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Multi-colony calibrations of coral Ba/Ca with a contemporaneous *in situ* seawater barium record

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Abstract

The coral skeleton barium to calcium ratio (Ba/Ca_{coral}), a proxy for seawater barium concentrations (Ba_{SW}), has been interpreted as a tracer of upwelling based on the characteristic "nutrient like" depth profile of Ba_{SW}. However, in some tropical regions, such as the Gulf of Panamá, substantial influence of terrestrial runoff inputs and differences between the vertical distribution of Ba_{SW} and that of the major nutrients (nitrate and phosphate) in the upper water column can complicate the interpretation of Ba/Ca_{coral} as an upwelled nutrient proxy. In the Gulf of Panamá, contemporaneous Ba/Ca_{coral} records from multiple colonies of *Porites lobata*, *Pavona gigantea*, and *Pavona clavus* corals record a nearly twofold change in surface water Ba_{SW} as a 20–70% increase in skeletal Ba/Ca with excellent correlation among Ba/Ca records from co-located colonies ($r = 0.86$–0.99). These results provide, for the first time, an absolute calibration of the coral Ba proxy with a contemporaneous Ba_{SW} record. Compiling the Ba/Ca_{coral} records from three co-located colonies of each species into taxon-specific composite regressions reveals strong statistically significant correlations with the Ba_{SW} time-series record ($p < 0.001$). Differences among taxa in regression slope, y-intercept, and average distribution coefficient, as well as a demonstration of the application of the *P. clavus* calibration to a previously published Ba/Ca_{coral} record, emphasize the necessity of using taxon-specific calibrations to reconstruct changes in Ba_{SW} with accuracy. These results support the application of Ba/Ca_{coral} to reconstruct past changes in absolute Ba_{SW} concentrations, adding an important tool to the collection of geochemical proxies for reconstructing surface ocean biogeochemical processes in the past.

1. INTRODUCTION

Surface-dwelling reef building corals provide the opportunity to reconstruct continuous centennial scale proxy records of environmental conditions at high (sub-seasonal) resolution. Isotopic and trace element ratios preserved in the banded aragonitic skeleton of surface dwelling coral colonies have been used as proxies for tropical sea surface temperature and salinity (e.g. Beck et al., 1992; Gagan et al., 1994; Nurhati et al., 2011; Carilli et al., 2014). Variations in seawater composition driven by upwelling, coastal runoff, and oceanographic circulation, have also been reconstructed using radiocarbon and trace elemental ratios in tropical coral skeleton (Δ^{14}C, Cd/Ca, P/Ca, and Ba/Ca: e.g. Shen et al., 1987;

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Lea et al., 1989; Guilderson and Schrag, 1998; Montaggioni et al., 2006; Fleitmann et al., 2007; Matthews et al., 2008; LaVigne et al., 2010; Moyer et al., 2012; Grottoli et al., 2013).

The ratio of barium to calcium in tropical surface coral skeleton (Ba/Ca_{coral}) has been shown to track upwelling and/or coastal runoff, depending upon the local sources of barium to surface waters (e.g. Lea et al., 1989; Sinclair and McCulloch, 2004b; Sinclair, 2005; Montaggioni et al., 2006; Fleitmann et al., 2007; Prouty et al., 2010; Maina et al., 2012; Moyer et al., 2012). Barium is removed from the dissolved phase in the upper water column by the precipitation of micron-scale barite crystals, formed in microenvironments of decaying organic matter and probably by other poorly described mechanisms as well (Dehairs et al., 1980; Bishop, 1988; Ganeshram et al., 2003). Barium is then returned to the dissolved phase in the thermocline and below, such that the resultant vertical concentration profile resembles that of silicate, which is remineralized deeper than nitrate and phosphate. Because of this "nutrient-like" Ba_{SW} water column profile, Ba/Ca in surface corals has been used to reconstruct changes in the upwelling of nutrient-rich thermocline waters (Lea et al., 1989; Fallon et al., 1999; Montaggioni et al., 2006; Allison and Finch, 2007). However, the increase of Ba_{SW} with depth is relatively subtle compared to the major nutrients nitrate and phosphate. Therefore, terrestrial runoff inputs of Ba to coastal upwelling sites can compromise the interpretation of Ba/Ca as an upwelling proxy in some locations. In coastal regions affected by riverine input, skeletal Ba/Ca has been shown to track changes in riverine sediment discharge, as barium desorbs from suspended sediment in low salinity estuarine waters, increasing Ba_{SW} and thus, skeletal Ba/Ca_{coral} (Li and Chan, 1979; Alibert et al., 2003; McCulloch et al., 2003; Sinclair and McCulloch, 2004a; Fleitmann et al., 2007; Prouty et al., 2008, 2010; Carriquiry and Horta-Puga, 2010; Horta-Puga and Carriquiry, 2012; Maina et al., 2012; Moyer et al., 2012; Mallela et al., 2013).

While the previous work discussed above has correlated Ba/Ca_{coral} variations to the occurrence of upwelling and terrestrial runoff events, the lack of a direct calibration of Ba/Ca_{coral} against Ba_{SW} has limited interpretations to *relative* changes in Ba/Ca_{coral} rather than quantitative reconstructions of absolute Ba_{SW}. Quantitative estimates of Ba_{SW} concentration from modern high-resolution coral records would allow for modeling seasonal-centennial variations in upwelling depth, riverine flux, or removal via primary production and barite formation (Lea et al., 1989).

Previous studies of foraminifera, deep sea corals, and inorganic precipitation of calcium carbonate have demonstrated that barium incorporates into calcite and aragonite in proportion to the Ba/Ca ratio of seawater (Kitano et al., 1971; Lea and Boyle, 1989; Lea et al., 1989; Lea and Spero, 1992; Dietzel et al., 2004; Anagnostou et al., 2011; Hönisch et al., 2011; LaVigne et al., 2011). Based on the assumption that cations in general incorporate into carbonates via inorganic substitution for calcium, distribution coefficients (D) have been used to relate the composition of these carbonates to that of the solution from which they precipitated (Morse and Bender, 1990).

$$D_{Ba} = \frac{Ba/Ca_{CaCO_3}}{Ba/Ca_{SW}} \tag{1}$$

Values for D_{Ba} have been found to be roughly similar for various species of aragonitic surface-dwelling and deep sea corals as well as inorganic aragonite (~1.2–1.4), suggesting that barium incorporation occurs via relatively simple ionic substitution and is not affected by the presence of symbionts or other vital effects (Lea and Boyle, 1989; Lea et al., 1989; Lea and Spero, 1992; Alibert et al., 2003; Dietzel et al., 2004; Anagnostou et al., 2011; Hönisch et al., 2011; LaVigne et al., 2011). Values of D_{Ba} that are estimated from coral analysis coupled to regional estimates of seawater barium concentrations, disconnected in time or space from the coral growth location, may lead to inaccuracies in the reconstruction of absolute Ba_{SW} concentration in the past. For example, acknowledging the lack of a direct calibration, Lea et al. (1989) used $D_{Ba} = 1.3$, estimated from mean Ba/Ca measured in Bermuda *Montastrea annularis* and *Diploria labyrinthiformis* corals and Ba_{SW} from a single GEOSECS station located 1700 km northeast of Bermuda to reconstruct Ba_{SW} variations in Galápagos from a *Pavona clavus* Ba/Ca_{coral} record. Little progress in refining measurements of D_{Ba} or exploring taxonomic or other dependencies of the Ba/Ca proxy has been made in the ensuing 25 years.

Recent work on previously established hermatypic coral proxies ($\delta^{18}O$, Sr/Ca, and Cd/Ca) has shown that averaged multi-colony records can yield more accurate seawater reconstructions (DeLong et al., 2007, 2011, 2013; Goodkin et al., 2007; Linsley et al., 2008; Matthews et al., 2008; Grottoli et al., 2013). Therefore, the natural variability in Ba/Ca_{coral} records among co-located colonies and taxa must be assessed to evaluate the reproducibility and accuracy of downcore Ba_{SW} reconstructions.

A field-based study carried out in the Gulf of Panamá in 2003 led to the first direct calibration of two trace elemental upwelling tracers in surface-dwelling corals: Cd/Ca and P/Ca (Matthews et al., 2008; LaVigne et al., 2010; Grottoli et al., 2013). This work revealed good intercolony reproducibility for P/Ca in *Pavona gigantea* and *Porites lobata* corals, however, Cd variability among co-located colonies suggests that Cd records derived from a single coral may not yield reliable upwelling reconstructions (Matthews et al., 2008; Grottoli et al., 2013). In this study, we take advantage of this unique set of seawater and coral samples to develop the first multi-colony calibrations for Ba/Ca_{coral} using a contemporaneous Ba/Ca_{SW} record.

2. METHODS

2.1. Samples

An archived set of replicate coral colonies and a time series of *in situ* seawater samples from a previous study in the Gulf of Panamá were analyzed to assess inter-colony Ba/Ca_{coral} reproducibility (Matthews et al., 2006, 2008; LaVigne et al., 2010; Grottoli et al., 2013). Full field study details are available in Matthews et al. (2008). In short, we analyzed nine coral colonies (three *P. lobata*, three

P. clavus, and three *P. gigantea*) reared at the same site (Isla Contadora, 1 m depth below mean low tide) with corresponding *in situ* seawater samples collected every three days through both upwelling and non-upwelling intervals. At the start of the experiment, all colony fragments were collected regionally from ~1 to 4 m depth, stained with Alizarin Red, and cemented to the reef at 1 m depth for the duration of the experiment. The *P. lobata* and *P. gigantea* colonies were collected within ~15 m of the study site. Because of the lack of individuals growing near the study site, the *P. clavus* colonies used in this experiment were transplanted from the North coast of Isla Contadora to the South coast study site (a distance of 1.1 km). Sea surface temperature (SST), salinity, and light intensity were measured from January to July 2003 at Isla Contadora with seawater samples collected at 1 m depth every three days, filtered, and acidified following trace metal clean procedures (Field et al., 2007; Matthews et al., 2008). The corals were stained *in situ* with Alizarin Red on 31 January 2003, 15 April 2003, and 13 July 2003 (marking the beginning, middle, and end of the six-month study period) and harvested in February 2004. Skeletal extension was measured between each pair of stain lines using a micrometer to calculate the skeletal extension rates (Fig. S1).

The skeletal Ba/Ca data shown here were collected during the ICP-MS analysis of these coral samples for P/Ca; the latter results were published previously (LaVigne et al., 2010). Full analytical details can be found in LaVigne et al. (2010). In brief, contiguous powdered samples (1–2 mg) were extracted from each colony, resulting in ~2–3 week temporal resolution over the period investigated for all samples except PG3, which resulted in ~6 week resolution. The powders were collected near the surface organic tissue layer, thus an oxidative/reductive solution cleaning technique was performed as a precaution on all samples to remove any residual non-skeletal matrix organic matter that could overprint the trace element signals incorporated into the aragonite matrix (Shen and Boyle, 1988).

These skeletal transects covered ~1 year of growth: the ~6 months prior to the study as well as the 6 month study period following transplantation and initiation of the seawater sampling. Only Ba/Ca$_{coral}$ data measured at or between the stain lines are reported in Fig. S1. Samples collected below (earlier than) the first stain line were used solely for Sr/Ca-SST age model reconciliation purposes (described below: Section 2.3). The Ba/Ca$_{coral}$ data collected below the first stain line (reported in Fig. S1) were excluded from the Ba/Ca calibrations since this skeletal material is likely a combination of carbonate deposited prior to the Ba$_{SW}$ sampling interval when corals were growing at different locations and skeletal material thickened during the study period. It is probable that some backfilling due to thickening of the skeleton may have affected all of the Gulf of Panamá coral skeleton used in this study. Although the samples below the last stain line likely included some material deposited after the study period, this would have occurred during late summer when all colonies were co-located and stable stratified conditions typically persist for several months.

2.2. Analyses

All sample preparation and high resolution inductively couple plasma mass spectrometry (HR-ICP-MS) and inductively couple plasma optical emission spectrometry (ICP-OES) analyses followed standard laboratory protocols for trace element analysis under Class 100 conditions. All solutions were made with ultrapure reagents (OPTIMA grade, Fisher Scientific) and Milli-Q (18.2 MΩ-cm, Millipore, MA, USA) water unless otherwise noted. Coral powders were dissolved in 1 N HNO_3 and analyzed following the solution phase HR-ICP-MS method described in LaVigne et al. (2010). In order to minimize differential plasma matrix effects between samples during analysis (de Villiers et al., 1994; Rosenthal et al., 1999), the dissolution volume of each sample was tailored to achieve 4 mM Ca and 1.0–1.5 mM Ca in 3% HNO_3 for HR-ICP-MS and ICP-OES measurement, respectively. The Ba/Ca measurements were carried out on an Element-XR (Thermo Scientific, Bremen, Germany) HR-ICP-MS equipped with a quartz spray chamber and a PFA MicroFlow nebulizer. The instrument was operated in low-resolution mode for analyzing barium and calcium using isotopes selected to maximize natural abundance and minimize polyatomic interferences (^{138}Ba and ^{48}Ca). The average analytical reproducibility for Ba/Ca measurements was ±5.8% based on replicate runs of an in-house matrix-matched coral consistency standard (9.9 ± 0.58 μmol/mol; 1 SD; $n = 24$) and duplicate dilutions of samples (average deviation from mean for $n = 9$ pairs of duplicates = 0.14 μmol/mol or 2.5% average deviation from mean). The Ba and Ca blanks subtracted from sample signals were <0.1% and <0.02% respectively. Six apparent outliers with high Ba/Ca values were selected from the data for reanalysis in a separate run. The data from four of the six re-analyzed samples did not agree with the initial Ba/Ca measurements (within uncertainty), therefore, these samples were excluded from further analysis. In addition, two outliers (PG1 7–9 mm and PL1 17–18 mm) were excluded from data analysis because of anomalously high Ba/Ca values compared against overlapping and/or neighboring data points and were likely a result of contamination or inefficient removal of organic matter during cleaning of those samples.

The filtered seawater samples were diluted by a factor of ten and analyzed for dissolved barium (Ba$_{SW}$) using a HR-ICP-MS method described by Field et al. (2007). The average analytical reproducibility for Ba$_{SW}$ measurements was ~2% based on the analysis of replicate dilutions of 10 samples (average deviation about mean = 1.173 nmol/kg 1 SD; $n = 10$ duplicate pairs). Repeat measurements of barium in a NASS-5 seawater standard reference material agree within the uncertainty of previous measurements of barium in this standard (5.33 ± 0.02 μg/L; 1 SD; $n = 6$; National Research Council Canada; Field et al., 2007).

The Sr/Ca data used in this study for the *P. lobata* and *P. gigantea* samples were generated using ICP-OES as described in LaVigne et al. (2010). The *P. clavus* corals were analyzed for Sr/Ca at Bowdoin College following the method described by (Schrag, 1999) using a MPX Vista ICP-OES (Varian, Inc., CA, USA) equipped with a cyclonic quartz spray chamber and a PFA microflow 100 (100 µL/min) nebulizer (Elemental Scientific, Inc., NE, USA). The emission line ratio calculated for data interpretation was Sr_{216}/Ca_{315}, which was determined to be most accurate and precise based on replicate analyses of an in-house matrix-matched coral standard and an otolith certified reference material for trace metals (FEBS-1; National Research Council Canada). The mean of repeat measurements of Sr/Ca in FEBS-1 (2.270 ± 0.0175 mmol/mol; 1SD; 0.77% RSD; $n = 12$) agreed within the uncertainty of previously published measurements (2.33 ± 0.14 mmol/mol: Robinson et al., 2009) and was accurate within 2% of the certified range of the standard (2.45 ± 0.13 mmol/mol). Reproducibility for Sr/Ca determinations of an in-house consistency standard ($n = 15$) and replicate dilutions of samples ($n = 8$ pairs of duplicates) over three days of analyses was 0.7% RSD.

2.3. Age model

Smoothing relative to short-term environmental variations was observed in the skeletal Ba/Ca records of all three coral taxa, similar to that seen in the P/Ca and Cd/Ca records from these samples (Matthews, 2007; LaVigne et al., 2010; Grottoli et al., 2013). This smoothing of geochemical signals most likely results from a combination of the ~1 mm (~2–3 week) sampling resolution as well as skeletal thickening caused by calcification throughout the coral tissue layer (Barnes and Lough, 1993; Taylor et al., 1993; Barnes et al., 1995). Skeletal thickening has been found to result in a "bio-smoothing" of Sr/Ca records within the tissue layer during skeletogenesis in *Porites* corals (Gagan et al., 2012). We assume that thickening affected Sr/Ca, Ba/Ca, and P/Ca equally, and thus, applied the same Sr/Ca-derived age model used for the P/Ca data to the corresponding Ba/Ca measurements from the *P. lobata* and *P. gigantea* coral samples (LaVigne et al., 2010). Because the *P. clavus* corals were not analyzed for Sr/Ca in the previous study, we followed the same approach to derive age models based on the new *P. clavus* Sr/Ca data.

In brief, following the method of (Swart et al., 2002), we used a Sr/Ca – SST chronology adjustment as an independent method of accounting for the timing offset between the incorporated coral records and *in situ* seawater records. The stain-line derived chronology was adjusted to align the Sr/Ca coral record with the *in situ* seawater SST measurements. Dates were assigned to three inflection points in the coralline Sr/Ca records to adjust the chronology of each colony so that Ba/Ca calibrations could be calculated appropriately (Fig. S2). Low-resolution evenly spaced sampling between the stain lines of corals with uneven growth rates and differences between stain-derived and Sr/Ca age models resulted in relatively short Ba/Ca records for some corals (e.g. PG1 and PG2). Unequal representation of seasons in coral records with variable growth rates has also been observed in isotopic records from the Galápagos upwelling region (Wellington et al., 1996). The skeletal Sr/Ca-SST age model adjustment described above accounts only for geochemical signal stretching caused by thickening. In addition to stretching the environmental signal, we also expected the skeletal thickening process and sampling integration to produce smoothed skeletal records relative to the high-resolution seawater signal (Cohen and Thorrold, 2007; Gagan et al., 2012). Therefore, to compensate for this effect, the Ba_{SW} data were smoothed using a 2–7 point moving average before re-sampling at the resolution of the coral data using the linear integration interpolation function of the AnalySeries program, as was performed for previous P/Ca-PO_{4SW} calibrations (Paillard et al., 1996; LaVigne et al., 2010). We identified the appropriate Ba_{SW} smoothing window to account for "bio-smoothing" in each colony (2–7 points of the seawater record: equivalent to ~1–3 weeks) by optimizing the coral Ba/Ca- smoothed Ba_{SW} correlation coefficient (LaVigne et al., 2010). This degree of smoothing occurs on a shorter timescale than the "bio-smoothing" found for Sr/Ca signals in *Porites* corals by Gagan et al. (2012: 3–12 months). We acknowledge, however, that any uncertainty in the Sr/Ca-derived age model would affect our estimate of Ba/Ca signal "bio-smoothing". Although Gagan et al. (2012) found that 3–12 month smoothing windows can attenuate environmental signals by 2–64% in *Porites* corals, we did not observe any attenuation of the seasonal Ba_{SW} signal in the Ba/Ca_{coral} records using the 1–3 week smoothing window that was found to be optimal for our samples. The similar range of smoothing windows required for all three coral taxa suggests that the signal smoothing observed for *Porites* by Gagan et al. (2012) also occurs in the *Pavona* species studied here.

2.4. Statistical analysis

Pearson correlation coefficients (r) were used to determine the degree of linear correlation between Ba/Ca_{coral} and Ba_{SW} for each colony analyzed. p-Values below 0.05 were considered statistically significant unless otherwise noted. Calibration slopes and y-intercepts were calculated to model the relationship between Ba/Ca_{coral} and Ba_{SW} using the Deming regression method, which accounts for uncertainties in both x and y variables. Statistical analyses were performed using Prism 6 software for Mac (Version 6.0d, October 2013, GraphPad Software, Inc.) and R (R Core Team, 2012).

3. RESULTS AND DISCUSSION

3.1. Dissolved barium variability in the Gulf of Panamá

The *in situ* SST, sea surface salinity (SSS), Cd_{SW}, and soluble reactive phosphate (PO_4) data collected throughout the study period have been used to calibrate Cd/Ca and P/Ca proxies in surface-dwelling corals (Matthews et al., 2008; LaVigne et al., 2010; Grottoli et al., 2013). New barium data measured in these seawater and coral samples now allow us to test the characteristics of the Ba/Ca_{coral} proxy. In addition, the Gulf of Panamá seawater data provide insight into the drivers of surface nutrient and trace element variability that could affect how these proxies are interpreted in corals from similar coastal upwelling regimes (Fig. 1). Early in the year (January–April), the ITCZ is located south of Panamá such that northerly winds

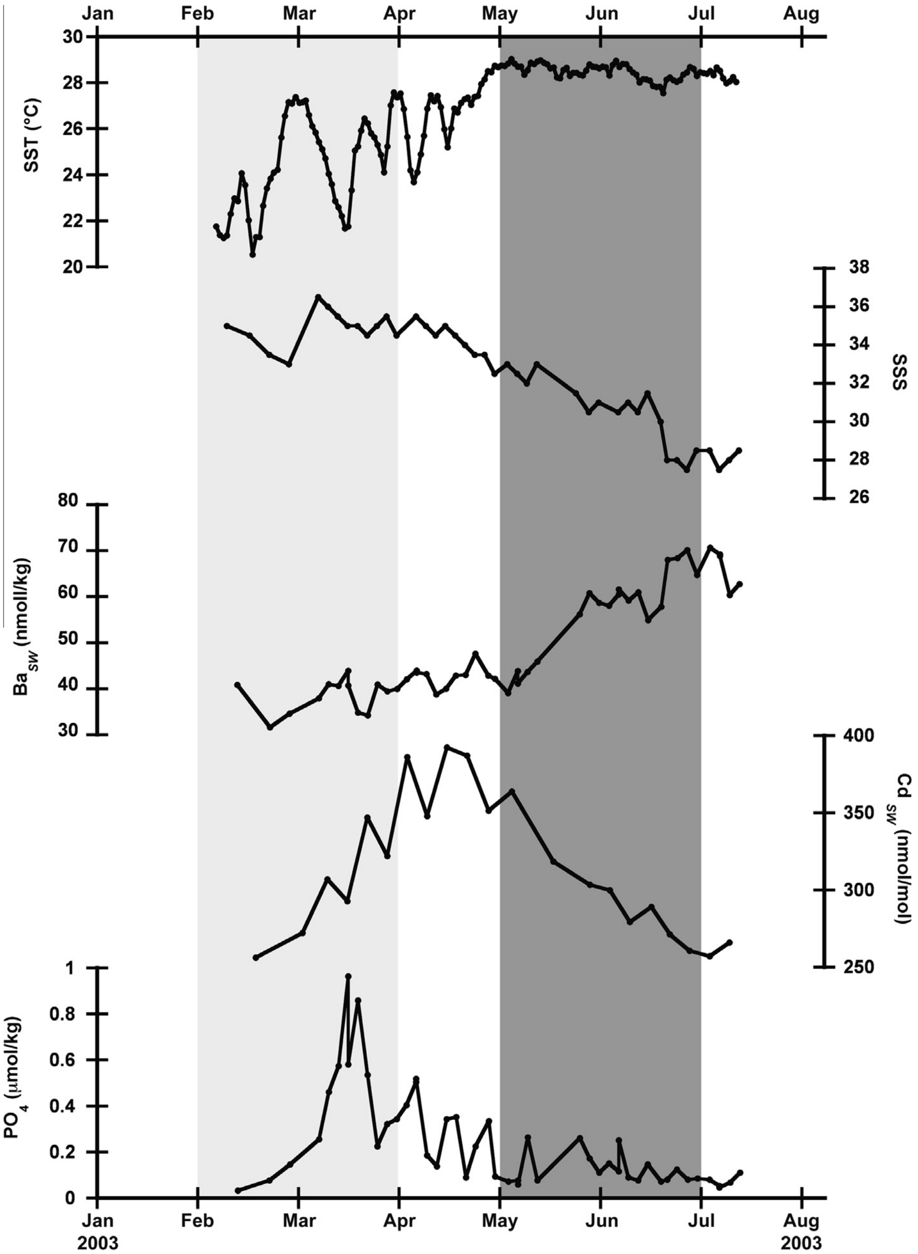

Fig. 1. *In situ* sea surface temperature (SST), sea surface salinity (SSS), dissolved barium (Ba_{SW}), cadmium (Cd_{SW}; Grottoli et al., 2013), and soluble reactive phosphate (PO_4; LaVigne et al., 2010) measured through the 2003 study period in the Gulf of Panamá. Uncertainties on Ba_{SW}, Cd_{SW}, and PO_4 measurements are 1.173 nmol/kg Ba (average deviation about the mean for $n = 10$ pairs of replicate dilutions), 6.3 nmol/kg Cd (RSD; $n = 10$), and 0.026 µmol/kg PO_4 (average deviation about the mean for $n = 14$ pairs of analytical duplicates). Typical seasons of runoff minimum (February–March) and maximum (May–June) identified by light and dark gray shading, respectively (Forsbergh, 1969; D'Croz et al., 1991). Tick marks on time axis are first day of month.

promote upwelling and dry atmospheric conditions in the Gulf. Summer months (May–December), however, are characterized by low atmospheric pressure, increased precipitation, and warm stratified conditions resulting from the more northerly position of the ITCZ (Forsbergh, 1969; D'Croz et al., 1991). The SST and SSS data collected in 2003 demonstrate this transition from the pulsed cool SST upwelling events prevailing in the relatively dry and higher salinity months of late Winter/early Spring to the warm stratified lower-salinity conditions common in the rainy summer season (Forsbergh, 1969; D'Croz et al., 1991; Fig. 1). The Cd_{SW}, PO_4, and Ba_{SW} time series data collected through this transition demonstrate the unique temporal behavior for each of these biogeochemically relevant properties in surface waters of a coastal upwelling site (Fig. 1).

Skeletal barium, cadmium, and phosphorus have all been considered as proxies for wind-driven upwelling in surface-dwelling corals based upon the general enrichment of these macro and micro nutrients with increasing depth in the ocean (e.g. Shen et al., 1987; Lea et al., 1989; Matthews et al., 2008; LaVigne et al., 2010; Grottoli et al., 2013). However, our data indicate that surface concentrations of these elements do not all vary concurrently with upwelling on sub-annual (weekly-monthly) timescales in the Gulf of Panamá (Fig. 1). Surface phosphate bears the closest resemblance to the pulsed upwelling signal with concentrations increasing during cool upwelling pulses in late Winter/early Spring and decreasing into the non-upwelling season. Dissolved cadmium, however, peaks later in the year (~mid-summer), previously suggested to be a result of biological uptake competing with upwelling supply during the highly productive Spring upwelling season, thus complicating the use of Cd/Ca as a direct proxy for upwelling (Matthews et al., 2008; Grottoli et al., 2013). Barium, which has been used as an upwelling tracer in other eastern equatorial Pacific corals, demonstrates a seasonal trend opposite to that of phosphate in Gulf of Panamá surface waters: increasing from winter to summer, with minimal apparent influence of the upwelling events that punctuate the SST and PO_4 records. Instead, Ba_{SW} has a strong inverse correlation with SSS ($r = -0.92$; $p < 0.0001$; Fig. 2), indicating that seasonal barium variability at this location is driven more by terrestrial runoff supply to surface waters during the rainy summer season than by upwelling supply from subsurface waters in winter (Fig. 1). Extrapolating our Panamá regression of Ba_{SW} to SSS (Ba_{SW} (nmol/kg) = −3.88 * SSS + 174.96) back to the approximate salinity of peak dissolved barium concentrations in estuaries (~4) yields a dissolved barium concentration of ~160 nmol/kg, which is in agreement with an average of peak barium concentrations in the Zaire, Amazon, Ganges, Chesapeake, and Delaware estuaries (salinity ~4 and 164 nmol/kg dissolved barium; Coffey et al., 1997). Freshwater flux to the Gulf during the high precipitation season likely causes barium to desorb from river-borne suspended particulate matter during transport from fresh to saline waters (Li and Chan, 1979; Coffey et al., 1997). Runoff into Panamá Bight is typically greatest in May–June and lowest in Feb–March (Forsbergh, 1969; Fig. 1). The sharp increase in Ba_{SW} following a minimum in ~Feb–March corresponds to this timing (Fig. 1). This suggests that instead of acting as a tracer of upwelling at this site, Ba/Ca_{coral} likely serves as a proxy for terrestrial runoff even in this strong upwelling region. Taken together, these data show that proxies typically considered to be tracers of upwelling in corals (e.g. Cd/Ca, P/Ca, Ba/Ca) must be carefully interpreted in light of local processes affecting surface water biogeochemistry. Conversely, studies using a well-calibrated multi-proxy approach could take full advantage of the variety of processes affecting these tracers to provide a more complete picture of the complex biogeochemical variations that may occur in such regions.

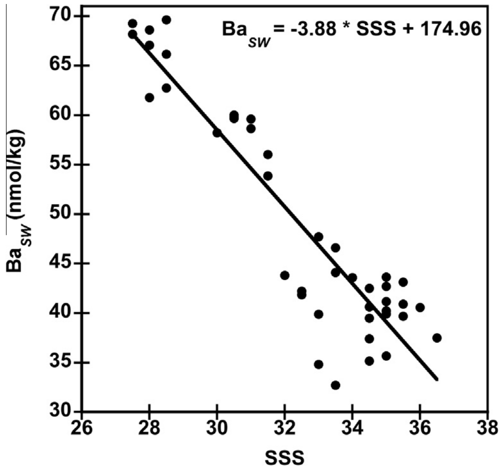

Fig. 2. Dissolved barium (Ba_{SW}; this study) vs. sea surface salinity (SSS; Matthews et al., 2008) for the coral growth site in the Gulf of Panamá, measured through the study period.

3.2. Ba/Ca_{coral} calibration against *in situ* Ba_{SW}

3.2.1. *Intercolony Ba/Ca reproducibility*

The unique set of replicate coral and contemporaneous *in situ* seawater samples collected from Isla Contadora, Panamá allows us to assess natural Ba/Ca variability among co-located coral colonies and taxa. All nine *P. lobata*, *P. gigantea*, and *P. clavus* colonies grew through the mid-year transition from dry to rainy conditions in 2003, and recorded the ~35 nmol/kg Ba_{SW} increase as a ~1–4 µmol/mol (20–70%) rise in skeletal Ba/Ca (Figs. S1 and 3). A similar degree of Ba/Ca increase has been observed during flood events in Great Barrier Reef *Porites* corals (McCulloch et al., 2003). The reproducibility among the replicate colony records plotted in Fig. 3 was evaluated by calculating correlation coefficients (r) between their Ba/Ca_{coral} records within each taxon. Each colony record was re-sampled at the timescale of each of the other corals using AnalySeries to construct common timescales such that correlation coefficients and p-values could be calculated. Within each taxon, we find excellent agreement between members of each pair of the replicate colony Ba/Ca_{coral} records ($r = 0.86$–0.99; Table 1). The correlation coefficients for the *P. gigantea* replicate corals and one of the *P. clavus* coral pairs, however, were not statistically significant ($p > 0.05$; Table 1). This is likely a result of the lower growth rates of the *P. gigantea* records resulting in lower resolution records and thus, fewer data points as compared to the other taxa (Table 1 and Fig. 3). The excellent agreement for the *P. lobata* and *P. clavus* corals, however, demonstrates a high level of intercolony reproducibility among the Ba/Ca_{coral} records. The Ba/Ca increase occurred at least 5–10 mm below the tissue layer in each coral and based on the agreement among colonies, the Ba/Ca increases measured are not a result of inefficient cleaning of organic tissue. Longer or higher resolution records from the *P. gigantea* corals are required to evaluate the significance of the apparent agreement among the co-located *P. gigantea* colonies studied here (Fig. 3; Table 1). Applying the Sr/Ca-derived age models to the high-resolution Ba/Ca_{coral} data (Section 2.3) allowed us to perform linear regressions against Ba_{SW} for each of the nine corals.

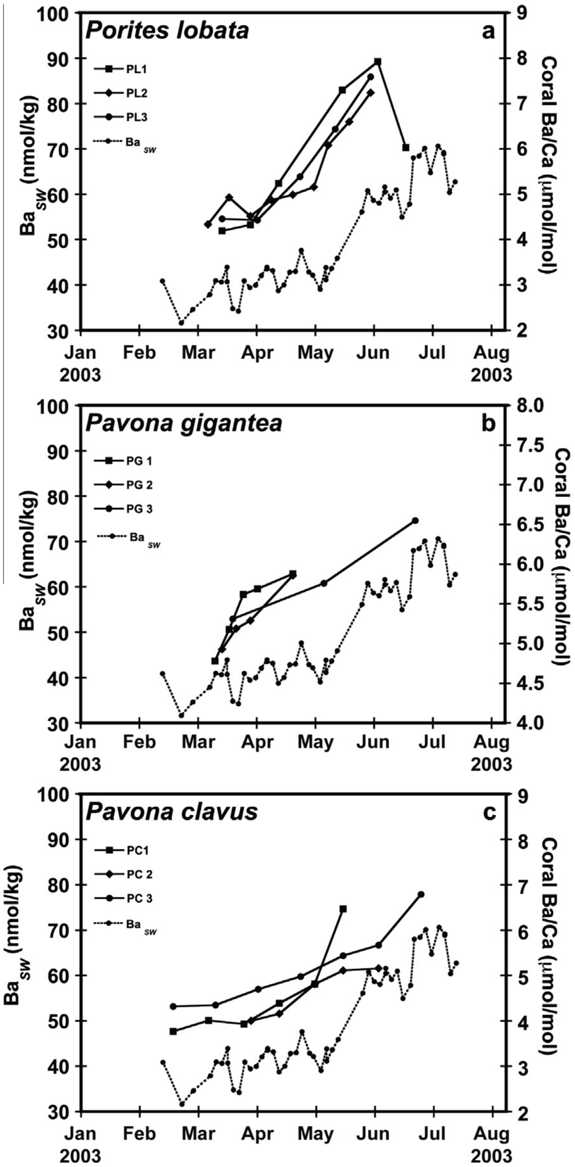

Fig. 3. *In situ* Ba_{SW} time series (dotted line; left y-axis) and contemporaneous timescale-adjusted coral Ba/Ca results (right y-axis) for triplicate colonies of *Porites lobata* (a) *Pavona gigantea* (b) and *Pavona clavus* (c) through the 2003 study period in the Gulf of Panamá. Uncertainty on coral Ba/Ca data points, based on repeat measurements of coral consistency standard, is 0.58 µmol/mol (1 SD; $n = 24$). Uncertainty in Ba_{SW} is 1.173 nmol/kg based on the average deviation about the mean for duplicate dilutions of 10 samples. Tick marks on time axis are first day of month.

3.2.2. Taxon-specific regressions

With Ba/Ca_{coral} data from multiple well-dated co-located coral colonies and a high-resolution contemporaneous *in situ* Ba_{SW} record, we can generate colony-specific Ba/Ca regressions and begin to evaluate inter-colony calibration reproducibility. Pearson correlation coefficients reveal a linear relationship between Ba/Ca_{coral} and Ba_{SW} for all nine coral colonies ($r = 0.70$–0.99), five of which are statistically significant ($p < 0.04$; Table S1). Regressions of Ba/Ca_{coral} against the re-sampled Ba_{SW} record were used to construct individual calibration equations for each of the nine colonies (Fig. 4 and Table S1).

Table 1
Correlation (r) between Ba/Ca records for replicate colonies of each taxa.

Porites lobata	PL2	PL3
PL1	0.96 ($p = 0.01$; $n = 5$)	0.97 ($p = 0.005$; $n = 5$)
PL2	–	0.99 (p = 0.002; n = 5)
PL3	–	–
Pavona gigantea	PG2	PG3
PG1	0.90 ($p = 0.1$; $n = 4$)	0.95 ($p = 0.2$; $n = 3$)
PG2	–	0.99 ($p = 0.09$; $n = 3$)
PG3	–	–
Pavona clavus	PC2	PC3
PC1	0.86 ($p = 0.06$; $n = 5$)	0.92 ($p = 0.01$; $n = 6$)
PC2	–	0.95 ($p = 0.01$; $n = 5$)
PC3	–	–

Within each genus, the individual colony regressions agree within the uncertainty of their calculated slopes and y-intercepts except for two colonies (PG3, which consists of only three data points and is not statistically significant, and PC1; Table S1). The lack of statistical significance for colonies PL1, PG1, and PC2 is likely a result of two factors influencing these data sets ($p = 0.09$–0.12; Table S1). First, low sampling resolution and growth rates for some colonies result in very few Ba/Ca measurements within the study period available for the regression calculations (e.g. PG3 $n = 3$). Second, the coral data from several colonies do not span a very large dynamic range in Ba_{SW}. This can occur as a result of evenly spaced sampling of corals that do not have constant growth rates (Wellington et al., 1996). For example, for colonies PG1, PG3, and PC2, most of the data points sampled from the coral fall in the early stable portion of the Ba_{SW} record (Figs. 3 and 4). Because the samples were drilled by hand at ~1 mm resolution on corals with varying growth rates, the sampling resolution and distribution of samples through the study period can vary from coral to coral. Compared to other seawater parameters (for example, phosphate), the Ba_{SW} transition occurs later in the study period (May 2003) during a period when fewer samples were extracted from the corals (Fig. 3). Thus, even though there is overlap between colony regression standard errors, the uncertainty associated with reconstructed Ba_{SW} measurements made with these individual colony-specific regressions would be too large for reliable proxy reconstructions (17–200% or ±7–80 nmol/kg Ba_{SW} for the range of Ba_{SW} values studied here: ~40–70 nmol/kg). The overall intercolony agreement is good among the Ba/Ca_{coral} records themselves, however additional work is needed to construct and compare higher-resolution calibrations from individual colonies.

Recently, multi-colony calibrations and reconstructions have been found to improve the accuracy and precision of coralline paleoceanographic reconstructions (e.g. DeLong et al., 2007, 2013, 2014; Goodkin et al., 2007; Linsley et al., 2008; Matthews et al., 2008; Pfeiffer et al., 2009;

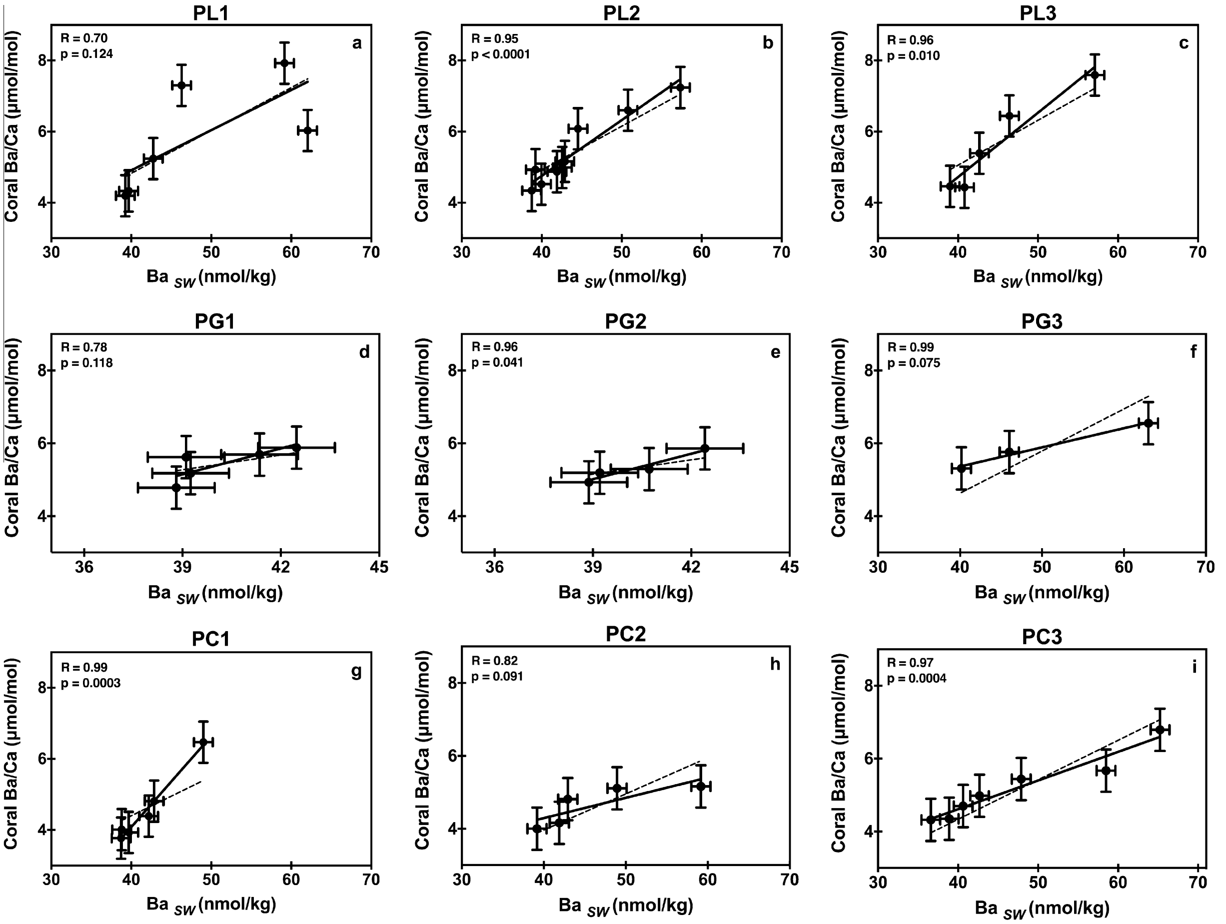

Fig. 4. Local Ba/Ca-Ba$_{SW}$ calibrations for individual colonies of Gulf of Panamá *Porites lobata* (a–c) *Pavona gigantea* (d–f) and *Pavona clavus* (g–i) colonies. Regressions were calculated from coral Ba/Ca (y-axis) and local re-sampled Ba$_{SW}$ time-series (x-axis; see text). X and Y error bars represent average deviation about the mean for duplicate Ba$_{SW}$ measurements ($n = 10$ pairs of replicate dilutions; avg. dev. = 1.173 nmol/kg Ba), and repeat measurements of coral consistency standard (SD = 0.58 µmol/mol; $n = 24$) respectively. Deming model II equations (solid black lines) and linear regressions forced through the origin (dashed lines) are plotted for each colony.

Grottoli et al., 2013; Williams et al., 2014). Given the inter-colony reproducibility in the Gulf of Panama Ba/Ca$_{coral}$ records and broad overlap in the standard error of the individual regression slopes and y-intercepts, we pooled the data from the three replicate colonies for each taxon studied into the following composite regressions (Fig. 5 and Table S1).

$$\mathrm{Ba/Ca}_{Porites\ lobata}(\mu\mathrm{mol/mol}) = [0.14 \pm 0.02] \cdot [\mathrm{Ba}_{SW}\ \mathrm{nmol/kg}] - [0.8 \pm 1.0] \quad (2)$$

$$\mathrm{Ba/Ca}_{Pavona\ gigantea}(\mu\mathrm{mol/mol}) = [0.06 \pm 0.01] \cdot [\mathrm{Ba}_{SW}\ \mathrm{nmol/kg}] + [3.0 \pm 0.6] \quad (3)$$

$$\mathrm{Ba/Ca}_{Pavona\ clavus}(\mu\mathrm{mol/mol}) = [0.09 \pm 0.015] \cdot [\mathrm{Ba}_{SW}\ \mathrm{nmol}/kg] + [0.9 \pm 0.7] \quad (4)$$

All multi-colony data sets reveal strong statistically significant relationships between Ba/Ca$_{coral}$ and Ba$_{SW}$ for the three taxa studied ($r = 0.8$; $p < 0.001$; Fig. 5). Using constructed linear mixed effects models in R using the lme4 package (R Core Team, 2012; Bates et al., 2012; Winter, 2013) to test for colony-specific effects, we found slopes and y-intercepts that agree within the uncertainty of the Deming regression for each taxon. In the mixed effect model analyses, we treated the relationship between Ba$_{SW}$ and Ba/Ca$_{coral}$ as a fixed effect, and colony-specific intercepts as a random effect. The uncertainty in absolute Ba$_{SW}$ values reconstructed using the composite calibrations (Eqs. (2)–(4)) is lower than that using the individual colony regressions (±~14–27 nmol/kg vs. up to ± 80 nmol/kg Ba$_{SW}$ for the range of Ba$_{SW}$ values studied here: ~40–70 nmol/kg), but suggests that the calibrations would benefit from further refinement. The *P. lobata* and *P. clavus* slopes and y-intercepts from the individual colony regressions agree within the uncertainty of the composite calibration equation except for one colony (PC1). The PC1 regression appears to be driven by a single data point at the high end of the regression (Fig. 4). The individual *P. gigantea* colony slopes and y-intercepts, however, do not all agree with the composite equation, which is likely a result of the narrow dynamic range covered by these records as discussed above. Because the composite regressions reveal more robust relationships between Ba/Ca$_{coral}$ and Ba$_{SW}$ compared to the individual colony regressions,

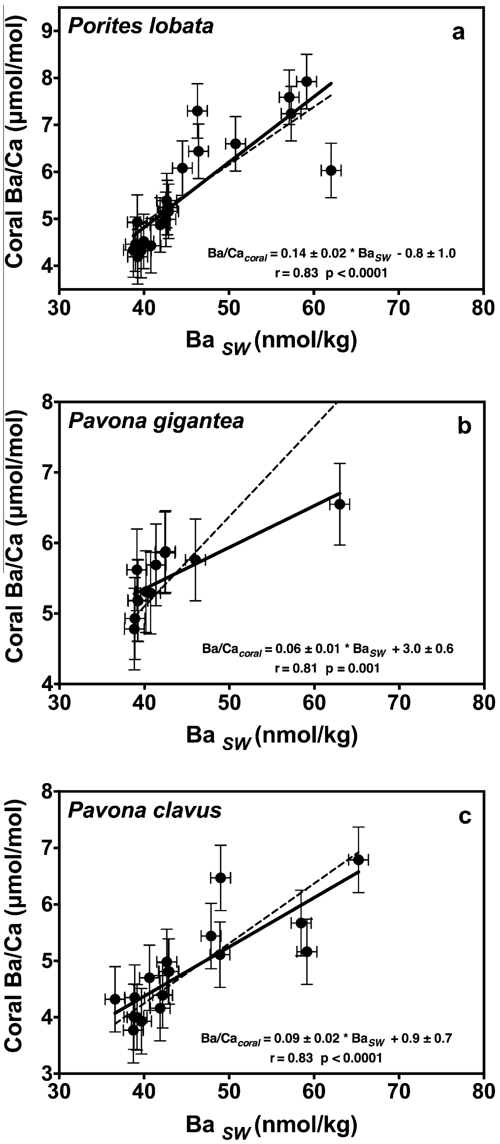

Fig. 5. Multi-colony composite Ba/Ca$_{coral}$ – seawater barium concentration (Ba$_{SW}$) calibrations for Gulf of Panamá *Porites lobata* (a) *Pavona gigantea* (b), and *Pavona clavus* (c) colonies. Regressions were calculated from coral Ba/Ca pooled from three replicate colonies (*y*-axis) and local re-sampled Ba$_{SW}$ time-series (*x*-axis; see text). *X* and *Y* error bars represent mean deviation for duplicate Ba$_{SW}$ measurements ($n = 10$ pairs of replicate dilutions; (avg. dev. = 1.173 nmol/kg Ba), and repeat measurements of coral consistency standard (SD = 0.58 µmol/mol; $n = 24$) respectively. Deming model II regression equations (solid black lines) and linear regressions forced through the origin (dashed lines) are plotted for each taxon.

multi-colony reconstructions of Ba$_{SW}$ would likely yield more precise results than single colony records. Future work with longer records covering a range of measured Ba$_{SW}$ would allow for a more sophisticated statistical analysis of the inter-colony reproducibility of the Ba/Ca$_{coral}$ calibrations, as has been accomplished recently for Sr/Ca and Mg/Ca in other coral archives (e.g. DeLong et al., 2007; Goodkin et al., 2007; Pfeiffer et al., 2009; DeLong et al., 2011, 2013; Williams et al., 2014).

3.2.3. Incorporation of barium and implications for reconstructions

Distribution coefficients (D_{Ba}) were calculated for each coral by dividing the mean Ba/Ca$_{coral}$ value for each colony by the mean of the Ba/Ca$_{SW}$ values calculated for each colony as described below (Eq. (1); Table S2). We find very good agreement among colony-specific *D*-values within each taxon (2–7% RSD; Table S2). This agreement among *D*-values and Ba/Ca$_{coral}$ records constructed from contemporaneous co-located colonies demonstrates a high level of intercolony reproducibility and supports the validity of the Ba/Ca coral proxy for *P. lobata*, *P. clavus* and *P. gigantea* corals.

We find D_{Ba} values ranging from ~1.0 to ~1.4 for the three coral genera included in this study (Table S2). These values are similar to those of other aragonitic surface and deep sea corals (~1.3–1.5), high-Mg calcite deep sea corals (~1.3), and inorganic aragonite precipitation experiments (~1.5), but differ from foraminiferal calcite (0.15), supporting the hypothesis that surface corals incorporate Ba via ionic substitution of Ba for Ca to form witherite ($BaCO_3$; Kitano et al., 1971; Lea et al., 1989; Dietzel et al., 2004; Anagnostou et al., 2011; Hönisch et al., 2011; LaVigne et al., 2011). Therefore, we also compared the composite taxa-specific regressions expressed as Ba/Ca$_{coral}$ vs. Ba/Ca$_{SW}$ (Fig. 6). In order to calculate Ba/Ca$_{SW}$ for these regressions, we coupled our Ba$_{SW}$ measurements with estimates of Ca$_{SW}$ scaled to salinity through the study period (based on average surface Ca$_{SW}$ of 10.2 mmol/kg and salinity of 35.09 for Pacific surface waters; de Villiers, 1998). The Ba/Ca$_{SW}$ record was smoothed and resampled in the same manner as the Ba$_{SW}$ record in order to assign Ba/Ca$_{SW}$ values to the Ba/Ca data points from each colony (Section 2.3).

Based on the evidence for an ionic substitution barium incorporation mechanism, we would expect that a coral grown in seawater containing no barium would have no skeletally incorporated Ba. Thus, we compared the unforced Deming regressions of Ba/Ca$_{coral}$ vs. Ba$_{SW}$ and Ba/Ca$_{SW}$ against ordinary least squares (OLS) regressions forced through the origin. We find that the OLS regressions of Ba/Ca$_{coral}$ vs. Ba$_{SW}$ forced through the origin fall within the standard errors of the unforced individual colony linear regressions for all but two colonies (PC1 and PG3). In addition, across the range of Ba$_{SW}$ values studied here, for *P. lobata* and *P. clavus*, the forced and unforced taxa-specific linear regressions of Ba/Ca$_{coral}$ vs. Ba$_{SW}$ and Ba/Ca$_{SW}$ agree within the uncertainty (Figs. 5 and 6). This agreement suggests that applying *D*-values (or Ba/Ca$_{coral}$–Ba/Ca$_{SW}$ regressions forced through the origin: Eqs. (5) and (6)) to *P. lobata* and *P. clavus* corals corresponding to the range of Ba/Ca values studied here would yield results that fall within the uncertainty of the Ba$_{SW}$ regression calibrations reported in Section 3.2.2 (Eqs. (2)–(4); if estimates of Ca$_{SW}$ variations with sea surface salinity were taken into account). In addition, the uncertainty in absolute Ba$_{SW}$ values reconstructed using Eqs. (5) and (6) would be much lower than that resulting from the unforced colony regressions reported above (±~2–4 nmol/kg Ba$_{SW}$ for the range of Ba$_{SW}$ values studied here: ~40–70 nmol/kg or ~5–6%).

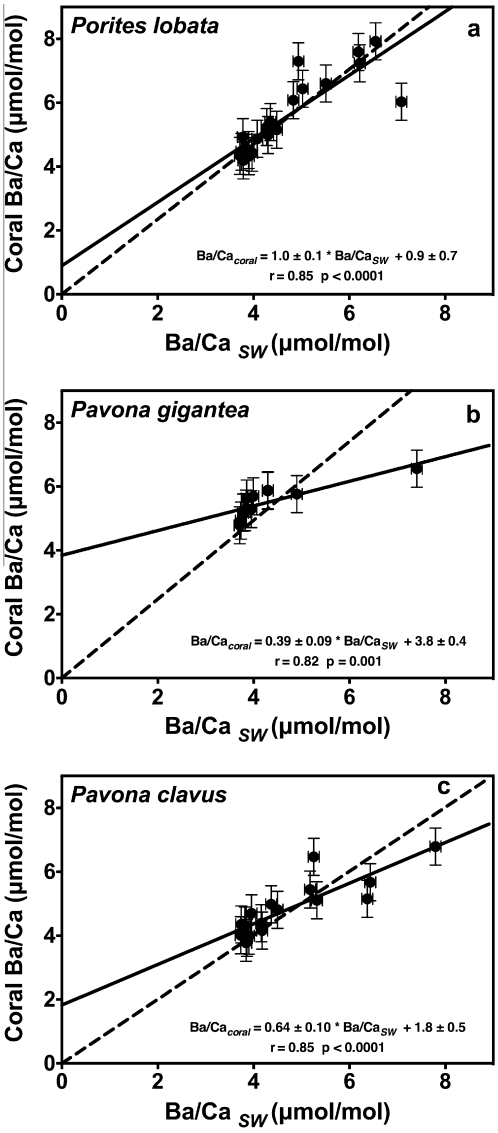

Fig. 6. Multi-colony composite Ba/Ca$_{coral}$ – seawater barium/calcium ratio (Ba/Ca$_{SW}$) calibrations for Gulf of Panamá *Porites lobata* (a) *Pavona gigantea* (b), and *Pavona clavus* colonies. Regressions were calculated from coral Ba/Ca pooled from three replicate colonies (y-axis) and local re-sampled Ba/Ca$_{SW}$ time-series (x-axis; see text). X error bars represent mean deviation for duplicate Ba$_{SW}$ measurements ($n = 10$ pairs of replicate dilutions avg. dev. = 1.173 nmol/kg Ba) propagated to estimated uncertainty on mean Ba/Ca$_{SW}$ calculated for the study period (5.324 µmol/kg). Y error bars represent Ba/Ca$_{coral}$ uncertainty based on repeat measurements of coral consistency standard (SD = 0.58 µmol/mol Ba/Ca; $n = 24$). Deming model II regression equations (solid black lines) and linear regressions forced through the origin (dashed lines) are plotted for each taxon.

For *P. gigantea* corals, however, the forced regressions do not fall within the uncertainty of the unforced regressions (Figs. 5c and 6c). The low number of data points in the upper range of the *P. gigantea* regressions suggests that additional data spanning a broader range of Ba$_{SW}$ values will likely be required before robust calibrations can be applied to *P. gigantea* coral records.

$$\mathrm{Ba/Ca}_{Porites\ lobata} = [1.18 \pm 0.03] \cdot [\mathrm{Ba/Ca}_{SW}];\ p < 0.0001; n = 20 \quad (5)$$

$$\mathrm{Ba/Ca}_{Pavona\ clavus} = [1.00 \pm 0.03] \cdot [\mathrm{Ba/Ca}_{SW}];\ p < 0.0001; n = 18 \quad (6)$$

Interestingly, the Ba/Ca$_{coral}$ regression slopes and y-intercepts calculated for the Panamá surface corals are comparable to those calculated for aragonitic and calcitic deep-sea corals (Fig. S3; Eqs. (5) and (6); Anagnostou et al., 2011; LaVigne et al., 2011). This agreement between surface and deep-sea corals and corals of different calcium carbonate polymorphs further supports an inorganic Ba incorporation mechanism that is not a function of so-called "vital effects" driven by factors such as the presence of symbionts.

In summary, our data support an inorganic substitution incorporation mechanism for barium in surface-dwelling corals, based on the following evidence: (1) A high degree of intercolony reproducibility in Ba/Ca$_{coral}$ records (Table 1 and Fig. 3) and D-values (Table S2), (2) overlap between unforced regression standard errors with those forced through the origin for *P. lobata* and *P. clavus* corals spanning the range of values studied here (Figs. 5 and 6), and (3) general agreement between surface coral barium D-values (or Ba/Ca$_{coral}$ vs. Ba/Ca$_{SW}$ regressions forced through the origin) and those of non-symbiont bearing deep-sea corals (Fig. S3).

3.2.4. Application of the Ba/Ca proxy

The first study to reconstruct upwelling trends from a Galápagos *P. clavus* Ba/Ca$_{coral}$ record lacked the species-specific calibration needed to quantify Ba$_{SW}$ (Lea et al., 1989). With the calibrations provided by this study, we can now evaluate the effect of using estimated D-values based on other coral species vs. species-specific calibrations. Lea et al. (1989) applied the best estimate of D_{Ba} available at the time (~1.3 based on Bermuda *M. annularis* and *D. labyrinthiformis* corals) to their *P. clavus* Ba/Ca$_{coral}$ record to estimate the degree of Ba$_{SW}$ variability through several upwelling periods. This revealed Ba$_{SW}$ values ranging from ~33 nmol/kg during warm stratified El Niño conditions to ~38 nmol/kg during the coolest SST upwelling intervals (Fig. 7). The D_{Ba} values calculated from our Panamá *P. clavus* corals (0.95–1.08) are lower than those used by Lea et al. (1989), suggesting that the Ba$_{SW}$ concentrations reported by Lea et al. may have been underestimated. Applying the *P. clavus* multi-colony calibration equation based on our Panamá corals to the *P. clavus* record (Lea et al. 1989; Fig. 7) suggests that Ba$_{SW}$ concentrations in Galápagos surface waters were ~7–10 nmol/kg higher than originally estimated. We find values closer to ~40 nmol/kg during warm stratified periods and 45–49 nmol/kg during cool upwelling periods. These values are in reasonable agreement with Ba$_{SW}$ measurements made more recently in a non-upwelling region of NE tropical Pacific ~35–42 nmol/kg (Esser and Volpe, 2002). The absolute change in Ba$_{SW}$ between warm and cool periods based on our calibration is roughly comparable to that estimated by Lea et al. (1989; ~9–10 nmol/kg vs. ~7 nmol/kg, respectively;

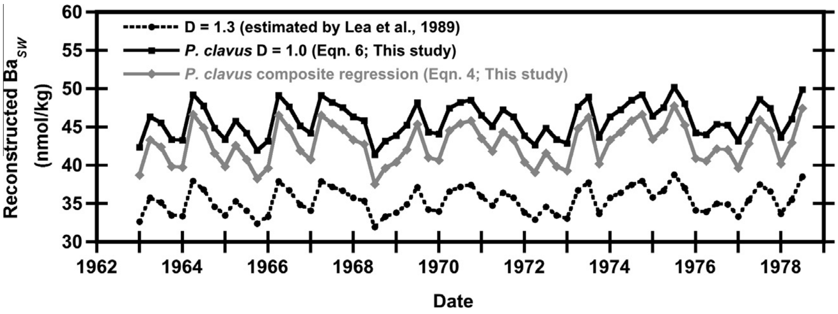

Fig. 7. Ba_{SW} values reconstructed from the Galápagos *Pavona clavus* Ba/Ca record published by Lea et al. (1989; data downloaded from http://hurricane.ncdc.noaa.gov/pls/paleox/f?p=519:1:::::P1_STUDY_ID:1849). Dashed line (black circles) represents Ba_{SW} calculated from D-value estimated by Lea et al., 1989 based on Bermuda *M. annularis* and *D. labyrinthiformis* corals ($D = 1.3$). Solid lines represent Ba_{SW} reconstructed from Gulf of Panama *P. clavus* data (this study) using *P. clavus* composite regression of Ba/Ca against Ba_{SW} (Eq. (4); gray diamonds) or $D = 1.0$ (Eq. (6); black squares). Reconstructions using D-values incorporate estimates of Ca_{SW} scaled with salinity from this region (Ca_{SW} of 10.2 mmol/kg and salinity of 34.3 for Pacific surface waters de Villiers, 1998; Sweet et al., 2007).

Fig. 7). This re-analysis of the Galápagos record demonstrates differences in Ba incorporation between taxa and underscores the importance of using species-specific calibrations or D_{Ba} values to reconstruct Ba_{SW} accurately (e.g. Pingatore et al., 1989; Pretet et al., 2014).

3.3. Other potential influences on coral Ba/Ca

3.3.1. Temperature

Sea surface temperature, a known driver of thermodynamically regulated incorporation of cations in marine carbonates, varies with upwelling intensity in the Gulf of Panamá. Although we cannot tease out the influence of SST on Ba/Ca in these corals because of co-variation in SST and Ba_{SW} at this site, it is unlikely that SST drives the incorporation of Ba observed in our data. Previous studies have suggested that barium incorporation in coral aragonite is inversely affected by temperature (Hart and Cohen, 1996; Dietzel et al., 2004; Gaetani and Cohen, 2006). Our data, however, reveal the opposite trend if any: with cool SST upwelling periods corresponding to lower Ba/Ca_{coral} values and vice versa during warm summer conditions (Figs. 1 and 3). Therefore, it is unlikely that SST is the primary driver of the seasonal Ba/Ca_{coral} variation apparent in our data. Even still, an inverse temperature effect on Ba/Ca_{coral} would only slightly dampen the increase in Ba/Ca_{coral} observed during the study period (by ~ -0.4 to -1 μmol/mol or a decrease in D of ~ 0.3: based on relationships reported by Dietzel et al. (2004) and Gaetani and Cohen (2006).

3.3.2. Salinity

Although our data reveal an inverse relationship between SSS and Ba/Ca_{coral}, this trend is more likely to result from barium delivery to the coastal surface waters by freshwater runoff than a salinity effect on barium incorporation. A recent study has shown that Ba/Ca_{coral} in other surface coral species (*Mimosa verrucosa, Acropora* sp., and *Stylophora pistillata*) is resistant to imposed changes in salinity ranging from 36 to 40 under experimental culturing conditions (Pretet et al., 2014).

4. CONCLUSIONS

The data presented here support the continued interpretation of skeletal Ba/Ca in shallow water hermatypic corals as a tracer of surface water barium concentration. Collectively, our high-resolution seawater and skeletal coral trace element records demonstrate the complexities associated with using indirect nutrient proxies to reconstruct upwelling in coastal areas (Matthews et al., 2008; LaVigne et al., 2010; Grottoli et al., 2013). These studies reveal the value of combining multiple surface coral proxies to provide a detailed understanding of biogeochemical dynamics of upwelling regimes in the past. Using data from triplicate coral colonies we present the first taxa-specific Ba/Ca_{coral} calibrations based on multiple co-located colonies and a contemporaneous *in situ* Ba_{SW} seawater record. These equations can now be applied to downcore records from *P. lobata* and *P. clavus* corals to quantify high-resolution changes in absolute Ba_{SW} concentration, a substantial improvement over interpreting relative changes in Ba/Ca_{coral} alone. These results suggest that larger corals from regions where precipitation is influenced by ITCZ position could be used to reconstruct ITCZ and ENSO variability using runoff records derived from Ba/Ca_{coral}. The calibrations presented here could also be used to quantify paleo-Ba_{SW} concentration from fossilized surface corals to reconstruct millennial-scale changes in paleo Ba_{SW} inventory and water mass distribution resulting from variations in circulation, riverine input, upwelling, or removal from surface waters via barite formation (e.g. Lea and Boyle, 1990, 1991). Additional work constructing longer-term calibrations and evaluating inter-colony reproducibility will likely lead to even more robust calibrations with reduced uncertainty, allowing for the broad application of the Ba/Ca_{coral} proxy.

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APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.gca.2015.12.038.

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