provide information on the extent of earlier ice sheets, since it can be assumed that no substantial meltwaters would have entered the Gulf unless the southward extent of the ice sheet was greater than the latest Wisconsin limit about 11,200 years ago (Fig. 1). Such an approach will be of particular value since little is known about earlier episodes of deglaciation, because succeeding glacial advances have redistributed the older deposits.

JAMES P. KENNETT
Graduate School of Oceanography,
University of Rhode Island,
Kingston 02881

N. J. SHACKLETON
Sub-department of Quaternary
Research, University of Cambridge,
Cambridge, England

References and Notes

1. H. E. Wright and D. G. Frey, Eds., *The Quaternary of the United States* (Princeton Univ. Press, Princeton, N.J., 1965).
2. J. T. Andrews, *Arct. Alp. Res.* **5**, 185 (1973).
3. J. Bird, *ibid.*, p. 165.
4. V. K. Prest, *Geol. Surv. Can. Map 1257A* (1969).
5. V. K. Prest, in *Geology and Economic Minerals of Canada*, R. J. Douglas, Ed. (Geological Survey of Canada, Ottawa, 1970), pp. 676–764.
6. R. A. Bryson, W. M. Wendland, J. D. Ives, J. T. Andrews, *Arct. Alp. Res.* **1**, 1 (1969).
7. Oxygen isotopic analyses were made for approximately the last 25,000 years for K 97 and K 139 and the last 50,000 years for K 120 (*9*).
8. Details of locations and lengths of cores are given in Kennett and Huddlestun (*9*).
9. J. P. Kennett and P. Huddlestun, *Quat. Res.* **2**, 38 (1972).
10. The following sedimentation rates were calculated by using 11,000 years ago for the age of the Z-Y boundary and assuming that the rates were constant: (K 97) 27, (K 139) 9, and (K 120) 7 cm per 1000 years.
11. J. P. Kennett and P. Huddlestun, *Quat. Res.* **2**, 384 (1972); H. Clark and J. P. Kennett, *Earth Planet. Sci. Lett.* **19**, 267 (1973).
12. We used

$$\delta^{18}O = \left[\frac{(^{18}O/^{16}O)\text{sample}}{(^{18}O/^{16}O)\text{PDB1}} - 1\right] \times 10^3$$

where PDB is the standard Pee Dee Belemnite. For means of calibration, see N. J. Shackleton, *Colloq. Int. Cent. Natl. Rech. Sci.* **219**, 203 (1974).
13. C. Emiliani, *Quaternaria* **2**, 87 (1955).
14. E. Olausson, *Progr. Oceanogr.* **3**, 221 (1965).
15. Analytical techniques are described in N. J. Shackleton and N. D. Opdyke, *Quat. Res.* **3**, 39 (1973).
16. C. Emiliani, *Science* **154**, 851 (1966).
17. W. S. Broecker, in *The Quaternary of the United States*, H. E. Wright and D. G. Frey, Eds. (Princeton Univ. Press, Princeton, N.J., 1965), p. 737; W. S. Broecker, M. Ewing, B. C. Heezen, *Am. J. Sci.* **253**, 429 (1960).
18. D. B. Ericson and G. Wollin, *Science* **162**, 1227 (1968).
19. No evidence indicates that the Z-Y boundary is diachronous between the Gulf of Mexico and the Caribbean. It is, however, possible that this boundary may be slightly younger in the Gulf because of delayed migration of tropical *G. menardii* to a cooler Gulf near the end of the last glaciation.
20. A. W. H. Bé and L. Lott, *Science* **145**, 823 (1964).
21. N. J. Shackleton, *Nature (Lond.)* **215**, 15 (1967); W. Dansgaard and H. Tauber, *Science* **166**, 499 (1969).
22. At 197 cm in K 97 the oxygen isotopic compositions of the four species measured are as follows: *G. ruber*, −1.72; *G. sacculifer*, −1.14; *N. dutertrei*, −0.21; and *G. truncatulinoides*, +1.35 per mil.
23. C. Emiliani, *Am. J. Sci.* **252**, 149 (1954).
24. J. I. Jones, *Micropaleontology N.Y.* **13**, 489 (1967); W. F. Ruddiman, *Geol. Soc. Am. Bull.* **82**, 283 (1971).
25. T. H. Clark and C. W. Stearn, *Geological Evolution of North America* (Ronald, New York, 1968).
26. J. R. Curray, in *The Quaternary of the United States*, H. E. Wright and D. G. Frey, Eds. (Princeton Univ. Press, Princeton, N.J., 1965), p. 723.
27. V. K. Prest, *Geol. Surv. Can. Pap. 71-6* (1971).
28. E. Uchupi, *Trans. Gulf Coast Assoc. Geol. Soc.* **17**, 161 (1967).

29. Isotope analysis was supported under National Environment Research Council grant GR3/1762 to N.J.S. The mass spectrometer was operated by M. A. Hall. We thank C. Holmes for his assistance in supplying core materials, V. K. Prest for valuable advice on the continental glacial record, and G. Kukla for useful criticism of the manuscript. Support to J.P.K. was by NSF grant GA-36191X (Geological Oceanography).

29 November 1974; revised 5 February 1975 ■

Submarine Barite-Opal Rocks of Hydrothermal Origin

Abstract. *Unusual submarine rocks consisting of barite, opal, and volcanic detritus were recovered from the Lau Basin northeast of Australia. It is proposed that these rocks were formed when hydrothermal solutions emanating from a fracture zone offsetting the active spreading center in the Lau Basin came into contact with cooler ocean waters.*

Submarine barite-opal volcanic rocks were recovered from the Lau Basin, a marginal basin located northeast of Australia. The rocks were obtained by dredge from atop the Peggy Ridge, presently believed to be a fracture zone offsetting the active spreading center in the Lau Basin. The spreading center generally trends northeast-southwest dividing the Lau and Tonga ridges (*1*). The whole basin is less than 10 to 15 million years old, and the sediment cover is sparse, occurring in linear, probably fault-controlled troughs (*2*). Barite-opal rocks of this young age are not common in the marine environment and their origin is considered in this report.

Dredge hauls from the Peggy Ridge in the Lau Basin consist of ocean ridge type tholeiitic basalts exhibiting various degrees of weathering, together with pumice from the Tonga and Lau ridges. In only one dredge, 7 TOW-86D (16°55.4′S, 176°49.5′W; water depth 1990 to 1664 m), unusual barite-opal rocks were sampled. They are opal-cemented hyaloclastites containing fragments of tholeiitic basalt as glass, palagonite, plagioclase, and rare augite in addition to authigenic montmorillonite, phillipsite, and barite crystals.

There is considerable variation in the percentages of opal, hyaloclastite, and particularly barite in the total rocks (*3*). The relative abundances obtained by point counts on thin sections generally compare favorably with those obtained by other methods, except in rock K, where the discrepancy is probably due to the irregular opal distribution in layers and veins.

The euhedral barite crystals average 200 μm in length, with some crystals as large as 500 μm. The crystals are larger than those generally found in deep-sea sediments. Church (*4*) usually found barites smaller than 5 μm and only rarely in the size range 30 to 100 μm. In two rocks (A and B) barite is uniformly distributed, whereas in rock K it occurs only as a vein lining. The opal lines the intergranular cavities and cements the clasts. It has a botryoidal or colloform texture, with individual hemispheres 10 to 25 μm in diameter. This texture is well illustrated in Fig. 1, A and B. The occurrence of an opal vein cutting both a volcanic clast and the opal cement in rock K indicates at least two periods of opal deposition. In Fig. 1B the opal lines a cavity and surrounds a euhedral barite crystal. Optically, the opal is isotropic and has a refractive index varying between 1.440 and 1.444. X-ray diffraction of the opal gives a low broad peak between 19° and 26° with a maximum of 22° (values are 2θ for CuKα radiation, where θ is the Bragg angle); this classifies it as opal-A according to the scheme of Jones and Segnit (*5*). Opal-A commonly occurs in sediments from the deep sea, but only as radiolarians, diatoms, silicoflagellates, and sponge remains. Inorganic opal-A is not observed, probably because silica concentrations in pore waters rarely approach the equilibrium solubility value for amorphous opal, but possibly also because it is difficult to distinguish from organic opal. Organic opal-A, opal-CT (disordered cristobalite-tridymite), and quartz are the forms of silica found in deep-sea sediments (*6*). Opal-CT, in such sediments, characteristically exhibits a bladed and spherulitic growth habit (*7*) and does not resemble the opal-A shown in Fig. 1B. Opal-CT is also found as the diagenetic alteration product of volcanic detritus (*8*). No opal-CT was detected in the rocks we examined; however, Griffin *et al.* (*9*) found opal-CT in sediments from the Lau Basin.

Possible sources for the silica to form inorganic opal precipitates in the marine environment include (i) dissolution of biogenous opal and subsequent precipitation; (ii) devitrification and diagenesis of volcanic debris, followed by precipitation at normal deepwater temperatures; and (iii) precipitation from hydrothermal solutions which have leached silica out of volcanic material.

Sediment cover in the Lau Basin is sparse and its opal content is low, ranging from 0 to 9 percent, with an average value of 5 percent (*10*). The barite-opal rocks were dredged from the Peggy Ridge, which lies about 750 m above the basin floor and, according to seismic data, is essentially free of sediments (*2*). Therefore, it is unlikely that biogenous opal is the source of the cement in these rocks. Opal rocks were not sampled in other dredge hauls from the area.

Precipitation of amorphous silica (opal-A) at normal seawater temperatures is an unlikely source of these rocks. From his studies of chert in some cores obtained by the Deep Sea Drilling Project (DSDP), Heath (*11*) showed that, during the normal diagenetic processes, empty foraminiferal chambers are first infilled with chalcedony, and this is followed by replacement of the micritic matrix with cristobalite. The foraminiferal shell is then replaced by chalcedony. However, in the Lau Basin opal rocks, foraminifera occur in the cavities surrounded by the opal and have not undergone any infilling or alteration. Clearly, the diagenetic sequence of chert formation observed in the DSDP cores has not been followed here.

Heath (*11*) explained the finding of chert in relatively young sediments (Miocene age in the Panama Basin) by suggesting that high thermal gradients could speed up the process of chert formation. The Lau Basin is undergoing active spreading, and the Peggy Ridge is considered to be a leaky fracture zone in an area with variable but generally high heat flow (*12*). For example, the nearest heat flow value, obtained approximately 28 km away, is 4.22 μcal cm^{-2} sec^{-1}. In such areas seawater could be circulating through fractures in the rocks. During its passage it could be warmed and could dissolve such constituents of the rocks as silica (*13*). On percolating into normal seawater it would be cooled and would become supersaturated, precipitating opal-A. The opal-A from the Lau Basin silicifies young rocks and morphologically resembles the hydrothermal deposits of opal found in the upper portions of a borehole in Yellowstone National Park in the western United States [compare Fig. 1B with figure 4 in (*14*)]. The opal at Yellowstone is thought to have formed below 104°C since it was found only in the upper portions, where the temperature was less than 104°C (*14*).

A temperature of formation of about 41°C for the opal-A in rock K was obtained from oxygen isotopic measurements on the opal [$\delta Si^{18}O_2$ of +31.1 per mil SMOW (*15*)], using Labeyrie's equation $t = 5 - 4.1(\delta Si^{18}O_2 - \delta H_2{}^{18}O - 40)$ (*16*) and assuming $\delta H_2{}^{18}O$ equals zero. This temperature must be interpreted with extreme care since contamination with volcanic detritus and the presence of water in the opal-A structure could have affected the oxygen isotopic value (*17*). Still, a temperature considerably higher than that of normal deep ocean water is indicated.

Barite concretions are rare in the marine environment but have been found in the Japan Sea; off the coast of California; from Kaipara Harbour, New Zealand; off the borderland of southern India; and now in the Lau Basin (*18–20*). The Lau Basin samples are the only ones that do not occur in relatively shallow water. In addition, barite is commonly dispersed in marine sediments and can reach concentrations of up to 10 percent by weight on a carbonate-free basis on the East Pacific Rise (*21, 22*). The origins of these barites have been variously considered to be biologic activity (*4*), continental weathering (*19*), hydrothermal solutions (*21*), and combinations of these (*18*). Both hydrothermal and sedimentary

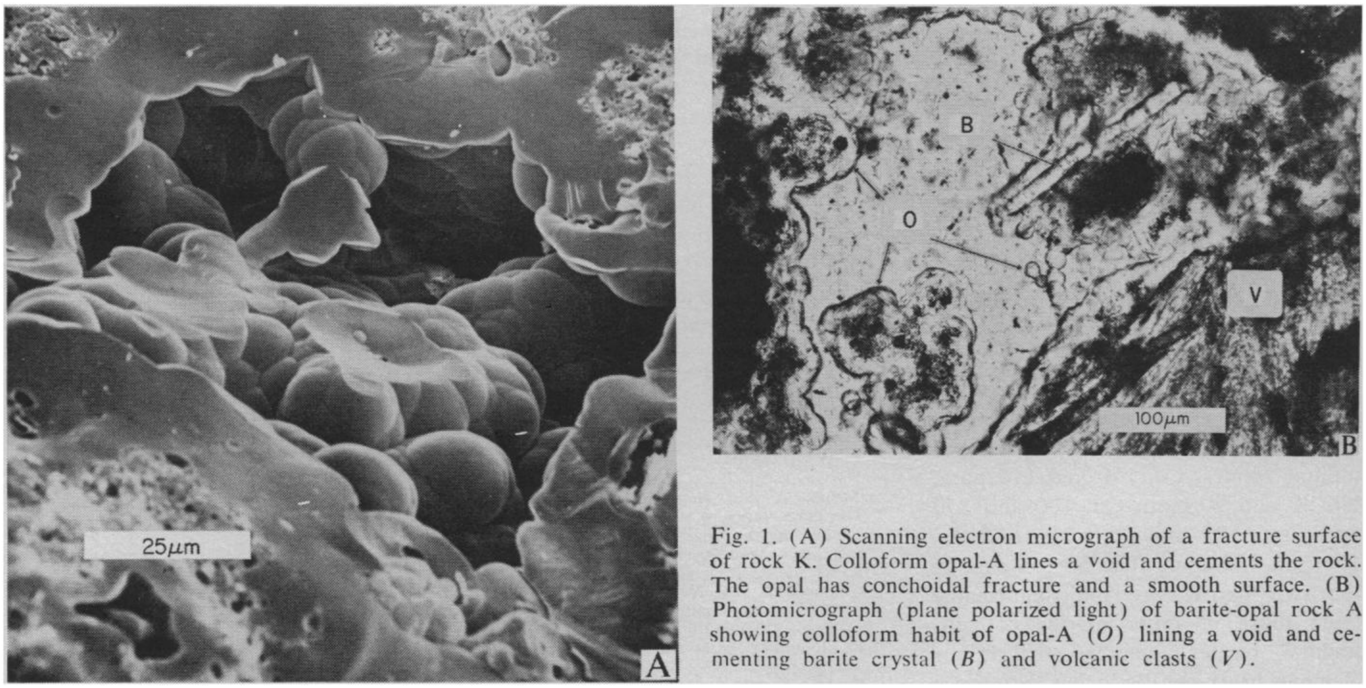

Fig. 1. (A) Scanning electron micrograph of a fracture surface of rock K. Colloform opal-A lines a void and cements the rock. The opal has conchoidal fracture and a smooth surface. (B) Photomicrograph (plane polarized light) of barite-opal rock A showing colloform habit of opal-A (*O*) lining a void and cementing barite crystal (*B*) and volcanic clasts (*V*).

processes have been used to explain continental deposits of barite (*23*). Barite is undersaturated in normal oceanic waters (*4*). Most theories require an additional source for barium—either hydrothermal solutions or biological activity—to bring about the precipitation of barite.

Both isotopic and chemical analyses have been used to determine the origins of marine barites. The sulfur and oxygen isotopic ratios for barites A and B (*24*) are compared to those for other continental and marine barites in Fig. 2. Bacterial sulfate reduction is indicated by the arrows. The sulfur isotopic compositions of the two barites are similar to each other and to the value of present-day seawater sulfate (+20.3 ± 0.5 per mil). Thus the barites could not have formed from meteoritic waters or in areas with high bacterial reduction of sulfate, both of which would have changed the sulfur isotopic composition. The oxygen isotopes are from 4 to 6 per mil heavier than those in present-day seawater sulfate (+9.7 per mil), which are not in isotopic equilibrium with seawater (*25*). Exchange of oxygen isotopes between dissolved sulfate and water proceeds very slowly at neutral *p*H and Earth surface temperatures, but is considerably accelerated at higher temperatures and in acidic solutions (*25*). The two barites reported here are showing such a shift toward the equilibrium seawater sulfate value of +38 per mil. Church (*4*) showed that freshly precipitated barite had the same oxygen isotopic composition as the seawater sulfate it was precipitated from. Hence, if one assumes that the shifts toward equilibrium result solely from temperature changes, a temperature of formation can be calculated. Using Lloyd's (*25*) formula, $\ln \alpha = (3251/T^2) - 0.0056$, we calculate the temperature of the seawater from which the barites precipitated as 117°C for barite A and 134°C for barite B. These temperatures are slightly higher than that indicated for the opal. This is not inconsistent since the opal was deposited after the barite.

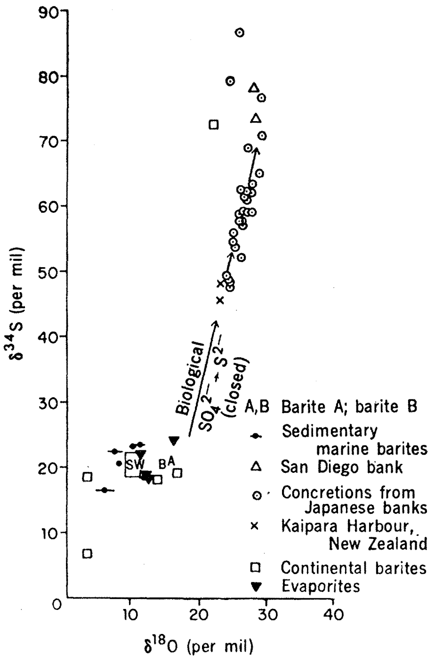

Fig. 2. Comparison of δ^{18}O and δ^{34}S for barites A and B with values for other marine and continental barites. Isotopic changes during sulfate reduction are shown by the arrow. Data sources: sedimentary marine barites and San Diego bank, from Church (*4*); concretions from Japanese banks and evaporites, from Sakai (*18*); Kaipara Harbour, New Zealand, from Rafter and Mizutani (*20*).

The chemical compositions of barites A and B, respectively, are: Sr, 2.0 and 1.4 percent; Fe, 460 and 710 parts per million (ppm); Co, 150 and 110 ppm; Ni, 90 and 90 ppm; Cu, 100 and 130 ppm; Zn, 125 and 95 ppm; and As, 190 and 130 ppm. The Sr contents of the two barites are indistinguishable from those of other marine or continental barites, whereas the minor elements are generally higher than those reported by Church (*26*) and probably reflect their deposition in an area of high ferromanganese deposition (*10*).

Both the opal and the barite show evidence of having been deposited under higher temperatures than that of normal seawater. It is therefore suggested that the barite and opal were precipitated inorganically when hydrothermal solutions came into contact with cooler ocean waters. The hydrothermal solutions are related to the presence of an active spreading center in the Lau Basin.

K. K. BERTINE
San Diego State University,
San Diego, California 92115

J. B. KEENE
Scripps Institution of Oceanography,
La Jolla, California 92037

References and Notes

J. G. Sclater, J. W. Hawkins, J. Mammerickx, C. G. Chase, *Geol. Soc. Am. Bull.* **83**, 505 (1972).

2. J. W. Hawkins, in *Geology of Continental Margins*, C. Burk and C. Drake, Eds. (Springer-Verlag, New York, 1974), p. 505.
3. The percentages of opal, barite, and volcanic detritus in the rocks are as follows. Opal, rock A, 41 and 30; rock B, 51 and 50; rock K, 63 and 25 [first value by method of E. D. Goldberg, *J. Mar. Res.* **17**, 178 (1958); second by thin section point count (500)]. Barite, rock A, 34 and 30; rock B, 6 and 5; rock K, 1 and 2 [first value, gravimetric after leaching with HCl, HNO_3, and HF: second by thin section point count (500)]. Volcanic detritus, rock A, 25 and 40; rock B, 43 and 45; rock K, 36 and 73 [first value by difference; second by thin section point count (500)].
4. T. Church, thesis, University of California, San Diego (1970).
5. J. B. Jones and E. R. Segnit, *J. Geol. Soc. Aust.* **18**, 57 (1971).
6. G. R. Heath and R. Moberly, in *Initial Reports of the Deep Sea Drilling Project* (Government Printing Office, Washington, D.C., 1971), vol. 7, p. 991; Y. Lancelot, in *Initial Reports of the Deep Sea Drilling Project* (Government Printing Office, Washington, D.C., 1973), vol. 17, p. 377.

F. M. Weaver and S. W. Wise, *Nature (Lond.)* **237**, 56 (1972).

N. Güven and R. E. Grim, *Clays Clay Mineral.* **20**, 89 (1972); S. W. Wise, F. M. Weaver, N. Güven, *Proc. Electron. Microsc. Soc. Am. 31st Annu. Meet.* (1973), p. 157.

9. J. J. Griffin, M. Koide, A. Höhndorf, J. W. Hawkins, E. D. Goldberg, *Deep-Sea Res.* **19**, 139 (1972).

K. K. Bertine, *Geochim. Cosmochim. Acta* **38**, 629 (1974).

11. G. R. Heath, in *Initial Reports of the Deep Sea Drilling Project* (Government Printing Office, Washington, D.C., 1973), vol. 16, p. 609.
12. J. G. Sclater, U. G. Ritter, F. S. Dixon, *J. Geophys. Res.* **77**, 5697 (1972).
13. J. B. Corliss, *ibid.* **76**, 8128 (1971).
14. S. Honda and L. J. P. Muffler, *Am. Mineral.* **55**, 1714 (1970).
15. Analysis by H. Sakai, Institute for Thermal Spring Research, Okayama University, Misasa, Japan.

L. P. Labeyrie, *Nature (Lond.)* **248**, 40 (1974).

L. P. Knauth and S. Epstein, *Earth Planet. Sci. Lett.* **25**, 1 (1975).

18. H. Sakai, *Geochem. J.* **5**, 79 (1971).

E. D. Goldberg, B. L. K. Somayajulu, J. Galloway, I. R. Kaplan, G. Faure, *Geochim. Cosmochim. Acta* **33**, 287 (1969).

20. T. A. Rafter and Y. Mizutani, *N.Z. J. Sci.* **10**, 816 (1967).

G. Arrhenius and E. Bonatti, *Progr. Oceanogr.* **3**, 7 (1965).

22. K. Boström and M. N. A. Peterson, *Econ. Geol.* **61**, 1258 (1966).
23. See, for example, A. C. Durham and J. S. Hanor, *Econ. Geol.* **62**, 82 (1967); D. R. Shawe, F. G. Poole, D. A. Brobst, *ibid.* **64**, 245 (1969).
24. The sulfur and oxygen isotopic ratios are calculated as

$$\delta^{18}O = \left[\frac{(^{18}O/^{16}O)\text{sample}}{(^{18}O/^{16}O)\text{SMOW}} - 1 \right] \times 10^3$$

where SMOW is Standard Mean Ocean Water, and

$$\delta^{34}S = \left[\frac{(^{34}S/^{32}S)\text{sample}}{(^{34}S/^{32}S)\text{CDT}} - 1 \right] \times 10^3$$

where CDT is Canyon Diablo Troilite. The values (per mil) were: δ^{18}O, barite A, + 14.2 ± 0.1 and + 15.9 ± 0.3; barite B, + 30.6 ± 0.1 and + 14.1 ± 0.1; δ^{34}S, barite A, + 22.2 ± 0.2 and + 20.4 ± 0.2; barite B, + 21.4 ± 0.2 and + 19.9 ± 0.2. The first value in each pair was obtained by H. Sakai, Institute for Thermal Spring Research, Okayama University, Misasa, Japan, and the second by the Department of Scientific and Industrial Research, Institute of Nuclear Sciences, Lower Hutt, New Zealand. The disparity in the δ^{18}O values for rock B found by the two laboratories may be due to inhomogeneities, since different portions were sampled; because of its similarity to the isotopic value of barite A, the lower value is plotted in Fig. 2.

25. R. M. Lloyd, *J. Geophys. Res.* **73**, 6099 (1968). In Lloyd's formula $\alpha = (^{18}O/^{16}O)\text{sulfate}/(^{18}O/^{16}O)\text{water}$.
26. Compare to Church's (*4*) average values for marine barites: Sr, 1.0 percent, range 0.2 to 3.4 percent; Fe, 260 ppm; Cr < 100 ppm; Zn, 200 ppm; and Cu, 1 ppm.

27. Supported by the San Diego State University Foundation (grant 263029-908) and ONR contract USN-N00014-75-C-0152. The samples were collected on the Scripps Institution of Oceanography expedition Seven Tow, which was supported by funds from the National Science Foundation and the Office of Naval Research. M. Kastner and E. D. Goldberg reviewed the manuscript.

21 November 1974