

dicted from the Na/Cl ratio of seawater by only 1 $\mu\text{eq liter}^{-1}$. However, Mg^{2+} is much less closely linked to Na^+ and Cl^- , probably because it is also related significantly to the agricultural components of Ca^{2+} and NH_4^+ . Like Ca^{2+} , Mg^{2+} is a component of windblown soil.

A three-cluster analysis (BMDP, K-means, no standardization) of the 49 sites studied in 1981 reveals a geographical pattern of concentric rings related to concentrations of the major pollutant ions, SO_4^{2-} , H^+ , and NO_3^- . All three are high at 15 sites subject to severe air pollution in northern Illinois and Indiana through Ohio, West Virginia, Virginia, and Pennsylvania to New York. The same ions are of intermediate concentration at 16 surrounding sites in Michigan, southern Illinois, Tennessee, the Carolinas, New York, New Hampshire, and southern Maine. A third group, low in these ions, forms an outer ring of 18 sites in Minnesota, Wisconsin, Upper Michigan, Arkansas, Mississippi, Florida, Georgia, Tennessee, North Carolina, and northern Maine. In the most polluted group of sites, H^+ averages 61.7 $\mu\text{eq liter}^{-1}$ (pH 4.21) and is almost twice the concentration of the summed base cations ($\text{NH}_4^+ + \text{Ca}^{2+}$), whereas in the least polluted group it averages 21.4 $\mu\text{eq liter}^{-1}$ (pH 4.67) and about equals the sum of the two base cations. Wet SO_4^{2-} deposition in the most polluted group is approximately twice as great (31 $\text{kg ha}^{-1} \text{ year}^{-1}$) as in the least polluted group (15 $\text{kg ha}^{-1} \text{ year}^{-1}$).

EVILLE GORHAM

Department of Ecology and
Behavioral Biology, University of
Minnesota, Minneapolis 55455

FRANK B. MARTIN

JACK T. LITZAU

Statistical Center, University of
Minnesota, St. Paul 55108

References and Notes

1. C. V. Cogbill and G. E. Likens, *Water Resour. Res.* **10**, 1133 (1974); J. N. Galloway, G. E. Likens, E. S. Edgerton, in *Proceedings of the First International Symposium on Acid Precipitation and the Forest Ecosystem*, L. S. Dochinger and T. A. Seliga, Eds. (U.S. Department of Agriculture Forest Service General Technical Report NE-23, Washington, D.C., 1976).
2. D. W. Fisher, *U.S. Geol. Surv. Water-Supply Pap.* 1535-M (1968), p. 21; D. G. Shannon and L. Fine, *Environ. Sci. Technol.* **8**, 1026 (1974); R. Soderlund and B. H. Svensson, Eds., *Report No. 7, Scientific Committee on Problems of the Environment (SCOPE)* (Ecological Bulletin of the Swedish Natural Science Research Council No. 22, Stockholm, 1976); N. C. Lau and R. J. Charlson, *Atmos. Environ.* **16**, 1633 (1982).
3. E. Gorham, *Q. J. R. Meteorol. Soc.* **84**, 274 (1958).
4. L. Granat, *Tellus* **24**, 550 (1972); A. Skartveit, *Atmos. Environ.* **16**, 2501 (1982).
5. P. A. P. Moran, *J. Multivar. Anal.* **1**, 232 (1971).
6. D. J. McNaughton, *Atmos. Environ.* **15**, 1075 (1981).
7. E. S. Verry, *Water Resour. Res.* **19**, 454 (1983).
8. J. N. Galloway and G. E. Likens, *Atmos. Environ.* **15**, 1081 (1981).

9. R. C. Harriss, personal communication.
10. J. O. Reuss, *Report EPA-660/3-75-032* (Environmental Protection Agency, Ecological Research Series, Washington, D.C., 1975).
11. A. Henriksen, *Nature (London)* **278**, 542 (1979); L. S. Evans, G. R. Hendrey, G. J. Stensland, D. W. Johnson, A. J. Francis, *Water Air Soil Pollut.* **16**, 469 (1981); *Atmosphere-Biosphere Interactions: Toward a Better Understanding of the Ecological Consequences of Fossil Fuel Combustion* (National Academy Press, Washington, D.C., 1981).
12. Recommended by Canadian members of work group I on impact assessment, final report under the United States-Canada Memorandum of Intent on Transboundary Air Pollution, 1983.
13. J. N. Galloway, G. E. Likens, W. C. Keene, J. M. Miller, *J. Geophys. Res.* **87**, 8771 (1982).
14. J. W. Munger and S. J. Eisenreich, *Environ. Sci. Technol.* **17**, 32A (1983).
15. J. N. Galloway and D. M. Whelpdale, *Atmos. Environ.* **14**, 409 (1980).
16. We thank J. H. Gibson and the National Atmospheric Deposition Program for supplying screened and corrected data, and E. B. Cowling, S. J. Eisenreich, J. N. Galloway, R. C. Harriss, G. E. Likens, J. W. Munger, M. Oppenheimer, W. Stumm, M. F. Uman, and D. M. Whelpdale for advice and encouragement. The National Science Foundation provided a grant (DEB 7922142) to one of us (E.G.). Limnological Research Center Contribution 292.

15 September 1983; accepted 14 December 1983

Thermogenic Gas Hydrates in the Gulf of Mexico

Abstract. *Thermogenic gas hydrates were recovered from the upper few meters of bottom sediments in the northwestern Gulf of Mexico. The hydrates were associated with oil-stained cores at a water depth of 530 meters. The hydrates apparently occur sporadically in seismic "wipeout" zones of sediments in a region of the Gulf continental slope at least several hundred square kilometers in area.*

We report here the occurrence of thermogenic gas hydrates in ocean sediments. The hydrates were discovered fortuitously during geochemical surveys involving piston coring operations at 27°47'N and 91°30'W in 530 to 560 m of water in the northwestern Gulf of Mexico. Hydrates were observed dispersed in carbonate rubble in three cores and ranged in size from minute crystals to objects several centimeters in diameter. Although the cores were severely disrupted by gas expansion during the 10- to 15-minute interval between coring and retrieval on deck, the gas hydrates appeared to be distributed from the top of the core to a sediment depth of at least several meters. Samples of the hydrates were preserved in liquid nitrogen for laboratory analysis.

Gas hydrates are solid icelike clathrate structures in which gases are occluded in a crystalline water lattice under appropriate conditions of high pressure and low temperature. Hydrates can exist in two forms. Structure I gas hydrates have a symmetrical shape and exclude molecules larger than ethane. Structure II hydrates are slightly larger and can accommodate not only methane and ethane but also propane and isobutane. Molecules as large or larger than *n*-butane cannot be accommodated in either lattice structure (1). The stability zone of gas hydrates in marine sediments is generally found in continental slope areas where water depths are greater than 500 m and water temperatures at the bottom are near 0°C. Although a wide range of molecules (methane, ethane, propane, isobutane, CO_2 , N_2 , O_2 , and H_2S) can form hydrates, methane and possibly CO_2 are the only gases found in sufficient

quantities in deep-sea sediments to form gas hydrates. Under conditions of temperature and pressure appropriate for hydrate stability, gas concentrations must exceed solubility levels before hydrates can form. Therefore, methane hydrates can be found only in regions where there is significant biogenic methane production or where there is migration of thermogenic gases from deeper horizons. Thermogenic gases do not form hydrates at their site of production because the ambient temperatures are outside the stability zone of hydrates.

The presence of gas hydrates in marine sediments has long been suspected on the basis of laboratory stability studies and the existence, in some sediments, of a bottom-simulating reflector (BSR)—an anomalous acoustic reflector that approximately parallels the bottom topography, cutting across bedding planes and deepening with increasing water depth (2). The BSR is thought to represent the lower boundary of gas hydrate stability, below which gas hydrates decompose because of increased temperatures. The existence of hydrates has been inferred in many ocean areas on the basis of seismic records (3). Gas hydrates appear to be common in the continental margins of all the oceans. However, to our knowledge the only direct observations of gas hydrates in marine sediments have been in shallow cores from the Black Sea (4); at a subbottom depth of 238 m on leg 76 of the Deep Sea Drilling Project/International Phase of Ocean Drilling (DSDP/IPOD) in the Blake Outer Ridge of the Atlantic Ocean (5); and on DSDP/IPOD legs 66, 67, and 84 in the Middle America Trench off Mexico and Guatemala (6). Because hydrates are not stable at atmo-

Table 1. Data on the molecular and isotopic composition of hydrate gas and water obtained after decomposition in a pressure device consisting of a 23-cm² sample holder, gauge block, and gas sampling port with septum (Parr Instrument). Two experiments were performed with separate hydrate samples taken from a depth in the core of 1.0 to 1.5 m. N.D., not determined.

Parameter	Experiment 1	Experiment 2
<i>Gas (all compositions in percent)*</i>		
Methane	55.1 (−44.6)	67.5 (−44.8)
Ethane	2.6 (−29.3)	4.5
Propane	14.4 (−18.6)	14.9
Isobutane	4.4 } (−28.6)	4.2
n-Butane	0.2 }	0.2
Carbon dioxide	3.4 (18.5)	3.9 (13.3)
Nitrogen	N.D.	4.1
O ₂ + argon	N.D.	<0.1
Methane/ethane + propane	3.2	3.5
Total components	83.3	99.2
3D, methane (per mil)	−189	
<i>Water (ionic compositions in parts per thousand)†</i>		
Salinity (refractive index)	9	9
Chlorinity	5.9	4.8
Na ⁺	3.5	3.0
Mg ²⁺	0.21	0.16
K ⁺	0.14	0.11
Ca ²⁺	0.20	0.16
Sr ²⁺	0.0054	N.D.

*Numbers in parentheses are carbon isotopic ($\delta^{13}\text{C}$) values in per mil. †Chlorinity was determined by Mohr titration and the cations by inductive coupled plasma.

spheric pressure (even at -20°C), only the sample from DSDP/IPOD leg 84 was successfully collected for laboratory study prior to the discovery reported here. The four previous samplings of gas hydrates yielded predominantly biogenic hydrocarbon gases (mainly methane) on decomposition.

The thermogenic nature of the hydrates collected in this study is indicated by (i) molecular compositions containing large amounts of ethane, propane, and isobutane, (ii) carbon isotopic compositions, and (iii) the presence of oil in the cores. Results of the molecular and isotopic analyses of gas and water obtained

from the decomposing hydrate samples are summarized in Table 1 (7). The hydrates had a gas:fluid ratio of 70:1 on decomposition. The large amounts of propane and isobutane indicate that a structure II hydrate was present. Hydrocarbons larger than isobutane were detected at very low concentrations. The large amounts of ethane, propane, and isobutane and the heavy carbon isotopic ratio (−45 per mil relative to Pee Dee belemnite) of the hydrate gases are characteristic of thermogenic gases produced deep in the sedimentary column (8). The large amounts of nonmethane gases in the hydrate must stabilize the hydrate

lattice, since the 6° to 8°C temperature of water at 530 m in this part of the Gulf of Mexico is outside the temperature limit of methane hydrate stability. Since the presence of thermogenic hydrates in shallow sediments implies that the hydrate gas has migrated upward from deep in the sedimentary column, thermogenic hydrates could exist as deep in the sediment column as their stability would allow.

The three cores that contained gas hydrates were also oil-stained. Results of chemical analysis of two of the hydrate cores are presented in Table 2. The cores contained as much as 12.1 percent hexane-extractable material. Column chromatography was used to separate the extractable organic matter into saturate, aromatic, and polar compound types (9). The oil was extensively biodegraded, with both the saturate and aromatic gas chromatograms being dominated by the unresolved complex mixture. Column chromatography of the extractable material indicated that most of the degraded oil was aromatic in nature (23.1 percent saturate, 44.6 percent aromatic, and 7.6 percent polar compounds for oil in the 0- to 5-cm section of core 165). The large amounts of calcium carbonate in the core may be the result of microbial oxidation of petroleum. Chlorinities in the interstitial waters in excess of seawater levels may be due to the presence of a salt diapir underlying the site. The erratic distribution of chlorinities may reflect the fact that hydrates exclude salts from the clathrate structure because of the size of their ionic radii.

Although the area where the three hydrate cores were collected is restricted

Table 2. Data on sediment and interstitial water in two hydrate-containing cores. N.D., not determined (some sections contained large amounts of oil, making certain analyses impossible).

Station	Depth (cm)	Extractables (%)	Organic carbon* (%)	CaCO ₃ (%)	Sulfur (%)	Refractive index (per mil)	Chlorinity (per mil)	SCO ₂ (milligrams of carbon per liter)
166	0 to 5	1.2	3.2	16.8	1.0	37	19.1	14.2
166	20 to 25	3.1	2.4	18.8	1.2	38	19.3	3.1
166	40 to 45	1.3	2.8	19.3	1.2	37	19.2	21.6
166	60 to 65	3.2	14.3	N.D.	0.6	N.D.	N.D.	N.D.
166	80 to 85	12.1	11.9	N.D.	0.8	N.D.	N.D.	N.D.
165	0 to 5	2.7	3.8	44.9	0.76	38	18.4	54.2
165	20 to 25	3.5	4.5	31.5	0.84	N.D.	N.D.	N.D.
165	40 to 45	2.1	3.0	37.7	0.88	N.D.	N.D.	N.D.
165	80 to 85	0.8	3.0	65.0	0.51	N.D.	N.D.	N.D.
165	140 to 145	1.8	2.8	30.8	1.21	55	30.9	25.9
165	160 to 165	0.4	1.1	16.9	1.20	72	41.2	29.2
165	180 to 185	0.2	1.1	19.3	1.37	73	41.8	19.7
165	200 to 205	0.6	1.6	8.2	1.37	64	35.6	47.0
165	220 to 225	0.3	1.4	15.7	1.55	72	41.5	36.1
165	240 to 245	0.5	1.7	7.2	1.68	60	35.2	37.5
165	260 to 265	0.4	1.4	14.2	1.66	61	34.6	30.4
165	280 to 285	0.3	1.3	10.0	1.87	72	39.3	31.8

*Organic carbon content was highly variable in many sections because of a separate oil phase.

in size (a few square kilometers), there is evidence that thermogenic gas hydrates may be widespread on the Gulf continental slope. Anderson *et al.* (10) recently reported oil-stained sediments containing large amounts of gas over a 20-km² area of the upper slope. Some of the sediment gases they collected contained large amounts of isobutane but little *n*-butane, suggesting that hydrates were originally present in these cores. Our report expands the area where oil, and probably hydrates, occur intermittently in surface sediments to ~250 km². The migration of thermogenic gas and oil to the surface in this area occurs along faults and fractures created by salt tectonics in the area. Since these processes are pervasive over large areas of the Gulf Coast, hydrates associated with thermogenic hydrocarbon seepage may be common along the continental slope.

Little seismic evidence for gas hydrates in the Gulf of Mexico has been reported. BSR's have not been reported for the northern Gulf of Mexico, although they have been reported along the Mexican Ridge systems (2). Sidner *et al.* (11) observed anomalous seismic features described as chaotic facies (gas-charged sediments). The gas hydrates sampled in this study were associated with chaotic facies or gas "wipeout" zones. Sections reported as chaotic facies may in reality be the top of a sediment section containing disseminated gas hydrates (12).

The discovery of thermogenic hydrates associated with oil-stained cores in the Green Canyon area of the Gulf of Mexico will necessitate more detailed chemical, geological, and biological studies of the area. The extent and distribution of hydrates, their seismic signature, and their possible association with active oil and gas seepage are only a few of the areas of interest suggested by this discovery. Many complicating processes in these cores need further study, such as (i) the response of the microbial ecosystem to seeping oil and gas and dissolving salt; (ii) the effect of the microbial processes on isotopic fractionation in the oil, methane, and carbon dioxide, and (iii) geochemistry associated with carbonate formation from degradation of the seeping oil. Because of the apparent widespread occurrence of oil in slope sediments from natural seepage, questions are also raised as to our ability to differentiate between natural seepage and petroleum pollution in the Gulf of Mexico and to determine baseline levels. The effect of solid hydrates and oil-stained sediments on the benthic ecology of an area is unknown. Gas hydrates may

also represent a recoverable resource if they exist in significant quantities in the subsurface.

J. M. BROOKS
M. C. KENNICUTT II
R. R. FAY
T. J. McDONALD

Department of Oceanography, Texas
A&M University, College Station 77843

ROGER SASSEN
Getty Oil Company Research Center,
Houston, Texas 77042

References and Notes

1. D. W. Davidson, M. K. El-Defrawy, M. O. Fuglem, A. S. Judge, paper presented at the Third International Conference on Permafrost, Calgary, 1978.
2. T. H. Shipley *et al.*, *Am. Assoc. Pet. Geol. Bull.* **63**, 2204 (1979).
3. K. A. Kvenvolden and M. A. McMenamin, *U.S. Geol. Surv. Circ.* **825**, 1 (1980); K. A. Kvenvolden and L. A. Barnard, paper presented at the Hedberg Conference, Tulsa, 1983.
4. A. G. Yefremova and B. P. Zhizhchenko, *Dokl. Akad. Nauk SSSR* **214**, 1179 (1974).
5. J. M. Brooks, L. A. Barnard, D. A. Wiesen-burg, M. C. Kennicutt II, K. A. Kvenvolden, *Initial Rep. Deep Sea Drill. Proj.* **76**, 377 (1983).
6. J. C. Moore *et al.*, *Geotimes* **24**, 20 (1979); R. von Huene *et al.*, *Geol. Soc. Am. Bull.* **91**, 421

(1980); K. A. Kvenvolden and T. J. McDonald, *Initial Rep. Deep Sea Drill. Proj.*, in press.

7. A portion of the hydrate was allowed to decompose in a pressure vessel. Samples obtained from the pressurized vessel were analyzed as described by Brooks *et al.* (5). Carbon isotope values are reported as per mil deviations from the Pee Dee belemnite standard:

$$\delta^{13}\text{C} = \frac{(^{13}\text{C}/^{12}\text{C})_{\text{sample}} - (^{13}\text{C}/^{12}\text{C})_{\text{std}}}{(^{13}\text{C}/^{12}\text{C})_{\text{std}}} \times 1000$$

The δD value is reported relative to standard mean ocean water.

8. B. B. Bernard, J. M. Brooks, W. M. Sackett, paper presented at the Offshore Technology Conference, Houston, 1977.
9. The silica gel-alumina column chromatography was similar to that described by M. C. Kennicutt and L. M. Jeffrey [*Mar. Chem.* **10**, 367 (1981)]. High-resolution fused silica capillary chromatography on saturate and aromatic fractions was performed on a Hewlett-Packard 5880 gas chromatograph.
10. R. K. Anderson, R. S. Scanlan, P. L. Parker, E. W. Behrens, *Science* **222**, 619 (1983).
11. B. R. Sidner, S. Gartner, W. R. Bryant, *Tex. A&M Univ. Tech. Rep.* 77-5-T (1977).
12. W. R. Bryant, private communication.
13. Supported by the Marine Chemistry Program of the National Science Foundation through grant OCE-8020560 and by the Office of Naval Research through contract N00014-80-C-00113. We thank Conoco, Inc., Cities Service Oil and Gas Corp., and Getty Oil Co. for releasing the hydrate cores for study. A. Jeffrey, D. D. Sheu, and R. Pflaum provided the isotopic analysis of the hydrate gas; R. Burke the δD analysis; and S. Schofield the ionic analysis.

9 April 1984; accepted 22 May 1984

An El Niño Signal in Atmospheric Angular Momentum and Earth Rotation

Abstract. Anomalously high values of atmospheric angular momentum and length of day were observed in late January 1983. This signal in the time series of these two coupled quantities appears to have been a consequence of the equatorial Pacific Ocean warming event of 1982–1983.

Interest in the angular momentum budget of the earth-atmosphere system has been sparked in recent years by the availability of routine global analyses of atmospheric wind fields and improved astronomical measurements of the rotation of the earth. Studies (1–3) have

demonstrated that, on time scales of about a year and less, changes in the angular momentum of the atmosphere are strongly coupled to changes in the rotation rate of the solid earth, that is, to changes in the length of day (ΔLOD). We show here that, starting in late January

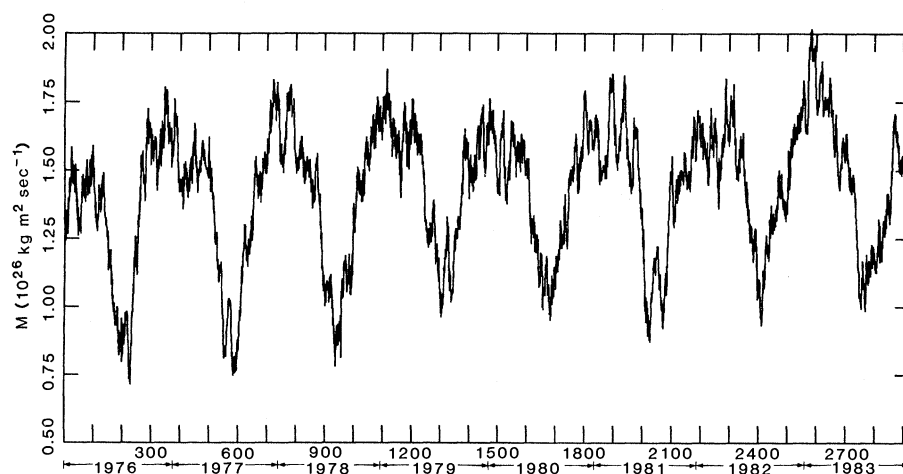


Fig. 1. Twice-daily values of the angular momentum of the atmosphere above the globe between 1000 and 100 mbar for the period 1 January 1976 to 31 December 1983. Time is marked along the abscissa in units of days.