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Black Carbon in Deep-Sea Sediments

C. A. Masiello and E. R. M. Druffel

Black carbon (BC) enters the ocean through aerosol and river deposition. BC makes up 12 to 31 percent of the sedimentary organic carbon (SOC) at two deep ocean sites, and it is 2400 to 13,900 carbon-14 years older than non-BC SOC deposited concurrently. BC is likely older because it is stored in an intermediate reservoir before sedimentary deposition. Possible intermediate pools are oceanic dissolved organic carbon (DOC) and terrestrial soils. If DOC is the intermediate reservoir, then BC is 4 to 22 percent of the DOC pool. If soils are the intermediate reservoir, then the importance of riverine carbon in the ocean carbon cycle has been underestimated.

Black carbon is a chemically heterogeneous, biologically refractory class of carbon compounds produced during biomass burning and fossil fuel combustion. Estimates of modern BC production are 50 to 260 teragrams of carbon per year (Tg C/year) from biomass burning (1) and 12 to 24 Tg C/year from fossil fuel combustion (2) (1 Tg = 10^{12} g). Although humans have recently increased environmental concentrations, BC has always been a product of natural biomass burning. The atmospheric lifetime of BC aerosols is 40 hours to 1 month (3), providing enough time for BC to reach even the most remote oceanic sites. BC has been detected in marine sediments from the Cretaceous-Tertiary boundary (4) and in Pacific sediments from a range of geologic time periods (5, 6).

Initially, most BC is likely incorporated into soils; however, some submicrometer-sized particles remain airborne and become part of the background planetary aerosol (2). BC makes up ~10% by weight of the aerosol over the Northern Hemisphere open oceans (7, 8). BC that reaches the ocean surface eventually reaches the ocean sea floor, and at least some [~ 10 Tg/year (9)] sedimentary BC is preserved (5, 10).

The mass of organic carbon stored globally in ocean sediments is ~ 160 Tg/year (11). BC makes up approximately 6% of this carbon, and its concentration in sediments has been widely measured (5, 6, 12–14). BC has been shown to constitute up to 50% of SOC in some continentally influenced oligotrophic sites [for example, the north and equatorial Atlantic Ocean (14)]. Although biomass burning can produce millimeter-sized BC particles, almost no BC larger than 2 μm in diameter is airborne during a biomass burning event (13), and long-distance transport selects effectively for the smaller fraction of BC aerosols (3). When BC is deposited to the ocean's surface, the majority of particles are

likely within the DOC size class [less than 1 μm , according to the definition used for radiocarbon measurements (15)].

Fossil fuel-produced BC contains no radiocarbon and thus has a ^{14}C age of more than 50,000 years ($\Delta^{14}\text{C} \sim -1000$ per mil). Modern BC from biomass burning has a $\Delta^{14}\text{C}$ signature greater than 0 per mil, indicating the presence of bomb ^{14}C produced in the late 1950s and early 1960s from thermonuclear weapons testing. Here we use radiocarbon measurements to infer storage pools and residence times for BC in the ocean (16).

In December 1995, we collected a 152-cm gravity core from 54°00.00'S, 176°39.99'W (between New Zealand and Antarctica, within the seasonal ice zone). The sea floor at this site was at a depth of

5314 m, and the surface water phytoplankton concentration was high (17). We also took two cores in October 1996 in the northeastern Pacific at a well-studied time series site, Station M (18), located on the Pacific abyssal plain at ~ 4100 m depth. The first was a subcore 8 cm in diameter and 14 cm long of a box core collected from 34°55.87'N, 123°1.98'W with a Free Vehicle Grab Respirometer (18). The second was a 194-cm gravity core collected at 34°38.40'N, 123°9.39'W. We report the gravity core data in the top 50 cm, as this is the range where SOC and BC ^{14}C ages are both less than $\sim 50,000$ years. The ^{14}C age of the bulk sedimentary organic carbon at 50 cm in both the Pacific and Southern Ocean gravity cores is $\sim 25,000$ years.

These two sites were selected because they were not expected to have significant riverine sources of carbon. The northeastern Pacific site is on the abyssal plain, 220 km west of central California. The land closest to the Southern Ocean site is 500 km northwest (the Antipodes Islands).

To extract BC, we treated sediments with a mixture of dichromate and sulfuric acid (10, 19). The average mass yield of BC per total SOC (dry weight, salt corrected) of all sediment samples from the two northeast Pacific sites was $15 \pm 2\%$. BC is a significant component of the SOC at this site (Fig. 1A). The mass yield of BC per SOC at the Southern Ocean site was $21 \pm 6\%$, with higher yields lower in the core

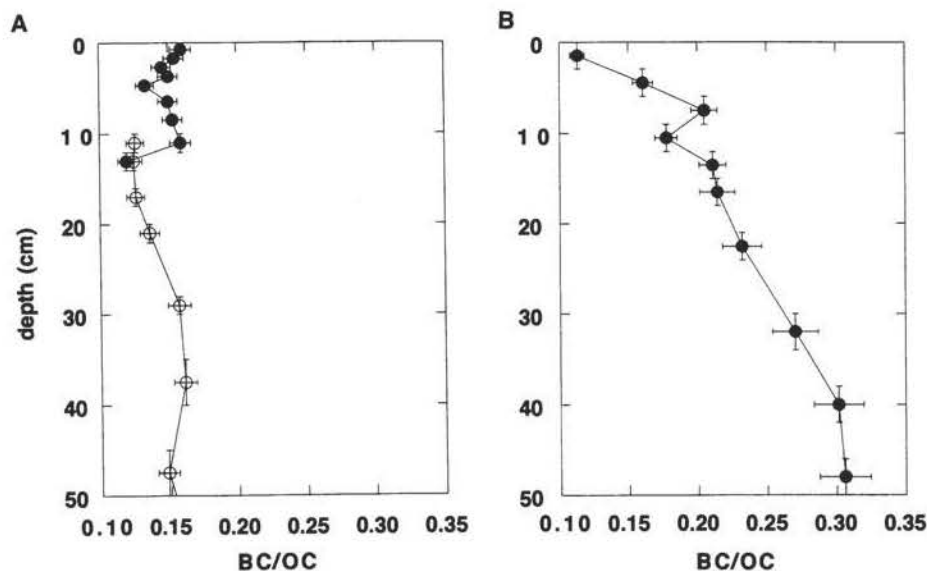


Fig. 1. (A) BC per total SOC in the northeastern Pacific box core and gravity core. Solid circles represent the box core, and open circles represent the gravity core. Approximately 10 cm of the gravity core was lost on board during core collection and sampling, and samples from this core have a ± 3 cm uncertainty in depth assignments. The ^{210}Pb -derived sedimentation rate in the mixed layer for this site is 28.4 cm per thousand years (cm/kyr) (36); ^{14}C -derived (non-BC SOC) sedimentation rate below the mixed layer is 1.9 ± 0.6 cm/kyr. Error bars are based on the reproducibility of the dichromate and sulfuric acid extraction on replicate sediment samples. (B) BC per total SOC in the Southern Ocean gravity core. The sedimentation rate, from the ^{14}C value of non-BC SOC, is 2.3 ± 1.4 cm/kyr.

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(Fig. 1B). The increase in the BC/SOC ratio with depth in the Southern Ocean may be the result of preferential remineralization of non-BC SOC. Alternatively, the BC production rate could have been higher during the last glacial period (14).

Radiocarbon ages from the two north-east Pacific cores (20) are offset at 12 cm depth (Fig. 2A) because of uncertainties in the depth assignments of samples from the gravity core (see Fig. 1A caption) or regional variability in sedimentary depositional processes or both. Despite this uncertainty, there is a continuous age offset between the ^{14}C age of BC and non-BC SOC of 2400 ± 120 years in the box core and 5400 ± 520 years in the deeper gravity core. Likewise, there is an average age offset of $13,900 \pm 3900$ years between the BC and non-BC SOC from the Southern Ocean core (Fig. 2B).

At Stu M, the sediment is bioturbated from the surface down to ~ 12 cm (21), and the sedimentation rates at both sites are quite low (see Fig. 1A caption). The presence of BC from fossil fuel combustion would appear as an increase in the age difference between BC and non-BC SOC in this modern bioturbated layer relative to deeper parts of the core. We do not observe this effect in any of our cores. This, combined with low sedimentation rates, rules out fossil fuel BC as a cause of the age difference between BC and non-BC SOC.

To explain the differences between BC and non-BC SOC ages in our cores we must consider the ^{14}C signatures of each carbon pool when the BC was produced and the processes that transport BC and SOC from their sources to ocean sediments. Before humans began combusting globally significant amounts of fossil fuels, virtually all BC was produced from terrestrial biomass burning and had the radiocarbon signature of the terrestrial biosphere. The residence time for carbon in the living terrestrial biosphere is less than 50 years (22), giving a modern radiocarbon signature ($\Delta^{14}\text{C} \sim 0$ per mil). Before the ocean's surface was contaminated with bomb ^{14}C , organic material produced in the ocean through photosynthesis also had an essentially modern radiocarbon signature [with a small reservoir effect (23)]. This surface organic material is the source of most suspended and sinking particulate organic carbon (POC), which travels to the sea floor in less than 10 years (24, 25). If BC also traveled from production directly to the ocean floor, then its radiocarbon age would not be substantially different from concurrently deposited non-BC SOC. However, we see a substantial age offset between BC and non-BC SOC in all cores sampled.

These age differences can be explained if BC is stored in at least one intermediate carbon pool between terrestrial production and deposition in ocean sediments. Candi-

date intermediate pools are terrestrial soils and the ocean DOC pool. Terrestrially stored soil BC could arrive at the ocean via either river transport or aerosol deposition.

River-derived, terrestrial organic matter tracers disperse and settle as river plumes depart continental shelves (26). Most evidence suggests that river-borne soil carbon does not reach remote, open ocean sites such as those described here (27). However, the BC measured in this report does not have chemical or stable isotopic signatures that make it easily distinguished from bulk oceanic carbon pools. Few of the original organic compounds from plants that serve as biomarkers (for example, lignins) remain in biomass-derived BC. The average $\delta^{13}\text{C}$ values of our BC samples are -23.9 ± 0.6 per mil in the northeastern Pacific ($n = 16$) and $-18.6 \pm 1.4\%$ in the Southern Ocean ($n = 9$). [The $\delta^{13}\text{C}$ of biomass-produced BC is controlled by the relative proportions of C3 and C4 plants combusted and by isotopic fractionation during combustion (28)]. The $\delta^{13}\text{C}$ values of our BC samples are close enough to those of oceanic DOC [$\delta^{13}\text{C}$ from -20 to -22 per mil (29)] that it would be difficult to identify the presence of BC in the bulk DOC pool using $\delta^{13}\text{C}$ measurements. Evidence suggests that river-transported BC is less than modern (30). This leaves open the possibility that riverine BC, aged thousands of years in terrestrial soils, contributes significantly to oceanic DOC and remote sedimentary SOC.

However, given the current understanding of the fate of river carbon, it is more plausible that the material extracted from our remote cores arrived at the ocean surface via aerosol deposition. The atmospheric residence time of BC aerosols is short (3), so before the late 19th century, newly produced aerosol BC probably reached the ocean surface with the modern radiocarbon signature of the terrestrial biosphere.

Wind erosion of aged soil BC has not been included as a detectable source in atmospheric BC budgets (2, 31, 32). BC aerosol concentrations correlate well with gaseous tracers of combustion (33) and poorly with tracers of soil-derived aerosols (34). We conclude that before humans began producing BC from fossil fuel combustion, BC arrived at the ocean's surface with a modern $\Delta^{14}\text{C}$ signature.

Because ocean organic carbon also arrives at ocean sediments with its initial ^{14}C signature changed only slightly (35), we can use the age difference between BC and concurrently deposited non-BC SOC to infer residence times of BC in the water column. From the age differences observed in our cores, these residence times are 2400 to 5400 years for our Pacific site and 13,900 years for our Southern Ocean site. For these residence

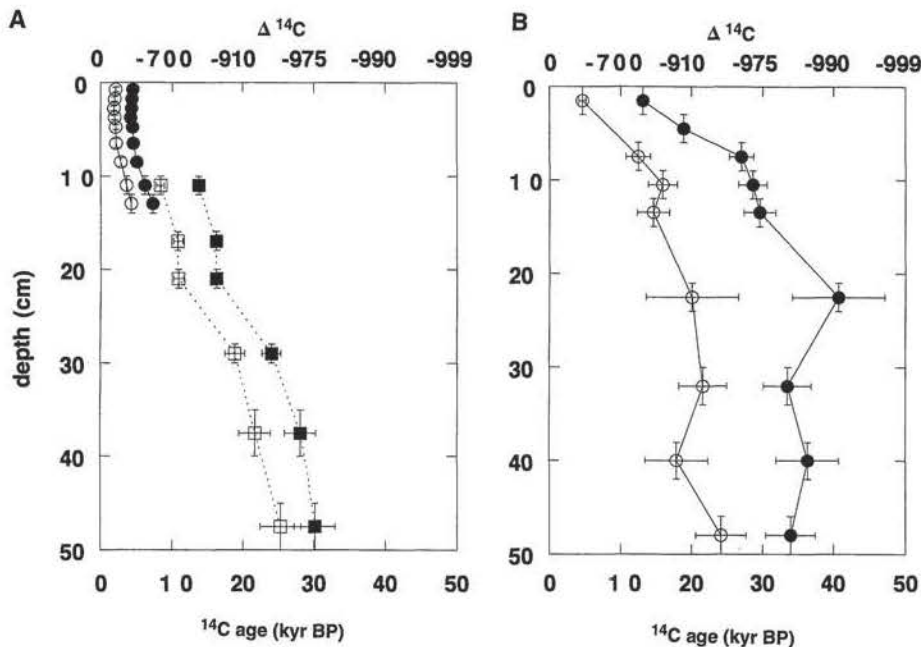


Fig. 2. (A) $\Delta^{14}\text{C}$ and ^{14}C age of BC and non-BC SOC in the northeastern Pacific box core and gravity core. Circles represent the box core; squares represent the gravity core; open symbols represent non-BC SOC, and solid symbols represent BC. B.P. is ^{14}C years before present, where "present" is 1950. Error bars are based on the reproducibility of the chromic and sulfuric acid extraction on replicate samples, and when not visible are smaller than the data point. (B) $\Delta^{14}\text{C}$ and ^{14}C age of BC and non-BC SOC in the Southern Ocean gravity core.

times (2400 to 13,900 years), an approximate flux of BC per year to the world's oceans of 8.4×10^{17} μmol (9) and an average deep ocean DOC concentration of 39 μM (29) we calculate that BC could be 4 to 22% of the total deep ocean DOC pool.

Within this calculation are a number of first-order approximations about BC in the oceans. Among them are the assumptions that (i) suspended BC resides only in the DOC pool and not the POC pool; (ii) oceanic BC has one homogeneous age; (iii) river inputs of BC to remote sediments are not significant; and (iv) BC (and DOC) removal processes are similar between oceans. All of these approximations are reasonable given the available information; however, it is likely that they simplify the actual environmental processes. Small changes in each of these variables could result in site-to-site variability in the estimated residence time of BC in the water column, variabilities such as those observed between our northeastern Pacific and Southern Ocean sites (2400 to 5400 years and 13,900 years, respectively). For example, if the largest BC particles are removed closer to shore, the age difference between BC and non-BC SOC would be smaller closer to continents (providing one possible explanation for the difference between our Southern and Pacific ocean cores). Once the causes of these site-to-site differences are better understood, it may be possible to use sedimentary BC as a tracer of water column and sedimentary carbon cycle processes.

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20. The non-BC SOC fraction modern (FM) was calculated by mass balance by solving the equation $FM_{\text{SOC total}} = (FM_{\text{BC}} \times \text{fraction BC}) + (FM_{\text{non-BC SOC}} \times \text{fraction non-BC SOC})$ for the variable $FM_{\text{non-BC SOC}}$.
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Elasticity of Single-Crystal MgO to 8 Gigapascals and 1600 Kelvin

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The cross pressure (P) and temperature (T) dependence of the elastic moduli (C_{ij}) of single-crystal samples of periclase (MgO) from acoustic wave travel times was measured with ultrasonic interferometry: $\partial^2 C_{11}/\partial P \partial T = (-1.3 \pm 0.4) \times 10^{-3}$ per kelvin; $\partial^2 C_{110}/\partial P \partial T = (1.7 \pm 0.7) \times 10^{-3}$ per kelvin; and $\partial^2 C_{44}/\partial P \partial T = (-0.2 \pm 0.3) \times 10^{-3}$ per kelvin. The elastic anisotropy of MgO decreases with increasing pressure at ambient temperature, but then increases as temperature is increased at high pressure. An assumption of zero cross pressure and temperature derivatives for the elastic moduli underestimates the elastic anisotropy and overestimates the acoustic velocities of MgO at the extrapolated high-pressure and high-temperature conditions of Earth's mantle.

Periclase has the cubic rock salt (B1) structure. It has traditionally been regarded as a standard solid for testing new experimental techniques developed for elasticity measurements (1–5) and for theoretical modeling and analyses of thermoelastic properties of solids at elevated pressure and temperature (6–8). It is an important mineral in geophysics because mineralogical models of Earth's lower mantle contain magnesiowüstite, (Mg_x, Fe_{1-x})O (9), on the basis of high

pressure–high temperature phase equilibrium experiments (10). Its availability and stability over a wide range in the pressure–temperature space have prompted its use as a pressure standard in high pressure–high temperature x-ray diffraction experiments in diamond anvil cells and multianvil apparatus (11, 12).

Although the elastic properties of MgO have been the subject of numerous experimental and theoretical investigations over the past 30 years, direct measurements of the acoustic velocities with the techniques of physical acoustics have been made primarily at high pressure (≤ 8 GPa) but ambient temperature (2–4), or at high temperature (≤ 1800 K) but ambient pressure (5). A previous effort to map the elasticity of this mineral at simultaneous elevated pressures and temperatures covered the range

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