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**Key Points:**

- Dissolved organic carbon (DOC) ages similarly to dissolved inorganic carbon (DIC) in deep water as it flows north from the Southern Ocean to the east Pacific
- The lowest DOC $\Delta^{14}C$ value yet obtained (−578‰) may be the result of input of ancient DOC produced in hydrothermal systems
- Deep DOC $\delta^{13}C$ are variable and lower close to the East Pacific Rise, supporting that hydrothermal input of DOC is feasible

**Supporting Information:**

Supporting Information may be found in the online version of this article.

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# Dissolved Organic Radiocarbon in the Eastern Pacific and Southern Oceans

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**Abstract** We report marine dissolved organic carbon (DOC) concentrations, and DOC $\Delta^{14}C$ and $\delta^{13}C$ values in seawater collected from the Southern Ocean and eastern Pacific GOSHIP cruise P18 in 2016/2017. The aging of $^{14}C$ in DOC in circumpolar deep water northward from 69°S to 20°N was similar to that measured in dissolved inorganic carbon in the same samples, indicating that the transport of deep waters northward is the primary control of $^{14}C$ in DIC and DOC. Low DOC $\Delta^{14}C$ and $\delta^{13}C$ measurements between 1,200 and 3,400 m depth may be evidence of a source of DOC produced in nearby hydrothermal ridge systems (East Pacific Rise).

**Plain Language Summary** Dissolved organic carbon (DOC) is the most abundant form of reduced carbon in the ocean, and is believed to originate mostly from photosynthesis in surface waters. Yet, the $^{14}C$ age of DOC is thousands of years old, leaving a gap in our understanding of how long DOC persists in the deep ocean. We find aging of DOC and dissolved inorganic carbon (DIC) in the deep ocean from 69°S to 20°N is equal. We hypothesize that the transport and mixing of deep waters northward is the primary control of $^{14}C$ in DIC and DOC in circumpolar deep water.

## 1. Introduction

The concentration of dissolved organic carbon (DOC) in seawater is only ~2%–4% that of dissolved inorganic carbon (DIC), making DOC more sensitive to small changes in its sources and sinks than that for DIC. Also, the sources and sinks of DIC in seawater are well understood (gas exchange with atmospheric $CO_2$, photosynthesis, respiration, and dissolution of calcium carbonate). Sources and sinks of DOC are complex, including photosynthesis, respiration, microbial transformations (Jiao, et al., 2010), river input (Meybeck, 1982), gel formation (Verdugo et al., 2004), chemoautotrophy (Hansman et al., 2009; Ingalls et al., 2006), changes of the composition of low molecular weight DOC (T. Broek et al., 2020), dissolution of surface POC (Druffel et al., 2016; Smith et al., 1992), and hydrothermal processes (Lang et al., 2006; McCarthy et al., 2011). There is also radioactive decay causing "aging" of DOC (and DIC) as water is transported along the deep ocean conveyor (Druffel et al., 2019; Key et al., 2004). A $^{14}C$ mass balance shows that surface ocean DOC is made of a 1:1 mixture of old DOC from deep water and newly produced, post-bomb DOC from surface water (Williams & Druffel, 1987).

There is a wide range of $\Delta^{14}C$ values for the various organic compound classes of DOC (I. Voparil and M. McCarthy, unpublished data; T. A. B. Broek et al., 2017; Loh et al., 2004; Zigha et al., 2017), dissolved black carbon (Coppola & Druffel, 2016; Ziolkowski & Druffel, 2010), and dissolved carbohydrates and sugars (Repeta & Aluwihare, 2006). Isotopic diversity of DOC is important for understanding the oceanic DOC cycle. The focus of this work lies with the carbon isotopic signatures of bulk DOC and understanding the trends in the data spatially and with depth in the eastern Pacific and Southern Oceans.

Ongoing research aims to understand the mechanisms controlling old ages of deep ocean DOC. The dilution hypothesis explains that the existence of refractory DOC in the deep ocean is the low concentrations of labile organic compounds, not recalcitrance, as the reason for low prokaryotic growth in the deep sea (Arrieta et al., 2015). Jiao, et al. (2015) reanalyzed the data from Arrieta et al. (2015) and found alternative

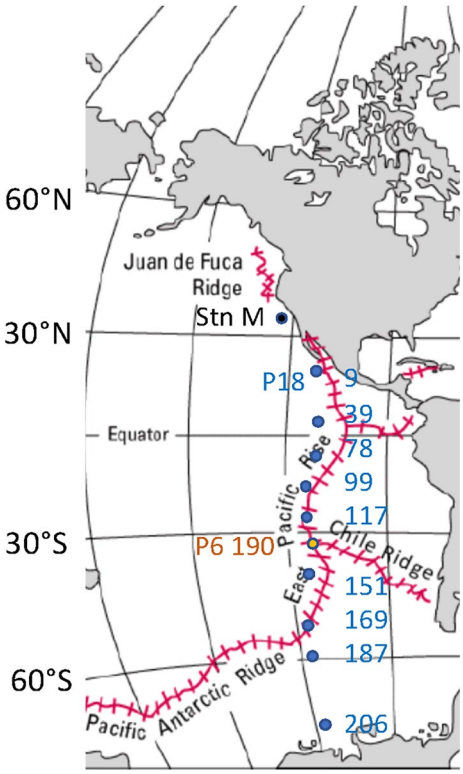


**Figure 1.** Station locations occupied during the P18 cruise (blue circles), Stn M cruises (black circle) (34°50′N 123°0′W) (Beaupré & Druffel 2009) and the P6 cruise (orange circle) (Druffel & Griffin, 2015). Positions and names of spreading ridges appear on the ocean floor.

explanations for their data, yet this concept remains an active study area. Another hypothesis predicts that a large amount of young DOC (~30%) is present in the deep ocean (Follett et al., 2014). However, 30% far exceeds new production measurements (Falkowski, 2014), net additions of refractory DOC to the deep Atlantic (Romera-Castillo et al., 2019), and calculations of POC dissolution in the deep Atlantic and Arctic using DOC $\Delta^{14}C$ measurements (Druffel et al. 2016, 2017).

Hansell and Carlson (2013) hypothesized localized sinks of refractory DOC in the Pacific, though these sinks remain unidentified. From bioassay experiments of Atlantic water, Shen and Benner(2018) found that photodegradation and photoenhanced biodegradation are responsible for over half of the removal of refractory DOC from deeper waters that cycle to the surface in the Atlantic. Beaupré et al. (2019) showed that freshly produced, primary marine aerosol contained 19%–40% refractory DOC. These studies provide sink mechanisms for refractory DOC from the ocean.

Chemoautotrophy at off-axis, hydrothermal systems has been invoked as a source of DOC to deep seawater (Druffel & Griffin, 2015; Estes et al., 2019; Lang et al., 2006; McCarthy et al., 2011), suggesting that low DOC $\delta^{13}C$ and $\Delta^{14}C$ values can be explained by this process. Shah Walter et al. (2018) report that deep DOC is removed from crustal rocks surrounding the Mid-Atlantic ridge, and are consistent with microbe-mediated oxidation. The microbial carbon pump is hypothesized as responsible for the production of refractory DOC (Jiao et al., 2010). Walker et al. (2016) found that organic matter is more chemically degraded as it decreases in size, and that small particles and molecules persist in the ocean longer than their larger counterparts. These studies addressing sources and sinks of marine DOC are primary motivations for the present work.

We show that DOC $\Delta^{14}C$ in deep water (2,000–3,500 m) from the eastern Pacific and Southern Oceans (along ~110°W) ranges from −480‰ to −578‰, a larger range than that found for the central Pacific and Southern Oceans (−500‰ to−560‰) (Druffel et al. 2019). Aging of circumpolar deep water (CDW) with latitude from 69°S in the Southern Ocean to 20°N in the eastern Pacific was equal in both DIC (Key & McNichol, 2020) and DOC (this work). We find that DOC $\Delta^{14}C$ values for water samples from P18 correlate with $\delta^{3}He$ measurements from a previous P18 cruise in 1994 (Jenkins, 2014). The DOC $\delta^{13}C$ values in deep waters are variable, with some low values at stations close to the East Pacific Rise. We suggest that hydrothermal influence of DOC near the East Pacific Rise may be contributing to low DOC $\Delta^{14}C$ and $\delta^{13}C$ values in this region.

## 2. Collection and Methods

Seawater was collected from two legs of the GO-SHIP P18 cruise along 103°–110°W from 20°N to 69°S aboard the NOAA Ship Ronald H. Brown (November 2016–February 2017) (Figure 1). Samples collected from nine stations are reported here (Table S1). DOC samples shallower than 400 m were filtered using precombusted (540°C, 2 hr), GFF (0.7 μm) filters. DOC samples were collected in precombusted, 1L Amber Boston Round glass bottles with acid cleaned (10% HCl), polytetrafluorethylene (PTFE)-lined caps with additional PTFE sheet liners (cleaned in Chromerge), and frozen at −20°C at an angle to prevent breakage at −20°C until analysis.

In the lab, DOC samples were thawed by immersion in hot water and shaken to fully dissolve salt crystals (Beaupré et al. (2007)). Samples were diluted with 18.2 Ω MQ water ([DOC] = 0.8 ± 0.3 μM), acidified with 85% phosphoric acid, and stripped of DIC with ultrapure He gas. The sample was then UV oxidized

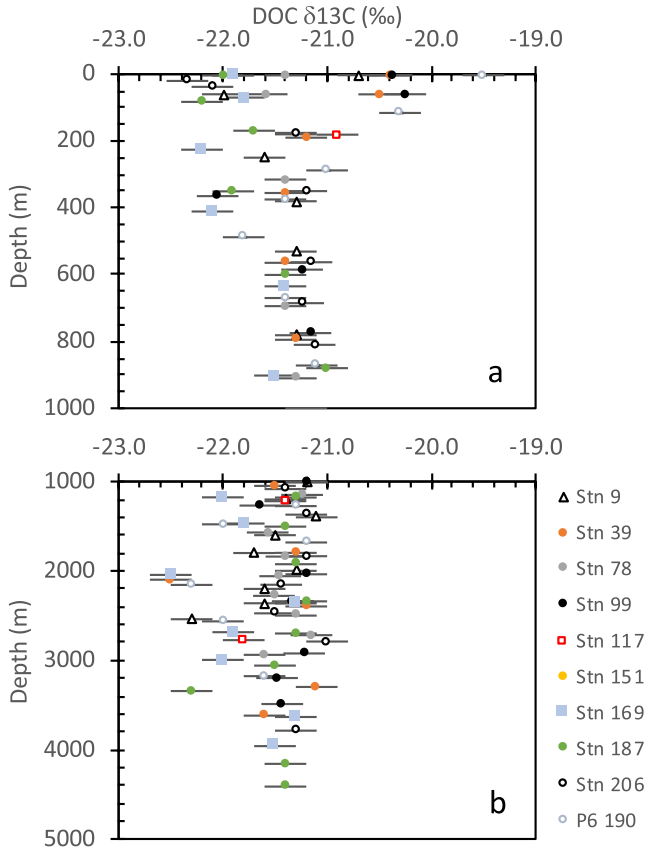


**Figure 2.** DOC $\delta^{13}C$ values versus depth for samples collected on the P18 cruise and station 190 on the P6 cruise at 32.5°S 115.9°W in 2010 from (a) 0–1,000 m, and (b) 1,000–5,000 m depth.

to produce $CO_2$ for 4 hr in a quartz reactor and collected as described by Beaupré et al. (2007) and B. D. Walker et al. (2019). Reported [DOC] (uncertainty ± 1.3 μM) were corrected for $CO_2$ loss due to breakthrough from the Horibe glass trap cooled with liquid nitrogen during collection, whose mass was quantified via integration using an infrared $CO_2$ gas analyzer (LI-COR Inc., model LI-6252; B. D. Walker et al., 2019). For $\Delta^{14}C$ measurements, samples were converted from $CO_2$ to graphite by reduction on iron catalyst using the zinc method (Walker & Xu, 2019; Xu et al., 2007). Radiocarbon measurements were made by us at the Keck Carbon Cycle AMS Laboratory at the University of California, Irvine (Santos et al., 2010).

Radiocarbon results are reported as $\Delta^{14}C$ values that are corrected for date of collection according to convention (Stuiver & Polach, 1977). Total uncertainty of the $\Delta^{14}C$ analyses are ±5‰. The $\delta^{13}C$ value of each sample was measured on a split of the $CO_2$ that was produced from UV oxidation of the DOC sample using a Gas Bench II and Thermo Electron Delta Plus isotope ratio mass spectrometer, with a total analytical uncertainty of ±0.2‰.

## 3. Results

### 3.1. DOC Concentrations

At 9 stations sampled on the P18 cruise, DOC concentrations ([DOC]) were highest in the upper 70 m of the water column (39.6–84.3 μM; Figure S1 and Table S2). Concentrations decreased rapidly by 1,000 m depth, and ranged from 35.4–55.2 μM between 71 and 1,000 m. The average [DOC] values below 1,000 m for most stations were similar within error, ranging from 35.0 ± 2.3 μM (stn 99) to 40.2 ± 2.0 μM (stn 169). These values are within statistical uncertainty to averages of [DOC] measurements reported for nearby or the same stations on this P18 cruise (Hansell, 2019).

### 3.2. DOC $\delta^{13}C$ Measurements

The DOC $\delta^{13}C$ values ranged from −22.4‰ (stn 206) to −20.3‰ (stn 99) in the upper 1,000 m of the water column (Figure 2 and Table S2). Values were less variable below 1,000 m, where station averages ranged from −21.8 ± 0.4‰ (stn 169) to −21.3 ± 0.2‰ (stn 206). Twelve low values (−22.5 to −21.8‰) were found between 1,200 and 3,400 m at stations 9, 39, 117, 169, 187 and 190 (P6). Most of these low $\delta^{13}C$ values are found at stations located close to the East Pacific Rise, a hydrothermal ridge system (see Section 4.4).

### 3.3. DOC $\Delta^{14}C$ Measurements

The DOC $\Delta^{14}C$ values for surface samples collected from nine stations on the P18 cruise ranged from −444‰ (stn 206) to −200‰ (stn 9) (Figure 3a and Table S2). Lower values (−444‰ to −355‰) were observed for samples at high latitudes (stns 169, 187 and 206) (Figure 3b). Values decreased quickly with depth in the upper 1,000 m, which include Subantarctic Mode Water (SAMW) and Antarctic Intermediate Water (AAIW) (see Section 4.1). The DOC $\Delta^{14}C$ values below 1,000 m ranged from −578‰ (stn 117) to −471‰ (stn 206).

## 4. Discussion

The discussion is presented in four parts. First, we discuss the presence of bomb $^{14}C$ in DOC in the upper 1,000 m of the Pacific water column that includes SAMW and AAIW. Second, we evaluate the correlation between the DOC and DIC $\Delta^{14}C$ values for samples from the same niskin bottles and the implications for the

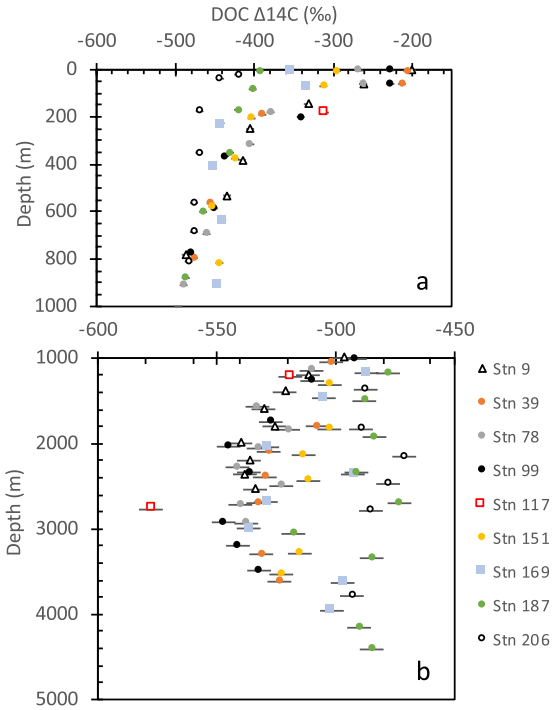


**Figure 3.** DOC Δ14C values versus depth for samples collected from 9 stations on the P18 cruise in 2016/17 from (a) 0–1,000 m, and (b) 1,000–5,000 m depth.

carbon cycle and presence of bomb $^{14}C$. Third, we compare the $^{14}C$ aging of DOC and DIC in the northward flowing CDW of the Pacific and Southern Oceans. Implications are discussed regarding the primary control on DOC $^{14}C$ aging in the deep Southern and eastern Pacific oceans. Fourth, we discuss the low DOC $\Delta^{14}C$ and $\delta^{13}C$ values between 1,200 and 3,400 m at six stations and possible explanations for these low isotopic values.

### 4.1. DOC Isotopic Distributions in Water Masses of the Upper Ocean

In addition to naturally produced $^{14}C$, DOC in the upper 1,000 m of the water column contains bomb $^{14}C$ that was produced in the late 1950s and early 1960s by testing of thermonuclear bombs in the stratosphere (Druffel et al. 2019; Williams & Druffel, 1987). This is implied because bomb $^{14}C$ was found in oceanic DIC in the Pacific (<1,000 m) during the 1960s (Bien et al., 1965), 1970s (Östlund & Stuiver, 1980) and 1990s (Key et al., 2004).

In our P18 data set, the highest DOC $\Delta^{14}C$ values (−268‰ to −200‰) are found in the surface (<20 m) of the tropical and subtropical Pacific (stns 9, 39, 78, and 99) (Figure 3a and Table S2). Lower surface values (−421‰ to −295‰) are found at higher latitudes (stn 151, 169, 187, and 206), where deeper isopycnals intersect the sea surface, and lower $\Delta^{14}C$ waters come to the surface. This upwelling is especially intense in the Southern Ocean (stns 187 and 206) where surface DOC $\Delta^{14}C$ values are −393‰ and −421‰, respectively (Figure 3a and Table S2). These results agree with earlier surface DOC $\Delta^{14}C$ results from the Southern Ocean (Bercovici et al., 2018; Druffel & Bauer, 2000) and the central Pacific (Druffel et al., 2019).

There is a significant correlation between surface DOC $\delta^{13}C$ values (from 3 to 20 m) and sea surface temperatures (SSTs; Figure S3). This is similar to the correlation between surface DOC $\delta^{13}C$ and SST found for samples from the central Pacific (Druffel et al., 2019) (Figure S3). Rau et al. (1989) determined that the correlation between SST and plankton $\delta^{13}C$ values was due to an inverse relationship between plankton $\delta^{13}C$ and dissolved $CO_2$ concentration, due to intracellular carbon fixation. This relationship is consistent with surface primary producers as the main control on the carbon isotopic signature of DOC in the surface ocean.

SAMW is produced in the sub Antarctic region of the Pacific (sigmaΘ 25.4–26.9, ~200–500 m), flows northwestward toward the equator, and then eastward in the Equatorial Undercurrent (Rodgers et al., 2003; Toggweiler et al., 1991). Samples of SAMW lie between 41°S and 5°N (stns 151, 117, 99, 78, and 39), and have DOC $\Delta^{14}C$ values ranging from −462‰ to −341‰ (Figure S2 and Table S2). Formed in the Antarctic convergence zone (50°–60°S), AAIW has low salinity (34.3–34.6) and density (sigmaΘ 26.9–27.45). Samples in AAIW are found between 59.5°S and 5°N (stns 187, 151, 117, 99, 78, and 39) and have DOC $\Delta^{14}C$ values that range from −519‰ to −424‰ (Figure S2 and Table S2). There are no significant trends in DOC $\Delta^{14}C$ with latitude in either SAMW or AAIW, which is expected because the transport times of these water masses from the Southern Ocean to the equator is of the order of decades (Toggweiller et al., 1991) and is not discernable in the decay of $^{14}C$ over this short time period.

### 4.2. Correlation Between $\Delta^{14}C$ of DOC and DIC in the Southern Ocean and East Pacific

A significant correlation is found between DOC $\Delta^{14}C$ (this work) and DIC $\Delta^{14}C$ (Key & McNichol, 2020) values obtained in samples from the same niskin bottles at eight of the stations on the P18 cruise (Figure S4). The Model II geometric mean regression of all DOC $\Delta^{14}C$ versus DIC $\Delta^{14}C$ values reveals a significant correlation ($r^2 = 0.84$). This is in agreement with central Pacific measurements that also showed a significant correlation between DOC $\Delta^{14}C$ versus DIC $\Delta^{14}C$ values (Druffel et al., 2019).

Keeling plots of $[DOC]^{-1}$ versus DOC $\Delta^{14}C$ have shown significant linear correlations at several open ocean sites, although diapycnal transport throughout the entire water column does not occur (Beaupré & Aluwihare 2010). This conundrum was recently addressed by Beaupré et al. (2020) who introduced a new tool, fractionation- and decay-corrected concentration of $^{14}C$ atoms in DOC and DIC. They found that higher resolution depth profiles are needed in order to identify regions with unique DOC biogeochemistry. Notwithstanding, the correlation between DOC and DIC $\Delta^{14}C$ values in the open ocean likely indicates that the depth of penetration of bomb $^{14}C$ is similar in DOC and DIC pools (<1,000 m).

### 4.3. Comparison Between $^{14}C$ Aging of DOC and DIC in CDW

We calculate the aging of DOC and DIC in CDW that flows generally northward in the eastern Pacific as defined by Roussenov et al. (2004). Roussenov et al. (2004) studied the mechanisms that control DIC $\Delta^{14}C$ distribution in the deep Pacific using an isopycnic ocean general circulation and tracer model. Their model results show that the deepest water in the eastern Pacific along 110°W (sigma4 45.84) flows generally northward from 30°S to 10°S and 20°N to 50°N, and eastward in the tropics.

DOC $^{14}C$ ages were calculated from $\Delta^{14}C$ values for samples whose densities (sigma4) ranged from 45.75 to 45.80 (~2,500–3,600 m depth) and were plotted versus latitude for water samples from P18 (this work), one station in the southeastern Pacific (P6 stn 190 32.5°S, 87.53°W in 2010; Druffel & Griffin, 2015) and one station in the northeastern Pacific (stn M 34.8°N 123.0°W; Beaupré and Druffel 2009) (Figure S5a in the supporting information). The Model II geometric mean regression of DOC $^{14}C$ ages versus latitude ($r^2 = 0.61$) is significant, showing a decrease from 69°S (5,440 ± 140 $^{14}C$ years) to 34.8°N (6,620 ± 140 $^{14}C$ years) of 1,180 ± 280 $^{14}C$ years. The high $^{14}C$ age for the DOC sample (6,900 $^{14}C$ years) at 25°S (stn 117) is anomalous. There is an apparent plateau in $^{14}C$ ages between 32°S and 20°N.

We compare DOC aging to that of DIC from measurements made on the same P18 cruise in 2016/17 (Key & McNichol, 2020), the P6 cruise in 2010 (stn 190) and stn M, which are plotted versus latitude (Figure S5b in the supporting information; Beaupré and Druffel 2009; Masiello et al., 1998; McNichol & Key, 2019). The Model II geometric mean regression displays a significant relationship ($r^2 = 0.87$). The decrease of the DIC $^{14}C$ age at 69°S (1,430 ± 30 $^{14}C$ years) and 34.8°N (2,450 ± 30 $^{14}C$ years) is 1,020 ± 60 $^{14}C$ years, equivalent within error to that obtained for DOC. In addition, the Model II regression slopes for both DOC (11.3 ± 2.1) and DIC (9.81 ± 0.49) versus latitude are equal within error. We also notice a plateau in $^{14}C$ DIC ages, although the range (between 20°S and 20°N) is narrower than that observed for the $^{14}C$ DOC ages (between 32°S and 20°N). The cause of these plateaus is not clear at this time, though we note that deep water transport is generally northward between 30°S and 10°S, and eastward between 10°S and 10°N (Roussenov et al., 2004).

It is apparent that both DOC and DIC age similarly in CDW as it flows generally northward from the Southern Ocean to the eastern Pacific. However, this measure of aging is likely a minimum estimate, due to the mixing between CDW and the North Pacific Deep Water that lies above it (Lavergne et al., 2017; Roussenov et al., 2004). This finding, that circulation is the primary control on $^{14}C$ content of DOC in CDW, indicates that the deep DOC is refractory on timescales of >1,000 years.

A rough measure of rate of utilization of DOC in CDW can be made using the transit time calculated above and the average decrease in [DOC] from the deep Southern Ocean to the deep northeast Pacific. It has been reported that [DOC] decreases with latitude northward from 40 μmol C $kg^{-1}$ in the Southern Ocean to 38 μmol C $kg^{-1}$ in the northeast Pacific Ocean (Hansell & Carlson, 2013). Thus the utilization rate of refractory DOC in CDW is 0.002 ± 0.001 μmol C $kg^{-1}$ $yr^{-1}$ (2 ± 1 μmol $kg^{-1}$/1,180 ± 280 $^{14}C$ yr). Hansell et al. (2012) report a removal rate of refractory DOC in the subsurface ocean of 0.0027 μmol C $kg^{-1}$ $yr^{-1}$, similar to the rate we calculate.

### 4.4. Are Low DOC $\Delta^{14}C$ and $\delta^{13}C$ Values Evidence of Hydrothermal DOC?

The deep DOC $\Delta^{14}C$ values along the P18 section (Figure S2) generally decrease from the Southern Ocean into the east Pacific from about −500‰ to −540‰. This is in contrast to the central Pacific, where there were low DOC $\Delta^{14}C$ values (−540‰ to −570‰) between 2,000 m and 3,500 m in the North Pacific extending

from 10°N to 53°N (Druffel et al., 2019); this was attributed to southward flowing North Pacific Deep Water returning to the south Pacific.

An unusually low DOC $\Delta^{14}C$ value is found at 25°S (stn 117), −578 ± 5‰ at 2,775 m, and is starkly different from the other measurements in the eastern Pacific from 50°S to 20°N that range from −510‰ to −547‰ (Figures 3b and S2 in the supporting information). There are low $\delta^{13}C$ values found for 12 samples (−22.4 to −21.8‰) between 1,200 and 3,400 m at stations 9, 39, 117, 169, 187, and 190 (P6) (Figure 2b). Most of these low $\delta^{13}C$ values are found at stations located close to the hydrothermal ridge system of the East Pacific Rise (Figure 1).

The low $\Delta^{14}C$ and $\delta^{13}C$ values may be explained in several ways: (a) the presence of $^{14}C$-free contamination (e.g., oil) in the samples, (b) utilization of young DOC, leaving behind old DOC, or c) the presence of hydrothermally influenced DOC. First, the presence of carbon contamination is not suspected, because the [DOC] of the sample with a low DOC $\Delta^{14}C$ value (35.8 ± 1.2 μM) was similar to those measured at the other stations (average 37.6 ± 1.8 μM Table S2). A mass balance calculation reveals that a $\Delta^{14}C$ value of −578‰ (assuming the actual value is equal to the average of surrounding stations >1,000 m depth, −520‰) would require 12% carbon of the sample to have $\Delta^{14}C = -1{,}000$‰, and a [DOC] of 46 μM. It is also unlikely that utilization of young DOC, leaving behind old DOC in the deep water could explain the low DOC $\Delta^{14}C$ value at 25°S, because the [DOC] in the sample was equal to the average of those from the other stations. This indicates that there was no measurable loss of DOC in the sample from the 25°S station compared to those from the other stations.

Third, the low DOC $\Delta^{14}C$ and $\delta^{13}C$ values may be explained by ancient DOC emanating from hydrothermal venting of ocean water through porous ocean crust. Ridge-flank systems have been shown to strip out oceanic DOC onto porous basalts (Lang et al., 2006) and deliver chemoautotrophically produced DOC with low $\Delta^{14}C$ (−772 to −835‰) and low $\delta^{13}C$ (−26 to −34.5‰) values (McCarthy et al., 2011) to the deep northeast Pacific. DOC concentrations would not be expected to increase during this process (Lang et al., 2006).

To test this hypothesis, we use excess $^{3}He$ ($\delta^{3}He$) in seawater, which is a tracer of input of hydrothermal waters from ridges and flanks into the deep ocean (Lupton and Craig 1981). A Model II geometric mean regression of all DOC $\Delta^{14}C$ values versus $\delta^{3}He$ values (>1,000 m from nearby stations from the P18 cruise in 1994; Lott & Jenkins, 1998; Jenkins, Doney, Fendrock, Fine, et al., 2018a, 2018b) shows a significant correlation ($r^2 = 0.55$, $y = -0.29 \pm 0.03 \cdot x - 129 \pm 7$) (Figure S6). This is equal within error to that found for the south Pacific data along 32.5°S on the P6 cruise in 2010 ($r^2 = 0.86$, $y = -0.30 \pm 0 .02 \cdot x - 135 \pm 11$) (Druffel & Griffin, 2015). This comparison is not ideal, because 22 years have elapsed between the collection of the P18 $\delta^{3}He$ samples and the DOC $\Delta^{14}C$ samples reported here. However, the similarity of the DOC $\Delta^{14}C$ and $\delta^{3}He$ correlations in the eastern and southern (Druffel & Griffin, 2015) Pacific Ocean indicates that hydrothermal processes may be influencing DOC in regions of the Pacific Ocean where there is known influence by hydrothermal inputs on the East Pacific Rise (Figure 1) (J. Lupton, 1998).

## 5. Implications for the DOC Cycle and Future Work

We have demonstrated that the aging of DOC and DIC in the deep eastern Pacific and Southern Oceans is equal within error, indicating that transport northward is the primary control of $^{14}C$ decay on both forms of dissolved carbon. This has also been shown for DOC and DIC in northward flowing Antarctic Bottom Water in the central Pacific (Druffel et al., 2019). A large fraction of the DOC in the deep ocean is refractory (Hansell, 2013), and it would appear that there is little change in this refractory DOC during transport in the deep Pacific. Shen and Benner (2018) report that the mass of refractory DOC could increase as circulation slows in a warming ocean. This makes understanding the residence time of DOC in the ocean crucial for predicting how the global carbon cycle will adjust as the Earth's climate changes.

Further studies of the input of DOC from hydrothermal sources are needed to assess the magnitude of ancient DOC entering the deep ocean. Comparison of the low DOC $\Delta^{14}C$ and $\delta^{13}C$ values reported here with measurements of $\delta^{3}He$ in samples from the P18 cruise in 2016/17 are essential. Estes et al. (2019) observed that both high and low temperature hydrothermal vents at the East Pacific Rise (9°50′N 104°17.5′W) vent

field are a source of submicron, abiotically produced graphite. The magnitude of a hydrothermal source(s) of DOC remains an open question.

If hydrothermal vents are adding ancient DOC to the deep sea, it may be leading us to overestimate the ocean's ability to store refractory DOC. Thus, the higher the hydrothermal DOC source, the lower the time that the deep ocean may actually store refractory DOC.

Additionally, molecular techniques are needed to identify the source or sources of DOC to the deep Pacific. Optical analyses, Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FTICR-MS), and untargeted metabolomics have been used to analyze vent fluid DOC to find evidence of organic sulfur compounds and amino acids that have been interpreted as evidence of chemosynthesis (Grandy et al., 2020; Longnecker et al., 2018; Rossel et al., 2015). In situ analysis of vent fluid has been accomplished with Raman spectroscopy and liquid chromatography mass spectrometry (LC-MS) (Camilli et al., 2009; White et al., 2006). Recently, in situ solid phase microextraction of DOC that utilized a protein-resistant coating on the resin that protected metabolites from degradation after extraction was reported (Grandy et al., 2020). This approach, or a similar one that preserves the chemosynthetic signal, could prove invaluable for diagnosing hydrothermal-derived DOC.

## Data Availability Statement

Data from the P18 cruise are available in Table S2 and at the Repeat Hydrography Data Center at the CCHDO website (https://doi.org/10.7289/v5cv4g1w) using the expocode 33RO20161119. There are no real or perceived financial conflicts of interests for any author.

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## References

Arrieta, J., Mayol, E., Hansman, R. L., Herndl, G. J., Dittmar, T., & Duarte, C. M. (2015). Dilution limits dissolved organic carbon utilization in the deep ocean. *Science*. https://doi.org/10.1126/science.1258955

Beaupré, S. R., & Aluwihare, L. (2010). Constraining the 2-component model of marine dissolved organic radiocarbon. *Deep Sea Research Part II: Topical Studies in Oceanography*, *57*(16), 1494–1503. https://doi.org/10.1016/j.dsr2.2010.02.017

Beaupré, S. R., & Druffel, E. R. M. (2009). Constraining the propagation of bomb-radiocarbon through the dissolved organic carbon (DOC) pool in the northeast Pacific Ocean. *Deep Sea Research Part I: Oceanographic Research Papers*, *56*(10), 1717–1726. https://doi.org/10.1016/j.dsr.2009.05.008

Beaupré, S. R., Druffel, E. R. M., & Griffin, S. (2007). A low-blank photochemical extraction system for concentration and isotopic analyses of marine dissolved organic carbon. *Limnology and Oceanography: Methods*, *5*, 174–184. https://doi.org/10.4319/lom.2007.5.174

Beaupré, S. R., Kieber, D. J., Keene, W. C., Long, M. S., Maben, J. R., Lu, X., et al. (2019). Oceanic efflux of ancient marine dissolved organic carbon in primary marine aerosol. *Science Advances*. https://doi.org/10.1126/sciadv.aax6535

Beaupré, S. R., Walker, B. D., & Druffel, E. R. M. (2020). The two–component model coincidence: Evaluating the validity of marine dissolved organic radiocarbon as a stable–conservative tracer at Station M. *Deep-Sea Research II*, *173*, 104737. https://doi.org/10.1016/j.dsr2.2020.104737

Bercovici, S. K., McNichol, A. P., Xu, L., & Hansell, D. A. (2018). Radiocarbon content of dissolved organic carbon in the South Indian Ocean. *Geophysical Research Letters*, *45*(2), 872–879. https://doi.org/10.1002/2017gl076295

Bien, G. S., Rakestraw, N. W., & Suess, H. E. (1965). Radiocarbon in the Pacific and Indian oceans and its relation to deep water movements. *Limnology & Oceanography*, *10*, R25–R37. https://doi.org/10.4319/lo.1965.10.suppl2.r25

Broek, T. A. B., Walker, B. D., Guilderson, T. P., & McCarthy, M. C. (2020). Low molecular weight dissolved organic carbon: Aging, compositional changes, and selective utilization during global ocean circulation. *Global Biogeochemical Cycles*. http://10.1029/2020GB006547

Broek, T. A. B., Walker, B. D., Guilderson, T. P., & McCarthy, M. D. (2017). Coupled ultrafiltration and solid phase extraction approach for the targeted study of semi-labile high molecular weight and refractory low molecular weight dissolved organic matter. *Marine Chemistry*, *194*, 146–157. https://doi.org/10.1016/j.marchem.2017.06.007

Camilli, R., Mallios, A., Sakellariou, D., Bingham, B., Eustice, R., & Goudreau, J. (2009). *Real-time in-situ chemical and localization sensors integration in human occupied submersible for studying hydrothermal vents*. In Proceedings of the 9th Hellenic Symposium of Oceanography and Fishery. Patra, Greece.

Coppola, A. I., & Druffel, E. R. M. (2016). Cycling of black carbon in the ocean. *Geophysical Research Letters*, *43*, 4477–4482. https://doi.org/10.1002/2016GL068574

Druffel, E. R. M., & Bauer, J. E. (2000). Radiocarbon distributions in Southern Ocean dissolved and particulate organic matter. *Geophysical Research Letters*, *27*(10), 1495–1498. https://doi.org/10.1029/1999GL002398

Druffel, E. R. M., & Griffin, S. (2015). Radiocarbon in dissolved organic carbon of the South Pacific Ocean. *Geophysical Research Letters*, *42*, 4096–4101. https://doi.org/10.1002/2015GL063764

Druffel, E. R. M., Griffin, S., Coppola, A. I., & Walker, B. D. (2016). Radiocarbon in dissolved organic carbon of the Atlantic Ocean. *Geophysical Research Letters*, *43*, 5279–5286. https://doi.org/10.1002/2016GL068746

Druffel, E. R. M., Griffin, S., Glynn, C. S., Benner, R., & Walker, B. D. (2017). Radiocarbon in dissolved organic and inorganic carbon of the Arctic Ocean. *Geophysical Research Letters*, *44*, 2369–2376. https://doi.org/10.1002/2016GL072138

Druffel, E. R. M., Griffin, S., Wang, N., Garcia, N. G., McNichol, A. P., Key, R. M., & Walker, B. D. (2019). Dissolved organic radiocarbon in the central Pacific Ocean. *Geophysical Research Letters*, *46*, 5396–5403. https://doi.org/10.1029/2019GL083149

Estes, E. R., Berti, D., Coffey, N. R., Hochella, M. F., Wozniak, A. S., & Luther, G. W. (2019). Abiotic synthesis of graphite in hydrothermal vents. *Nature Communications*, *10*. https://doi.org/10.1038/s41467-019-13216-z

Falkowski, P. G. (2014). Biogeochemistry of Primary Production in the Sea Treatise on geochemistry, *Biogeochemistry*, *10*, 163–187. https://doi.org/10.1016/b978-0-08-095975-7.00805-6

Follett, C. L., Repeta, D. J., Rothman, D. H., Xu, L., & Santinelli, C. (2014). Hidden cycle of dissolved organic carbon in the deep ocean. *Proceedings of the National Academy of Sciences of the United States of America*, *111*, 16706–16711. https://doi.org/10.1073/pnas.1407445111

Grandy, J. J., Onat, B., Tunnicliffe, V., Butterfield, D. A., & Pawliszyn, J. (2020). Unique solid phase microextraction sampler reveals distinctive biogeochemical profiles among various deep-sea hydrothermal vents. *Scientific Reports*, *10*, 1360. https://doi.org/10.1038/s41598-020-58418-4

Hansell, D. A. (2013). Recalcitrant Dissolved Organic Carbon Fractions. *Annual Review of Marine Science*, *5*, 421–445. https://doi.org/10.1146/annurev-marine-120710-100757

Hansell, D. A. (2019). *DOC/DON data from P18 cruise in 2016/2017. expo code 33RO20161119*. Retrieved from https://www.ncei.noaa.gov/data/oceans/ncei/ocads/data/0171546/33RO20161119.exc.csv

Hansell, D. A., & Carlson, C. A. (2013). Localized refractory dissolved organic carbon sinks in the deep ocean. *Global Biogeochemical Cycles*, *27*. https://doi.org/10.1002/gbc.20067

Hansell, D. A., Carlson, C. A., & Schlitzer, R. (2012). Net removal of major marine dissolved organic carbon fractions in the subsurface ocean. *Global Biogeochemical Cycles*, *26*(1), GB1016. https://doi.org/10.1029/2011GB004069

Hansman, R. L., Griffin, S., Watson, J. T., Druffel, E. R. M., Ingalls, A. E., Pearson, A., & Aluwihare, L. I. (2009). The radiocarbon signature of microorganisms in the mesopelagic ocean. *Proceedings of the National Academy of Sciences*, *106*, 6513–6518. https://doi.org/10.1073/pnas.0810871106

Ingalls, A. E., Shah, S. R., Hansman, R. L., Aluwihare, L. I., Santos, G. M., Druffel, E. R. M., & Pearson, A. (2006). Quantifying archeal community autotrophy in the mesopelagic ocean using natural radiocarbon. *Proceedings of the National Academy of Sciences*, *103*(17), 6442–6447. https://doi.org/10.1073/pnas.0510157103

Jenkins, W. (2014). *δ3He data set from P06 cruise January-April 2010, and from P16N February-April 1991*. Retrieved from http://cdiac.ornl.gov/ftp/oceans/CLIVAR/P06_2009/

Jenkins, W. J., Doney, S. C., Fendrock, M. A., Fine, R. A., et al. (2018a). *A comprehensive global oceanic dataset of discrete measurements of helium isotope and tritium during the hydrographic cruises on various ships from 1952-10-21 to 2016-01-22 (NCEI Accession 0176626)*. NOAA National Centers for Environmental Information. Dataset. https://doi.org/10.25921/c1sn-9631

Jenkins, W. J., Doney, S. C., Fendrock, M. A., Fine, R. A., et al. (2018b). *A comprehensive global oceanic dataset of discrete measurements of helium isotope and tritium during the hydrographic cruises on various ships from 1952-10-21 to 2016-01-22 (NCEI Accession 0176626)*. NOAA National Centers for Environmental Information. Dataset. https://doi.org/10.25921/c1sn-9631

Jiao, N., Herndl, G. J., Hansell, D. A., Benner, R., Kattner, G., Wilhelm, S. W. (2010). Microbial production of recalcitrant dissolved organic matter: Long-term carbon storage in the global ocean. *Nature Reviews Microbiology*, *8*, 593–599. https://doi.org/10.1038/nrmicro2386

Jiao, N., legendre, L., Robinson, C., Thomas, H., Luo, Y.-W., Dang, H., et al. (2015). Comment on "Dilution limits dissolved organic carbon utilization in the deep ocean". *Science*, *350*(6267), 1483. https://doi.org/10.1126/science.aab2713

Key, R. M., Kozyr, A., Sabine, C. L., Lee, K., Wanninkhof, R., Bullister, J. L., et al. (2004). A global ocean carbon climatology: Results from Global Data Analysis Project (GLODAP). *Global Biogeochemical Cycles*, *18*, GB4031. https://doi.org/10.1029/2004GB002247

Key, R. M., & McNichol, A. P. (2020). *DIC-14C data from P18 cruise legs 1 and 2 in 2016/17. expo code 33RO20161119*. https://doi.org/10.7289/v5cv4g1w

Lang, S. Q., Butterfield, D. A., Lilley, M. D., Paul Johnson, H., & Hedges, J. I. (2006). Dissolved organic carbon in ridge-axis and ridge-flank hydrothermal systems. *Geochimica et Cosmochimica Acta*, *70*, 3830–3842. https://doi.org/10.1016/j.gca.2006.04.031

Lavergne, C., Madec, G., Roquet, F., Holmes, R. M., & McDougall, T. J. (2017). Abyssal Ocean overturning shaped by seafloor distribution. *Nature*, *551*(7679), 181–186. https://doi.org/10.1038/nature24472

Loh, A. N., Bauer, J. E., & Druffel, E. R. M. (2004). Variable aging and storage of dissolved organic components in the open ocean. *Nature*, *430*(7002), 877–881. https://doi.org/10.1038/nature02780

Longnecker, K., Sievert, S. M., Sylva, S. P., Seewald, J. S., & Kujawinski, E. B. (2018). Dissolved organic carbon compounds in deep-sea hydrothermal vent fluids from the East Pacific Rise at 9°50′N. *Organic Geochemistry*, *125*, 41–49. https://doi.org/10.1016/j.orggeochem.2018.08.004

Lott, D. E., & Jenkins, W. J. (1998). Advances in the analysis and shipboard processing of tritium and helium samples. *International WOCE Newsletter*, *30*, 27–30.

Lupton, J. (1998). Hydrothermal helium plumes in the Pacific Ocean. *Journal of Geophysical Research*, *103*(C8), 15853–15868. https://doi.org/10.1029/98jc00146

Lupton, J. E., & Craig, H. (1981). A Major Helium-3 Source at 15 S on the East Pacific Rise. *Science*, *214*, 13–18. https://doi.org/10.1126/science.214.4516.13

Masiello, C. A., Druffel, E. R. M., & Bauer, J. E. (1998). Physical controls on dissolved inorganic radiocarbon variability in the California Current. *Deep Sea Research Part II: Topical Studies in Oceanography*, *45*(4–5), 617–642. https://doi.org/10.1016/s0967-0645(97)00096-9

McCarthy, M. D., Beaupré, S. R., Walker, B. D., Voparil, I., Guilderson, T. P., & Druffel, E. R. M. (2011). Chemosynthetic origin of 14C-depleted dissolved organic matter in a ridge-flank hydrothermal system. *Nature Geoscience*, *4*, 32–36. https://doi.org/10.1038/ngeo1015

McNichol, A. P., & Key, R. (2019). *DIC-14C data from P16N cruise leg 1 in 2015. expo code 33RO20150419*. https://doi.org/10.7289/v5cv4g1w

Meybeck, M. (1982). Carbon, nitrogen, and phosphorus transport by World Rivers. *American Journal of Science*, *282*, 401–450. https://doi.org/10.2475/ajs.282.4.401

Östlund, H. G., & Stuiver, M. (1980). Geosecs Pacific radiocarbon. *Radiocarbon*, *22*(1), 25–53. https://doi.org/10.1017/s0033822200004707

Rau, G. H., Takahashi, T., & Marais, D. J. D. (1989). Latitudinal variations in plankton δ13C: Implications for $CO_2$ and productivity in past oceans. *Nature*, *341*(6242), 516–518. https://doi.org/10.1038/341516a0

Repeta, D. J., & Aluwihare, L. I. (2006). Radiocarbon analysis of neutral sugars in high-molecular-weight dissolved organic carbon: Implications for organic carbon cycling. *Limnology & Oceanography*, *51*, 1045–1053. https://doi.org/10.4319/lo.2006.51.2.1045

Rodgers, K. B., Blanke, B., Madec, G., Aumont, O., Ciais, P., & Dutay, J.-C. (2003). Extratropical sources of equatorial Pacific upwelling in an OGCM. *Geophysical Research Letters*, *30*(2), 1084. https://doi.org/10.1029/2002GL016003

Romera-Castillo, C., Pelegri, J. L., Hansell, D. A., & Alvarez-Salgado, X. A. (2019). Net additions of recalcitrant dissolved organic carbon in the deep Atlantic Ocean. *Global Biogeochemical Cycles*, *33*(9). https://doi.org/10.1029/2018GB006162

Rossel, P. E., Stubbins, A., Hach, P. F., & Dittmar, T. (2015). Bioavailability and molecular composition of dissolved organic matter from a diffuse hydrothermal system. *Marine Chemistry*, *177*, 257–266. https://doi.org/10.1016/j.marchem.2015.07.002

Roussenov, V., Williams, R. G., Follows, M. J., & Key, R. M. (2004). Role of bottom water transport and diapycnic mixing in determining the radiocarbon distribution in the Pacific. *Journal of Geophysical Research*, *109*. C06015. https://doi.org/10.1029/2003JC002188

Santos, G. M., Southon, J. R., Drenzek, N. J., Ziolkowski, L. A., Druffel, E., Xu, X., et al. (2010). Blank assessment for ultra–small radiocarbon samples: Chemical extraction and separation vs. AMS. *Radiocarbon 52*(3), 1322–1335. https://doi.org/10.1017/s0033822200046415

Shaw Walter, S. R., Jaekel, U., Osterholz, H., Fisher, A. T., Huber, J. A., Pearson, A., et al. (2018). Microbial decomposition of marine dissolvedorganic matter in cool oceanic crust. *Nature Geoscience*, *11*. https://doi.org/10.1038/s41561-018-0109-5

Shen, Y., & Benner, R. (2018). Mixing it up in the ocean carbon cycle and the removal of refractory dissolved organic carbon. *Scientific Reports*. https://doi.org/10.1038/s41598-018-20857-5

Smith, K. L. J., Baldwin, R. J., & Williams, P. M. (1992). Reconciling particulate organic carbon flux and sediment community oxygen consumption in the deep North Pacific. *Nature*, *359*, 313–315. https://doi.org/10.1038/359313a0

Stuiver, M., & Polach, H. A. (1977). Discussion: Reporting of 14C data. *Radiocarbon*, *19*(3), 355–363. https://doi.org/10.1017/s0033822200003672

Toggweiler, J. R., Dixon, K., & Broecker, W. S. (1991). The Peru upwelling and the ventilation of the South Pacific thermocline. *Journal of Geophysical Research*, *96*(C11), 20467–20497. https://doi.org/10.1029/91JC02063

Verdugo, P., Alldredge, A. L., Azam, F., Kirchmand, D. L., Passowe, U., & Santschif, P. H. (2004). The oceanic gel phase: A bridge in the DOM–POM continuum. *Marine Chemistry*, *92*, 67–85. https://doi.org/10.1016/j.marchem.2004.06.017

Walker, B. D., Beaupré, S. R., Griffin, S., & Druffel, E. R. M. (2019). UV photochemical oxidation and extraction of marine dissolved organic carbon at UC Irvine: Status, surprises, and methodological recommendations. *Radiocarbon*, *61*(5), 1603–1617. https://doi.org/10.1017/RDC.2019.9

Walker, B. D., & Xu, X. (2019). An improved method for the sealed-tube zinc graphitization of microgram carbon samples and 14C AMS measurement. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, *438*, 58–65. https://doi.org/10.1016/j.nimb.2018.08.004

Walker, B. W., Beaupré, S. R., Guilderson, T. P., McCarthy, M. D., & Druffel, E. R. M. (2016). Pacific carbon cycling constrained by organic matter size, age and composition relationships. *Nature Geoscience*. https://doi.org/10.1038/ngeo2830

White, S. N., Dunk, R. M., Peltzer, E. T., Freeman, J. J., & Brewer, P. G. (2006). In situ Raman analyses of deep-sea hydrothermal and cold seep systems (Gorda Ridge and Hydrate Ridge). *Geochemistry, Geophysics, Geosystems*, *7*(5). https://doi.org/10.1029/2005GC001204

Williams, P. M., & Druffel, E. R. M. (1987). Radiocarbon in dissolved organic carbon in the central North Pacific Ocean. *Nature*, *330*, 246–248. https://doi.org/10.1038/330246a0

Xu, X., Trumbore, S. E., Zheng, S., Southon, J. R., McDuffee, K. E., Luttgen, M., & Liu, J. C. (2007). Modifying a sealed tube zinc reduction method for preparation of AMS graphite targets: Reducing background and attaining high precision. *Nuclear Instruments and Methods in Physics Research B*, *259*, 320–329. https://doi.org/10.1016/j.nimb.2007.01.175

Zigha, P., McNichol, A., Xu, L., Johnson, C., Santinelli, C., Karl, D. M., & Repeta, D. J. (2017). Allochthonous sources and dynamic cycling of ocean dissolved organic carbon revealed by carbon isotopes. *Geophysical Research Letters*, *44*. https://doi.org/10.1002/2016GL071348

Ziolkowski, L., & Druffel, E. R. M. (2010). Aged black carbon identified in marine dissolved organic carbon. *Geophysical Research Letters*, *37*, L16601. https://doi.org/10.1029/2010GL043963

## References from the Supporting Information

McNichol, A. P., & Key, R. (2015). *DIC-14C data from P6E cruise leg 2 in 2010. expo code 318M20091121*. https://doi.org/10.1002/2015GL063764