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Radiocarbon and stable carbon isotope compositions of organic compound classes in sediments from the NE Pacific and Southern Oceans

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Abstract

Radiocarbon ($\Delta^{14}\text{C}$) abundance and stable carbon isotope ($\delta^{13}\text{C}$) compositions were measured for total lipid, total hydrolyzable amino acids (THAA), total carbohydrates (TCHO), and acid-insoluble organic fractions separated from phytoplankton, zooplankton, and sediment cores collected from two abyssal sites, one in the northeast (NE) Pacific Ocean and one in the Southern Ocean. These results are compared with those obtained for a separate core from the NE Pacific and reported by Wang et al. [Geochim. Cosmochim. Acta 62 (1998) 1365.]. An uncharacterized acid-insoluble fraction dominated (43–57%) the sediment TOC pool at both sites. Sediment collected from the NE Pacific exhibited higher TOC, TN, and higher $\Delta^{14}\text{C}$ values and contained both labile (THAA and TCHO) and refractory (lipid and acid-insoluble) fractions. In contrast, sediment from the Southern Ocean had much lower TOC and $\Delta^{14}\text{C}$ values, which indicated that organic matter was extremely refractory. Sedimentation rates calculated from ^{14}C ages of TOC for both sites indicate that the differences in the organic composition and $\Delta^{14}\text{C}$ signatures of organic matter in the sediments likely resulted from the differences in production and deposition of organic matter to the sediment, and the diagenetic stages of sedimentary organic matter in the two oceans.

Unlike $\Delta^{14}\text{C}$, stable carbon isotopic ($\delta^{13}\text{C}$) compositions of TOC in the sediments of the two oceans had similar values, which reflect not only the organic matter input from marine-derived sources but also the nature of degraded, predominately uncharacterized organic fraction in these sediments. The differences in $\delta^{13}\text{C}$ values among the compound classes in sediments at both sites can be attributed to the carbon isotopic signatures in original sources during photosynthesis and associated environmental factors. Preferential degradation of organic matter and heterotrophic effects may also play important roles for the observed $\delta^{13}\text{C}$ variations and these effects need to be further investigated. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Radiocarbon; Stable carbon isotope; Organic compound

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1. Introduction

Deep-sea sediments, as one of the largest carbon reservoirs in the ocean, not only play an important role in the global carbon and biogeochemical cycles (Emerson and Hedges, 1988), but also provide the most complete record of past and present-day oceans. Our knowledge of the circulation and chemistry of the past ocean is based in part on the isotopic and geochemical studies of sedimentary organic carbon. Therefore, it is important to understand the sources and the processes, which control the contents and carbon isotopic signatures of organic matter in the deep-sea sediments.

Radiocarbon (^{14}C) is the radioactive form of carbon produced by cosmic-ray secondaries in the stratosphere and during thermonuclear bomb testing in the late 1950s and early 1960s. It provides an ideal tracer to study the transformation and cycling of carbon in the ocean (Druffel and Williams, 1992; Druffel et al., 1998). Previous studies (Wang et al., 1996, 1998) reported $\Delta^{14}\text{C}$ values in organic compound classes: total lipid, total hydrolyzable amino acids (THAA), total carbohydrates (TCHO), and acid-insoluble (uncharacterized) organic fractions separated from particulate organic matter and sediments collected from an abyssal site (station M) in the northeast (NE) Pacific Ocean. These results showed that organic matter preserved in the sediment is a mixture of organic carbon of different sources and with different diagenetic stages. Lipids exhibited much lower $\Delta^{14}\text{C}$ signatures than THAA and TCHO fractions in the sediments. We suggested that differential decomposition of organic matter and sorption and/or biological incorporation of 'old' (low $\Delta^{14}\text{C}$) dissolved organic carbon (DOC) (Druffel and Williams, 1990) onto sediment could be the major processes controlling the observed $\Delta^{14}\text{C}$ signatures and abundances of the organic fractions.

In this paper, we report the results of our further investigations of $\Delta^{14}\text{C}$ activities and stable carbon isotopic ($\delta^{13}\text{C}$) compositions of total lipid, THAA, TCHO and acid-insoluble organic fractions in sediments collected from two abyssal sites, one in the NE Pacific Ocean and one in the Southern Ocean. For the NE Pacific site, we report and compare the new results obtained from a different gravity core (65 cm) with those reported previously for a separate

core collected from the same site (station M, Wang et al., 1998). We also compared the $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ results from the NE Pacific Ocean sediment with the results obtained from a gravity core collected from the Southern Ocean. Distinct differences in sedimentary geochemistry, and $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ values among the organic fractions were found between the two cores and the processes which likely control the observed differences were discussed.

2. Methods

2.1. Study site

Sediment samples used in this study were collected from two abyssal sites: one in the NE Pacific Ocean and one in the Southern Ocean. The NE Pacific site (station M, $34^{\circ}50'\text{N}$, 123°W) is located 220 km west of Point Conception, CA. The water depth at station M is 4100 m and there is a strong southward-flowing California Current down to about 150-m depth in the region (Lynn and Simpson, 1987). The sediment at station M contained mainly silty clay. Strong seasonal variability in primary production with maximum organic fluxes in late spring and early fall has been observed in the region (Michaelsen et al., 1988; Smith et al., 1994). From 1989 to 1996, a time-series seasonal study was carried out at station M to determine the coupling of near-bottom organic carbon fluxes and benthic processes (Smith and Druffel, 1998). Our sampling at station M was in collaboration with K. Smith at the Scripps Institution of Oceanography.

The Southern Ocean site (54°S , 176°W) is in the South Pacific sector in the Antarctic Circumpolar Current region. Water depth is 5300 m at the station and sediment contained mainly fine clay minerals. We collected phytoplankton, zooplankton, and sediment samples for this study from the station during a cruise to study DOC and particulate organic carbon (POC) cycling in the Southern Ocean.

2.2. Sampling

A sediment core was collected from each site. At station M, NE Pacific site, a 2" diameter gravity core

was collected on the R/V New Horizon in April 1996. This was a separate core from that reported earlier by Wang et al. (1998). The sediment core was sectioned at 1-cm intervals in the top 10 cm, and at 2–5-cm intervals from 10 to 65 cm. All sections were stored in glass jars at -20°C within a few hours after collection. A 2"-diameter gravity core was collected from the Southern Ocean site on the R/V Melville in December 1995. The sediment core was sectioned at 0.5–1-cm intervals in the top 10 cm, and 2–5-cm intervals down to 120 cm and stored in glass jars at -20°C within a few hours after collection.

Plankton samples were also collected from the Southern Ocean. Phytoplankton was collected using a 33- μm net at the surface water (0–1 m). This mesh size is too large to collect picoplankton that might have been missed. Samples were filtered by gentle vacuum filtration onto pre-combusted quartz-fiber filters (Whatman Ultrapure, QM-A, 43-mm diameter; nominal pore size 1.0 μm) and frozen in glass jars at -20°C . Zooplankton was collected using a 335- μm mesh, meter-net towed at 25–100 m depth for 30 min/deployment and samples were stored in glass jars and frozen at -20°C after collection. All glass jars used were acid washed and baked at 550°C for 2 h.

2.3. Compound class extraction and isolation

We measured $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ of TOC and the THAA, TCHO, lipid, and acid-insoluble organic fractions. The method used to separate the organic fractions of plankton and sediments is described in detail in a previous paper (Wang et al., 1998). Briefly, samples were oven-dried at 50°C . Total lipid was first extracted using a 2:1 v/v mixture of methylene chloride/methanol (both of high purity, Burdick and Jackson) by ultrasonication. After lipid extraction, samples were divided into two portions for THAA and TCHO hydrolyses. For THAA, the samples were hydrolyzed with 6 N HCl (Ultrex pure, J.T. Baker) under N_2 at 100°C for 19 h and THAA were isolated using cation exchange column chromatography. After hydrolysis, organic material left in the solid was defined as the acid-insoluble fraction. For TCHO, samples were hydrolyzed with H_2SO_4 (98% Ultrex pure, J.T. Baker) at 100°C for 3

h. After neutralizing the sample with $\text{Ba}(\text{OH})_2$ and centrifuging to separate the resulting BaSO_4 , the TCHO fraction was isolated using mixed cation/anion column chromatography (Cowie and Hedges, 1984). Our previous study showed that the amino acids and total sugars accounted for $97 \pm 16\%$ and $94 \pm 12\%$ of the carbon isolated in the THAA and TCHO fractions, respectively, as measured by high pressure liquid chromatography for amino acids and spectrophotometrical detection of MBTH assay for sugars (Wang et al., 1998).

2.4. Sample combustion and isotope measurements

Portions of dried phytoplankton, zooplankton, and sediments were weighed directly into 13-mm pre-combusted (850°C) quartz tubes for TOC $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ measurements. All TOC and organic fraction samples were acidified in the combustion tubes with 1–2 ml 1% H_3PO_4 to remove residual carbonates. After adding pre-combusted CuO (50–100 mg) and Ag foil (5–10 mg), all samples were dried in vacuo and the tubes flame-sealed under vacuum and combusted at 850°C for 1 h according to standard techniques (Druffel et al., 1992). CO_2 volume was measured for the combusted samples and split into subsamples for isotope analyses (Wang et al., 1998).

The CO_2 subsamples for ^{14}C analyses were converted to graphite targets according to the method of Vogel et al. (1987). $^{14}\text{C}/^{13}\text{C}$ ratios were measured using accelerator mass spectrometry (AMS) at the Lawrence Livermore National Laboratories (LLNL) and radiocarbon values are reported as $\Delta^{14}\text{C}$ (the per mil deviation from the 'standard' activity of 19th century wood) as defined by Stuiver and Polach (1977) for geochemical samples without known age. CO_2 for $\delta^{13}\text{C}$ analyses was measured using a VG Micromass 602E isotope ratio mass spectrometer at the Woods Hole Oceanographic Institution with an overall uncertainty of $\pm 0.10\%$. All $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ values reported are corrected for blank CO_2 produced during the sample processing and combustion steps (Wang et al., 1998). TOC and TN contents of the samples were measured using a Carlo Erba 200 CHN analyzer with uncertainties of $\pm 8\%$ and $\pm 10\%$ of the mean for TOC and TN for replicate analyses of samples, respectively.

3. Results

3.1. TOC, TN, and C/N ratios

Results of TOC, TN, and C/N mole ratios measured for plankton and sediment cores are summarized in Table 1 and plotted in Fig. 1. Phytoplankton and zooplankton collected from the Southern Ocean had lower carbon contents (19–31%) than those values (40–50%) from the NE Pacific plankton (Table 1, Wang et al., 1998). In comparison, TN content of phytoplankton (3.2%) is higher and TN content of zooplankton (5.4%) is lower in the Southern Ocean (Table 1) than those values in phytoplankton (2.8%) and zooplankton (8.2%) from the NE Pacific (Wang et al., 1998).

In the NE Pacific sediment, TOC and TN contents ranged from 0.61–1.6% to 0.11–0.19% of dry weight, respectively. TOC content showed variations with depth where TN did not (Fig. 1a). For the Southern Ocean core, TOC, and TN contents were much lower, ranging from 0.03% to 0.25% for TOC and from 0.014% to 0.044% for TN. Both TOC and TN values decreased rapidly in the top 10 cm and then remained constant down to 120 cm (Fig. 1b). C/N mole ratios also showed large differences in the sediments between the two oceans. For the NE Pacific, C/N ratios were in the range of 6.5–10.3 and varied with depth (Fig. 1c). In comparison, the C/N ratios in the Southern Ocean core ranged from 2.1 to 8.5 and the values decreased rapidly in the top 10 cm and then remained constant at depth (Fig. 1c).

3.2. Distribution and abundance of organic fractions

The abundances of THAA, TCHO, lipid, and acid-insoluble fractions determined for the plankton and sediments are plotted in Fig. 2 for the two oceans. For comparison, the results for phytoplankton and zooplankton at station M were from our previous study (Wang et al., 1998). As shown in Fig. 2, THAA, TCHO, and lipid are the major organic compound classes contained in both phytoplankton and zooplankton collected from both NE Pacific and the Southern Ocean. They accounted for > 90% of the biomass C in the plankton. However, the abundance of the compound classes in plankton showed

some differences between the two oceans. The lipid fractions were more abundant in zooplankton (48%) than in phytoplankton (14%) and THAA fraction was more abundant (35%) in phytoplankton than that in zooplankton (25%) in the Southern Ocean compared with the values for the NE Pacific. These values, in general, are comparable with the values reported by Parsons et al. (1961) in which they showed that protein, carbohydrate, and lipids accounted for 40–60%, 20–40%, and 5–23% of biomass in phytoplankton.

In sediments, the three organic fractions only accounted for < 40% of TOC and uncharacterized acid-insoluble fraction was the dominant (43–57%) fraction of TOC in both oceans (Fig. 2). Among the three compound classes, THAA fraction was more abundant than TCHO and lipid fractions in the sediments of both oceans. In their recent study, Wakeham et al. (1997) also reported that 80% of TOC buried in the surface sediments in the central equatorial Pacific was uncharacterized. Sedimentary organic carbon dominated by the uncharacterized organic fraction in the deep sea indicates the extensive diagenetic alteration of surface produced organic matter during transformation from water column to sediments (Lee and Wakeham, 1988; Wakeham and Lee, 1989). More labile fractions (lipids, amino acids, carbohydrates) produced in the surface water are decomposed preferentially during particle sinking and the material being buried in the sediments become more refractory (acid-insoluble).

3.3. $\Delta^{14}\text{C}$ results

Values of $\Delta^{14}\text{C}$ in phytoplankton and zooplankton collected from the Southern Ocean were 22‰ and 21‰, respectively. These values are 35–60‰ lower than the $\Delta^{14}\text{C}$ values of plankton collected from the NE Pacific (Table 1, Wang et al., 1998). Values of $\Delta^{14}\text{C}$ of organic fractions separated from the Southern Ocean phytoplankton and zooplankton ranged from 1‰ to 21‰ (Table 2) and all of these values showed post-bomb $\Delta^{14}\text{C}$ signatures (> -160‰, Stuiver et al., 1983).

Values of $\Delta^{14}\text{C}$ in sediments also showed large differences between the two sites (Table 1, Fig. 3). In the NE Pacific sediment, $\Delta^{14}\text{C}$ of TOC ranged

Table 1

TOC, TN, C/N mole ratios, $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ measurements of TOC in plankton and sediment samples collected from the northeast Pacific Ocean and the Southern Ocean

Sample and depth	TOC (wt.%)	TN (wt.%)	C/N (mol)	UCID#	TOC	
					$\delta^{13}\text{C}$ (‰)	$\Delta^{14}\text{C}$ (‰)
<i>Northeast Pacific Ocean</i>						
Phytoplankton (1 m) ^a	40	2.8	16.7	1281	−18.3	59 ± 7
Zooplankton (85 m) ^a	50	8.2	7.1	1282	−21.8	81 ± 6
Sediment core (cm)						
0–1	1.3	0.17	8.9	1748	−21.6	−283 ± 4
1–2	1.3	0.18	8.4	1749	−21.7	−284 ± 4
3–4	1.2	0.17	8.2	1751	−21.8	−339 ± 4
7–8	1.2	0.14	10.0	1753	−22.0	−493 ± 3
9–10	1.6	0.18	10.3	1754	−21.8	−372 ± 4
12–14	1.3	0.19	8.0	1755	−21.7	−446 ± 3
16–18	1.1	0.17	7.6	1756	−21.6	−572 ± 3
20–22	1.4	0.16	10.2	1757	−21.7	−575 ± 3
26–28	0.85	0.13	7.6	1758	−22.2	−772 ± 2
30–35	0.77	0.11	8.2	1759	−22.4	−825 ± 2
35–40	0.61	0.11	6.5	1760	−22.2	−597 ± 3
40–45	1.2	0.15	9.3	1761	−21.5	−562 ± 3
45–50	1.4	0.16	10.2	1793	−22.2	−411 ± 4
50–55	1.4	0.17	9.6	1794	−21.8	−426 ± 4
55–60	1.1	0.16	8.0	1795	−21.8	−622 ± 3
60–65	1.1	n.d.	n.d.	1763	−21.9	−695 ± 3
<i>Southern Ocean</i>						
Phytoplankton (1 m)	19	3.2	6.9	1659	−23.9	22 ± 7
Zooplankton (25 m)	31	5.4	6.7	1660	−26.2	21 ± 6
Sediment core (cm)						
0–1	0.25	0.044	6.6	1646	−21.3	−454 ± 4
1–2	0.24	0.036	7.8	1647	−21.2	−510 ± 3
2.5–3	0.19	0.026	8.5	1648	−21.4	−662 ± 3
3–4	0.19	0.037	6.0	1649	−22.5	−711 ± 3
5–6	0.07	0.021	3.9	1650	−21.4	−895 ± 2
8–9	0.06	0.019	3.7	1651	−21.4	−949 ± 2
10–11	0.04	0.019	2.5	1652	−21.7	−976 ± 2
17–19	0.03	0.017	2.1	1653	−21.4	−994 ± 2
31–36	0.03	0.015	2.3	1654	−21.5	−993 ± 2
51–56	0.03	0.014	2.5	1655	−20.7	−997 ± 2
71–76	0.03	0.015	2.3	1656	−20.8	−987 ± 2
91–96	0.03	0.016	2.2	1657	−21.0	−1000 ± 2
116–120	n.d.	n.d.	n.d.	1658	−20.8	−1000 ± 2

TOC and TN (wt.%) were salt-corrected assuming a salinity of 35.00‰.

$\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ values were blank-corrected. The errors for $\Delta^{14}\text{C}$ are AMS counting statistical errors.

^aPhytoplankton and zooplankton data for the Northeast Pacific Ocean is from Wang et al. (1998) for comparison.

from −283‰ to −825‰ and the values decreased from the surface down to 35 cm and then increased to 50 cm before decreasing below that (Fig. 3a). As shown in Fig. 3a, $\Delta^{14}\text{C}$ values of TOC in the top 10 cm sediment of the gravity core from the NE Pacific

are similar to the values we measured previously for a separate push core from the same site (Wang et al., 1998) suggesting that there was no significant loss of the surface sediment during our gravity core sampling and recovery at station M. However, no such

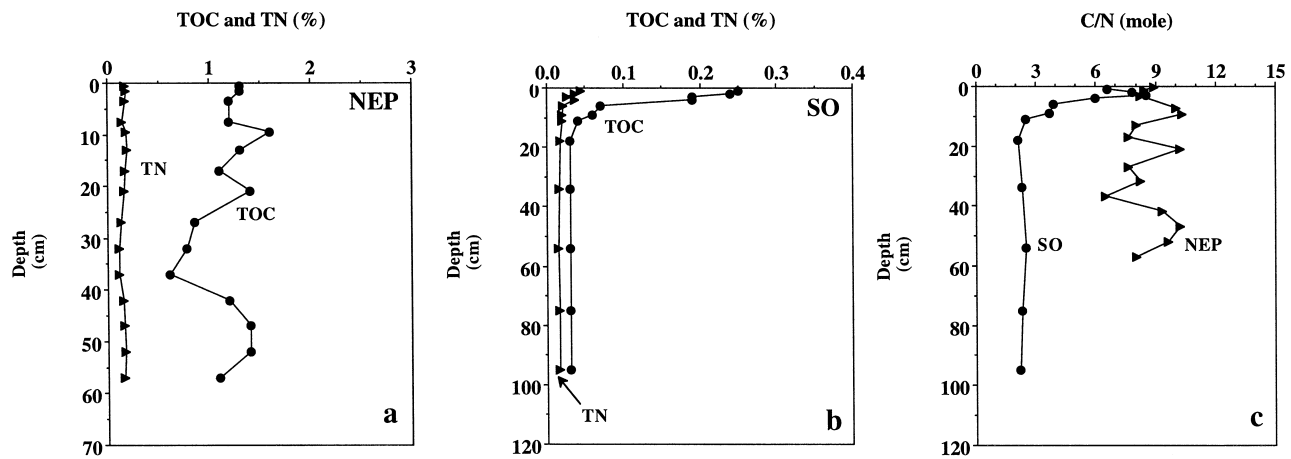


Fig. 1. Concentration profiles of TOC and TN (both as percentage of dry weight) in sediments of (a) station M, Northeast Pacific (NEP), and (b) Southern Ocean (SO), and (c) profiles of C/N mole ratios in both sediments.

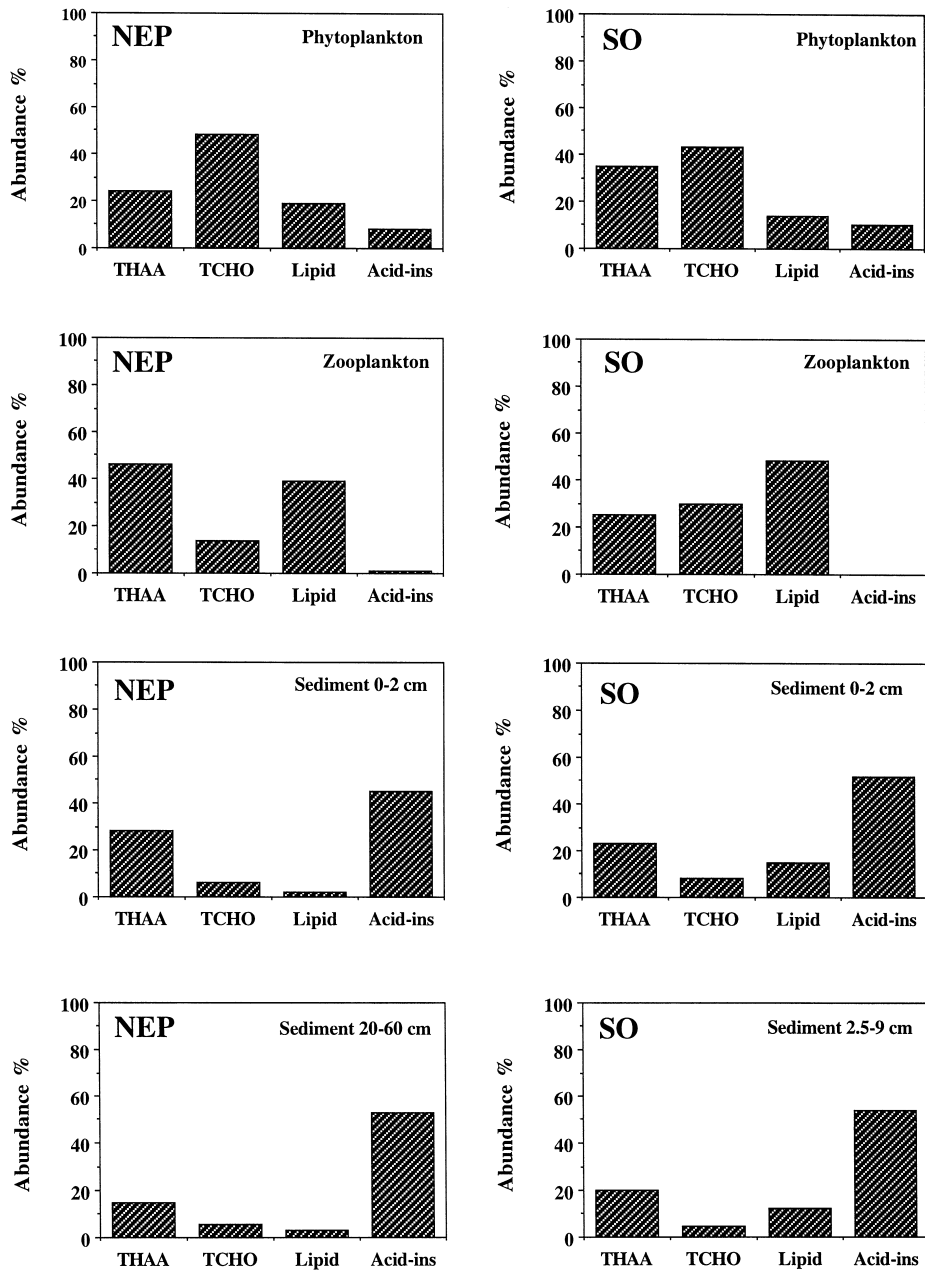


Fig. 2. A comparison of relative abundance (as percentage of TOC) of THAA, TCHO, lipid, and acid-insoluble organic fractions separated from phytoplankton, zooplankton, and sediments of station M, NEP and the SO. For comparison, phytoplankton and zooplankton data for NEP was from Wang et al. (1998).

comparison is available for the Southern Ocean core. In the Southern Ocean core, $\Delta^{14}\text{C}$ of TOC ranged

from -454‰ to -1000‰ , which are much lower than the $\Delta^{14}\text{C}$ values of TOC in the station M core.

Table 2
 $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ measurements of TOC, THAA, TCHO, lipid, and acid-insoluble fractions in samples collected from the northeast Pacific Ocean and the Southern Ocean

Sample and depth	TOC			THAA fraction			TCHO fraction			Lipid fraction			Acid-insoluble		
	UCID#	$\delta^{13}\text{C}$ (‰)	$\Delta^{14}\text{C}$ (‰)	UCID#	$\delta^{13}\text{C}$ (‰)	$\Delta^{14}\text{C}$ (‰)	UCID#	$\delta^{13}\text{C}$ (‰)	$\Delta^{14}\text{C}$ (‰)	UCID#	$\delta^{13}\text{C}$ (‰)	$\Delta^{14}\text{C}$ (‰)	UCID#	$\delta^{13}\text{C}$ (‰)	$\Delta^{14}\text{C}$ (‰)
<i>Northeast Pacific Ocean</i>															
Phytoplankton (1 m)	1281	-18.3	59 ± 7	1299	-18.2	53 ± 12	1308	-16.6	79 ± 11	1272	-21.1	80 ± 10	1290	-19.6	51 ± 15
Zooplankton (25 m)	1282	-21.8	81 ± 6	1300	-18.9	45 ± 11	1309	-17.5	n.d.	1273	-25.1	58 ± 8	1291	-24.1	n.d.
Sediment core (cm)															
0–2	1748, 1749	-21.7	-284 ± 8	1930	-20.5	-322 ± 4	2123	-18.4	-111 ± 5	1796	-24.3	-468 ± 4	1812	-23.4	-388 ± 4
3–4	1751	-21.8	-339 ± 4	1931	-17.5	-214 ± 5	2124	-17.7	-138 ± 5	1797	-23.5	-535 ± 3	1813	-23.0	-451 ± 3
7–8	1753	-22.0	-493 ± 3	1932	-19.6	-442 ± 3	2125	-18.8	-354 ± 4	2316	-23.8	-561 ± 3	1814	-22.8	-597 ± 3
12–14	1755	-21.7	-446 ± 3	1933	-22.3	-598 ± 2	lost			1799	-23.6	-551 ± 3	1815	-22.6	-472 ± 3
20–22	1757	-21.7	-575 ± 3	1934	-21.0	-251 ± 5	2127	-15.6	-487 ± 3	1800	-23.2	-711 ± 3	1816	-22.6	-656 ± 2
30–35	1759	-22.4	-825 ± 2	2020	-19.8	-540 ± 3	2128	-15.3	-673 ± 3	2011	-24.2	-756 ± 2	2024	-23.1	-833 ± 2
35–40	1760	-22.2	-597 ± 3	1935	-18.4	-369 ± 4	2129	-17.6	-258 ± 4	1801	-23.6	-545 ± 3	1817	-23.2	-493 ± 3
40–45	1761	-21.5	-562 ± 3	2021	-19.4	-379 ± 4	2130	-17.7	-215 ± 4	2012	-24.1	-684 ± 2	2025	-22.9	-620 ± 2
45–50	1793	-22.2	-411 ± 4	lost			2131	-17.3	-394 ± 3	2013	-24.9	-612 ± 2	2026	-23.3	-617 ± 2
50–55	1794	-21.8	-426 ± 4	1843	-19.0	-376 ± 3	2132	-17.6	-327 ± 4	1802	-23.5	-572 ± 3	1818	-22.7	-505 ± 3
60–65	1763	-21.9	-695 ± 3	2023	-19.2	-517 ± 3	lost			2014	-23.4	-696 ± 2	2027	-23.0	-652 ± 2
<i>Southern Ocean</i>															
Phytoplankton (1 m)	1659	-23.9	22 ± 7	1844	-21.7	11 ± 6	2117	-21.9	21 ± 6	1665	-27.1	lost	1807	-22.9	1 ± 6
Zooplankton (1 m)	1660	-26.2	21 ± 6	2318	-20.9	10 ± 5	2320	-20.5	lost	2317	-29.7	10 ± 6	2322	-26.1	18 ± 5
Sediment core (cm)															
0–1	1646	-21.3	-454 ± 4	lost			2119	-17.5	-160 ± 4	1667	-28.8	-542 ± 3	1808	-21.6	-554 ± 3
1–2	1647	-21.2	-510 ± 3	2017	-18.7	-444 ± 3	lost			1668	-27.3	-461 ± 5	1809	-21.2	-600 ± 3
2.5–4	1648, 1649	-22.0	-687 ± 6	2018	-22.3	-654 ± 2	2121	-16.0	-205 ± 11	1669	-29.0	-552 ± 3	1810	-21.3	-657 ± 2
4.5–9	1650, 1651	-21.4	-922 ± 4	2019	-21.5	-860 ± 2	2122	-20.9	lost	1670	-33.2	-679 ± 3	1811	-20.9	-937 ± 2

For comparison, phytoplankton and zooplankton data for the Northeast Pacific Ocean is from Wang et al. (1998). Values for $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ are blank-corrected and errors for $\Delta^{14}\text{C}$ are AMS counting statistical errors except for phytoplankton and zooplankton $\Delta^{14}\text{C}$ errors, which include both sample processing blanks and AMS counting statistical errors.

n.d.: Samples were either too small (< 0.1 mg C) for $\Delta^{14}\text{C}$ measurements or did not give any ion current during AMS analysis.

Duplicate measurements were made for 3 sediment samples and they agreed to within +/−1 and 50 per mil for $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$, respectively.

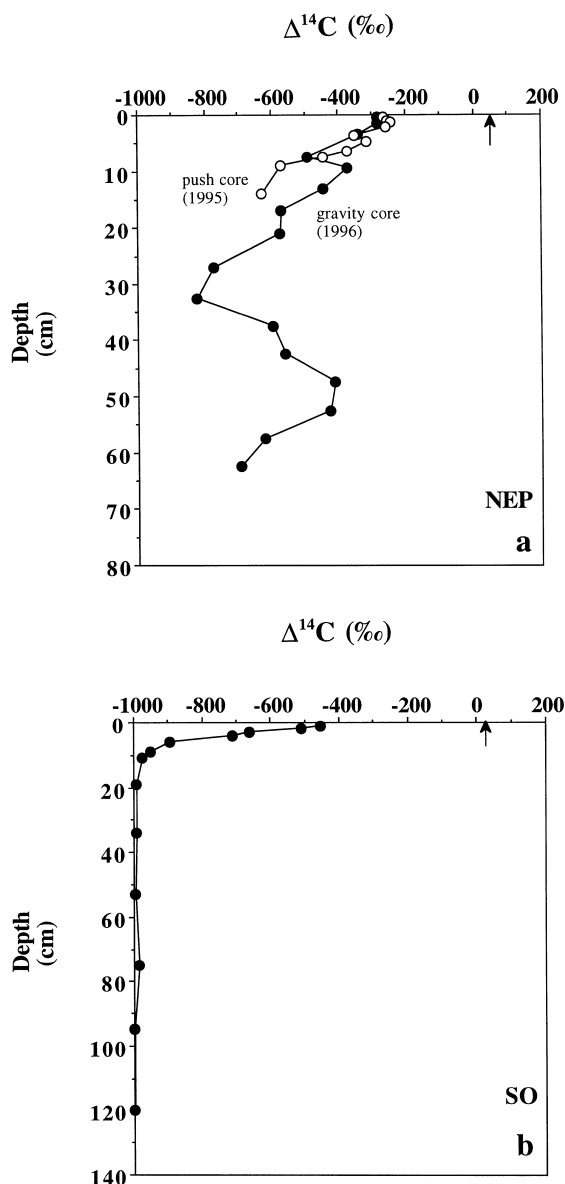


Fig. 3. $\Delta^{14}\text{C}$ profiles of TOC in sediments of (a) station M, NEP. Values from a separated push core (Wang et al., 1998) were also plotted for comparison, and (b) the SO. The arrow indicates the average value of $\Delta^{14}\text{C}$ measured for phytoplankton and zooplankton from the two oceans.

$\Delta^{14}\text{C}$ values of TOC in the Southern Ocean core decreased very rapidly in the top 10 cm and were devoid of ^{14}C (-1000‰) at greater sediment depths (Fig. 3b).

Values of $\Delta^{14}\text{C}$ of organic fractions separated from sediments also showed differences between the two oceans (Fig. 4). In the NE Pacific core, the lipid fraction exhibited lower $\Delta^{14}\text{C}$ signatures, ranging from -468‰ to -696‰ , than those of THAA (-214‰ to -598‰), and TCHO (-111‰ to -673‰) fractions (Fig. 4a). The acid-insoluble fractions had $\Delta^{14}\text{C}$ values close to the values of the lipid fractions. In general, $\Delta^{14}\text{C}$ profiles of all four frac-

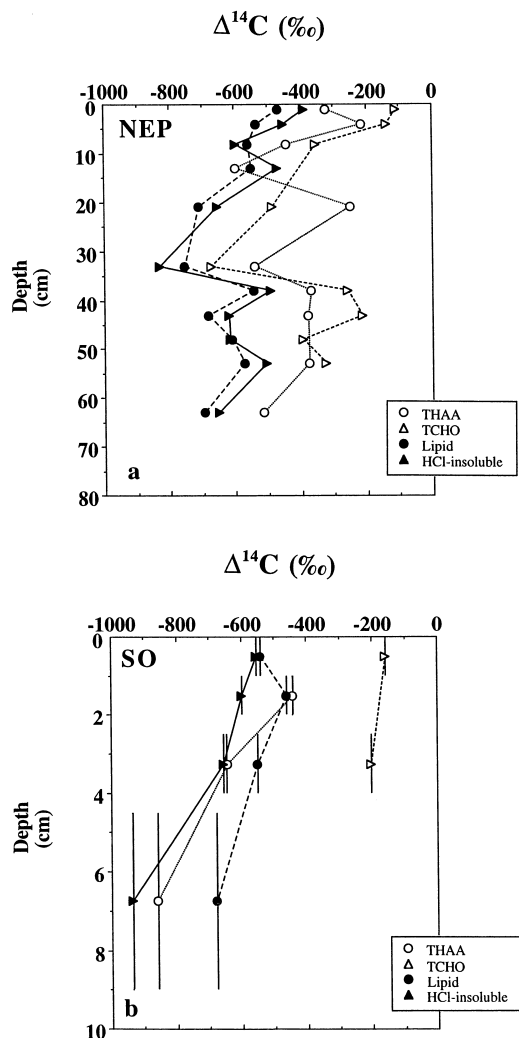


Fig. 4. $\Delta^{14}\text{C}$ profiles of THAA, TCHO, lipid and acid-insoluble organic fractions in sediments of (a) station M, NEP and (b) the SO. Note the change in depth scales between (a) and (b).

tions showed similar trends with depth in the sediment. For the Southern Ocean core, we only separated organic fractions from the top 9 cm due to the very low TOC contents in the deeper sediment. As shown in Fig. 4b, the TCHO fractions had higher $\Delta^{14}\text{C}$ values (-160‰ to -205‰) than the THAA, lipid, and acid-insoluble fractions. Unlike the NE Pacific core, the lipid fractions did not exhibit lower $\Delta^{14}\text{C}$ signatures than the other organic fractions in the sediment. In general, $\Delta^{14}\text{C}$ values of all organic fractions decreased with depth (Fig. 4b). At both sites, the TCHO $\Delta^{14}\text{C}$ values were significantly higher than those in the other organic fractions in the surface sediment (0–4 cm).

3.4. $\delta^{13}\text{C}$ results

$\delta^{13}\text{C}$ values of TOC in phytoplankton and zooplankton collected from the Southern Ocean were -23.9‰ and -26.2‰ , respectively (Table 1). These values were about 5‰ lower than those reported previously for the samples collected from the NE Pacific Ocean (Table 1, Wang et al., 1998). In both oceans, $\delta^{13}\text{C}$ values of zooplankton were about 3‰ lower than that of phytoplankton.

The $\delta^{13}\text{C}$ values of TOC in the sediment core from the NE Pacific were relatively constant with depth, ranging from -21.5‰ to -22.4‰ (Table 1). $\delta^{13}\text{C}$ values of TOC in the Southern Ocean core ranged from -20.7‰ to -22.5‰ and were also constant with depth (Table 1). The $\delta^{13}\text{C}$ values of TOC in sediments did not show significant differences as observed for the plankton between the two oceans.

$\delta^{13}\text{C}$ values measured for the organic fractions showed large variations (Fig. 5). For phytoplankton and zooplankton collected from the Southern Ocean, $\delta^{13}\text{C}$ values ranged from -21.7‰ to -27.1‰ and -20.5‰ to -29.7‰ , respectively. $\delta^{13}\text{C}$ values of lipid in phytoplankton and zooplankton were 6–7‰ lower than the values of THAA and TCHO fractions (Fig. 5b). In general, $\delta^{13}\text{C}$ values of THAA, TCHO and lipid fractions in phytoplankton and zooplankton in the Southern Ocean were 2–6‰ lower than those in samples collected from the NE Pacific. The variations of $\delta^{13}\text{C}$ among the organic fractions in plankton in the Southern Ocean were also larger overall

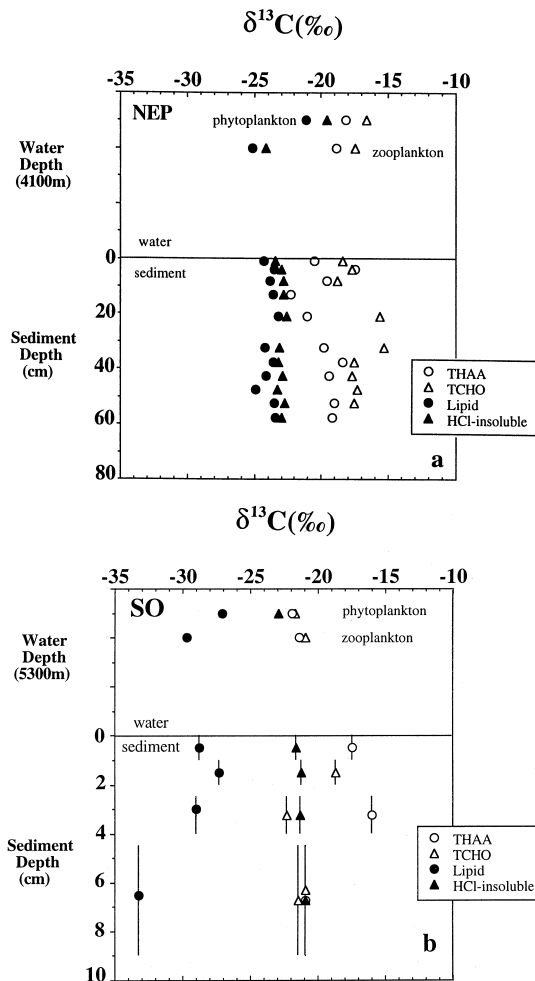


Fig. 5. $\delta^{13}\text{C}$ profiles of THAA, TCHO, lipid, and acid-insoluble fractions in the sediments of (a) station M, NEP, and (b) the SO. Values of $\delta^{13}\text{C}$ measured for the organic fractions in phytoplankton and zooplankton from the two oceans were also plotted for comparison.

than those in the NE Pacific plankton that we measured previously (Fig. 5a and Wang et al., 1998).

$\delta^{13}\text{C}$ values of organic fractions separated from sediments also showed large variations. In the NE Pacific sediment, the TCHO fractions had higher $\delta^{13}\text{C}$ values (-15.3‰ to -18.8‰) than THAA (-17.5‰ to -22.3‰), acid-insoluble (-22.6‰ to -23.4‰) and lipid (-23.2‰ to -24.9‰) fractions (Fig. 5a). $\delta^{13}\text{C}$ compositions in THAA and TCHO

fractions showed more variations with depth than those of lipid and acid-insoluble fractions. In the Southern Ocean core (Fig. 5b), THAA and TCHO fractions had higher $\delta^{13}\text{C}$ values ranging from -16.0‰ to -22.3‰ and decreased with depth. $\delta^{13}\text{C}$ values in the lipid fractions (-27.3‰ to -33.2‰) were more depleted than the acid-insoluble fractions, which had constant $\delta^{13}\text{C}$ values ranging from -20.9‰ to -21.6‰ .

4. Discussion

4.1. Sedimentary geochemical differences in the two oceans

TOC, TN, and C/N ratios in sediment reflect a combination of the sources, deposition and diagenetic stages of organic matter. TOC and TN in the NE Pacific sediment were 5–20 times higher than these in the Southern Ocean sediment, indicating that there was a more rapid and higher organic matter deposition and preservation in the sediments at the NE Pacific site. This is also supported by the sedimentation rates calculated from our sedimentary TOC ^{14}C ages and $\delta^{13}\text{C}$ results as described in later sections. The fluctuations of TOC content with depth in the sediment in the NE Pacific (Fig. 1a) may reflect the variations in organic production and deposition in the past. Based on carbon and oxygen isotopic measurements in sediments collected across the California Current in the North Pacific, Lyle et al. (1992) reported that during the last glacial maximum, both primary production and organic carbon deposition rate were doubled in the region. However, as described later, our $\Delta^{14}\text{C}$ results do not support this possibility for the observed TOC increase in the core. The observed TOC variations with depth in the core therefore, could be affected by strong bioturbation in the sediment as reported for station M (Reimers et al., 1992; Cai et al., 1995). In comparison, the rapid decreases of both TOC and TN in the sediment of the Southern Ocean indicate that decomposition of organic matter likely took place in the upper 10 cm and the organic matter preserved in the deep sediment of the Southern Ocean is much more refractory. The rapid decrease of C/N ratios with depth in the

Southern Ocean sediment compared to the NE Pacific sediment was likely due to the large fraction of ammonium sorbed onto clay minerals, which reduce the observed C/N ratios as reported for the sediments in the Central Pacific (Müller, 1977). This was well demonstrated in Fig. 6; a significant fraction of inorganic nitrogen (the intercept of TN% at TOC% zero) was present in both sediments. Since the TOC in the Southern Ocean sediment was much lower (Fig. 6b) compared to the values of the NE Pacific sediment (Fig. 6a), the influence of C/N ratio by sedimentary inorganic nitrogen was much greater for the Southern Ocean sediment.

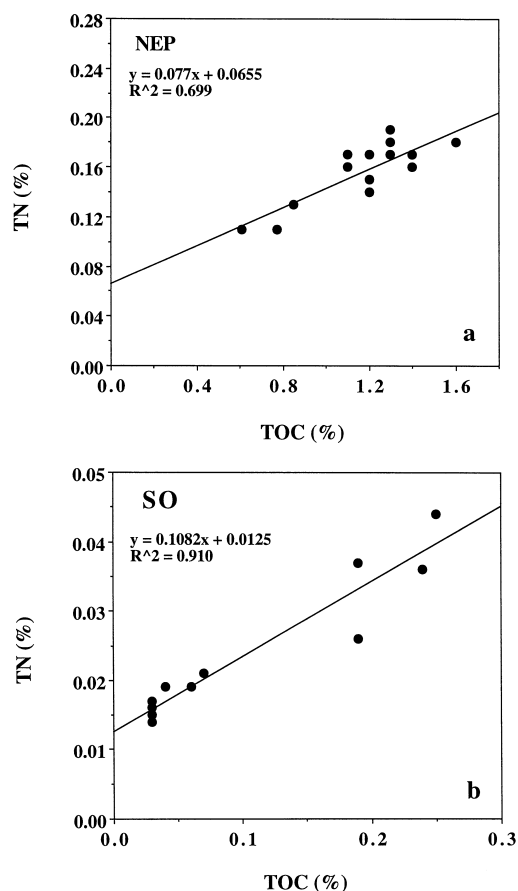


Fig. 6. Plots of TN (%) vs. TOC (%) for the sediments cores collected from (a) station M, NEP and (b) the SO. Lines are linear regression fits to the data.

4.2. ^{14}C sedimentation rate

Due to its long half life (5730 years) and assuming a constant organic C deposition rate to the sediments in the past, we calculated the sedimentation rate using ^{14}C ages of sediment TOC for the two oceans. For the NE Pacific, we used ^{14}C ages from the depth of 10–35 cm to avoid the bioturbation effect. For the Southern Ocean core, we used $\Delta^{14}\text{C}$ values in the uppermost 20-cm where steady state ^{14}C decay appeared to have been occurring. As shown in Fig. 7, significant linear relationships ($r^2 = 0.96\text{--}0.98$) were obtained for both sites. The calculated sedimentation rate for the NE Pacific site is

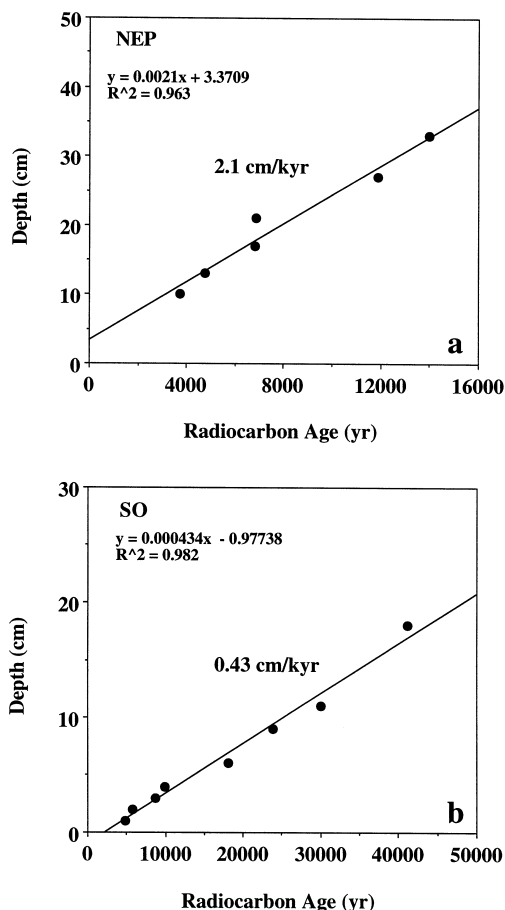


Fig. 7. Plots of radiocarbon age (year) of TOC vs. depth (cm) for the sediment cores collected from (a) station M, NEP and (b) the SO. The slope of the line taken as sedimentation rate was 2.1 cm/kyr for NEP and 0.434 cm/kyr for SO, respectively.

2.1 cm/kyr, about five times higher than the sedimentation rate of 0.43 cm/kyr obtained for the Southern Ocean site. This difference in sedimentation rate supports our hypothesis above that variations in organic carbon deposition to the sediments is likely the major controlling factor for the differences in TOC and TN contents and carbon isotope signatures observed in the sediments between the two oceans.

Our study site in the Southern Ocean is in the region of Antarctic open water where water column stability and primary production are both low compared to the Antarctic coastal regions (US Joint Global Ocean Flux Study — Southern Ocean Process Study, 1992). In general, the average primary production in Antarctic open water ($16 \text{ gC m}^{-2} \text{ yr}^{-1}$) is much lower than the value ($55 \text{ gC m}^{-2} \text{ yr}^{-1}$) in the NE Pacific (Smith et al., 1992). Evidence for the difference in organic deposition to sediments of the two oceans also came from sediment trap studies conducted in the two oceans. Based on their 5-year time-series sediment traps studies, Baldwin et al. (1998) reported that the mean annual flux at 3500 m water depth at station M, NE Pacific ranged from 45 to $83 \text{ mg m}^{-2} \text{ day}^{-1}$. This is much higher than the mean annual flux values of 22 and $1.1 \text{ mg m}^{-2} \text{ day}^{-1}$ measured by sediment trap at 2700 and 900 m water depths in the Southern Ocean (Honjo, 1996; Fisher et al., 1988). Considering a water depth of 5300 m at our Southern Ocean station, the particle flux to the deep water and surface sediment has to be lower than that at NE Pacific. There also could have been scouring of sediment by bottom currents at our location, which would explain the low $\Delta^{14}\text{C}$ values in the surface sediment; however, we presently have no evidence to support or refute this possibility.

Our calculated ^{14}C sedimentation rate for the NE Pacific core, however, could not explain the high $\Delta^{14}\text{C}$ values measured in the deeper sediment (Fig. 3). It is not clear why a fraction of much 'younger' organic matter (-400‰ to -800‰) was preserved between 35 and 60 cm depth in the sediment. As discussed above, if the high TOC content in this depth range reflects the high organic matter input during the glacial period, the age of the TOC at this depth should correspond to the age of 16,000–28,000 years based on the sedimentation rate rather than

4100 to 12,900 ^{14}C years. It is possible that the sedimentation rate at station M had varied greatly with time and organic deposition was affected by variations of marine and terrestrial fluxes in the past as observed in the sediments collected across the California Current transect (Lyle et al., 1992). It is also possible that a ‘younger’ organic C source (e.g., dead animal) or recent bioturbation (worm activity) could have been active at this depth of the core. Williams et al. (1978) and Druffel et al. (1984) reported that for sediments collected from the central North Pacific Ocean, significant $\Delta^{14}\text{C}$ values of organic matter were detected below the sediment mixed layer where all carbon should have $\Delta^{14}\text{C}$ values of $\sim -1000\text{‰}$. They suggested that the major mechanism for injecting the recent carbon to the deeper sediment was burrowing by large worms.

4.3. Comparison of $\Delta^{14}\text{C}$ signatures in sediments of the two oceans

As discussed above, the differences in $\Delta^{14}\text{C}$ of TOC and of organic C fractions in sediments from the two sites are affected by the differences in source, deposition rate, and diagenetic stage of organic matter in the sediments of the two oceans. The ‘old’ $\Delta^{14}\text{C}$ values (-284‰ to -454‰) measured for TOC in the surface sediments at both NE Pacific and the Southern Ocean indicate that a significant fraction of the surface sedimentary organic matter was from ‘old’ carbon inputs. Some of the ‘old’ organic C in surface sediments could be contributed from transport of terrestrial and fossil sources and reworked marine carbon source as well. Using $\Delta^{14}\text{C}$ measurements of individual organic compounds, Eglinton et al. (1997) found that organic matter preserved in the surface 2–4 cm sediment in the Arabian Sea reflects very different C sources with $\Delta^{14}\text{C}$ values ranged from -33‰ to -724‰ . The ‘old’ *n*-alkanes (-594‰ to -724‰) in the sediment were mainly from higher plants and fossil carbon inputs. Comparing the values of $\Delta^{14}\text{C}$ of TOC in the surface (0–2 cm) sediment, TOC in the Southern Ocean sediment was about 2600 ^{14}C years ‘older’ than TOC in the NE Pacific station M surface sediment. The ‘old’ TOC in the Southern Ocean surface sediment suggests that organic matter de-

posited to the sediment was much more refractory and contained lower amounts of labile (surface produced) organic carbon.

The rapid decrease of $\Delta^{14}\text{C}$ of TOC in the Southern Ocean core may indicate that bioturbation in the sediment was not strong and organic matter deposited to the surface sediment remineralized and decayed away rapidly in the upper 10 cm depth. Based on the profiles of ^{210}Pb and ^{14}C measured in the sediments collected from Antarctic abyssal and continental margin regions, DeMaster et al. (1991) reported that bioturbation was negligible. For the Southern Ocean site, however, we do not know whether bottom currents had affected the organic matter deposited in the surface sediment and influenced the observed $\Delta^{14}\text{C}$ profile. It is clear that the higher $\Delta^{14}\text{C}$ values of TOC in NE Pacific sediment indicate that a significant amount of labile organic matter (THAA and TCHO) was deposited and preserved in the sediment with depth.

The differences of $\Delta^{14}\text{C}$ values among the organic fractions in the sediments between the two oceans could also be explained by the differences in source, deposition, and decomposition stages of organic matter. As discussed above, higher sedimentation rate of organic matter at the NE Pacific site resulted in higher TOC content in the sediments and a significant fraction of ‘young’ labile organic matter (THAA, TCHO) preserved with depth. These labile organic compounds could be adsorbed strongly onto particle surfaces, which would slow down their rates of degradation (Henrichs and Sugai, 1993; Keil et al., 1994; Wang and Lee, 1995). In comparison, organic matter deposited and preserved in the Southern Ocean sediments was extensively degraded and a small ‘young’ organic fraction (TCHO) was present in the upper few centimeter (Fig. 4b). At both sites, the younger than expected TCHO fraction in the surface sediments is surprising. In the Southern Ocean surface sediment (0–4 cm), TCHO fraction had ^{14}C ages of 1400–1800 years. If these compound classes were all produced during photosynthesis in surface water and deposited to the sediment at the same time, then they should all have similar ^{14}C ages at the same depth in the sediment. It is not clear why such ‘young’ TCHO fraction was preserved in the sediments. In her study, Aluwihare (1999) found that carbohydrate (monosaccharide) isolated from DOC

in the deep northeast Pacific (1000 m) had a post-bomb $\Delta^{14}\text{C}$ value ($> -50\text{‰}$) which is much higher than the value of bulk DOC (-556‰) measured at the same depth from the same site (Bauer et al., 1998). It seems that carbohydrates in the ocean may be controlled by different biogeochemical processes, which require further study.

The explanation for the 'old' lipid fraction in station M sediments (Fig. 4a) is also not clear. It appears that most of the labile lipids were decomposed preferentially in the water column (Wakeham and Canuel, 1988; Wakeham et al., 1997) and in sediments (Sun and Wakeham, 1994). Studies by Volkman et al. (1983) and Wakeham et al. (1984) on the coast of Peru, the North Atlantic, and the North Pacific have shown that more insoluble and hydrophobic components, consisting of storage lipids and membrane lipids, were more likely to survive degradation during sinking of POM and become incorporated into sediments from the coast of Peru and the North Atlantic and North Pacific. The 'old' lipid fraction preserved in the sediments may reflect different C sources to this pool. Bacterial utilization of bulk DOC in the deep water ($\Delta^{14}\text{C} = -549 \pm 10\text{‰}$ ($n = 21$) for DOC measured at 1600–4050 m depths at station M, Bauer et al., 1998) and in sediment and subsequent incorporation of that carbon into bacterial membrane lipids could contribute 'old' carbon to the lipid pool. This could also be true for the Southern Ocean sediments (Fig. 4b). The relatively constant $\Delta^{14}\text{C}$ values of the lipid fractions in the surface sediment (0–9 cm) may suggest that much of the lipid carbon was from heterotrophic synthesis and bacterial incorporation of the deep water or pore water DOC into the sediment ($\Delta^{14}\text{C}$ of DOC in the deep water of Southern Ocean is $\sim -500\text{‰}$, Druffel and Bauer, 2000). In their biomarker study, Dachs et al. (1998) found that the lipids in sinking particles collected in the Alboran Sea had significant contribution from bacterial inputs and the composition was largely affected by bacterial activities. More recently, Cherrier et al. (1999) reported that $\Delta^{14}\text{C}$ measured in bacterial nucleic acids isolated from the surface water at station M in the NE Pacific was higher than the values of DOC but lower than that of dissolved inorganic carbon (DIC) and suspended POC. They suggest that bacteria in the surface water at station M utilize both modern

and older DOC as C sources. We expect that in the deep water and sediment, bacterial assimilation of old DOC could be more significant.

4.4. Comparison of $\delta^{13}\text{C}$ signatures in plankton and sediments of the two oceans

Carbon isotopic fractionations among organic compound classes in phytoplankton has been well-recognized (Abelson and Hoering, 1961; De Niro and Epstein, 1977; Descolas-Gros and Fontugne, 1990; Fischer, 1991). During photosynthesis, phytoplankton fix dissolved inorganic C (DIC) in the surface water into organic biomass C by enzymatic carboxylation reactions (Descolas-Gros and Fontugne, 1990; Fogel and Cifuentes, 1993; Goericke et al., 1993). Environmental factors such as water temperature and light intensity also play important roles in $\delta^{13}\text{C}$ composition of phytoplankton in the ocean (Sackett, 1991). Studies have found that a negative relationship generally exists between $\delta^{13}\text{C}$ of phytoplankton and CO_2 concentrations in seawater (Fontugne and Duplessy, 1978, 1981; Rau et al., 1982, 1989; Francois et al., 1993).

Phytoplankton and zooplankton collected from the surface Southern Ocean waters (SST = 8°C) were 5‰ lower in $\delta^{13}\text{C}$ compared to the samples collected from the warm regions where $p\text{CO}_2$ concentrations were lower. Wada et al. (1987) have suggested that the low $\delta^{13}\text{C}$ compositions measured for Antarctic phytoplankton were likely due to the high $p\text{CO}_2$ in the surface water and slow growth rates under low light intensities. This trend was also found in our samples. The $\delta^{13}\text{C}$ values (-23.9‰ , -26.2‰) we measured for the Southern Ocean plankton are in good agreement with the values (-23‰ to -27‰) reported for the diatom *Thalassiosira* spp. collected in the Atlantic sector of the Southern Ocean. The lower $\delta^{13}\text{C}$ values (by 3‰) in zooplankton relative to phytoplankton in both oceans is likely due to the higher lipid content of zooplankton (Fig. 2). It has been recognized that lipids are more depleted in $\delta^{13}\text{C}$ than amino acids and carbohydrates during biosynthetic pathways (Abelson and Hoering, 1961; De Niro and Epstein, 1977; Monson and Hayes, 1982).

$\delta^{13}\text{C}$ signatures in sedimentary organic matter reflect a variety of controlling factors such as the

organic carbon inputs, the carbon source utilized, biosynthetic and metabolic effects, and heterotrophic fractionation (Hayes, 1993). In spite of the differences in $\delta^{13}\text{C}$ values of phytoplankton and zooplankton in the two oceans, $\delta^{13}\text{C}$ values of TOC in sediments were the same. $\delta^{13}\text{C}$ of TOC in the Southern Ocean sediment is 2–5‰ higher than those values in the plankton. The loss of labile organic fractions during organic decomposition will cause the shift of $\delta^{13}\text{C}$ between surface plankton and sedimentary TOC. Preferential decomposition of lipids during particle sinking as observed in the ocean (Wakeham et al., 1984; Wakeham and Canuel, 1988; Wakeham et al., 1997) will also result in $\delta^{13}\text{C}$ enrichment in sediment in both oceans. In addition to the differences in organic degradation, Fischer (1991) reported that shorter food chains and different types of bacteria reworking the deposited organic carbon could also cause the isotope shift between POC and organic C in sediments. The heterotrophic effect on the carbon isotope composition of organic matter in marine sediments is still not well understood and needs to be studied further.

5. Summary

The data presented in this paper reinforce results from our previous studies indicating that distinct differences in $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ exist among the organic compound classes of total lipid, THAA, and TCHO in marine sediments. Variations in organic carbon sources, despite the uncertainty in source inputs to these sedimentary regimes, primary production, sedimentation, decomposition, and biosynthesis of organic matter during early diagenesis in sediments, are major processes that contribute to the observed $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ differences among the compound classes in the sediments of the two abyssal sites we studied. The higher organic matter with relatively ‘young’ $\Delta^{14}\text{C}$ signatures in the NE Pacific sediment indicates that a significant amount of labile organic matter (THAA, TCHO) was preserved in the sediment to greater depth than expected, due to the higher organic sedimentation rate and perhaps a subsurface bioturbation effect. Adsorption of the compounds onto sediment particles may play an important role in preservation of the labile organic matter

in the sediment. The Southern Ocean site, on the other hand, had much lower organic carbon contents with ‘old’ $\Delta^{14}\text{C}$ signatures indicating the extensively degraded and refractory nature of the organic matter preserved in the sediment. In both sediments, the poorly characterized insoluble fraction represents not only the most abundant organic fraction, but also dominates the carbon isotopic signatures of sedimentary TOC. The chemical composition and formation of this fraction certainly needs to be carefully studied in the future.

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References

- Abelson, P.H., Hoering, T.C., 1961. Carbon isotope fractionation in formation of amino acids by photosynthetic organisms. *Proc. Natl. Acad. Sci.* 47, 623–632.
- Aluwihare, L., 1999. High molecular weight (HMW) dissolved organic matter (DOM) in seawater: Chemical structure, sources and cycling. PhD Dissertation, MIT/WHOI Joint Program, 224 pp.
- Baldwin, R.J., Glatts, R.C., Smith, K.L., 1998. Particulate matter fluxes into the benthic boundary layer at a long time-series

- station in the abyssal NE Pacific: composition and fluxes. *Deep-Sea Res.* 45, 643–665.
- Bauer, J.E., Druffel, E.R.M., Williams, P.M., Wolgast, D.M., Griffin, S., 1998. Inter- and Intra-annual variability in isotopic (^{14}C and ^{13}C) signatures of dissolved organic carbon in the eastern North Pacific Ocean. *J. Geophys. Res.* 103, 2867–2882.
- Cai, W.J., Reimers, C.E., Shaw, T., 1995. Microelectrode studies of organic carbon degradation and calcite dissolution at a California Continental rise site. *Geochim. Cosmochim. Acta* 59, 497–511.
- Cherrier, J., Bauer, J.E., Druffel, E.R.M., Coffin, R.B., Chanton, J.P., 1999. Radiocarbon in marine bacteria: evidence for the ages of assimilated carbon. *Limnol. Oceanogr.* 44, 730–736.
- Cowie, G.L., Hedges, J.I., 1984. Determination of neutral sugars in plankton, sediments, and wood by capillary gas chromatography of equilibrated isomeric mixtures. *Anal. Chem.* 56, 504–510.
- Dachs, J., Bayona, J.M., Fowler, S.W., Miquel, J., Albaiges, J., 1998. Evidence for cyanobacterial inputs and heterotrophic alteration of lipids in sinking particles in the Alboran Sea (SW Mediterranean). *Mar. Chem.* 60, 189–201.
- DeMaster, D.J., Nelson, T.M., Harden, S.L., Nittrouer, C.A., 1991. The cycling and accumulation of biogenic silica and organic carbon in Antarctic deep-sea and continental margin environments. *Mar. Chem.* 35, 489–502.
- De Niro, M.J., Epstein, S., 1977. Mechanism of carbon isotope fractionation associated with lipid synthesis. *Science* 197, 261–263.
- Descolas-Gros, C., Fontugne, M., 1990. Stable carbon isotope fractionation by marine phytoplankton during photosynthesis. *Plant, Cell Environ.* 13, 207–218.
- Druffel, E.R.M., Bauer, J.E., 2000. Radiocarbon in Southern Ocean dissolved and particulate organic carbon. *Geophys. Res. Lett.* 27, 1495–1498.
- Druffel, E.R.M., Williams, P.M., 1990. Identification of a deep source of particulate organic carbon using bomb ^{14}C . *Nature* 347, 172–174.
- Druffel, E.R.M., Williams, P.M., 1992. Importance of isotope measurements in marine organic geochemistry. *Mar. Chem.* 39, 209–215.
- Druffel, E.R.M., Williams, P.M., Livingston, H.D., Koide, M., 1984. Variability of natural and bomb-produced radionuclide distributions in abyssal red clay sediments. *Earth Planet. Sci. Lett.* 71, 205–214.
- Druffel, E.R.M., Williams, P.M., Bauer, J.E., Ertel, J.R., 1992. Cycling of dissolved and particulate organic matter in the open ocean. *J. Geophys. Res.* 97, 15639–15659.
- Druffel, E.R.M., Griffin, S.M., Bauer, J.E., Wolgast, D., Wang, X.-C., 1998. Distribution of particulate organic carbon and radiocarbon in the water column from the upper slope to the abyssal NE Pacific Ocean. *Deep-Sea Res.* 45, 667–687.
- Eglinton, T.I., Benitez-Nelson, B.C., Pearson, A., McNichol, A.P., Bauer, J.E., Druffel, E.R.M., 1997. Variability in radiocarbon ages of individual organic compounds from marine sediments. *Science* 277, 796–799.
- Emerson, S., Hedges, J.I., 1988. Processes controlling the organic carbon content of open ocean sediments. *Paleoceanography* 3, 621–634.
- Fischer, G., 1991. Stable carbon isotope ratios of plankton carbon and sinking organic matter from the Atlantic sector of the Southern Ocean. *Mar. Chem.* 35, 581–596.
- Fisher, G., Fuetterer, D., Gersonde, R., Honjo, S., Ostermann, D.R., Wefer, G., 1988. Seasonal variability of particle flux in the Weddell Sea and its relation to ice cover. *Nature* 335, 426–428.
- Fogel, M.L., Cifuentes, L.A., 1993. Isotope fractionation during primary production. In: Engel, M.H., Macko, S.A. (Eds.), *Organic Geochemistry: Principles and Applications*. Plenum, New York, pp. 73–100.
- Fontugne, M.R., Duplessy, J.-C., 1978. Carbon isotope ratio of marine plankton related to surface water masses. *Earth Planet. Sci. Lett.* 41, 365–371.
- Fontugne, M.R., Duplessy, J.-C., 1981. Carbon isotopic fractionation by marine plankton in the temperature range -1 to 31°C . *Oceanol. Acta* 4, 85–90.
- Francois, R., Altabet, M.A., Goericke, R., McCorkle, D.C., Brunet, C., Poisson, A., 1993. Changes in the $\delta^{13}\text{C}$ of surface water particulate organic matter across the subtropical convergence in the SW Indian Ocean. *Global Biogeochem. Cycles* 7, 627–644.
- Goericke, R., Montoya, J.P., Fry, B., 1993. Physiology of isotope fractionation in algae and cyanobacteria. In: Lajtha, K., Michener, B. (Eds.), *Stable Isotope in Ecology*. Academic Press, New York.
- Hayes, J.M., 1993. Factors controlling ^{13}C contents of sedimentary organic compounds: principles and evidence. *Mar. Geol.* 113, 111–125.
- Henrichs, S.M., Sugai, S.F., 1993. Adsorption of amino acids and glucose by sediments of Resurrection Bay (Alaska): functional group effects. *Geochim. Cosmochim. Acta* 57, 823–835.
- Honjo, S., 1996. Fluxes of particles to the interior of the open ocean. In: Ittekkot, V., Schafer, P., Honjo, S., Depetris, P.J. (Eds.), *Particle Flux in the Ocean*. Wiley, pp. 91–154, SCOPE.
- Keil, R.G., Montlucon, D.B., Prahl, F.G., Hedges, J.I., 1994. Sorption preservation of labile organic matter in marine sediments. *Nature* 370, 549–552.
- Lee, C., Wakeham, S.G., 1988. Organic matter in seawater: biogeochemical processes. In: Riley, J.P. (Ed.), *Chemical Oceanography* vol. 9. Academic Press, pp. 1–51.
- Lyle, M., Zahn, R., Prahl, F., Dymond, J., Collier, R., Pisias, N., Suess, E., 1992. Paleoproductivity and carbon burial across the California Current: the multitracers transect, 42°N . *Paleoceanography* 7, 251–272.
- Lynn, R.J., Simpson, J.J., 1987. The California Current System: the seasonal variability of its physical characteristics. *J. Geophys. Res.* 92, 12,947–12,966.
- Michaelsen, J., Zhang, X., Smith, R.C., 1988. Variability of pigment biomass in the California Current System as determined by satellite imagery: 2. Temporal variability. *J. Geophys. Res.* 93, 10,883–10,896.
- Monson, K.D., Hayes, J.M., 1982. Carbon isotopic fractionation in the biosynthesis of bacterial fatty acids: ozonolysis of

- unsaturated fatty acids as a means of determining the intramolecular distribution of carbon isotopes. *Geochim. Cosmochim. Acta* 46, 139–149.
- Muller, P.J., 1977. C/N ratios in Pacific deep-sea sediments: effect of inorganic ammonium and organic nitrogen compounds sorbed by clays. *Geochim. Cosmochim. Acta* 41, 765–776.
- Parsons, T.R., Stephens, K., Strickland, J.D.H., 1961. On the chemical composition of eleven species of marine phytoplankters. *J. Fish. Res. Board Can.* 18, 1001–1016.
- Rau, G.H., Sweeney, R.E., Kaplan, I.R., 1982. Plankton C-13:C-12 ratio changes with latitude: differences between northern and southern oceans. *Deep-Sea Res.* 29, 1035–1039.
- Rau, G.H., Takahashi, T., Des Marais, D.J., 1989. Latitudinal variations in plankton $\delta^{13}\text{C}$: implications for CO_2 and productivity in past oceans. *Nature* 341, 516–518.
- Reimers, C.E., Jahnke, R.A., McCorkle, D.C., 1992. Carbon fluxes and burial rates over the continental slope and rise off central California with implications for the global carbon cycle. *Global Biogeochem. Cycles* 6, 199–224.
- Sackett, W.M., 1991. A history of the $\delta^{13}\text{C}$ composition of oceanic plankton. *Mar. Chem.* 34, 153–156.
- Smith, K.L., Druffel, E.R.M., 1998. Long time-series monitoring of an abyssal site in the NE Pacific: an introduction. *Deep-Sea Res.* 45, 573–586.
- Smith, W., Nelson, D., DeMaster, D., 1992. Major scientific goals for a US JGOFS study in the Southern Ocean, characteristics of a comprehensive science plan and logistical considerations. US JGOFS Planning Report 16, 104–109.
- Smith, K.L., Kaufmann, R.S., Baldwin, R.J., 1994. Coupling of near-bottom pelagic and benthic processes at abyssal depths in the eastern North Pacific Ocean. *Limnol. Oceanogr.* 39, 1101–1118.
- Stuiver, M., Polach, H.A., 1977. Discussion: reporting of ^{14}C data. *Radiocarbon* 19, 355–363.
- Stuiver, M., Quay, P.D., Ostlund, H.G., 1983. Abyssal water carbon-14 distribution and the age of the world oceans. *Science* 219, 849–854.
- Sun, M.Y., Wakeham, S.G., 1994. Molecular evidence for degradation and preservation of organic matter in the anoxic Black Sea Basin. *Geochim. Cosmochim. Acta* 58, 3395–3406.
- US Joint Global Ocean Flux Study — Southern Ocean Process Study, 1992. US JGOFS Planning Report, No. 16.
- Vogel, J., Nelson, D., Southon, J., 1987. ^{14}C background level in an accelerator mass spectrometry system. *Radiocarbon* 29, 323–333.
- Volkman, J.K., Farrington, J.W., Gagosian, R.B., Wakeham, S.G., 1983. Lipid composition of coastal marine sediments from the Peru upwelling region. In: Bioroy, M. (Ed.), *Advances in Organic Geochemistry 1981*. Wiley, pp. 228–240.
- Wada, E., Terazaki, M., Kabaya, Y., Nemoto, T. et al., 1987. ^{15}N and ^{13}C abundances in the Antarctic Ocean with emphasis on the biochemical structure of the food web. *Deep-Sea Res.* 34, 829–841.
- Wakeham, S.G., Canuel, E.A., 1988. Organic geochemistry of particulate matter in the eastern tropical North Pacific Ocean: implications for particle dynamics. *J. Mar. Res.* 46, 183–213.
- Wakeham, S.G., Lee, C., 1989. Organic geochemistry of particulate matter in the ocean: the role of particles in oceanic sedimentary cycles. *Org. Geochem.* 14, 83–96.
- Wakeham, S.G., Lee, C., Farrington, J.W., Gagosian, R.B., 1984. Biogeochemistry of particulate organic matter in the oceans: results from sediment trap experiments. *Deep-Sea Res.* 31, 509–528.
- Wakeham, S.G., Lee, C., Hedges, J.I., Hernes, P.J., Peterson, M.L., 1997. Molecular indicators of diagenetic status in marine organic matter. *Geochim. Cosmochim. Acta* 61, 5363–5369.
- Wang, X.-C., Lee, C., 1995. Adsorption and desorption of aliphatic amines and amino acids in anoxic salt marsh sediment. *Geochim. Cosmochim. Acta* 59, 1787–1797.
- Wang, X.-C., Druffel, E.R.M., Lee, C., 1996. Radiocarbon in organic compound classes in particulate organic matter and sediment in the deep Northeast Pacific Ocean. *Geophys. Res. Lett.* 23, 3583–3586.
- Wang, X.-C., Druffel, E.R.M., Griffin, S., Lee, C., Kashgarian, M., 1998. Radiocarbon studies of organic compound classes in plankton and sediment of the Northeast Pacific Ocean. *Geochim. Cosmochim. Acta* 62, 1365–1378.
- Williams, P.M., Stenhouse, M.C., Druffel, E.M., Koide, M., 1978. Organic ^{14}C activity in an abyssal marine sediment. *Nature* 276, 698–701.