6. Richard, P. & Gräber, P. Kinetics of ATP synthesis catalyzed by the H$^+$-ATPase from chloroplasts (CF$_0$F$_1$) reconstituted into liposomes and coreconstituted with bacteriorhodopsin. *Eur. J. Biochem.* **210**, 287–291 (1992).

7. Pitard, P., Pitard, B. & Rigaud, J.-L. ATP synthesis by the F$_0$F$_1$-ATPase from the thermophilic *Bacillus* PS3 co-reconstituted with bacteriorhodopsin into liposomes. *J. Biol. Chem.* **270**, 21571–21578 (1995).

8. Fromme, P. & Gräber, P. Activation/inactivation and uni-site catalysis by the reconstituted ATP-synthase from chloroplasts. *Biochim. Biophys. Acta* **1016**, 29–42 (1990).

9. Girault, G., Berger, G., Galmiche, J.-M. & Andre, F. Characterization of six nucleotide-binding sites on chloroplast coupling factor 1 and one site on its purified β subunit. *J. Biol. Chem.* **263**, 14690–14695 (1988).

10. Cladera, J. *et al.* Functional reconstitution of photosystem I reaction center from cyanobacterium *Synechocystis* sp PCC6803 into liposomes using a new reconstitution procedure. *J. Bioenerg. Biomembr.* **28**, 503–515 (1996).

11. Pitard, B., Richard, P., Duñach, M. & Rigaud, J.-L. ATP synthesis by the F$_0$F$_1$ ATP synthase from thermophilic *Bacillus* PS3 reconstituted into liposomes with bacteriorhodopsin. *Eur. J. Biochem.* **235**, 779–788 (1996).

12. Richard, P., Rigaud, J.-L. & Gräber, P. Reconstitution of CF$_0$F$_1$ into liposomes using a new reconstitution procedure. *Eur. J. Biochem.* **193**, 921–925 (1990).

13. Petitou, M., Tuy, F. & Rosenfeld, C. A simplified procedure for organic phosphorus determination from phospholipids. *Anal. Biochem.* **91**, 350–353 (1978).

Ocean margins as a significant source of organic matter to the deep open ocean

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Continental shelves and slopes comprise less than 20% of the world ocean area, yet they are proposed to be quantitatively important sources of the organic matter that fuels respiration in the open ocean's interior[1,2]. At least certain regions of the coastal ocean produce more organic carbon than they respire[3], suggesting that some fraction of this non-respired, unburied organic carbon is available for export from the coastal to the open ocean[4]. Previous studies of carbon fluxes in ocean margins[1,5,6] have not considered the potential roles of dissolved organic carbon (DOC) and suspended particulate organic carbon (POC$_{susp}$), even though both pools are quantitatively far larger than sinking POC. Here we report natural radiocarbon (^{14}C) abundance measurements that reveal continental slope and rise waters to contain both DOC and POC$_{susp}$ that are concurrently older and in higher concentrations than DOC and POC$_{susp}$ from the adjacent North Atlantic and North Pacific central gyres. Mass-balance calculations suggest that DOC and POC$_{susp}$ inputs from ocean margins to the open ocean interior may be more than an order of magnitude greater than inputs of recently produced organic carbon derived from the surface ocean. Inputs from ocean margins may thus be one of the factors contributing to the old apparent age of organic carbon observed in the deep North Atlantic and Pacific central gyres[7–9].

The radioisotopic form of carbon, ^{14}C (half-life, 5,730 yr), can be used as an indicator of the average age of bulk marine organic carbon pools such as DOC and POC. In addition to natural cosomogenically produced ^{14}C, the increase in the global inventory of ^{14}C as a result of nuclear weapons testing during the late 1950s and early 1960s also allows us to use bomb-produced ^{14}C to constrain the age of more recently formed (over the past ~40 years) organic carbon pools[10]. The Δ^{14}C (defined as the deviation in parts per thousand (‰) from the ^{14}C activity of nineteenth century wood) values of natural marine organic carbon have been found to range from as low as around −525‰ (^{14}C age of ~6,000 yr BP) for deep ocean DOC[8] to as high as about +140‰ for suspended POC samples containing bomb ^{14}C in the mid- to late 1980s (ref. 9).

Samples for ^{14}C isotope analysis of DOC and POC$_{susp}$ were collected from the western North Atlantic (WNA) and eastern North Pacific (ENP) continental margins. In April 1994, samples were collected from 4 depths at each of three WNA sites located over the continental slope in the Middle Atlantic Bight region between eastern Long Island, New York, and Cape Hatteras, North Carolina. The Bight is characterized by a permanent thermohaline front between continental shelf and slope waters and a net southwestward flow of slope water, of which ~50% is entrained across the front into slope waters and the remainder is advected offshore near Cape Hatteras[5]. The depth of the WNA mid-slope sites ranged from ~1,100–1,500 m. Samples were also collected from the eastern North Pacific from 1991 to 1993 at a time-series site located at the base of the continental rise (~4,100 m depth) at 34° 50′ N, 123° 00′ W[11,12], and previously in 1985 at a site in the Santa Monica basin of the California continental borderland[13]. The ENP site is located ~220 km off the coast of central California within the California current system and is influenced by spring–summer maxima in primary productivity and sinking POC fluxes as a result of seasonal upwelling[14].

The Δ^{14}C values of DOC from shallow surface waters (5 m depth) of the WNA continental slope were highly variable, ranging over ~200‰ (Fig. 1a). In mid-depth slope waters (~300 m and 750 m; Fig. 1a), Δ^{14}C-DOC values were significantly lower (that is, more negative in Δ^{14}C) by 75 to 150‰ relative to DOC from similar depths in the central north Atlantic gyre (−276 to −260‰ in the Sargasso Sea (SS)[8,9]. By 1,000 m depth, the Δ^{14}C-DOC profiles of WNA slope water and those of SS water converged towards similar values. These data indicate the presence of ^{14}C-depleted DOC at mesopelagic depths in WNA slope waters. On the basis of its δ^{13}C values (δ^{13}C range: −21.3 to −22.4‰; J.E.B., unpublished data), this DOC appears to be predominantly marine in origin (fully marine DOC has δ^{13}C values ranging from about −22 to −18‰).

The Δ^{14}C values of POC$_{susp}$ from the WNA ranged from −190 to +80‰ and were significantly lower than Δ^{14}C of POC$_{susp}$ from the SS[9] (Fig. 1b). Δ^{14}C values more positive than about −70 to −40‰ are considered to be post-bomb (that is, later than early 1950s to early 1960s thermonuclear weapons testing) because the pre-bomb Δ^{14}C of the temperate and tropical surface ocean was in this range[15]. The δ^{13}C values in POC$_{susp}$ (range: −22.9 to −24.9‰; J.E.B., unpublished data) suggest that terrestrial carbon (with an assumed average δ^{13}C ≈ −27‰) may have contributed slightly more to POC$_{susp}$ than to DOC in WNA slope waters. The similar offsets in Δ^{14}C for both DOC and POC$_{susp}$ between the WNA and the SS (Fig. 1a, b) suggest that the same or related mechanisms may control inputs of ^{14}C-depleted DOC and POC$_{susp}$ to WNA slope waters.

Similar to the WNA, profiles from the ENP also indicate a net depletion in ^{14}C (that is, more negative Δ^{14}C values) of both DOC and POC$_{susp}$ relative to the central North Pacific (CNP) gyre[7,9] (Fig. 1c, d). The lowest Δ^{14}C-DOC values in the ENP occurred, also like the WNA, at shallow to intermediate depths (0–700 m), and Δ^{14}C-DOC values in the ENP were lower than in the CNP at all depths samples (Fig. 1c). The Δ^{14}C-DOC values in Santa Monica basin were also, with the exception of the single 850-m sample, lower than values in the CNP (Fig. 1c). Significantly lower Δ^{14}C values of POC$_{susp}$ were likewise observed at all depths in both the ENP and Santa Monica Basin[13] relative to the CNP gyre (Fig. 1d). The average difference in Δ^{14}C-DOC between WNA and SS waters was greater than the corresponding margin-central gyre difference in the North Pacific (compare Fig 1a, c); the margin-central gyre offset in Δ^{14}C of POC$_{susp}$ was also greater overall in the North Atlantic (compare Fig. 1b, d). The corresponding δ^{13}C values for DOC (range: −20.5 to −21.7 (ref. 12)) and POC$_{susp}$ (range: −20.0 to −22.9‰ (ref. 11)) in ENP waters were greater (more positive) as a whole than for DOC and POC$_{susp}$ from the WNA.
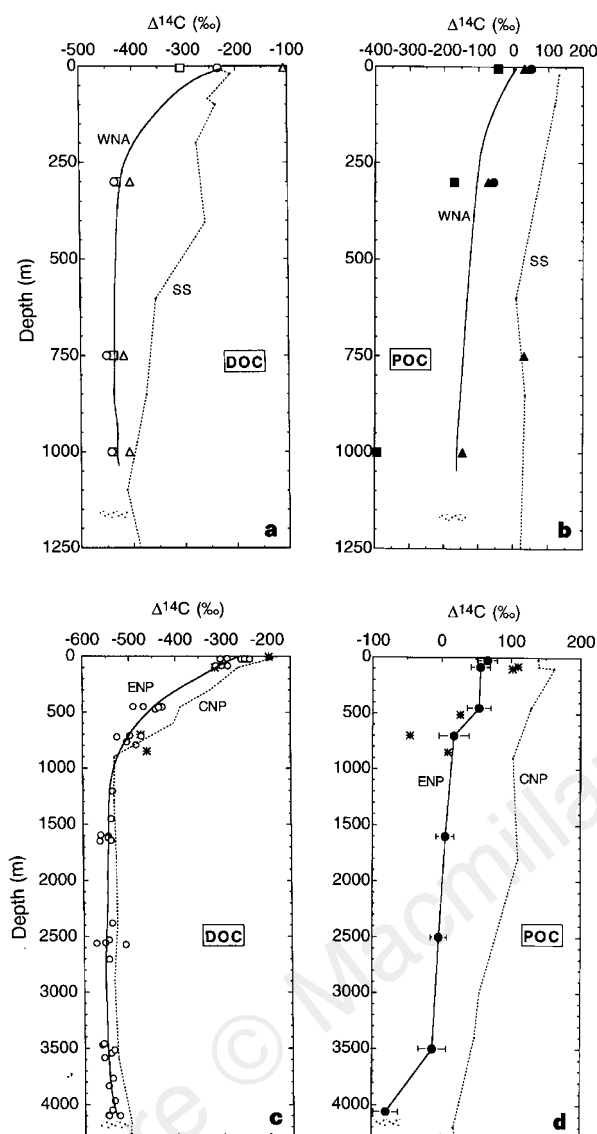
Concentrations of DOC were greatest in shallow (0 to $\sim$100 m) WNA (J.E.B., unpublished data) and ENP[12] slope and rise waters and decreased with increasing depth. With the exception of $\sim$300 m depth in the WNA and 0 to 700 m depth in the ENP, DOC in slope and rise waters exceeded by 4–9 μM those concentrations measured previously in North Atlantic and Pacific central gyre waters[7-9] (Table 1). Suspended POC concentrations were up to an order of magnitude higher in surface waters of the slope and rise than in surface waters of both the SS (J.E.B., unpublished data; ref. 9) and CNP[9]. At depths $\geqslant\sim$500 m, POC_{susp} concentrations in slope and rise waters were in all cases $\sim$2–3 times (2–3 μg C l^{-1}) greater than in the deep SS and CNP, where POC_{susp} concentrations were $\sim$0.6–1 μg C l^{-1} (Table 1).

The elevated DOC and POC_{susp} concentrations in slope (in the WNA) and rise (in the ENP) waters, together with lower $\Delta^{14}C$ values in both pools, indicate that organic matter older than that in the North Atlantic and Pacific central gyres is present in ocean margins and that it is potentially available for export to the open ocean. The origin(s) of this old, ^{14}C-depleted carbon to continental slope and rise waters is (are) not known, but several possibilities may be considered. In the WNA, the reintroduction to the water column of old sedimentary organic carbon (both as DOC and POC_{susp}) from weathered shelf and upper slope sediments[16,17] may contribute to the highly ^{14}C-depleted ($\Delta^{14}C$ as low as about -700‰) colloidal and dissolved organic carbon observed in near-bottom waters in the Middle Atlantic Bight[18] as well as to the ^{14}C-depleted POC_{susp} (Fig. 1b). The WNA may also at times be influenced by upwelled Antarctic Intermediate Water[19] which could contain a component of older, higher-concentration DOC. However, this mechanism is unlikely to account for the elevated concentrations of ^{14}C-depleted POC_{susp} also found in the WNA (Fig. 1b). Finally, the presence of trace amounts of hydrocarbons (with $\Delta^{14}C$ of about 1,000‰) from submarine seeps off California[20] could impart lower-than-average $\Delta^{14}C$ values to the DOC pool (but less likely so to the POC_{susp} pool) of the ENP compared with areas remote from seepage (such as the CNP). Thus, the older DOC and POC_{susp} in these two ocean margin systems may arise from multiple system-specific sources or from a common source such as weathered shelf and slope sediments.

The DOC of surface open ocean waters can be shown conceptually to consist of a mixture of both old, conservative material that has aged in the deep ocean and of young labile material recently

Figure 1 $\Delta^{14}C$ values of DOC and POC in North Atlantic and North Pacific waters. **a**, Values of $\Delta^{14}C$ (deviation in parts per thousand from the ^{14}C activity of nineteenth century wood) of DOC (open symbols with solid line-of-best-fit added), and **b**, POC_{susp} (solid symbols with solid line-of-best-fit added) from 3 stations between 35°39.06′ N, 74°36.78′ W and 39°37.72′ N, 71°37.78′ W (circles, northern slope station; triangles, central slope station; squares, southern slope station) along the Middle Atlantic Bight continental slope in the western North Atlantic (WNA). Also shown are $\Delta^{14}C$-DOC and $\Delta^{14}C$-POC_{susp} profiles determined previously for the Sargasso Sea (SS, dashed lines)[8,9]. DOC and POC_{susp} collection and sample-processing techniques are given in refs 9 and 12. Briefly, DOC samples (650 ml of 0.7-μm-filtered sea water) were oxidized to CO_2 by high-energy (2,400 W) ultraviolet irradiation for 2 h. POC_{susp} samples were collected from up to several thousand litres of sea water using *in situ* pumps with 0.7-μm quartz-fibre filters followed by sealed-tube combustion of sample filters to produce CO_2. Procedures for conversion of sample CO_2 to graphite and subsequent ^{14}C analysis by accelerator mass spectrometry (AMS) are presented in ref. 30. All ^{14}C data are corrected for sample $\delta^{13}C$ (data not shown) and are reported using the conventions of Stuiver and Pollach[31]. Errors associated with $\Delta^{14}C$ AMS analysis are smaller than the symbols and averaged ±6‰. Errors due to blank corrections for $\Delta^{14}C$-POC_{susp} samples from the WNA only (filled symbols) are as follows: 5-m samples, $\leqslant$±11‰; 300–1,000-m samples, ±40–60‰, with the exception of one 300-m sample (-171‰), which had an error of -80‰. All DOC samples from the WNA slope were significantly depleted in $\Delta^{14}C$ relative to the SS $\Delta^{14}C$-DOC profile, with the exception of the single 1,000-m sample ($\Delta^{14}C = -408$‰) which has not significantly different, and the single 5-m sample ($\Delta^{14}C = -107$‰)

which was significantly greater. All POC_{susp} samples from the WNA slope were significantly depleted in $\Delta^{14}C$ relative to the Sargasso Sea $\Delta^{14}C$-POC_{susp} profile, with the exception of the single 750-m sample, which was not significantly different. **c**, Values of $\Delta^{14}C$ of DOC (open circles with solid line-of-best-fit added), and **d**, POC_{susp} (filled circles) from the eastern North Pacific (ENP) including a continental rise site off central California at 34°50′ N, 123°00′ W and Santa Monica basin (star symbols) in the southern California continental borderland[13]. Symbols for $\Delta^{14}C$ of DOC in the ENP (open circles) represent individual samples measured on six separate occasions between July 1991 and July 1993. Symbols for $\Delta^{14}C$ of POC_{susp} in the ENP (solid circles) represent mean values ($\pm1\sigma$) of four profiles measured between February 1992 and July 1993 (ref. 11). Also shown are profiles of $\Delta^{14}C$-DOC and $\Delta^{14}C$-POC_{susp} (both dashed lines) determined previously for the central North Pacific (CNP)[7,9]. Errors associated with $\Delta^{14}C$ AMS analyses of both DOC and POC_{susp} are smaller than symbols and averaged ±6‰ ($\pm1\sigma$). For $\Delta^{14}C$-DOC in the CNP, single profiles measured in 1985 and 1987 showed minimal differences from each other[9]; the average standard deviation of these $\Delta^{14}C$-DOC profiles in the upper 1,000 m was 12‰, equivalent to the 2σ measurement error. All DOC and POC_{susp} samples from both eastern North Pacific sites were significantly depleted in $\Delta^{14}C$ relative to the corresponding central N. Pacific profiles, with the exception of the 900-m Santa Monica basin DOC sample which was not significantly greater. Note the differences in $\Delta^{14}C$ scales between all panels and in depth scales between WNA (in **a** and **b**) and ENP (in **c** and **d**) profiles. Stippled area under WNA and ENP profiles indicates approximate depth of the sea floor at these sites.

produced in the photic zone[9,21,22]. Using a mass-balance approach, it has been calculated[9] that surface seawater Δ^{14}C-DOC values for the central North Pacific and North Atlantic Oceans are -155‰ and -214‰, respectively, which agree well with measured values of -153‰ and -210‰, respectively. A similar calculation is made here for surface (5 m) slope water of the central WNA, which has the highest Δ^{14}C-DOC value (-107‰; Fig. 1a) of all WNA slope waters examined. The background DOC from deeper ($300–1,000$ m) waters of the central WNA slope has a mean concentration of 52 μM (J.E.B., unpublished data) and a mean Δ^{14}C of -421‰ (Fig. 1a). The DOC concentration of surface slope water is $\sim$91 μM (J.E.B., unpublished data), giving a calculated Δ^{14}C of the 'excess' surface DOC component (with a concentration of 91 μM minus 52 μM, or 39 μM) of $+311$‰. This Δ^{14}C value is high and similar to previous measurements of humic substances in Amazon river water made in 1984 (Δ^{14}C = $+230$‰)[23] and reflects the input of post-bomb, terrestrial carbon to shallow central WNA slope waters which are influenced by inputs from rivers and estuaries.

The same calculation when applied to southern WNA waters yields a different conclusion. Using a deep, background mean DOC concentration of 51 μM (J.E.B., unpublished data) and a Δ^{14}C-DOC value of -435‰ (Fig. 1a) and a DOC concentration and Δ^{14}C-DOC value in shallow slope waters of 83 μM (J.E.B., unpublished data) and -306‰ (Fig. 1a), respectively, then the Δ^{14}C of the 'excess' surface DOC component (with a concentration of 83 μM minus 51 μM, or 32 μM) is calculated to be -100‰. This Δ^{14}C-depleted component of excess DOC added to southern WNA surface slope water (about 400‰ lower than the 'excess' component in central WNA slope surface waters) is reflective of an older source of carbon to the surface DOC pool, perhaps originating from shelf and slope porewaters and sediments[16,17,24] that are advected seaward. Similar calculations for POC$_{susp}$ using this simple model are not justified because of the $\sim$10-fold greater concentrations of POC$_{susp}$ in surface compared with deeper waters. For DOC, however, it is clear that sources having highly disparate Δ^{14}C may contribute to the surface ocean pool, leading to the high degree of variability observed in the WNA.

The existence of positive concentration gradients between the margins and deep open ocean and between the surface and deep open oceans indicates that both margins and the surface ocean may serve as sources of DOC and POC$_{susp}$ to the deep central gyres (Table 1). We can estimate by ^{14}C mass balance the relative potential contributions of each of these sources to the deep North Atlantic and Pacific using the following simplifying assumptions: (1) the deep central North Atlantic and Pacific are in steady state with respect to Δ^{14}C values and concentrations of DOC and POC$_{susp}$ (refs 7–9); (2) the two dominant sources of DOC and POC$_{susp}$ to the deep central gyres are lateral inputs of ^{14}C-depleted material derived from the margins and vertical inputs of 'modern', ^{14}C-enriched material derived from surface ocean production[11]; and (3) the margin-to-deep open ocean and surface-to-deep open ocean gradients observed in these studies are representative of the North Atlantic and Pacific as a whole. We find that in order to maintain the observed average DOC Δ^{14}C values in the deep central gyres, the input of DOC from the margins is calculated to be as much as 25–100 times that of modern, surface ocean-derived carbon; for POC$_{susp}$, the contribution from margins is smaller than that for DOC but still 5–19 times greater than the contribution of material from the surface (Table 1). These estimates of margin and surface contributions to the deep open ocean have two principal implications: (1) inputs of 'aged' organic carbon from the margins to the deep open ocean may surpass inputs derived from recent surface ocean production, and (2) in view of the much larger surface-to-deep than margin-to-deep concentration gradients, most young, surface-derived material must be degraded, allowing a smaller but more highly refractory margin component to contribute proportionally more to the deep central gyres.

Lateral transport of organic matter from margins to pelagic and abyssal environments has been invoked previously to help explain carbon and oxygen imbalances in the deep ocean[14,25]. Transport of ^{14}C-depleted DOC and even POC$_{susp}$ from ocean margins to the central gyres may be facilitated by isopycnal (that is, lateral) eddy diffusion, which can be 10^3–10^7 times greater than vertical eddy diffusive transport[26]. Although vertical transport of recently produced surface material to the central gyres may also be enhanced by such processes as seasonal thermocline breakdown[27] and rapidly sinking organic particles[9,11,14], we would expect this younger organic carbon to be relatively more susceptible to microbial remineralization[21,22,28] than older margin-derived material. Thus, although the open ocean undoubtedly receives inputs from both its margins and surface production, the Δ^{14}C and concentration profiles of DOC and POC$_{susp}$ in the deep central gyres may be maintained by greater relative inputs from the margins than from recent surface production.

Table 1 Relative contributions of margin and surface ocean organic carbon to the deep central gyres

Dissolved organic carbon

	Margin component		Modern surface component		Margin fraction*	Surface fraction*	Margin: surface ratio
	$\Delta-\Delta^{14}$C$_{DOC}$†	Δ[DOC]‡	$\Delta-\Delta^{14}$C$_{DOC}$§	Δ[DOC]‖			
North Atlantic	-78‰	9 μM	$+520$‰	34 μM	0.96	0.04	25
North Pacific	-39‰	4 μM¶	$+665$‰	23 μM	0.99	0.01	100

Suspended particulate organic carbon

	$\Delta-\Delta^{14}$C$_{POC}$†	Δ[POC]‡	$\Delta-\Delta^{14}$C$_{POC}$§	Δ[POC]‖			
North Atlantic	-167‰	3 μg l^{-1}#	$+93$‰	28 μg l^{-1}	0.84	0.16	5.2
North Pacific	-83‰	2 μg l^{-1}#	$+94$‰	31 μg l^{-1}	0.95	0.05	19

Estimates of the relative contributions of margin and surface ocean-derived DOC and suspended POC to the deep central North Atlantic and Pacific gyres. Shown are DOC and suspended POC Δ^{14}C and concentration gradients between the deep open North Atlantic and North Pacific Oceans, their respective margins (WNA and ENP, respectively), and modern surface ocean organic carbon. Also shown are the fractions of margin and surface ocean DOC and POC required to maintain the observed steady-state Δ^{14}C profiles of DOC and suspended POC in the deep North Atlantic and Pacific central gyres.
* Relative contributions of margin and surface-derived DOC and POC required to maintain the observed average Δ^{14}C values of DOC and POC in the deep central North Atlantic and Pacific gyres. The contribution of each component is described by the mass balance equation (here shown for DOC): $x[(\Delta-\Delta^{14}$C$_{DOC})_{margin}(\Delta$[DOC]$_{margin}/$[DOC]$_{deep\,central\,gyre})+y[(\Delta-\Delta^{14}C_{DOC})_{surface}(\Delta$[DOC]$_{surface}/$[DOC]$_{deep\,central\,gyre})] = (\Delta-\Delta^{14}C_{DOC})_{deep\,central\,gyre}$, where x is the margin component, y is the surface component, and $x+y = 1$. Note that by definition $(\Delta-\Delta^{14}$C$_{DOC})_{deep\,central\,gyre} = 0$. For calculating the margin and surface-derived suspended POC components, POC values are substituted for DOC values in the above equation. Average values used for [DOC]$_{deep\,central\,gyre}$ were 43 and 35 μM for the SS and CNP, respectively; the average value used for [POC]$_{deep\,central\,gyre}$ was 0.72 μg l^{-1} for both the SS and CNP[9].
† Mean observed gradients in Δ^{14}C values of DOC and POC between margins and deep central gyres.
‡ Mean observed gradients in concentrations of DOC and POC between margins and deep central gyres.
§ Mean observed gradients in Δ^{14}C values of DOC and POC derived from recent photosynthetically fixed surface ocean organic carbon and that present in deep central gryres. The average Δ^{14}C values of surface-derived, photosynthetically fixed carbon measured at the time each central gyre site was sampled were $+120$‰ and $+140$‰ for the Sargasso Sea and central North Pacific, respectively[9].
‖ Mean observed gradients in concentrations of DOC and POC between surface (average of 0–20 m depth for DOC; average of particle maximum zone for POC$_{susp}$, typically 20–85 m depth) and deep ($>1,000$ m depth) central gyre waters[9].
¶ Excludes 0 to $\sim$700 m depth interval.
# Excludes shallowest depths sampled where concentrations were up to 30 times greater in margins.

Shallow continental shelf and slope waters may also act as low-salinity conduits of younger terrestrial organic matter (J.E.B., unpublished data, and ref. 18), where margins are affected significantly by rivers and estuaries. However, most of this material must also be degraded in nearshore waters or sequestered in sediments as it does not appear to comprise a significant component of open ocean DOC^{29} and POC_{susp} seaward of the shelf-slope front. The isotope signatures of DOC and POC_{susp} at the coastal–open ocean boundaries (that is, slope and rise waters) here indicate that this carbon has mainly a non-recent marine origin and is older than organic carbon from the North Atlantic and Pacific central gyres. If this material propagates seaward, possibly along isopycnal surfaces, it may represent a source of old DOC and POC to intermediate and deep waters of the interior ocean[4]. □

1. Walsh, J., Rowe, G., Iverson, R. & McRoy, C. Biological export of shelf carbon is a sink of the global CO_2 cycle. *Nature* **292**, 196–201 (1981).
2. Smith, S. & MacKenzie, F. The ocean as a net heterotrophic system: implications for the carbon biogeochemical cycle. *Global Biogeochem. Cycles* **1**, 187–198 (1987).
3. Smith, S. & Hollibaugh, T. Coastal metabolism and the oceanic organic carbon balance. *Rev. Geophys.* **31**, 75–89 (1993).
4. Wollast, R. in *Ocean Margin Processes in Global Change* (eds Mantoura, R., Martin, J.-M. & Wollast, R.) 365–381 (Wiley, New York, 1991).
5. Biscaye, P., Flagg, C. & Falkowski, P. The Shelf Edge Exchange Processes experiment, SEEP-II: an introduction to hypotheses, results and conclusions. *Deep-sea Res. II* **41**, 231–252 (1994).
6. Walsh, J., Biscaye, P. & Csanady, G. The 1983–1984 Shelf Edge Exchange Processes (SEEP)-I experiment: hypotheses and highlights. *Cont. Shelf Res.* **8**, 435–456 (1988).
7. Williams, P. & Druffel, E. Radiocarbon in dissolved organic matter in the central North Pacific Ocean. *Nature* **330**, 246–248 (1987).
8. Bauer, J., Williams, P. & Druffel, E. ^{14}C activity of dissolved organic carbon fractions in the north-central Pacific and Sargasso Sea. *Nature* **357**, 667–670 (1992).
9. Druffel, E., Williams, P., Bauer, J. & Ertel, J. Cycling of dissolved and particulate matter in the open ocean. *J. Geophys. Res.* **97**, 15,639–15,659 (1992).
10. Trumbore, S. & Druffel, E. in *Role of Nonliving Organic Matter in the Earth's Carbon Cycle* (Zepp, R. G. & Sonntag, C.) 7–22 (Wiley and Sons, New York, 1995).
11. Druffel, E., Bauer, J., Williams, P., Griffin, S. & Wolgast, D. Seasonal variability of radiocarbon in particulate organic carbon in the northeast Pacific. *J. Geophys. Res.* **101**, 20,543–20,552 (1996).
12. Bauer, J. E., Druffel, E., Williams, P. M., Wolgast, D. & Griffin, S. Temporal variability in dissolved organic carbon and radiocarbon in the eastern North Pacific Ocean. *J. Geophys. Res.* (in the press).
13. Williams, P., Robertson, K., Souter, A., Griffin, S. & Druffel, E. Isotopic signatures (^{14}C, ^{13}C, ^{15}N) as tracers of sources and cycling of soluble and particulate organic matter in the Santa Monica Basin. *Prog. Oceanogr.* **30**, 253–290 (1992).
14. Smith, K., Kaufman, R. & Baldwin, R. Coupling of near-bottom pelagic and benthic processes at abyssal depths. *Limnol. Oceanogr.* **39**, 1101–1118 (1994).
15. Stuiver, M., Pearson, G. W. & Braziunas, T. Radiocarbon age calibration of marine samples back to 9000 cal yr B.P. *Radiocarbon* **28**, 980–1021 (1986).
16. Anderson, R., Rowe, G., Kemp, P., Trumbore, S. & Biscaye, P. Carbon budget for the mid-slope depocenter of the Middle Atlantic Bight. *Deep-sea Res. II* **41**, 669–703 (1994).
17. Churchill, J., Wirick, C., Flagg, C. & Pietrafesa, L. Sediment resuspension over the continental shelf east of the Delmarva Peninsula. *Deep-sea Res. II* **41**, 341–363 (1994).
18. Guo, L., Santschi, P., Cifuentes, L. & Trumbore, S. Cycling of high-molecular-weight dissolved organic matter in the Middle Atlantic Bight as revealed by carbon isotopic (^{13}C and ^{14}C) signatures. *Limnol. Oceanogr.* **41**, 1242–1252 (1996).
19. Tanaka, N., Monaghan, M. & Turekian, K. ^{14}C balance for the Gulf of Maine, Long Island Sound and the northern Middle Atlantic Bight: evidence for the extent of the Antarctic Intermediate Water contribution. *J. Mar. Res.* **48**, 75–87 (1990).
20. Bauer, J., Spies, R., Vogel, J., Nelson, D. & Southon, J. Natural ^{14}C evidence of fossil carbon cycling in sediments of a marine hydrocarbon seep off California. *Nature* **348**, 230–232 (1990).
21. Carlson, C. & Ducklow, H. Dissolved organic carbon in the upper ocean of the central Equatorial Pacific, 1992: daily fine-scale vertical variations. *Deep-sea Res. II* **42**, 639–656 (1995).
22. Cherrier, J., Bauer, J. & Druffel, E. Utilization and turnover of labile dissolved organic matter by bacterial heterotrophs in eastern North Pacific waters. *Mar. Ecol. Prog. Ser.* **139**, 267–279 (1996).
23. Hedges, J. *et al.* Organic ^{14}C in the Amazon River system. *Science* **231**, 1129–1131 (1986).
24. Bauer, J., Reimers, C., Druffel, E. & Williams, P. Isotopic constraints on carbon exchanges between deep ocean sediments and seawater. *Nature* **373**, 686–689 (1995).
25. Jahnke, R., Reimers, C. & Craven, D. Intensification of recycling of organic matter at the sea floor near ocean margins. *Nature* **348**, 50–54 (1990).
26. Knauss, J. A. *Introduction to Physical Oceanography* (Prentice-Hall, Englewood Cliffs, NJ, 1978).
27. Carlson, C. A., Ducklow, H. W. & Michaels, A. F. Annual flux of dissolved organic carbon from the euphotic zone in the northwestern Sargasso Sea. *Nature* **371**, 405–408 (1994).
28. Kirchman, D., Suzuki, Y., Garside, C. & Ducklow, H. High turnover rates of dissolved organic carbon during a spring phytoplankton bloom. *Nature* **352**, 612–614 (1991).
29. Opsahl, S. & Benner, R. Distribution and cycling of terrigenous dissolved organic matter in the ocean. *Nature* **386**, 480–482 (1997).
30. Vogel, J., Nelson, E. & Southon, J. ^{14}C background levels in an accelerator mass spectrometry system. *Radiocarbon* **29**, 323–333 (1987).
31. Stuiver, M. & Polach, H. Discussion: reporting of ^{14}C data. *Radiocarbon* **19**, 355–363 (1977).

The deep structure of a sea-floor hydrothermal deposit

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Hydrothermal circulation at the crests of mid-ocean ridges plays an important role in transferring heat from the interior of the Earth[1–3]. A consequence of this hydrothermal circulation is the formation of metallic ore bodies known as volcanic-associated massive sulphide deposits. Such deposits, preserved on land, were important sources of copper for ancient civilizations and continue to provide a significant source of base metals (for example, copper and zinc)[4–6]. Here we present results from Ocean Drilling Program Leg 169, which drilled through a massive sulphide deposit on the northern Juan de Fuca spreading centre and penetrated the hydrothermal feeder zone through which the metal-rich fluids reached the sea floor. We found that the style of feeder-zone mineralization changes with depth in response to changes in the pore pressure of the hydrothermal fluids and discovered a stratified zone of high-grade copper-rich replacement mineralization below the massive sulphide deposit. This copper-rich zone represents a type of mineralization not previously observed below sea-floor deposits, and may provide new targets for land-based mineral exploration.

Transects of boreholes drilled on the Ocean Drilling Program (ODP) Leg 169 defined the extent and composition of the Bent Hill massive sulphide (BHMS) deposit in Middle Valley on the northern Juan de Fuca spreading centre (Fig. 1), and is the first geometric characterization of a complete sea-floor hydrothermal system. A 500-m-deep hole through the apex of the massive sulphide deposit provided a complete vertical section of the hydrothermal system, penetrating the feeder zone, the underlying sediment column and the uppermost volcanic basement.

Middle Valley is the northern extension of the Endeavor segment of the Juan de Fuca ridge. Due to its proximity to the continent and

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