Isotopic composition of carbonate-bound organic nitrogen in deep-sea scleractinian corals: A new window into past biogeochemical change

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A R T I C L E   I N F O

A B S T R A C T

Over the last two decades, the skeletal remains of deep-sea corals have arisen as a geochemical archive of Pleistocene oceanographic change. Here we report the exploration of the isotopic composition of the carbonate-bound organic nitrogen (hereafter, CB-δ^{15}N) in the deep-sea scleractinian coral *Desmophyllum dianthus* as a possible tool for reconstructing past changes in the ocean nitrogen cycle. The measurement protocol is adapted from a high-sensitivity method for foraminifera shell-bound δ^{15}N. We explored the variability of CB-δ^{15}N within specimens, among corals collected at different depths in a given ocean region, and among different ocean regions. Modern *D. dianthus* CB-δ^{15}N is strongly correlated with the δ^{15}N of N export as estimated from sediment traps, shallow subsurface nitrate, and surface sediments, suggesting that CB-δ^{15}N is a reliable proxy for δ^{15}N of N export. *D. dianthus* CB-δ^{15}N is consistently 8–9‰ higher than δ^{15}N of N export, indicating that *D. dianthus* acquires its nutrition primarily from suspended particulate organic matter (POM) that derives from sinking POM, not directly from sinking POM.

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1. Introduction

Biologically available (fixed) nitrogen (N) is a limiting nutrient for phytoplankton growth across much of the global ocean (Dugdale and Goering, 1967), and changes in the marine fixed N inventory would have major impacts on the productivity and ecology of the global ocean (Falkowski, 1997; Zehr and Kudela, 2011). Better constraints on past changes in the N cycle will improve our mechanistic understanding of ocean biogeochemistry and its interaction with climate, illuminating its role in past CO$_2$ change and also informing our expectations for ocean biogeochemical change into the coming decades and centuries.

The primary existing archives of the past marine N cycle are ocean sediments. However, sedimentary δ^{15}N records do have limitations, and some have major pitfalls. First, sedimentary organic matter is often affected by diagenesis and contamination with allochthonous N (Altabet and François, 1994; Robinson et al., 2012).

While the effects of these processes may be minor in high productivity environments with rapid sediment accumulation rates (Altabet et al., 1999; Prokopenko et al., 2006), there are many indications of problems in regions of moderate or low productivity, especially those close to ocean margins (e.g. Altabet, 2007; Meckler et al., 2011; Ren et al., 2009, 2012; Straub et al., 2013). For this reason, methods have been developed for measuring the δ^{15}N of organic matter protected from diagenesis in diatoms and foraminifera tests preserved in marine sediments (Robinson et al., 2004; Robinson and Sigman, 2008; Ren et al., 2009, 2012). These archives and their biases are yet to be fully defined (Ren et al., 2012; Horn et al., 2011; Morales et al., 2013). Furthermore, there is uneven distribution of ocean sediments suited for N isotopic analysis of either bulk sediments or microfossils. For example, bulk sedimentary N is an unreliable reflection of the δ^{15}N of N export from oligotrophic subtropical surface waters, diatom microfossils are constrained to certain high silicate environments, and foraminifera species and their preservation vary strongly with space and time. Finally, marine sediments rarely allow for better than centennial resolution in the context of generally modest accumulation rates and the effects of bioturbation. To improve the
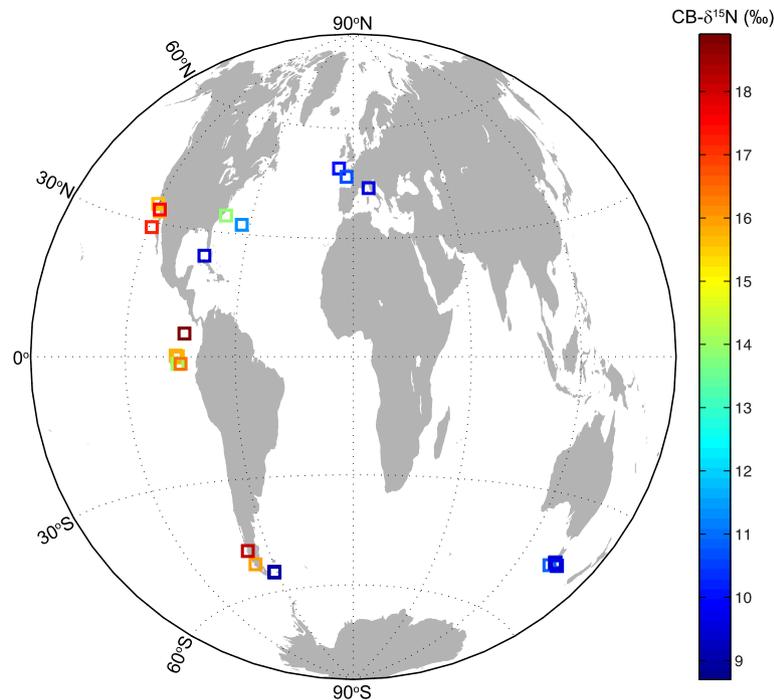
Fig. 1. Locations and coral-bound δ^{15}N (‰ vs. air) of the *D. dianthus* samples analyzed in this study.

geographic and temporal resolution of existing δ^{15}N paleo-archives, we evaluated the δ^{15}N of organic nitrogen bound within the carbonate skeleton of deep-sea scleractinian corals as an additional proxy for past changes in the marine N cycle.

Deep-sea corals have been shown to be a powerful paleoceanographic tool (Robinson et al., 2014). They can be precisely dated using U–Th disequilibrium techniques (Cheng et al., 2000; Mangini et al., 1998; Smith et al., 1997), and their radiocarbon content has yielded much information about past ocean circulation (e.g. Adkins et al., 1998; Burke and Robinson, 2012; Frank et al., 2004; Mangini et al., 1998; Robinson et al., 2005). Measurements of neodymium isotopes (ε_{Nd}) in scleractinian skeletons (e.g. van de Flierdt et al., 2010) demonstrated the utility of deep-sea corals for tracing past changes in ocean circulation. Distribution of nutrients in the past has been explored by analyzing Cd/Ca, P/Ca, and Ba/Ca ratios in scleractinian corals (Adkins et al., 1998; Anagnostou et al., 2011; LaVigne et al., 2011). The use of δ^{13}C, δ^{18}O, Sr/Ca, Mg/Ca and clumped isotopes as proxies is complicated by vital effects (Adkins et al., 2003; Gagnon et al., 2007; Thiagarajan et al., 2011), but progress has made using the "method of lines" (e.g. Smith et al., 2002).

Deep-sea proteinaceous corals (octocorals) that contain layers rich in organics are already being tapped as a tool for reconstructing the past marine N cycle (e.g., Guilderson et al., 2013; Sherwood et al., 2014). However, the organic layers of proteinaceous corals are not isolated from the environment, may be affected by diagenesis, and are generally not well preserved for more than a few thousand years. In contrast, the organic matter that is bound within the carbonate skeletons of scleractinian corals is protected by the aragonite/calcite matrix of the fossil (e.g. Muscatine et al., 2005) and thus may be preserved as long as the carbonate itself. The carbonate-bound organics are secreted directly by corals to facilitate the calcification process (e.g. Cusack and Freer, 2008), so they likely record the δ^{15}N of coral tissue at the time of calcification. However, the concentration of organics preserved within the carbonate skeleton is minute (<10 µmol of N per gram of carbonate skeleton) and has not been measured for δ^{15}N due to the associated analytical challenges. Here, we report the adaptation

of a protocol from foraminifera-bound δ^{15}N analysis (Ren et al., 2009, 2012) for the measurement of the δ^{15}N of carbonate-bound organic nitrogen in deep-sea coral (coral-bound δ^{15}N, CB-δ^{15}N) and our first explorations of the potential of CB-δ^{15}N as a proxy for the past marine N cycle. We focus here on the solitary species of *Desmophyllum dianthus* (Esper, 1794). Modern/near-modern *D. dianthus* samples were used to explore the variation of CB-δ^{15}N within and among the septa of a single specimen, with water column depth at a given collection region, and among sites from across the global ocean.

2. Materials and methods

All *D. dianthus* samples used in this study are from modern/near-modern corals, recently collected, and cover a wide range of regions and depths (Fig. 1 and Table S1). A patch of a coral theca was mechanically cleaned with a diamond disk and/or diamond drill bit using a dremel or small dental drill. Small pieces of a septum from the cleaned region of the theca were cut out with a diamond disk and the septum surfaces were further cleaned with a small drill bit. For studies of small-scale variability, the whole septum was cut out and cleaned. Modern corals collected live have little of the ferromanganese crust that often covers fossil coral specimens (Adkins et al., 1998; Cheng et al., 2000); hence, only very light mechanical cleaning was needed.

The protocol for nitrogen isotope analysis was adapted from a method for foraminifera shell-bound organic N (Ren et al., 2009, 2012). Briefly, 5–10 mg of coral septum is ground into coarse powder (with a grain size of a few hundred micrometers) and sonically cleaned for 5 min in 2% sodium polyphosphate to remove any detrital material attached to the sample. The sample is rinsed (by filling, centrifugation, and decanting) three times with deionized water (DIW) and reductively cleaned using sodium bicarbonate buffered dithionite-citrate reagent to remove any metal coatings (Mehra and Jackson, 1958), similar to the method used by Lomitschka and Mangini (1999). After 3–4 rinses with DIW, the sample is cleaned for 24 h using 13% sodium hypochlorite to remove external organic N contamination and again rinsed 3–4 times
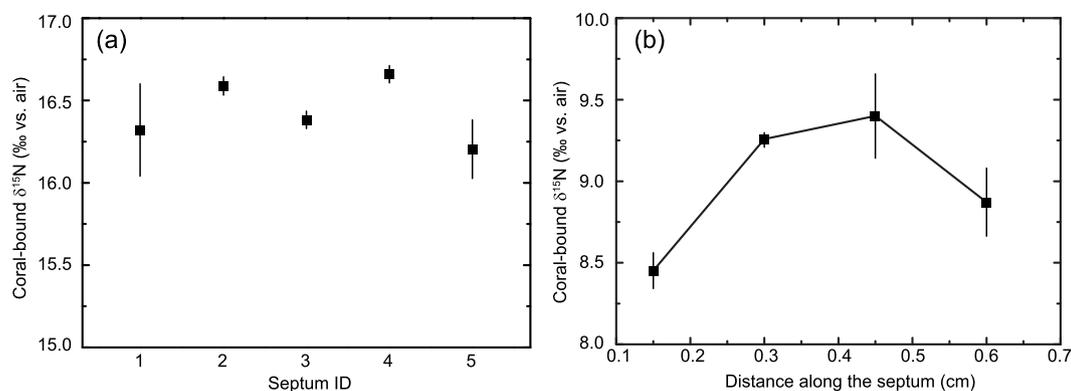
Fig. 2. Variations of coral-bound δ^{15}N on one specimen. (a) Coral-bound δ^{15}N of five different septa of the same generation (S1) on a modern *D. dianthus* specimen from southern Chile. The samples are approximately contemporary. (b) Coral-bound δ^{15}N of four samples along the growth direction of one septum from a modern *D. dianthus* specimen from Drake Passage. Errors (1 sd) were calculated from duplicates.

with DIW. After cleaning, the sample is dried in a clean oven at 60 °C and dissolved in 4 N hydrochloric acid. The released organic matter is oxidized into nitrate using a basic potassium persulfate solution (Nydahl, 1978). The resulting dissolved nitrate is converted bacterially into nitrous oxide, which is measured for its δ^{15}N by automated extraction and gas chromatography-isotope ratio mass spectrometry (Sigman et al., 2001). Each ground sample was processed in duplicate through the entire protocol. An in-house coral standard was used in each batch of analysis as quality control and yields a long-term precision better than 0.3‰ (1σ).

3. Results and discussion

3.1. Variability of CB-δ^{15}N within a specimen

We examined the variability of CB-δ^{15}N within individual *D. dianthus* specimens, seeking information on (i) variation among the septa (radial units of carbonate) precipitated at a given time and (ii) temporal variation within an individual septum (Fig. 2). *D. dianthus* belongs to the subclass of *Hexacorallia* and grows its septa in multiples of six in one generation. After first generation (S1) septa are in place, generation (S2) grows in between and so on (Sorauf and Jell, 1977). To examine the intra-septa variability of CB-δ^{15}N within a specimen from a fjord in southern Chile, we took samples from 5 different septa of the (S1) generation of a specimen. Efforts were made to sample approximately contemporary pieces (the very top parts of the intact S1 septa). The inter-septum variation was shown to be similar to the analytical error (Fig. 2(a)). The lack of significant inter-septum variability suggests that there is little spatial variability in the δ^{15}N of an individual polyp, at least with regard to the organic matter involved in biomineralization. At a practical level, it would appear that the CB-δ^{15}N is independent of which septum is chosen from a given septum generation.

To evaluate the temporal variability of CB-δ^{15}N over the life span of an individual coral from Drake Passage in the Southern Ocean, we cut pieces ∼1.5 mm wide along the growth direction (across the growth bands) of one septum (Fig. 2(b)). Over a distance of ∼6 mm, CB-δ^{15}N varies by ∼1‰. Given a linear growth rate of 0.5–2.0 mm yr^{-1} for *D. dianthus* (Adkins et al., 2004), CB-δ^{15}N varied by ∼1‰ over 3–12 years of growth at Drake Passage. This variability is comparable to the CB-δ^{15}N of the organic layers of proteinaceous coral on decadal timescales (Sherwood et al., 2014).
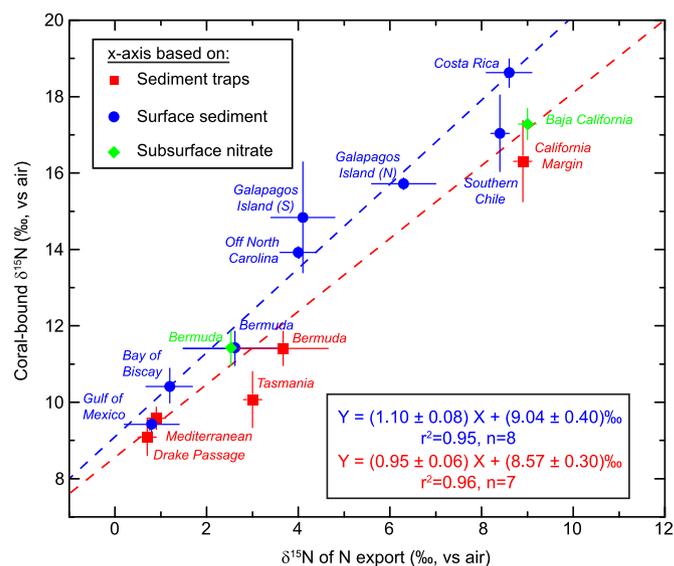

Fig. 3. Cross-plot of ocean region-averaged coral-bound δ^{15}N of *D. dianthus* versus δ^{15}N of N export. For ocean regions where δ^{15}N of N export from sediment traps (red squares) are not available, δ^{15}N of N export are estimated from surface bulk sedimentary δ^{15}N (blue circles), using the empirical relationship proposed by Galbraith et al. (2013): δ^{15}N of N export = surface bulk sedimentary δ^{15}N − 0.75 ± 0.25‰ (km water depth)$^{-1}$. Subsurface nitrate δ^{15}N is used to estimate δ^{15}N of N export at Baja California (green diamond), where the surface nutrient utilization is complete. At Bermuda, there are constraints on the δ^{15}N of N export from sediment traps (Altabet, 1988; Altabet et al., 1991), surface sediments (Altabet, 2006) and shallow subsurface nitrate (Knapp et al., 2005) from the nearby BATS site, and all three are shown. Regression lines (least squares cubic) are shown separately for surface sediments (blue line) and sediment traps plus subsurface nitrate (red line). The errors for coral-bound δ^{15}N were calculated from all the samples measured at a given ocean region; while the errors for δ^{15}N of N exported are from the references (Table 1) and/or propagated through the estimation.

3.2. CB-δ^{15}N as a proxy for δ^{15}N of N export

The corals analyzed for CB-δ^{15}N were compared with the estimated δ^{15}N of N export at their respective sites (Fig. 3). Where sinking POM δ^{15}N had been measured in sediment traps, these data were compared to CB-δ^{15}N. Sediment trap δ^{15}N often declines with depth (Fig. 4(b); Altabet et al., 1991; Thunell et al., 2004), the significance of which is not understood. Where sediment trap data from multiple depths existed, the data from the shallowest trap were used. There is an ongoing discussion about the accuracy with which sediment traps (and different models of sediment trap; Buesseler et al., 2000) capture the sinking flux and

its chemical and isotopic composition. In addition, where sediment traps have been deployed for multiple years, substantial seasonal, interannual, and apparently stochastic variability in sediment trap $\delta^{15}N$ is observed, raising the question of the degree to which the period of a given sediment trap deployment was representative of longer term conditions (Altabet et al., 1991; Lourey et al., 2003; Thunell et al., 2004). Nevertheless, it is the best estimate of $\delta^{15}N$ of N export that is broadly available for comparison with CB-$\delta^{15}N$.

At many of the coral sites, no sediment trap data were available. At these sites, if nearby surface bulk sedimentary $\delta^{15}N$ is available, this is the basis for the estimate of the $\delta^{15}N$ of N export. Given the known influence of diagenesis on bulk sedimentary $\delta^{15}N$ (Altabet and François, 1994), a depth-varying correction proposed by Galbraith et al. (2013) is applied. However, this correction probably does not fully account for the variation in the "diagenetic offset" (Altabet, 2006), nor does it account for the variable importance of terrestrial N contamination.

At the Baja California site where no nearby surface bulk sedimentary $\delta^{15}N$ data exist, the $\delta^{15}N$ of shallow subsurface nitrate is used to estimate the $\delta^{15}N$ of N export (Sigman et al., 2005). We believe that this a robust approach for settings where nitrate consumption is complete in surface waters (Ren et al., 2012). In regions with persistent surface nitrate pool (incomplete seasonal drawdown), the $\delta^{15}N$ of N export must be estimated by calculating the $\delta^{15}N$ of nitrate consumed based on nitrate isotope data from throughout the shallow water column, introducing additional uncertainties. In any case, lack of nitrate isotope data from near most of the coral sites prevents us from using subsurface nitrate as the dominant point of comparison for the CB-$\delta^{15}N$. For the Bermuda coral, there are constraints from sediment traps (Altabet, 1988; Altabet et al., 1991), surface sediments (Altabet, 2006) and shallow subsurface nitrate (Knapp et al., 2005) from the nearby BATS site, and all three are shown (Fig. 3).

The corals derive from regions that cover a broad range in estimated $\delta^{15}N$ (0 to 9‰, Fig. 3) of the N export. One cause for this variation is the $\delta^{15}N$ of subsurface nitrate, as controlled by the hydrography and biogeochemistry of the ocean region. Corals from Baja California and the Channel Islands off California Margin are in regions where water column denitrification elevates the $\delta^{15}N$ of subsurface nitrate (e.g., Sigman et al., 2005), which is then upwelled and/or mixed into the euphotic zone, leading to a high $\delta^{15}N$ for the N export (Altabet et al., 1999). In contrast, corals from the Gulf of Mexico and Bermuda are from regions where shallow subsurface nitrate $\delta^{15}N$ is low, apparently due to N fixation in the tropical and subtropical North Atlantic (Karl et al., 2002; Knapp et al., 2005, 2008; Meckler et al., 2011). The low $\delta^{15}N$ observed in the subsurface nitrate and exported POM in the Mediterranean Sea may also be due to N fixation (Pantoja et al., 2002), although low-$\delta^{15}N$ atmospheric N inputs have also been implicated (e.g., Mara et al., 2009). The second driver for variation in the $\delta^{15}N$ of N export is the degree of nitrate consumption in surface waters. Incomplete consumption of surface nitrate in the Southern Ocean waters of the Drake Passage and south of Tasmania, coupled with the isotope discrimination during nitrate assimilation, leads to a low $\delta^{15}N$ for sinking POM in these regions (Altabet and François, 1994; Lourey et al., 2003). Conversely, in the fjords off the southern coast of Chile, high-$\delta^{15}N$ residual nitrate from the Southern Ocean is advected into the region (Sigman et al., 1999; De Pol-Holz et al., 2009). At some sites, both drivers are at play. Near the Galapagos Islands and in the Costa Rica Dome, subsurface nitrate $\delta^{15}N$ is elevated (albeit relatively weakly; Rafter et al., 2012) by eastern tropical Pacific denitrification, while nitrate consumption at the surface is incomplete, lowering the $\delta^{15}N$ of N export relative to the nitrate supply (Dubois and Kienast, 2011).

The CB-$\delta^{15}N$ of the modern corals collected within these oceanic provinces cover a $\sim10‰$ range and show a strong

Table 1
Ocean region-averaged coral-bound $\delta^{15}N$ of *D. dianthus* and corresponding $\delta^{15}N$ of N export.

Ocean region	Coral-bound $\delta^{15}N$ (‰)	sd[a]	# of specimen	Coral depth (m)	$\delta^{15}N$ of N export (‰)	sd	Adjacent surface sedimentary $\delta^{15}N$ (‰)	Water depth (m) for sedimentary $\delta^{15}N$ (‰)	Source for $\delta^{15}N$ of N export	Reference
Drake Passage	9.09	0.48	4	728–900	0.7	0.2			Sediment trap (960 m)	Khim et al. (2007)
Gulf of Mexico	9.42	0.24	1	1064	0.8	0.6	2.50	2249	Surface sediment[b]	Meckler et al. (2011)
Mediterranean	9.58	0.29	1	~700	0.9	0.2			Sediment trap (1508 m)	Mobius et al. (2010)
Tasmania	10.07	0.73	11	1460–2395	3.0	0.2			Sediment trap (1060 m)	Lourey et al. (2003)
Bay of Biscay	10.38	0.45	2	205–1050	1.2	0.5	2.80	2172	Surface sediment	Galbraith et al. (2013)
Bermuda-1[d]	11.41	0.45	1	~500	3.7	0.9			Sediment trap (100 m)	Altabet (1988)
Bermuda-2	11.41	0.45	1	~500	2.5	0.2			Subsurface nitrate[c]	Knapp et al. (2005)
Bermuda-3	11.41	0.45	1	~500	2.6	1.2	6.00	4600	Surface sediment	Altabet (2006)
Off North Carolina	13.92	0.15	1	~1800	4.0	0.4	5.30	1742	Surface sediment	Galbraith et al. (2013)
Galapagos Islands (S)	14.84	1.45	3	554–651	4.1	0.7	6.09	2650	Surface sediment	Farrell et al. (1995)
Galapagos Islands (N)	15.72	0.10	3	402–806	6.3	0.7	8.52	2942	Surface sediment	Dubois and Kienast (2011)
California Margin	16.31	1.06	3	137–839	8.9	0.2			Sediment trap (550 m)	Collins et al. (2011)
Southern Chile	17.04	1.00	2	636–821	8.4	0.2	9.10	868	Surface sediment	De Pol-Holz et al. (2009)
Baja California	17.28	0.41	1	313	9.0	0.2	9.00		Subsurface nitrate	Sigman et al. (2005)
Costa Rica	18.63	0.40	2	617–700	8.6	0.5	10.10	2045	Surface sediment	Dubois and Kienast (2011)

[a] sd of coral-bound $\delta^{15}N$ is calculated from all the measured specimen at each ocean region.
[b] $\delta^{15}N$ of N export = surface bulk sedimentary $\delta^{15}N - 0.75 \pm 0.25‰ \cdot$ (km water depth)$^{-1}$ as suggested by Galbraith et al. (2013).
[c] In a steady state, subsurface nitrate $\delta^{15}N$ should equal the $\delta^{15}N$ of N export in ocean regions where surface nutrient utilization is complete.
[d] For the Bermuda coral, there are constraints on the $\delta^{15}N$ of N export from sediment traps, surface sediments and subsurface nitrate from the nearby BATS site, and all three are shown.
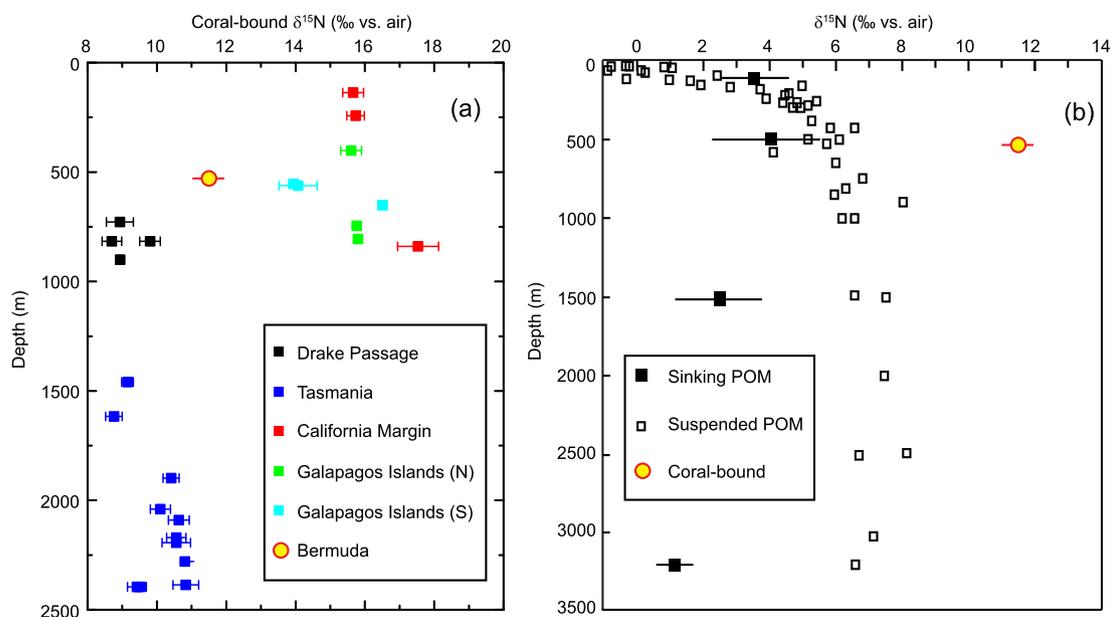
Fig. 4. (a) Depth profiles of coral-bound δ^{15}N at Drake Passage, Tasmania, California Margin, Northern Galapagos Islands and Southern Galapagos Islands. Only ocean regions with three or more coral specimens are shown here with Bermuda the one exception (shown for comparison with the right panel). Errors (1 sd) were calculated from duplicates or triplicates of the same specimen. (b) Depth profiles of sinking POM, suspended POM and coral-bound δ^{15}N at Bermuda. Sinking POM and suspended POM δ^{15}N data are from Altabet et al. (1991).

correlation with the estimated δ^{15}N of N export (Fig. 3 and Table 1). Because of the uncertainties associated with these different constraints on the δ^{15}N of N export, separate least squares cubic regressions (York, 1966; York et al., 2004) are generated for corals compared to sediment trap (and nitrate isotope) data (Fig. 3, red dashed line) and corals compared to surface bulk sedimentary δ^{15}N data (Fig. 3, blue dashed line). The correlations are strong in either case (Fig. 3, $R^2 = 0.96$ and 0.95, respectively), suggesting that *D. dianthus* CB-δ^{15}N is a reliable indicator of the δ^{15}N of N export. CB-δ^{15}N is substantially (8–10‰) higher than the δ^{15}N of N export, a finding with important implications for the food source of *D. dianthus*, which are discussed below in Section 3.3.

There is a small offset (∼0.4‰) in the intercepts between the regression lines of two datasets (Fig. 3, blue and red regressions). We also calculated the average difference between CB-δ^{15}N and δ^{15}N of N export for each dataset (Table 1), with CB-δ^{15}N on average 9.4‰ higher than the δ^{15}N of N export based on surface sediments while CB-δ^{15}N is on average 8.1‰ higher than the δ^{15}N of N export from sediment traps and shallow subsurface nitrate. The 1.3‰ difference between the two datasets may be due to the effects of diagenesis and allochthonous inputs on bulk sedimentary δ^{15}N, as well as the uncertainty in the effort to correct for them (Robinson et al., 2012). Hereafter, we take the sediment trap-based comparison (with a mean difference of 8.1‰ from the available sites) as our best estimate of the difference between the δ^{15}N of N export and CB-δ^{15}N.

3.3. Implications for coral nutrition: sinking POM vs. suspended POM

The nutrition of deep-sea corals has been studied relatively little in comparison to surface-dwelling symbiotic corals (Watling et al., 2011). Orejas et al. (2001) examined the gastrovascular cavity contents of polyps of two species of anthozoans (*Clavularia cf. frankliniana* and *Anthomastus bathyproctus*) collected from seafloor in the upper 400 m on the Antarctic Peninsula and found diatoms, protozoans, foraminifera, nematodes, invertebrate larvae and remnants of salps. The authors concluded that the Antarctic octocorals are opportunistic feeders that consume any available food source. Orejas et al. (2003) examined the diet of two Antarctic octocorals

collected from above 500 m and carried out feeding experiments, finding that the octocorals do consume zooplankton but that prey smaller than zooplankton (ciliates, dinoflagellates, and other phytoplankton) is also actively consumed. Feeding experiments suggest that deep-sea scleractinian corals such as *Lophelia pertusa* are also opportunistic feeders (Mueller et al., 2014). Given that these corals are from relative shallow waters, where living plankton are at maximal concentrations, the main significance of these feeding investigations for our kilometers-deep corals is that they indicate that corals are able to feed on a wide range of food sources, including micrometer-sized particles (Mueller et al., 2014). The capacity to consume even particles as small as bacteria and cyanobacteria has been observed in various scleractinian corals, symbiotic and asymbiotic (Houlbreque and Ferrier-Pages, 2009). In the deep sea, the dominant form of large particle is dead sinking POM, while the most abundant form of small particle (and thus the dominant form of particles in general) is suspended POM.

Based on the presence of modern nuclear bomb radiocarbon signal in the gorgonin fraction of gorgonian corals as well as on the gorgonin δ^{15}N, Sherwood et al. (2005) concluded that gorgonian corals feed mainly on zooplankton and/or sinking POM, not on suspended POM or dissolved organic matter (DOM). However, there is also a bomb signal in deep suspended POM (Druffel et al., 1992), giving it a radiocarbon content that is indistinguishable from that measured in the gorgonin (Sherwood et al., 2005). Sherwood et al. (2009) observed much higher δ^{15}N (6–9‰ higher than the sinking POM δ^{15}N) of organic nodes of bamboo corals from Tasmanian seamounts and suggested that the bamboo corals feed on suspended POM and/or large zooplankton.

Although the comparison of our *D. dianthus* CB-δ^{15}N with δ^{15}N of N export shows a very good correlation, the 8–9‰ difference between CB-δ^{15}N and δ^{15}N of N export (Fig. 3) suggests that *D. dianthus* does not feed directly on sinking POM, as this difference is roughly twice that of the 3–3.5‰ increase expected per trophic level elevation (Deniro and Epstein, 1981; Iken et al., 2001). The difference is best explained as an indication that *D. dianthus* feeds primarily on suspended POM that derives from sinking POM, as the δ^{15}N of deep suspended POM is generally ∼4–5‰ higher than that of sinking POM (Fig. 4(b); Altabet et al., 1991; Casciotti et al., 2008;

Saino and Hattori, 1987), such that the CB-δ^{15}N of *D. dianthus* is ~3‰ higher than deep suspended POM, equivalent to one trophic level. This explanation is supported by the directly measured δ^{15}N difference (2–3‰) between coral tissue and surrounding suspended POM on *Lophelia pertusa* and *Madrepora oculata* from North Atlantic (Kiriakoulakis et al., 2005; Duineveld et al., 2007). An alternative explanation is that *D. dianthus* relies on zooplankton consuming sinking POM, but this would more accurately yield a 6‰ difference, given that 3‰ is typical for the trophic δ^{15}N increase per trophic level in deep sea ecosystems (Iken et al., 2001). Thus, if zooplankton dominated the diet of *D. dianthus*, then they would need to rely to a substantial degree on carnivorous zooplankton. Reliance on zooplankton would be surprising, as zooplankton occur at very low concentration in the deep ocean, representing a minor fraction of the entire suspended POM pool (Clegg and Whitfield, 1990), and carnivorous zooplankton would be especially rare. Reliance on a specific food type that occurs at low concentration does not fit with the observation that deep-sea corals are opportunistic feeders with a broad food spectrum (Iken et al., 2001; Orejas et al., 2001).

The implicit assumption behind drawing conclusions regarding food sources from the comparison of CB-δ^{15}N with the δ^{15}N of sinking and suspended POM is that the CB-δ^{15}N of deep-sea corals is similar to the coral tissue δ^{15}N at the time of calcification. Although we did not directly compare CB-δ^{15}N to coral tissue δ^{15}N, there are coral tissue δ^{15}N data from the literature that supports this assumption. The 8–9‰ difference between CB-δ^{15}N and the δ^{15}N of N export that we observe is similar to the observed δ^{15}N difference between coral tissue (9.3±0.5‰ for *Lophelia pertusa* and 9.5±0.2‰ for *Madrepora oculata*) and sinking POM (2.2±0.9‰) on the NE Atlantic margin (Duineveld et al., 2004). In the bamboo corals collected on the Tasmanian seamounts, the δ^{15}N values of both the living tissue and underlying gorgonin were reported to be 9–12‰ (Sherwood et al., 2009), similar to our *D. dianthus* CB-δ^{15}N (9.98 ± 0.76‰) from the same location. In the southern Chilean fjord, the δ^{15}N of *D. dianthus* tissue from shallower depths (subtidal zone, <200 m) was reported to be 14.5 ± 0.8‰ ($n = 21$) (Mayr et al., 2011), also similar to our CB-δ^{15}N (15.94 ± 0.23‰) at ~600 m, especially if we take into account the tendency for suspended POM δ^{15}N to increase with depth (see Section 3.4).

Given the tendency of deep-sea corals to be found on seafloor with high relief and strong bottom currents (Dorschel et al., 2007), the habitat of the species seems consistent with reliance on suspended POM. On the seamounts and continental slopes where the coral resides, the lateral transport of suspended POM is likely to be far greater than the sinking POM flux. Even without strong lateral currents, the availability of suspended POM should far outstrip that of sinking POM. Below a depth of 500 m, more than 80% of the mass of total POM is composed of suspended POM with a diameter of <2 μm (Clegg and Whitfield, 1990). Particles adequately large to sink occur at exceedingly low concentration (Clegg and Whitfield, 1990), and it would seem unlikely that corals could meet their food requirements by passively waiting for sinking particles to settle onto them.

3.4. CB-δ^{15}N with water depth

D. dianthus occurs over a broad depth range (200–2500 m) (Addamo et al., 2012). The sample set of this study allows for a preliminary examination of the variability of CB-δ^{15}N with water column depth. The variation of modern CB-δ^{15}N with depth is less than 2‰ in all the depth profiles (Fig. 4(a)), indicating the ~10‰ range of CB-δ^{15}N observed in different ocean regions (Fig. 3) cannot be driven by depth-related variation. Three or four out the five depth profiles show a slight increase with depth (Fig. 4(a)), while none suggests a δ^{15}N decline with depth.

While sinking POM δ^{15}N typically holds constant or decreases with increasing depth below 100 m (Casciotti et al., 2008; Lourey et al., 2003; Voss et al., 1996), suspended POM increases sharply in the first ~200–300 m, asymptoting at greater depth (Fig. 4(b)) (Altabet, 1988; Casciotti et al., 2008; Saino and Hattori, 1987). A similar pattern is also observed in the δ^{15}N of suspension feeders in the Weddell Sea (Mintenbeck et al., 2007). If *D. dianthus* feeds mostly on suspended POM, as we concluded above, we might expect CB-δ^{15}N to increase with depth. While most of the individual sites do tend to show a weak δ^{15}N rise with depth, the data in hand neither confirm nor preclude a depth increase comparable to that observed in suspended POM δ^{15}N. This is because most of the depth increase in suspended POM δ^{15}N occurs within the upper ~200–300 m of the water column (Fig. 4(b)), while most of our specimens generally derive from deeper in the water column and/or do not cover a substantial depth range (Fig. 4(a)).

Moreover, suspended POM δ^{15}N (and thus CS-δ^{15}N) depth variations may record more dynamic processes than we have so far discussed. The Tasmanian corals arguably show the clearest signs of an increase in CB-δ^{15}N with depth. Yet this is largely driven by the CB-δ^{15}N increase from ~1500 m to below 2000 m, and such deep structure is difficult to explain in terms of progressively greater degradation of deeper suspended POM. An alternative explanation is that the lower CB-δ^{15}N at ~1500 m is caused by the particles advected into the subsurface by Antarctic Intermediate Water (AAIW) from the Antarctic surface, where surface suspended POM δ^{15}N is lower than further north (Altabet and François, 1994, 2001; Lourey et al., 2003). Moreover, in the deepest Tasmanian corals analyzed, the CB-δ^{15}N is ~1–2‰ lower than modestly shallower corals. This may be due to the sedimenting of rapidly sinking particles onto the extensive area of seafloor concentrated at this depth, yielding effectively fresher suspended POM at the coral depths that are more similar to that of the abyssal seabed across the region.

3.5. Implications for paleoceanography

Relative to other species of deep-sea coral, *D. dianthus* appears to have several advantages as an archive in paleoceanography. First, *D. dianthus* is the best studied deep-sea coral species in terms of paleoceanographically relevant analyses, allowing a comparison with other geochemical proxies back to the last glacial period (e.g. Burke and Robinson, 2012). Second, *D. dianthus* is widely distributed from coastal Antarctica to the Arctic Circle and has a depth range of 200 to 2500 m (Addamo et al., 2012). Substantial collections of samples are already available (e.g., Thiagarajan et al., 2013; Burke and Robinson, 2012). Third, the high U content in aragonitic scleractinian corals such as *D. dianthus* allows accurate dating back to ~500 ka (Cheng et al., 2000). Fourth, *Desmophyllum* has a long lifespan (up to 200 yr) and relatively slow growth rates (0.5–2 mm per year) (Adkins et al., 2004; Robinson et al., 2014). This allows for high-resolution measurements on one single septum that nevertheless cover meaningful intervals of time (Adkins et al., 1998; Eltgroth et al., 2006).

Given that only 5–10 mg of coral is required for replicate analysis of CB-δ^{15}N, decadal resolution should be possible in most specimens, and annual/sub-annual resolution may be possible in selected specimens. It is not yet clear whether the skeletally bound organic N in *D. dianthus* records such fine time scales. The potential benefits of this high resolution include insight into the inherent variability of past oceanic environments as well as the possibility of precisely dating important biogeochemical transitions. There are also potential pitfalls, including the possibility that a single measurement from a coral will capture a rare unrepresentative δ^{15}N for a given time interval. These issues will be straightforward (although time-consuming) to address as the approach matures.

A related and possibly more fundamental set of issues surround the time scales of variation that are recorded in the δ^{15}N of the coral's food source, which we have argued to be dominantly suspended POM. Suspended POM does appear susceptible to isotopic change on the timescale of seasons and years, due to changes in the sinking POM that generates it (Druffel et al., 1998). Suspended POM δ^{15}N at a given site on the seafloor could also potentially change very rapidly due to a shift in the contact zone between water masses with different origins. However, deep suspended POM has relatively lower radiocarbon content than sinking POM (Druffel et al., 1992, 1996), implying both a substantial time scale for degradation in the water column and/or resuspension of aged organic matter from the seabed (Druffel et al., 1998; Hwang et al., 2004). If the latter process is as important as suggested (Hwang et al., 2004), then deep suspended POM δ^{15}N (and CB-δ^{15}N) may include a continuum of time scales of response extending to as much as hundreds/thousands of years. Of course, it is possible that resuspended organic matter, which is likely to be more recalcitrant, is less actively processed by deep-sea corals.

These attributes of *D. dianthus* aside, individual coral species tend to vary dramatically with time, depth, and location (Robinson et al., 2014), with cases where some corals expand in a given region as others decline. Thus, inter-calibration of different deep sea corals should be undertaken to allow a given paleoceanographic study to make use of multiple species.

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Appendix A. Supplementary material

Supplementary material related to this article can be found online at http://dx.doi.org/10.1016/j.epsl.2014.05.048.

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