Available online at www.sciencedirect.com
ScienceDirect
Geochimica et Cosmochimica Acta 74 (2010) 1282–1293
Geochimica et Cosmochimica Acta
www.elsevier.com/locate/gca

Coral skeleton P/Ca proxy for seawater phosphate: Multi-colony calibration with a contemporaneous seawater phosphate record

Michèle LaVigne [a,*], Kathryn A. Matthews [b], Andréa G. Grottoli [c], Kim M. Cobb [d], Eleni Anagnostou [a], Guy Cabioch [e], Robert M. Sherrell [a,f]

[a] *Institute of Marine and Coastal Sciences, Rutgers University, New Brunswick, NJ, USA*
[b] *Los Alamos National Laboratory, Los Alamos, NM, USA*
[c] *School of Earth Sciences, The Ohio State University, Columbus, OH, USA*
[d] *School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, GA, USA*
[e] *Institut de Recherche pour le Développement, Bondy CEDEX, France*
[f] *Department of Earth and Planetary Sciences, Rutgers University, Piscataway, NJ, USA*

Received 14 May 2009; accepted in revised form 29 October 2009; available online 10 November 2009

Abstract

A geochemical proxy for surface ocean nutrient concentrations recorded in coral skeleton could provide new insight into the connections between sub-seasonal to centennial scale nutrient dynamics, ocean physics, and primary production in the past. Previous work showed that coralline P/Ca, a novel seawater phosphate proxy, varies synchronously with annual upwelling-driven cycles in surface water phosphate concentration. However, paired contemporaneous seawater phosphate time-series data, needed for rigorous calibration of the new proxy, were lacking. Here we present further development of the P/Ca proxy in *Porites lutea* and *Montastrea sp*. corals, showing that skeletal P/Ca in colonies from geographically distinct oceanic nutrient regimes is a linear function of seawater phosphate ($PO_{4\ SW}$) concentration. Further, high-resolution P/Ca records in multiple colonies of *Pavona gigantea* and *Porites lobata* corals grown at the same upwelling location in the Gulf of Panamá were strongly correlated to a contemporaneous time-series record of surface water $PO_{4\ SW}$ at this site ($r^2 = 0.7$–0.9). This study supports application of the following multi-colony calibration equations to down-core records from comparable upwelling sites, resulting in ±0.2 and ±0.1 μmol/kg uncertainties in $PO_{4\ SW}$ reconstructions from *P. lobata* and *P. gigantea,* respectively.

$$P/Ca_{Porites\ lobata}\ (\mu mol/mol) = (21.1 \pm 2.4)PO_{4\,SW}(\mu mol/kg) + (14.3 \pm 3.8)$$
$$P/Ca_{Pavona\ gigantea}\ (\mu mol/mol) = (29.2 \pm 1.4)PO_{4\,SW}(\mu mol/kg) + (33.4 \pm 2.7)$$

Inter-colony agreement in P/Ca response to $PO_{4\ SW}$ was good (±5–12% about mean calibration slope), suggesting that species-specific calibration slopes can be applied to new coral P/Ca records to reconstruct past changes in surface ocean phosphate. However, offsets in the *y*-intercepts of calibration regressions among co-located individuals and taxa suggest that biologically-regulated "vital effects" and/or skeletal extension rate may also affect skeletal P incorporation. Quantification of the effect of skeletal extension rate on P/Ca could lead to corrected calibration equations and improved inter-colony P/Ca agreement. Nevertheless, the efficacy of the P/Ca proxy is thus supported by both broad scale correlation to mean surface water phosphate and regional calibration against documented local seawater phosphate variations.

* Corresponding author. Current address: University of California Davis, Bodega Marine Laboratory, 2099 Westside Road, Bodega Bay, CA 94923, USA. Tel.: +1 707 875 1911.
E-mail address: lavigne@marine.rutgers.edu (M. LaVigne).

0016-7037/$ - see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.gca.2009.11.002

1. INTRODUCTION

An understanding of past tropical euphotic zone nutrient dynamics would provide a critical link between climate oscillations, biological carbon fixation, and surface ocean nutrient supply (e.g. Sarmiento et al., 2004). The distribution of modern open ocean phosphate and nitrate measurements is sparse both globally and temporally and a direct proxy for these essential macronutrients has been an elusive goal for the paleoceanographic community. Indirect coralline geochemical proxies (Cd/Ca, Ba/Ca and $\delta^{13}C$) have been used to reconstruct relative changes in seawater nutrients and upwelling (Shen et al., 1987, 1992; Lea et al., 1989; Felis et al., 1998). These proxies, however, are not calibrated quantitatively against surface water nitrate or phosphate, and variability among co-located colonies suggests that records derived from a single coral may not yield accurate nutrient reconstructions (Grottoli and Wellington, 1999; Grottoli, 2002; Montaggioni et al., 2006; Matthews et al., 2008).

Recent work has indicated that hermatypic surface-dwelling corals act as high-resolution recorders of surface water phosphate. The skeletal element ratio P/Ca was shown to track annual upwelling cycles in a single *Pavona gigantea* coral over a 4-year record (LaVigne et al., 2008). This study also revealed that ~90% of coral skeleton P is incorporated as an intracrystalline phase resistant to solution cleaning of finely ground coral aragonite. Of this intracrystalline P, however, >60% was not detectable by soluble reactive phosphate analysis on acid-dissolved aragonite, indicating that ionic substitution of orthophosphate for carbonate is not the primary locus for skeletal P, and that organic P phases may be involved, though the incorporation mechanism is not fully understood. Previous studies have also suggested that *Porites, Montastrea,* and *Diploria* corals record coastal phosphorus runoff and pollution as increased P/Ca, incorporated in the skeleton as both inorganic and organic P phases (Dodge et al., 1984; Shotyk et al., 1995; Kumarsingh et al., 1998; Alibert et al., 2003). In addition to these studies on surface corals, a deep-water phosphate proxy calibration was published for the solitary deep-sea coral *Desmophyllum dianthus* (Montagna et al., 2006). While these studies have provided the initial proof of concept for surface coral P/Ca as a $PO_{4\ SW}$ recorder, further efforts are needed to calibrate the proxy against contemporaneous seawater phosphate data. The natural variability in P/Ca records among colonies and taxa must be assessed carefully to determine the degree of reproducibility possible for reliable $PO_{4\ SW}$ reconstructions. 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 reconstructions of climate (DeLong et al., 2007; Goodkin et al., 2007; Linsley et al., 2008; Matthews et al., 2008).

Further development of this promising phosphate proxy is needed to provide the quantitative foundation for generation of sub-seasonal records that are crucial to understanding variations in oceanic nutrient and primary production on decadal to centennial timescales, more directly than can be achieved using available paleo-SST/upwelling proxies alone. In this study, we provide P/Ca results from broadly distributed corals, justifying further validation of this emerging nutrient proxy, and present the first P/Ca calibrations against contemporaneous ambient $PO_{4\ SW}$ concentration. These findings demonstrate inter-colony reproducibility in P/Ca response to $PO_{4\ SW}$, support further development and application of the P/Ca proxy, and identify the possibility that species offsets, extension rate or biological regulation of P incorporation ("vital effects") may be secondary influences on coralline P/Ca.

2. METHODS

2.1. Samples

2.1.1. Global P/Ca distribution

Surface coral samples collected from several distinct oceanic nutrient regimes were analyzed for P/Ca. Multi-year P/Ca records were averaged to acquire mean skeletal P/Ca for two *Montastrea faveolata* (Biscayne National Park, FL; and Martinique, Caribbean) and five *Porites lutea* (Gulf of Aqaba/Eilat, Red Sea; Rarotonga and New Caledonia, South Pacific; Christmas Island and Fanning Island, Central Equatorial Pacific) colonies (Table 1; Linsley et al., 2000; Desenfant, 2004 ; Nurhati et al., 2009). Since skeletal P sampled below the organic tissue layer has been shown to be resistant to rigorous chemical cleaning (LaVigne et al., 2008), the powders extracted from distilled-water rinsed slabs were not cleaned chemically prior to analysis for the globally distributed samples. Mean P/Ca values for *Montastrea sp.* and *Porites lutea* corals were regressed against mean $PO_{4\ SW}$ concentration for each site to evaluate the relationship between seawater and coralline phosphorus (Table 1).

2.1.2. Local calibrations

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 (Matthews et al., 2006, 2008; Matthews, 2007) were analyzed to assess inter-colony P/Ca reproducibility and to calibrate coral P/Ca with $PO_{4\ SW}$ concentration. Full details of the previous study methods are available in Matthews et al. (2008). In short, we analyzed nine coral colonies (3 *Porites lobata*, 3 *Pavona clavus*, and 3 *Pavona gigantea*) reared within meters of each other at the same site (Isla Contadora, 1 m depth below mean low tide) with corresponding *in situ* seawater samples collected periodically through both upwelling (high $PO_{4\ SW}$) and non-upwelling (low $PO_{4\ SW}$) intervals. At the start of the experiment, all colonies were collected from ~1 to 4 m depth 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) was measured every 30 min from January to July 2003 at Isla Contadora with seawater samples collected at 1 m depth every 3 days, filtered, and acidified following

Table 1
Coral and seawater samples used to establish global P/Ca distribution (Fig. 1).

Location	Coral P/Ca data					Seawater phosphate data				
	Species	Date range sampled	Number of samples averaged (n)	Mean skeletal P/Ca (μmol/mol)	Skeletal P/Ca: Average deviation from mean (Fig. 1 error bars)	$PO_{4\ SW}$ data range	$PO_{4\ SW}$ mean (μmol/kg)	$PO_{4\ SW}$ average deviation from mean (Fig. 1 error bars)	$PO_{4\ SW}$ data source	Number of samples averaged (*n*)
Gulf of Eilat (Israel)	*Porites lutea*	2003–2007	35	6.50	1.07	2003–2007	0.03	0.02	Israeli National Monitoring Program**	23
New Caledonia (South Pacific)	*Porites lutea*	1991–1993	16	9.95	1.69	2005	0.15	0.02	World Ocean Atlas	2
Rarotonga (South Pacific)	*Porites lutea*	1996	4	9.02	1.54	2005	0.17	0.01	World Ocean Atlas	4
Fanning Island (Central Eq. Pacific)	*Porites lutea*	1994–1999	70	12.27	2.16	August–September 2005	0.20	0.02	Dinsdale et al. (2008)	32
Christmas Island (Central Eq. Pacific)	*Porites lutea*	1979–1993	240	14.64	8.56	August–September 2005	0.30	0.04	Dinsdale et al. (2008)	32
Biscayne National Park, USA (Atlantic): Time-series Maximum	*Montastrea faveolata*	January–March 2000	2	22.00	0.99	January–March 2000	0.12	0.011	SERC-FIU Water Quality Monitoring Network***	2
Biscayne National Park, USA (Atlantic): Time-series Minimum	*Montastrea faveolata*	1998–1999	4	13.49	0.28	1998–1999	0.02	0.003	SERC-FIU Water Quality Monitoring Network***	4
Curacao (Caribbean)*	*Montastrea annularis*	1973–1981	16	17.18	1.34	July–October 1994	0.06	0.020	van Duyl et al. (2002)	9
Martinique (Caribbean)	*Montastrea faveolata*	1998–2000	14	15.44	1.91	April 1988 and May 1989	0.07	0.029	Littler et al. (1993), Oxenford et al. (1994)	16

* Data from 2 "control" corals from Dodge et al. (1984).

** Data were provided Y. Shaked, Israeli National Monitoring Program, The Interuniversity Institute, Eilat, Israel.

*** Data were provided by the SERC-FIU Water Quality Monitoring Network which is supported by SFWMD/SERC Cooperative Agreement #4600000352 as well as EPA Agreement #X7–96410603-3.

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 the first and last stain line using a micrometer, and divided by the study duration to calculate the average skeletal extension rate of each colony. The width of each stain was measured to determine whether skeletal thickening, the deposition of new aragonite over existing intra-skeletal structures, occurred in these corals (Barnes et al., 1995). We analyzed the filtered seawater samples for both PO_4 (soluble reactive phosphate (SRP)) and total dissolved phosphorus (TDP) by standard colorimetric (Koroleff, 1983) and ICP-MS methods (Field et al., 2007), respectively. We calculated dissolved organic phosphorus (DOP) by subtraction ($DOP_{SW} = TDP_{SW} - PO_{4\,SW}$).

Fifteen to twenty powdered samples (1–2 mg) were extracted from each colony at ~1–2 mm sampling resolution. Sample transects covered ~1 year of growth starting ~6 months prior to the initial collection and including the 6 month study period, resulting in ~2 to 3 week temporal resolution. Samples collected below the first stain line were used solely for age model reconciliation purposes (Section 3.2.1) and were excluded from the P/Ca calibrations since this skeletal material included carbonate deposited prior to the experimental interval. The Gulf of Panamá powders were extracted from skeletal material near the surface organic layer. An oxidative/reductive solution cleaning technique modified from Shen and Boyle (1988), was thus performed on all drilled samples to remove residual organics that could have overprinted the P signal incorporated into the aragonite matrix given the proximity to the tissue layer.

2.2. Analyses

All sample preparation and analyses followed standard laboratory protocols for trace element analysis under Class 100 conditions. All solutions were made with ultrapure reagents (OPTIMA grade, Seastar Chemicals Inc., BC, Canada) and Milli-Q (18.2 MΩ-cm, Millipore, MA, USA) water unless otherwise noted.

2.2.1. Sample preparation

In order to minimize differential plasma matrix effects between samples during analysis (de Villiers et al., 1994; Rosenthal et al., 1999), the dissolution volume for each sample was individually adjusted to achieve 80 mM Ca (±10%) in 1 N ultrapure HNO_3, based on mass of drilled powder prepared for dissolution. Samples were further diluted to 4 mM Ca and 1.5 mM Ca in 3% HNO_3 for analysis by ICP-MS (P/Ca) and ICP-OES (Sr/Ca), respectively.

Measurements of P/Ca were carried out on an Element-XR (Thermo Scientific, Bremen, Germany) high-resolution inductively coupled plasma mass spectrometer (HR-ICP-MS) operated in both low and medium resolutions ($M/\Delta M = 300$ and 4000, respectively) and E-scan detection mode (using a combination of magnet jumps and electrostatic peak scanning). Adapted from Rosenthal et al. (1999), the sample introduction system consisted of a microautosampler (SC-E2) connected to a self-aspirating PFA MicroFlow nebulizer (PFA-100; <100 μL/min flow rate), a PFA o-ring free PureCap endcap, and a PFA PureChamber spray chamber (Elemental Scientific Inc., NE, USA). A grounded metal shield inserted between the load coil and the torch was used to increase sensitivity. Extra gas flows (Ar, 0.1–0.2 L/min and NH_3, 0.071 L/min) were added via a single additional gas port on the end cap of the spray chamber to supplement the cool, auxiliary, and sample gas flows required.

Samples were standardized against two separate standard curves: one multi-element standard addition curve (including P) was made by spiking an in-house coral consistency standard; a second single element standard curve for Ca was made up in 3% HNO_3. To optimize P/Ca accuracy, we calculated elemental ratios offline using concentrations determined from the two separate standard curves rather than adopting the elemental ratio method developed for the determination of precise Mg/Ca ratios in foraminifera (Rosenthal et al., 1999). Indium, which was analyzed in both medium and low resolutions, was used to monitor and correct for instrument drift (typically ~30 to 40%) in the calculation of data. An in-house matrix-matched coral consistency standard was analyzed as an unknown six times through each analytical run to check reproducibility within and between days (±2.0 μmol/mol external precision for P/Ca, $n = 26$, corresponding to ±7% RSD precision for mean sample P/Ca). The phosphorus blank subtracted from sample signals was typically <10%. Coral solutions ranged from ~1 to 7 ppb P, ~10–100× the detection limit of 0.05–0.1 ppb P (3× SD of blank acid).

For Sr/Ca analysis, a Vista-Pro CCD simultaneous radially viewed ICP-OES (Varian, Inc., CA, USA) was equipped with a cyclonic quartz spray chamber and a PFA MicroFlow 100 (100 μL/min) nebulizer (Elemental Scientific Inc., NE, USA). The samples were introduced into the plasma using an ASX-100 autosampler (CETAC, NE, USA) in free aspiration mode. The emission line ratio calculated for data interpretation was Sr_{407}/Ca_{318} as determined optimal by Andreason et al. (2006). Separate Sr and Ca matrix-matched standard curves, consistency standards, and blanks were used, similar to the HR-ICP-MS method. An internal standard of 100 ppb Y was used to correct for instrument drift. Reproducibility of Sr/Ca for the consistency standard was <0.3% RSD ($n = 9$).

2.2.2. Statistical analysis

The least squares method of linear regression was used to assess the relationship between coral P/Ca and $PO_{4\,SW}$ concentration for both the global distribution samples (Section 3.1) and for each colony analyzed from the Gulf of Panamá (Section 3.2). Species-specific multi-colony regression coefficients and associated errors were determined by calculating the average deviation about mean slopes and *y*-intercepts for each of the triplicate *P. lobata* and *P. gigantea* colonies. *P*-levels below 0.05 were considered statistically significant. Regression analyses were performed using the regression data analysis add-in feature of Microsoft Office Excel 2003 Professional Edition for Windows (©1985–2003 Microsoft Corporation).

3. RESULTS AND DISCUSSION

3.1. Global P/Ca distribution

To test the global applicability of the P/Ca–$PO_{4\ SW}$ proxy, we compared mean skeletal P/Ca for globally—distributed *Porites lutea* and *Montastrea sp.* samples with mean surface ocean phosphate for each location (Fig. 1; Table 1). For both coral genera, we found that individuals growing under naturally elevated $PO_{4\ SW}$ conditions incorporate more skeletal phosphorus than those in low $PO_{4\ SW}$ environments. The strong linear relationship between multi-year mean coralline P/Ca and mean $PO_{4\ SW}$ concentration ($r^2_{Porites\ lutea} = 0.93$; $r^2_{Montastrea\ sp.} = 0.91$), justifies further development of this proxy in a broad range of oceanic nutrient regimes. Although linear regressions fit the data well for both species, the calculated slopes and *y*-intercepts for the two genera differ substantially suggesting that taxonomic differences in skeleton formation or extension rates likely influence P incorporation ($P/Ca_{Porites\ lutea} = 31.9\ (PO_{4\ SW}) + 5.12$; $P/Ca_{Montastrea\ sp.} = 84.8\ (PO_{4\ SW}) + 11.6$). These globally based equations present good first-order estimates of the relationship between coral P/Ca and $PO_{4\ SW}$ concentration, but rigorous calibration of this relationship requires additional *in situ* time-series data before the proxy can be applied down-core. As evidenced by the range of $PO_{4\ SW}$ and P/Ca_{coral} averaged at each location, there is considerable uncertainty in these regressions, likely resulting from a lack of local $PO_{4\ SW}$ data contemporaneous with the growth period sampled for each coral (Table 1). The inter-genus difference in these regression equations could be a result of (1) different P incorporation sensitivities to ambient $PO_{4\ SW}$ between the two genera or (2) possible influence of additional forms of P in seawater (e.g., dissolved organic phosphorus (DOP), or particulate phosphorus (PP)) on skeletal P. The potential influences of seawater P speciation, temperature, and extension rate on the P/Ca–$PO_{4\ SW}$ proxy are discussed in Section 3.4. While these uncertainties justify further development of the P/Ca proxy with local time-series calibrations, the global distribution data show that bulk skeletal P/Ca in geographically distant corals, growing under different phosphate regimes, broadly reflect the PO_4 content of ambient seawater.

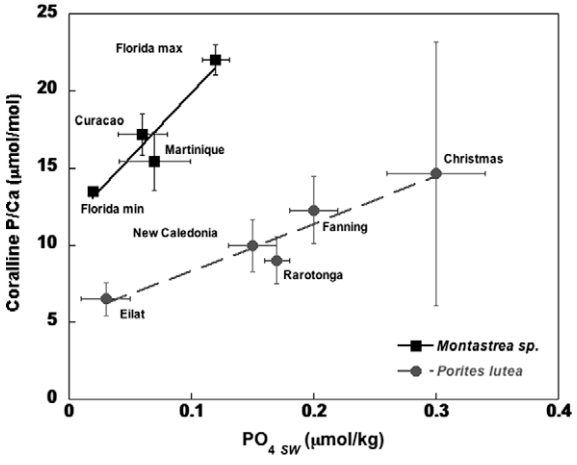

Fig. 1. Average coralline P/Ca for *Porites lutea* (grey circles) and *Montastrea sp.* (black squares) plotted against mean local seawater phosphate concentration ($PO_{4\ SW}$). Sources and date ranges of seawater and coral data are summarized in Table 1. Each data point represents average $PO_{4\ SW}$ concentration for the site indicated (*x*-axis) and a mean P/Ca value calculated from multi-year P/Ca record (*y*-axis). Error bars represent deviation from mean for seawater data (*x*) and the coral subsamples used to calculate mean P/Ca (*y*) covering time periods indicated in Table 1 ($n = 2$–240, see Table 1; Florida min error bars are smaller than symbol). Dashed grey and solid black lines represent linear regressions of plotted data.

3.2. Multi-colony P/Ca calibration with *in situ* $PO_{4\ SW}$ concentration

Sufficient evidence has now been presented both in global distribution and down-core periodicity (LaVigne et al., 2008) to warrant additional testing of the hermatypic coral P/Ca–$PO_{4\ SW}$ proxy. Natural P/Ca variability among co-located coral colonies and species-specific calibrations with contemporaneous seawater data was therefore assessed. All six *P. gigantea* and *P. lobata* colonies at Isla Contadora grew through the transition from upwelling to non-upwelling conditions, and recorded the ~0.6 µmol/kg $PO_{4\ SW}$ decrease as an ~10 µmol/mol drop in skeletal P/Ca (Figs. 2 and 3; Supplementary Fig. S1). This change in P/Ca with upwelling is apparently smaller than that previously measured in a comparable coral record from Isla Contadora covering 1975–1979; which gave ~30–50 µmol/mol P/Ca annual change with upwelling (LaVigne et al., 2008). Without an *in situ* $PO_{4\ SW}$ time-series corresponding to the 1975–1979 coral sample, a rigorous comparison of P/Ca sensitivity to $PO_{4\ SW}$ was impossible for these samples, given the degree of interannual variability in upwelled nutrient concentrations at this site (D'Croz et al., 1991; D'Croz and Robertson, 1997; D'Croz and O'Dea, 2007). In contrast to *P. gigantea* and *P. lobata*, we found that only one *P. clavus* coral recorded the change in upwelled $PO_{4\ SW}$ concentration as a change in P/Ca (Fig. 2). While it is possible that the lack of P/Ca signal in the colonies analyzed in this study is a result of physiological stress caused when the coral fragments were transplanted prior to the experiment, it may also be that *P. clavus* corals are unreliable P/Ca recorders. Given this uncertainty, the *P. clavus* samples were not analyzed for Sr/Ca for age model adjustment nor carried through further statistical analysis or discussion.

3.2.1. Age model

While all *P. gigantea* and *P. lobata* colonies recorded upwelling as a peak in both P/Ca (indicating seawater phosphate increase) and Sr/Ca (indicating SST decrease), the corals recorded the geochemical signals of this ~3 month long upwelling period over ~6 to 12 months of skeletal growth (Figs. S2 and S3). This smoothed geochemical signal is similar in shape to the multi-year Sr/Ca and P/Ca cycles for the 1975–1979 Isla Contadora *P. gigantea* coral sampled both at higher resolution by laser ablation (~0.42 mm/sample = 3 week resolution) and by bulk sampling (drilling and solution analysis), indicating that the

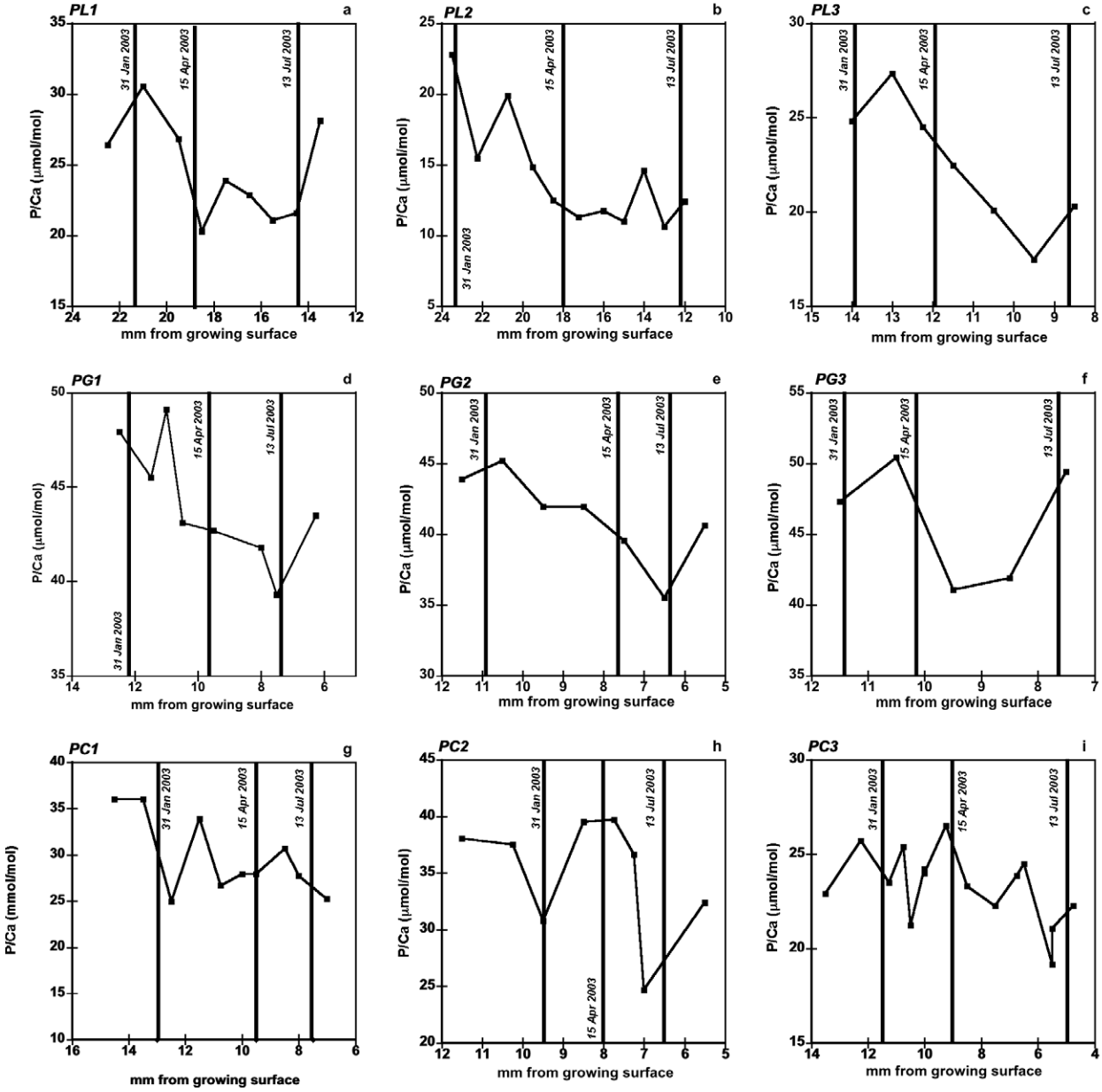

Fig. 2. Coral P/Ca for *Porites lutea* (a–c), *Pavona gigantea* (d–f) and *Pavona clavus* (g–i) colonies plotted on mm-scale from growing surface. Location of the upper edge of *in situ* stain lines shown as vertical lines (staining dates indicated).

P/Ca smoothing effect is not a result of coarser resolution sampling by the drilling method (~1 mm/ sample = ~1 to 2 month resolution; LaVigne et al., 2008). Geochemical smoothing was also observed in laser ablation Cd/Ca records of these corals (Matthews, 2007), and is most likely a result of skeletal thickening, which is caused by calcification throughout the coral tissue layer, extending into the surface of the bulk skeleton (Barnes and Lough, 1993; Taylor et al., 1993; Barnes et al., 1995; Matthews, 2007). Barnes and Lough (1993) showed that the thickening of skeletal structures can occur over several months of coral growth. Models of this process have shown that skeletal thickening can distort geochemical records of both annual and short pulse environmental variations (Barnes et al., 1995; Taylor et al., 1995), causing time discrepancies between forcing functions and chronological markers such as density bands (Barnes and Lough, 1996). Measurements of stain line thickness in each sample used in this study showed that the *P. lobata* and *P. gigantea* corals incorporated the 1-day stain over an equivalent of 1–6 weeks and 2.5–3 months of skeletal growth (0.5–1.4 mm and 1.9–2.4 mm), respectively. Therefore, we suggest that skeletal thickening is responsible for the apparent signal smoothing and timing offset between the incorporated coral signals and the *in situ* seawater records. Similar timing offsets have been found in stained coral fragments, where Sr/Ca-SST chronologies were used instead of stain-line derived dates (Swart et al., 2002). We assumed that thickening affected both

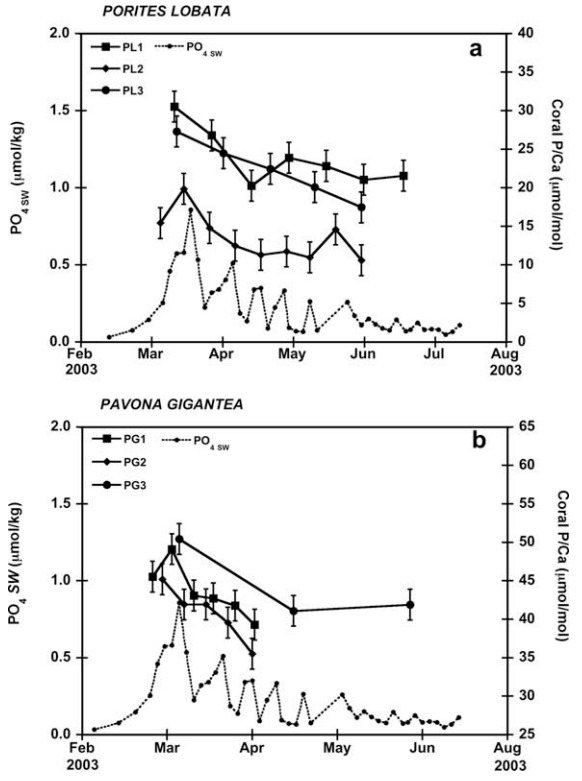

Fig. 3. *In situ* $PO_{4\ SW}$ concentration time-series (dotted line; *y*-axis 1) and contemporaneous timescale-adjusted coralline P/Ca results (*y*-axis 2) for triplicate colonies of *Porites lobata* (a) and *Pavona gigantea* (b) through the 2003 study period in the Gulf of Panamá. Error bars on coral P/Ca data points represent mean standard deviation of repeat measurements of coral consistency standard (SD = 2 µmol/mol; $n = 26$). Tick marks on time axis are first day of month.

Sr/Ca and P/Ca equally, and 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 stretched 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 P/Ca calibrations could be calculated appropriately (Figs. S2 and S3). The *P. gigantea* corals required larger age model corrections than the *P. lobata* colonies, corresponding to the higher degree of thickening of *P.gigantea* stain lines, and likely due to differences in skeletal structure and degree of thickening between *Porites* and *Pavona* (Cohen and Thorrold, 2007).

The skeletal Sr/Ca-SST age model adjustment accounts only for geochemical signal stretching caused by thickening. 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). To compensate for this effect, $PO_{4\ SW}$ data were smoothed using a 3–7 day moving average before resampling at the resolution of the coral data using the linear integration interpolation function of the AnalySeries program (Paillard et al., 1996). We identified the appropriate $PO_{4\ SW}$ smoothing window (from 3–7 days) for each colony by optimizing the smoothed coral P/Ca-$PO_{4\ SW}$ correlation coefficients. The slopes and *y*-intercepts reported varied by less than 10% and r^2 values were greater than 0.6 for all trials in the 3–7 day smoothing window range. Further investigations of P/Ca with finer resolution sampling of skeletal microstructures could lead to a better understanding of how skeletal thickening and smoothing affects incorporated P signals. The calibrations reported here are, however, appropriate to bulk sampling methods often employed in paleo-proxy reconstructions.

3.2.2. Inter-colony calibration reproducibility

Regression analysis revealed a strong linear relationship between $PO_{4\ SW}$ and coral P/Ca for all six *P. gigantea* and *P. lobata* colonies ($r^2 = 0.7$–0.9; Fig. 4 and Table 2). The

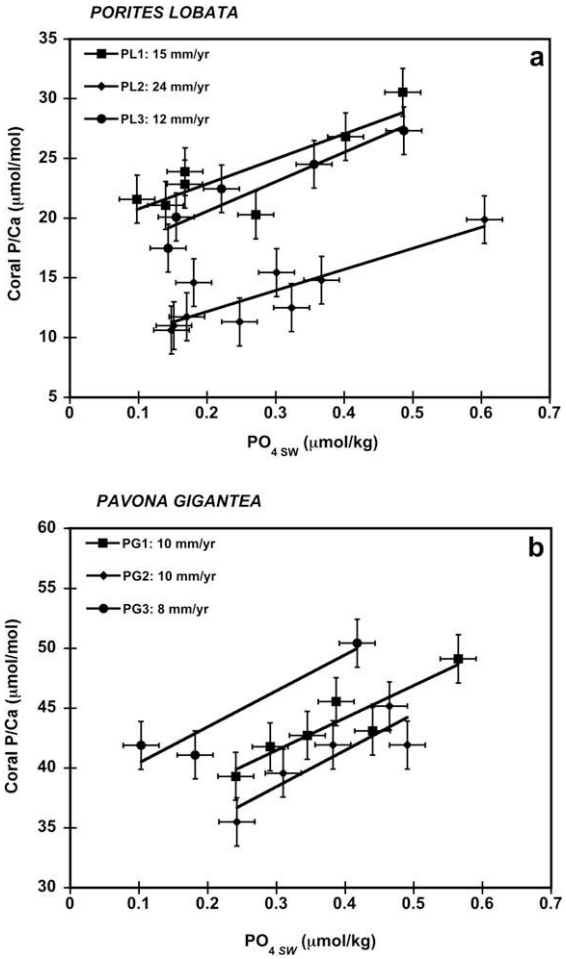

Fig. 4. Local $PO_{4\ SW}$–P/Ca calibrations for Gulf of Panamá *Porites lobata* (a) and *Pavona gigantea* (b) colonies. Linear regression lines were calculated from local re-sampled $PO_{4\ SW}$ time-series (*x*-axis) and coral P/Ca (*y*-axis; see text). *X* and *Y* error bars represent mean deviation for duplicate $PO_{4\ SW}$ measurements ($n = 14$ analytical duplicates; (mean deviation = ± 0.026 µmol/kg PO_4), and repeat measurements of coral consistency standard (SD = 2 µmol/mol; $n = 26$), respectively. Solid black lines represent linear regression equations calculated for each colony. The extension rate of each colony along sampled growth axis is indicated in the figure legend.

Table 2
Linear regression analysis.

	Slope	*y*-intercept	r^2	*p*-value	df	Colony extension rate (mm/year)	Extension during upwelling (distance between stain 1 and 2; mm)	Extension during non-upwelling (distance between stain 2 and 3; mm)
Porites lobata								
PL1	20.9	18.7	0.70	0.019	6	14.8	2.5	4.3
PL2	17.7	8.65	0.76	0.002	8	24.1	5.3	5.8
PL3	24.8	15.6	0.91	0.012	4	11.5	2	3.3
P. lobata mean	21.1	14.3						
P. lobata average deviation from mean ($n = 3$ colonies)	2.4	3.8						
P. lobata inter-colony agreement (avg % deviation from mean)	12%	26%						
Pavona gigantea								
PG1	27.1	33.4	0.85	0.009	5	10.4	2.5	2.3
PG2	30.4	29.3	0.78	0.048	4	10.0	3.3	1.3
PG3	30.0	37.4	0.90	0.204	2	8.3	1.3	2.5
P. gigantea mean	29.2	33.4						
P. gigantea average deviation from mean ($n = 3$ colonies)	1.4	2.7						
P. gigantea inter-colony agreement (avg % deviation from mean)	5%	8%						

regressions were statistically significant ($p < 0.05$), except that of the PG3 colony, which had an insufficient number of data points ($p = 0.204$; $n = 3$). The *P. gigantea* and *P. lobata* colony regressions showed good inter-colony agreement in calculated slopes (±5–12% average deviation about mean) within each species. This confirms that most (70–90%) of the variation in the P/Ca of an individual coral can be explained by changes in $PO_{4\,SW}$. The remaining 10–30% variability in P/Ca could result from other factors including biologically-regulated "vital effects", extension rate (de Villiers et al., 1995; Sinclair et al., 2006), or the influence of additional seawater conditions on P incorporation (Section 3.4).

The mean slope and *y*-intercept, with average deviation for both ($n = 3$ colonies per species), were calculated from the individual colony regressions to create the following multi-colony calibrations.

$$\mathrm{P/Ca}_{Porites\ lobata}\ (\mu\mathrm{mol/mol}) = (21.1 \pm 2.4)\mathrm{PO}_{4SW}\ (\mu\mathrm{mol/kg}) + (14.3 \pm 3.8)$$

$$\mathrm{P/Ca}_{Pavona\ gigantea}\ (\mu\mathrm{mol/mol}) = (29.2 \pm 1.4)\mathrm{PO}_{4SW}\ (\mu\mathrm{mol/kg}) + (33.4 \pm 2.7)$$

Based on the Gulf of Panamá $PO_{4\,SW}$ concentration range (0.1–0.6 μmol/kg), the error associated with the above multi-colony calibrations, and analytical error on P/Ca (±2 μmol/mol), we calculated ±0.2 and ±0.1 μmol/kg error on $PO_{4\,SW}$ reconstructed from *P. lobata and P. gigantea* P/Ca, respectively. The variability in slopes and *y*-intercepts calculated for the *P. lobata* colonies is largely a function of one individual (PL2) (Fig. 4a). The *P. lobata* uncertainty on reconstructed $PO_{4\,SW}$ improves to ±0.1 μmol/kg if PL2 is excluded from the error calculation. The factor of ~2 higher extension rate of PL2 relative to the other colonies indicates that extension rate may influence skeletal P incorporation (Section 3.4.1). Nonetheless, inter-colony slope and *y*-intercept agreement is good given the relatively short study period, and encourages further proxy development.

3.2.3. Inter-genus agreement

All *P. gigantea* and *P. lobata* colonies gave a combined multi-genus calibration slope of 25.1 ± 4.0 (μmol/mol) $(\mu\mathrm{mol/kg})^{-1}$. The fact that all colonies recorded $PO_{4\,SW}$ changes with very similar sensitivity is encouraging for the use of this proxy in other locations and species for reconstruction of past surface water nutrient concentrations. We do find, however, a difference between the two genus-specific *y*-intercepts (mean *y*-intercept$_{P.\ lobata}$ = 14.3 ± 3.8 μmol/mol; mean *y*-intercept$_{P.\ gigantea}$ = 33.4 ± 2.7 μmol/mol; Table 2), similar to the inter-genus *y*-intercept offsets observed in the global distribution analyses (Section 3.1). This offset indicates that, similar to coralline $\delta^{18}O$ (Erez, 1978; Juillet-Leclerc et al., 2009) and other trace elements (Sinclair, 2005), biological "vital effects", species offsets and/or extension rate likely influence P incorporation, and require further investigation.

3.3. Global distribution versus local calibration

With these results, the global and local relationships between $PO_{4\,SW}$ and P/Ca for *Porites* can be compared. Significant differences are observed in both slope (31.9_{global} vs. 21.1_{local}) and *y*-intercept (5.12_{global} vs. 14.3_{local}). These offsets could be related to species-specific (*P. lobata* vs. *P. lutea*) differences in P incorporation or levels of inherent

skeletal P incorporation (inorganic or organic) upon which the seawater phosphate sensitivity is built. These slopes and *y*-intercept differences between the open ocean corals and colonies grown at the coastal Gulf of Panamá upwelling location, suggest that other environmental conditions such as additional forms of SW phosphorus may influence skeletal P incorporation (Section 3.4.3). These offsets suggest a need for additional down-core *in situ* calibrations in low DOP environments and further constraints on the skeletal P incorporation mechanism.

3.4. Other potential influences on P/Ca

3.4.1. Extension rate

We calculated similar slopes and *y*-intercepts for individuals of both species used in this study with extension rates of 8–15 mm/year (Table 2, Fig. 4). The *P. lobata* colony with the highest extension rate (PL2; 24 mm/year), however, had a significantly lower slope and *y*-intercept than the other two colonies of that species (Table 2, Fig. 4). This suggests that fluctuations in extension rate could influence P/Ca incorporation and thus down-core reconstructions of $PO_{4\ SW}$ concentration. Based on this result, absolute $PO_{4\ SW}$ concentration could be reconstructed with confidence from upwelling corals with extension rates of 8–15 mm/year. While this data set is insufficient to quantify rigorously the extension rate effect, we argue that the seasonal P/Ca response seen in the corals cannot be driven primarily by increased extension rate during non-upwelling vs. upwelling seasons. Skeletal extension was greater during the non-upwelling season for four of the colonies (PL1, PL2, PL3, PG3), and opposite for two colonies (PG1, PG2), yet all six corals recorded the decrease in $PO_{4\ SW}$ as decreased P/Ca (Table 2 and Fig. 2). We expect that further work could lead to the addition of an extension-rate correction component to calibration equations and therefore improved inter-colony P/Ca agreement, as has been found for Sr/Ca (Goodkin et al., 2007; Saenger et al., 2008).

3.4.2. Temperature

A number of surface ocean properties vary with upwelling intensity in the Gulf of Panamá. Sea surface temperature (SST), for example, is a known driver of thermodynamically regulated incorporation of cations in marine carbonates. Because P/Ca and Sr/Ca vary concomitantly with upwelling-driven $PO_{4\ SW}$ concentration and SST changes, the influence of SST on P/Ca incorporation cannot be tested independently at this site. Although P/Ca is negatively correlated with SST ($r = -0.89$), we do not expect skeletal incorporation of P to be driven directly by SST. First, although the P incorporation mechanism remains uncertain, a significant component of skeletal P apparently exists as an organic phase (LaVigne et al., 2008), suggesting that traditional ionic substitution thermodynamics do not apply to this proxy. Second, data from the Florida *Montastrea faveolata* coral included in the global distribution analysis do not show a relationship between P/Ca and SST for a location where large seasonal variations in SST are independent of changes in $PO_{4\ SW}$ concentration.

3.4.3. Additional forms of seawater phosphorus

We find a strong linear relationship between P/Ca and surface water $PO_{4\ SW}$ concentration globally (Section 3.1) and in local time-series (Section 3.2), supporting the hypothesis that ambient seawater PO_4 is the primary driver of P/Ca variations in corals. However, while 90% of skeletal P has been shown to be "intracrystalline", skeletal orthophosphate may not be the primary form of skeletal P, and both inorganic and organic skeletal P phases may respond independently to $PO_{4\ SW}$ (Dodge et al., 1984; Shotyk et al., 1995; Kumarsingh et al., 1998; LaVigne et al., 2008). To determine the variability in P/Ca that could be attributed to DOP_{SW} or TDP_{SW}, rather than $PO_{4\ SW}$, in the Gulf of Panamá corals, we compared r^2 values calculated from linear regressions of P/Ca against TDP_{SW} and DOP_{SW} records derived from the *in situ* seawater samples. We found that a higher proportion of P/Ca variability can be ascribed to $PO_{4\ SW}$ than to DOP_{SW} or TDP_{SW} variability (mean $r^2_{PO4\ SW} = 0.82$; mean $r^2_{DOP\ SW} = 0.18$; mean $r^2_{TDP\ SW} = 0.75$). This suggests that coralline P/Ca is primarily a function of $PO_{4\ SW}$ rather than DOP_{SW} or the combined TDP_{SW} signal. However, the possibility that other forms of P in seawater (such as DOP and PP) could also be incorporated into coral skeleton, influencing the measured P/Ca response to upwelling, cannot yet be ruled out.

Lacking a clear understanding of the skeletal P incorporation mechanism at present, we cannot identify how additional forms of seawater P could introduce the 5–26% inter-colony variability in regression coefficients we calculated. It is not surprising, however, that physiological processes could influence skeletal P incorporation as biological "vital effects" given that phosphate is an essential nutrient biologically, and uptake is carrier-mediated in both corals and zooxanthellae (Godinot et al., 2009).

We can imagine, for example, that the degree of feeding, heterotrophy vs. autotrophy, or internal nutrient cycling could differ between colonies or genera and result in variable proportions of PP_{SW}, DOP_{SW}, and $PO_{4\ SW}$ incorporation (Porter, 1974; Falkowski et al., 1993; Palardy et al., 2005). Nevertheless, given the good reproducibility in slope among colonies at the same site, we expect that these influences affect the P/Ca response to $PO_{4\ SW}$ similarly among co-located colonies.

Based on these observed species and inter-colony offsets and indication that both organic and inorganic forms of P are likely present in coral skeleton, we can speculate upon the source of two possible pools of skeletal P (Shotyk et al., 1995; Kumarsingh et al., 1998; LaVigne et al., 2008). We hypothesize that a background level of P is skeletally incorporated as an organic component inherent to biocalcification and dictated by the organism's species and/or growth rate, thus setting the coral's calibration *y*-intercept, above which inorganic skeletal P varies consistently in response to changes in $PO_{4\ SW}$ (calibration slope). Further work is needed to constrain the relative roles of these potential influences, and variability on longer timescales. Until then, we must consider the uncertainty in slope (±5–12%) and *y*-intercept (±8–26%) as natural variability among specimens, and treat this as a source of error in coral-based $PO_{4\ SW}$ reconstructions. The possible influence of additional forms of P (e.g., DOP, PP) on skeletal P/Ca adds

uncertainty to the application of calibrations (particularly the *y*-intercept) from the Gulf of Panamá (DOP = 0.3–0.6 μmol/kg) to distinct nutrient environments such as low DOP open ocean sites (typical DOP range = 0.075–0.2 μmol/kg; (Case, 2001; Karl et al., 2001; Ammerman, 2003). Since we observed better agreement among individuals and species for calibration slopes than for *y*-intercepts, we suggest that the mean species-specific slopes calculated from the Gulf of Panamá corals can be used in future down-core studies to reconstruct changes in $PO_{4\ SW}$. At different locations, measurements of modern coral P/Ca and $PO_{4\ SW}$, and the genus-specific calibration slope determined in this study, could be used to determine a site-specific *y*-intercept for down-core $PO_{4\ SW}$ reconstructions.

We expect that continued efforts to evaluate multi-year and multi-colony calibrations with contemporaneous seawater PO_4 data for additional species, locations, and individuals will further reduce the level of uncertainty in future down-core records.

4. CONCLUSIONS

The data presented here show that P/Ca acts as a paleophosphate proxy with only moderate inter-colony variability. The skeletal phosphorus content of multiple coral genera and species is linearly related to ambient seawater phosphate concentrations in both local time-series and global temporal-mean distributions. Triplicate *Porites lobata* and *Pavona gigantea* P/Ca records from corals grown at the same site were highly correlated with variations in seawater phosphate caused by seasonal upwelling ($r^2 = 0.7$–0.9), with good agreement among colony regressions (±5–12% agreement in slope).

Mean slopes, *y*-intercepts, and inter-colony error calculated from multi-colony linear regressions can now be applied to down-core *P. lobata* and *P. gigantea* P/Ca records in comparable coastal upwelling regimes. The local reproducibility and global linearity of P/Ca demonstrated in this study strongly encourages further development and application of this novel proxy. Additional work constructing longer term calibrations for distinct nutrient regimes, constraining the skeletal P incorporation mechanism, and quantifying the sensitivity of P/Ca to biological "vital effects", variations in extension rate, and potential incorporation of other forms of seawater phosphorus will likely lead to robust species-specific calibrations and the broad application of this proxy to open ocean sites.

ACKNOWLEDGMENTS

We thank B. Linsley, B. Lazar, D. Poore, T. D. Hickey, C. Reich, K. DeLong, A. Véron, and F. Desenfant, for global P/Ca distribution samples; C. Theodore, I.S. Nurhati, and Y. Matsui for sample preparation and analyses; L. D'Croz of the Smithsonian Tropical Research Institute for Gulf of Panamá oceanographic data and field logistics; J. Palardy for extensive field work assistance, Y. Rosenthal, J. Reinfelder, S. Sosdian, T. Babila, and P. Field for valuable discussions on trace elements in corals and proxy development. Funding support was provided by the Canon National Park Science Scholars Fellowship to M. LaVigne, the Donors of the American Chemical Society Petroleum Research Fund (ACS PRF Grant 47625-AC2 to R. Sherrell and 41740-G2 to A. Grottoli), the National Science Foundation (OCE 0752544 to R. Sherrell and 0610487 to A. Grottoli), the Andrew Mellon Foundation (to A. Grottoli), and the Evolving Earth Foundation (to K. Matthews). The reviews of T. McConnaughey, Associate Editor A. Cohen, and an anonymous reviewer greatly improved the quality of the manuscript.

APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.gca.2009.11.002.

REFERENCES

Alibert C., Kinsley L., Fallon S., McCulloch M., Berkelmans R. and McAllister F. (2003) Source of trace element variability in Great Barrier Reef corals affected by the Burdekin flood plumes. *Geochim. Cosmochim. Acta* **67**, 231–246.

Ammerman, J. W., 2003. Phosphorus deficiency in the Atlantic: An emerging paradigm in oceanography. *Eos* **84**, 165, 170.

Andreason, D. H., Sosdian, S., Perron-Cashman, S., Lear, C. H., deGaridel-Thoron, T., Field, P. and Rosenthal, Y. (2006) Fidelity of radially viewed ICP-OES and magnetic-sector ICP-MS measurement of Mg/Ca and Sr/Ca ratios in marine biogenic carbonates: Are they trustworthy together? *Geochemistry Geophysics Geosystems* 7, Q10P18.

Barnes D. J. and Lough J. M. (1993) On the nature and causes of density banding in massive coral skeletons. *J. Exp. Mar. Biol. Ecol.* **167**, 91–108.

Barnes D. J. and Lough J. M. (1996) Coral skeletons: storage and recovery of environmental information. *Global Change Biol.* **2**, 569–582.

Barnes D. J., Taylor R. B. and Lough J. M. (1995) On the inclusion of trace materials into massive coral skeletons. Part II: distortions in skeletal records of annual climate cycles due to growth processes. *J. Exp. Mar. Biol. Ecol.* **194**, 251–275.

Case, D. A., 2001. *The Inventory, Seasonality and Stoichiometry of the Major Phosphorus Pools in the Sargasso Sea*. Texas A&M University.

Cohen A. L. and Thorrold S. R. (2007) Recovery of temperature records from slow-growing corals by fine scale sampling of skeletons. *Geophys. Res. Lett.* **34**, L17706.

D'Croz L., Del Rosario J. B. and Gomez J. A. (1991) Upwelling and phytoplankton in the Bay of Panama. *Rev. Biol. Trop.* **39**, 233–241.

D'Croz L. and O'Dea A. (2007) Variability in upwelling along the Pacific shelf of Panama and implications for the distribution of nutrients and chlorophyll. *Estuar. Coast. Shelf Sci.* **73**, 325–340.

D'Croz, L. and Robertson, D. R. (1997) Coastal oceanographic conditions affecting coral reefs on both sides of the Isthmus of Panama. In *8th International Coral Reef Symposium*.

de Villiers S., Nelson B. K. and Chivas A. R. (1995) Biological controls on coral Sr/Ca and $\delta^{18}O$ reconstructions of sea surface temperatures. *Science* **269**, 1247–1249.

de Villiers S., Shen G. T. and Nelson B. K. (1994) The Sr/Ca-temperature relationship in coralline aragonite: Influence of variability in $(Sr/Ca)_{sewater}$ and skeletal growth parameters. *Geochim. Cosmochim. Acta* **58**, 197–208.

DeLong, K. L., Quinn, T. M. and Taylor, F. W. (2007) Reconstructing 20th century SST variability in the Southwest Pacific: a replication study using multiple coral Sr/Ca records from New Caledonia. *Paleoceaongraphy* **22**, PA4212.

Desenfant, F. (2004) *Tracage des circulations atmosphériques et océaniques en Atlantique Nord Subtropical à partir d'enregistrements géochimiques (Isotopes du Plomb et de l'oxygène) contenus dans le squelette des coraux massifs*. Universite de Droit, D'Economie et des Sciences d'Aix-Marseille Aix-Marseille III- Université Paul Cezanne.

Dinsdale E., Pantos O., Smriga S., Edwards R. A., Angly F., Wegley L., Hatay M., Hall D., Brown E., Haynes M., Krause L., Sala E., Sandin S. A., Thurber R. V., Willis B., Azam F., Knowlton N. and Rohwer F. (2008) Microbial ecology of four coral atolls in the Northern Line Islands. *PLos One* **3**, e1584.

Dodge R., Jickells T., Knap A., Boyd S. and Bak R. (1984) Reef-building coral skeletons as chemical pollution (phosphorus) indicators. *Mar. Pollut. Bull.* **15**, 178–187.

Erez J. (1978) Vital effect on stable-isotope composition in foraminifera and coral skeletons. *Nature* **273**, 199–202.

Falkowski P., Dubinski Z., Muscatine L. and McCloskey L. R. (1993) Population control in symbiotic corals. *BioScience* **43**, 606–611.

Felis T., Patzold J., Loya Y. and Wefer G. (1998) Vertical water mass mixing and plankton blooms recorded in skeletal stable carbon isotopes of a Red Sea coral. *J. Geophys. Res.* **103**, 30731–30739.

Field M. P., LaVigne M., Murphy K. R., Ruiz G. M. and Sherrell R. M. (2007) Direct determination of P, V, Mn, As, Mo, Ba, and U in seawater by SF-ICP-MS. *J. Anal. Atom. Spectrom.* **22**, 1145–1151.

Godinot C., Ferrier-Pagès C. and Grover R. (2009) Control of phosphate uptake by zooxanthellae and host cells in the scleractinian coral *Stylophora pistillata*. *Limnol. Oceanogr.* **54**, 1627–1633.

Goodkin, N. F., Hughen, K. A. and Cohen, A. L. (2007) A multicoral calibration method to approximate a universal equation relating Sr/Ca and growth rate to sea surface temperature. *Paleoceanography* **22**, PA1214.

Grottoli A. G. (2002) Effect of light and brine shrimp on skeletal δ13C in the Hawaiian coral *Porites compressa*: a tank experiment. *Geochim. Cosmochim. Acta* **66**, 1955–1967.

Grottoli A. G. and Wellington G. M. (1999) Effect of light and zooplankton on skeletal $\delta^{13}C$ values in the eastern Pacific corals *Pavona clavus* and *Pavona gigantea*. *Coral Reefs* **18**, 29–41.

Juillet-Leclerc A., Reynaud S., Rollion-Bard C., Cuif J. P., Dauphin Y., Blamard D., Ferrier-Pages C. and Allemand D. (2009) Oxygen isotopic signature of the skeletal microstructures in cultured corals: identification of vital effects. *Geochim. Cosmochim. Acta* **17**, 5320–5332.

Karl D. M., Bjorkman K. M., Dore J. E., Fjieki L., Hebel D. V., Houlihan T., Letelier R. M. and Tupas L. M. (2001) Ecological nitrogen-to-phosphorus stoichiometry at station ALOHA. *Deep-Sea Res. II* **48**, 1529–1566.

Koroleff, F. (1983) In *Methods of Seawater Analysis* (eds. M. Ehrhardt and K. Grasshoff). Verlag Chemie.

Kumarsingh K., Laydoo R., Chen J. and Siung-Chang A. (1998) Historic records of phosphorus levels in the Reef-building coral *Montastrea annularis* from Tobago, West Indies. *Mar. Pollut. Bull.* **36**, 1012–1018.

LaVigne M., Field M. P., Anagnostou E., Grottoli A. G., Wellington G. M. and Sherrell R. M. (2008) Skeletal P/Ca tracks upwelling in Gulf of Panamá coral: evidence for a new seawater phosphate proxy. *Geophys. Res. Lett.* **35**, L05604.

Lea D. W., Shen G. T. and Boyle E. A. (1989) Coralline barium records temporal variability in equatorial Pacific upwelling. *Nature* **340**, 373–375.

Linsley B. K., Wellington G. M. and Schrag D. P. (2000) Decadal sea surface temperature variability in the subtropical South Pacific from 1726 to 1997 A.D. *Science* **290**, 1145–1148.

Linsley, B. K., Zhang, P., Kaplan, A., Howe, S. S. and Wellington, G. M. (2008) Interdecadal-decadal climate variability from multicoral oxygen isotope records in the South Pacific Convergence Zone region since 1650 A.D. *Paleoceanography* **23**, PA2219.

Littler, M. M., Littler, D. S. and LaPointe, B. E. (1993) Modifications of tropical reef community structure due to cultural eutrophication: the Southwest Coast of Martinique. In *Proceedings of the Seventh International Coral Reefs Symposium*. Guam.

Matthews K., McDonough W. and Grottoli A. (2006) Cadmium measurements in coral skeleton using isotope dilution-inductively coupled plasma-mass spectrometry. *Geochem. Geophys. Geosyst.* **7**.

Matthews, K. A. (2007) *Cadmium in Coral Skeleton: Natural Variability and In situ Calibration*. Dissertation, University of Pennsylvania.

Matthews K. A., Grottoli A. G., McDonough W. F. and Palardy J. E. (2008) Upwelling, species, and depth effects on coral skeleton cadmium-to-calcium ratios (Cd/Ca). *Geochim. Cosmochim. Acta* **72**, 4537–4550.

Montaggioni L. F., Le Cornec F., Corrège T. and Cabioch G. (2006) Coral barium/calcium record of mid-Holocene upwelling activity in New Caledonia, South-West Pacific. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **237**, 436–455.

Montagna P., McCulloch M., Taviani M., Mazzoli C. and Vendrell B. (2006) Phosphorus in cold-water corals as a proxy for seawater nutrient chemistry. *Science* **312**, 1788–1791.

Nurhati I. S., Cobb K. M., Charles C. D. and Dunbar R. B. (2009) Late 20th century warming and freshening in the central tropical Pacific. *Geophys. Res. Lett.* **36**, L21606.

Oxenford H. A., Hunte W., Deane R. and Campana S. E. (1994) Otolith age validation and growth rate variation in flyingfish (Hirundichthys affinis) from the eastern Caribbean. *Mar. Biol.* **118**, 585–592.

Paillard D., Labeyrie L. and Yiou P. (1996) Macintosh program performs time-series analysis. *EOS Trans.* **77**, 379.

Palardy J. E., Grottoli A. G. and Matthews K. A. (2005) Effects of upwelling: depth, morphology and polyp size on feeding in three species of Panamanian corals. *Mar. Ecol. Prog. Ser.* **300**, 79–89.

Porter J. W. (1974) Autotrophy, heterotrophy, and resource partitioning in Caribbean reef-building corals. *Am. Nat.* **110**, 731–742.

Rosenthal Y., Field M. P. and Sherrell R. M. (1999) Precise determination of element/calcium ratios in calcareous samples using Sector Field Inductively Couple Plasma Mass Spectrometry. *Anal. Chem.* **71**, 3248–3253.

Saenger, C., Cohen, A. L., Oppo, D. W. Hubbard, D. (2008) Interpreting sea surface temperature from strontium/calcium ratios in *Montastrea* corals: link with growth rate and implications for proxy reconstructions. *Paleoceanography* **23**, PA3102.

Sarmiento J. L., Gruber N., Brzezinski M. A. and Dunne J. P. (2004) High-latitude controls of thermohaline nutrients and low latitude biological productivity. *Nature* **427**, 56–60.

Shen G. T. and Boyle E. A. (1988) Determination of lead, cadmium and other trace metals in annually-banded corals. *Chem. Geol.* **67**, 47–62.

Shen G. T., Boyle E. A. and Lea D. W. (1987) Cadmium in corals as a tracer of historical upwelling and industrial fallout. *Nature* **328**, 794–896.

Shen G. T., Cole J. E., Lea D. W., Linn L. J., McConnaughey T. and Fairbanks R. G. (1992) Surface ocean variability at Galapagos from 1936 to 1982: Calibration of geochemical tracers in corals. *Paleoceanography* **7**, 563–588.

Shotyk W., Immenhauser-Potthast I. and Vogel H. (1995) Determination of nitrate, phosphate, and organically bound phosphorus in coral skeletons by ion chromatography. *J. Chromatogr. A* **706**, 209–213.

Sinclair D. J. (2005) Correlated trace element 'vital effects' in tropical corals: a new geochemical tool for probing biomineralization. *Geochim. Cosmochim. Acta* **69**, 3265–3284.

Sinclair D. J., Williams B. and Risk M. (2006) A biological origin for climate signals in corals – trace element "vital effects" are ubiquitous in Scleractinian coral skeletons. *Geophys. Res. Lett.* **33**, L17707.

Swart, P. K., Elderfield, H. and Greaves, M. J. (2002) A high-resolution calibration of Sr/Ca thermometry using the Caribbean coral Montastraea annularis. *Geochem. Geophys. Geosyst.* **3**, 2002GC000306.

Taylor R. B., Barnes D. J. and Lough J. M. (1993) Simple models of density band formation in massive corals. *J. Exp. Mar. Biol. Ecol.* **167**, 109–125.

Taylor R. B., Barnes D. J. and Lough J. M. (1995) On the inclusion of trace materials into massive coral skeletons. 1. Materials occurring in the environment in short pulses. *J. Exp. Mar. Biol. Ecol.* **185**, 255–278.

Van Duyl F. C., Gast G. J., Steinhoff W., Kloff S., Veldhuis M. J. W. and Bak R. P. M. (2002) Factors influencing the short-term variation in phytoplankton composition and biomass in coral reef waters. *Coral Reefs* **21**, 293–306.

Associated editors: Anne Cohen