Earth and Planetary Science Letters 441 (2016) 125–132

Contents lists available at ScienceDirect

Earth and Planetary Science Letters

www.elsevier.com/locate/epsl

Influence of open ocean nitrogen supply on the skeletal $\delta^{15}N$ of modern shallow-water scleractinian corals

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ARTICLE INFO

Article history:
Received 29 September 2015
Received in revised form 6 February 2016
Accepted 16 February 2016
Editor: H. Stoll

Keywords:
nitrogen isotope
coral
marine nitrogen cycle
paleoceanography

ABSTRACT

The isotopic composition of skeleton-bound organic nitrogen in shallow-water scleractinian corals (hereafter, CS-$\delta^{15}N$) is an emerging tool for studying the marine nitrogen cycle in the past. The CS-$\delta^{15}N$ has been shown to reflect the $\delta^{15}N$ of nitrogen (N) sources to corals, with most applications to date focusing on the anthropogenic/terrestrial N inputs to reef environments. However, many coral reefs receive their primary N sources from the open ocean, and the CS-$\delta^{15}N$ of these corals may provide information on past changes in the open ocean regional and global N cycle. Using a recently developed persulfate/denitrifier-based method, we measured CS-$\delta^{15}N$ in modern shallow-water scleractinian corals from 8 sites proximal to the open ocean. At sites with low open ocean surface nitrate concentrations typical of the subtropics and tropics, measured CS-$\delta^{15}N$ variation on seasonal and annual timescales is most often less than 2‰. In contrast, a broad range in CS-$\delta^{15}N$ (of ~10‰) is measured across these sites, with a strong correlation between CS-$\delta^{15}N$ and the $\delta^{15}N$ of the deep nitrate supply to the surface waters near the reefs. While CS-$\delta^{15}N$ can be affected by other N sources as well and can vary in response to local reef conditions as well as coral/symbiont physiological changes, this survey indicates that, when considering corals proximal to the open ocean, the $\delta^{15}N$ of the subsurface nitrate supply to surface waters drives most of the CS-$\delta^{15}N$ variation across the global ocean. Thus, CS-$\delta^{15}N$ is a promising proxy for reconstructing the open ocean N cycle in the past.

1. Introduction

Coral skeleton-bound organic matter (CSOM) constitutes 0.01–0.1% of the skeleton material by weight; and research is ongoing to understand the synthesis, composition and role of organic matter during the calcification process (Drake et al., 2013; Tambutte et al., 2011). From a paleoceanographic and biogeochemical perspective, the CSOM is directly synthesized by coral at the time of calcification and may provide important information about coral reef environments in the past. For shallow-water scleractinian corals, CSOM has several key virtues as an archive of past conditions. First, CSOM is protected by the carbonate skeleton and may be preserved for tens or hundreds of millions of years (Muscatine et al., 2005). Second, shallow-water scleractinian corals are widely distributed in the low latitude ocean, and fossil coral samples are found throughout the Mesozoic and Cenozoic Eras (i.e. back to ~240 Ma). Third, shallow-water scleractinian corals have high linear extension rates (e.g., 2 cm/yr) and produce annual growth bands. Thus, appropriate techniques would allow for the generation of high-resolution records on individual coral cores.

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http://dx.doi.org/10.1016/j.epsl.2016.02.032
0012-821X/

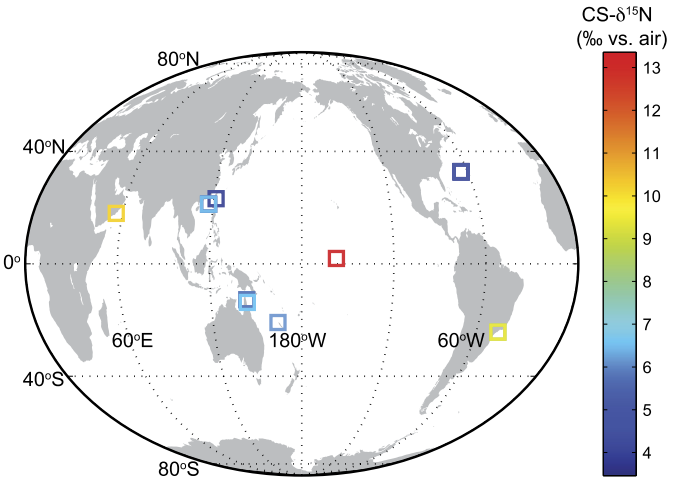

Fig. 1. Locations and average coral skeletal δ^{15}N (CS-δ^{15}N, ‰ vs. air) for each coral core or set of cores used in this study.

Due to the difficulty associated with analyzing this dilute form of organic matter, only a handful of measurements have been made on CSOM: total organic carbon and amino acid composition (Ingalls et al., 2003), carbon isotopes (Muscatine et al., 2005) and nitrogen isotopes (Erler et al., 2015; Hoegh-Guldberg et al., 2004; Marion et al., 2005; Muscatine et al., 2005; Wang et al., 2015). Among these measurements, a recent analytical advance in nitrogen isotopic analysis of CSOM (hereafter: CS-δ^{15}N) requires only 5–10 mg of carbonate material per measurement and yields a precision of 0.2‰ (Wang et al., 2015). Thus, this technique allows for the generation of seasonal or even monthly CS-δ^{15}N records on single coral cores that are comparable to other records made on the inorganic carbonate of corals (e.g., δ^{18}O, Metal/Ca ratio) (Erler et al., 2016).

CS-δ^{15}N in shallow-water scleractinian corals has been shown to reflect the δ^{15}N of N sources to corals. Most studies to date have focused on anthropogenic/terrestrial N input into the reefs (Erler et al., 2015; Hoegh-Guldberg et al., 2004; Jupiter et al., 2008; Marion et al., 2005). However, the water over many reefs exchanges freely with open ocean surface waters, and the CS-δ^{15}N in corals from these reefs is expected to reflect the δ^{15}N of open ocean N supply, an expectation that is supported by some recent data (Yamazaki et al., 2011; Wang et al., 2015). If this applies generally, then it would expand the range of potential applications of CS-δ^{15}N to studies of past changes in the open ocean N cycle, on timescales ranging from recent centuries to the distant geological past. In this study, using corals from 8 globally distributed sites, we test the hypothesis that CS-δ^{15}N of corals proximal to the open ocean is controlled by the δ^{15}N of oceanic nitrate supplied to the euphotic zone adjacent to the reefs.

2. Materials and methods

2.1. Corals

The coral samples used in this study are from the following sites (Fig. 1; Table 1): Bermuda in the North Atlantic, the Brazil margin in the South Atlantic, the Oman margin in the Indian Ocean, the northern Great Barrier Reef (GBR), New Caledonia, the Dongsha atoll and Green Island in the western Pacific, and Kiritimati Island in the central equatorial Pacific (CEP). The sampling was proximal to the open ocean, and there is no distinctively large terrestrial input to any of these sites, increasing the likelihood that the corals directly reflect the δ^{15}N of oceanic N sources. We have measured CS-δ^{15}N from such locations as the inshore Great Barrier Reef (Erler et al., 2015) and lagoon patch reefs nearby the islands of Bermuda (Wang et al., 2015), but these are not included in our analysis. From the Bermuda pedestal, we use only the offshore corals that we have measured (Wang et al., 2015). At each site, coral heads from one or multiple colonies were collected from living corals by scuba divers. Collection information for each site is given in Table 1 and supplementary Fig. 1. The Pacific and Indian Ocean coral samples in this study are *Porites. sp*., except for the New Caledonia coral (*Isopora palifera*); while the Atlantic coral samples include three species: *Diploria labyrinthiformis* for Bermuda; and *Mussismilia hispida* and *Madracis decactis* for Brazil Margin. Despite the species differences, all the corals used in this study are symbiotic (i.e. have zooxanthellae).

In the lab, a slab was cut from each coral head for *Porites* and *Diploria*. The *Porites* and *Diploria* slabs were rinsed with deionized water, dried, and then scanned by computed axial tomography (CAT) to determine the maximum growth axis. Age models of the *Porites* and *Diploria* slabs were determined by counting annual growth bands in CAT scan images or by correlating with Sr/Ca records in the same core. Along the maximum growth axis, powder samples were drilled out from each slab/piece at annual/seasonal resolution. For coral species other than *Porites* and *Diploria*, no age model was generated. Tissue from these corals was removed with a jet of deionized water. Then skeleton pieces were cut from the coral skeleton with a rotary tool and diamond-coated cutting wheel. The skeleton pieces were rinsed with deionized water, dried and crushed into fine powder with agate mortar and pestle. These pieces were estimated to represent several years' growth. Table 1 describes the samples accumulated into the average CS-δ^{15}N reported for each site.

2.2. CS-δ^{15}N measurements

The coral carbonate powders were analyzed for CS-δ^{15}N following the protocol in Wang et al. (2015). First, in an oxidative cleaning step, 10 mL sodium hypochlorite (10–15% available chlorine) is added to 5–10 mg of coral powder in 15 mL centrifuge tubes. These centrifuge tubes are placed on an orbital shaker for 24 hrs. The oxidative cleaning step has been demonstrated to be important for the removal of contaminant organic matter (Hendy et al., 2012; Ingalls et al., 2003; Ramos-Silva et al., 2013) and thus the analysis of CS-δ^{15}N (Erler et al., 2016; Wang et al., 2015). The cleaning reagent is decanted, and the sample is rinsed 3 times with deionized water by centrifugation and decanting and then dried at 60 °C. Once dry, the sample is weighed into a 4 mL borosilicate glass vial (precombusted for 5 hrs at 500 °C) and dissolved by reaction with 4 N HCl. After dissolution, an aliquot of 1 mL freshly combined persulfate oxidizing reagent (1 g recrystallized low-N potassium persulfate and 2 g ACS grade NaOH in 100 mL deionized water) is added, and the sample is autoclaved for 1.5 hr to completely oxidize to nitrate the organic nitrogen released during decalcification. After oxidation, the sample is centrifuged; the clear supernatant is transferred to another precombusted 4 mL borosilicate glass vial and the pH of the supernatant is adjusted to near 7 with HCl and NaOH. The nitrate concentration of the sample solution is analyzed by chemiluminescence (Braman and Hendrix, 1989), mostly to determine aliquot volumes for δ^{15}N measurement. The δ^{15}N of the nitrate is measured by conversion to N_2O with the "denitrifier method" (Sigman et al., 2001) followed by extraction, purification, and isotopic analysis of the N_2O product (Casciotti et al., 2002). Amino acid reference materials USGS 40 and 41 are used in each batch of analyses to correct for the reagent and operational blanks, which is typically less than 2% of the total N content in an oxidized sample. An in-house coral standard (CBS-1) provides a metric for reproducibility both within an analysis batch and across batches. The analytical precision (1sd) of our protocol is 0.2‰ (Wang et al., 2015). For each coral core, an average CS-δ^{15}N ($\pm$1sd) is calcu-