

Fig. 2. Histogram of  $S\!-\!P$  intervals for the twenty-seven local events recorded at Vanda.

The prominence of the S phase at Vanda must therefore be due to its path rather than its source, and suggests some guiding action of a surface layer of unusual uniformity. The path is, in fact, along young mountain ranges, unbroken by major geological inhomogeneities or sedimentary basins, whereas that to Scott Base traverses the western Ross Sea and McMurdo Sound, where there are likely to be great thicknesses of sediment and moraine as well as recent volcanic rock near Scott Base.

During January and February 1969, there thus appears to have been a localized source of seismic energy about 250 km north of McMurdo Sound, with lesser activity extending southwards about 100 km. These earthquakes could have been caused by ice movement, for cracks in ice can produce shocks of the observed magnitude<sup>3</sup>.

Another explanation is that the earthquakes are a swarm, such as occur in areas of recent volcanism in New Zealand<sup>5</sup>. These comprise numerous small earthquakes, with no one shock of significantly greater magnitude, and appear to comprise natural earthquakes in that they are unaccompanied by volcanic manifestations, and not closely related to present-day volcanic or geothermal activity. Young volcanism is present in Victoria Land, and geothermal activity has recently been reported from Mount Melbourne<sup>6</sup>, about 120 km from the earthquakes. From the observed occurrence of about one shock a day of magnitude 2, the usual magnitude-frequency relationship would lead to the expectation of several magnitude 4 shocks a year, and one of magnitude 5 every few years. Such activity would not go undetected, and its absence supports the suggestion that if the earthquakes are not due to ice movement they are an earthquake swarm.

A fault developed in the Vanda seismograph late in April 1969, but recording will be restarted there early in

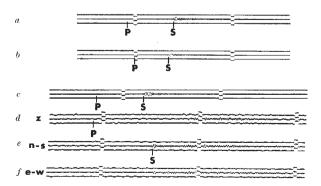


Fig. 3. a, Earthquake of 1969, January 31, 14 h, recorded at Vanda. S-P 29\frac{1}{2} \text{s.} b, Earthquake of 1969, January 31, 20 h, recorded at Vanda. S-P 20\frac{1}{2} \text{s.} Earthquake of 1969, January 12, 12 h, recorded at: c, Vanda; d, Scott Base, vertical component; c, Scott Base, n-s component; f, Scott Base, e-w component.

the 1969–70 season, when a temporary station will also be installed at Hallett, about 600 km to the north of Scott Base. This further study should throw more light on the nature of these earthquakes, which may be the first natural earthquakes to be located on the Antarctic continent, as distinct from those accompanying eruptions on the Graham Land Peninsula. The existence of such small natural earthquakes, however, will not alter the fact that Antarctica is substantially less seismic than any other continent.

I thank the seismograph operators at Scott Base and Vanda Station, K. G. Mandeno and S. K. Cutfield, and also W. L. Johns, who has helped greatly in the running of the Vanda seismograph.

R. D. Adams

Seismological Observatory, Geophysics Division. DSIR.

Wellington, New Zealand.

Received May 27; revised July 17, 1969.

<sup>1</sup> Evison, F. F., NZ J. Geol. Geophys., 10, 479 (1967).

<sup>2</sup> Hatherton, T., Geophys. J., 5, 252 (1961).

- Hatherton, T., and Evison, F. F., NZ J. Geol. Geophys., 5, 864 (1962).
  Browne-Cooper, P. J., Small, G. R., and Whitworth, R., NZ J. Geol. Geophys., 10, 443 (1967).
- <sup>5</sup> Eiby, G. A., Bull. Vol., 29, 61 (1966).
- <sup>6</sup> Nathan, S., and Schulte, F. J., NZ J. Geol. Geophys., 10, 422 (1967).

## Natural Radiocarbon Activity of the Dissolved Organic Carbon in the North-east Pacific Ocean

The "age" of the dissolved organic matter in the deep sea relative to its origin in the euphotic zone has been a matter of conjecture for some time<sup>1-3</sup>. Photosynthetic fixation of carbon dioxide into plant carbon by phytoplankton and subsequent biochemical oxidation or solubilization of organic carbon takes place primarily in the upper 0-300 m of the sea. A small, as yet unknown, fraction of this organic carbon is transferred into the deep water by physical processes such as turbulent mixing and sinking of surface water at high latitudes. In addition, particulate organic carbon which sinks from the surface may be converted into dissolved organic matter at depth. In order to determine how "old" this dissolved organic carbon is, its natural radiocarbon activity has been measured for two deep-water samples taken off southern California.

The dissolved organic carbon was converted to carbon dioxide (and subsequently to methane for radiocarbon counting) by photo-oxidation with high energy ultraviolet radiation<sup>4</sup> (Fig. 1). Seawater was collected with a 100 l. stainless steel sampler and stored in 200 l. pre-leached steel drums lined with polythene (no increase in organic carbon was detected during the storage period before analysis). Pre-filtration to remove particulate organic matter was not necessary because its concentration was less than 5  $\mu$ g/l. The seawater was acidified to pH 2 with hydrochloric acid, sparged free of inorganic carbon (99.97 per cent) with oxygen gas and irradiated in 60 l. batches for 20 h. using a 1,200 W mercury-are lamp (Hanovia Engelhardt '189 A'). The carbon dioxide so formed was sparged from the seawater with oxygen gas and trapped in strontium hydroxide as strontium carbonate. Complete oxidation was ascertained by comparison of the carbon dioxide in the irradiated seawater (detected by a Beckman model 15 infrared analyser) with the amount of carbon dioxide resulting from the wet combustion of the organic carbon in the seawater before oxidation<sup>5,6</sup>. The strontium carbonate was collected by filtration, washed with water in a nitrogen atmosphere and then dried in vacuo.

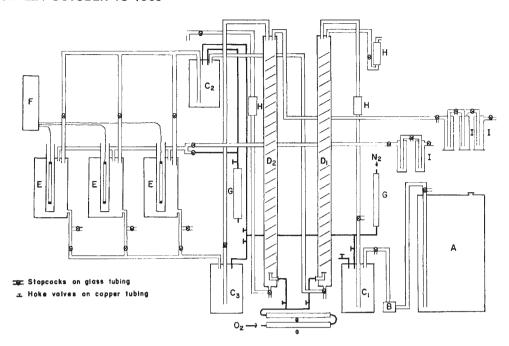


Fig. 1. Reactor for conversion of organic carbon to carbon dioxide. A, 200 l. polythene-lined steel drum; B, centrifugal pump;  $C_1$ , 20 l. glass carboy containing acidified seawater;  $C_2$ , same as  $C_1$ , containing seawater stripped of  $CO_2$ ;  $C_3$ , same as  $C_1$ , containing product from reactors (E);  $D_1$ , glass stripping column packed with broken glass to remove inorganic  $CO_2$ ;  $D_2$ , same as  $D_1$  to remove  $CO_2$  resulting from oxidation of organic carbon; E, 20 l. glass reactors fitted with mercury-are lamps in quartz tubes; F, ballasts to power lamps: G, absorption traps containing activated charcoal, molecular sieve and ascarite; H, liquid and gaseous flowmeters; I,  $Sr(OH)_2$  absorption traps. The  $N_2$  is used to transfer the seawater under positive pressure. All stopcocks and glass joints are lubricated with 80 per cent  $H_3PO_4$ . The acidified seawater flows into the top of column  $D_1$  at 17 ml,/min and  $O_2$  enters through the bottom fit at 4,000 ml,/min. After irradiation in the reactors E, the product  $CO_2$  is stripped from column  $D_2$  as in column  $D_1$ , and absorbed in the  $Sr(OH)_2$  traps.

The radiocarbon activity was determined by conversion of the carbon dioxide, derived from the strontium carbonate, into methane which was then counted in a 100 ml. counter similar to that described earlier, at pressures between 1.0 and 1.4 atmospheres. The background counting rate was 0.415 c.p.m. and each of the samples was counted twice. The activity of the samples was compared with 0.95 times the National Bureau of Standards oxalic acid. The results (Table 1) are expressed as  $\Delta^{14}{\rm C}$  where

$$\Delta^{14}C^{0}/_{00} = \delta^{14}C^{0}/_{00} - (2\delta^{13}C^{0}/_{00} + 50) \left[1 + \frac{\delta^{14}C^{0}/_{00}}{1,000}\right]$$

and the "age" equals

8,033 ln [ 
$$\frac{1}{1 + \Delta^{14}C^0/_{00}}$$
]

The  $\delta^{19}$ C value is  $-22\cdot5^{\circ}/_{00}$ , an average of three earlier determinations on the dissolved organic matter in seawater sampled at the same location and depth<sup>9</sup>.

The "age" of the inorganic carbon at 2,000 m at 30° 04′ N, 118° 02′ W was 2,194±70 yr in October 1959 (ref. 10) and 1,480±80 yr at 31° 53′ N, 119° 47′ W in July 1966 (unpublished results of P. M. W.). The dissolved organic matter is significantly "older" than either of these ages, which implies that it does not follow the same path as the inorganic carbon from their origin at the ocean surface. In effect, the dissolved organic carbon, or some fraction of it, is recycled through the system and some "young" carbon entering the deep sea is converted directly to CO<sub>2</sub>, rather than to dissolved organic carbon (the average age of 3,400 yr will represent a mean value for the total dissolved organic carbon where some fractions are "older"

and some are "younger"). The inorganic carbon may be "younger", because solution at depth of biogenic calcium carbonate and oxidation of particulate organic carbon sinking from the surface effects carbon-14 enrichment of the inorganic carbon. Recent results 11 on the carbon-13: carbon-12 ratios of the inorganic carbon in the oxygen minimum zone (200–1,000 m) in the Atlantic Ocean indicate a contribution from biogenic carbon dioxide to the total inorganic carbon, which again may lower the "age" of the inorganic carbon.

This apparent "age" of 3,400 yr for the dissolved organic carbon is also an indication of the amount of photosynthetically fixed carbon which enters the deep sea. The average amount of carbon fixed by phytoplankters is of the order of  $100 \text{ g/m}^2/\text{yr}$  (ref. 12), which for the world oceans  $(3.6 \times 10^{14} \text{ m}^2)$  becomes  $3.6 \times 10^{16} \text{ g/yr}$ . At 500 µg of carbon/l., the total reservoir of dissolved organic carbon in the deep sea, 300 m to 3,800 m (mean depth of the oceans), is  $6.3 \times 10^{17} \text{ g}$  of carbon. Thus

Residence time 
$$(yr) = \frac{amount in reservoir (g)}{input (g/yr)}$$

 $\quad \text{and} \quad$ 

Input = 
$$\frac{6.3 \times 10^{17} \text{ g}}{3,400 \text{ yr}}$$
 =  $1.85 \times 10^{14} \text{ g/yr}$ 

This means that 0.51 per cent of the fixed carbon (3.6  $\times$  10<sup>16</sup> g/yr) enters the deep sea in dissolved form assuming a steady-state situation.

The fact that the dissolved organic carbon is 3,400 yr "old" in the north-east Pacific supports the hypothesis that this organic matter, or a large percentage of it, is resistant to biochemical oxidation or bacterial utilization.

Table 1. A 14C ACTIVITIES AND AGE OF DISSOLVED ORGANIC ACID

	Depth	Sample	Total organic	∆14C	Age
Sampling location	collected (m)	volume (l.)	carbon ( $\mu g/l$ .)	(°/ <sub>00</sub> )	(yr B.P.)
30° 15.0′ N, 119° 49.0′ W. Collected June 18, 1968. Bottom depth, 3,300 m	1,880	420	400	$-351 \pm 27$	$3,470 \pm 330$
30° 16.9' N 119° 49.6' W Collected Japuary 10, 1969. Bottom depth, 3,500 m	1,920	440	350	$-341 \pm 25$	$3,350 \pm 300$

This work was supported by the US Atomic Energy Commission

P. M. WILLIAMS

Institute of Marine Resources, University of California, San Diego, La Jolla, California 92037.

H. OESCHGER

Physikalisches Institut. Universität Bern, Bern, Switzerland.

P. KINNEY

Institute of Marine Science. University of Alaska, College, Alaska.

Received June 30, 1969.

- <sup>1</sup> Krogh, A., Ecol. Monog., 4, 421 (1934).
- <sup>2</sup> Williams, P. M., Nature, 204, 462 (1964).
- <sup>3</sup> Menzel, D. W., and Ryther, J. H., Deep-Sea Res., 15, 327 (1968).
- Armstrong, F. A. J., Williams, P. M., and Strickland, J. D. H., Nature, 211, 481 (1966).
- <sup>5</sup> Menzel, D. W., and Vaccaro, R. F., Limnol. Oceanog., 9, 138 (1964).
- Williams, P. M., Limnol. Oceanog., 14, 297 (1969).
  Loosli, H. H., and Oeschger, H., Earth Planet. Sci. Lett., 5, 191 (1968).
- <sup>8</sup> Broecker, W. S., and Olson, E. A., Radiocarbon, 3, 176 (1961).
- 9 Williams, P. M., and Gordon, L. I., Deep-Sea Res. (in the press).
- <sup>10</sup> Bien, G. S., Rakestraw, N. W., and Suess, H. E., Limnol. Oceanog., 10 (suppl.), R25 (1965).
- <sup>11</sup> Deuser, W. G., and Hunt, J. M., Deep-Sea Res., 16, 221 (1969).
- <sup>12</sup> Ryther, J. H., in *The Sea* (edit. by Hill, M. N.), 2, 347 (John Wiley and Sons, New York and London, 1963).

## Diagenetic Changes in Interstitial Waters of Holocene Lake Constance Sediments

Many workers have investigated the chemical composition of interstitial waters in modern oceanic sediments1, but, to my knowledge, no similar extensive investigations have been carried out on fresh water sediments. I have studied two sediment cores, 3.70 m and 3.80 m long, from the shallow "Untersee" Basin of Bodensee (Lake Constance), Central Europe (Fig. 1), representing an age of approximately 2,000-4,000 years, if the present rate of sedimentation in this area (1-2 mm/year) is assumed2.

The sedimentation process in the Untersee is governed by the deposition of carbonate rich clayey silt muds resulting from suspended load of the Rhine River, by calcite produced in the littoral zone by blue-green algae and aquatic plants2,3 plus organic material derived from these plants and the phytoplankton4. Diatoms also occur, but are not very abundant. In most parts of the Untersee the sediment is black to grey due to the formation of FeS.nH<sub>2</sub>O and pyrite. The hydrochemistry of the Untersee lake water changes seasonally5. The variations are shown in Fig. 2.

Immediately after sampling, the interstitial waters were squeezed from the muds and subsequently analysed by the standard methods of water chemistry or atomic absorption spectroscopy.

The mineralogy of both cores is about the same; the main constituent being calcite and minor constituents, clay minerals (illite, smectite, chlorite), quartz and feldspars (both K-feldspar and Na-rich plagioclases), and dolomite. The total carbonate content, however, of core two from the "Gnadensee" is at any depth higher (61-80 per cent) than that of the other core one from the "Rheinsee" (44-64 per cent). This is also true for the content of organic material (about 4 per cent organic carbon as compared with about 2 per cent in core one). The clay fraction ( $< 2 \mu m$ ) in core two is less than in core one. In both cores the upper parts have lower clay contents than the deeper ones.

The water content of both sediment cores decreases with depth, but, in core one, water contents are always

higher at any depth than in core two. The electric conductivity of the interstitial waters increases with depth, at any depth the waters of core two showing higher values. Sodium content increases steadily with depth from 5.6 to 20.5 mg/l. in core one and from 7.4 to 26.1 mg/l. in core two; it is thus almost quadruplicated from top to bottom in both cores and the increase is much higher with regard to the supernating lake water. Potassium content is always higher (about 1.5 to 2 times) than in the lake water; in core one a tendency seems to exist towards an increase with depth. Magnesium content clearly increases with depth in core one, less clearly in core two, the increase compared with the lake water being more than 50 per cent. Calcium content does not reveal systematic changes. In core one it is lower than in the lake water, in core two slightly higher. Strontium content shows the same tendency as the calcium content. In core one, again, the concentration is lower than in the lake water. N(NH<sub>4</sub>) content in the uppermost sediment layer is already about 50-100 times higher in core one and about 150-300 times higher than in the lake. A clear tendency exists in both cores (especially in core one) towards an increase with depth. The SiO content is also much higher in the interstitial waters (up to ten-fold), and no dependence on depth can be observed. In the uppermost parts of both cores the P(PO<sub>4</sub>) content is several times higher. It decreases in core one to values similar to those found in the present lake water; in core two an increase with depth can be observed after reaching a minimum at a depth of 70 cm. The chloride content in core one decreases more or less steadily with depth, and at the bottom of the core it reaches only one-third of the Cl found in the lake water. In the uppermost and lowermost parts of core two the Cl values are about the same as in the lake water; between 0.70 and 1.70 m depth they are slightly lower. No SO<sub>4</sub> has been found in the interstitial waters of both cores. The HCO<sub>3</sub> content (not shown in Fig. 2) of core one is about twice as high, of core two twice to three times as high, as in the lake water and does not show dependence on depth. In some layers CO3 could also be proved; pH values (not shown in Fig. 2) were found to vary between 7.6 and 8.55, and no systematic change with depth was detected.

The results show that in the fresh water sediments of

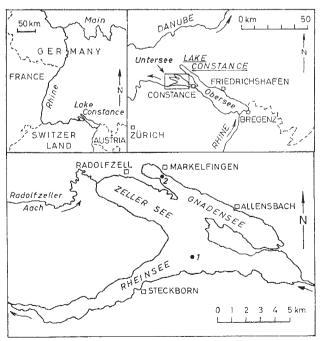


Fig. 1. Location of sediment cores one and two in the Untersee of Lake