



## Barium isotopes in cold-water corals

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### ABSTRACT

Recent studies have introduced stable Ba isotopes ( $\delta^{138/134}\text{Ba}$ ) as a novel tracer for ocean processes. Ba isotopes could potentially provide insight into the oceanic Ba cycle, the ocean's biological pump, water-mass provenance in the deep ocean, changes in activity of hydrothermal vents, and land-sea interactions including tracing riverine inputs. Here, we show that aragonite skeletons of various colonial and solitary cold-water coral (CWC) taxa record the seawater (SW) Ba isotope composition. Thirty-six corals of eight different taxa from three oceanic regions were analysed and compared to  $\delta^{138/134}\text{Ba}$  measurements of co-located seawater samples. Sites were chosen to cover a wide range of temperature, salinity, Ba concentrations and Ba isotope compositions. Seawater samples at the three sites exhibit the well-established anti-correlation between Ba concentration and  $\delta^{138/134}\text{Ba}$ . Furthermore, our data set suggests that Ba/Ca values in CWCs are linearly correlated with dissolved [Ba] in ambient seawater, with an average partition coefficient of  $D_{\text{CWC/SW}} = 1.8 \pm 0.4$  (2SD). The mean isotope fractionation of Ba between seawater and CWCs  $\Delta^{138/134}\text{Ba}_{\text{CWC-SW}}$  is  $-0.21 \pm 0.08\text{‰}$  (2SD), indicating that CWC aragonite preferentially incorporates the lighter isotopes. This fractionation likely does not depend on temperature or other environmental variables, suggesting that aragonite CWCs could be used to trace the Ba isotope composition in ambient seawater. Coupled [Ba] and  $\delta^{138/134}\text{Ba}$  analysis on fossil CWCs has the potential to provide new information about past changes in the local and global relationship between [Ba] and  $\delta^{138/134}\text{Ba}$  and hence about the operation of the past global oceanic Ba cycle in different climate regimes.

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### 1. Introduction

Aragonitic scleractinian cold-water corals (CWC) are distributed throughout the global oceans in waters ranging from just a few meters to abyssal depths of several thousand meters (Roberts et al., 2006). In contrast to traditional paleoceanographic archives such as sediment cores, reconnaissance and precise dating of CWCs is performed by  $^{14}\text{C}$  and U-series dating (Mangini et al., 1998; Cheng et al., 2000; Douville et al., 2010; Margolin et al., 2014; Spooner et al., 2016). With linear extension rates of several mm/a (e.g. Mortensen, 2001; Orejas et al., 2008) oceanic changes on centennial, decadal, yearly or even seasonal time scales can be elucidated from geochemical and isotope tracers in aragonite CWC skeletons. Despite this advantage, only a small number of paleoceanographic tracers have been established successfully and ap-

plied in CWCs (Robinson et al., 2014). For example, temperature, state of ventilation and water-mass provenance have been retrieved from various elemental and isotope tracers (Robinson et al., 2014). However, biological factors, so-called 'vital effects', often alter some elemental and isotope systems, e.g.  $\delta^{13}\text{C}$ ,  $\delta^{18}\text{O}$  or Li/Ca, limiting their use as oceanic tracers (Adkins et al., 2003; Rollion-Bard et al., 2009; Raddatz et al., 2013).

Barium has an enigmatic oceanic chemistry that has been studied for many years. The nutrient-like distribution of dissolved Ba in seawater,  $[\text{Ba}]_{\text{SW}}$ , is closely correlated with silicate and alkalinity ( $\text{Si}(\text{OH})_4$ ) (Chow and Goldberg, 1960; Wolgemuth and Broecker, 1970; Jeandel et al., 1996). But numerous studies suggested that the oceanic Ba cycle is not directly linked to the silicate or carbonate cycle (Bishop, 1988; Monnin et al., 1999). While regenerative dissolved Ba enriches deep ocean concentrations, its removal in the upper ocean is attributed to the precipitation of barite ( $\text{BaSO}_4$ ), even though seawater is mostly under-saturated in  $\text{BaSO}_4$ . This behaviour can possibly be explained by the decay of organic matter in settling particles releasing Ba and/or  $\text{SO}_4^{2-}$  into a microenvi-

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**Table 1**

Locations of CWC and seawater sample sites. For the exact coordinates of each cold water coral please refer to the supplementary material.

Station	Latitude	Longitude	Covered depths	Analysed depths (m)
<b>Iceland</b>				
Hafadjup CWC	63°16.82′–63°20.52′N	19°34.11′–19°35.75′W	363–680	363–680
Hafadjup SW	63°19.02′N	19°36.72′W	360–680	360–680
Reykjanes Ridge CWC	62°36.45′–63°5.13′N	24°59.27′–24°32.53′W	209–698	209–698
Reykjanes Ridge SW	62°53.34′N	24°50.88′W	238–338	238–338
<b>Equatorial Atlantic</b>				
Carter Seamount CWC	5°36.66′–9°13.37′N	21°16.49′–26°57.46′ W	265–2318	265–2318
JC094 CTD 2 SW	9°17.1′N	21°38.0′W	0–4524	0–4524
<b>Drake Passage</b>				
Burdwood Bank	54°50.26′–54°50.33′S	62°7.11′–62°14.99′W	334–1829	334–1829
NBP1103 CTD 21	55°3.25′S	62°81′W	0–4110	0–2250
571 NBP1103 CTD 100	60°33.85′S	65°29.57′W	0–3100	0–1500

ronment until a BaSO<sub>4</sub>-saturation is reached (Dehairs et al., 1980; Bishop, 1988; Paytan and Griffith, 2007; Horner et al., 2017).

A new-found ability to precisely measure naturally occurring fractionation between Ba isotopes enables further insight to be gained into the processes controlling the Ba cycle in the ocean. The isotope composition of Ba is defined with reference to the SRM NIST 3104a standard as

$$\delta^{138/134}\text{Ba}_{\text{NIST3104a}} = \left( \frac{{}^{138}\text{Ba}/{}^{134}\text{Ba}_{\text{sample}}}{{}^{138}\text{Ba}/{}^{134}\text{Ba}_{\text{NIST3104a}}} - 1 \right) \times 1000 \quad (1)$$

which we abbreviate to  $\delta^{138/134}\text{Ba}$ . Recent Ba isotope studies have focused on fractionation processes during experimental precipitation of BaCO<sub>3</sub>, BaSO<sub>4</sub> and BaMn[CO<sub>3</sub>]<sub>2</sub> (von Allmen et al., 2010; Böttcher et al., 2012; Mavromatis et al., 2016; van Zuilen et al., 2016), in igneous rocks (Miyazaki et al., 2014; Nan et al., 2015), in sediments and soils (Bridgestock et al., 2018; Bullen and Chadwick, 2016), and in seawater (Horner et al., 2015; Cao et al., 2016; Bates et al., 2017; Hsieh and Henderson, 2017). During barite, BaCO<sub>3</sub> and BaMn[CO<sub>3</sub>]<sub>2</sub> precipitation experiments, the solid phase preferentially incorporates the lighter isotopes, leaving the solution relatively heavy in Ba isotopes (von Allmen et al., 2010; Böttcher et al., 2012; van Zuilen et al., 2016). Upper ocean barite formation and its dissolution in the deep ocean lead to an inverse profile for Ba isotopes compared to dissolved Ba concentration, with light Ba isotope compositions in the deep ocean and heavier isotope compositions in surface waters (e.g. Horner et al., 2015). Further studies on Ba isotopes highlighted the potential to provide insight into the oceanic Ba cycle, the ocean's biological pump, deep water-mass provenance (Bates et al., 2017; Horner et al., 2015), riverine inputs (Cao et al., 2016), and possibly other inputs from sediment and/or hydrothermal inputs (Hsieh and Henderson, 2017). To investigate past changes in these processes, CWCs could be a promising archive.

Over the years, several studies have shown that the Ba/Ca ratio in foraminifera and calcitic corals reflects Ba concentrations in ambient seawater [Ba]<sub>sw</sub> (LaVigne et al., 2011; Lea and Boyle, 1993). Recently, calibration of the Ba/Ca in aragonitic CWCs to reconstruct past [Ba]<sub>sw</sub> has been a focus of research (Anagnostou et al., 2011; LaVigne et al., 2016; Spooner, 2016). However, only one study has included an assessment of Ba isotopes in coralline carbonate (Pretet et al., 2016). That study measured Ba isotopes in cultured tropical aragonitic scleractinian corals grown in Mediterranean seawater, revealing a variable fractionation (see Eq. (2)) between seawater and cultured coralline aragonite ranging from  $-0.02\%$  (Acropora sp. and Porite sp.) to  $-0.35\%$  (Stylophora sp. and Montipora sp.). The Ba isotope composition of natural CWCs was also

reported; two *Lophelia pertusa* (*L. pertusa*) samples from the Norwegian shelf were analysed and found to have  $\delta^{138/134}\text{Ba}$  values of  $0.25 \pm 0.11\%$  and  $0.3 \pm 0.11\%$ .

In this study we present the first detailed study of  $\delta^{138/134}\text{Ba}$  in natural CWCs in comparison to that of the seawater in which they grew. The data set includes thirty-six well-characterised aragonitic scleractinian specimens from eight different taxa, both solitary and colonial, recovered from three sites: the North Atlantic, the Equatorial Atlantic, and the Drake Passage. The samples cover a wide range of environmental conditions, Ba concentrations, and seawater Ba isotope compositions. This allows for a systematic assessment of the Ba isotope fractionation during coral growth and the use of CWCs as an archive for past seawater  $\delta^{138/134}\text{Ba}$ .

## 2. Materials and analytical methods

### 2.1. Samples

Thirty-six CWCs and ambient seawater samples from three ocean regions were selected for Ba isotope analysis. The locations were: south of Iceland in the North Atlantic (Reykjanes Ridge and Hafadjup), in the Equatorial Atlantic (Carter Seamount), and in the Drake Passage (Burdwood Bank) (Table 1). They were chosen to cover a wide range of temperature and salinity (e.g. T: 2–11.5 °C; S: 34.29–35.32 psu), Ba concentrations and Ba isotope compositions (Figs. 1, 2 and 6, supplementary material). Eight different colonial and solitary aragonite scleractinian coral taxa (identified to either genus or species level) of living or young (less than 1000 a) CWCs were sampled: *Lophelia pertusa* (*L. pertusa*), *Madrepora oculata* (*M. oculata*), *Desmophyllum dianthus* (*D. dianthus*), *Balanophyllia* sp., *Caryophyllia* sp., *Dasmomillia* sp., *Flabellum* sp. and *Javania* sp. (supplementary material). Corals off Iceland were collected during the ICECTD cruise in 2012 (Frank et al., 2012) using the ROV Victor 6000 (provided by IFREMER). Simultaneously, seawater samples (125 ml) were directly filled (unfiltered) into acid cleaned PEP bottles by the ROV. They were stored at room temperature. Three months prior to Ba isotope analysis, seawater samples were acidified to a pH of 1.5 by adding purified, concentrated HCl. Therefore, in these samples total dissolvable Ba concentrations and isotope compositions are analysed. Equatorial Atlantic samples from Carter Seamount were recovered during the JC094 cruise in 2013 (Robinson, 2014; Spooner et al., 2016). The corals were collected by the ROV Isis. Ambient seawater samples are from CTD station 2 and were analysed by Bates et al. (2017). In contrast to seawater samples from Iceland and the Drake Passage, Equatorial Atlantic samples were filtered with 0.4 µm Acropak cartridge filters before acidification. CWCs from Burdwood Bank in the Drake Passage were collected in 2011 during cruise NBP1103, using a small bas-

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