Chemical Geology 453 (2017) 146–168

Contents lists available at ScienceDirect

Chemical Geology

journal homepage: www.elsevier.com/locate/chemgeo

Neodymium isotopes and concentrations in aragonitic scleractinian cold-water coral skeletons - Modern calibration and evaluation of palaeo-applications

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ARTICLE INFO

Article history:
Received 23 September 2016
Received in revised form 21 January 2017
Accepted 24 January 2017
Available online 27 January 2017

Keywords:
Neodymium isotopes
Rare earth elements
Cold-water corals
Seawater
Sediments
Drake Passage

ABSTRACT

Cold-water corals (CWCs) are unique archives of mid-depth ocean chemistry and have been used successfully to reconstruct the neodymium (Nd) isotopic composition of seawater from a number of species. High and variable Nd concentrations in fossil corals however pose the question as to how Nd is incorporated into their skeletons.

We here present new results on modern specimens of *Desmophyllum dianthus*, *Balanophyllia malouinensis*, and *Flabellum curvatum*, collected from the Drake Passage, and *Madrepora oculata*, collected from the North Atlantic. All modern individuals were either collected alive or uranium-series dated to be <500 years old for comparison with local surface sediments and seawater profiles. Modern coral Nd isotopic compositions generally agree with ambient seawater values, which in turn are consistent with previously published seawater analyses, supporting small vertical and lateral Nd isotope gradients in modern Drake Passage waters. Two *Balanophyllia malouinensis* specimens collected live however deviate by up to 0.6 epsilon units from ambient seawater. We therefore recommend that this species should be treated with caution for the reconstruction of past seawater Nd isotopic compositions.

Seventy fossil Drake Passage CWCs were furthermore analysed for their Nd concentrations, revealing a large range from 7.3 to 964.5 ng/g. Samples of the species *D. dianthus* and *Caryophyllia* spp. show minor covariation of Nd with ^{232}Th content, utilised to monitor contaminant phases in cleaned coral aragonite. Strong covariations between Nd and Th concentrations are however observed in the species *B. malouinensis* and *G. antarctica*. In order to better constrain the source and nature of Nd in the cleaned aragonitic skeletons, a subset of sixteen corals was investigated for its rare earth element (REE) content, as well as major and trace element geochemistry. Our new data provide supporting evidence that the applied cleaning protocol efficiently removes contaminant lithogenic and ferromanganese oxyhydroxide phases. Mass balance calculations and seawater-like REE patterns rule out lithogenic and ferromanganese oxyhydroxide phases as a major contributor to elevated Nd concentrations in coral aragonite. Based on mass balance considerations, geochemical evidence, and previously published independent work by solid-state nuclear magnetic resonance (NMR) spectroscopy, we suggest authigenic phosphate phases as a significant carrier of skeletal Nd. Such a carrier phase could explain sporadic appearance of high Nd concentrations in corals and would be coupled with seawater-derived Nd isotopic compositions, lending further confidence to the application of Nd isotopes as a water mass proxy in CWCs.

1. Introduction

Aragonitic scleractinian cold-water corals (CWCs) are abundant in regions where availability of other palaeoceanographic archives is

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http://dx.doi.org/10.1016/j.chemgeo.2017.01.022

limited, such as the mid-depth North Atlantic (e.g., Frank et al., 2004; Robinson et al., 2007) or the mid-depth Southern Ocean (e.g., Burke et al., 2010; Thiagarajan et al., 2013; Margolin et al., 2014). Their skeletons can be dated accurately by uranium-series disequilibrium (e.g., Edwards et al., 1987; Cheng et al., 2000; Robinson et al., 2006), and growth rates from 0.5 to 2 mm/year in *Desmophyllum dianthus* (Risk et al., 2002; Adkins et al., 2004) and up to 26 mm/year in *Lophelia pertusa* (Gass and Roberts, 2006; recently synonymised to *Desmophyllum pertusum*, Addamo et al. 2016) can provide for high resolution geochemical archives (e.g., Adkins et al., 1998; Copard et al., 2012; Montero-Serrano et al., 2013; Wilson et al., 2014; Chen et al., 2015; Hines et al., 2015; Lee et al., 2017).

A powerful proxy to constrain past water mass changes is the neodymium (Nd) isotopic composition of seawater, which has been extracted from various marine archives (e.g., van de Flierdt and Frank, 2010), including CWCs (van de Flierdt et al., 2006a; Robinson and van de Flierdt, 2009; Colin et al., 2010; Copard et al., 2011, 2012; López Correa et al., 2012; Montero-Serrano et al., 2011, 2013; Wilson et al., 2014). While the proxy has been calibrated successfully in both modern colonial (reef - building) and solitary corals (van de Flierdt et al., 2006a; Copard et al., 2010, van de Flierdt et al., 2010), there are a number of questions that still need addressing. Firstly, the global calibration effort by van de Flierdt et al. (2010) was conducted on museum specimens, which were U-Th dated to be between 0 and 377 years old, with two ages however ranging back to the middle and early Holocene. Furthermore, coral Nd isotope results were compared to the most proximal site in the ocean where seawater results were published from the same water mass. In some cases, this was up to 2000 km away from the site of coral collection. A more direct calibration was performed by Copard et al. (2010), who analysed 13 corals collected alive for their Nd isotopic composition. Five of which were directly comparable to nearby seawater measurements. There is still a need to expand the current calibration to include a wider range of coral samples collected alive for comparison with ambient seawater.

Another point that needs revisiting for the application of Nd isotopes in CWCs as a palaeo water mass proxy is the observation of elevated Nd concentrations in thoroughly cleaned fossil coral skeletons (e.g., Crocket et al., 2014). Pioneering calibration studies showed that Nd concentrations in modern CWC specimens of ≤42.7 ng/g (Copard et al., 2010; van de Flierdt et al., 2010) are similar to observations in shallow-water corals (SWC), i.e., ≤55.5 ng/g (Shaw and Wasserburg, 1985; Sholkovitz and Shen, 1995; Akagi et al., 2004; Wyndham et al., 2004). Moreover, Copard et al. (2010) showed a weak dependence of Nd concentrations in modern specimens with water depth, qualitatively in agreement with the behaviour of dissolved Nd in seawater. Fossil specimens however revealed that Nd concentrations in cleaned aragonite can be significantly higher than cited above (up to 612 ng/g in Crocket et al., 2014 and 772 ng/g in Wilson et al., 2014), which has been speculated to result from incomplete removal of contaminant phases (Copard et al., 2010; Crocket et al., 2014). Colin et al. (2010) ruled out contributions from ambient sediments as no systematic relationship between sediment and coral Nd isotopic compositions could be observed downcore. Crocket et al. (2014), on the other hand, performed mass balance calculations to show that contamination from ferromanganese oxyhydroxide phases can account for a maximum of 27% of observed Nd concentration in cleaned aragonite, with no resolvable effect on the Nd isotopic composition. However, as most modern and fossil CWCs show Nd concentrations in excess of what is predicted from inorganic aragonite precipitation experiments (Terakado and Masuda, 1988; ~6–11 ng/g) it is necessary to identify the nature of skeletal Nd.

In this paper we present (i) a new Nd isotope calibration of live CWCs and local seawater from the Drake Passage and a location close to Iceland (Fig. 1), and (ii) a multi-element investigation to identify the dominant Nd carrier phase in CWC skeletons. Taken together our results improve the robustness of the Nd isotope signal extracted from (fossil) aragonitic CWC skeletons.

2. Samples

2.1. Seawater

In order to compare coral data and ambient seawater, three seawater profiles were collected for 10 to 12 depths each during NBP0805 (April to May 2008) on the *R/V Nathaniel B. Palmer* in the Drake Passage using the shipboard CTD system equipped with PVC Niskin bottles (Fig. 1 and Table 1). Ten litre samples were transferred from Niskin bottles into acid cleaned cubitainers using Tygon® tubing. Unfiltered samples were acidified to pH < 2 onboard using high purity HCl. Sampling stations were located in deep waters off Burdwood Bank (north of the Subantarctic Front), off the southern end of the Shackleton Fracture Zone (near the southern boundary of the ACC), and near Sars and Interim seamounts (near the Polar Front; Figs. 1 and 2). All major water masses were sampled: surface mixed layer, Subantarctic Mode Water (SAMW), Antarctic Intermediate Water (AAIW), Upper Circumpolar Deep Water (UCDW), and Lower Circumpolar Deep Water (LCDW) mixing with South Pacific Deep Water (SPDW) and Weddell Sea Deep Water (WSDW) at depth (Fig. 2).

2.2. Sediments

Sediment samples were collected during NBP0805 and NBP1103 (May to June 2011) on the *R/V Nathaniel B. Palmer* from a number of locations across the Drake Passage and at water depths between 333 and 4395 m (Figs. 1 and 2, Table 2). Coring was successful during NBP1103 at Burdwood Bank (Kasten core KC08, 333 m water depth), Interim seamount (Kasten core KC77, 3095 m) and at the WAP margin (Box core BC63, 597 m water depth). During NBP0805 small amounts of sediment samples were collected using a minicorer attached to the CTD to recover sediments from 4221 and 4395 m water depth near Sars and the SFZ, respectively. Additional gravel was collected from two dredges (DR18 and DR35; Table 3) at SFZ (2392 m) and Sars seamount (695 m; Figs. 1 and 2, Table 2). Samples were taken from respective top sections where possible (i.e., not applicable to dredge samples; Table 2). The lithology of the different samples is very heterogeneous reflecting the different depositional environments, but also different sampling methods; for example dredged sediments contain rock fragments. KC08 is characterised as quartz sand, including some darker minerals with an overall slightly green overgrowth. Sediment samples from Sars (DR35 and CTD04 minicore containing mud with pieces of rock) and Interim (KC77, sand) seamounts are dominated by light-brown and grey colours indicating unusually high carbonate contents. Sediments from SFZ (DR18 and CTD03 minicore) are grey to brown and contain mostly mud and rock fragments. BC63 sediments from the WAP contain various grain sizes in a grey-brown mud matrix.

2.3. Cold-water corals

Modern solitary coral specimens of *Desmophyllum dianthus* ($n = 3$), *Balanophyllia malouinensis* ($n = 4$) and *Flabellum curvatum* ($n = 1$; Fig. 3) were collected on Burdwood Bank by dredging and trawling during NBP0805 ($n = 6$ from one Blake Trawl at 816 m water depth) and LMG0605 (May–June 2006) on the *R/V Laurence M. Gould* ($n = 2$; both *B. malouinensis*; one from 120 m water depth and one from 854 m water depth; Figs. 2 and 3; Table 4). It should be noted that ‘modern samples’ in this case includes specimens collected alive ($n = 3$) and specimens to be <467 years old as confirmed by U-series dating (Table 4; Burke and Robinson, 2012; Burke, 2012; Burke et al., unpubl. data). The shallowest sample from 120 m water depth (*B. malouinensis*) was bathed in subsurface waters of the mixed layer, whereas the samples from 816 m (southern slope of Burdwood Bank) and 854 m water depth (northern slope of Burdwood Bank) were bathed in AAIW (Fig. 2; Table 4). *B. malouinensis* (Fig. 3) is a species that is very abundant