterns, better than 90 percent of the saturated and unsaturated hydrocarbons were contained within the unresolved, complex mixture. Large-scale alterations by these processes have been reported for petroleum in reservoirs and in salt domes (*8*). Biodegraded, thermogenic hydrocarbons have been reported in unconsolidated slope sediment from northern California (*9*). High sulfur content and high American Petroleum Institute (API) gravity values support the bacterial degradation model (*10*).

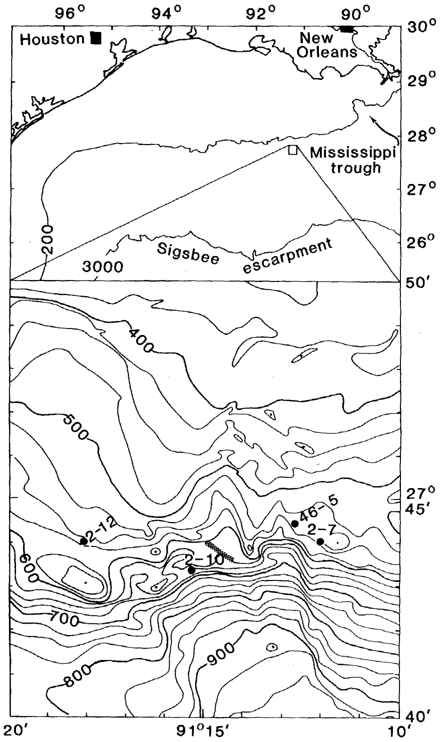

Fig. 1. Maps showing the locations of shallow cores containing unusually large quantities of petroleum-like organic matter. Depth contours are in meters.

The $\delta^{13}C$ values of the bitumen and fractions resemble those of other Gulf coast oils (*11*). The resemblance between IG-46-5 oil and the oil recovered from the Challenger Knoll in the central Gulf by the Deep Sea Drilling Program is striking. Oil released during the Ixtoc blowout in 1979, which was collected at the wellhead, was more negative by only 1 per mil. The ^{13}C-depleted carbon in the residue fraction, with $\delta^{13}C$ values of −36.7 and −30.6 (Table 1), is taken to be the result of microbial action on the oil, but the mechanism is unknown. The abundance of ^{13}C-depleted carbonates in these cores was certainly the result of microbial oxidation of organic matter to CO_2, which was then precipitated as calcium carbonate. The presence of large lumps of ^{13}C-depleted light carbonate in the upper section of the cores suggests that biodegradation took place late in the migration pathway, as oil approached the seawater-sediment interface.

Inspection of the cores in the cold room prior to subsampling indicated that gases were present. Gas samples were taken from cores IG-47-2-7 and IG-47-2-12 for chemical and isotopic analysis (*12*). High concentrations of hydrocar-

Table 2. Concentration and isotopic composition of natural gas hydrocarbons in cores. Tr, trace; N.D., not detected.

Depth (m)	Methane*	Ethane*	Propane*	Isobutane (ppm)	Butane (ppm)	Isopentane (ppm)	Pentane (ppm)	$\frac{C_1}{C_2+C_3}$	Relative % C_2+	Relative % C_3
					Core IG-47-2-7					
1.1	5,900	142	Tr	1,100	N.D.	N.D.	N.D.		17.5	
2.3	273,000 −56.5	608	N.D.	99	N.D.	N.D.	N.D.		0.3	
3.7	105,000 −54.2	290	Tr	92	N.D.	N.D.	N.D.		0.4	
5.7	196,000 −44.7	4,400	561	273	775	538	N.D.	39.5	3.2	0.28
7.4	645,000 −61.9	9,980	1,440	397	3,080	1,130	331	56.5	2.5	0.22
7.6	663,000 −61.8	10,600	1,510	334	2,880	906	290	54.7	2.4	0.22
9.2	659,000 −59.7	22,300 −28.6	9,630 −24.5	1,800	3,770	774	280	20.7	5.5	1.4
10.5	439,000 −61.0	14,200	5,830	1,104	3,525	963	456	21.9	5.6	1.2
					Core IG-47-2-12					
0.8	343,000 −48.1	32,000 −28.6	83,600 −24.5	21,000	3,680	257	Tr	3.0	29.1	17.3
1.5	45,500 −30.5	4,340	11,400	9,320	5,240	3,850	2,100	2.9	44.3	13.9
3.6	18,700 −53.7	9,890	25,800	13,100	5,530	2,660	1,360	0.52	75.7	33.5

*The upper value is the concentration (parts per million) of component as the volume of total recovered gas; the lower number is the $\delta^{13}C$ value of that component. †C_2+ is the sum of concentrations of hydrocarbons of molecular size greater than methane.

bon gases were detected, although the cores had been held for many days (Table 2). The ratio of methane to ethane plus propane [$C_1/(C_2 + C_3)$] and the $\delta^{13}C$ values of gases are used to distinguish biogenic from petrogenic hydrocarbons. A ratio greater than 1000 and $\delta^{13}C$ more negative than −60 per mil indicates bacterial methane (*2*). On the basis of these parameters, the gases in the cores are derived from deep, thermally produced sources (Table 2). The relative percentage of ethane to pentane and the percentage of propane (Table 2), as high as 75.7 and 33.5, respectively, suggest that a mechanism is available to concentrate these molecules. Anomalous seismic reflections suggest the presence of gas hydrates in western Gulf of Mexico sediments (*3*). Gas hydrate formation has been suggested as a possible mechanism for the retention of natural gas of unusual chemical composition (*13*).

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4. A simple long-wavelength ultraviolet source consisting of a GE-F6T5-BLB lamp in a camping lantern was used for the sample surveys.
5. High-resolution gas chromatography was carried out on the saturated and unsaturated hydrocarbon fractions with a Perkin-Elmer model 910 chromatograph with flame-ionization detector. A 25-m fused-silica, wall-coated open tubular column coated with OV-101 liquid phase was programmed from 100°C to 270°C at 7.5°C per minute. Silica-gel chromatography was done on a portion of the bitumen after the methanol-benzene solvent was removed by rotary vacuum evaporation and the material was dissolved in hexane. The hexane solution was placed on a silica-gel column (20 by 1 cm) (Activity-I, 60- to 200-mesh Woelm silica gel). The three fractions of total bitumen were successively eluted with hexane, benzene, and methanol. These fractions were then freed of solvent and used for GLC and isotope analysis.
6. Carbon isotope compositions are expressed as the difference (in parts per mil) between the standard (std) and the sample, based on the $\delta^{13}C$ notation:

$$\delta^{13}C = \frac{(^{13}C/^{12}C)_{\text{sample}} - (^{13}C/^{12}C)_{\text{std}}}{(^{13}C/^{12}C)_{\text{std}}} \times 10^3$$

   When Pee Dee belemnite is used as a standard, data for organic matter will be small negative numbers. The reproducibility is ± 0.2 per mil. We converted organic carbon to CO_2 for isotope analysis by the sealed tube method, using Pyrex glass and copper oxide [S. Sofer, *Anal. Chem.* **52**, 1389 (1980)]. Isotope measurements were made on a VG-Micromass model 602E isotope-ratio mass spectrometer. Carbonate samples were converted to CO_2 with phosphoric acid according to standard procedures.
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10. Bitumen sample IG-46-5 (280 to 285 cm) had an organic sulfur content of 2.5 percent as compared to 3.74 percent for the Challenger Knoll oil. The API gravity of the Challenger Knoll oil was 14.8; the corresponding values for the top six samples of core IG-46-5 were 10.7, 14.5, 16.2, 14.8, 16.3, and 17.6. High sulfur content is generally associated with low API gravity values.
11. R. S. Scalan, J. K. Winters, P. L. Parker, *Energy and Environmental Chemistry,* vol. 1, *Fossil Fuels*, L. H. Keith, Ed. (Ann Arbor Science, Ann Arbor, Mich., 1982), pp. 219–231; B. Koons and P. H. Monaghan, *Initial Rep. Deep Sea Drill. Proj.* **1**, 486 (1969). The $\delta^{13}C$ values for bitumen, saturated hydrocarbons, aromatic hydrocarbons, and polar compounds were, respectively, −26.6, −26.5, −26.8, and −26.5.
12. We took gas samples by puncturing the plastic core liner with a two-way needle and allowing gas to flow into a 20-ml Vacutainer. Gas components were separated by a combination of differential adsorption on silica-gel and packed-column chromatography. The components were oxidized to CO_2 for isotopic analysis in a vacuum apparatus adapted from H. Craig [*Geochim. Cosmochim. Acta* **3**, 53 (1953)].
13. K. A. Kvenvolden, private communication. J. M. Brooks has recently reported (private communication) finding gas hydrates in sediment samples taken from this same general location in the Gulf of Mexico.
14. This research was sponsored by Getty Oil, Gulf Oil Exploration and Production, Mobil Exploration and Production, Phillips Petroleum, Shell Development, and Tenneco Oil. This report is contribution 590 of the Marine Science Institute and 561 of the Institute of Geophysics, University of Texas.

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Nickel: An Essential Micronutrient for Legumes and Possibly All Higher Plants

Abstract. *Soybean plants deprived of nickel accumulated toxic concentrations of urea (2.5 percent) in necrotic lesions on their leaflet tips. This occurred regardless of whether the plants were supplied with inorganic nitrogen or were dependent on nitrogen fixation. Nickel deprivation resulted in delayed nodulation and in a reduction of early growth. Addition of nickel (1 microgram per liter) to the nutrient media prevented urea accumulation, necrosis, and growth reductions. This evidence suggests that nickel is essential for soybeans and possibly for higher plants in general.*

In contrast to the situation in animals, for which four new essential trace elements have been identified in the last decade (*1*), no new generally essential micronutrient for higher plants has been discovered since 1954 (*2*). Several investigators have suggested that nickel might be essential for plants, but conclusive evidence has not been reported (*3, 4*). The recent finding that urease is a nickel-metalloenzyme (*5*), however, suggested that nickel might have a specific function in higher plants. Nickel has been shown to stimulate growth when urea is the sole nitrogen source but to have slight or no effect with other nitrogen sources (*6, 7*). We report here that nickel is essential for nitrogen metabolism in soybeans [*Glycine max* (L.) Merr.], either when nitrogen is supplied as NO_3^- and NH_4^+ or when the plants are dependent on nitrogen fixation.

Soybeans (cultivar "Maple Presto") were grown in nutrient solutions that had been purified of nickel by chromatography with 8-hydroxyquinoline and controlled-pore glass beads (8HQ-CPG) (*8*). This technique, similar to that proposed by Hill (*9*), removed 99.99 percent of ^{63}Ni added. The purified nutrient solutions were estimated to have a nickel concentration of 0.06 μg liter^{-1}. Plants grown without nickel additions (Ni_0 treatment) developed necrotic lesions on 27.5 ± 3.2 percent (mean ± standard error) of their leaflet tips, and this injury was absent on plants that were supplied nickel at concentrations of either 1 (Ni_1) or 10 (Ni_{10}) μg liter^{-1} (*10*). Leaflet tip necroses were counted 56 days after imbibition, during mid-podfill (Fig. 1A). A urea concentration of 2.5 percent (weight/weight) was found in necrotic leaflet tips, whereas no urea could be detected in Ni_1 plants (*11*). Leaflet tips were also analyzed for potassium, calcium, magnesium, phosphorus, sulfur, iron, manganese, zinc, boron, and copper by inductively coupled argon plasma–optical emission spectrophotometry. All these concentrations were within the normal range for soybean leaves (*12*).

Shimada and Ando (*7*) found that nickel additions increased leaf urease activity in tomatoes and soybeans and that low-nickel plants, grown with urea as the sole nitrogen source, accumulated urea and developed necrotic leaflet tips. Thus, we conclude that the leaflet tip necrosis that we observed was caused by the accumulation of toxic concentrations of urea.

Seed yields were similar in all three treatments, and all gave 100 percent germination. Urease activity and the nickel concentration in the seed were increased when nickel was supplied (Table 1). Nickel concentrations in Ni_0 seed digests were comparable to blank values. A similar relationship in jack bean seed has been reported by Dixon *et al.* (*13*), but