frontiers in Marine Science

MINI REVIEW
published: 08 September 2020
doi: 10.3389/fmars.2020.540165

Open-Ocean Minima in $\delta^{13}C$ Values of Particulate Organic Carbon in the Lower Euphotic Zone

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Extensive studies in the 1980s–1990s led to the characterization of latitudinal variations in sea surface $\delta^{13}C$ values of particulate organic carbon ($\delta^{13}C_{POC}$), and relationships were found with CO_2 concentrations, temperature, growth rates, and cell geometries. Surprisingly, no large-scale efforts have been made to describe variations in $\delta^{13}C_{POC}$ values over depth in the water column. Here we compile published examples demonstrating a widespread isotopic pattern in particulate organic carbon (POC) of the upper water column. In 51 vertical profiles, $\delta^{13}C_{POC}$ values in the lower euphotic zone on average are 1.4‰ lower than $\delta^{13}C_{POC}$ values in the upper euphotic zone of open ocean settings. In a majority of locations this vertical decrease in $\delta^{13}C_{POC}$ values is >2‰ and up to 5‰, larger than the commonly recognized vertical $\delta^{13}C$ variation in dissolved inorganic carbon over the same depths. We briefly review hypotheses and supporting evidence offered by previous studies of individual water columns: The observed patterns could result from vertical differences in photosynthetic growth rates or community composition, biochemical composition of organic matter due to degradation, isotopic disequilibrium within the dissolved inorganic carbon pool, particle dynamics, or seasonal vertical mixing. Coordinated isotopic, biological, and seawater chemistry data are sparse, and consistent drivers of this widespread isotopic pattern are currently elusive. Further work is needed to adequately characterize the environmental conditions coinciding with this pattern, to test its origins, and to determine if the magnitude of upper water column $\delta^{13}C_{POC}$ variations could be a useful marker of upper ocean carbon cycle dynamics.

Keywords: carbon isotopes, particulate organic carbon, water column, marine organic carbon, phytoplankton

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Specialty section:
This article was submitted to Marine Biogeochemistry, a section of the journal Frontiers in Marine Science

Received: *03 March 2020*
Accepted: *13 August 2020*
Published: *08 September 2020*

Citation:
Close HG and Henderson LC (2020) Open-Ocean Minima in $\delta^{13}C$ Values of Particulate Organic Carbon in the Lower Euphotic Zone. Front. Mar. Sci. 7:540165. doi: 10.3389/fmars.2020.540165

INTRODUCTION

Particulate organic carbon (POC) is the major carrier of carbon from the surface to the deep ocean (the biological pump); therefore, quantifying POC and understanding its origins and degradation are important priorities. POC is defined as all combustible carbon captured on filters of pore size ~0.7 μm and remaining after removal of carbonates by acidification. POC therefore encompasses diverse organic structures contained in the biomass of phytoplankton, heterotrophic and chemoautotrophic microbes, and detrital materials such as dead cells, cell fragments, fecal pellets, other aggregated material, and terrigenous or resuspended allochthonous organic matter. The naturally occurring stable carbon isotope ratio of POC ($\delta^{13}C_{POC}$) is one of the only chemical characterizations that captures the entire POC pool, since individual, measurable chemical components constitute only a small proportion of the total (Kharbush et al., 2020; this issue). Accordingly, $\delta^{13}C_{POC}$ values preserved in seafloor sediments are important factors in interpreting earth's past carbon cycle (Kump and Arthur, 1999).

$\delta^{13}C_{POC}$ values in the surface ocean have been relatively well-characterized, largely motivated by the possibility of using preserved $\delta^{13}C_{POC}$ values as an indicator of photosynthetic responses to past and evolving sea surface CO_2 concentrations (e.g., Rau et al., 1989; Freeman and Hayes, 1992; Francois et al., 1993; Goericke and Fry, 1994; Young et al., 2013). Open-ocean $\delta^{13}C_{POC}$ values vary from −35‰ at high latitudes to −16‰ at low-mid latitudes (Goericke and Fry, 1994). In contrast, the $\delta^{13}C$ value of dissolved CO_2 used as a substrate for photosynthesis only varies by ∼2‰ across surface waters (Rau et al., 1989). To explain the $\delta^{13}C_{POC}$ variations, the expressed isotopic fractionation (ε_P) between CO_2 ($\delta^{13}C_{CO2}$) and photosynthetic biomass ($\delta^{13}C_P$) (Hayes, 1993, 2001) was found to correlate to some degree with CO_2 concentration, but also with phytoplankton growth rates and cell geometry (Laws et al., 1995; Popp et al., 1998, and others). Additional influence on ε_P can arise from the use of carbon concentrating mechanisms and the active uptake and/or fixation of bicarbonate (see Wilkes and Pearson, 2019).

In contrast, relatively few studies have focused explicitly on vertical patterns of $\delta^{13}C_{POC}$ extending below near-surface depths (Jeffrey et al., 1983; Saino, 1992), and to our knowledge no global data compilation exists. Individually, several studies have noted large (2–5‰) decreases in $\delta^{13}C_{POC}$ values between the near-surface ocean and the lower euphotic zone or upper pycnocline in open ocean settings, a depth range over which the values of $\delta^{13}C_{CO2}$ usually vary by only 0.5–2.0‰ (Schmittner et al., 2013; Meyer et al., 2016). Hypothesized mechanisms for creating vertical $\delta^{13}C_{POC}$ patterns include both photosynthetic and degradative processes. In this short review we compile data from published studies reporting $\delta^{13}C_{POC}$ values in the upper 250 m of open-ocean water columns in order to explore whether global patterns or environmental drivers can be detected, briefly review existing hypotheses for the observed vertical patterns, and make suggestions for future work.

DATA COMPILATION OF GLOBAL OCEAN $\delta^{13}C_{POC}$ PROFILES

Average $\delta^{13}C_{POC}$ Minimum in the Lower Euphotic Zone or Local Pycnocline

We compiled suspended $\delta^{13}C_{POC}$ data from 11 published studies representative of the global open ocean and containing 51 vertical profiles of $\delta^{13}C_{POC}$ extending from near-surface waters to depths of 250 m. Study locations spanned latitudes from −53° to 50° (**Figure 1A** and **Supplementary Tables S1, S2**) in the oligotrophic Atlantic (Pedrosa-Pàmies et al., 2018), equatorial Atlantic (Bishop et al., 1977; Jeffrey et al., 1983), Gulf of Mexico, Caribbean Sea, Eastern Tropical Pacific (Jeffrey et al., 1983), South Atlantic (Hurley et al., 2019), Southern Ocean (O'Leary et al., 2001; Trull et al., 2008), and North Pacific (Saino, 1992; Minagawa et al., 2001; Hernes and Benner, 2002; Druffel et al., 2003). Non-tabulated data points (Saino, 1992) and coordinates locations (Trull et al., 2008) were extracted using a built-in MATLAB function (ginput); data are compiled in **Supplementary Table S2**. We excluded some published studies from our numerical analysis due to a scarcity of depths sampled in the upper water column or due to likelihood of terrigenous inputs, low-oxygen metabolisms, or experimental manipulations (Williams and Gordon, 1970; Eadie and Jeffrey, 1973; Druffel et al., 1996; Benner et al., 1997; Trull and Armand, 2001; Hernes and Benner, 2006; Close et al., 2014; Krishna et al., 2018; Liu et al., 2018). We also did not include data from the Arctic region due to the prevalence of terrigenous or advected POC in these areas (e.g., Griffith et al., 2012; Xiang and Lam, 2020).

To compare across sites, we standardized reported sampling depth in two different ways: as a proportion of total euphotic zone depth, defined as 0.1% surface PAR (E_z, **Figure 1B**), and relative to the monthly and maximum annual mixed layer depths (MLD, **Figure 1C**). For the E_z standardization we retrieved global 1% surface PAR depths from the mapped MODIS-Aqua satellite data product (NASA Goddard Space Flight Center, 2018) produced using the method of Lee et al. (2007); determined to be within ∼14% of *in situ* measured values). The 4 × 4 km grid location closest to each published study site was extracted; results were similar (within 0.3 ± 1.7 m) when using an average of the surrounding data points. E_z was calculated based on first-order attenuation from 1% PAR at each location and ranged from 61 to 187 m. We retrieved monthly and maximum annual MLD from Holte et al. (2017), who compiled data from Argo float profiles and used a hybrid density algorithm to find MLD. We found the nearest points on the resulting 1 × 1° grid and used an average of the values at these points.

To account for known latitudinal variations in absolute values of $\delta^{13}C_{POC}$, the $\delta^{13}C_{POC}$ data for each individual vertical profile were normalized to the minimum $\delta^{13}C_{POC}$ value anywhere within the upper 250 m of the water column, i.e., the local minimum value was subtracted from each data value in an individual profile to calculate $\Delta\delta^{13}C_{POC}$ (**Figures 1B,C**). After depth and isotopic data were normalized, we compiled all data to assess global vertical trends. We compared the distribution of all $\Delta\delta^{13}C_{POC}$ values in the upper 0–50% and lower 50–100% of the E_z and below (**Figure 1B** and **Supplementary Figure S2A**). For the MLD standardization we compared all $\Delta\delta^{13}C_{POC}$ values above the monthly MLD, between the monthly and annual maximum MLD (local pycnocline), and below the annual maximum MLD (maximum pycnocline; **Figure 1C** and **Supplementary Figure S2B**). Due to normalization of the isotopic data to a zero value, the distributions were skewed and statistical tests were chosen accordingly for non-normally distributed data. A Wilcoxon rank sum test was used to assess significance pair-wise between the different depth ranges (**Supplementary Table S3**). $\delta^{13}C_{POC}$ values were found to be significantly lower in the lower euphotic zone

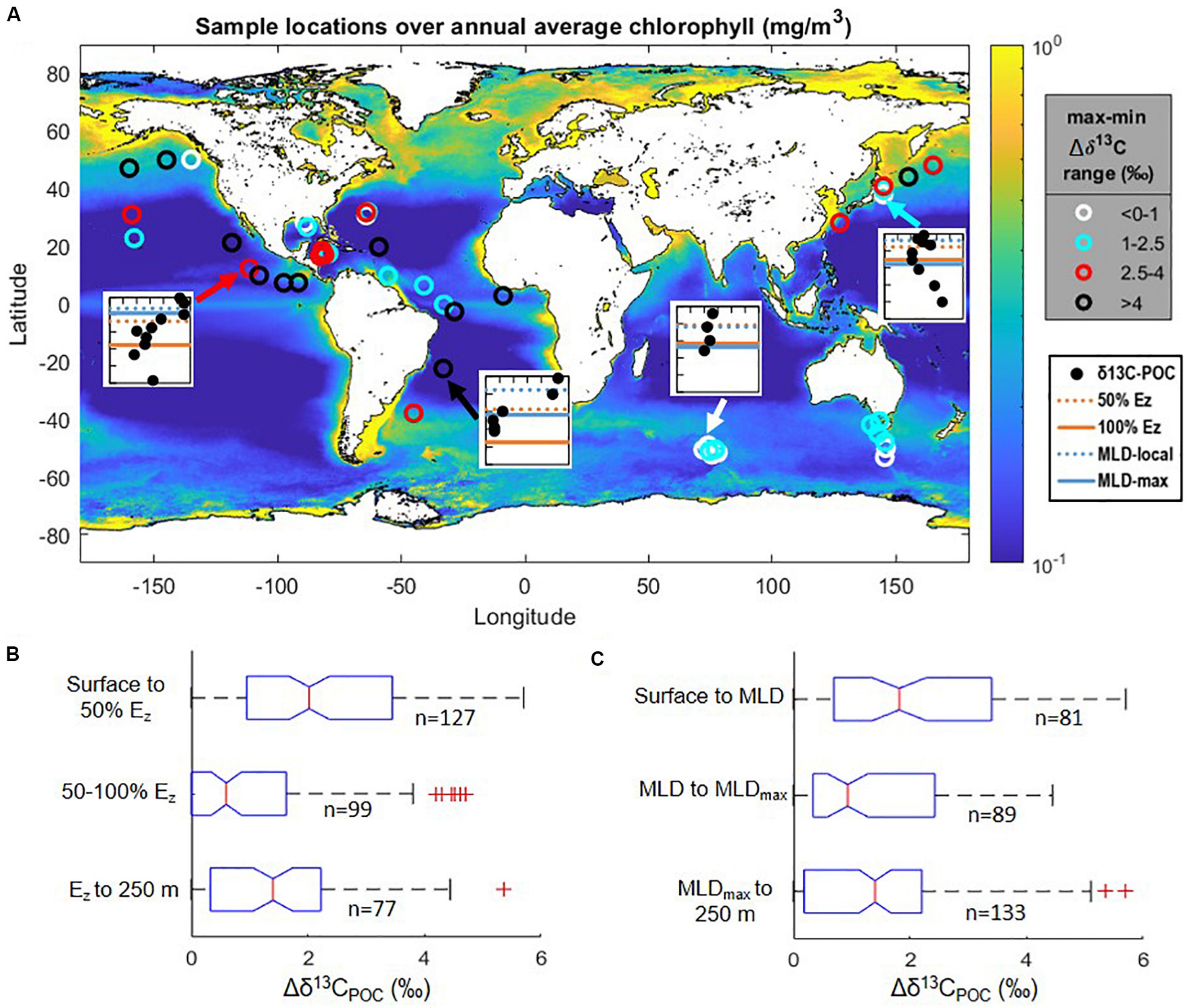

FIGURE 1 | (A) Data locations (open circles) shown over mapped annual climatological surface ocean chlorophyll concentrations from Melin (2013). Symbols are color-coded according to the ranges in $\Delta\delta^{13}C_{POC}$ values observed in the upper 250 m (overlying maximum minus underlying minimum; see **Figure 2**). Insets show examples of four vertical profiles of $\delta^{13}C_{POC}$ values (filled black circles): each inset spans from the surface down to 250 m on the vertical axis and a $\delta^{13}C$ range of −27 to −21‰ on the horizontal axis (see also **Supplementary Figure S1**); horizontal lines indicate depths of the mixed layer and euphotic zone as indicated in the legend. **(B,C)** Normalized $\Delta\delta^{13}C_{POC}$ values among all compiled data: medians (center vertical lines), interquartile range (boxes), 99% intervals (brackets), and outliers (individual points); **(B)** when grouped by standardized euphotic zone depth intervals (100% E_z, depth at which irradiance is 0.1% of surface values); **(C)** when grouped by local mixed layer depth (MLD) and maximum annual mixed layer depth (MLD_{max}). $\Delta\delta^{13}C_{POC}$ indicates $\delta^{13}C_{POC}$ values normalized to the minimum $\delta^{13}C_{POC}$ value found within the upper 250 m at each station, as described in the text. Depth ranges and statistical results are further outlined in **Supplementary Table S3**.

compared to the upper euphotic zone, with a difference in median $\Delta\delta^{13}C_{POC}$ values of 1.4‰ ($p < 10^{-8}$; **Figure 1B** and **Supplementary Table S3**). $\delta^{13}C_{POC}$ values were also significantly lower in depths between the monthly and maximum MLD when compared to those above the monthly MLD, with a difference in median $\Delta\delta^{13}C_{POC}$ values of 0.9‰ ($p < 0.01$; **Figure 1C** and **Supplementary Table S3**).

Generalizing the statistical results above, within the 51 compiled profiles, $\delta^{13}C_{POC}$ values in the lower euphotic zone and/or below the local mixed layer are significantly lower than values in the upper euphotic zone and/or above the local mixed layer. Further, when considering data distribution in relation to the euphotic zone depth, $\delta^{13}C_{POC}$ values in the lower euphotic zone (50–100% of E_z) defined a local minimum; they are lower than $\delta^{13}C_{POC}$ values both above and below this depth range ($p < 0.02$; **Figure 1B** and **Supplementary Table S3**).

Comparison of Individual $\delta^{13}C_{POC}$ Vertical Profiles to Environmental Data

The analysis above considered the compiled global data as a whole and examined differences between median $\delta^{13}C_{POC}$ values within coarse divisions of the upper water column. We also examined the overall magnitude of variation in $\delta^{13}C_{POC}$ values found within individual water columns, i.e., the upper water column max-min range in $\delta^{13}C_{POC}$ values ($\Delta\delta^{13}C_{POC}$ max-min). We calculated this range as the difference between the minimum $\delta^{13}C_{POC}$ value found anywhere in the upper 250 m of individual water columns and the maximum $\delta^{13}C_{POC}$ value found *above* this depth in order to focus on the pattern of higher $\delta^{13}C_{POC}$ overlying lower $\delta^{13}C_{POC}$ values. We found that 63% of individual water columns had a max-min range > 2‰, with the largest ranges >5‰ (**Figure 2A**). We attempted to assess whether the observed $\Delta\delta^{13}C_{POC}$ max-min range correlated with broad scale environmental features extracted from global datasets. Using linear regressions (MATLAB function polyfit), no correlation was found between the local max-min range and the absolute depth of the euphotic zone, chlorophyll *a*, nor modeled surface phytoplankton size or fecal pellet export (Melin, 2013; Siegel et al., 2014; linear regression, $r^2 < 0.1$). The only linear regressions resulting in $r^2 > 0.15$ were those comparing the local $\Delta\delta^{13}C_{POC}$ max-min range to net primary production (**Figure 2B**) and maximum annual mixed layer depth (**Figure 2C**).

Where possible, we extracted coinciding *in situ* vertical profiles of concentrations of POC, dissolved inorganic carbon (DIC), O_2, chlorophyll, and nutrient concentrations from the published studies, as well as C:N ratios. We also obtained annual climatological DIC concentrations, alkalinity, salinity, pH, and temperature data mapped at 1 × 1° resolution from GLODAP and World Ocean Atlas databases (Key et al., 2004), and we calculated CO_2 concentration profiles for each $\delta^{13}C_{POC}$ data location using the CO2SYS tool (Lewis and Wallace, 1998). We tested for pair-wise correlations between vertical profiles of these variables and $\delta^{13}C_{POC}$ values (both absolute values and $\Delta\delta^{13}C_{POC}$ values) where possible, and we did not find any significant relationships. Measured *in situ* $\delta^{13}C_{DIC}$ values were available from O'Leary et al. (2001) and Hurley et al. (2019). We normalized $\delta^{13}C_{DIC}$ and $\delta^{13}C_{POC}$ to near-surface values, using the data point closest to the surface to account for the known latitudinal variation in surface ocean $\delta^{13}C_{DIC}$ and $\delta^{13}C_{POC}$ values. In the nine individual profiles where this comparison was possible, we found that the vertical range in $\delta^{13}C_{POC}$ values was on average approximately four times larger than the vertical range in $\delta^{13}C_{DIC}$ over the same depths (slope = 4.17, $r^2 = 0.53$, linear regression).

DISCUSSION

Data Availability and Quality

While our compilation of published data here is likely not exhaustive, it is to our knowledge the first global examination of vertical profiles of $\delta^{13}C_{POC}$ in the upper water column. Global mapped 3-dimensional oceanographic data products for $\delta^{13}C_{POC}$ currently do not exist, and most major oceanographic programs do not include vertical $\delta^{13}C_{POC}$ as a standard parameter. Anecdotally, vertical $\delta^{13}C_{POC}$ values might be measured much more frequently than they are published or interpreted (e.g., Bishop et al., 1999). The scarcity of published data and lack of a database for $\delta^{13}C_{POC}$ values were barriers to identifying environmental commonalities underlying the observed patterns. We also note that low vertical resolution in many profiles likely means that the true minimum and maximum $\delta^{13}C_{POC}$ values in a given water column were not captured (**Supplementary Figure S1**).

Of the 11 studies from which we compiled data, 6 collected POC using *in situ* or submersible pumps to filter large volumes of water (>70 L). Jeffrey et al. (1983); Saino (1992), Wu et al. (1999); Minagawa et al. (2001), and Hernes and Benner (2002) instead collected seawater in large volumes (10–30 L) from Niskin bottles and filtered the water shipboard. Filtering POC from large volumes of water helps in obtaining a statistical sampling of the particle population; small sample volumes are subject to interference from the inconsistent capture of sparse large particles as well as a larger proportional blank contribution from dissolved organic matter (DOM) sorbed to the filter when POC loading is low. Discussion of DOM sorption and differential particle retention based on filtration media or pressures has been extensive in terms of effects on POC and pigment concentrations (e.g., Gardner et al., 2003; Nayar and Chou, 2003; Bishop et al., 2012). However, the effects of sampling methods and blank correction on $\delta^{13}C_{POC}$ values are under-discussed (Lorrain et al., 2003) and are of particular importance in the subsurface where POC concentrations are lower and blank contribution is proportionally higher. In addition, the most common, elemental analysis-based methods for bulk carbon isotope analysis are >99% inefficient, necessitating large sample quantities; broader use of "nano-scale" analytical methods could improve our ability to obtain better three-dimensional data coverage for oceanic $\delta^{13}C_{POC}$ measurements (see Close, 2019).

The size fraction(s) of particles studied also can be important. Most studies described here collected total POC onto 0.45, 0.7, 0.8, or 1.0 μm glass or quartz fiber filters, but the studies of Bishop et al. (1977) and Hurley et al. (2019) in the mid-latitude Atlantic included a prefilter of 53 μm mesh size. In these cases, the observed patterns of $\delta^{13}C_{POC}$ in the lower euphotic zone were a particular feature of small particles (∼0.7–53 μm), which constituted the majority of POC. Trull et al. (2008) included measurements of several particle size classes in a study of the Southern Ocean – where large phytoplankton and particles are more abundant that the above studies – and found heterogeneities in the $\delta^{13}C$ values across both size and depth, possibly relating to a combination of physiological effects on ε_P, different sinking rates, and temporal offsets between surface production and deeper particles (see below).

Photosynthetic Hypotheses for Origins of Low $\delta^{13}C_{POC}$ Values in the Lower Euphotic Zone or Upper Pycnocline

Several physiological, community, and environmental features of *in situ* photosynthesis have been suggested as drivers of systematic variations in $\delta^{13}C_{POC}$ values between the upper

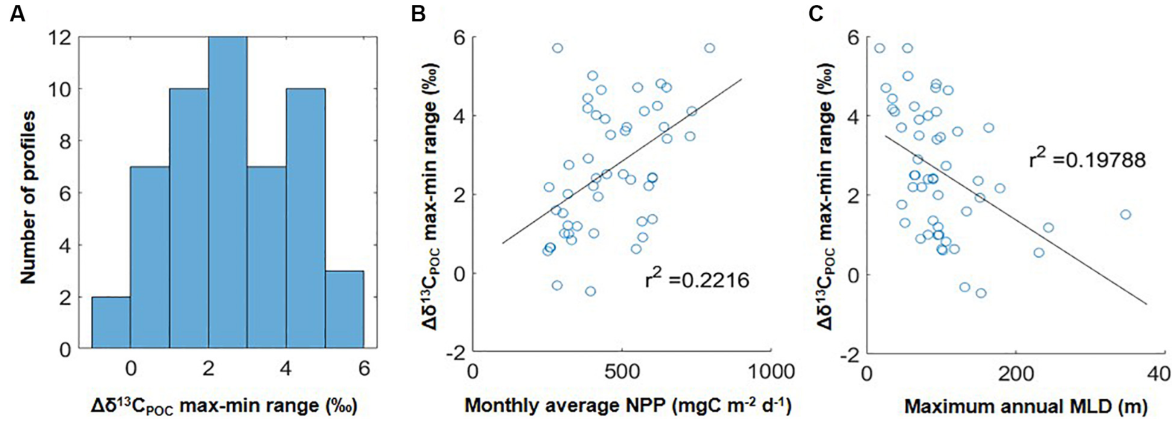

FIGURE 2 | (A) Distribution of upper water column ranges in $\Delta\delta^{13}C_{POC}$ values in the 51 individual water columns in this study, calculated as the overlying maximum $\delta^{13}C_{POC}$ value minus subsurface minimum $\delta^{13}C_{POC}$ value (i.e., maximum values occurring at depths below the minimum are not considered here). Negative values indicate profiles in which the minimum $\delta^{13}C_{POC}$ value was found at the shallowest data point. **(B)** Comparison of $\Delta\delta^{13}C_{POC}$ max-min ranges in **(A)** to climatological net primary production (NPP) at each location. **(C)** Comparison of $\Delta\delta^{13}C_{POC}$ max-min ranges in **(A)** to maximum annual mixed layer depth (MLD_{max}) at each location. One extreme outlier was omitted from **(B)** with an NPP value of 1250 mg m^{-2} d^{-1} and $\Delta\delta^{13}C_{POC}$ max-min range of 1.8‰.

and lower euphotic zones. Saino (1992) noted "a subsurface minimum near the base of the euphotic zone" when examining $\delta^{13}C_{POC}$ values at study sites adjacent to the Kuroshio Current and suggested photosynthetic mechanisms. Models and culture studies (e.g., Popp et al., 1998; Cassar et al., 2006) have demonstrated that ε_P depends on an interplay between the growth rate of an organism and the supply rate of CO_2; higher CO_2 supply rates and/or slower growth rates will lead to a larger ε_P, and therefore lower values of $\delta^{13}C_P$. Saino (1992) suggested that both conditions likely exist in the lower euphotic zone: CO_2 concentrations here are higher than the surface due to the net removal of CO_2 by photosynthesis at the surface and the net respiration of CO_2 in the lower euphotic zone, and growth rates are likely lower due to light limitation. O'Leary et al. (2001) also found low $\delta^{13}C_{POC}$ values in the lower euphotic zone in a study of the subantarctic water column, and their model results pointed to slow photosynthetic growth rates as the cause. Decreases in photosynthetic growth rate with increasing depth in the euphotic zone are frequently observed in the open ocean (e.g., Laws, 2013), and relationships between growth rates and photosynthetic fractionation of carbon isotopes have been demonstrated in culture (Laws et al., 1995; Bidigare et al., 1997; Popp et al., 1998).

A smaller average cell size of phytoplankton in the lower euphotic zone/upper pycnocline than in the upper euphotic zone/mixed layer also is a frequent observation in open-ocean settings (e.g., Poulton et al., 2006; Barone et al., 2015). Trull and Armand (2001) demonstrated that a smaller average cell size (higher surface area: volume ratio) of phytoplankton in the lower euphotic zone could result in lower $\delta^{13}C_{POC}$ values, an isotopic relationship previously established in phytoplankton cultures and models by Rau et al. (1996); Popp et al. (1998), and others, stemming from faster CO_2 diffusion rates.

Conversely, targeted studies of individual photosynthetic taxa or biomarkers have sometimes suggested a pattern of increasing or unchanging $\delta^{13}C$ values over increasing depth in the euphotic zone (Prahl et al., 2005; Popp et al., 2006; Tolosa et al., 2008; Radabaugh et al., 2014). The recent model of Wilkes and Pearson (2019) suggests that increasing $\delta^{13}C$ values over depth could be a phenomenon specific to eukaryotic phytoplankton with intracellular CO_2 partitioning or carbon concentrating strategies, with carbon isotopic fractionation varying according to whether growth is limited by low nutrient concentrations (upper euphotic zone/mixed layer) or other factors such as light [lower euphotic zone/upper pycnocline; also explored by Laws et al. (2002) and Cassar et al. (2006)]. Some phytoplankton also employ active uptake and/or fixation of bicarbonate (HCO_3^-), thereby also complicating relationships between cell size, CO_2 concentrations, and $\delta^{13}C_P$ (e.g., Bentaleb et al., 1998; Cassar et al., 2004). Due to such variations in photosynthetic physiologies, the isotopic sensitivity of a whole phytoplankton community to its local seawater environment (CO_2 concentrations, light and nutrient availability) will depend also on the taxonomic composition of photosynthesizing organisms present (e.g., Leboulanger et al., 1995; Bentaleb et al., 1998; Trull et al., 2008).

Saino (1992) also discussed how slow isotopic equilibrium relative to chemical equilibrium within the DIC system could lead to relatively high values of $\delta^{13}C_{CO2}$ in the mixed layer compared to the lower euphotic zone. Notably, $\delta^{13}C_{CO2}$ usually is calculated from measured $\delta^{13}C_{DIC}$ using constants that assume the system is at both chemical and isotopic equilibrium (Freeman and Hayes, 1992).

Some compound-specific isotope analyses of lipids have supported a photosynthetic origin of low $\delta^{13}C_{POC}$ values in the lower euphotic zone. Close et al. (2014) found that $\delta^{13}C$ values of lipid biomarkers for *in situ* production paralleled $\delta^{13}C_{POC}$ values throughout the euphotic zone in the Eastern Tropical North Pacific, which ruled out the degradative accumulation of lipids (see section "Degradative or Dynamical Hypotheses for Origins of Low $\delta^{13}C_{POC}$ Values in the Lower Euphotic Zone or Upper Pycnocline") as a driver behind low $\delta^{13}C$ values in the lower euphotic zone. Similarly, O'Leary et al. (2001) demonstrated that $\delta^{13}C$ values of photosynthetic sterols paralleled vertical profiles of $\delta^{13}C_{POC}$ in subantarctic waters.

Degradative or Dynamical Hypotheses for Origins of Low $\delta^{13}C_{POC}$ Values in the Lower Euphotic Zone or Upper Pycnocline

Equally common in published interpretations of upper water column $\delta^{13}C_{POC}$ variations are hypotheses relating to degradation or alteration processes. Jeffrey et al. (1983) noted that "the upper part of the pycnocline (i.e., below the local mixed layer) is marked by lighter POC-$\delta^{13}C$ values at almost all the stations occupied" in a broad-ranging study of the Eastern Tropical North Pacific, Gulf of Mexico, Caribbean, and western south Atlantic. These authors suggested a degradative mechanism, following the interpretations of Eadie and Jeffrey (1973) and based on the results of Degens (1969): below the local mixed layer POC concentrations decrease rapidly due to high rates of respiration. Amino acids and sugars comprise quickly degrading, ^{13}C-enriched components of POC, potentially leaving remaining POC at these depths with a relatively high abundance of ^{13}C-depleted lipids. This explanation was cited by Druffel et al. (2003), who noted relatively low $\delta^{13}C$ values of POC in the upper 200 m at study sites in the North Central Pacific and Sargasso Sea.

Bishop et al. (1977) noted "a depletion in ^{13}C of 4‰ over the depth interval between 32 and 50 m," but could not attribute this to the degradative explanation of Eadie and Jeffrey (1973) because a preponderance of lipids should result in an increase in C:N ratios. Instead C:N ratios were invariant over these depths, and the authors suggested that secondary production by bacteria could lead to low $\delta^{13}C$ values. However, the proportional contribution of lipids may increase without being accompanied by an increase in C:N, if proteinaceous (low C:N) material is also abundant, as suggested by Pedrosa-Pàmies et al. (2018). There are few broad organic compositional studies of POC that are accompanied by carbon isotopic data. One such study by Sannigrahi et al. (2005) did not find a strong relationship between organic composition and $\delta^{13}C_{POC}$ values in the upper water column at Station ALOHA [isotopic data previously reported by Hernes and Benner (2002)]; in particular the lipid composition was not proportionally higher at the lower euphotic $\delta^{13}C_{POC}$ minimum than it was at shallower depths.

Hernes and Benner (2002, 2006) suggested that low subsurface $\delta^{13}C_{POC}$ values in the oligotrophic subtropical Pacific and Sargasso Sea were the result of an advected source of terrigenous organic matter, based on a correlation with lignin concentration. However, this correlation existed mainly in POM below the euphotic zone. The local minimum in $\delta^{13}C_{POC}$ values observed in the lower euphotic zone did not correlate with the proportional contribution of lignin to total POC at that depth. Advection of POC from adjacent waters often cannot explain the range of $\delta^{13}C_{POC}$ values observed in a single water column (e.g., Lourey et al., 2004), although this is more commonly cited in the Arctic (Griffith et al., 2012; Xiang and Lam, 2020).

Overall, organic compositional effects on $\delta^{13}C_{POC}$ values seem to be more apparent at advanced stages of organic matter degradation that occur below the euphotic zone, in deep mesopelagic and bathypelagic waters. Here decreases in $\delta^{13}C_{POC}$ values are more clearly related to increasing C:N ratios or changing biochemical composition than they are in the upper water column (see Minagawa et al., 2001; Hwang and Druffel, 2003; Sannigrahi et al., 2005). Analogous to the patterns recognized for particulate $\delta^{15}N$ values (Altabet et al., 1991), shallower, earlier degradation of macromolecules may lead first to increases in $\delta^{13}C_{POC}$ values as bonds containing ^{12}C are more quickly hydrolyzed or respired in upper mesopelagic waters (e.g., Bishop et al., 1977; Jeffrey et al., 1983; Wu et al., 1999). Accordingly, slightly higher $\delta^{13}C_{POC}$ values were found below E_z compared to the lower euphotic zone in our data compilation (**Figure 1B** and **Supplementary Table S3**), and this pattern is more apparent in individual water column profiles (**Supplementary Figure S1**; see also Cavagna et al., 2013).

Particle, seasonal, and water column dynamics also may lead to vertical variations in $\delta^{13}C_{POC}$. Studies of size-fractionated POC or plankton frequently find size-based differences in $\delta^{13}C$ values. Typically large particles are assumed to sink more quickly through the euphotic zone; those originating in the surface can carry their $\delta^{13}C_{POC}$ values below the mixed layer, possibly also being disaggregated into small particles therein. Large phytoplankton often have higher $\delta^{13}C_{POC}$ values than small phytoplankton and therefore would tend to contribute ^{13}C-enriched rather than ^{13}C-depleted material into the subsurface through such a mechanism (Bishop et al., 1977; Fry and Wainright, 1991; Wu et al., 1999; Trull and Armand, 2001; Trull et al., 2008). Heterogeneous sinking rates and $\delta^{13}C$ values have also been used to explain temporal offsets in the origins of upper and lower water column $\delta^{13}C_{POC}$ values, especially in locations with strong seasonality. That is, POC in the subsurface may represent export from the surface ocean during growth conditions (growth rates, CO_2 concentrations, phytoplankton community composition) typical of preceding seasons (Lourey et al., 2004; Cavagna et al., 2013). In high latitude areas seasonal changes in MLD can also distribute surface biomass throughout the euphotic zone and create temporal and spatial offsets between the formation and observation of POC (Grenier et al., 2015).

Zooplankton egesta and/or methane production by gut microbiota also have been cited as possibly affecting $\delta^{13}C_{POC}$ values (Cavagna et al., 2013). Fecal pellets can be highly ^{13}C-depleted in comparison to zooplankton diet (Tamelander et al., 2006). In addition, relatively ^{13}C-depleted methane has been observed reaching maximum concentrations in the pycnocline of oxygenated open-ocean water columns (Holmes et al., 2000; Sasakawa et al., 2008), likely linked to bacterial degradation of dissolved organic compounds (Repeta et al., 2016). Bacteria may incorporate this methane into biomass during oxidative metabolism (Sasakawa et al., 2008), but it is unclear if biomass quantities would be sufficient to affect overall $\delta^{13}C_{POC}$ values.

Unique Geochemical Signatures of the Lower Euphotic Zone or Upper Pycnocline: Potential Implications

One objective of this review is to motivate wider measurement and/or reporting of vertically resolved $\delta^{13}C_{POC}$ data. Regardless of the underlying primary or degradative drivers of this pattern, better data coverage – especially at higher vertical resolution – will allow more precise definition of the depths at which $\delta^{13}C_{POC}$ minima occur and the overall magnitude of variation in upper water column $\delta^{13}C_{POC}$ values; both could prove to be a useful diagnostic of underlying ecosystem processes or carbon dynamics as described above.

The current data compilation suggests that there is a widespread pool of POC in the ocean with $\delta^{13}C$ values that are significantly different from those modeled as "source" photosynthetic values in the surface ocean. POC in the lower euphotic zone or upper pycnocline is abundant and serves as a food source for subsurface biota; studies such as Liu et al. (2018) have discussed how variations in $\delta^{13}C_{POC}$ values in deep chlorophyll maxima can influence how $\delta^{13}C$ values are interpreted in food web studies. The depths of the lower euphotic zone or upper pycnocline, which usually include deep chlorophyll maxima when present, can also be a location of net particle formation and export (Kemp et al., 2000; Benitez-Nelson et al., 2001; Umhau et al., 2019). Recognizing subsurface sources for exported material can be important to the interpretation of the sedimentary geochemical record (e.g., Luo et al., 2014; Hurley et al., 2018). Interestingly, an analog exists in terrestrial systems; plant matter growing in the upper canopy of forests consistently has higher $\delta^{13}C$ values than plant matter growing below (the "canopy effect"; Van der Merwe and Medina, 1991). The differential preservation and dietary usage of these two signatures can affect the interpretation of terrestrial soil records and food webs (e.g., Bonafini et al., 2013).

Finally, global biogeochemical models include the carbon isotope fractionation of photosynthetic organisms according to relationships with growth rate and CO_2 concentrations established in culture (Tagliabue and Bopp, 2008; Schmittner et al., 2013). However, it is unclear whether current models already can adequately reproduce observed vertical $\delta^{13}C_{POC}$ patterns; these models have instead focused on validation of surface ocean $\delta^{13}C_{POC}$ values or vertical $\delta^{13}C_{DIC}$ patterns. A more comprehensive dataset of vertical $\delta^{13}C_{POC}$ values could help validate such isotope-enabled carbon cycle models.

CONCLUSION

Existing published works demonstrate that $\delta^{13}C_{POC}$ values can be significantly lower in the lower euphotic zone or upper pycnocline compared to the upper euphotic zone or local surface mixed layer in a wide range of global open-ocean locations. While individual studies have offered hypotheses for the origin of this vertical pattern, a global compilation of $\delta^{13}C_{POC}$ profiles with coinciding oceanographic data is necessary to test whether there are consistent environmental drivers. We suggest that high-quality isotopic data coverage of the global open ocean is needed, particularly with better data density throughout the euphotic zone and with coinciding CO_2 system data, cell size characterization, and $\delta^{13}C_{DIC}$ data. The large water sample volume needed to obtain sufficient material for $\delta^{13}C_{POC}$ measurements is currently a barrier to including this parameter in many global-scale oceanographic programs, but improvements in the efficiency of isotopic measurement could mitigate this issue. Compound-specific isotope approaches, autotrophic and heterotrophic rate measurements (including substrate-specific photosynthetic uptake, bicarbonate vs. CO_2), particle dynamics characterization, and relevant enzyme expression data all would aid in discerning between potential hypothesized mechanisms. Further, we suggest that an isotope-specific database such as the emergent IsoBank (Pauli et al., 2017)[1] would be an appropriate place to aggregate both published and unpublished $\delta^{13}C_{POC}$ data that currently may be dispersed across various oceanographic databases.

AUTHOR CONTRIBUTIONS

HC and LH designed the study. LH conducted the data analysis and contributed to the manuscript. HC wrote the manuscript. Both authors contributed to the article and approved the submitted version.

FUNDING

Publication was funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) project number 422798570. This work was partially inspired by discussions at a workshop on Marine Organic Biogeochemistry that was held in Delmenhorst, Germany in April 2019 and funded by the Hanse-Wissenschaftskolleg and the Geochemical Society. LH was supported by a University of Miami Fellowship.

ACKNOWLEDGMENTS

We thank Ellen Druffel and Rut Pedrosa-Pámies for providing tabulated data from Druffel et al. (2003) and Pedrosa-Pàmies et al. (2018), Igor Belkin for advice in recovering data from Saino (1992), and David Siegel for providing modeled climatologies from Siegel et al. (2014). We are grateful for comments by MM, Yuan Shen, and TT which resulted in considerable improvements to this mini-review.

SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fmars.2020.540165/full#supplementary-material

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[1] http://isobank-qa.tacc.utexas.edu/en/

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Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.