

## Barium isotopes in cold-water corals

Hemsing Freya <sup>1,2,\*</sup>, Hsieh Yu-Te <sup>2</sup>, Bridgestock Luke <sup>2</sup>, Spooner Peter T. <sup>3</sup>, Robinson Laura F. <sup>3</sup>, Frank Norbert <sup>1</sup>, Henderson Gideon M. <sup>2</sup>

<sup>1</sup> Heidelberg Univ, Inst Environm Phys, Neuenheimer Feld 229, D-69120 Heidelberg, Germany.

<sup>2</sup> Univ Oxford, Dept Earth Sci, South Parks Rd, Oxford OX1 3AN, England.

<sup>3</sup> Univ Bristol, Sch Earth Sci, Queens Rd, Bristol BS8 1RJ, Avon, England.

\* Corresponding author : Freya Hemsing, email address : [freya.hemsing@iup.uni-heidelberg.de](mailto:freya.hemsing@iup.uni-heidelberg.de)

### Abstract :

Recent studies have introduced stable Ba isotopes ( $\delta^{138/134}\delta^{138/134}\text{Ba}$ ) 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  $\delta^{138/134}\delta^{138/134}\text{Ba}$  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  $\delta^{138/134}\delta^{138/134}\text{Ba}$ . 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  $\text{DCWC/SW} = 1.8 \pm 0.4$  (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  $\delta^{138/134}\delta^{138/134}\text{Ba}$  analysis on fossil CWCs has the potential to provide new information about past changes in the local and global relationship between [Ba] and  $\delta^{138/134}\delta^{138/134}\text{Ba}$  and hence about the operation of the past global oceanic Ba cycle in different climate regimes.

### Highlights

► First detailed study of Ba isotope fractionation in modern cold-water corals. ► Eight genera from the Atlantic and Southern Oceans were analysed. ► Constant fractionation between coral aragonite and seawater of  $-0.21 \pm 0.08\text{‰}$  (2SD). ► Ba isotopes in cold-water corals have the potential to trace past seawater  $\delta^{138/134}\text{Ba}$ . ► Combined Ba/Ca and isotope analysis can reconstruct past changes in oceanic Ba cycle.

**Keywords** : barium isotope fractionation, cold-water corals, calibration, Ba/Ca, paleoceanography

## 31 1. Introduction

32 Aragonitic scleractinian cold-water corals (CWC) are distributed throughout the global oceans in waters  
33 ranging from just a few meters to abyssal depths of several thousand meters (Roberts et al., 2006). In  
34 contrast to traditional paleoceanographic archives such as sediment cores, reconnaissance and precise  
35 dating of CWCs is performed by  $^{14}\text{C}$  and U-series dating (Mangini et al., 1998; Cheng et al., 2000;  
36 Douville et al., 2010; Margolin et al., 2014; Spooner et al., 2016). With linear extension rates of several  
37 mm/a (e.g. Mortensen, 2001; Orejas et al., 2008) oceanic changes on centennial, decadal, yearly or even  
38 seasonal time scales can be elucidated from geochemical and isotope tracers in aragonite CWC  
39 skeletons. Despite this advantage, only a small number of paleoceanographic tracers have been  
40 established successfully and applied in CWCs (Robinson et al., 2014). For example, temperature, state  
41 of ventilation and water-mass provenance have been retrieved from various elemental and isotope  
42 tracers (Robinson et al., 2014). However, biological factors, so-called 'vital effects', often alter some  
43 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  
44 al., 2003; Rollion-Bard et al., 2009; Raddatz et al., 2013).

45 Barium has an enigmatic oceanic chemistry that has been studied for many years. The nutrient-like  
46 distribution of dissolved Ba in seawater,  $[\text{Ba}]_{\text{sw}}$ , is closely correlated with silicate and alkalinity  
47 ( $\text{Si}(\text{OH})_4$ ) (Chow and Goldberg, 1960; Wolgemuth and Broecker, 1970; Jeandel et al., 1996). But  
48 numerous studies suggested that the oceanic Ba cycle is not directly linked to the silicate or carbonate  
49 cycle (Bishop, 1988; Monnin et al., 1999). While regenerative dissolved Ba enriches deep ocean  
50 concentrations, its removal in the upper ocean is attributed to the precipitation of barite ( $\text{BaSO}_4$ ), even  
51 though seawater is mostly under-saturated in  $\text{BaSO}_4$ . This behaviour can possibly be explained by the  
52 decay of organic matter in settling particles releasing Ba and/or  $\text{SO}_4^{2-}$  into a microenvironment until a  
53  $\text{BaSO}_4$ -saturation is reached (Dehairs et al., 1980; Bishop, 1988; Paytan and Griffith, 2007; Horner et  
54 al., 2017).

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

$$58 \delta^{138/134}\text{Ba}_{\text{NIST3104a}} = \left( \frac{^{138}\text{Ba}/^{134}\text{Ba}_{\text{sample}}}{^{138}\text{Ba}/^{134}\text{Ba}_{\text{NIST3104a}}} - 1 \right) \times 1000 \quad (1)$$

59 which we abbreviate to  $\delta^{138/134}\text{Ba}$ . Recent Ba isotope studies have focussed on fractionation processes  
60 during experimental precipitation of  $\text{BaCO}_3$ ,  $\text{BaSO}_4$  and  $\text{BaMn}[\text{CO}_3]_2$  (von Allmen et al., 2010; Böttcher  
61 et al., 2012; Mavromatis et al., 2016; van Zuilen et al., 2016), in igneous rocks (Miyazaki et al., 2014;  
62 Nan et al., 2015), in sediments and soils (Bridgestock et al., 2018; Bullen and Chadwick, 2016), and in  
63 seawater (Horner et al., 2015; Cao et al., 2016; Bates et al., 2017; Hsieh and Henderson, 2017). During  
64 barite,  $\text{BaCO}_3$  and  $\text{BaMn}[\text{CO}_3]_2$  precipitation experiments, the solid phase preferentially incorporates  
65 the lighter isotopes, leaving the solution relatively heavy in Ba isotopes (von Allmen et al., 2010;  
66 Böttcher et al., 2012; van Zuilen et al., 2016). Upper ocean barite formation and its dissolution in the  
67 deep ocean lead to an inverse profile for Ba isotopes compared to dissolved Ba concentration, with light  
68 Ba isotope compositions in the deep ocean and heavier isotope compositions in surface waters (e.g.  
69 Horner et al., 2015). Further studies on Ba isotopes highlighted the potential to provide insight into the  
70 oceanic Ba cycle, the ocean's biological pump, deep water-mass provenance (Bates et al., 2017; Horner  
71 et al., 2015), riverine inputs (Cao et al., 2016), and possibly other inputs from sediment and/or  
72 hydrothermal inputs (Hsieh and Henderson, 2017). To investigate past changes in these processes,  
73 CWCs could be a promising archive.

74 Over the years, several studies have shown that, the Ba/Ca ratio in foraminifera and calcitic corals  
75 reflects Ba concentrations in ambient seawater  $[\text{Ba}]_{\text{sw}}$  (LaVigne et al., 2011; Lea and Boyle, 1993).  
76 Recently, calibration of the Ba/Ca in aragonitic CWCs to reconstruct past  $[\text{Ba}]_{\text{sw}}$  has been a focus of  
77 research (Anagnostou et al., 2011; LaVigne et al., 2016; Spooner, 2016). However, only one study has  
78 included an assessment of Ba isotopes in coralline carbonate (Pretet et al., 2016). That study measured  
79 Ba isotopes in cultured tropical aragonitic scleractinian corals grown in Mediterranean seawater,  
80 revealing a variable fractionation (see EQ.2) between seawater and cultured coralline aragonite ranging  
81 from  $-0.02\text{‰}$  (*Acropora sp.* and *Porite sp.*) to  $-0.35\text{‰}$  (*Stylophora sp.* and *Montipora sp.*). The Ba  
82 isotope composition of natural CWCs was also reported; two *Lophelia pertusa* (*L. pertusa*) samples  
83 from the Norwegian shelf were analysed and found to have  $\delta^{138/134}\text{Ba}$  values of  $0.25 \pm 0.11\text{‰}$  and  $0.3 \pm$   
84  $0.11\text{‰}$ .

85 In this study we present the first detailed study of  $\delta^{138/134}\text{Ba}$  in natural CWCs in comparison to that of  
86 the seawater in which they grew. The data set includes thirty-six well-characterised aragonitic

87 scleractinian specimens from eight different taxa, both solitary and colonial, recovered from three sites:  
88 the North Atlantic, the Equatorial Atlantic, and the Drake Passage. The samples cover a wide range of  
89 environmental conditions, Ba concentrations, and seawater Ba isotope compositions. This allows for a  
90 systematic assessment of the Ba isotope fractionation during coral growth and the use of CWCs as an  
91 archive for past seawater  $\delta^{138/134}\text{Ba}$ .

92

## 93 **2. Materials and analytical methods**

### 94 **2.1 Samples**

95 Thirty-six CWCs and ambient seawater samples from three ocean regions were selected for Ba isotope  
96 analysis. The locations were: south of Iceland in the North Atlantic (Reykjanes Ridge and Hafadju), in  
97 the Equatorial Atlantic (Carter Seamount), and in the Drake Passage (Burdwood Bank) (Tab.1). They  
98 were chosen to cover a wide range of temperature and salinity (e.g. T: 2 – 11.5°C; S: 34.29 – 35.32 psu),  
99 Ba concentrations and Ba isotope compositions (Fig. 1, 2 & 7, supplementary material). Eight different  
100 colonial and solitary aragonite scleractinian coral taxa (identified to either genus or species level) of  
101 living or young (less than 1000 a) CWCs were sampled: *Lophelia pertusa* (*L. pertusa*), *Madrepora*  
102 *oculata* (*M. oculata*), *Desmophyllum dianthus* (*D. dianthus*), *Balanophyllia* sp., *Caryophyllia* sp.,  
103 *Dasmomillia* sp., *Flabellum* sp. and *Javania* sp. (supplementary material). Corals off Iceland were  
104 collected during the ICECTD cruise in 2012 (Frank et al., 2012) using the ROV Victor 6000 (provided  
105 by IFREMER). Simultaneously, seawater samples (125 ml) were directly filled (unfiltered) into acid  
106 cleaned PEP bottles by the ROV. They were stored at room temperature. Three months prior to Ba  
107 isotope analysis, seawater samples were acidified to a pH of 1.5 by adding purified, concentrated HCl.  
108 Therefore, in these samples total dissolvable Ba concentrations and isotope compositions are analysed.  
109 Equatorial Atlantic samples from Carter Seamount were recovered during the JC094 cruise in 2013  
110 (Robinson, 2014; Spooner et al., 2016). The corals were collected by the ROV *Isis*. Ambient seawater  
111 samples are from CTD station 2 and were analysed by Bates et al., 2017. In contrast to seawater samples  
112 from Iceland and the Drake Passage, Equatorial Atlantic samples were filtered with 0.4  $\mu\text{m}$  Acropak  
113 cartridge filters before acidification. CWCs from Burdwood Bank in the Drake Passage were collected

114 in 2011 during cruise NBP1103, using a small basket dredge and trawls (Chen et al., 2015; Margolin et  
115 al., 2014; Robinson and Waller, 2011). Depths and coordinates given here are the average for each  
116 retrieval event. Seawater samples are from CTD station 21 and were taken unfiltered in Niskin bottles,  
117 acidified with 4 ml concentrated HCl and stored at room temperature. As Burdwood Bank is positioned  
118 north of the Subantarctic front an additional unfiltered seawater profile close to Sars Seamount between  
119 the Subantarctic and the Polar front was analysed (cruise NBP1103, station 100). Temperature and  
120 salinity were determined following Spooner et al. (2016). Further details regarding the coral samples  
121 are summarised in the supplementary material.

122

## 123 **2.2 Ba extraction and analysis**

124 All samples (corals and seawater), except for the seawater samples analysed by Bates et al., 2017 (CTD  
125 2, cruise JC094), were prepared and analysed at the Earth Sciences Department of the University of  
126 Oxford. Ba isotopes, for both seawater and CWC samples, were measured on a thermal ionisation mass  
127 spectrometer (TIMS; Thermo Scientific Triton), using a  $^{137}\text{Ba}$ - $^{135}\text{Ba}$  double spike to correct for mass  
128 fractionation during the chemical procedure and instrumental analysis (Hsieh and Henderson, 2017).  
129 For seawater analyses, about 50 ml of seawater was precisely weighed and spiked with a known quantity  
130 of the double spike. After an equilibration period of 24h, 3 ml of 0.9M  $\text{Na}_2\text{CO}_3$  solution was added to  
131 co-precipitate Ba with  $\text{CaCO}_3$ . The precipitate was centrifuged and cleaned with MilliQ water. After  
132 dissolving the precipitate in HCl, column separation was applied twice using the cation exchange resin  
133 AG50-X8 (200 – 400mesh) to purify Ba from the matrix elements (Table S2 and S3 in supplementary  
134 material of (Bridgestock et al., 2018) after (Horner et al., 2015; Foster et al., 2004; Nan et al., 2015)).  
135 To remove organics leached from the resin, 7.5M  $\text{HNO}_3$  and 9.8M  $\text{H}_2\text{O}_2$  were alternately added to the  
136 samples and evaporated. This procedure was repeated three times.

137 CWC samples were rinsed with fresh water on-board ship. Living corals were bleached to remove  
138 external organic tissue and washed again in fresh water. All corals were dried and stored at room  
139 temperature until analysis. The cleaning procedure was adapted from Copard et al. (2010) and Pretet et  
140 al. (2016). CWCs were thoroughly mechanically cleaned using a dremel tool, removing FeMn-coatings

141 and organic residues. To remove any further contamination coral pieces were then washed three times  
142 in MilliQ water in acid cleaned Teflon vials and leached in very dilute HCl. Leaching was performed  
143 by covering the sample with MilliQ water and adding drops of 2M HCl until small bubbles could be  
144 seen around the aragonite. Leaching lasted for five minutes before rinsing three times with MilliQ water  
145 again. Afterwards, samples were dried and weighed (45 – 70 mg). The sample size was chosen to have  
146 more than 300 ng of Ba for isotope measurements. Although small intra-skeletal variabilities of around  
147 11% were observed for the aragonitic CWC species *L. pertusa* between theca walls and centres of  
148 calcification (Raddatz et al., 2016), sample size tests on two *Desmophyllum* (5-40 mg) showed that  
149 different sizes did not affect the obtained Ba/Ca result significantly and tended towards better  
150 reproducibilities for larger CWC pieces (Spooner, 2016). Therefore, the sample size used here  
151 potentially reduces the small influence of intra-skeletal Ba/Ca variability. Coral pieces were dissolved  
152 in 5 ml 7.5M HNO<sub>3</sub> and spiked with a known quantity of <sup>137</sup>Ba-<sup>135</sup>Ba double spike (Hsieh and  
153 Henderson, 2017). To ensure spike equilibration, samples were heated to 90 – 100°C for at least 12h  
154 following spike addition. Coral samples were subsequently dried down, dissolved in 3M HCl, dried  
155 again and redissolved in 1 ml 3M HCl. Ba purification by cation exchange chromatography followed  
156 the procedure for seawater samples (Table S2 and S3 in supplementary material of (Bridgestock et al.,  
157 2018)).

158 At least two total procedural blanks were determined alongside each batch of samples processed through  
159 the chemical separation procedure. For seawater samples these were between 0.19 and 1.6 ng (n=4),  
160 representing a maximum of 0.16% of Ba processed in samples. Most of the Ba blank is added with the  
161 Na<sub>2</sub>CO<sub>3</sub> used for co-precipitation, so blanks for coral samples processed without this step were  
162 significantly lower: 0.02 – 0.24 ng (n=5) accounting for a maximum of 0.02% of the total Ba processed  
163 in samples. Therefore, no blank correction was applied to either seawater or coral samples.

164 Purified samples were dissolved in 1 – 2 µl 2M HCl and loaded on a previously outgassed single Re  
165 filament, adding 1 – 2 µl Ta<sub>2</sub>O<sub>5</sub>-H<sub>3</sub>PO<sub>4</sub> activator (Hsieh and Henderson, 2017). To stabilise the ion  
166 beams during the analysis the activator was loaded on the filament prior to the samples.

167 For coral samples, typical ion beams during the analysis on the TIMS were 8 – 10 V for <sup>138</sup>Ba<sup>+</sup>. Seawater  
168 samples yielded slightly smaller Ba beams of 3 – 7 V <sup>138</sup>Ba<sup>+</sup> and frequently showed a less stable signal.

169 Seven Faraday cups simultaneously detected the masses  $138^+$ ,  $137^+$ ,  $136^+$ ,  $135^+$ ,  $134^+$   $140^+$  and  $139^+$ ,  
170 with the latter reflecting  $^{140}\text{Ce}^+$  and  $^{139}\text{La}^+$ , which were monitored to account for possible isobaric  
171 interferences on  $^{136}\text{Ba}$  and  $^{138}\text{Ba}$ . No  $140^+$  and  $139^+$  signals were detected above background during any  
172 analysis. A single analysis consisted of 54 blocks, each containing 10 isotope ratio measurements, with  
173 a measurement integration time of 8.4s. To monitor the electronic baseline the X-Symmetry of the  
174 instrument was adjusted to divert the ion beams before each block. Blank analyses were measured for  
175 20 – 30 blocks. To correct for instrumental mass bias using the double spike composition, all raw data  
176 were processed offline (Hsieh and Henderson, 2017). The isotope analysis together with the known  
177 spike mass also provide Ba concentration measures.  
178 The standard JCp-1, consisting of powdered coral (Okai et al., 2002), was also analysed three times. It  
179 was prepared in the same way as CWCs samples but without the mechanical and chemical cleaning  
180 steps.

181

## 182 **3 Results**

### 183 **3.1 Reproducibility**

184 Repeat analyses of the SRM NIST 3104a standard using similar beam sizes for seawater samples lead  
185 to a long-term external reproducibility of  $\pm 0.03\%$  (2SD; (Bridgestock et al., 2018; Hsieh and  
186 Henderson, 2017)). Repeat analysis of the coral standard JCp-1 yielded a  $\delta^{138/134}\text{Ba}$  of  $0.25 \pm 0.03\%$   
187 (2SD, n=3), which is within error of analyses in two other laboratories with values of  $0.29 \pm 0.03\%$   
188 (Horner et al., 2015) and  $0.26 \pm 0.1\%$  (Pretet et al., 2016). Several duplicates of seawater and coral  
189 samples confirm the reproducibility of  $\pm 0.03\%$  (supplementary material). Bridgestock et al., (2018)  
190 and Hsieh and Henderson (2017), studies also undertaken at University of Oxford, further verify this  
191 level of reproducibility for seawater and sediment samples. Two analyses were discarded because they  
192 yielded a larger internal standard error for  $\delta^{138/134}\text{Ba}$  than the standard reproducibility ( $\pm 0.03\%$ ) and  
193 were considered unreliable. Both of these samples were subsequently successfully re-analysed.  
194 The reproducibility for the Ba concentration of the repeated coral standard (JCp-1) and seawater sample  
195 measurements (Bridgestock et al., 2018; Hsieh and Henderson, 2017) was  $\pm 2$  to  $3\%$  (1SD), which is  
196 presumably dominated by weighing uncertainties (2 – 3%) and taken as the uncertainty for Ba

197 concentrations of corals and seawater measured in this study. Converting the concentration to Ba/Ca by  
198 assuming a Ca concentration of 40% per mass of the coral (Roberts et al., 2009), the average Ba/Ca in  
199 JCp-1 obtained in this study,  $7.94 \pm 0.22 \mu\text{mol/mol}$  ( $n=3$ ; 3% 2SD), is within uncertainty of previous  
200 studies (e.g.  $7.465 \pm 0.655$ ; (Hathorne et al., 2013)). For seawater samples a Ca concentration of 10.3  
201 mmol/kg (Henderson and Henderson, 2009) was taken to convert Ba concentrations into Ba/Ca<sub>sw</sub>  
202 values.

203

### 204 **3.2 $\delta^{138/134}\text{Ba}$ in seawater profiles**

205 The seawater profile from the Burdwood Bank in the Drake Passage shows the established anti-  
206 correlation between  $[\text{Ba}]_{\text{sw}}$  and  $\delta^{138/134}\text{Ba}$  (Fig. 1; (Bridgestock et al., 2018; Hsieh and Henderson, 2017;  
207 Bates et al., 2017; Pretet et al., 2016; Horner et al., 2015)). Note, that seawater data from the South  
208 China Seas were reported to exhibit a different correlation between  $[\text{Ba}]_{\text{sw}}$  and  $\delta^{138/134}\text{Ba}$  (Cao et al.,  
209 2016) and were therefore excluded in the compilation of published data (Fig. 1).  $[\text{Ba}]_{\text{sw}}$  is 55.2 nmol/kg  
210 in surface waters and increases to 102 nmol/kg at 2250 m water depth. The isotope composition of Ba  
211 decreases with depth from 0.5‰ to 0.25‰.

212 Tropical Atlantic water samples measured and described in detail by Bates et al. (2017) (CTD 2, cruise  
213 JC094) show a similar distribution with Ba concentrations increasing from 37.9 (11 m) to 84.6 nmol/kg  
214 at 4512 m depth and  $\delta^{138/134}\text{Ba}$  decreasing from 0.57‰ to 0.31‰ (Fig. 1). Note, that Ba concentration  
215 for station CTD 2 were initially given in nM (Bates et al., 2017) and have been recalculated here to  
216 nmol/kg by assuming a seawater density of 1.027 kg/l.

217 Seawater samples from south of Iceland, at Reykjanes Ridge and within Hafad Jup basin, cover the depth  
218 range of 238 to 680 m, coinciding with the depths of coral retrieval (Fig. 1). Over this depth interval  
219 both  $[\text{Ba}]_{\text{sw}}$  and  $\delta^{138/134}\text{Ba}$  are nearly constant within uncertainties: 49.3 – 52.9 nmol/kg and 0.51 –  
220 0.53‰ respectively.

221 The seawater samples analysed in this study cover nearly the total range of presently available seawater  
222  $\delta^{138/134}\text{Ba}$  and confirm published data (Fig. 2; (Bridgestock et al., 2018; Hsieh and Henderson, 2017;  
223 Bates et al., 2017; Pretet et al., 2016; Horner et al., 2015)). Isotope compositions of Ba from publications  
224 originally reporting in  $\delta^{137/134}\text{Ba}$  were converted to  $\delta^{138/134}\text{Ba}$  by multiplying by a factor of 1.3 (after



225 Horner et al.; 2015). The closest seawater profiles were used to compare seawater  $\delta^{138/134}\text{Ba}$  with the  
226 coral analyses. To obtain  $\delta^{138/134}\text{Ba}_{\text{sw}}$  at the water depths in which the analysed corals grew, the values  
227 of seawater samples at adjacent depths were linearly interpolated.

228

### 229 **3.3 Ba/Ca in cold-water corals**

230 Ba/Ca for corals varied between 7.5 and 16.3  $\mu\text{mol/mol}$  (Fig. 3a, supplementary material), while  
231 seawater samples spanned 3.9 to 9.7  $\mu\text{mol/mol}$  (Fig. 3a, supplementary material). Ba/Ca results of  
232 different discrete subsamples of some corals from the Equatorial Atlantic and the Drake Passage and  
233 analysis of JCp-1 ( $6.96 \pm 0.08$  2SE,  $n=13$ ) were also carried out in the Bristol Isotope Group (Spooner,  
234 2016). Accounting for analytical deviations between the laboratories seen in the JCp-1 analysis, the  
235 measurements of both laboratories agree for all subsampled corals, despite the use of two different  
236 measurement approaches. The double spike method with Ba purification used here, analysed on a TIMS,  
237 was compared to direct Ba/Ca measurements of dissolved coral fragments using a ThermoFinnigan  
238 Element 2 ICP-MS (Spooner, 2016).

239 A linear least squares regression gives  $\text{Ba/Ca}_{\text{CWC}} = 1.8 (\pm 0.4, 2\text{SE}) \text{Ba/Ca}_{\text{sw}} + 0.7 (\pm 2.6)$  with a  
240 correlation factor of  $r^2 = 0.67$ . Therefore, the overall partition coefficient  $D_{\text{CWC/SW}}(\text{Ba})$  (i.e.  
241  $\text{Ba/Ca}_{\text{CWC}}/\text{Ba/Ca}_{\text{sw}}$ ) observed is  $1.8 \pm 0.4$  (2SE). The partition coefficient calculated separately for each  
242 CWC in this study covers a range from 1.5 to 2.4.

243

### 244 **3.4 $\delta^{138/134}\text{Ba}$ in cold-water corals**

245 CWCs of four different taxa were analysed from Burdwood Bank (Fig. 3b – 6, supplementary material).  
246 Taxa from Burdwood Bank included five *Balanophyllia sp.*, two *Flabellum sp.*, two *Caryophyllum sp.*  
247 and three *D. dianthus*, with samples taken from depths ranging from 334 to 1829 m. Isotope  
248 compositions  $\delta^{138/134}\text{Ba}$  are 0.24‰ in shallow corals and 0.03‰ in the deeper corals (Fig. 4), reflecting  
249 the decrease in seawater  $\delta^{138/134}\text{Ba}$  with depth. At each depth, coral  $\delta^{138/134}\text{Ba}$  values agree with each  
250 other within external reproducibility ( $\pm 0.03\%$ ), regardless of species.

251 The fractionation of Ba between corals and seawater can be expressed by the isotope fractionation factor  
252  $\alpha = R_{\text{CWC}}/R_{\text{sw}}$  or the enrichment factor

253 
$$\varepsilon = (\alpha - 1) \times 1000 \approx \Delta^{138/134}\text{Ba}_{\text{CWC-SW}} = \delta^{138/134}\text{Ba}_{\text{CWC}} - \delta^{138/134}\text{Ba}_{\text{SW}} \quad (2)$$

254 with an external analytical 2SD of  $\pm 0.04\%$  propagated from the analytical 2SD of  $\delta^{138/134}\text{Ba}$  ( $\pm 0.03\%$ ).

255 Individual enrichment factors in CWCs from Burdwood Bank range from  $-0.19$  to  $-0.29\%$  with an  
 256 average of  $-0.24 \pm 0.06\%$ . The uncertainty of the average is assumed to be the larger of either the  
 257 propagated external reproducibility or the 2SD obtained when averaging over a number of corals.

258 Taxa analysed from Carter Seamount include two *Dasmosillia sp.*, six *Caryophyllia sp.*, and four *Javania*  
 259 *sp.* covering water depths from 265 to 2318m.  $\delta^{138/134}\text{Ba}$  varies from  $0.18$  to  $0.40\%$  associated with  
 260 enrichment factors of  $-0.16$  to  $-0.27\%$ , with a mean of  $-0.19 \pm 0.07\%$ .

261 Corals analysed from Iceland only cover shallow water depths between 206 and 698m. Three species,  
 262 six *D. dianthus*, five *L. pertusa*, and one *M. oculata*, show an isotope composition of  $0.28 - 0.36\%$ . The  
 263 enrichment  $\Delta^{138/134}\text{Ba}_{\text{CWC-SW}}$  between seawater and coral  $\delta^{138/134}\text{Ba}$  is  $-0.16$  to  $-0.24\%$  also averaging to  
 264  $-0.19 \pm 0.05\%$ .

265 The fractionation  $\Delta^{138/134}\text{Ba}_{\text{CWC-SW}}$  between CWCs and seawater averaged over all locations and species  
 266 is  $-0.21 \pm 0.08\%$  (2SD; 2SE =  $\pm 0.01\%$ ) ( $\alpha_{\text{Ba}} = 0.99979 \pm 0.00008$ ) (Fig. 5). Averaging for each species  
 267 separately leads to a Ba fractionation between  $-0.17$  and  $-0.25\%$  (Fig. 5 and supplementary material).  
 268 The genus *Balanophyllia sp.* (n=5) shows the largest Ba fractionation of  $-0.25 \pm 0.05\%$  (2SD) while  
 269 *Javania sp.* (n=4) fractionates Ba by only  $-0.17 \pm 0.04\%$ . The two genera with the highest variability in  
 270  $\Delta^{138/134}\text{Ba}$  were *D. dianthus* (n=9) with values ranging from  $-0.16\%$  to  $-0.28\%$  and averaging  $-0.22 \pm$   
 271  $0.08\%$ , and *Caryophyllia sp.* (n=8) covering a range of  $-0.16\%$  to  $-0.27\%$  and averaging  $-0.21 \pm 0.$   
 272  $07\%$ .

273

## 274 **4 Discussion**

### 275 **4.1 Constancy of $D_{\text{CWC/SW}}$ (Ba)**

276 The mean partition coefficient derived by a linear fit to all data is  $D_{\text{CWC/SW}}(\text{Ba}) = 1.8 \pm 0.4$  (2SE, see  
 277 Fig. 3a) covering a range from 1.5 to 2.4 for separate samples. These values are similar to those in  
 278 previous studies (Anagnostou et al., 2011; Spooner, 2016). The study by Anagnostou et al., 2011  
 279 ( $\text{Ba}/\text{Ca}_{\text{CWC}} = 1.4 (\pm 0.3) \text{Ba}/\text{Ca}_{\text{SW}} + 0 (\pm 2)$ ) did not reveal a significant correlation between the partition  
 280 coefficient and seawater temperature, salinity or pH. Spooner (2016) analysed possible environmental

281 impacts on  $D_{\text{CWC/SW}}(\text{Ba})$  in more detail, confirming the findings of Anagnostou et al. (2011), and  
282 indicating that  $D$  is independent of seawater nutrient content ( $\text{PO}_4$ ) and oxygen concentrations. Data in  
283 this study support the previous finding that incorporation of Ba into CWCs does not depend on seawater  
284 temperature (Fig. 7(a)), water depth, salinity, pH or nutrient content but seems to occur at a constant  $D$   
285 value (Tab. A1 in supplementary material). Within the stated uncertainty of 0.4, no clear inter-species  
286 or location effect is resolved. Analysis at higher precision and a considerably larger data set might  
287 resolve variations smaller than the resolution here. At the stated uncertainty of 0.4, however, we consider  
288  $D$  constant which favours the use of CWCs to reconstruct past oceanic Ba concentrations, with potential  
289 application to assess past biogeochemical cycling of Ba and/or ocean circulation.

290

#### 291 **4.2 Constancy of $\Delta^{138/134}\text{Ba}_{\text{CWC-SW}}$**

292 With a mean enrichment factor  $\Delta_{\text{BaSO}_4\text{-SW}}$  of  $-0.21 \pm 0.08\text{‰}$  (Fig. 5) all thirty-six coral samples analysed  
293 in this study are enriched in lighter Ba isotopes compared to ambient seawater (Fig. 4). The incorporation  
294 of lighter isotopes during carbonate formation is similar to other isotope systems such as Ca (e.g. Böhm  
295 et al., 2006; Fantle and DePaolo, 2007), Sr (e.g. Fietzke and Eisenhauer, 2006; Raddatz et al., 2013),  
296 Mg (e.g. Yoshimura et al., 2011) and Li (e.g. Marriott et al., 2004; Rollion-Bard et al., 2009). The most  
297 likely explanation for the fractionation is a kinetic effect combined with biological impacts (e.g. Böhm  
298 et al., 2006; DePaolo, 2004).

299 The offset towards light Ba isotopes during incorporation into a mineral phase is similar to that seen in  
300 limited previous studies. Pretet et al. (2016) analysed two *L. pertusa* from the Norwegian margin and  
301 found  $\delta^{138/134}\text{Ba}$  of  $0.25 \pm 0.11\text{‰}$  and  $0.3 \pm 0.11\text{‰}$ , but without accompanying seawater measurements.  
302 The coral values in that study are, however, identical within uncertainties to North Atlantic corals from  
303 this study. Further analyses in Pretet et al. (2016) on cultured tropical aragonitic scleractinian corals  
304 showed a more variable fractionation than observed here, varying between  $-0.02\text{‰}$  (*Acropora sp.* and  
305 *Porite sp.*) and  $-0.38\text{‰}$  (*Stylophora sp.* and *Montipora sp.*) (Fig. 6).

306 Previous inorganic precipitation experiments of  $\text{BaSO}_4$  and  $\text{BaMn}[\text{CO}_3]_2$  showed a similar preference  
307 for incorporation of lighter isotopes, with a fractionation of  $-0.33 \pm 0.04\text{‰}$  and  $-0.17 \pm 0.028\text{‰}$   
308 respectively (Fig. 6; (von Allmen et al., 2010; Böttcher et al., 2012)). Reported Ba isotope fractionation

309 during BaCO<sub>3</sub> precipitation is between  $-0.25 \pm 0.028\text{‰}$  (von Allmen et al., 2010) and  $-0.07 \pm 0.04\text{‰}$   
310 (Mavromatis et al., 2016). The fractionation observed for CWCs analysed in this study lies roughly in  
311 the middle of the fractionation range reported on precipitates or cultured aragonite tropical corals (Fig.  
312 6; (von Allmen et al., 2010; Böttcher et al., 2012; Pretet et al., 2016)). Analysis of the relationship  
313 between [Ba] and  $\delta^{138/134}\text{Ba}$  in seawater also suggests that Ba isotopes incorporated into BaSO<sub>4</sub> during  
314 precipitation in the water column are lighter than seawater, with  $\Delta_{\text{BaSO}_4\text{-SW}} = -0.28 \pm 0.10\text{‰}$  (Horner et  
315 al., 2015) or  $-(0.4 - 0.5)\text{‰}$  (Bridgestock et al., 2018; Horner et al., 2017). The results in this study for  
316 coral aragonite are at the lower limit of this range.

317 At the precision of our measurements, there is no correlation between water temperature (between 2 and  
318 12°C) and Ba isotope fractionation ( $\Delta^{138/134}\text{Ba}$ ) observed in this study (Fig. 7(b), supplementary  
319 material). No previous study has assessed the temperature dependency of  $\Delta^{138/134}\text{Ba}$  on CaCO<sub>3</sub>  
320 formation, although no temperature dependency of fractionation in laboratory grown BaCO<sub>3</sub> precipitates  
321 was found (von Allmen et al., 2010). A possible effect of precipitation rates was observed for Ba  
322 fractionation into BaCO<sub>3</sub> precipitates with a larger fractionation for slower precipitation rates.  
323 Transferring this observation to the higher variance seen in the cultured corals compared to the natural  
324 coral analysed in this study cannot explain the observed discrepancy. Known linear extension rates of  
325 the taxa analysed in this study span a wide range, from e.g. 0.5 – 3.1 mm/a for *D. dianthus* and 5 – 26  
326 mm/a for *L. pertusa* (Gass and Roberts, 2006; Mortensen, 2001; Orejas et al., 2008), and no significant  
327 impact on Ba fractionation could be observed at the precision achieved in this study.

328 No substantial correlation between fractionation and nutrient availability (PO<sub>4</sub>) could be observed  
329 (supplementary material). Analyses of other environmental factors like depth, pH and salinity provided  
330 no clear evidence for significant impacts on Ba fractionation (supplementary material). At the precision  
331 achieved here, there is also no influence of dissolved Ba concentration in seawater on Ba isotope  
332 fractionation (Fig. 7(c)).

333 Different species span a range of enrichment factors from  $-0.17\text{‰}$  (*Javania sp.*) to  $-0.25\text{‰}$   
334 (*Balanophyllia sp.*) (Fig. 5). However, this possible inter-species difference is barely resolved at the  
335 0.03‰ level of our analytical uncertainty and compounded by the possibility of regional variations. All  
336 species lie well within the 2SD (0.08‰) of the average fractionation between seawater and CWCs

337 ( $\Delta^{138/134}\text{Ba}_{\text{CWC-SW}} = -0.21\text{‰}$ ). The isotope offset of CWCs at the Drake Passage may also be subtly  
338 different from that in the Atlantic (Fig. 4), but again any difference is very close to analytical uncertainty  
339 and lies well within the 2SD of the average fractionation. It is possible that species or local effects may  
340 become apparent with future higher precision or a significant larger data set, but at the stated uncertainty  
341 of 0.08‰ the offset between seawater and CWC Ba isotopes is constant.

342

### 343 **4.3 $\delta^{138/134}\text{Ba}$ : a new proxy for paleoceanography**

344 Recent studies have demonstrated a strong linear relationship between  $\delta^{138/134}\text{Ba}$  and [Ba] in seawater  
345 (Bates et al., 2017; Hsieh and Henderson, 2017; Horner et al., 2015; Bridgestock et al., 2018). Local  
346 deviations from this relationship could provide evidence for local inputs of Ba with distinct isotope  
347 compositions. Variation in the nature of the global relationship may occur in the past, and would indicate  
348 changes in the global biogeochemical cycling of Ba through time. The fact that, within the uncertainties  
349 stated in this study, both  $D_{\text{CWC/SW}}(\text{Ba})$  and  $\Delta^{138/134}\text{Ba}_{\text{CWC-SW}}$  are found to be constant for CWCs regardless  
350 of the growth environment suggests that measurements on fossil corals would allow reconstruction of  
351 the past ocean relationship between [Ba] and  $\delta^{138/134}\text{Ba}$ . Analysis of coralline Ba/Ca can provide  
352 information about the [Ba] of the water the coral grew in, with possible implications for changing  
353 productivity and/or water circulation. However, measurements of this parameter alone cannot provide  
354 information about local inputs of Ba, nor possible changes in the whole oceanic Ba cycle but can be  
355 constrained by additional  $\delta^{138/134}\text{Ba}$  analyses. Thus, our observations suggest future applications  
356 regarding the reconstruction of the past marine Ba cycle using coupled Ba/Ca and Ba isotope  
357 measurements in CWCs.

358 Based on the data presented here we can test the potential accuracy of seawater Ba reconstructions from  
359 CWCs. The constancy of both the elemental partition coefficient and isotope fractionation for Ba in  
360 combination with the safe assumption that the seawater Ca content remained similar on long timescales,  
361 enables reconstruction of past seawater [Ba] and  $\delta^{138/134}\text{Ba}$  from coral data. Within uncertainty the  
362 reconstructed linear correlation for seawater has slope and intersect values that are equal to the  
363 relationship directly measured in seawater samples (Fig. 8).

364 To avoid the possibility of circular reasoning by using the same coral set to both define and test  $D_{CWC/SW}$   
365 (Ba) and  $\Delta^{138/134}\text{Ba}_{CWC-SW}$  to reconstruct seawater, we ran repeated Monte-Carlo cross validations  
366 splitting the data set in two halves. The cross validation was run 1000 times to assess the predictive  
367 capability of our calibration for  $D_{CWC/SW}$  (Ba) and  $\Delta^{138/134}\text{Ba}_{CWC-SW}$  (supplementary material). The  
368 distribution obtained confirms the results when using all thirty-six CWCs for both the elemental partition  
369 and isotope fractionation, and slope and y-intersect of the seawater  $\delta^{138/134}\text{Ba}$ -[Ba] correlation. The  
370 average  $\delta^{138/134}\text{Ba}$  deviation of each reconstructed seawater value from the best-fit regression through  
371 the seawater observations is 0.03‰, indicating the expected uncertainty in future studies on past  
372 seawater reconstructions. This level of uncertainty is similar to the uncertainty of an individual Ba  
373 isotope analysis, suggesting that the range of values observed for the fractionation  $\Delta^{138/134}\text{Ba}_{CWC-SW}$  and  
374 partition coefficient  $D_{CWC/SW}$  (Ba) are largely due to measurement uncertainty, rather than systematic  
375 biases within the data set. Furthermore, the level of uncertainty is small relative to the observed  
376 geographical variation in the modern ocean (Fig. 2), supporting the strength of coupling Ba/Ca and Ba  
377 isotope measurements on CWCs to provide novel assessment of the past Ba cycle in the past.  
378 This approach might be used to trace changes in nutrient cycling, upwelling, and water-mass circulation  
379 (Bates et al., 2017; Bridgestock et al., 2018; Horner et al., 2015). Changes in the general relationship of  
380  $\delta^{138/134}\text{Ba}$  and [Ba] in the past might also be used to identify whole-ocean changes in the Ba-cycle and  
381 deviations from the relationship used to assess inputs in the past ocean (e.g. from rivers or in the deep  
382 ocean) (Cao et al., 2016; Hsieh and Henderson, 2017).

383

## 384 5 Conclusions

385 Barium isotopes ( $\delta^{138/134}\text{Ba}$ ) in eight different taxa of colonial and solitary aragonitic scleractinian cold-  
386 water corals (CWC), taken from sites in the North Atlantic, the Equatorial Atlantic, and the Drake  
387 Passage, show a surprisingly constant isotope offset towards lighter values with a mean of  $\epsilon_{\text{Ba}} \approx$   
388  $\Delta^{138/134}\text{Ba}_{CWC-SW} = -0.21 \pm 0.08\%$ . Within this reproducibility no relationship with species or location  
389 and the environmental variables dissolved Ba concentration, depth, temperature, salinity, pH or  
390 phosphate concentration is observed. The mean partition coefficient for Ba ( $D_{CWC/SW}$  (Ba) =  $1.8 \pm 0.4$ )  
391 is within the range found in previous studies, regardless of the growth environment. The constancy of

392 elemental partitioning and isotope fractionation indicate that coupled [Ba] and  $\delta^{138/134}\text{Ba}$  analysis in  
393 CWCs can be used to reconstruct changes in the local and global relationship between [Ba] and  
394  $\delta^{138/134}\text{Ba}$ . New information about inputs of Ba to the ocean, and the past global oceanic cycling of Ba,  
395 might thus be gained and past changes in riverine and hydrothermal inputs to the ocean assessed.

396

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406

407

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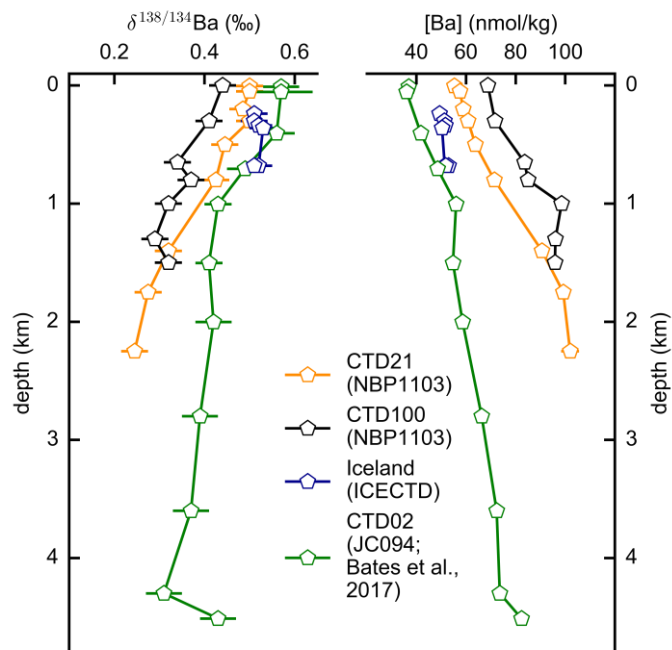
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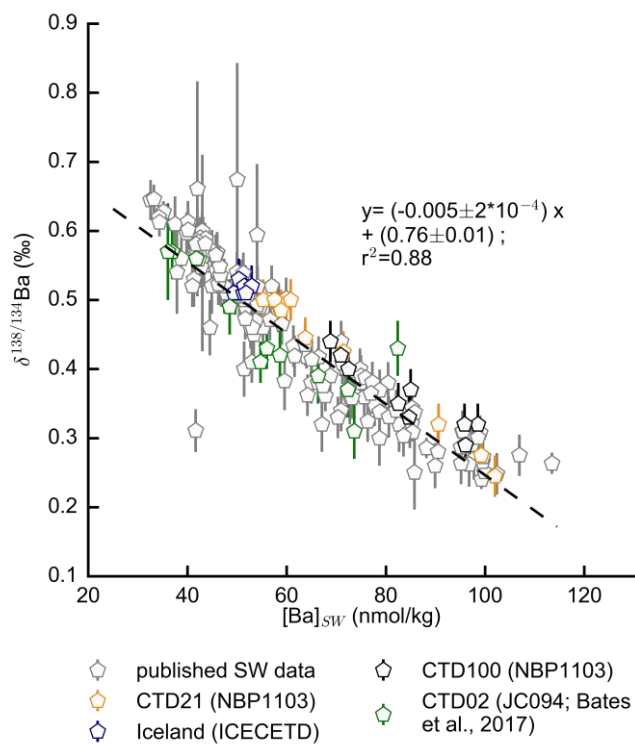
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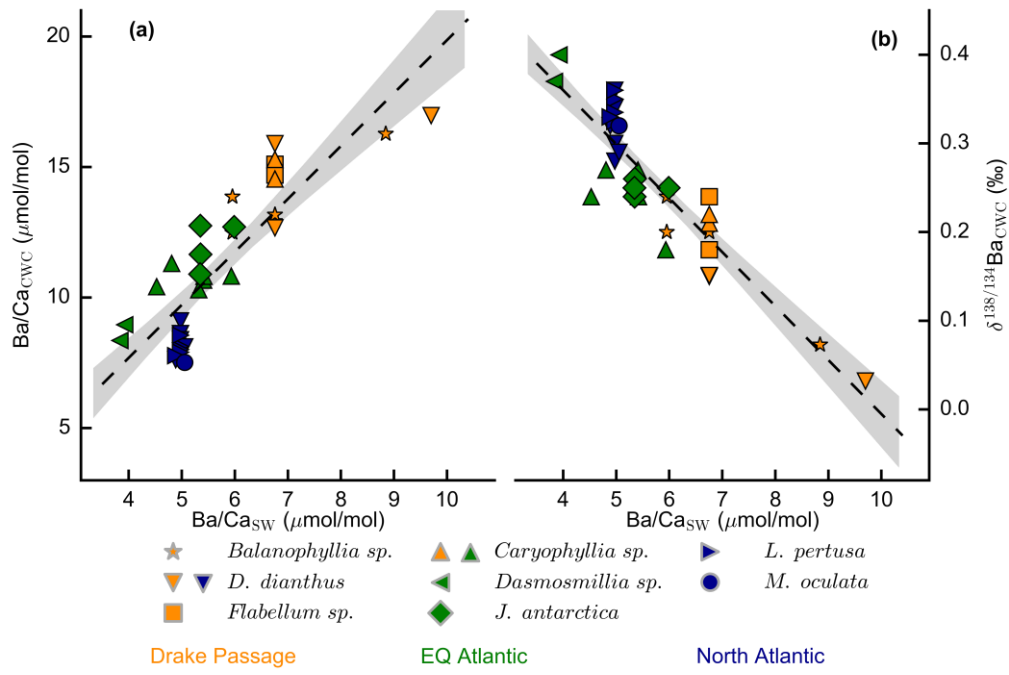
552 *Figure 1*

553



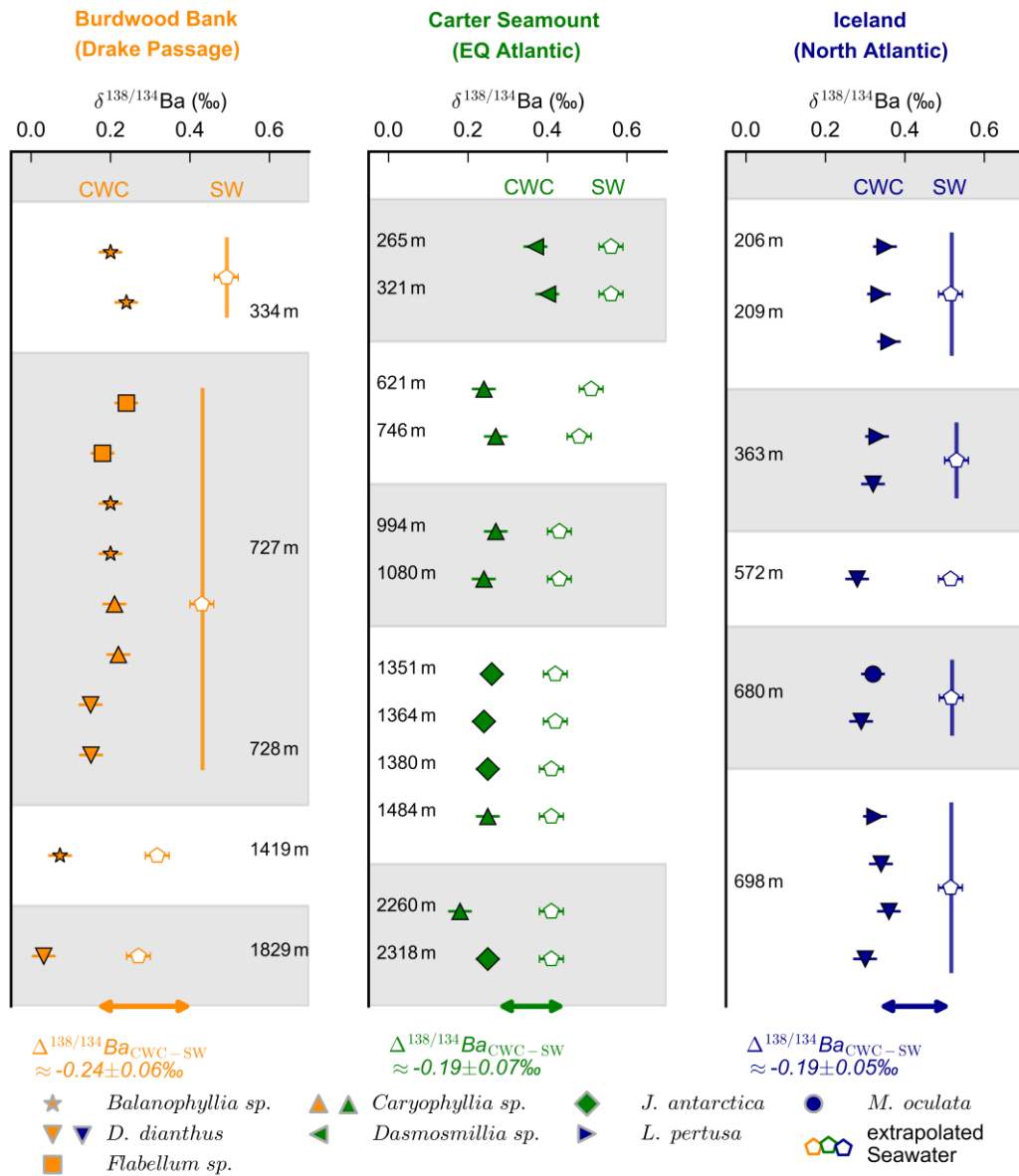
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555 *Figure 2*



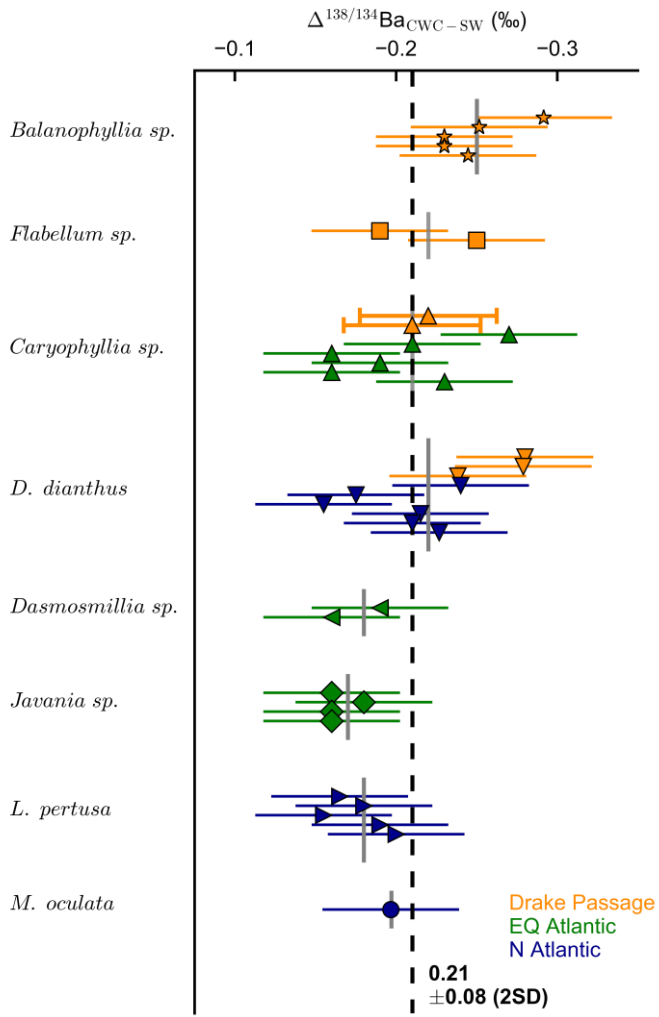
556

557 Figure 3



558

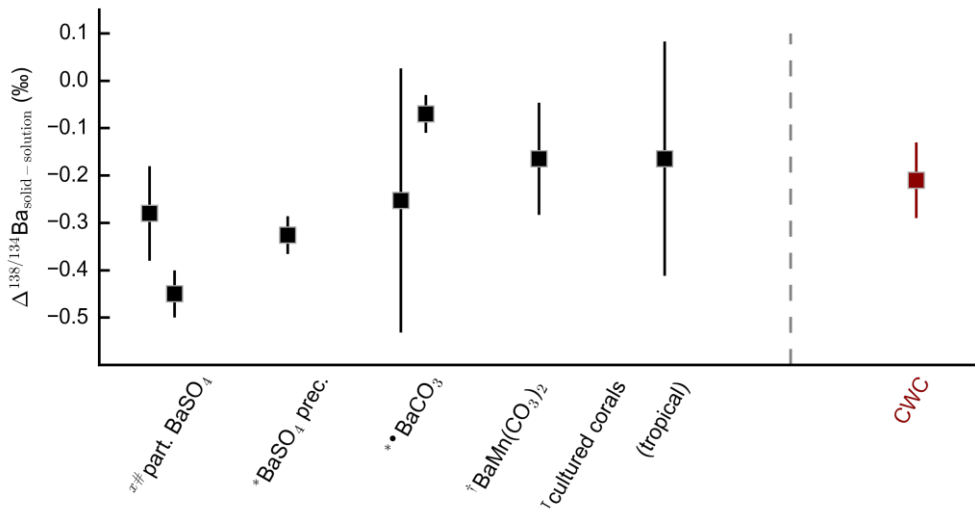
559 Figure 4



560

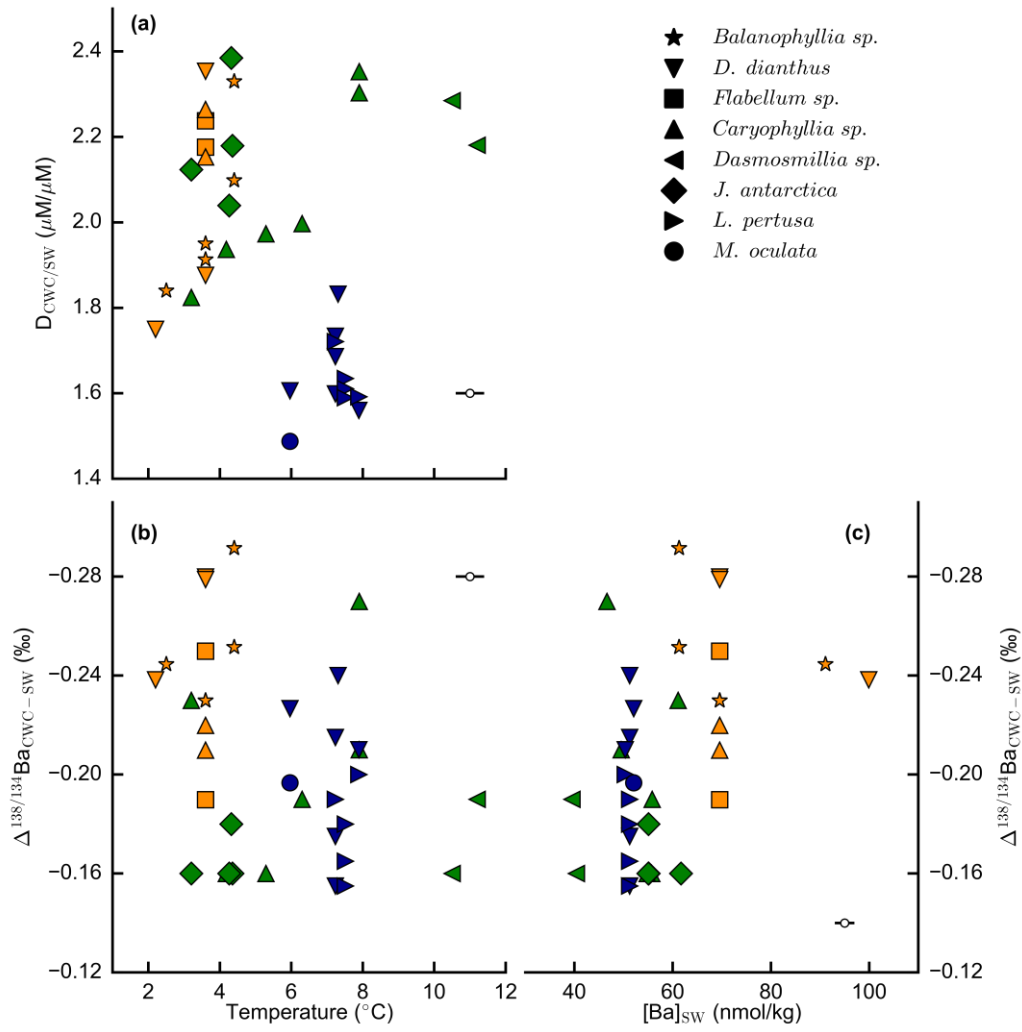
561 Figure 5

562



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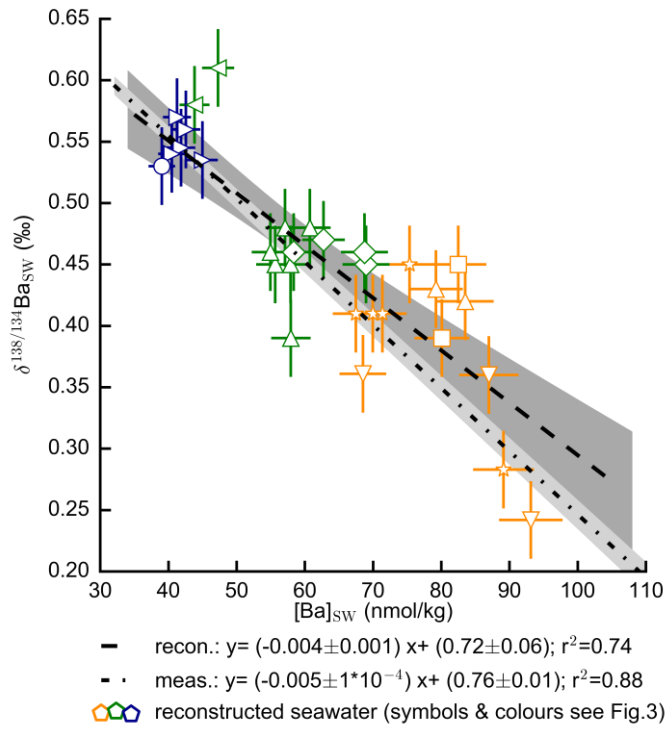
564 Figure 6



565

566 Figure 7





567

568 *Figure 8*

569

570 *Table 1*

station	latitude	longitude	covered depths	analysed depths (m)
Iceland				
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
Equatorial Atlantic				
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
Drake Passage				
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
NBP1103 CTD 100	60° 33.85' S	65° 29.57' W	0 – 3100	0 – 1500

571

572 **Figure and table captions**

573

574 Figure 1:

575 Seawater profiles for dissolved Ba concentrations [Ba] and Ba isotope compositions  $\delta^{138/134}\text{Ba}$ .

576 At all locations, station CTD21 (Burdwood Bank, orange), CTD100 (Sars Seamount, black), Iceland

577 (Reykjanes Ridge and Hafadjup, blue), and CTD02 (Carter Seamount) (Bates et al., 2017), the well-

578 established anti-correlation between [Ba] and  $\delta^{138/134}\text{Ba}$  can be observed. Both profiles from cruise

579 NBP1103 reach deeper, but were not analysed in abyssal depths as only depths with coral growth were

580 considered for this study. Station CTD100 will not be discussed further as corals from Sars seamount

581 were not analysed here.

582

583 Figure 2:

584  $\delta^{138/134}\text{Ba}_{\text{sw}}$  against  $[\text{Ba}]_{\text{sw}}$  for samples from this study and published data (Bridgestock et al., 2018;

585 Hsieh and Henderson, 2017; Bates et al., 2017; Pretet et al., 2016; Horner et al., 2015). Data from Bates

586 et al. (2017) were used in this study for considerations of corals from the Equatorial Atlantic (green

587 symbols). Cao et al. (2016) data were not included in this summary as their seawater samples exhibited

588 a different correlation with higher Ba isotope compositions. Our data agree well with the other studies.

589 Note that seawater Ba isotope composition at the coral sites cover nearly the total observed range of

590  $\delta^{138/134}\text{Ba}$  reported in the other studies.

591

592 Figure 3:

593 Ba/Ca in CWCs and ambient seawater (a) and seawater Ba/Ca<sub>sw</sub> influence on coralline  $\delta^{138/134}\text{Ba}$  (b).

594 (a) A linear fit (black dashed line) through the data gives:  $\text{Ba}/\text{Ca}_{\text{CWC}} = 1.8 (\pm 0.4) \text{Ba}/\text{Ca}_{\text{sw}} + 0.7 (\pm 2.6)$

595 with a correlation factor of  $r^2 = 0.67$  (0.95 confidence interval as shaded grey area).

596 (b) Similar to seawater  $\delta^{138/134}\text{Ba}$ , a close anti-correlation to Ba concentration (here as Ba/Ca<sub>sw</sub>) can be

597 observed for coralline  $\delta^{138/134}\text{Ba}$ . The correlation factor  $r^2$  is 0.82.

598

599 Figure 4:

600  $\delta^{138/134}\text{Ba}$  in CWCs (filled symbols) at all three sites compared to ambient seawater (open symbols).  
601 Seawater values are extrapolated to the depth each coral grew at. All CWCs are isotopically lighter than  
602 ambient seawater, with higher Ba isotope compositions in shallower depths than in deeper waters.  
603 Within uncertainties all sites show a similar mean fractionation. The overall fractionation of Burdwood  
604 Bank corals is  $\Delta^{138/134}\text{Ba}_{\text{CWC-SW}} = -0.24 \pm 0.06\text{‰}$ , while Carter Seamount and Iceland corals both  
605 fractionate Ba by  $-0.19\text{‰}$  with a 2SD of  $\pm 0.07\text{‰}$  and  $\pm 0.05\text{‰}$  respectively.

606

607 Figure 5:

608  $\Delta^{138/134}\text{Ba}_{\text{CWC}}$  for each species/ genus separately.

609 The overall fractionation between corals and seawater is  $\Delta^{138/134}\text{Ba}_{\text{CWC}} = -0.21 \pm 0.08\text{‰}$  (2SD and 0.01‰  
610 SE). The maximum species specific fractionation is  $\Delta^{138/134}\text{Ba}_{\text{CWC}} = -0.25 \pm 0.05\text{‰}$  for *Balanophyllia*  
611 *sp.* and the minimum  $\Delta^{138/134}\text{Ba}_{\text{CWC}} = -0.17 \pm 0.04\text{‰}$  for *Javania sp.* (uncertainties are the larger of  
612 external reproducibility and 2SD from averaging). The species *D. dianthus* shows the largest variability  
613 in  $\Delta^{138/134}\text{Ba}_{\text{CWC}}$ , ranging from  $-0.16$  to  $-0.28\text{‰}$  and an average of  $-0.22 \pm 0.08\text{‰}$ .

614

615 Figure 6:

616 Comparison of  $\Delta^{138/134}\text{Ba}$  to published assessments. Particulate  $^{\#}\text{BaSO}_4$  (part.) were estimated by  
617 Horner et al., 2015,  $^{\#}\text{BaSO}_4$  (part.) by Bridgestock et al., 2018 and Horner et al., 2017, precipitates of  
618  $^{\#}\text{BaSO}_4$  (prec.) and  $^{\#}\text{BaCO}_3$  were analysed by von Allmen et al., 2010, of  $^{\#}\text{BaCO}_3$  by Mavromatis et al.,  
619 2016, of  $^{\dagger}\text{BaMn}[\text{CO}_3]_2$  by Böttcher et al., 2012 and  $^{\top}$ cultured tropical corals were investigated by Pretet  
620 et al., 2016. Uncertainties are 2SE for repeat analysis of one sample.

621 The variation seen in precipitates is larger than for all thirty-six natural CWCs investigated in this study  
622 (red). CWCs are separately analysed for location and species in Fig. 4 and 5.

623

624 Figure 7:

625 Temperature dependency of  $D_{\text{CWC/SW}}$  (a) and  $\Delta^{138/134}\text{Ba}_{\text{CWC}}$  (b), and correlation between  $[\text{Ba}]_{\text{SW}}$  and  
626  $\Delta^{138/134}\text{Ba}_{\text{CWC}}$  (c). No correlation of  $D_{\text{CWC/SW}}$  with temperature ( $r^2 = 0.02$ ) and  $\Delta^{138/134}\text{Ba}_{\text{CWC}}$  with

627 temperature ( $r^2 = 0.12$ ) and  $[\text{Ba}]_{\text{SW}}$  ( $r^2 = 0.16$ ) can be observed (for colours see e.g. Fig. 4). Uncertainties  
628 for temperature and  $[\text{Ba}]_{\text{SW}}$  are displayed with the extra open data point.

629

630

631 Figure 8:

632 Comparison between the established seawater  $[\text{Ba}]_{\text{SW}}$  and  $\delta^{138/134}\text{Ba}$  correlation (meas.: dash-dot line)  
633 and the seawater characteristic 'reconstructed' from the CWCs (reconstructed: dashed line). The  
634 reconstruction was achieved by applying a constant partition coefficient and isotope fractionation for  
635 Ba to the measured CWC data, obtaining the open coloured symbols (for symbols see e.g. Fig. 3).  
636 Uncertainties shown are the external reproducibilities from our measurements. Within uncertainties  
637 (grey envelopes) the 'reconstructed' seawater data and  $[\text{Ba}]_{\text{SW}}$  and  $\delta^{138/134}\text{Ba}$  correlation agree with the  
638 well-known seawater anti-correlation for  $[\text{Ba}]_{\text{SW}}$  and  $\delta^{138/134}\text{Ba}$ .

639

640 Table 1:

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