

1 **Response to review comments**

2

3 Dear Editor and Referees,

4

5 We thank two anonymous referee for the constructive reviews, and sincerely appreciate the
6 comment which helped us to improve this manuscript. Please find our responses to the
7 general and specific comments below.

8

9 Sincerely yours,

10

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12 *****

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20

1 **Reviewer#1**

2
3 My main concern with this manuscript is that it duplicates large portions of the companion
4 isotope manuscript (sections 3.2, 4.2.1, 4.2.2) and those duplicated sections are some of the
5 strongest of this report. The Ba/Ca data show a convincing linear correlation with seawater Ba
6 concentrations, which is consistent with previous studies on octocorals, bamboo corals and
7 aragonitic deep-sea corals. While not significantly novel, this result is worth publication,
8 although I recommend some changes below. In contrast, the B/Ca and U/Ca data should be
9 combined with the companion isotope manuscript, so that redundancies can be eliminated.
10 Because both manuscripts are short and the Ba/Ca data merely confirm previous studies, I
11 would recommend combining all data in one manuscript.

12 → We have split the results of trace element partitioning and isotopic fractionation of
13 calcitic corals in two paper because the main topics discussed in O & C isotope ratios and
14 Ba/Ca ratios were very different, and their research areas were ocean acidification and
15 paleoceanography, respectively. But we combined all data in this manuscript (trace
16 element paper) according to Reviewer #1 and #2 suggestions. We also added
17 Supplementary materials.

18
19 The combined manuscript should reason why these specific elements are worthwhile to be
20 studied, and the mechanism for U/Ca variations in response to carbonate chemistry changes
21 needs to be reviewed in the introduction as well.

22 → We added the sentences below in Introduction.

23 "In seawater, uranium exists in several different carbonate complexes, uranyl
24 triscarbonate ($\text{UO}_2(\text{CO}_3)_3^{4-}$), bicarbonate ($\text{UO}_2(\text{CO}_3)_2^{2-}$) and monocarbonate (UO_2CO_3^0)
25 complexes (Djogic et al., 1986). As pH decreases, a preferential uptake of $\text{UO}_2(\text{CO}_3)_2^{2-}$
26 and/or UO_2CO_3^0 can explain the inverse relationship between U/Ca in CaCO_3 and
27 seawater pH. Early studies show convincing annual U/Ca cycles in the reef corals (Min et
28 al., 1995; Shen and Dunbar, 1995), and the primary objective of this paleotracer is to
29 evaluate them as seawater pH or $[\text{CO}_3^{2-}]$ proxies (e.g., Anagnostou et al., 2011; Inoue et
30 al., 2011; Raitzsch et al., 2011; Raddatz et al., 2014). Although the large discrepancy in
31 pH dependence found between coral and foraminifera is due to the different CaCO_3
32 polymorphs (Reeder et al., 2000) and species-specific calcification mechanisms, U/Ca
33 ratios decrease as seawater $[\text{CO}_3^{2-}]$ increases (Russel et al., 2004; Anagnostou et al., 2011;
34 Inoue et al., 2011; Raitzsch et al., 2011; Raddatz et al., 2014). In planktonic foraminifera
35 calcite, the core-top empirical calibration shows that U/Ca is significantly affected by
36 calcification temperature and preferential dissolution effect (Yu et al., 2008). The
37 empirical calibration and intra-shell variation of U/Ca in calcitic corals also offers the
38 possibility of examining the use of this proxy as an indicator of past ocean conditions
39 (Sinclar et al., 2011)."

1 While validating proxies in living organisms from known chemical and physical conditions is
2 a valuable and broadly applied approach, data interpretation is often challenging due to
3 several environmental parameters varying simultaneously. The authors acknowledge that the
4 current manuscript suffers from this difficulty, in that pH and temperature both decrease with
5 water depth and thus preclude unequivocal association of decreasing B/Ca and U/Ca ratios
6 with either one of these parameters. This complicates direct relation of oxygen isotopes to
7 seawater acidity, for which B/Ca may be a proxy. However, the observed patterns are
8 consistent with previous observations in foraminifera and corals (Spero et al. 1997,
9 McConnaughey et al. 1989), where d18O decreases at lower pH (i.e. lower B/Ca ratios at
10 greater depths, but also lower temperatures at depth). While the data shown in Figure 3 are
11 consistent with this expectation, the text is erroneous. For instance, in the abstract (page 414,
12 line 17) the authors say that “that d18O and d13C are enriched in light isotopes when
13 conditions are less alkaline”, page 426, line 24: “If B/Ca is assumed to be a function of the pH
14 of the ECF, then light isotopes would be enriched in the calcifying fluid under less alkaline
15 conditions, because B/Ca is positively correlated with d18O and d13C values. B/Ca versus
16 d18O regressions are shown as positive (Table 2)”. These interpretations and correlations are
17 erroneous because the relationship between B/Ca and d18O is inverse, as obvious in Figure 3.
18 Such an inverse relationship agrees with theoretical studies on O and C isotope partitioning in
19 seawater. The authors should read the studies of Zeebe (1999, 2001). This study still requires
20 removal of the temperature effect on d18O before any pH effect can be evaluated, but I
21 assume the companion manuscript deals with that. Plots of DIC, temperature and pH should
22 be provided.

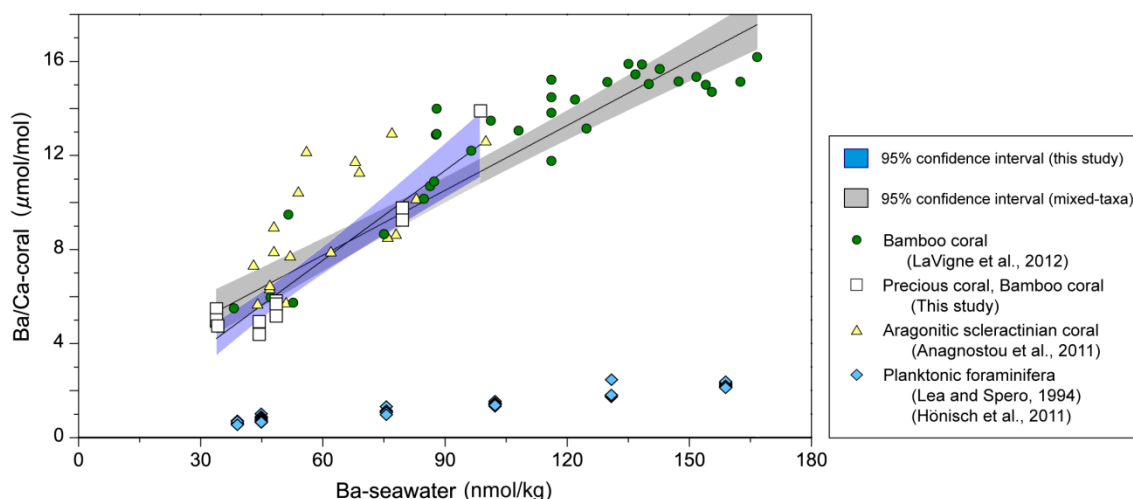
23 → As Reviewer #1 pointed out, pH proxies, B/Ca, and U/Ca ratios presented in this study
24 are simultaneously affected by seawater carbonate chemistry and water temperature, i.e.
25 pH and temperature both decrease with water depth, thus this precludes unequivocal
26 association of decreasing B/Ca and U/Ca ratios with either one of these parameters. We
27 changed related sentences in 4.2.2.

28

29 The Ba/Ca correlation with the seawater Ba concentration is convincing but the data
30 presentation should be modified to include plots of these relationships in aragonitic cold-
31 water scleractinian corals published by Anagnostou et al. (2011) and in calcitic planktic
32 foraminifers by Hönisch et al. (2011). While the relationship of Anagnostou et al. (2011)
33 appears similar to the ones presented in Figure 4, it falls above those relationships, and the
34 foraminifer equation presented by Hönisch et al. (2011) falls below them, consistent with
35 observations from inorganic studies presented in the text.

36 Section 4.2.1 should be corrected accordingly.

37 → We added the data of cold-water corals and planktonic foraminifera in the Fig. 4 as
38 suggested.



1
2

3 There are several redundancies in the text, some typos and some rephrasing is required in
 4 various sentences, however, given the substantial rewriting that this manuscript should
 5 undergo, I find it premature to dwell on such minor aspects. An aspect that the authors should
 6 focus on is a better presentation of the sampling strategy of the individual coral species.
 7 Which portion of the skeleton was sampled and how? This is well explained for the intra-
 8 skeletal transect but not for the other samples.

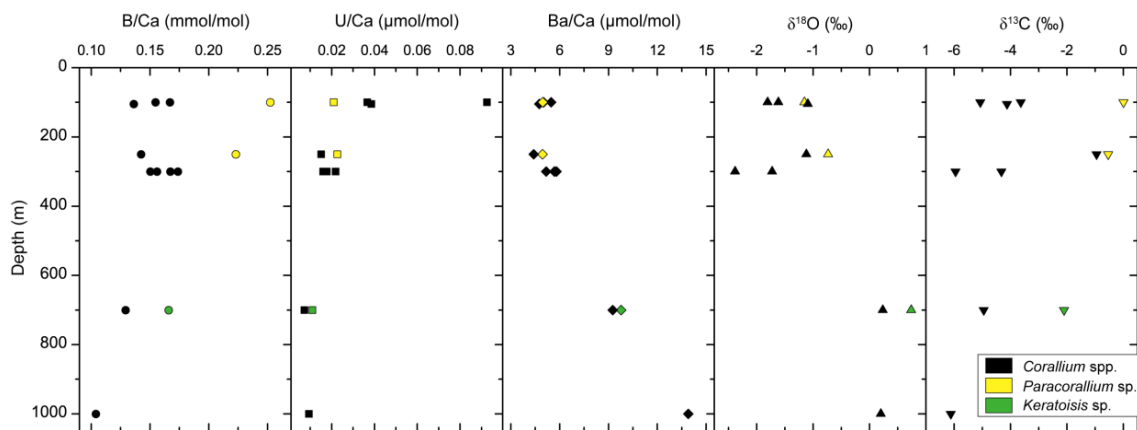
9 ➔ The samples were cleaned with ultrapure H₂O₂ and distilled water in an ultrasonic bath to
 10 remove organic compounds. After the chemical treatment, the coral skeletons were cut
 11 along the growth axis and sliced into slabs with a diamond saw. Most of the skeleton was
 12 red or pink, with the core showing some white. The whitish core part was traceable along
 13 the growth direction. We separated the core from the outer part of the skeleton using the
 14 diamond saw, and then crushed it into sand-sized particles in an agate mortar. The coral
 15 skeletons were ground to powder in an agate mortar before ICP-MS analysis.

16

17 Furthermore, data of the same species should be plotted with the same symbol in Figure 3, so
 18 that species-specific patterns can be identified. It should be discussed how the intra-skeletal
 19 variations observed on one specimen relate to octocorals in general. Is this one observation
 20 significant for all corals or could it be specific to this one species, or even just this specimen?

21 ➔ We changed the symbol in Fig. 3 as suggested. The skeletal macro- and micro-structures
 22 can greatly influence element partitioning during skeletal growth. We investigated the
 23 distributions and chemical forms of minor and major elements in the skeleton of precious
 24 corals (*Paracorallium japonicum*, *Corallium elatius*, *C. rubrum*) using synchrotron
 25 radiation micro-XRF (Tamenori et al., 2014, *J. Struct. Biol.*; Nguyen et al., 2014,
 26 *Geochem. Cosmochim. Acta*; and unpublished data). For example, as in the case of major
 27 elements, the core part of the precious coral skeletons are generally enriched in Mg and
 28 depleted in S (unpublished data). Similar phenomenon is observed in the aragonitic
 29 scleractinian cold-water coral *Desmophyllum* (Yoshimura et al., 2014, *Geo-Mar. Lett.*).
 30 Two major structural components in septa, centers of calcification (COC) and the

1 surrounding fibrous region, were morphologically and compositionally different. The
 2 COCs were characterized by higher concentrations of P and Mg and lower concentrations
 3 of O and Sr. In this study, elevated Ba/Ca ratios were observed at the central axis of the
 4 skeleton, and similar Ba enrichment has been reported previously in particular skeletal
 5 microstructures (please see 4.1.2.). Hasegawa et al. (2012) *J. Exp. Mar. Biol. Ecol.*
 6 reported that barium is homogeneously across the cross-sections of the skeleton of
 7 Japanese white coral (*Corallium konojoi*). Distinct distributional patterns are apparent for
 8 each element and for each genus. The variation in intra-skeletal Ba, U, and B distribution
 9 have yet to be investigated fully, but practically speaking, the inner part of the skeletons
 10 fibrous is less suitable for paleoceanographic reconstruction. This is ongoing topic in our
 11 lab.
 12



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 14
 15
 16 Finally, the authors should read and cite Uchikawa et al. (2015), who performed inorganic
 17 precipitation experiments for B/Ca. The authors cite Sanyal et al. (2000) but that study did not
 18 measure B/Ca ratios but estimated them from B concentration experiments by isotope dilution.
 19 The Uchikawa data are more accurate and provide much deeper insight into B uptake into
 20 inorganic calcite.

21 ➔ We changed Discussion in consideration of the latest paper by Uchikawa et al. (2015)
 22 regarding B incorporation into synthetic calcite.

23
 24 Figure 6 is not discussed or introduced in the text and should be removed.

25 ➔ Fig. 6 is introduced in the text (p. 426, Line 13). The relationship between water depth
 26 and previously reported skeletal growth rates of calcitic Octocorallia 10 coral taxa (Gri_n
 27 and Dru_el, 1989; Dru_el et al., 1990; Garrabou and Harmelin, 2002; Marschal et al.,
 28 2004; Andrews et al., 2005; Bramanti et al., 2005; Roark et al., 2006; Bruckner and
 29 Roberts, 2009; Gallmetzer et al., 2010; Nguyen et al., 2013; Vielzeuf et al., 2013) (Fig. 6)
 30 indicates a growth rate decrease per meter of depth. In corals living at intermediate and
 31 deep depths, differences in the availability of nutrients at habitat water depths may affect

1 coral calcification rates.

2
3 Please not also that Yu and Elderfield (2007) studied benthic foraminifers, which follow
4 different B incorporation patterns than planktic foraminifers and respond to Delta Carbonate
5 Ion. The text should be corrected accordingly. Also, Allen and Hönisch (2012) argue against a
6 temperature effect in planktic foraminifers, this study is cited in a somewhat misleading way.
7 However, the observations made in planktic foraminifers are not necessarily true for corals,
8 where B/Ca has been shown to be sensitive to temperature (e.g. Fallon et al. 2003).
9 Discussion of environmental controls on B/Ca in corals needs to be improved.

10 → As pointed out by Reviewer #1, calcification physiology of foraminifera is very different
11 from that of corals. As in the case of aragonitic corals, there is a growing number of
12 boron paper (both B/Ca and $\delta^{11}\text{B}$). On contrary, there is still a few paper dealing with
13 B/Ca partitioning in calcitic coral skeletons. Generally speaking, the extent of trace
14 element uptake by CaCO_3 is controlled primarily by the crystal lattice structure, so we
15 considered foraminifera results in order to discuss possible controlling factors of B/Ca
16 ratios in calcitic corals. We corrected the text according to Reviewer's comments.

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18
19 **Reviewer#2**

20
21 Studies with octocorals are in their infancy and the results from this study will be an
22 important contribution. However, the results as summarized in the abstract are unclear. Ba/Ca
23 reflects seawater Ba/Ca, pH or carbonate ion, and is a nutrient proxy? I think they mean B/Ca
24 is a pH proxy and Ba/Ca is a nutrient proxy, thus a typo in abstract. There is no mention of
25 boron results in the abstract yet it warrants mention in the title? U is mentioned in the last
26 sentence only in relation to Ba/Ca.

27 → We changed Abstract as suggested. Please see revised manuscript.

28
29 However, upon further review of the paper, I found a duplication of results between two
30 papers in review with the same journal. The inclusion of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ data were found for
31 this paper (Table 1), this data is presented in another paper currently in discussion in the same
32 journal (Mechanism of O and C isotope fractionation in magnesian calcite skeletons,
33 Biogeosciences Discuss., 12, 389–412, doi:10.5194/bgd-12- 389-2015, 2015). Table 1 is same
34 in both papers and Table 2 is largely duplicated.

35 Figure 2 presents the same data for $\delta^{13}\text{C}_{\text{dic}}$ as the Figure 1 in the other paper. The other
36 paper is not cited in any of the relevant captions except Figure 3 nor in the methods and the
37 first mention of the other paper is in the results section 3.2. Additionally, the other paper has a
38 B/Ca vs. $\delta^{18}\text{O}$ figure that seems like it was in this paper at one point. The magnesium data in
39 Table 1 is presented first in another paper by the authors (Yoshimura, T., Tanimizu, M., Inoue,

1 M., Suzuki, A., Iwasaki, N., and Kawahata, H.: Mg isotope fractionation in biogenic
2 carbonates of deep-sea coral, benthic foraminifera, and Hermatypic coral, Anal. Bioanal.
3 Chem., 401, 2755–2769, 2011) but is not reference in the table caption but it is mentioned in
4 the methods section. The authors probably did not mean to do anything egregious but they
5 should clearly state there is a companion paper reporting on the same data at the start of this
6 paper. I suggest either combining the papers, since $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ are central to their
7 interpretations presented in this paper, or develop two papers as a part one and part two that it
8 clearly show the two papers are related like “ ^{13}C and ^{18}O isotopic disequilibrium in
9 biological carbonates: I. Patterns and II. In vitro simulation of kinetic isotope effects
10 (McConnaughey, 1989a, b). The second option will clearly tie the two papers together in the
11 same journal.

12 → We combined all data in this manuscript (trace element paper) according to Reviewer #1
13 and #2 suggestions. We also added reference of Mg/Ca data (Yoshimura et al., 2011) in
14 the table caption.

15

16 Individual scientific questions/issues ("specific comments"): One specimen examined is a
17 bamboo coral, *Keratoisis* sp. where as the others are precious corals of *Corallium* sp. These
18 corals belong to the same subclass, Octocorallia but differ in families and morphologies. I
19 would suggestion caution and/or additional support to include the bamboo coral in this study
20 or include in the discussion the possibility of a species effect. Early work with isotopes in
21 ahermatypic corals found differences between coral families and order (Weber, 1973a) and
22 differences in trace elements in hermatypic corals has been found at the genus level between
23 corals in close proximity and same reef environmental conditions (DeLong et al., 2011). Table
24 1 shows there are differences between oxygen and carbon isotopes and trace element ratios
25 between *C. konojoi* and *P. japonicum* at the same site and water depth. It is unclear if there is
26 a species effect (Weber, 1973b) among deep sea corals at the same location and environmental
27 conditions but the authors should consider this.

28 → As Reviewer #2 pointed out, the variations in the isotope ratios were greater at some
29 depths than they were between the surface and the deepest depths. The variation in local
30 habitat characteristics and individual coral physiology (species effect) can account for the
31 large variation in growth rates, trace element partitioning and $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ at certain
32 depths. We added sentences about species effect in Discussion 4.2.2. We also changed the
33 colors of symbol of Fig. 3 in order to distinguish three different genera (*Corallium*,
34 *Paracorallium*, *Keratoisis*).

35

36 Technical corrections: There are many technical issues to list but I withhold a detailed list
37 until the paper structure of the two papers can be resolved. $\delta^{18}\text{O}$ is sometimes referred to δ^{18}
38 in the text and abstract, this may be an issue with special character but other occurrences are
39 correct.

40 → We corrected typos in the text. Sorry for overlooking these in the proof.

41

1 Table 2 Should p-value for B/Ca and U/Ca be the same in both occurrences? One is 0.000 and
2 the other is 0.6092.

3 → Sorry for the erratum. This table and Figures of the companion paper are shown as
4 supplement material.

5

6 References Cited

7 DeLong, K.L., Flannery, J.A., Maupin, C.R., Poore, R.Z., Quinn, T.M., 2011. A coral Sr/Ca
8 calibration and replication study of two massive corals from the Gulf of Mexico.
9 *Palaeogeography Palaeoclimatology Palaeoecology* 307, 117-128.

10 McConnaughey, T., 1989a. ^{13}C and ^{18}O isotopic disequilibrium in biological carbonates: II.
11 In vitro simulation of kinetic isotope effects. *Geochimica et Cosmochimica Acta* 53, 163-171.

12 McConnaughey, T., 1989b. ^{13}C and ^{18}O isotopic disequilibrium in biological carbonates: I.
13 Patterns. *Geochimica et Cosmochimica Acta* 53, 151-162.

14 Weber, J.N., 1973a. Deep-sea ahermatypic scleractinian corals - isotopic composition of
15 skeleton. *Deep-Sea Research* 20, 901-909.

16 Weber, J.N., 1973b. Incorporation of strontium into reef coral skeletal carbonate. *Geochimica*
17 *et Cosmochimica Acta* 37, 2173-2190.

18 → Thank you for a list of suggested readings. We changed the text according to these
19 references.

20

1 Ba, B, and U element partitioning in magnesian calcite 2 skeletons of Octocorallia corals

3

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14

15 Abstract

16 Octocorallia corals are geologically important producers of biominerals, and they provide
17 long-term records (up to hundreds of years) of environmental conditions in the deep ocean.
18 Barium, boron and uranium element partitioning and oxygen and carbon isotope fractionation
19 of high-Mg calcite skeletons of Octocorallia corals were investigated. Here we clarify the
20 suitability of Ba/Ca, B/Ca, and U/Ca ratios in the skeletons of calcitic corals as potential
21 archives of environmental and physicochemical parameters of water masses, such as nutrient
22 concentrations and pH. The dissolved Ba concentration in seawater and the coral Ba/Ca ratio
23 showed a clear positive correlation. The empirically derived barium partition coefficient is
24 comparable to previous data for not only calcitic corals but also intermediate- to deep-water-
25 dwelling scleractinian corals whose skeletons are composed of aragonite. Our data suggest
26 that Ba/Ca ratios in Octocorallia corals support the use of this proxy for nutrients in
27 intermediate and deep waters. The B/Ca and U/Ca ratios, a possible proxy for pH or carbonate
28 ion concentration in seawater, tended to be negatively related to water depth, and substantial
29 interspecimen differences were observed in both ratios at each habitat depth. B/Ca showed the

1 largest correlation with carbon isotope ratio among the examined parameters. This result
2 implies that the pH of the extracytoplasmic calcifying fluid (ECF) simultaneously influences
3 O and C isotope ratios and B/Ca ~~by influencing the relative contributions of dissolved carbon~~
4 ~~sources in the ECF. Positive correlations of B/Ca with $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ suggest that $\delta^{18}\text{O}$ and~~
5 ~~$\delta^{13}\text{C}$ are enriched in light isotopes when conditions are less alkaline, suggesting a potential~~
6 ~~role of biological alkalinity pumping becomes more favorable with decreasing calcifying fluid~~
7 ~~pH.~~ Substantial inter- and intra-specimen variations in U/Ca suggest that physicochemical
8 factors do not exert a dominant systematic control on U incorporation. ~~Seawater pH and~~
9 ~~temperature both decrease with water depth, and this precludes unequivocal association of~~
10 ~~decreasing B/Ca and U/Ca ratios with either one of these parameters. However, the empirical~~
11 ~~calibration of B/Ca and U/Ca ratios in calcitic corals would introduce complexity beyond a~~
12 ~~simple pH dependence.~~

13

14 **1 Introduction**

15 The chemical compositions of the hard parts of calcifying organisms, such as coral skeletons
16 and foraminifer, brachiopod, and mollusk shells, are crucial as tracers of past environmental
17 conditions. Calcium carbonate (CaCO_3) is one of the most abundant biominerals, and the
18 chemical composition, ultrastructure, and organic components of carbonate minerals
19 ultimately determine their physicochemical properties. Corals are a geologically important
20 producer of biominerals that provide long-term records of environmental conditions over a
21 wide range of water depths, from the surface to deep water. Non-symbiotic corals, which are
22 distributed at water depths ranging from several dozen to thousands of meters (Iwasaki, 2010),
23 can provide millennial-scale records of environmental conditions in intermediate and deep
24 waters (e.g., Smith et al., 1997; Adkins et al., 1998; Sherwood et al., 2005; Eltgroth et al.,
25 2006; Montagna et al., 2006; van de Flierdt et al., 2006). Octocorallia (Anthozoa) coral
26 skeletons are composed of high-Mg calcite, and the longevity of these corals means that they
27 can provide long-term records of environmental conditions.

28 The use of minor and trace metal compositions of biogenic CaCO_3 as proxies for
29 paleoenvironmental conditions has also been of great value. Despite their potential utility for
30 decadal- to centennial-scale records in intermediate and deep waters, however, only a few
31 studies, have investigated depth-sensitive trace-element partitioning of calcitic corals
32 (LaVigne et al., 2011; Sinclair et al., 2011; McCulloch et al., 2012; Hasegawa et al., 2012).

1 Intermediate- and deep-water chemistry are affected by decadal-scale climate changes via
2 changes in ocean circulation and ventilation and in biochemical and geochemical cycling. The
3 dissolved barium concentration in the ocean shows significant variations that depend on water
4 depth and locality, and it behaves similarly to nutrients such as dissolved silica (e.g., Bacon
5 and Edmond, 1972). Therefore, barium concentrations are higher in deep waters and in areas
6 of nutrient upwelling. Moreover, Ba/Ca ratios in the skeletons of calcitic corals can be reliably
7 used as a proxy for nutrients in the intermediate water masses in which such corals live
8 (Sinclair et al., 2011; LaVigne et al., 2011; Hasegawa et al., 2012).

9 In addition, pH-sensitive tracers such as boron isotopes and B/Ca (Foster et al., 2008; Allen
10 and Hönisch, 2012), and U/Ca (Reeder et al., 2000; Russell et al., 2004; Inoue et al., 2011)
11 have been used to study past ocean pH. These tracers are linked to the ocean's inorganic
12 carbon cycle, which plays a central role in climate change. Boron-based pH proxies rely on
13 the fact that the relative abundances and B isotopic compositions of the two aqueous species
14 of boron in seawater, $B(OH)_3$ and $B(OH)_4^{2-}$, are pH dependent (e.g., Kakihana et al., 1977).
15 Data on boron partitioning in inorganic calcite show that changes in the relative proportions
16 of these dissolved species are clearly recorded in the B/Ca ratio (Sanyal et al., 2000;
17 Uchikawa et al., 2015). Recently, robust pH tracers for use in paleoceanography have been
18 explored by a biological species-specific approach (e.g., Allen and Hönisch, 2012, and
19 references therein), but only one study has examined boron isotopes in calcite skeletons of
20 intermediate- and deep-water-dwelling corals (McCulloch et al. 2012), and that study did not
21 systematically evaluate the B/Ca ratio of calcitic corals.

22 In seawater, uranium exists in several different carbonate complexes, uranyl tricarbonate
23 ($UO_2(CO_3)_3^{4-}$), bicarbonate ($UO_2(CO_3)_2^{2-}$) and monocarbonate ($UO_2CO_3^0$) complexes
24 (Djogic et al., 1986). As pH decreases, a preferential uptake of $UO_2(CO_3)_2^{2-}$ and/or $UO_2CO_3^0$
25 can explain the inverse relationship between U/Ca in $CaCO_3$ and seawater pH. Early studies
26 show convincing annual U/Ca cycles in the reef corals (Min et al., 1995; Shen and Dunbar,
27 1995), and the primary objective of this paleotracer is to evaluate them as seawater pH or
28 $[CO_3^{2-}]$ proxies (e.g., Anagnostou et al., 2011; Inoue et al., 2011; Raitzsch et al., 2011;
29 Raddatz et al., 2014). Although the large discrepancy in pH dependence found between coral
30 and foraminifera is due to the different $CaCO_3$ polymorphs (Reeder et al., 2000) and species-
31 specific calcification mechanisms, U/Ca ratios decrease as seawater $[CO_3^{2-}]$ increases (Russel
32 et al., 2004; Anagnostou et al., 2011; Inoue et al., 2011; Raitzsch et al., 2011; Raddatz et al.,

1 2014). In planktonic foraminifera calcite, the core-top empirical calibration shows that U/Ca
2 is significantly affected by calcification temperature and preferential dissolution effect (Yu et
3 al., 2008). The empirical calibration and intra-shell variation of U/Ca in calcitic corals also
4 offers the possibility of examining the use of this proxy as an indicator of past ocean
5 conditions (Sinclair et al., 2011).

6 In this study, we investigated B, Ba, and U element partitioning in the calcite skeletons of
7 Octocorallia corals collected from sites at a range of water depths. Our aim was to investigate
8 whether past environmental changes can be inferred from Ba/Ca, B/Ca, and U/Ca values
9 recorded in deep-sea coral skeletons.

10

11 **2 Materials and Methods**

12 We selected 13 specimens of deep-sea coral (*Paracorallium japonicum*, *Corallium elatius*, *C.*
13 *konojoi*, *Corallium* sp., and *Keratoisis* sp.) from several sampling localities at water depths of
14 30–1500 m in the western, northwestern, and northern Pacific (Table 1). Mean annual water
15 temperatures at the sampling localities range from 2.5 to 19.5 °C (water temperatures are from
16 Levitus94; <http://ingrid.ldeo.columbia.edu/SOURCES/.LEVITUS94/>) (Levitus and Boyer,
17 1994). The coral skeletons were cut along the growth axis and sliced into slabs with a
18 diamond saw. Most of the precious coral skeleton was red or pink, with the core showing
19 some white. The whitish core part was traceable along the growth direction. The samples
20 were cleaned with ultrapure H₂O₂ and distilled water in an ultrasonic bath to remove organic
21 compounds. After the chemical treatment, we separated the core from the outer part of the
22 skeleton using the diamond saw, and then crushed it into sand-sized particles in an agate
23 mortar. The coral skeletons were ground to powder in an agate mortar before analysis. The
24 Mg/Ca ratios and the Mg isotope ratios of these specimens have already been reported by
25 Yoshimura et al. (2011). In addition, a semi-fossilized coral skeleton (*Corallium elatius*)
26 collected at 200-300 m depth at 25°N, 126°E was cut perpendicular to the growth axis and a
27 dental drill was used to sample the skeleton along the maximum growth line from the central
28 axis to the outer margin at 1-mm intervals in order to examine intra-specimen changes in trace
29 metal profiles (Fig. 1).

30 Oxygen and carbon isotope ratios were measured with an isotope ratio mass spectrometer
31 (Micromass ISOPRIME) at the National Institute for Advanced Industrial Science and

1 Technology. Isotopic data are reported as per mil (‰) deviations relative to Vienna Peedee
2 Belemnite (VPDB). The NBS-19 carbonate standard was used for calibration of the VPDB
3 scale. Analytical precision was $\pm 0.1\%$ for both $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$.

4 The ratios of minor and trace elements to Ca were measured with a quadrupole inductively
5 coupled plasma mass spectrometer (iCAP Qc; Thermo Scientific, Bremen, Germany) at the
6 Japan Agency for Marine-Earth Science and Technology and calibrated using the JcP-1
7 (prepared from a modern reef-building coral) and JcT-1 (Holocene fossil giant clam shell)
8 carbonate reference materials from the Geological Survey of Japan (Okai et al., 2004) and
9 mono-element standard reagents from Kanto Chemical. To reduce Ca matrix effects and
10 control for instrumental drift, internal standards (Be, Sc, Y, and In) were added to the solution.
11 Additionally, standard solutions were measured after every fifth sample for data correction.
12 All element concentrations are given as molar ratios relative to Ca.

13 For proxy evaluations (see Table S1), we used $\delta^{18}\text{O}$, $\delta^{13}\text{C}$, and $[\text{CO}_3^{2-}]$ data from the inorganic
14 carbon chemistry database, Global Ocean Data Analysis Project (GLODAP,
15 <http://cdiac.ornl.gov/oceans/glodap/>; Key et al., 2004). The $\delta^{18}\text{O}$ values used were 0‰ for
16 most samples, and +0.2‰ for DPC-V1 and DPC-V4. We selected $\delta^{13}\text{C}$, alkalinity, and
17 dissolved inorganic carbon (DIC) data that had been collected at points in the Pacific Ocean
18 close to the deep-sea coral sampling localities, and we calculated other inorganic carbon data
19 with the CO2SYS program (Lewis and Wallace, 1998). Dissolved barium concentrations
20 ($[\text{Ba}]_{\text{sw}}$) determined at habitat depths near the coral sampling locations were used for
21 calibration of the barium partitioning coefficient (Oba and Kato, 2012). To calculate
22 fractionation and partitioning coefficients, we used values based on $\delta^{13}\text{C}$ -depth and $[\text{Ba}]_{\text{sw}}$ -
23 depth relationships determined near the coral sampling sites (Fig. 2).

24

25 **3 Results**

26 **3.1 Trace element concentrations**

27 The profiles of inorganic carbon dioxide and of oceanic tracers with nutrient-like behaviors in
28 ambient seawater changed markedly with depth. The B/Ca, Ba/Ca, and U/Ca ratios of the
29 suite of Octocorallia corals were plotted in relation to the habitat depths of the corals (Fig. 3).
30 B/Ca and U/Ca values ranged from 0.104 to 0.252 mmol/mol, and from 0.007 to 0.093
31 $\mu\text{mol/mol}$, respectively (Fig. 3), and substantial interspecimen differences were observed in

1 both ratios at each habitat depth. Nevertheless, both elements tended to be negatively related
2 to water depth. Such inverse relationships with depth might reflect a positive relationship
3 between these ratios and ambient water temperature or inorganic carbon chemistry, and B/Ca
4 and U/Ca showed moderate correlations with some habitat environmental parameters (Table
5 S1).

6 Unlike B/Ca and U/Ca, Ba/Ca exhibited a clear increasing trend with depth, and
7 interspecimen differences were small (Fig. 3). To evaluate Ba/Ca partitioning in the skeletons,
8 we used dissolved Ba concentrations in seawater measured at Northwest Pacific sites nearest
9 to the coral sampling locations (Oba and Kato, 2012). The dissolved Ba concentration
10 increased from the surface to 1000 m depth by a factor of ~3 (Fig. 2, black squares), and
11 Ba/Ca in the coral skeletons showed a strong positive correlation with the ambient dissolved
12 Ba ($[Ba]_{SW}$) ($r = 0.95$; $p < 0.0001$; Fig. 4). The following equation was obtained by linear
13 regression:

$$14 \text{Ba/Ca}_{\text{coral}} = (0.127 \pm 0.012) * [Ba]_{SW} - (0.093 \pm 0.688) \quad (1)$$

15 The central axis of the skeleton of the semi-fossilized *C. elatius* (DPC-15) was characterized
16 by higher B/Ca and Ba/Ca, and lower U/Ca, compared with their values in more marginal
17 samples, and clear growth bands were apparent along the growth axis (Fig. 5). In this
18 specimen, B/Ca ranged from 0.102 to 0.166 mmol/mol and Ba/Ca ranged from 4.361 to 5.261
19 $\mu\text{mol/mol}$, and both B and Ba concentrations were markedly higher at the central axis (Fig. 5,
20 Table 2). In the outer part of the skeleton, however, B and Ba showed relatively small
21 variability, indicating that on the whole, their concentrations remained the same throughout
22 the life of the coral. In contrast, U/Ca showed a clear increasing trend from 0.034 to 0.326
23 $\mu\text{mol/mol}$ with growth of the coral, although it decreased to $\sim 0.23 \mu\text{mol/mol}$ near the margin
24 of the specimen (Fig. 5). Average Mg/Ca ratios were stable (average, around 126 mmol/mol)
25 along the sampling transect, but they showed an overall seasonal variation of 5.9% relative to
26 the average.

27 **3.2 Oxygen and carbon isotope ratios**

28 ~~The oxygen and carbon isotope data of the specimens are previously published in Yoshimura~~
29 ~~et al. (2014).~~ In the coral skeletons, $\delta^{18}\text{O}$ varied from -2.38‰ to -0.74‰ , and $\delta^{13}\text{C}$ varied
30 from -6.12‰ to 0.00‰ (Table 1). We observed a large interspecimen variation in the
31 relationship between these isotope ratios and water depths (Fig. 3). The Mg content of calcite

1 is known to substantially increase the isotope fractionation factor α at a given temperature
2 (Tarutani et al., 1969; Jimenez-Lopez et al., 2004; Mavromatis et al., 2012). Therefore, to
3 estimate the influence of [vital effect and Mg concentrations](#) on isotope fractionation in the
4 corals, we first calculated the difference values $\Delta^{18}\text{O}$ ($\delta^{18}\text{O}_{\text{coral}} - \delta^{18}\text{O}_{\text{calc}}$), and $\Delta^{13}\text{C}$ ($\delta^{13}\text{C}_{\text{coral}}$
5 $- \delta^{13}\text{C}_{\text{calc}}$), where $\delta^{18}\text{O}_{\text{coral}}$ and $\delta^{13}\text{C}_{\text{coral}}$ are the observed isotopic compositions of the corals,
6 and $\delta^{18}\text{O}_{\text{calc}}$ and $\delta^{13}\text{C}_{\text{calc}}$ are those estimated by examining the effect of both temperature and
7 Mg content on calcite–fluid isotope fractionation equilibria in synthetic magnesian calcite
8 (Jimenez-Lopez et al., 2006; Mavromatis et al., 2012).

9 In the coral samples, the Mg/Ca ratio ranged from 73.75 to 137.40 mmol/mol and showed a
10 clear positive correlation with water temperature (Yoshimura et al., 2011). Previous studies
11 have examined the effect of Mg on oxygen isotope fractionation equilibria by theoretical
12 calculations (Schauble et al., 2006; Chacko and Deines, 2008), but these theoretical models
13 tend to underestimate the effect of Mg at lower temperatures and to overestimate its effect at
14 higher temperatures, relative to data obtained empirically by experimental precipitation of
15 magnesian calcite (Mavromatis et al., 2012). [Because Tarutani et al. \(1969\), Jimenez-Lopez et](#)
16 [al. \(2004\), and Mavromatis et al. \(2012\) estimated different \$\alpha\$ values, we compared the](#)
17 [relationships between magnesium content and \$\delta^{18}\text{O}\$ at various temperatures between](#)
18 [empirically determined fractionation factors \(Mavromatis et al., 2012\) and fractionation](#)
19 [factors calculated ab initio by Chacko and Deines \(2008\). The theoretical \$\alpha\$ values yielded](#)
20 [positive \$\Delta^{18}\text{O}\$ values when the resulting calculated \$\delta^{18}\text{O}\$ values were subtracted from those of](#)
21 [the corals, indicating \$^{18}\text{O}\$ enrichment in the coral skeletons as high as \$\sim 2\%\$ \(Fig. 6\).](#)
22 [Theoretical \$\alpha\$ values determined by Schauble et al. \(2006\) yielded even more positive values.](#)
23 [In contrast, the empirically obtained \$\alpha\$ values \(Mavromatis et al., 2012\) yielded negative \$\Delta^{18}\text{O}\$](#)
24 [values for all samples \(Fig. 6\). The reason for this difference between empirical and](#)
25 [theoretical \$\alpha\$ values is still uncertain, and its examination is beyond the scope of this study,](#)
26 [but biogenic carbonates generally contain less \$^{18}\text{O}\$ and \$^{13}\text{C}\$ than inorganic calcite precipitated](#)
27 [slowly from solution \(e.g., Cohen and McConnaughey, 2003\). If we estimate the effect of the](#)
28 [Mg content by using the empirically determined oxygen and carbon isotope fractionation](#)
29 [factors reported by Mavromatis et al. \(2012\) and Jimenez-Lopez et al. \(2006\), the resulting](#)
30 [difference values for \$\delta^{18}\text{O}\$ and \$\delta^{13}\text{C}\$ range from \$-4.66\$ to \$-1.53\$ and from \$-7.34\$ to \$-1.75\$,](#)
31 [respectively \(Table 1, \[Yoshimura et al., 2014\]\(#\)\).](#) These results indicate that both the oxygen and

1 carbon isotope ratios of the calcitic corals in this study were depleted in heavier isotopes
2 compared with the ratios of inorganic magnesian calcite.

3

4 **4 Discussion**

5 **4.1 Ba/Ca as a proxy for past nutrient status**

6 **4.1.1 Calibration regressions**

7 Ba/Ca ratios in coral skeletons of various taxa have been used as a proxy for nutrient load in
8 the ocean (McCulloch et al., 2003; Montaggioni et al., 2006). Oceanic barium and silica are
9 similarly distributed in the water column and both show a nutrient-like behavior, having
10 higher concentrations in areas of high productivity. In this study, the change in skeletal Ba/Ca
11 with depth parallels that in the dissolved barium concentration in Pacific seawater (Fig. 2;
12 Bernat et al., 1972; Chan et al., 1976; Oba and Kato, 2012), and our results are in excellent
13 agreement with earlier results for gorgonian corals (LaVigne et al., 2011; Sinclair et al., 2011).
14 Regression equation (1) obtained in this study is very similar to that reported for gorgonian
15 corals (LaVigne et al., 2011), the skeletons of which are also composed of high-Mg calcite.
16 Both previously published data and our data show strong positive linear correlations between
17 the Ba/Ca ratio in corals of multiple taxa and the dissolved Ba concentration in seawater (Fig.
18 4), as follows:

$$19 \text{Ba/Ca}_{\text{coral}} = (0.092 \pm 0.013) * [\text{Ba}]_{\text{SW}} + (2.246 \pm 1.334) \quad (2)$$

20 where $r = 0.906$, $n = 46$, and $p < 0.001$. Moreover, this multi-taxa calibration equation
21 obtained using the data by this study and by LaVigne et al. (2011) agrees well with the
22 observed Ba partitioning in scleractinian cold-water coral skeletons (*Desmophyllum*;
23 Anagnostou et al., 2011):

$$24 \text{Ba/Ca}_{\text{coral}} = (0.104 \pm 0.024) * [\text{Ba}]_{\text{SW}} + (2.415 \pm 1.536) \quad (3)$$

25 Generally speaking, the distribution coefficients of minor elements in calcium carbonates are
26 strongly controlled by the lattice structures of calcite and aragonite, the predominant
27 polymorphs of biogenic CaCO_3 , where calcite has a rhombohedral and aragonite an
28 orthorhombic structure. Despite the differences in the carbonate mineralogy of calcitic and
29 aragonitic corals, however, Ba partitioning behavior is surprisingly similar between them.

1 This fact has already been pointed out by LaVigne et al. (2011), who concluded that the
2 skeletal Ba incorporation mechanism must be relatively simple, without any strong biological
3 or taxonomic influences or dependence on temperature, salinity, or carbonate ion
4 concentrations. Because neither mineral-specific nor species-specific partitioning is observed,
5 the use of Ba/Ca ratios in both calcitic and aragonitic intermediate- and deep-water corals as
6 an indicator of dissolved Ba is justifiable if the skeletal portion to be analyzed is carefully
7 selected, as discussed in the following section.

8 **4.1.2 Ba incorporation mechanisms**

9 Because the ultimate aim is to more accurately calculate changes in paleonutrient dynamics in
10 intermediate and deep waters, the intraskeletal distributions of Ba, B, U, and Mg were
11 measured along the growth transect of the semi-fossilized *C. elatius* specimen (Fig. 5).
12 Elevated Ba/Ca ratios were observed at the central axis of the skeleton, and similar Ba
13 enrichment has been reported previously in particular skeletal microstructures and along the
14 central axis in bamboo corals (Sinclair et al., 2011; LaVigne et al., 2011), despite differences
15 in sample types and habitat environments. Repeated observations of Ba enrichment along the
16 skeletal axis suggests a biological artifact along the central axis as a result of different modes
17 of skeletal growth or secondary mineral. In this regard, LaVigne et al. (2011) suggested that the
18 association between the skeletal central axis and higher Ba/Ca ratios might be attributable to
19 the presence of organic-rich calcite deposited during the juvenile stage of skeletal growth
20 (Noé and Dullo, 2006). The localized occurrence of elevated Ba spanning a few millimeters
21 along the central axis (Fig. 5) might affect the accuracy and precision of quantitative [Ba²⁺]
22 reconstruction and lead to the overestimation of past ocean Ba concentrations.

23 The use of Ba/Ca as a proxy is based on the assumption that mineralogical factors, rather than
24 the biological factors mentioned above, dominantly control Ba incorporation, but possible
25 mineralogical factors have not been well examined at the molecular scale (Finch et al., 2010,
26 and references therein). The ionic radius of Ba²⁺ (1.47 Å) is larger than that of Ca²⁺ (1.18 Å).
27 As a result, Ba is thought to preferentially coprecipitate with aragonite over calcite, because
28 the aragonite structure allows incorporation of larger ions into the crystal lattice. Inorganic
29 coprecipitation of Ba with CaCO₃ is well studied, and the concentration of Ba in aragonite is
30 approximately two orders of magnitude higher than its concentration in calcite (e.g., Kitano et
31 al., 1971; Tesoriero and Pankow, 1996; Dietzel et al., 2004). These results are inconsistent

1 with the finding of no apparent differences in Ba partitioning between calcitic and aragonitic
2 corals.

3 The Mg content of calcite can be low or high, and the amount of Mg incorporated into the
4 crystal lattice of calcite influences its physicochemical properties. For example, the Mg
5 content affects thermodynamic stability and step morphology of calcite as well as the rate of
6 crystal growth during CaCO₃ precipitation (e.g., Mucci and Morse, 1983; Davis et al., 2000;
7 Morse et al., 2007). The incorporation of Ba into low-Mg calcite foraminiferal shells is known
8 to be an order of magnitude smaller than that into high-Mg-calcite coral skeletons (Lea and
9 Spero, 1994; Hönisch et al., 2011), but data on the crystallographic control of Ba
10 incorporation in high-Mg calcite are still scarce. Tamenori et al. (2014) suggested that crystal
11 lattice distortion induced by the presence of minor elements influence minor- and trace-
12 element incorporation; for example, the substitution of tetrahedral sulfate for planar carbonate
13 ions causes distortion of the calcite unit cell along the c-axis and allows the substitution of
14 other elements for Ca ions (Kontrec et al., 2004). The spatial distributions of minor elements
15 such as magnesium and sulfate in the coral skeleton are closely related (Vielzeuf et al., 2013;
16 Tamenori et al., 2014; Nguyen et al., 2014), and the distribution of Ba may be governed partly
17 by the influence of other important minor elements. Analyses of the microscale distributions
18 of trace and minor elements and of in situ chemical speciation are needed to investigate the
19 robustness of key environmental parameters affecting the composition of the coral skeleton.

20 Many marine organisms do not directly record local environmental parameters in their
21 biominerals, because they produce their biominerals under strict biological controls (so-called
22 vital effects). Nevertheless, the excellent empirical agreement between dissolved Ba in
23 seawater and the Ba/Ca ratio in multiple taxa of calcitic corals suggests that skeletal the
24 Ba/Ca of deep-sea corals is a valuable proxy for the nutrient status in deep waters of the
25 paleo-ocean.

26

27 **4.2 Biological controls on boron and uranium partitioning**

28 **4.2.1 Do B/Ca and U/Ca reflect the pH of the ECF?**

29 B/Ca partitioning during inorganic calcite growth in the laboratory shows a significant
30 sensitivity to changes in pH and the carbonate ion concentration in the ambient fluid (Sanyal

1 et al., 2000). ~~Furthermore, observed increases in B/Ca of biogenic and inorganic carbonates~~
2 ~~with increasing pH is related to changes in the $[B(OH)_4^-]/[HCO_3^-]$ ratio (Yu and Elderfield,~~
3 ~~2007).~~ Because the basis of the B/Ca pH proxy of marine carbonates is the dependence of pH
4 on the relative proportions of dissolved boron species in seawater, the large variation in B/Ca
5 observed in coral skeletons should relate to the inorganic carbon chemistry during
6 calcification (Fig. 3). ~~Recently, empirical results of Uchikawa et al. (2015) obtained by~~
7 ~~experiments which systematically varied pH, total boron ($[B_T]$), dissolved inorganic carbon~~
8 ~~([DIC]), and Ca^{2+} concentrations have shown that B/Ca in calcite increases with both fluid pH~~
9 ~~and total boron concentration ($[B(OH)_3] + [B(OH)_4^-]$), and Uchikawa et al. (2015) proposed~~
10 ~~that the mode of B incorporation into synthetic calcite depends on the fluid $[B_T]/[DIC]$ ratio~~
11 ~~and the precipitation rate R .~~

12 In reef-building corals, variations of $\delta^{11}B$, which is regarded as the best pH indicator, are
13 controlled principally by biological factors via modification of the pH near calcification sites
14 (Rollion-Bard et al., 2003). As in intermediate-depth and deep-water corals, in aragonitic
15 corals the pH- $\delta^{11}B$ curve lies above the pH-dependent inorganic seawater borate equilibrium
16 curve. However, the calcitic coral *Corallium* sp. specimen measured by McCulloch et al. has
17 a significantly low $\delta^{11}B$, corresponding to a theoretical pH of ~ 0.3 , compared with aragonitic
18 corals, and also a low B concentration (McCulloch et al., 2012). This marked difference
19 between aragonitic and calcitic corals implies that the ability of this calcitic coral species to
20 regulate the pH of the calcifying fluid is much less (McCulloch et al., 2012). A large
21 biological control of $\delta^{11}B$ variation has also been reported for foraminiferal calcite (Allen and
22 Hönisch, 2012). Possible alternative controlling factors, other than ambient pH, are ambient
23 temperature, calcification rate, and in vivo microenvironments (Ni et al., 2007; Yu et al.,
24 2007; Tripathi et al., 2011; ~~Allen and Hönisch, 2012~~). Because the depth profile of dissolved B
25 species is linked to large changes in the carbonate system and is affected to some extent by
26 water temperature, it is difficult to separate pH effects from direct temperature effects in the
27 natural specimens used in the present study. However, the high B/Ca variability at a certain
28 habitat depths (Fig. 3) suggests that B/Ca profiles in calcitic corals may be primarily a result
29 of strong biological controls rather than temperature effects. At present, because B/Ca ratios
30 seem to be consequences of ECF conditions rather than of seawater chemistry, any
31 environmental effects were likely overridden by biological processes. Further validation, for
32 example, by demonstrating in situ $\delta^{11}B$ and $\delta^{18}O$ systematics as has been done in reef-
33 building corals (Rollion-Bard et al., 2003), is needed. Thus, better understanding of the

1 incorporation of boron into calcitic coral skeletons is a challenging problem awaiting future
2 research.

3 Like B/Ca, U/Ca is a candidate pH proxy that also showed significant interspecimen variation
4 in this study (Fig. 3). Although seawater temperature and pH may contribute to skeletal U/Ca
5 ratios (Reeder et al., 2000; Russell et al., 2004; Inoue et al., 2011), the intra- and intercolony
6 variation of U/Ca cannot be attributed to variations in environmental parameters. In the semi-
7 fossilized specimen DPC-15, U/Ca increased markedly, by a factor of ~10, from the central
8 axis to the margin (Fig. 5, Table 2). Large-amplitude variations, which were not reproduced
9 along different measurement transects in the U/Ca profile of a bamboo coral, possibly
10 reflected early diagenesis of the coral specimen (Sinclair et al., 2011). Moreover, uranium is
11 readily leachable from calcite because of its disordered coordination environment in the
12 calcite crystal (Reeder et al., 2000). Other possible mechanism accounting for the observed
13 variation of U/Ca may include controls of calcifying fluid chemistry during uranium
14 incorporation into ECF or high-Mg calcite as observed in the B incorporation. In considering
15 U/Ca ratios of biogenic CaCO_3 generally decrease as seawater $[\text{CO}_3^{2-}]$ increases (Russel et al.,
16 2004; Anagnostou et al., 2011; Inoue et al., 2011; Raitzsch et al., 2011; Raddatz et al., 2014),
17 a increasing trend along the growth axis of DPC-15 from 0.034 to 0.326 $\mu\text{mol/mol}$ suggests
18 that pH of the ECF decrease in the older coral age if pH influences U/Ca.

19 **4.2.2 $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ disequilibrium and mechanisms of their relationship** 20 **to boron and uranium partitioning**

21 Studies have reported significant isotopic disequilibrium in both aragonitic and calcitic coral
22 skeletons (e.g., Weber, 1973a; Heikoop et al., 2002; Noé et al., 2008). A significant
23 variability of oxygen and carbon isotope fractionation, and the fractionation factors calculated
24 for the coral specimens varied from the expected values calculated using the empirically
25 determined isotope fractionation factors (Jimenez-Lopez et al., 2006; Mavromatis et al.,
26 2012) ~~from environmental signals (Yoshimura et al., 2014)~~, after taking into account their
27 dependence on temperature, $\delta^{13}\text{C}_{\text{DIC}}$ and Mg contents. The coral skeletons were enriched in
28 light isotopes (^{16}O and ^{12}C) relative to the expected values (Fig. 6). The $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values
29 of scleractinian coral skeletons, which are composed of aragonite, are several permil lower
30 than those of inorganic aragonite precipitated slowly from solution (e.g., Cohen and
31 McConnaughey, 2003). Skeletal $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values are biased particularly by the inorganic
32 carbon dynamics, which are affected by the coral calcification physiology (Cohen and

1 McConnaughey, 2003; Adkins et al., 2003; Rollion-Bard et al., 2003; Suzuki et al., 2005;
2 Omata et al., 2008). The relationship between the stable isotope ratios of carbon and oxygen
3 is strongly linear in aragonitic corals (e.g., McConnaughey, 1989; Adkins et al., 2003).
4 ~~Simultaneous depletion of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ in calcitic coral skeletons was observed relative to~~
5 ~~the calculated isotopic compositions for synthetic high-Mg calcite (Table 1, Yoshimura et al.,~~
6 ~~2014), and i~~Intra-individual $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values also show a linear relationship in corals
7 with high-Mg calcite skeleton (Hill et al., 2011; Kimball et al., 2014). The empirical
8 calibration studies have shown that the intercept value of the regression equation for the coral
9 $\delta^{18}\text{O}$ - $\delta^{13}\text{C}$ relationship is a function of ambient water temperature (Smith et al., 2000), and
10 the "lines method" of calibrating paleothermometers are used for reconstructing past ocean
11 temperatures in calcite producers (Hill et al., 2011; Kimball et al., 2014).

12 ~~Because O and C isotope fractionation shows strong linear correlation in both aragonitic and~~
13 ~~calcitic corals that grow at intermediate and deep depths, the degree of biological control on~~
14 ~~isotope fractionation in aragonite and calcite must be similar. Adkins et al. (2003) proposed~~
15 ~~the existence of an interplay between two carbon pools, (1) dissolved carbon entering the~~
16 ~~calcification sites by diffusion through the calcicoblastic cell wall (CO_2 -cew) and (2) seawater~~
17 ~~DIC leak, during the mineralization process in the semi-isolated calcification space.~~ Because
18 coral internal processes probably control the isotopic composition of the coral skeleton
19 (Yoshimura et al., 2014), the key to understanding skeletal $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values is
20 information about the coral calcification physiology. In corals living at intermediate and deep
21 depths, differences in the availability of nutrients at habitat water depths may affect coral
22 calcification rates. The relationship between water depth and previously reported skeletal
23 growth rates of calcitic Octocorallia coral taxa (Griffin and Druffel, 1989; Druffel et al., 1990;
24 Garrabou and Harmelin, 2002; Marschal et al., 2004; Andrews et al., 2005; Bramanti et al.,
25 2005; Roark et al., 2006; Bruckner and Roberts, 2009; Gallmetzer et al., 2010; Nguyen et al.,
26 2013; Vielzeuf et al., 2013) (Fig. 67) indicates a growth rate decrease per meter of depth.
27 Despite the large habitat depth range represented by these corals, however, the variations in
28 the isotope ratios were greater at some depths than they were between the surface and the
29 deepest depths. The supposed relationship between water depth and higher pH or CaCO_3
30 saturation state of the extracytoplasmic calcifying fluid (ECF), calcification would be
31 enhanced and growth rates would be higher, but the variation in local habitat characteristics
32 and individual corals physiology can account for the large variation in growth rates, trace

1 element partitioning and $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ at certain depths. There would be a species effect
2 (Weber, 1973b) among deep sea corals at the same location and environmental conditions.

3 As previously ~~discussed~~ mentioned, corals regularly experience fluctuations in multiple
4 environmental and physiological parameters that affect variations in calcifying fluid pH.
5 Among the parameters studied, B/Ca showed the highest correlation with $\Delta^{13}\text{C}$ (Table S1). If
6 B/Ca is assumed to be a function of the pH of the ECF, then light isotopes would be enriched
7 in the calcifying fluid under less alkaline conditions, because B/Ca is positively correlated
8 with $\Delta^{13}\text{C}$ values (Table 2). ~~Assuming the existence of an interplay between two carbon pools,~~
9 ~~these results suggests that declines in calcifying fluid pH were possibly accompanied by the~~
10 ~~higher $[\text{CO}_2]$ contributions relative to isotopically heavy seawater DIC, suggesting a~~
11 ~~potential role of biological alkalinity pumping becomes more favorable with decreasing~~
12 ~~calcifying fluid pH (Yoshimura et al., 2014).~~ Corals exert strong physiological control on their
13 calcifying fluid pH by the ability to up-regulate pH at the site of calcification (McCulloch et
14 al., 2012; Anagnostou et al., 2012; Venn et al., 2013). These ~~findings~~ results imply that ECF
15 conditions influenced both B element partitioning and O and C isotopic compositions
16 simultaneously via variations in the dissolved carbon dynamics in the coral calcifying fluid,
17 e.g. an interplay between coral carbon sources (Adkins et al., 2003). However, the B/Ca, and
18 U/Ca ratios presented in this study are simultaneously affected by seawater carbonate
19 chemistry and water temperature, i.e. pH and temperature both decrease with water depth,
20 thus this precludes unequivocal association of decreasing B/Ca and U/Ca ratios with either
21 one of these parameters. Moreover, we found no significant correlation between B/Ca and
22 U/Ca, suggesting the element partitioning of either of the boron or uranium are not likely
23 driven mainly by seawater carbonate chemistry. Early studies reported substantial $\delta^{18}\text{O}$ and
24 $\delta^{13}\text{C}$ variations between ahermatypic coral families and order (Weber et al., 1973a), and
25 differences in Sr/Ca in hermatypic corals have been found at the genus level between corals in
26 close proximity (tens of meters) and thus the same environmental conditions (DeLong et al.,
27 2011). Such biogenic biases (called “vital effects”, Weber, 1973b) are also expected to
28 influence on the isotope fractionation and element partitioning. Although these proxies still
29 needs to be further investigated, the empirical calibration of B/Ca and U/Ca ratios in calcitic
30 corals would introduce complexity beyond a simple pH or $[\text{CO}_3^{2-}]$ dependence. ~~Our data on~~
31 ~~inter-colony variations suggest that differences in a biologically induced pH gradient in the~~
32 ~~calcifying region can explain a large variability of the boron partitioning behavior in high-~~
33 ~~Mg calcite coral skeletons.~~

1

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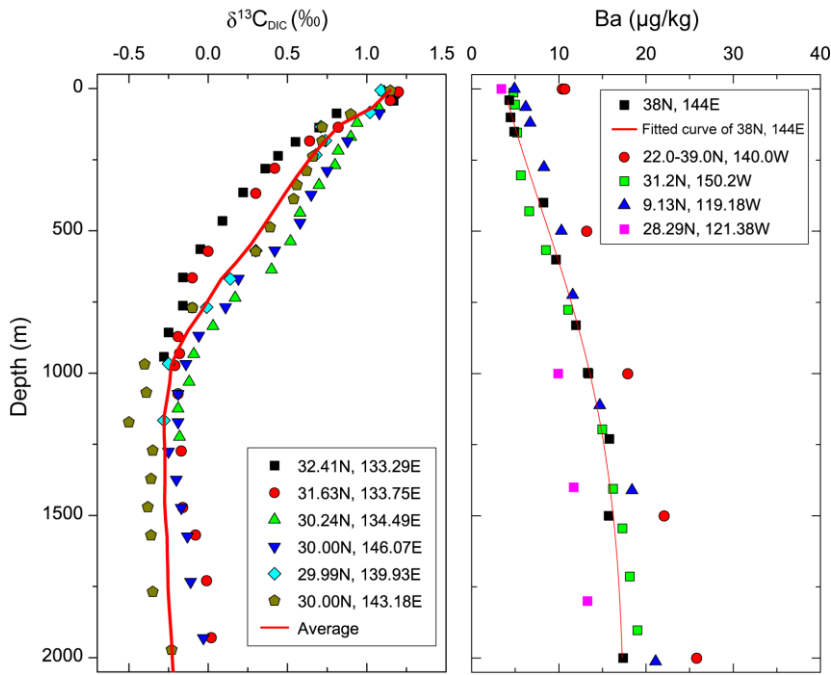
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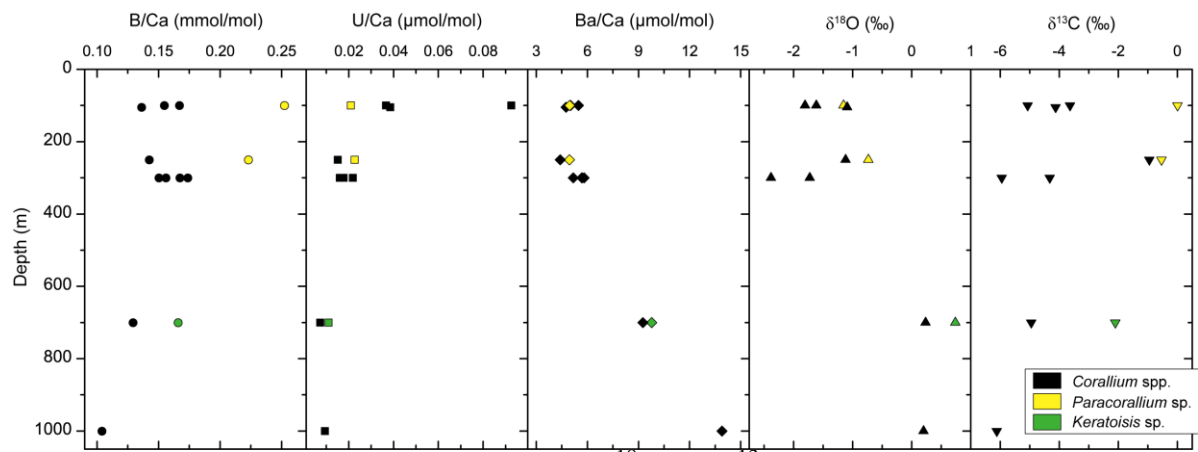
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2 **Figure 1.** Photograph of a specimen of the deep-sea coral DPC-11 *Corallium elatius* (left),
3 and a cross section of a semi-fossilized specimen DPC-15 *C. elatius* (right). The white arrow
4 denotes the transect along which samples were obtained by micromilling (17-mm in length).
5 The outermost part of the DPC-15 skeleton was not sampled because of notable bioerosion
6 caused by marine sponges.
7



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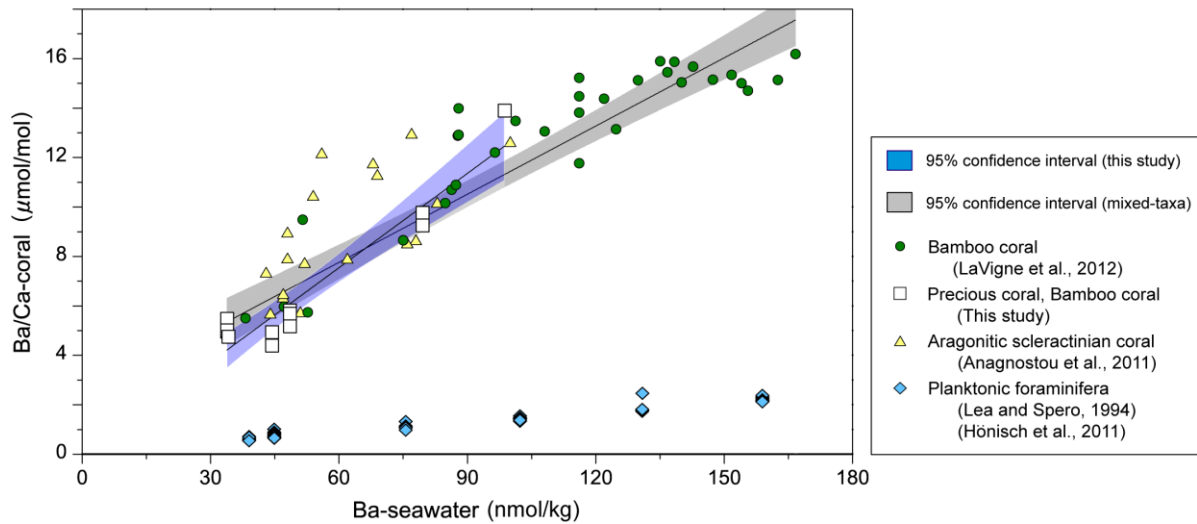
2 **Figure 2.** Comparison of $\delta^{13}\text{C}_{\text{DIC}}$ –depth and $[\text{Ba}^{2+}]$ –depth relationships among North Pacific
 3 sites. We selected published data collected at points close to the sampling localities of the
 4 corals analyzed in this study. The $\delta^{13}\text{C}$ carbon data were collected along sections P02, P09,
 5 and P10 in the Pacific Ocean distributed by the Global Ocean Data Analysis Project. The
 6 $\delta^{13}\text{C}_{\text{DIC}}$ values used to evaluate proxies were estimated from the curve obtained by averaging
 7 data from the Northwest Pacific sites. Values from a curve fitted to dissolved Ba
 8 concentrations from the western Pacific (38°N – 144°E , Oba and Kato, 2012) were used for the
 9 Ba/Ca proxy calibration. Published $[\text{Ba}^{2+}]$ data from GEOSECS cruises of eastern Pacific
 10 sampling stations (green squares, Chan et al., 1976; blue triangles, Bernat et al., 1972; purple
 11 squares, Bender et al, 1972; and red circles, Wolgemuth and Broecker, 1970) are also plotted
 12 for reference.

13

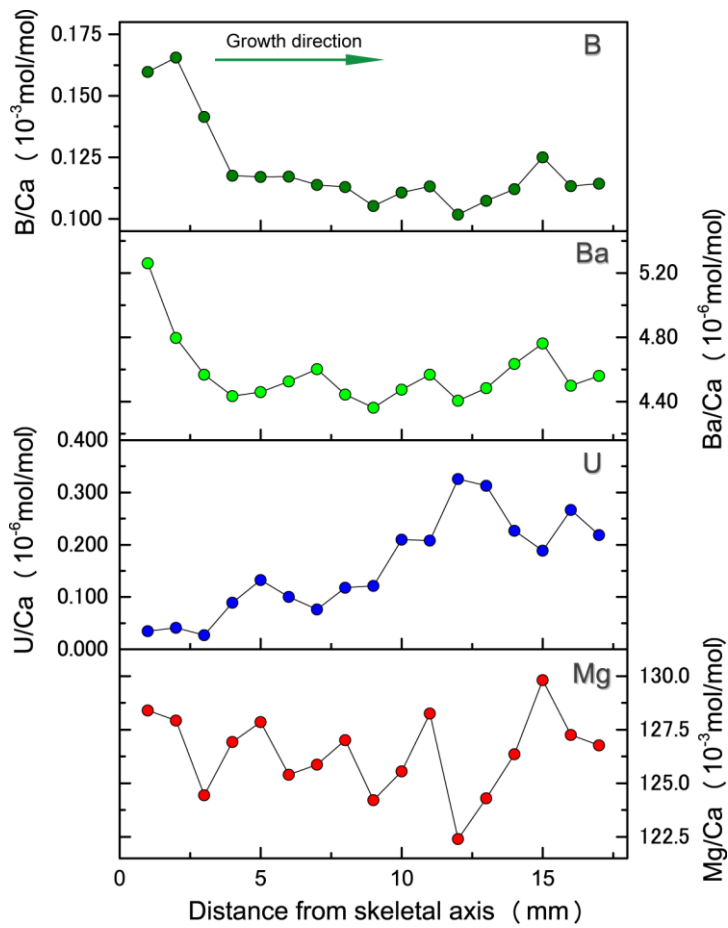


1
 2 **Figure 3.** Scatter plots of B/Ca, Ba/Ca, U/Ca, δ¹⁸O and δ¹³C of Octocorallia corals versus
 3 their habitat depth. [The oxygen and carbon isotope data of the specimens are previously](#)
 4 [published in Yoshimura et al. \(2014\).](#)

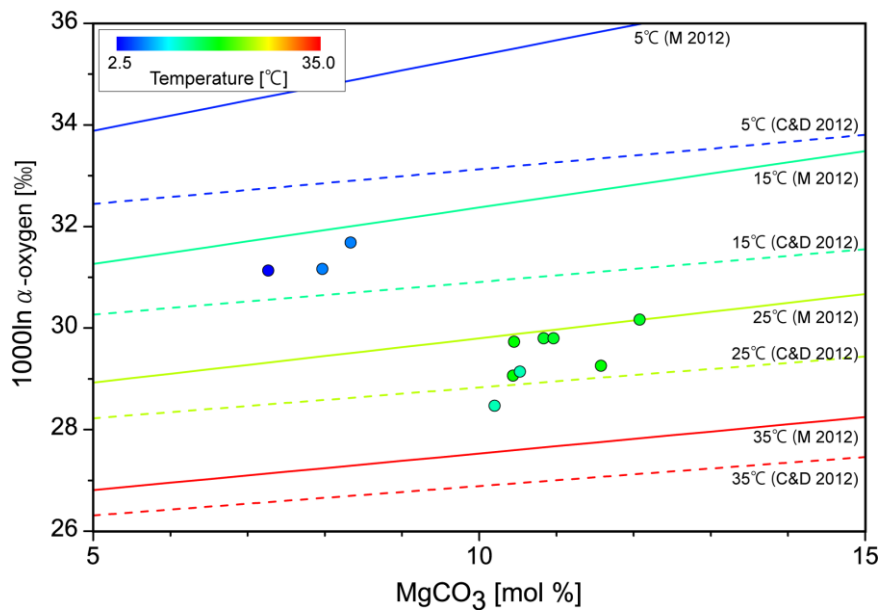
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2 **Figure 4.** Measured Ba/Ca ratios of high-Mg calcite skeletons of Octocorallia corals
3 (Ba/Ca_{coral}) plotted against dissolved Ba concentrations ([Ba]_{SW}) from Oba and Kato (2012).
4 For comparison, data from Lavigne et al. (2011) are also shown. The solid lines are regression
5 equation (1) (see text), $Ba/Ca_{coral} = (0.127 \pm 0.012) * [Ba]_{SW} - (0.093 \pm 0.688)$ ($r = 0.95$; $n =$
6 13 ; $p < 0.0001$), and regression equation (2) for multiple taxa calibration, $Ba/Ca_{coral} = (0.092$
7 $\pm 0.013) * [Ba]_{SW} + (2.246 \pm 1.334)$ ($r = 0.906$, $n = 46$, $p < 0.0001$). It is noteworthy that the
8 multi-taxa calibration equation for aragonitic cold-water scleractinian corals published by
9 Anagnostou et al. (2011), $Ba/Ca_{coral} = (0.104 \pm 0.024) * [Ba]_{SW} + (2.415 \pm 1.536)$, agrees well
10 with these equations for calcitic corals.



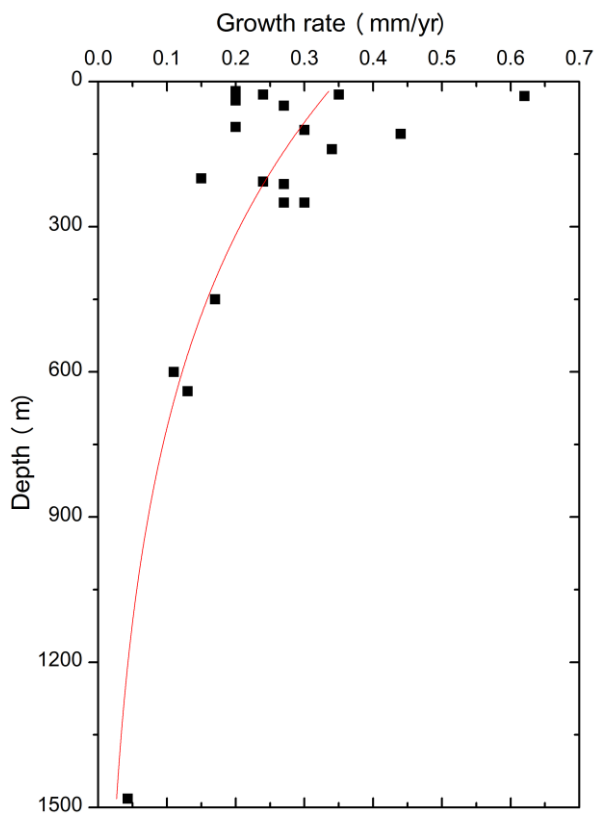
1
 2 **Figure 5.** Profiles of B/Ca, Ba/Ca, U/Ca, and Mg/Ca along the growth transect of a semi-
 3 fossilized specimen of *Corallium elatius*. A slab cut perpendicular to the growth axis was
 4 sampled with a micromill drill along the growth transect at 1-mm intervals from the central
 5 axis to the margin (white arrow in Fig. 1).
 6



1

2 **Figure 6.** Relationships between oxygen isotope fractionation factor (α) and Mg/Ca (shown
 3 as $[\text{MgCO}_3]$) at different temperatures, calculated by using α values determined empirically
 4 from inorganically precipitated high-Mg calcite (solid lines: Mavromatis et al., 2012) and
 5 theoretically (dashed lines: Chacko and Deines, 2008). The measured $\delta^{18}\text{O}$ and Mg/Ca ratios
 6 of the corals (blue and green circles) are also plotted. The colors of the lines and symbols
 7 indicate the formation temperature of the calcite.

8



1

2 **Figure 67.** Relationship between water depth and growth rate in Octocorallia Corallidae
 3 corals. The solid line is the linear regression obtained using published data for various taxa
 4 (Griffin and Druffel, 1989; Druffel et al., 1990; Garrabou and Harmelin, 2002; Marschal et al.,
 5 2004; Andrews et al., 2005; Bramanti et al., 2005; Roark et al., 2006; Bruckner and Roberts,
 6 2009; Gallmetzer et al., 2010; Nguyen et al., 2013; Vielzeuf et al., 2013). The curve is an
 7 exponential fit through data of a growth rate change (y) and meter of depth (x): $y = -0.022 +$
 8 $0.360 \cdot \exp(-0.0012 \cdot x)$.

9

Sample ID		Latitude /Longitude	Depth m	Temp. °C	$\delta^{18}\text{O}$	$\Delta^{18}\text{O}$	$\delta^{13}\text{C}$	$\Delta^{13}\text{C}$	B/Ca	Ba/Ca	U/Ca	Mg/Ca
					‰VPDB	‰	‰VPDB	‰	mmol/mol	μmol/mol	μmol/mol	mmol/mol
DPC-01	<i>C. konojoi</i>	32°N 134°E	100	19.5	-1.80	-2.20	-3.63	-5.38	0.17	5.5	0.09	116.56
DPC-12	<i>P. japonicum</i>	32°N 134°E	100	19.5	-1.15	-1.53	0.00	-1.75	0.25	5.0	0.02	116.71
DPC-K1	<i>P. japonicum</i>	25°N 126°E	200-300	18.0	-0.73	-1.83	-0.54	-2.00	0.22	4.9	0.02	137.40
DPC-0812	<i>C. elatus</i>	25°N 126°E	200-300	18.0	-1.12	-1.94	-0.95	-2.41	0.14	4.4	0.02	121.52
DPC-14	<i>Keratois</i> sp.	27°N 142°E	700	7.0	0.74	-2.58	-2.10	-2.97	0.17	9.8	0.01	90.93
DPC-K4	<i>Corallium</i> sp.	32°N 132°E	100	19.5	-1.61	-2.22	-5.07	-6.81	0.15	5.0	0.04	130.94
DPC-K3	<i>Corallium</i> sp.	27°N 142°E	700	6.5	0.24	-3.15	-4.95	-5.82	0.13	9.3	0.01	86.59
DPC-K5	<i>Corallium</i> sp.	28°N 177°E	1000	3.5	0.20	-3.89	-6.12	-6.70	0.10	13.9	0.01	78.40
DPC-V1	<i>Corallium</i> sp.	9°N 109°E	200-400	10-15	-2.38	-4.66	-5.95	-7.34	0.16	5.7	0.02	113.58
DPC-V4	<i>Corallium</i> sp.	9°N 109°E	200-400	10-15	-1.72	-4.06	-4.32	-5.71	0.17	5.2	0.02	117.69
DPC-951	<i>Corallium</i> sp.	35°N 139°E	105	17.5	-1.09	-2.10	-4.12	-5.85	0.14	4.7	0.04	123.13

1
2 **Table 1.** Sampling locations, water depth and temperature, stable oxygen and carbon isotope
3 ratios, and trace element concentrations of the coral samples. The $\Delta^{18}\text{O}$ and $\Delta^{13}\text{C}$ were
4 calculated by using isotope fractionation factors for inorganic magnesian calcite (Mavromatis
5 et al., 2012; Jimenez-Lopez, 2006). [The Mg/Ca data of the specimens are previously](#)
6 [published in Yoshimura et al. \(2011\).](#)

7

Sample ID	B/Ca	Ba/Ca	U/Ca	Mg/Ca
	mmol/mol	μmol/mol	μmol/mol	mmol/mol
DPC-K15-1	0.16	5.3	0.03	128.39
DPC-K15-2	0.17	4.8	0.04	127.92
DPC-K15-3	0.14	4.6	0.03	124.44
DPC-K15-4	0.12	4.4	0.09	126.92
DPC-K15-5	0.12	4.5	0.13	127.85
DPC-K15-6	0.12	4.5	0.10	125.40
DPC-K15-7	0.11	4.6	0.08	125.87
DPC-K15-8	0.11	4.4	0.12	127.01
DPC-K15-9	0.11	4.4	0.12	124.21
DPC-K15-10	0.11	4.5	0.21	125.56
DPC-K15-11	0.11	4.6	0.21	128.26
DPC-K15-12	0.10	4.4	0.33	122.40
DPC-K15-13	0.11	4.5	0.31	124.30
DPC-K15-14	0.11	4.6	0.23	126.35
DPC-K15-15	0.13	4.8	0.19	129.81
DPC-K15-16	0.11	4.5	0.27	127.25
DPC-K15-17	0.11	4.6	0.22	126.76

1

2 **Table 2.** Trace element (B, Ba, and U) concentrations in a semi-fossilized coral (specimen
3 DPC-15 *Corallium elatius*, Fig. 1). Sample #1 was obtained at the central axis and sample
4 #17 was at the outermost.

5

1 *Supplement of*

2 **Ba, B, and U element partitioning in magnesian calcite skeletons of Octocorallia corals**

3

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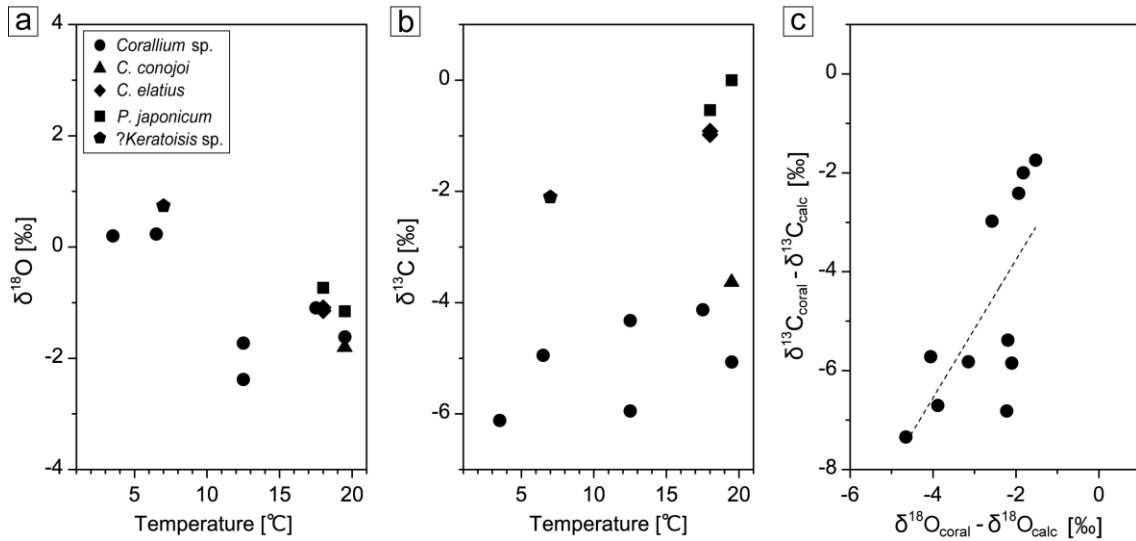
12

		Temp.	pH	$p\text{CO}_2$	HCO_3^-	CO_3^{2-}	$\text{HCO}_3^-/\text{CO}_3^{2-}$	B/Ca	U/Ca
$\delta^{18}\text{O}_{\text{coral}} - \delta^{18}\text{O}_{\text{calc}}$	<i>r</i>	0.652*	0.727*	-0.696*	-0.750*	0.733*	-0.620*	0.478	0.342
	<i>sig.</i>	0.03	0.011	0.017	0.008	0.01	0.042	0.137	0.303
$\delta^{13}\text{C}_{\text{coral}} - \delta^{13}\text{C}_{\text{calc}}$	<i>r</i>	0.318	0.332	-0.372	-0.325	0.304	-0.327	0.678*	-0.133
	<i>sig.</i>	0.34	0.318	0.261	0.329	0.364	0.327	0.022	0.696
B/Ca	<i>r</i>	0.552	0.542	-0.565	-0.537	0.525	-0.571	--	0.095
	<i>sig.</i>	0.079	0.085	0.07	0.089	0.097	0.067	--	0.782
U/Ca	<i>r</i>	0.576	0.614*	-0.545	-0.635*	0.645*	-0.537	0.095	--
	<i>sig.</i>	0.064	0.045	0.083	0.036	0.032	0.088	0.782	--

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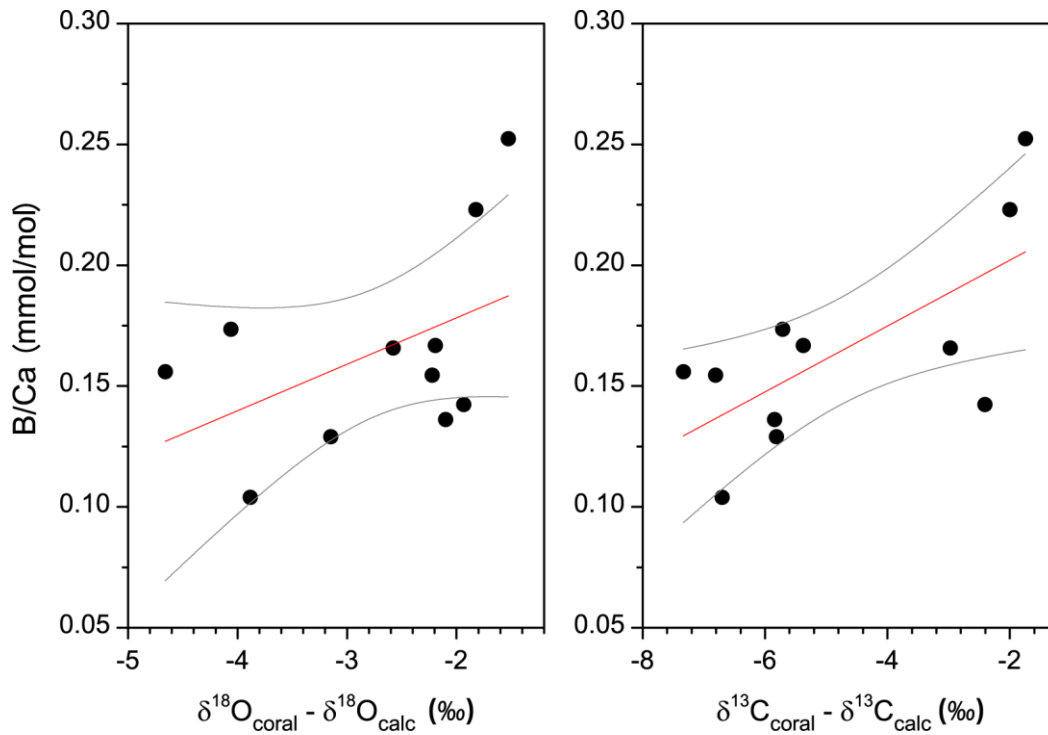
2 **Table S1.** Pearson correlation coefficients (*r*) and significance obtained by regressing $\Delta^{18}\text{O}$
3 ($\delta^{18}\text{O}_{\text{coral}} - \delta^{18}\text{O}_{\text{calc}}$), and $\Delta^{13}\text{C}$ ($\delta^{13}\text{C}_{\text{coral}} - \delta^{13}\text{C}_{\text{calc}}$), B/Ca, and U/Ca against various parameters
4 (*: 95% confidence level). The inorganic carbon data were calculated from alkalinity and total
5 dissolved inorganic carbon data made available by the Global Ocean Data Analysis Project.

1

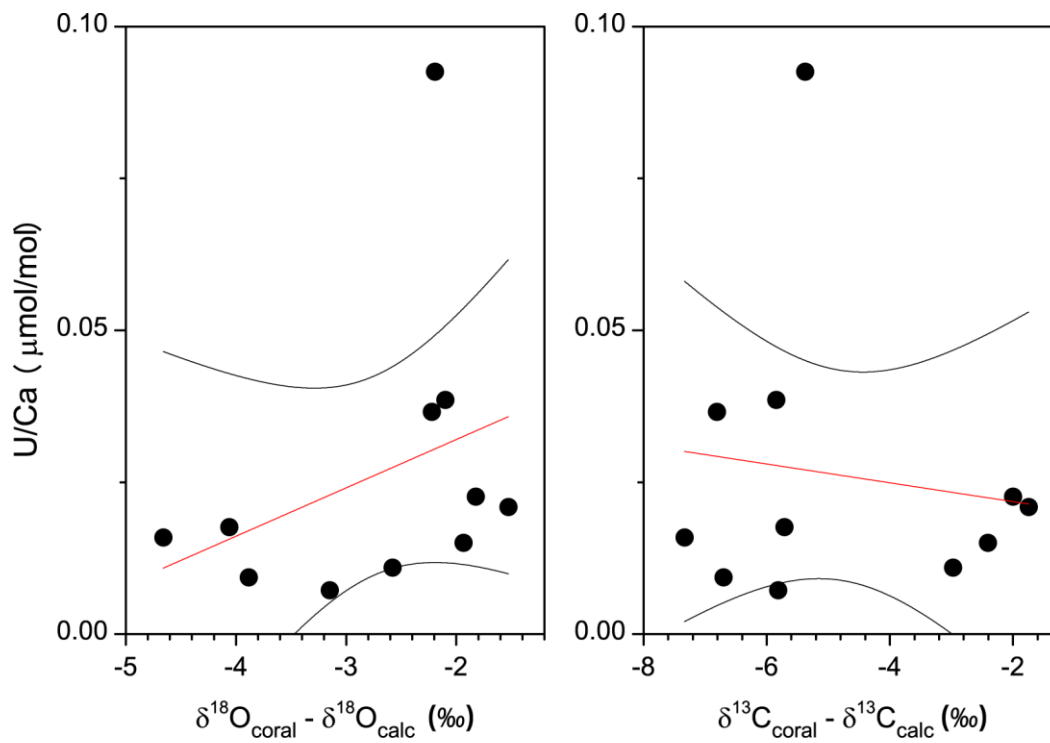


2

3 **Figure S1.** (a) Scatter plots of $\delta^{18}\text{O}$ and (b) $\delta^{13}\text{C}$ versus temperature for a suite of Octocorallia
 4 deep-sea corals collected from a large range of depths. (c) Scatter plot of $\Delta^{13}\text{C}$ ($\delta^{13}\text{C}_{\text{coral}} -$
 5 $\delta^{13}\text{C}_{\text{calc}}$) versus $\Delta^{18}\text{O}$ ($\delta^{18}\text{O}_{\text{coral}} - \delta^{18}\text{O}_{\text{calc}}$) for Octocorallia corals. $\delta^{18}\text{O}_{\text{calc}}$ and $\delta^{13}\text{C}_{\text{calc}}$ values
 6 were calculated by using empirically determined fractionation factors for inorganic calcite
 7 (Mavromatis et al., 2012; Jimenez-Lopez, 2006); and $\delta^{18}\text{O}_{\text{coral}}$ and $\delta^{13}\text{C}_{\text{coral}}$ values were
 8 calculated from the water temperature and Mg/Ca ratios of the corals (Yoshimura et al., 2011)
 9 using the equations of Mavromatis et al. (2012) and Jimenez-Lopez (2006), respectively.



1
 2 **Figure S2.** Scatter plots of measured B/Ca ratios of high-Mg calcite skeletons of Octocorallia
 3 corals against the difference values ($\delta^{18}\text{O}_{\text{coral}} - \delta^{18}\text{O}_{\text{calc}}$ and $\delta^{13}\text{C}_{\text{coral}} - \delta^{13}\text{C}_{\text{calc}}$) estimated by
 4 examining the effect of both temperature and Mg content on calcite–fluid isotope
 5 fractionation in synthetic magnesian calcite (Jimenez-Lopez et al., 2006; Mavromatis et al.,
 6 2012). The regression lines are shown with 95% confidence bounds.



1

2 **Figure S3.** Scatter plots of measured U/Ca ratios of high-Mg calcite skeletons of *Octocorallia*
 3 corals against the difference values ($\delta^{18}\text{O}_{\text{coral}} - \delta^{18}\text{O}_{\text{calc}}$ and $\delta^{13}\text{C}_{\text{coral}} - \delta^{13}\text{C}_{\text{calc}}$) estimated by
 4 examining the effect of both temperature and Mg content on calcite–fluid isotope
 5 fractionation in synthetic magnesian calcite (Jimenez-Lopez et al., 2006; Mavromatis et al.,
 6 2012). The regression lines are shown with 95% confidence bounds.

7