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

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ABSTRACT

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.

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

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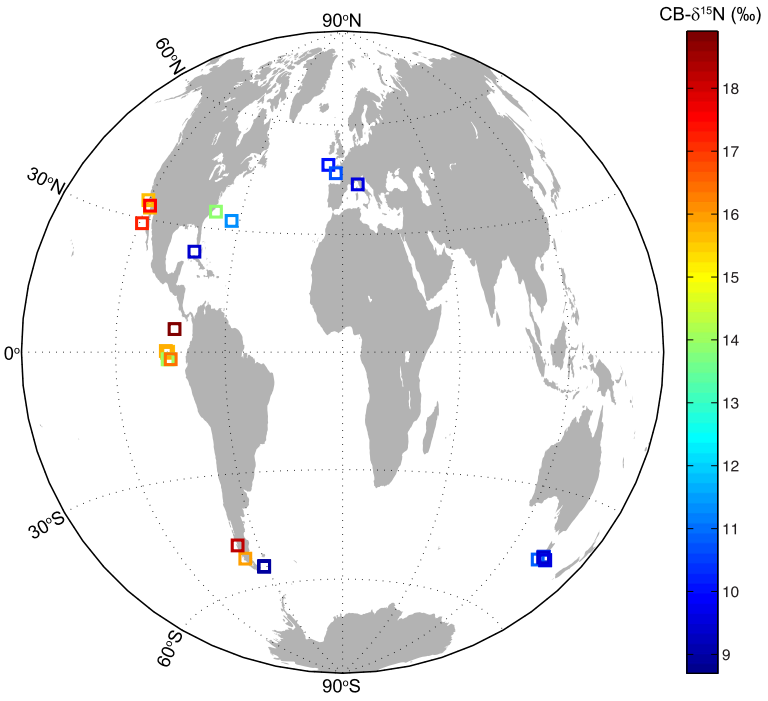

Fig. 1. Locations and coral-bound δ^{15}N (‰ vs. air) of the *D. dianthus* samples analyzed in this study.

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 been 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