

ORIGINAL RESEARCH ARTICLE

Constraints on barium isotope fractionation during aragonite precipitation by corals

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Keywords

Aragonite, Ba isotope fractionation, Barium isotopes, in situ growth experiment, isotope proxy, Mediterranean seawater, natural/cultured scleractinian corals.

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ABSTRACT

We present a barium (Ba) isotope fractionation study of marine biogenic carbonates (aragonitic corals). The major aim is to provide first constraints on the Ba isotope fractionation between modern surface seawater and coral skeleton. Mediterranean surface seawater was found to be enriched in the heavy Ba isotopes compared to previously reported values for marine open ocean authigenic and terrestrial minerals. In aquarium experiments with a continuous supply of Mediterranean surface water, the Ba isotopic composition of the bulk sample originating from cultured, aragonitic scleractinian corals ($\delta^{137/134}\text{Ba}$ between $+0.16 \pm 0.12\text{‰}$ and $+0.41 \pm 0.12\text{‰}$) were isotopically identical or lighter than that of the ambient Mediterranean surface seawater ($\delta^{137/134}\text{Ba} = +0.42 \pm 0.07\text{‰}$, 2SD), which corresponds to an empirical maximum value of Ba isotope fractionation of $\Delta^{137/134}\text{Ba}_{\text{coral-seawater}} = -0.26 \pm 0.14\text{‰}$ at 25°C. This maximum Ba isotope fractionation is close and identical in direction to previous results from inorganic precipitation experiments with aragonite-structured pure BaCO_3 (witherite). The variability in measured Ba concentrations of the cultured corals is at odds with a uniform distribution coefficient, $D_{(\text{Ba}/\text{Ca})}$, thus indicating stronger vital effects on isotope than element discrimination. This observation supports the hypothesis that the Ba isotopic compositions of these corals do not result from simple equilibrium between the skeleton and the bulk seawater. Complementary coral samples from natural settings (tropical shallow-water corals from the Bahamas and Florida and cold-water corals from the Norwegian continental shelf) show an even wider range in $\delta^{137/134}\text{Ba}$ values ($+0.14 \pm 0.08$ to $+0.77 \pm 0.11\text{‰}$), most probably due to additional spatial and/or temporal seawater heterogeneity, as indicated by recent publications.

INTRODUCTION

The earth alkaline element barium (Ba) has attracted significant attention in the biogeochemistry community. In the photic zone of marine surface waters, Ba is incorporated in or adsorbed on organic matter (Sternberg *et al.*, 2005) and planktonic carbonate tests, causing depletion of dissolved Ba (Cardinal *et al.*, 2005) and resulting in a nutrient-like distribution in the water column (Wolgemuth & Broecker, 1970; Chan *et al.*, 1976; Church, 1979;

Monnin *et al.*, 1999; Chester, 2009). Therefore, variation in the accumulation rates of Ba in marine sediments is thought to be indicative of variations in marine biological productivity through time (Schmitz, 1987; François *et al.*, 1995; Paytan *et al.*, 1996; McManus *et al.*, 1999; Martinez-Ruiz *et al.*, 2000; Babu *et al.*, 2002; Paytan & Griffith, 2007; Hull & Norris, 2011). Furthermore, Ba/Ca ratios in the shells of foraminifers are used to reconstruct past ocean alkalinity and circulation patterns (Lea *et al.*, 1989; Hall & Chan, 2004; Weldeab *et al.*, 2007a) or act as a

continental run-off proxy in coastal waters (Weldeab *et al.*, 2007b; Sprovieri *et al.*, 2008).

The marine Ba cycle, however, is not fully understood (Dymond *et al.*, 1992; Paytan & Kastner, 1996; Dickens *et al.*, 2003). Different Ba sources to the ocean and their relative contributions in the past are still difficult to quantify. If different Ba sources could be distinguished based on their respective isotopic composition, the relative contribution of these sources to the marine Ba pool could be approached by mass balance models. Further, transport, dissolution-reprecipitation or vital processes may induce resolvable Ba isotope fractionation in sediments and biogenic carbonate. Thus, the analysis of the Ba isotopic composition of different Ba sources in seawater and marine sediments bears the potential to improve the understanding of the Ba cycle.

Eugster *et al.* (1969) measured various meteorites, reagents Ba and one terrestrial standard and concluded that there is no anomaly present in Ba isotope abundances in excess of 1‰. Subsequently, only a very limited number of studies have dealt with Ba isotopes in natural terrestrial samples (von Allmen *et al.*, 2010; Miyazaki *et al.*, 2014; Horner *et al.*, 2015; Nan *et al.*, 2015; Cao *et al.*, 2016), or experimental carbonate and sulphate precipitates (von Allmen *et al.*, 2010; Böttcher *et al.*, 2012). Von Allmen *et al.* (2010) found that synthetic witherite (BaCO_3) and barite (BaSO_4) are generally depleted in the heavy Ba isotopes down to -0.3‰ in $\Delta^{137/134}\text{Ba}_{\text{solid-liquid}}$. The calculated total amounts of Ba precipitated in those experiments were below 5%, that is, the results were not significantly influenced by Rayleigh effects. Terrestrial Ba gangue minerals (four barites, one norsethite [$\text{BaMg}(\text{CO}_3)_2$]) were all close to standard solutions. In contrast, a $\delta^{137/134}\text{Ba}$ value of -0.5‰ was found in a diagenetic barite sample from ODP Leg 207 that formed under reducing diagenetic conditions. It is only recently that modern seawater data have been published for Ba. Open ocean water profiles in the South Atlantic (Horner *et al.*, 2015) and the East China Sea (Cao *et al.*, 2016) showed consistently a general decrease in $\delta^{137/134}\text{Ba}$ of about 0.2 to 0.3‰ with water depth. The actual depth in which the transition to lower $\delta^{137/134}\text{Ba}$ values starts and the Ba isotopic composition of (sub)surface waters, however, are variable. The latter varies between 0.45‰ in $\delta^{137/134}\text{Ba}$ in the South Atlantic (Horner *et al.*, 2015) and 0.8‰ in the East China Sea (Cao *et al.*, 2016), recalculated relative to the Fluka $\text{Ba}(\text{NO}_3)_2$ standard used here (see ‘MC-ICP-MS analysis’ below).

In this study, the Ba isotope composition of cultured coral skeletons is investigated and compared to the composition of the ambient seawater. Corals were chosen because they are abundant in the photic zone where Ba is depleted. Given the observed fractionated Ba isotope values in (sub)surface waters (Horner *et al.*, 2015; Cao *et al.*,

2016) and Ba depletion related to microorganism activity, corals may record changes in productivity and seawater heterogeneities with respect to their Ba isotopic compositions. In order to use coral skeletons as archives, however, the fractionation factor between carbonate and ambient seawater must be known. Next to isotope effects due to carbonate precipitation (von Allmen *et al.*, 2010), vital effects accompanying coral growth may contribute to the overall Ba isotope fractionation in an analogous manner to that observed in the Ca-isotope system. For example, Inoue *et al.* (2015) found significant difference in $\Delta^{44/40}\text{Ca}_{(\text{solid-solution})}$ in cultured *Porites australiensis* compared to published data from inorganic aragonite precipitates, what these authors attributed to coral-specific bio-mineralization processes. In contrast, vital effects on stable Sr isotope ratios are ambiguous. Constant $\Delta^{88/86}\text{Sr}$ values of -0.20‰ were reported for various samples of *Lophelia pertusa* derived from different locations along the European continental margins (Raddatz *et al.*, 2013). Fietzke & Eisenhauer (2006), on the other hand, reported temperature-dependent strontium isotope fractionation during calcium carbonate precipitation. Natural coral samples from *Pavona clavus* yielded a steeper temperature gradient than inorganically precipitated aragonite.

Here, the experimental setup with different coral species (Fig. 1) and constant ambient conditions allowed the

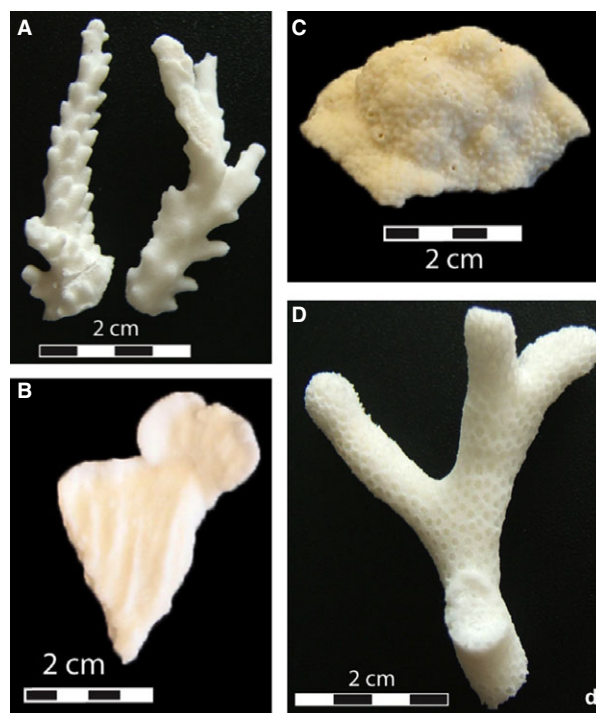


Fig. 1. Cultured Coral from this study (newly grown parts only). The bulk of the pictured samples was powdered for analysis (A) *Acropora* sp.; (B) *Montipora* sp.; (C) *Porites* sp., (D) *Stylophora* sp.

number of factors involved to be reduced and, in particular, the Ba isotopic composition of the ambient water to be measured. Thus, the magnitude and direction of Ba isotope fractionation during coral growth can be investigated. In addition, corals from different natural settings (tropical shallow-water corals: Bahamas/Florida; deep, cold-water corals: Norwegian continental shelf, Fig. 2) were analysed to get a first indication of Ba isotope fractionation in natural habitats. Further, a set of five

Mediterranean surface water samples taken over a distance of >2200 km east to west provides a first glimpse of surface water homogeneity at this scale (Fig. 3). The purpose of this study is to evaluate (i) if Ba isotope fractionation in corals is on the same order as that of abiogenic precipitation or if significant vital effects are observable; and (ii) if corals from natural settings show larger variations than explainable by precipitation, that is, are there indications for isotopically heterogeneous seawater.

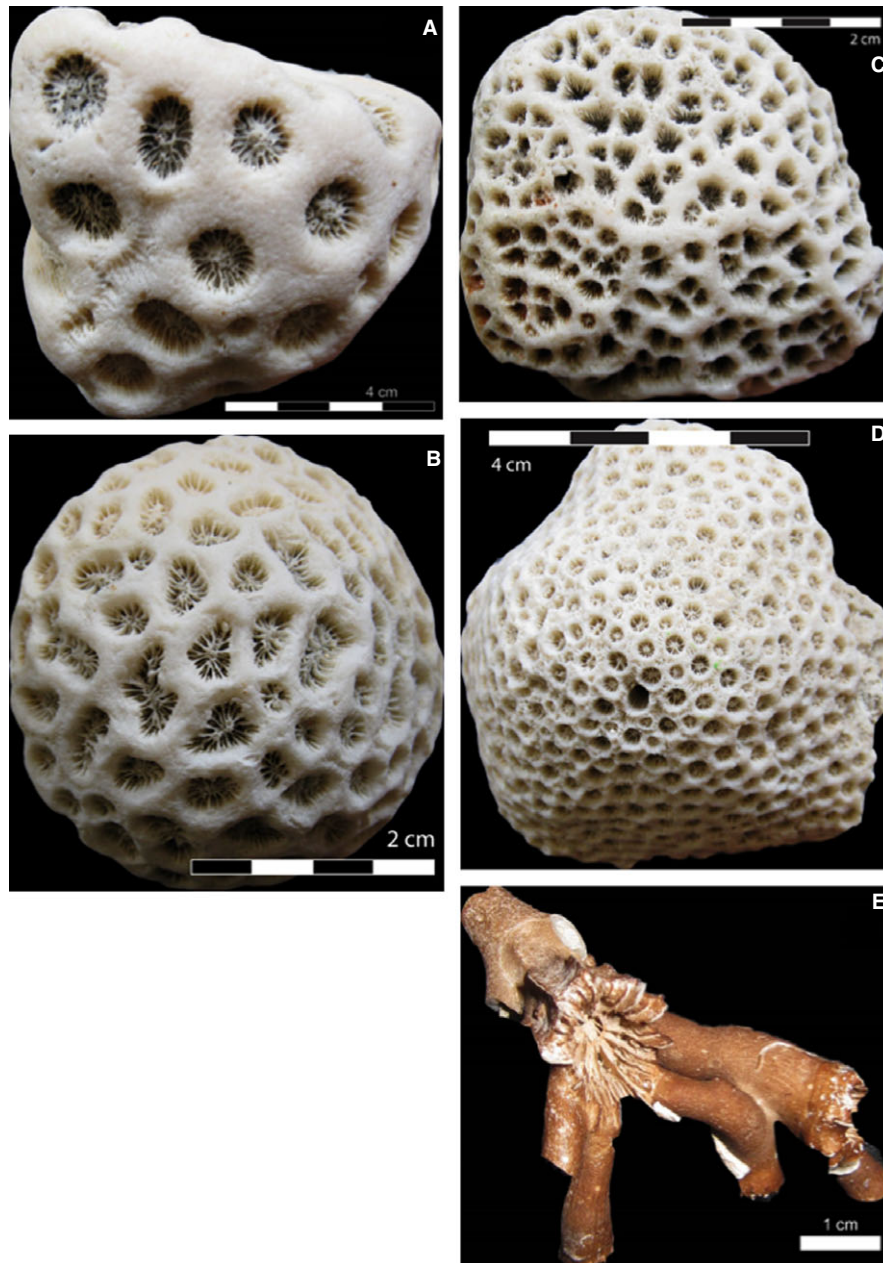


Fig. 2. Corals from natural habitats. The bulk of the samples pictured was powdered for analysis. (A and B) *Favia fragum*; (C) *Agaricia agaricites*; (D) *Montastraea cavernosa*; (E) *Lophelia pertusa*.



Fig. 3. Locations of the analysed natural and cultured coral samples, as well as Mediterranean seawater samples.

MATERIAL AND METHODS

Coral skeleton and seawater samples, experimental approaches and sampling environments

Characteristics of the coral samples are summarized in Tables 1 and 2. Two sets of samples consisting of tropical scleractinian corals (cultured and from natural settings), a standardized coral powder and a cold-water scleractinian coral were analysed.

The first sample set is composed of *Porites* sp., *Acropora* sp., *Stylophora* sp. and *Montipora* sp. cultured under constantly monitored conditions at the Centre Scientifique de Monaco. The aquaria were supplied with Mediterranean seawater pumped from a site situated at 50 m depth and 30 m off the coastline (Centre Scientifique de Monaco, Fig. 3). The salinity was monitored using a conductivity meter (Mettler LF 196) and was found to stay almost constant at 38. Seawater was maintained at a temperature of 25°C using a temperature controller (EW, PC 902/T). Metal halide lamps (Philips HPIT, 400 W) provided irradiance of $204 \pm 3 \mu\text{mol m}^{-2} \text{s}^{-1}$ on a 12 : 12 photoper-

iod. The seawater was continuously aerated with ambient air. A water sample was collected in the aquarium, representing the ambient seawater in which the cultured corals grew ('Monaco seawater'). Prior to grinding of the coral tips in an agate mortar, coral skeletons were bleached for 24 h with NaClO (10%), ultrasonic-cleaned and rinsed with Milli-Q water in order to remove organic matter.

The second sample set comprises sub-Recent tropical corals *Montastraea cavernosa*, collected off Mayaguana Island (Bahamas, Fig. 3; 22°25'2.47"N, 73°8'8.99"W) in 2008, and *Favia fragum* and *Agaricia agaricites* from the Florida Keys (Florida, USA; 24°44'23.94"N, 80°58'51.54"W) collected in 2004. The samples were ultrasonic-cleaned in Milli-Q water and powdered in an agate mortar prior to analysis. Unlike the other samples, the coral skeletons from the Bahamas and Florida are not pristine as their aragonite content ranges from 79.6 to 89.4% (Table 2), that is, up to 20% of aragonite is recrystallized into secondary calcite. In addition, a standardized coral powder (JCP-1, Geological Survey of Japan) was analysed. JCP-1 is used as an international reference material in coral skeleton studies (Okai *et al.*, 2002; Inoue *et al.*, 2004). This sample comes from a colony of *Porites* sp. off Japan and consists of 100% aragonite.

A sub-Recent *Lophelia pertusa* from the Norwegian continental shelf collected at a depth of around 200 m (Freiwald *et al.*, 2002) represents a cold-water scleractinian coral specimen. Prior to analysis, the coral sample was ultrasonic-cleaned in Milli-Q to remove attached sedimentary particles. The aragonitic skeleton of cold-water corals like *L. pertusa* may be coated post-mortem by a ferromanganese oxyhydroxide crust (Lomitschka & Mangini, 1999) as is the case for our sample (Fig. 2E). To test the potential influence of this coating on Ba isotope data, a portion of the sample was treated with 0.1M HCl to remove the coating (Copard *et al.*, 2010). Barium contents were very similar prior to ($15 \pm 0.7 \text{ mg kg}^{-1}$, Loph-1) and after this procedure ($13 \pm 0.6 \text{ mg kg}^{-1}$,

Table 1. Classification of the studied coral genera

Order	Suborder	Family	Species
Scleractinia	Astrocoeniina	Acroporidae	<i>Acropora</i> sp.
			<i>Montipora</i> sp.
		Pocilloporidae	<i>Stylophora</i> sp.
	Fungiina	Agariciidae	<i>Agaricia agaricites</i>
		Poritidae	<i>Porites</i> sp.
	Faviina	Faviidae	<i>Favia fragum</i>
		<i>Montastrea cavernosa</i>	
	Caryophylliina	Caryophylliidae	<i>Lophelia pertusa</i>

Classification based on Veron *et al.* (1996) with cultured species in bold.

Table 2. Sample characteristics and geochemical data set

Location	Nature	Species/name	Ba (mg kg ⁻¹)	Ba (nmol kg ⁻¹)	Position	Aragonite (%)	$\delta^{137/134}\text{Ba}$ (‰)	2SD	n	Ca (ppm)	Ba/Ca ($\mu\text{M Mol}^{-1}$)	$D_{(\text{Ba}/\text{Ca})}$
<i>Cultured corals</i>												
CSM	Tropical coral	<i>Acropora</i> sp. (1)	8.2	5.99E+04	Aquaria	100	0.34	0.17	2	379 700	6.3	1.4
CSM	Tropical coral	<i>Acropora</i> sp. (2)	8.8	6.41E+04	Aquaria	100	0.36	0.21	3	379 700	6.7	1.5
CSM	Tropical coral	<i>Montipora</i> sp.	56.9	4.15E+05	Aquaria	100	0.22	0.09	3	383 900	43.2	9.8
CSM	Tropical coral	<i>Porites</i> sp.	21.7	1.58E+05	Aquaria	100	0.41	0.12	2	n.d.	16.6*	3.8
CSM	Tropical coral	<i>Stylophora</i> sp.	8.2	5.94E+04	Aquaria	100	0.16	0.12	2	377 600	6.3	1.4
<i>Natural settings</i>												
Florida	Tropical coral	<i>Favia fragum</i> (1)	23.6	1.72E+05	Lagoon	85	0.55	0.08	8			
Florida	Tropical coral	<i>Favia fragum</i> (2)	5.7	4.15E+04	Lagoon	89	0.56	0.08	3			
Florida	Tropical coral	<i>Agaricia agaricites</i>	5.2	3.81E+04	Lagoon	88	0.77	0.11 [†]	1			
Bahamas	Tropical coral	<i>Montastraea cavernosa</i>	5.6	4.07E+04	Lagoon	80	0.49	0.04	2			
Japan (Standard)	Tropical coral	JCP-1	9.0	6.58E+04	Reef channel	100	0.16	0.01	2			
Norwegian Shelf	Cold-water coral	<i>L. pertusa</i> (Loph-1) [‡]	14.7	1.07E+05	200 m depth	100	0.14	0.08	6			
Norwegian Shelf	Cold-water coral	<i>L. pertusa</i> (Loph-2) [§]	12.5	9.08E+04	200 m depth	100	0.18	0.08	3			

n = number of measurement from one spiked and separated solution.

^{*}Ca set to 380 000 mg kg⁻¹.

[†]2 s_p(cf. Text).

[‡]Before removal of surface coating.

[§]After removal of surface coating.

Loph-2). Moreover, the two aliquots have identical $\delta^{137/134}\text{Ba}$ values (Table 2). We therefore conclude that coating by ferromanganese oxyhydroxides has a negligible influence on the Ba isotope composition of the coral skeleton analysed in this study. A previous study has shown that dissolved Mn does not affect the measured Ba isotope signal (Böttcher *et al.*, 2012).

A set of four surface seawater samples was taken on a transect through the Mediterranean Sea (Fig. 3) on-board R/V *Maria S. Merian* (Cruise MSM33) in November, 2013. Continuously supplied surface water from about 5 m water depth (MSM on-board sampling system) was sampled with 60 cm³ plastic syringes, filtered through 0.2 μm syringe filters (Minisart, Sartorius) into pre-conditioned polyethylene bottles, and acidified to final 1 vol % HNO₃ (Winde *et al.*, 2014) according to established procedures of filtering alkaline seawater through the membrane filters for earth alkaline element analyses. Seawater salinity and temperature data as well as geographical site coordinates were obtained from the standard MSM board equipment.

Sample preparation and analytical procedures

The analytical procedure of Ba extraction for isotope ratio measurements was conducted using PFA labware in a class 100 laminar flow hood. All acids were distilled before application. A detailed description of the chromatographic purification of Ba from carbonate matrices can be found in Pretet (2013). In brief, several grams of bulk coral material (see Figs 1 and 2) were powdered and homogenized. Aliquots comprising 2 μg of Ba – corresponding to 40 to 400 mg per analysis – were first mixed with an appropriate amount of ¹³⁰Ba-¹³⁵Ba double-spike, following the procedure reported in von Allmen *et al.* (2010). The spiked carbonate samples were then digested in 5 ml of 6.4 M HCl at 90°C for 12 h. After digestion, the samples were dried down and then redissolved in 0.6 ml of 2.5 M HCl to be loaded onto the column. The column chemistry was performed in PFA micro-columns (4.0 mm ID; Savillex, Eden Prairie, MN, USA) equipped with 4 mm PFA frits (30 μm pore size) and filled with 1 cm³ of Dowex[®] 50WX8 cation-exchange resin (200 to 400 mesh). First, the resin was cleaned with 10 ml of 6.4 M HCl and conditioned with 4 ml of 2.5 M HCl. Sample loading and removal of the matrix were conducted with 8.9 ml of 2.5 M HCl in total. Finally, Ba was eluted in 6 ml of 6.4 M HCl and taken to dryness.

A modified chromatographic procedure was applied for Ba separation from seawater, consisting of two cation-exchange columns. Before purification, 15 ml of Mediterranean seawater, corresponding to *ca* 100 ng Ba, were

double-spiked and evaporated at 100°C. This aliquot size provides enough Ba for one isotope measurement, while minimizing the amount of matrix elements. The precipitated salt was then equilibrated with 0.5 ml of 2.5 M HCl for about 10 h prior to ion-exchange purification. Remaining salt that did not re-dissolve was removed by centrifugation and discarded. Barium recovery from the evaporates was found to be quantitative, that is, less than 1% of total Ba was lost. In a first column, we removed the largest fraction of major elements. For this we used Spectrum® PP Columns 104704 (Spectrum Chromatography, Houston, TX, USA) filled with 2 cm³ of Dowex® 50WX8 cation-exchange resin. Cleaning and conditioning of the resin was done with 20 ml of 6.4 M HCl and 7 ml of 2.5 M HCl, respectively. The samples were loaded in 0.5 ml of 2.5 M HCl, followed by matrix removal with 5.5 ml of 2.5 M HCl and 2 ml of 6.4 M HCl. Barium was collected in 15 ml of 6.4 M HCl. The Ba yield of this first column was ca 90%. Removal of Na, Mg and K was close to 100%, whereas ca 15% of Ca and ca 55% of Sr were eluted together with Ba. Therefore, Ba was further purified from the remaining matrix in a second step, following the procedure outlined above for carbonate samples. The total Ba yield of our chromatographic separation from seawater was ca 80%. To test for potential analytical isotope fractionation, four aliquots of one seawater sample were spiked at different, successive analytical steps. They gave identical $\delta^{137/134}\text{Ba}$. Thus, despite the non-quantitative recovery of Ba, no impact on the Ba isotope signatures was recognized. Furthermore, the applied double-spike technique in addition corrects for analytical mass-dependent isotope fractionation when spiking is done before purification.

Following the chromatographic separation, remaining organic matter from the sample or from the ion-exchange resin was effectively oxidized using ca 150 μl of suprapure 30% H₂O₂ and 650 μl of 7M HNO₃, heated to 90°C for about 7 h. Prior to measurements, samples were evaporated and re-dissolved in 0.5 M HNO₃. The total blank for the chemical procedure was below 3 ng.

MC-ICP-MS analysis

Barium isotope analyses were performed using a double focusing Nu Instrument® ‘Nu plasma’ multi-collector ICP-MS at the Institute of Geological Sciences, Bern. Samples were introduced via a PFA nebulizer connected to an ESI® Apex-Q. The measurements were controlled for isobaric interferences of tellurium (Te), affecting mass ¹³⁰Ba, and of xenon (Xe) on ¹³⁰Ba, ¹³²Ba and ¹³⁴Ba. No Te was detected during the measurements. Signal intensities of ¹³⁰Xe, ¹³²Xe and ¹³⁴Xe were calculated based on the ¹³¹Xe beam and Xe isotope ratios taken from IUPAC

(de Laeter *et al.*, 2003), which were exponentially corrected for instrumental isotope fractionation.

Data acquisition included three to five blocks of 10 cycles of 10 seconds, depending on the available quantity of sample Ba. Peak centring was performed prior to each block. The isotopic values were expressed relative to a Ba nitrate ICP-OES standard solution from Fluka-Aldrich® as (expressed in ‰):

$$\delta^{137/134}\text{Ba} = \left(\frac{(^{137}\text{Ba}/^{134}\text{Ba})_{\text{sample}}}{(^{137}\text{Ba}/^{134}\text{Ba})_{\text{standard}}} - 1 \right) \times 1000$$

The Fluka Ba(NO₃)₂ standard used as reference solution was previously introduced and calibrated against IAEA standards (IAEA-SO-5 #34, IAEA-SO-6 #34, IAEA-CO-9 # 56) by von Allmen *et al.* (2010). A minimum of five standards (one after each three samples) was measured per analytical session. The $\delta^{137/134}\text{Ba}$ values of the samples reduced by the double-spike routine were further corrected with the average value of the standard solution measurements during each session. The long-term (2011 to 2013) intermediate precision of the reference solution was $\pm 0.10\text{‰}$ (2sd, $n = 270$). To assess the precision of coral sample analyses, the pooled standard deviation (2s_p) was calculated, giving an average deviation of all repeated samples of $\pm 0.11\text{‰}$ (2s_p). The intermediate precision of four Mediterranean water samples analysed in 2015 was $<0.08\text{‰}$, due to improved analytical conditions.

Accuracy of the analyses can be assessed by comparison of the coral standard JCp-1 with other studies. Two replicate measurements of JCp-1 resulted in a $\delta^{137/134}\text{Ba}$ value of $0.16 \pm 0.01\text{‰}$. Horner *et al.* (2015) measured a $\delta^{138/134}\text{Ba}$ value of $0.29 \pm 0.03\text{‰}$ relative to NIST SRM 3104a. Assuming mass-dependent behaviour, this value can be recalculated to $\delta^{137/134}\text{Ba} = 0.22\text{‰}$. Furthermore, we can relate this result to Fluka Ba(NO₃)₂ by using $\Delta^{137/134}\text{Ba}_{\text{IAEA-CO-9-SRM 3104a}} = 0.017 \pm 0.049\text{‰}$ (Nan *et al.*, 2015) and $\Delta^{137/134}\text{Ba}_{\text{IAEA-CO-9-Fluka}} = -0.03 \pm 0.06\text{‰}$ (von Allmen *et al.*, 2010). The recalculated $\delta^{137/134}\text{Ba}$ of JCp-1 from Horner *et al.* (2015) is 0.19‰ relative to Fluka Ba(NO₃)₂, which is within analytical uncertainty identical to the value of 0.16‰ measured here. Note that all data from Horner *et al.* (2015) cited here were recalculated accordingly. Similarly, data from Cao *et al.* (2016), that are originally given relative to a Ba(NO₃)₂ solution from Inorganic Ventures, were recalculated using IAEA-SO-5 ($\delta^{137/134}\text{Ba}_{\text{Ba(NO}_3)_2} = 0.12 \pm 0.10\text{‰}$) and $\Delta^{137/134}\text{Ba}_{\text{IAEA-SO-5-Fluka}} = 0.02 \pm 0.05\text{‰}$ (von Allmen *et al.*, 2010). The Ba concentration of JCp-1 was measured to be 9 mg kg^{-1} , which is in good agreement with results of Okai *et al.* (2002) ($10.5 \pm 0.3 \text{ mg kg}^{-1} \pm 3\%$ RSD) and Inoue *et al.* (2004) ($8 \text{ mg kg}^{-1} \pm 3\%$ RSD).

RESULTS

Barium concentrations

Barium concentrations in skeletal material are commonly normalized to calcium (Ca) and reported as Ba/Ca ratios. A distribution coefficient $D_{(Ba/Ca)}$ is then applied to derive the respective composition of seawater from the analysed skeleton (Lea & Spero, 1994; Böttcher & Dietzel, 2010), which is defined according to the following equation:

$$(Ba/Ca)_{\text{carbonate}} = D_{(Ba/Ca)} * (Ba/Ca)_{\text{solution}} \quad (1)$$

However, as $(Ba/Ca)_{\text{solution}}$ is constant for the cultured corals $(Ba/Ca)_{\text{carbonate}}$ ratios bear the same information on relative variations as $D_{(Ba/Ca)}$. Furthermore, Ba concentrations vary by one order of magnitude in the corals, while the range of Ca concentrations is smaller than 2% (Table 2). Thus, in the data set of cultured corals, Ba concentrations basically carry the same information as Ba/Ca ratios or $D_{(Ba/Ca)}$.

Mediterranean seawater barium isotope composition

Sampling of the seawater supplied for the aquarium experiments showed a Ba isotopic composition of $0.42 \pm 0.18\text{‰}$ in $\delta^{137/134}\text{Ba}$ (2sd, Table 2). In order to estimate potential variations in modern surface seawater, a further set of four samples from Mediterranean surface waters were analysed for their Ba isotope composition (Table 3). Results range from 0.38 to 0.46‰ with individual uncertainties of ≤ 0.07 (2sd; Fig. 4). These data indicate an essentially homogeneous $\delta^{137/134}\text{Ba}$ for Mediterranean surface waters. The Ba isotope composition of deeper water masses in the Mediterranean may differ from those of the surface waters and are the subject of further investigations.

Barium isotope composition of coral skeleton

The $\delta^{137/134}\text{Ba}$ values of scleractinian coral skeletons, comprising different coral families and genera, range

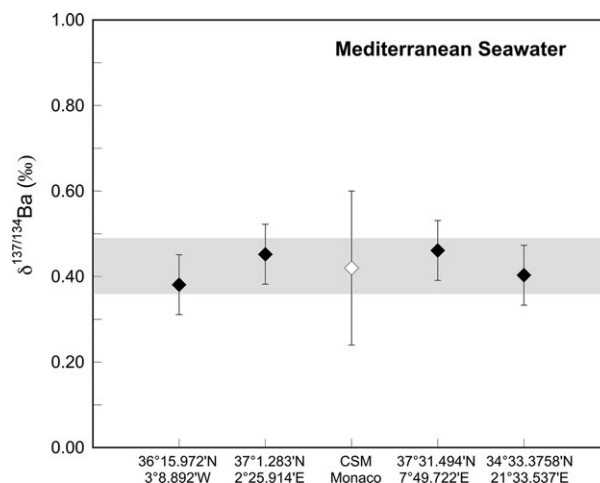


Fig. 4. Mediterranean seawater $\delta^{137/134}\text{Ba}$ values. Open symbol represents aquarium water (see Table 2).

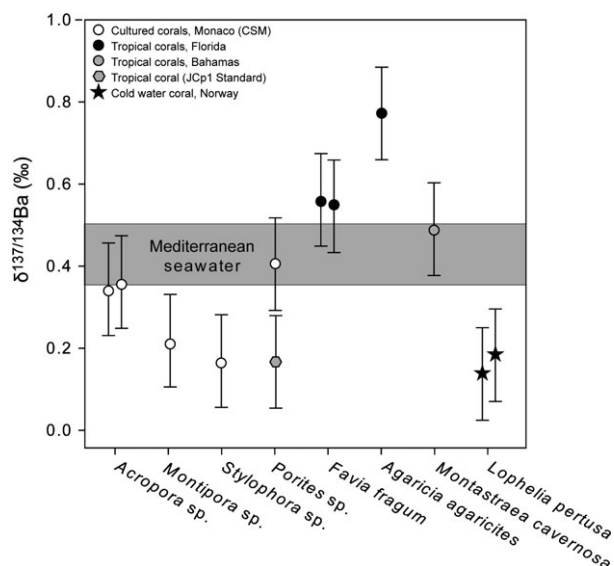


Fig. 5. $\delta^{137/134}\text{Ba}$ of coral skeletons ($\pm 2\text{sp}$) and average Mediterranean surface water ($0.42 \pm 0.07\text{‰}$), indicated by the grey area. Cultured corals: open circles, tropical corals (Florida): black circles, tropical coral (Bahamas): light grey circle, standard JCP-1: dark grey hexagon and cold-water coral from Norway: stars.

Table 3. Mediterranean seawater

Sample	Location	Sampling date (2013)	Salinity (S)	T (°C)	Ba (nmol kg ⁻¹)	$\delta^{(137}\text{Ba}/^{134}\text{Ba})\text{‰}$	2sd	n
MSM_033_685, #2	36°15.972'N, 3°8.892'W	November 2nd	36.7	19.14	43	0.38	0.06	2
MSM_033_688, #5	37°1.283'N, 2°25.914'E	November 3rd	36.7	21.8	42	0.45	0.07	2
MSM_033_690, #7	37°31.494'N, 7°49.722'E	November 4th	37.8	22.6	50	0.46	0.08*	1
MSM_033_707, #17	34°33.3758'N, 21°33.537'E	November 5th	39.4	22.5	54	0.40	0.03	2
Aquarium	Monaco CSM		38.0	25.0	58	0.42	0.18	5
Average	Mediterranean				49.3	0.42	0.07	

*Intermediate precision of the reference solution during analytical period: <0.08 (cf. Text).

between 0.14 ± 0.11 and $0.77 \pm 0.11\text{‰}$ ($2s_p$, Table 2; Fig. 5). Cultured tropical corals from the Monaco aquarium exhibit a range in $\delta^{137/134}\text{Ba}$ values between 0.16 and 0.41‰ . Compared to the Monaco seawater, the corals have identical (*Acropora* sp. and *Porites* sp.) or slightly, but significantly, lower $\delta^{137/134}\text{Ba}$ values (*Stylophora* sp. and *Montipora* sp.), giving a range of Ba isotope fractionation between -0.01 and -0.26‰ in $\Delta^{137/134}\text{Ba}_{\text{coral-seawater}}$. There is no significant correlation between $\delta^{137/134}\text{Ba}$ values and Ba concentration in the coral data (Fig. 6). Also, the values are independent from the systematic position of the respective genera and species (cf. Table 1).

The range in $\delta^{137/134}\text{Ba}$ of the analysed natural corals is much larger (0.14 to 0.56 , with one specimen yielding $0.77 \pm 0.11\text{‰}$, Table 2) than that of the cultured species. Here, significant differences exist between the cold-water coral *Lophelia pertusa* ($\delta^{137/134}\text{Ba} = 0.18 \pm 0.08\text{‰}$) and the tropical corals (Florida and the Bahamas; *A. agaricites*, *F. fragum* and *M. cavernosa*).

INTERPRETATION AND DISCUSSION

Barium concentrations and empirical distribution coefficients

The $D_{(\text{Ba}/\text{Ca})}$ values of cultured corals vary between 1.4 and 9.8 (Table 2). Most values are in agreement with the pioneering work of Lea *et al.* (1989), who found average $D_{(\text{Ba}/\text{Ca})}$ values of 1.41 ± 0.14 and 1.27 ± 0.03 for two different coral species and locations. The $D_{(\text{Ba}/\text{Ca})}$ values

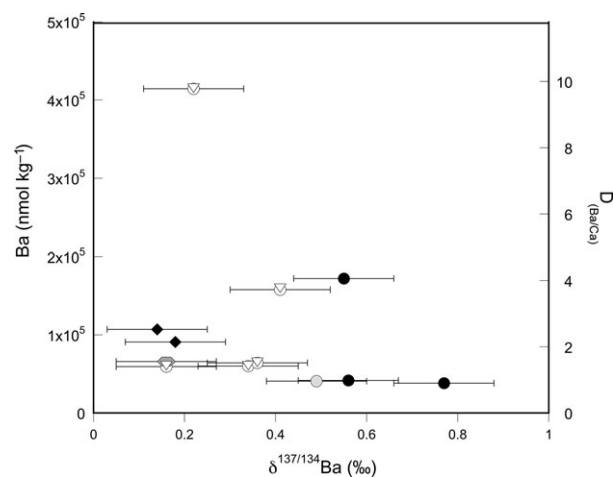


Fig. 6. $\delta^{137/134}\text{Ba}$ ($\pm 2s_p$) of coral skeletons (Cultured corals: open circles; tropical corals (Florida): black circles; tropical coral (Bahamas): light grey circle; standard JCP-1: dark grey hexagon; and cold-water coral from Norway: black diamonds) plotted against the Ba concentration (for cultured corals also against $D_{(\text{Ba}/\text{Ca})}$, shown as triangles).

for aragonite that was abiogenetically precipitated under laboratory conditions were found to be in the range of about 1.0 to 2.6 , and to be inversely correlated with temperature (Dietzel *et al.*, 2004; Gaetani & Cohen, 2006). Thus, estimated $D_{(\text{Ba}/\text{Ca})}$ values of all but one cultured coral are close to the range of experimental results for abiogenic Ba incorporation into aragonite at high precipitation rates. However, the pronounced $D_{(\text{Ba}/\text{Ca})}$ of one aquarium coral of 9.8 is too high to be explained as dominated by abiogenic Ba incorporation and cannot be reconciled by a unique $D_{(\text{Ba}/\text{Ca})}$ value. Thus, it appears reasonable to consider additional vital effects, as suggested previously by Gaetani & Cohen (2006), impacting internal pool sizes or crystallization kinetics beyond the scale considered in experiments so far.

The Ba concentrations of the corals from natural settings presented here (5 to 24 mg kg^{-1}) largely overlap with the cultured corals (8 to 57 mg kg^{-1}).

Coral skeleton Ba isotope fractionation

Barium isotope fractionation between seawater and coral skeleton is derived from the data of cultured corals (Table 2). As $\delta^{137/134}\text{Ba}_{\text{skeleton}}$ is close to or lower than $\delta^{137/134}\text{Ba}_{\text{seawater}}$, Ba stable isotope fractionation during biogenic Ba uptake seems to be similar to isotope effects during precipitation of aragonite-structured BaCO_3 (with-erite) (von Allmen *et al.*, 2010). It is further comparable to isotope fractionation of Sr (Krabbenhöft *et al.*, 2009), Mg (Yoshimura *et al.*, 2011), and Ca (Böhm *et al.*, 2006) in coral skeletons (see introduction). The experiments performed by von Allmen *et al.* (2010) suggest that different supersaturation degrees, and associated precipitation rates, influenced the reaction and the enrichment of light isotopes in the precipitates. The maximal observed Ba isotope fractionation between seawater and cultured corals (-0.26‰ in $\Delta^{137/134}\text{Ba}_{\text{coral-seawater}}$) is still consistent both in direction and magnitude with previous precipitation experiments (von Allmen *et al.*, 2010; Böttcher *et al.*, 2012). A similar fractionation factor was approximated by Horner *et al.* (2015), whose minimum estimate of $\alpha_{\text{BaSO}_4\text{-seawater}}$ corresponds to a $\Delta^{137/134}\text{Ba}_{\text{BaSO}_4\text{-seawater}}$ of -0.21‰ .

Substantial differences in $\delta^{137/134}\text{Ba}$ values for corals from the same environment, that is, the aquarium, cannot be attributed to simple, quasi abiogenic precipitation processes in isotope exchange equilibrium with bulk (aquarium) water, as already indicated by the variable $D_{(\text{Ba}/\text{Ca})}$ values. A simple first order model for this observation is that variable fractions of the given amount of seawater were precipitated during the bio-mineralization process. The question whether skeletogenesis in corals includes an open or semi-closed calcification compartment, is still a matter of intense debate (Böhm *et al.*, 2006; Cohen &

Holcomb, 2009; Cohen & Gaetani, 2010; Allemand *et al.*, 2011; Gaetani *et al.*, 2011; Tambutté *et al.*, 2011; Gagnon *et al.*, 2012). A semi-closed calcification compartment might provide the restricted reservoir needed for a Rayleigh-type Ba isotope fractionation. Taken at face value, the variations in $\delta^{137/134}\text{Ba}$ of the cultured corals could reflect a range of 25 to 99% of Ba from a given amount of seawater precipitated in a Rayleigh-type fractionation process, using a model with a Mediterranean $\delta^{137/134}\text{Ba}_{\text{seawater}}$ value as initial seawater value ($0.42 \pm 0.07\text{‰}$, 2sd) and a theoretical $\Delta^{137/134}\text{Ba}_{\text{precipitate-fluid}}$ of -0.3‰ (von Allmen *et al.*, 2010). However, a semi-closed calcification compartment is just one hypothesis to explain isotope fractionation in corals. For example, Inoue *et al.* (2015) reported combined $\delta^{44/40}\text{Ca}$ and Sr/Ca of *Porites australiensis* samples from multiple culture experiments. They conclude that their results are not compatible with a Rayleigh-type fractionation directly from a fluid, which is seawater-like in terms of $\delta^{44/40}\text{Ca}$ and Sr/Ca. Therefore, Inoue *et al.* (2015) favoured Ca-isotope fractionation in corals to be the result of Ca transmembrane transport (Tambutté *et al.*, 1996). Although these data give indications of isotope fractionation in corals also for Ba, the fractionation is comparatively small given the associated uncertainties and, thus, do not allow us to make conclusions on the competing hypotheses on bio-mineralization.

Diagenetic recrystallization

Following the experimentally derived Ba isotope fractionation factor during carbonate precipitation and the results of our coral culture experiments, the $\delta^{137/134}\text{Ba}$ value of a bulk coral is not higher than that of the ambient seawater, unless secondary processes contribute to the overall isotope fractionation. This finding is consistent with results for Sr or Ca (see introduction). In the coral samples from Florida and the Bahamas, up to 20% of the aragonite is recrystallized into calcite (Table 2), a process that may change the Ba isotopic compositions significantly. However, only very low amounts of Ba can be incorporated into the lattice of secondary calcite during recrystallization (Böttcher, 1997; Böttcher & Dietzel, 2010) or nano-scale dissolution-reprecipitation. Accordingly, calcitic fossils show $D_{(\text{Ba}/\text{Ca})}$ values consistently <1 [e.g. foraminifers (Lea & Spero, 1994; Hönisch *et al.*, 2011) and calcitic bivalve *Mytilus eludes* (Gillikin *et al.* 2006)]. Pingitore & Eastman (1985) investigated the Ba partitioning during recrystallization of coral aragonite to calcite. They compared altered and unaltered corals from the Pleistocene reef terraces exposed on Barbados, West Indies, and reported a Ba decrease from typical ranges of 8 to 15 mg kg⁻¹ in aragonite to 1 to 3 mg kg⁻¹ in secondary calcite. Therefore, the bulk carbonate

$\delta^{137/134}\text{Ba}$ should remain dominated by the composition of the original aragonite fraction. This phenomenon can be illustrated by a simple mass balance model. To increase an aragonitic skeleton $\delta^{137/134}\text{Ba}$ value of 0.4 (Mediterranean-like seawater) to 0.8 (like *A. agaricites* from the Florida setting), considering a 12% fraction of recrystallized calcite (as observed), and a Ba concentration five times lower in calcite than in primary aragonite (based on Pingitore & Eastman, 1985), the calcite fraction would have to carry a $\delta^{137/134}\text{Ba}$ value as high as +16‰. Therefore, partial diagenetic carbonate recrystallization is deemed unlikely to alter the primary Ba isotopic composition of a coral significantly.

Heterogeneity of the Ba isotopic composition of seawater

Precipitation of carbonate causes Ba isotope fractionation towards lower $\delta^{137/134}\text{Ba}$ values in a solid. Currently no data are available that would indicate a process that drives the Ba isotopic composition of a precipitate to $\delta^{137/134}\text{Ba}$ values above the corresponding dissolved Ba. This holds generally also true for isotope systems of other Earth alkaline elements (Nielsen *et al.*, 2012). Observed exceptions are Ca-isotope fractionation between aqueous solutions and inorganic solids that trap the hydrated ion in the lattice (Colla *et al.*, 2013) and the equilibrium Mg isotope fractionation factor between inorganic hydrous magnesium sulphate and aqueous MgSO₄ solutions (e.g. epsomite MgSO₄*7H₂O, Li *et al.*, 2011).

The $\delta^{137/134}\text{Ba}$ value of *A. agaricites* from Florida ($0.77 \pm 0.11\text{‰}$) is significantly higher than that of Mediterranean seawater ($0.42 \pm 0.07\text{‰}$). Given the above outlined conditions, carbonates of *A. agaricites* cannot have been precipitated from seawater with a Ba isotopic composition identical to that of Mediterranean surface waters. Indeed, recent studies indicate heterogeneous Ba isotopic compositions of surface ocean waters, ranging in $\delta^{137/134}\text{Ba}$ from 0.45 to 0.8‰ (Horner *et al.*, 2015; Cao *et al.*, 2016). Similarly, the vertical seawater heterogeneity, with shifts in $\delta^{137/134}\text{Ba}$ of about 0.2 to 0.3‰ (Horner *et al.*, 2015; Cao *et al.*, 2016), could be an explanation for the lower $\delta^{137/134}\text{Ba}$ values of the cold-water coral *L. pertusa* of $0.18 \pm 0.08\text{‰}$. We thus tentatively interpret the variations in the Ba isotopic composition of the investigated natural corals as indicators of spatial and/or temporal differences in the barium isotope composition of seawater.

CONCLUSIONS

Culture experiments at the Centre Scientifique de Monaco allowed for the first time the investigation of stable Ba

isotope fractionation between seawater and coral skeletons under controlled standard state conditions (25°C, 1 atm total pressure).

The seawater sample of the supply for the aquarium experiments and a set of four additional surface water samples from the Mediterranean Sea, collected over a distance of >2200 km from east to west, support a homogeneous Ba isotopic composition for Mediterranean surface waters with an average $\delta^{137/134}\text{Ba}$ value of $0.42 \pm 0.07\text{‰}$.

The cultured corals show either no Ba isotope fractionation relative to ambient seawater or slight enrichment in the lighter Ba isotopes ($\Delta^{137/134}\text{Ba}_{\text{coral-seawater}}$ between -0.01‰ and -0.26‰). The direction and magnitude of Ba isotope fractionation during coral growth is comparable with fractionation during precipitation of inorganic carbonates observed by a previous experimental study. The observed range of $D_{(\text{Ba}/\text{Ca})}$ values in the cultured corals in part exceed previously reported Ba distribution in abiotic experiments, and indicate additional vital effects leading to reservoir effects or crystallization velocities beyond the conditions of previous experimental calibrations. However, no correlation between $D_{(\text{Ba}/\text{Ca})}$ and the Ba isotopic composition of the corals is found in the growth experiments of this study. Instead, isotope fractionation might be governed by the efficiency of Ba incorporation into the coral skeleton. The number of investigated samples and the analytical resolution, however, do not allow further conclusions to be drawn.

One naturally grown tropical coral from Florida (*A. agaricites*) exhibits a $\delta^{137/134}\text{Ba}$ value significantly higher than that of Mediterranean surface water, suggesting heterogeneous Ba isotope compositions of surface seawaters, which is consistent with recently published data by Horner *et al.* (2015) and Cao *et al.* (2016). While the Ba isotope system is still in its infancy, these findings provide support to the use of coral Ba isotopes as a palaeo-proxy for water masses and the productivity related isotope composition they carried.

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The data will be available after publication on the PANGAEA repository (<http://www.pangaea.de>).

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