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Upwelling, species, and depth effects on coral skeletal cadmium-to-calcium ratios (Cd/Ca)

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Abstract

Skeletal cadmium-to-calcium (Cd/Ca) ratios in hermatypic stony corals have been used to reconstruct changes in upwelling over time, yet there has not been a systematic evaluation of this tracer's natural variability within and among coral species, between depths and across environmental conditions. Here, coral skeletal Cd/Ca ratios were measured in multiple colonies of *Pavona clavus*, *Pavona gigantea* and *Porites lobata* reared at two depths (1 and 7 m) during both upwelling and nonupwelling intervals in the Gulf of Panama (Pacific). Overall, skeletal Cd/Ca ratios were significantly higher during upwelling than during nonupwelling, in shallow than in deep corals, and in both species of *Pavona* than in *P. lobata*. *P. lobata* skeletal Cd/Ca ratios were uniformly low compared to those in the other species, with no significant differences between upwelling and nonupwelling values. Among colonies of the same species, skeletal Cd/Ca ratios were always higher in all shallow *P. gigantea* colonies during upwelling compared to nonupwelling, though the magnitude of the increase varied among colonies. For *P. lobata*, *P. clavus* and deep *P. gigantea*, changes in skeletal Cd/Ca ratios were not consistent among all colonies, with some colonies having lower ratios during upwelling than during nonupwelling. No statistically significant relationships were found between skeletal Cd/Ca ratios and maximum linear skeletal extension, $\delta^{13}C$ or $\delta^{18}O$, suggesting that at seasonal resolution the Cd/Ca signal was decoupled from growth rate, coral metabolism, and ocean temperature and salinity, respectively. These results led to the following conclusions, (1) coral skeletal Cd/Ca ratios are independent of skeletal extension, coral metabolism and ambient temperature/salinity, (2) shallow *P. gigantea* is the most reliable species for paleoupwelling reconstruction and (3) the average Cd/Ca record of several colonies, rather than of a single coral, is needed to reliably reconstruct paleoupwelling events.

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1. INTRODUCTION

Upwelling in the eastern equatorial Pacific plays a major role in the oceanography and climatology of the tropical Pacific Ocean by driving nutrient-rich waters to the surface, stimulating productivity and increasing the net flux of carbon dioxide from the atmosphere to the ocean. This upwelling region is one of the most studied in the world, yet the frequency, intensity and duration of these events are poorly characterized because of temporal and spatial gaps in oceanographic monitoring (Hayes et al., 1991; Sharp and McLain, 1992). However, the massive hermatypic stony corals found in tropical oceans are potential recorders of upwelling activity. With distinct annual skeletal banding, centennial-scale longevity, high growth rate, and their incorporation of a variety of environmental tracers into

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their aragonite skeleton (see reviews in Gagan et al., 2000; Grottoli and Eakin, 2007), stony corals may provide multi-century, sub-annual resolution records of paleoupwelling in the tropics.

The trace metal cadmium (Cd) is a promising, direct tracer of upwelling due to its behavior and distribution in the water column. Similar to the macronutrient phosphorous, Cd is depleted at the ocean surface via biological activity (e.g., Xu et al., 2008) and enriched at depth by the dissolution of sinking organic material (Boyle et al., 1976; Bruland et al., 1978). During upwelling events, cool deep water is pulled to the surface, bathing reefs in Cd-rich seawater. Coral skeleton appears to record these fluctuating Cd concentrations in seawater (Shen et al., 1987, 1992; Linn et al., 1990; Shen and Sanford, 1990; Delaney et al., 1993; Reuer et al., 2003). Although there are no similar studies of coral aragonite, culturing studies of foraminifera found Cd^{2+} substitution for Ca^{2+} in their calcite lattice (Mashiotta et al., 1997). In the first paper to describe this upwelling proxy in coral, Shen et al. (1987) estimated the seawater-coral distribution coefficient to be ≈1. However the single coral core and the seawater Cd data used to determine that coeffiecient were taken from different regions (the Galápagos and a sampling transect between California and Panama). In addition, although stony corals can be active heterotrophs (e.g., Palardy et al., 2005, 2006), the Cd content of their food (e.g., zooplankton, $[Cd]_{zp}$) is not considered to be a significant source of Cd to the skeleton.

While variations in coral skeletal Cd/Ca ratios (hereafter referred to as Cd/Ca) along the growth axis appear to record paleoupwelling conditions on seasonal to centennial timescales, the variability in the Cd/Ca response among coral colonies of the same species, among multiple coral species, or in colonies at different depths has not been evaluated. Previous research was unable to assess natural variability since only one or two records were available at any single site (Shen et al., 1987; Linn et al., 1990; Shen and Sanford, 1990; Delaney et al., 1993; Reuer et al., 2003). Comparison of four *Pavona clavus* records from the Galápagos Urvina Bay uplift area found that two colonies had higher average Cd/Ca, with a larger range in ratios, than the others (Delaney et al., 1993). Cd/Ca records from two Caribbean coral species showed very low correlation over a 20-year period (Reuer et al., 2003). In a nonupwelling region, Cd/Ca varied widely among same-species fragments from a single site (Ward, 2006). This variation among corals from the same sites suggests that factors other than the concentration of Cd in the seawater influence the coral Cd/Ca signal. The identification of, and accounting for, sources of Cd/Ca variation is necessary for the accurate reconstruction and interpretation of upwelling proxy records.

Previous studies have evaluated the natural variability present in other proxies such as $\delta^{18}O$ [$\delta^{18}O$ = permil deviation of the ratio of $^{18}O/^{16}O$ relative to the Vienna Peedee Belemnite Limestone standard (v-pdb)], a sea surface temperature (SST) and sea surface salinity (SSS) proxy (e.g., Linsley et al., 1994; Wellington et al., 1996), and $\delta^{13}C$ [$\delta^{13}C$ = permil deviation of the ratio of $^{13}C/^{12}C$ relative to v-pdb], a coral feeding and light level proxy (e.g., Felis et al., 1998; Grottoli, 1999, 2002; Grottoli and Wellington,

1999). Rigorous assessments of $\delta^{18}O$ and $\delta^{13}C$ found significant species, depth, growth rate and/or kinetic effects on these proxies (Wellington, 1982; McConnaughey, 1989a,b; Wellington et al., 1996; Grottoli, 1999; Grottoli and Wellington, 1999; Suzuki et al., 2005). Although similarly rigorous quantitative studies of trace metal ratios have not been published, qualitative surveys of coral skeletal Sr/Ca, Mg/Ca, U/Ca and B/Ca ratio variation among multiple *Porites* spp. colonies found generally consistent results for Sr/Ca, but poorer signal reproducibility for the other elements (Fallon et al., 1999; Stephans et al., 2004). Nonetheless, skeletal growth rates affect the incorporation of Sr into the mineral lattice at micrometer (e.g., Allison and Finch, 2004; Cohen and McConnaughey, 2003) and centimeter scales (e.g., de Villiers et al., 1994, 1995). Sinclair and others (Sinclair, 2005; Sinclair et al., 2006) found strong evidence for biologically-driven "vital effects" on Sr, Mg and U incorporation into seven *Porites* spp. fragments at both fine and seasonal scales. Thus, given the variations in Cd and other trace elements in coral, a systematic assessment of Cd/Ca was deemed necessary in order to accurately construct, interpret and compare paleoupwelling records from different locations, species and depths.

Here, we evaluated the effects of species, depth and upwelling on Cd/Ca in the seasonally upwelling Gulf of Panama (Pacific). Using coral fragments from multiple colonies from three species of corals at two depths, with stain lines marking the upwelling and nonupwelling intervals, the following hypotheses were tested: (1) Cd/Ca is higher during upwelling than nonupwelling, (2) Cd/Ca varies among species and across depth, and (3) Cd/Ca is correlated to other proxies that respond to upwelling-influenced conditions (i.e., SST/SSS via $\delta^{18}O$, feeding/light levels via $\delta^{13}C$).

2. MATERIALS AND METHODS

2.1. Site description

The low-pressure Inter-Tropical Convergence Zone (ITCZ) determines the seasonal pattern of wind, rainfall, and upwelling along the Pacific coast of Panama. During the nonupwelling "rainy" season (∼April–December), the ITCZ lies over or slightly to the north of Panama, with variable light winds, high cloud cover and rainfall. These conditions are coupled with higher SST, and lower SSS (due to rainfall) and nutrient levels (D'Croz et al., 1991). The upwelling "dry" season (∼January–April) occurs when the ITCZ migrates south of Panama, bringing strong north to northeast trade winds, minimal cloud cover and precipitation. Trade winds displace the warm surface water offshore, drawing cooler, more saline deep water to the surface. Upwelling can be directly observed with lower SST, and higher SSS and nutrient levels (Forsbergh, 1969; D'Croz et al., 1991; D'Croz and Robertson, 1997; D'Croz and O'Dea, 2007).

The study site was located in the Pearl Islands, Gulf of Panama (Fig. 1). This archipelago, centrally located in the Gulf, is a shallow rise surrounded by deeper water on all sides. The patch reefs off Playa Cacique, Contadora Island (8°38′N, 79°03′W) were chosen because they are (1) fully
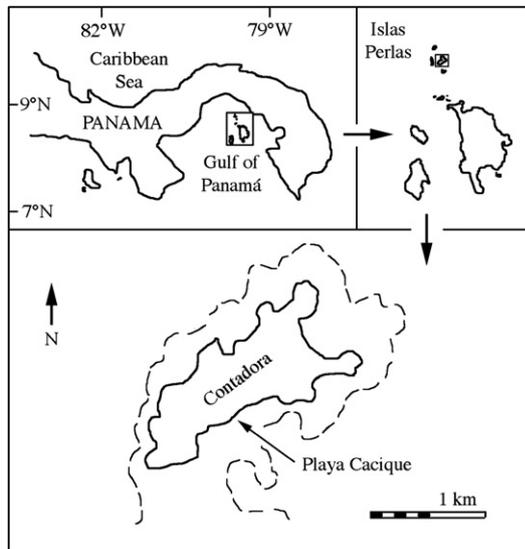
Fig. 1. The Pearl Islands and Contadora Island, Gulf of Panama, Panama. (From U.S. Defense Mapping Agency Chart numbers 21605 and 21607 redrafted from Wellington, 1982).

exposed to upwelling and nonupwelling waters (D'Croz et al., 1991), (2) located >30 km from major population centers and pollution sources, and (3) well studied, with a suite of existing complementary information on coral growth (Glynn, 1977; Wellington and Glynn, 1983), stable isotopic (Wellington and Dunbar, 1995; Grottoli and Wellington, 1999), and elemental (Shen and Sanford, 1990) ratios. Tides at Contadora are semidiurnal with a mean spring range of 7.2 m (Wellington, 1982). Patch reefs and isolated coral heads surround the island (Glynn and Maté, 1997).

2.2. Experimental design

Pavona clavus, *Pavona gigantea* and *Porites lobata* are the most common mounding corals in the Gulf of Panama (Glynn and Maté, 1997; Glynn and Ault, 2000) and are among the species most frequently used for paleoclimate reconstruction. In January 2003, 10 fragments (5–10 cm in diameter) each from *P. clavus*, *P. gigantea* and *P. lobata* colonies were collected at approximately 4 m depth (below mean low tide) and five of each species were deployed to the 1- and 7-m study sites (5 fragments × 3 species × 2 depths). On 31 January 2003, at the beginning of upwelling, all corals were stained *in situ* with Alizarin Red and cemented to the reef. Two and a half months later, on 15 April 2003 at the approximate end of the upwelling season as determined by observed sustained increases in SST, corals were re-stained and replaced on the reef to continue growing under nonupwelling conditions. Three months later, on 13 July 2003, corals were stained a final time and left to grow past the last stain line, minimizing any potential interference of the tissue layer on the skeletal isotopic and trace metal analyses (Esslemont et al., 2000). This also allowed for the completion of any possible skeletal "backfilling" (Barnes and Lough, 1993; Taylor and Lough, 1993) during the latter part of the study period.

January through July 2003 equally straddled the upwelling and nonupwelling seasons in the Gulf of Panama, thus exposing the corals to the maximum range of local ocean conditions. In February 2004 after seven months of growth beyond the final stain line, all corals were collected, surface tissue removed, and transported to the laboratory for geochemical analyses (see below).

Seawater conditions and chemistry were monitored at the site from January to July 2003. Seawater temperature and downwelling light intensity on the reef were monitored *in situ* using submerged temperature loggers (at 1 and 7 m depths; 2 readings/h) and a light meter (at 1 m depth; 1 reading/h) (Onset Computer Corporation, MA, USA). Salinity measurements were taken every 3 days using a hand-held refractometer. Sub-surface (1 m) seawater samples were collected every 3 days. Additional seawater samples from 5 m depth ($n = 5$) were taken over the course of the study period for comparative purposes. For each sample, 1 L of seawater was collected in a high-density polyethelyne (HDPE) bottle (rinsed three times with seawater prior to collection). A 20-mL subsample was filtered with a 0.4-μm filter and immediately preserved with mercuric chloride for stable oxygen and dissolved inorganic carbon isotopic analyses of the seawater ($\delta^{18}O_{sw}$ and $\delta^{13}C_{DIC}$). An additional 250-mL seawater subsample was processed for dissolved Cd ($[Cd]_{sw}$) analysis according to Field et al. (1999). Briefly, 250-mL of seawater were vacuum-filtered using an acid-cleaned 0.22-μm polycarbonate filter, acidified to a pH of 2 using ultra-clean concentrated HCl (Optima Grade, Fisher Chemical, NJ, USA), and stored in an acid-leached 250-mL HDPE bottle. Procedural blanks were taken by filtering MilliQ water (18 MΩ; Millipore, MA, USA) in lieu of seawater. Zooplankton samples were collected at nautical twilight as described in Palardy et al. (2006) during upwelling and nonupwelling periods. A subsample of the bulk zooplankton sample was isolated onto a pre-cleaned polycarbonate filter, and then frozen for cadmium analysis ($[Cd]_{zp}$). Though not considered to be a significant source of Cd to the coral skeleton, these zooplankton samples were analyzed for $[Cd]_{zp}$ to test this assumption.

2.3. Laboratory analyses

Each coral fragment was cut into a ~1-cm-thick slab along the axis of maximum linear skeletal extension (MLSE) to expose the stain lines, then cleaned with pressurized MilliQ water, sonicated in MilliQ water, and dried at 60 °C for at least 5 days. Photographs and X-radiographs were taken to compare stain lines and skeletal growth bands (Fig. 2). The MLSE between each stain line was measured on each fragment using a dissecting microscope and calipers. Bulk coral samples were extracted along the axis of maximum growth for upwelling and nonupwelling conditions by milling a section 1 mm wide by 1 mm deep for the entire length of growth between the first two (upwelling) and last two (nonupwelling) stain lines. Each sample was homogenized using an acid-washed agate mortar and pestle. A subsample was removed for stable isotopic analysis and the remainder used for Cd analysis.
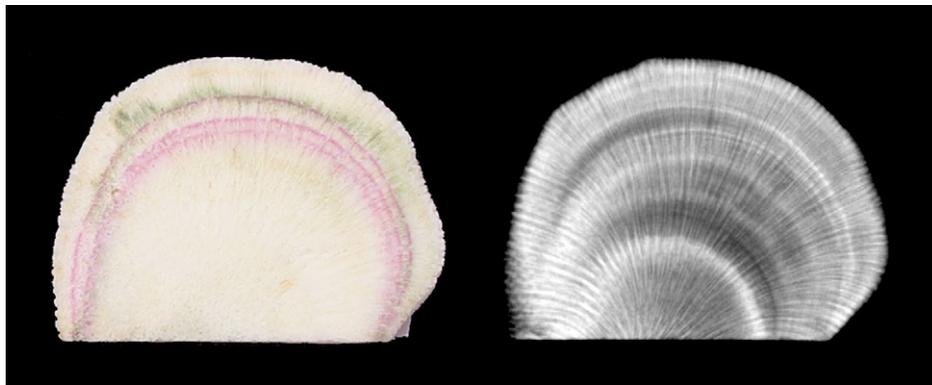
Fig. 2. Photograph and X-radiograph negative of a *Pavona clavus* fragment from 1 m depth, Playa Cacique, Contadora Island, Gulf of Panama. The base of the fragment is 5 cm across. The stain lines mark, from bottom to top, 31 January 2003, 15 April 2003 and 13 July 2003. The coral was collected on 13 February 2004.

2.3.1. Cadmium analyses

All solutions were made with MilliQ water and ultrapure reagents, unless otherwise noted. All labware was cleaned using acid leaching prior to sample handling. Coral, seawater and plankton samples were processed in a Class 100 clean room.

Coral samples and standards were cleaned and analyzed for skeletal Cd concentration ($[Cd]_{coral}$) and Cd/Ca ratios using isotope dilution-inductively coupled plasma-mass spectrometry (ID-ICP-MS) according to the method detailed in Matthews et al. (2006). In brief, ~25 mg of each bulk sample were cleaned using a procedure adapted from Martin and Lea (2002) and Reuer (2002). This process included oxidative and reductive steps to remove organics and oxides, respectively, as well as multiple leaches with weak nitric acid and multiple rinses in MilliQ water. The samples were then weighed, spiked with a known amount of ^{113}Cd (Oak Ridge National Laboratory, TN, USA) and dissolved. A 100-μL aliquot of solution was removed and analyzed for Ca using gravimetric standards with a yttrium internal standard for signal normalization. The remaining solution was passed through a chromatographic column to remove alkaline earth elements. This Cd-bearing eluant, as well as the Ca-bearing aliquot, were analyzed using an Element2 single-collector ICP-MS (Thermo Electron Corp., Bremen, Germany) with dry desolvation introduction (Aridus; CETAC Technologies, NE, USA). At least 10% of all samples were run in duplicate, along with an in-house coral standard (PPC-1) and certified reference materials which were used to monitor accuracy and precision. The relative first standard deviation (RSD; standard deviation as a percent of Cd/Ca or $[Cd]_{coral}$ value) of repeated measurements of Cd/Ca in PPC-1 was $\pm 2.0\%$ ($n = 12$). The RSD of $[Cd]_{coral}$ results for PPC-1 was $\pm 2.2\%$ ($n = 12$). The limit of determination (LoD = mean blank signal + 6[SD of blank signal]) ranged from 0.013 ppb (0.012 nmol/mol) to 0.057 ppb Cd (0.047 nmol/mol).

Seawater was analyzed using a method adapted from Field et al. (1999). A direct, 10-fold dilution of each filtered, acidified seawater sample was passed through the Aridus desolvator and delivered to the Element2 ICP-MS. Cd concentration of the seawater samples and the CASS-4 seawa-

ter standard (National Research Council, Canada) were determined by normalized standard addition. Repeated measurements of this standard yielded an RSD of $\pm 2.2\%$ ($n = 10$), with a LoD of 10.6 ppt.

Measurements of Cd concentration in the zooplankton samples were made using a method modified from Arslan et al. (2000). Zooplankton samples were thawed, rinsed three times with MilliQ water and allowed to dry under clean conditions. Samples were completely digested in closed beakers at 80 °C using strong HNO_3 and HF, dried down and reconstituted in 2% HNO_3. Using indium-spiked gravimetric standards, Cd concentrations were measured using normalized standard addition. Measurements of an internal zooplankton standard had an RSD of $\pm 7.8\%$ ($n = 6$), with a LoD of 0.011 ppm.

2.3.2. Stable isotope analyses

For each sample, 80–100 μg of coral powder were acidified with 100% H_3PO_4 in an automated carbonate Kiel device at 70 °C. $\delta^{13}C$ and $\delta^{18}O$ values of the resulting CO_2 gas were measured with a Finnigan MAT 252 triple collecting stable isotope ratio mass spectrometer (SIR-MS) and reported relative to the v-pdb standard. Repeated measurement of the NBS 19 standard ($n = 25$) had a standard deviation of $\pm 0.03\%$ for $\delta^{13}C$ and $\pm 0.06\%$ for $\delta^{18}O$. The $\delta^{13}C_{DIC}$ measurements were carried out by acidifying the seawater on a vacuum line, cryogenically isolating the CO_2 gas into sealed glass ampoules, and then introducing the gas via a multiport inlet system into the Finnigan 252 SIR-MS for isotopic analysis. For $\delta^{18}O_{sw}$ measurements, samples were equilibrated with CO_2 gas of known isotopic composition and then analyzed by SIR-MS (reported relative to v-pdb). Repeated measurement of internal standards for $\delta^{13}C_{DIC}$ ($n = 44$) and $\delta^{18}O_{sw}$ ($n = 7$) had standard deviations of $\pm 0.02\%$ and $\pm 0.1\%$, respectively. At least 10% of all stable isotopic measurements were made in duplicate.

2.4. Statistical analyses

Student's *t*-tests were used to determine if the mean upwelling and nonupwelling values of SSS, light intensity,

$[Cd]_{sw}$, $\delta^{13}C_{DIC}$, $\delta^{18}O_{sw}$ and $[Cd]_{zp}$ were significantly different from each other. A two-way Model I Analysis of Variance (ANOVA) tested for significant effects of depth (1 and 7 m) and interval (upwelling and nonupwelling) on SST. A three-way Model I ANOVA analyzed the effects of species (*P. clavus*, *P. gigantea*, *P. lobata*), depth, and interval on skeletal Cd/Ca, MLSE, $\delta^{13}C$ and $\delta^{18}O$. Species, depth and interval were fixed effects, and all effects were fully crossed. Post hoc Tukey tests were used to determine which means significantly differed within each effect. *A posteriori* slice tests (e.g., tests of simple effects, Winer, 1971) determined if upwelling and nonupwelling Cd/Ca averages significantly differed from each other within species and depth. Monte Carlo tests with 10,000 iterations determined, for sample sizes of 1 through 5, the probabilities of, (1) the experimental mean ΔCd/Ca (ΔCd/Ca = Cd/Ca$_{upwelling}$ − Cd/Ca$_{nonupwelling}$ for each fragment) falling within 1SD of the mean ΔCd/Ca generated by the Monte Carlo procedure and (2) the mean ΔCd/Ca from the Monte Carlo procedure falling within 1SD of the experimental mean of ΔCd/Ca. Linear correlation analysis modeled the relationship between coral Cd/Ca and coral MLSE, $\delta^{13}C$ and $\delta^{18}O$.

Data were normally distributed as determined from plots of the residuals versus the predicted values for each variable. Statistical analyses were generated using SAS software, Version 8.02 of the SAS System for Windows. [Copyright ©1999–2001 SAS Institute Inc. SAS and all other SAS Institute Inc. product or service names are registered trademarks or trademarks of SAS Institute Inc., Cary, NC, USA.] *P*-levels $\leqslant 0.05$ were considered significant unless otherwise noted.

3. RESULTS

3.1. Physical and chemical oceanographic conditions

The complete SST and SSS records illustrate clear variation with respect to upwelling (Fig. 3). Large cold pulses of seawater characterized the January–April 2003 period and were followed by warmer and less variable SSTs through
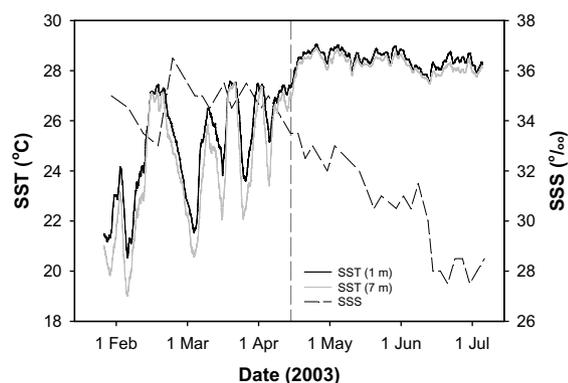

Fig. 3. Sea surface temperature (SST; twice hourly, with the application of a 48-point running mean), and sea surface salinity (SSS; sampled every 3 days) at Contadora Island, Gulf of Panama from January to July, 2003. Coral colonies used in this study were stained in late January (start of data collection), mid-April (vertical dashed line) and mid-July (end of data collection).

Table 1
Average values ±1 standard error during upwelling (January–April 2003) and nonupwelling (April–July 2003) intervals for various monitored parameters at Contadora Island, Gulf of Panama

Parameter	Upwelling	Nonupwelling	p
SST at 1 m (°C)	24.79 ± 0.04	28.34 ± 0.01	<0.0001*
SST at 7 m (°C)	23.83 ± 0.05	28.10 ± 0.01	<0.0001*
SSS (‰)	34.91 ± 0.20	30.78 ± 0.44	<0.0001*
Light intensity (W/m^2)	0.32 ± 0.02	0.15 ± 0.01	<0.0001*
$[Cd]_{sw}$ (10^{-12} g/g [ppt])	35.4 ± 2.2	34.2 ± 1.4	0.728
$\delta^{13}C_{DIC}$ (‰, v-pdb)	0.96 ± 0.11	1.06 ± 0.05	0.384
$\delta^{18}O_{sw}$ (‰, v-pdb)	-29.68 ± 0.02	-30.43 ± 0.11	<0.0001*
$[Cd]_{zp}$ (10^{-6} g/g dry weight [ppm])	2.5 ± 0.6	1.9 ± 0.4	0.227

Sea surface temperature (SST) was measured every 30 min; light intensity every 60 min; sea surface salinity (SSS), dissolved Cd in seawater ($[Cd]_{sw}$), the carbon isotope ratio of dissolved inorganic carbon in seawater ($\delta^{13}C_{DIC}$), and the oxygen isotope ratio of seawater ($\delta^{18}O_{sw}$) every 3 days. Six zooplankton samples were collected in June 2003 (nonupwelling) and two in February 2004 (upwelling) and analyzed for Cd content ($[Cd]_{zp}$). The Student's *t*-test determined significance and parameters with significantly different means ($p \leqslant 0.05$) are marked with a ∗ symbol.

July 2003 (Fig. 3). SSS also behaved as expected, with more saline water during upwelling, followed by freshening with the onset of the nonupwelling (rainy) season (Fig. 3). SST was significantly colder, by 3.91 °C, during the upwelling versus nonupwelling intervals, and by 0.60 °C at 7 m compared to 1 m depth (Table 1). In addition, the difference in SST between the 1 and 7 m depths was significantly greater during the upwelling interval (0.96 °C) than during the nonupwelling interval (0.24 °C) (Table 2). Average SSS, light intensity, and $\delta^{18}O_{sw}$ were all significantly higher during upwelling compared to the nonupwelling interval (Table 1). Average $\delta^{13}C_{DIC}$, $[Cd]_{sw}$ and $[Cd]_{zp}$ were not significantly different between upwelling and nonupwelling intervals (Table 1).

To determine if $[Cd]_{sw}$, $\delta^{13}C_{DIC}$ or $\delta^{18}O_{sw}$ differed between the 1- and 7-m depths, five pairs of 1- and 5-m water samples were taken concurrently over the course of the field season. Within instrumental error, no differences in the $\delta^{18}O_{sw}$, $[Cd]_{sw}$ and most of the $\delta^{13}C_{DIC}$ values were detected. Despite two $\delta^{13}C_{DIC}$ samples with slightly higher $\delta^{13}C_{DIC}$ ratios at 1 m than at 7 m, average $\delta^{13}C_{DIC}$ ratios were not significantly different between depths.

Table 2
Results of a two-way Model I ANOVA of sea surface temperature (SST) assessing effects of depth (1 and 7 m) and interval (upwelling and nonupwelling) at Contadora Island, Panama ($n = 14,878$)

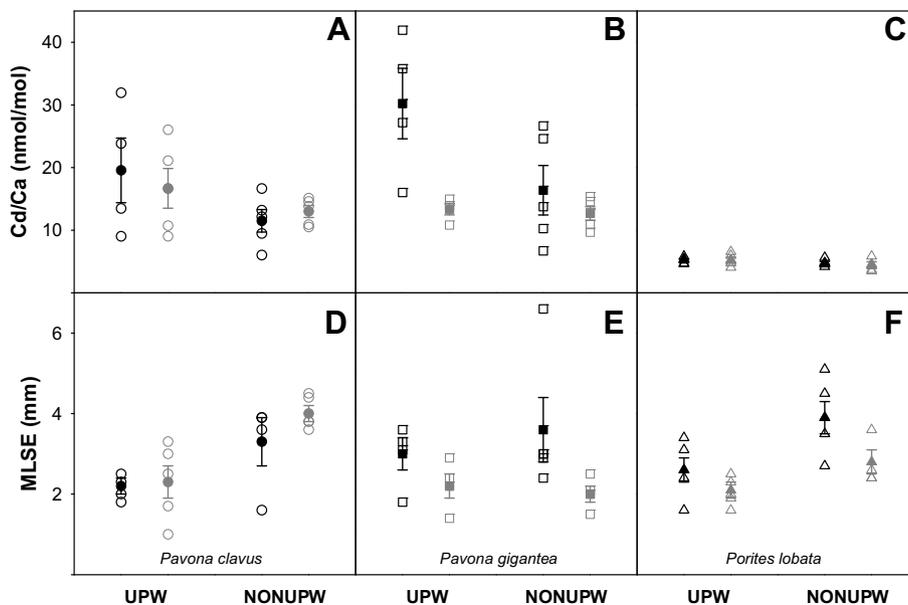| Source	df	SST	
		SS	Pr > F
Model	1	54,610.6	<0.0001*
Depth	1	94.7	<0.0001*
Interval	1	21,990.0	<0.0001*
Depth × interval	1	422.3	<0.0001*
Error	14,877	44,643.4	

Significant *p* values are marked with a ∗ symbol.

Fig. 4. Cd/Ca and maximum linear skeletal extension (MLSE) in *Pavona clavus* (A,D), *Pavona gigantea* (B,E) and *Porites lobata* (C,F) during upwelling (UPW, January–April) and nonupwelling (NONUPW, April–July) intervals. Open symbols represent individual sample measurements; closed symbols show means ± 1 standard error. Black = 1 m; gray = 7 m depth.

3.2. Coral Cd, MLSE, $\delta^{13}C$, $\delta^{18}O$

Of the 30 fragments deployed for the experiment (5 fragments × 3 species × 2 depths), 29 were recovered at the conclusion of the study period (one *P. gigantea* colony was lost). Of the possible 58 intervals (29 fragments × 2 intervals), two were lost during processing. In total, 56 bulk coral samples were taken and each analyzed for skeletal Cd/Ca, [Cd]$_{coral}$, MLSE, $\delta^{13}C$ and $\delta^{18}O$ (*P. clavus* n = 19, *P.*

gigantea n = 18, *P. lobata* n = 19) (Figs. 4, 5). Cd/Ca varied significantly among species (*P. gigantea* = *P. clavus* ≫ *P. lobata*), between depths (1 m > 7 m), and between intervals (upwelling > nonupwelling) (Table 3, Fig. 4). *P. lobata* was markedly different from the other two species, with much lower mean concentration and within-species variability. The species by depth interaction was significant, indicating that the magnitude of the Cd/Ca response to depth differed among coral species. Since the leverage plots of the interac-
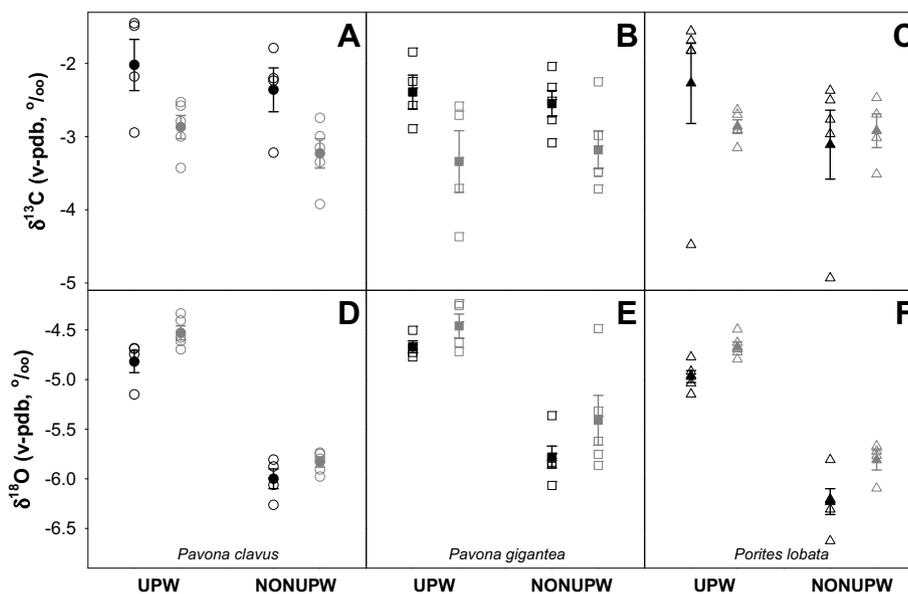

Fig. 5. Skeletal $\delta^{13}C$ and $\delta^{18}O$ (reported relative to the Vienna PeeDee Belemnite (v-pdb) standard) in *Pavona clavus* (A,D), *Pavona gigantea* (B,E) and *Porites lobata* (C,F) during upwelling (UPW, January–April) and nonupwelling (NONUPW, April–July) intervals. Open symbols represent individual sample measurements; closed symbols show means ± 1 standard error. Black = 1 m; gray = 7 m depth.

Table 3
Results of a three-way Model I ANOVA assessing species, depth (1 and 7 m), and interval (upwelling and nonupwelling) effects on skeletal $[Cd]_{coral}$ and Cd/Ca in *Pavona clavus*, *Pavona gigantea* and *Porites lobata* at Contadora Island, Panama ($n = 56$)

Source	df	$[Cd]_{coral}$		Cd/Ca	
		SS	Pr > F	SS	Pr > F
Model	11	1550.1	<.0001*	2659.7	<0.0001*
Species	2	1299.1	<.0001*	1728.3	<0.0001*
Depth	1	9.2	0.7491	189.8	0.0162*
Interval	1	149.7	0.0079*	289.0	0.0035*
Species × depth	2	47.4	0.5048	297.7	0.0120*
Species × interval	2	67.3	0.0849	112.9	0.1677
Depth × interval	1	8.4	0.7844	112.4	0.0608
Species × depth × interval	1	6.9	0.9356	107.5	0.1820
Error	44	645.7		1335.6	

Significant *p* values are marked with a * symbol.

tion term do not cross, main effects remain interpretable. Additional *a posteriori* slice tests revealed that Cd/Ca was significantly lower during nonupwelling than during upwelling in the shallow *P. clavus* and *P. gigantea* species only. $[Cd]_{coral}$ also significantly differed between species (*P. gigantea* = *P. clavus* ≫ *P. lobata*) and intervals (upwelling > nonupwelling), but not between depths (Table 3). No interaction effects were significant for $[Cd]_{coral}$.

MLSE did not significantly differ among species, but was significantly lower at 7 m compared to 1 m, and during upwelling compared to nonupwelling (Table 4). The *a posteriori* slice tests coupled with the significant species by depth interaction effect shows that unlike the other species, *P. clavus* grew faster at depth (Table 4, Fig. 4). Coral skeletal $\delta^{13}C$ did not significantly differ among species, was significantly more enriched in colonies growing at 1 m than at 7 m, and did not significantly differ between intervals (Table 4). Coral skeletal $\delta^{18}O$ significantly differed among species (*P. gigantea* > *P. clavus* > *P. lobata*), was significantly more enriched at 7 m compared to 1 m, and during upwelling compared to nonupwelling (Table 4 and Fig. 5). No interaction effects were significant.

The magnitude of Cd/Ca change within individual coral colonies ($\Delta Cd/Ca = Cd/Ca_{upwelling} - Cd/Ca_{nonupwelling}$ for

each colony) was calculated. Sample loss (one *P. clavus* upwelling section, one *P. lobata* nonupwelling section) prevented the determination of those fragments' $\Delta Cd/Ca$, thus only 26 values are reported here. Although the majority of the $\Delta Cd/Ca$ values were positive as expected, six out of the 26 values were negative (Fig. 6). The change in Cd/Ca between upwelling and nonupwelling was significantly greater in shallow than in deep corals. Results from the Monte Carlo tests suggested that when using the mean $\Delta Cd/Ca$ of three fragments there is a 75% probability that the "true" $\Delta Cd/Ca$ is within error of the estimated mean for both shallow *P. gigantea* and *P. clavus*, although that probability drops to ∼50% when $n = 2$ (Table 5).

The relationships between coral skeletal Cd/Ca and MLSE, $\delta^{13}C$ and $\delta^{18}O$ were evaluated with correlation analyses (Fig. 7). In all cases, (i.e., for comparisons of individual species, and for pooled *Pavona* spp.) there were no statistically significant correlations between any tested parameters (Table 6).

4. DISCUSSION

4.1. Oceanographic conditions

SST and SSS fluctuated in response to the distinct upwelling event (Fig. 3). Pulses of cold, deep, saline water (e.g., 21 °C, 35‰) characterized the upwelling interval from January to mid-April. In mid-April, SST increased abruptly and then stabilized at ∼28.5 °C, while SSS decreased gradually with the onset of the rainy season to a low of 27.5‰. The pattern and range of SST and SSS recorded between January and April 2003 were similar to those observed by Wellington and Glynn (1983), D'Croz et al. (1991), D'Croz and Robertson (1997) and D'Croz and O'Dea (2007), indicating that this upwelling season was typical for the region.

This upwelling interval was further distinguished by high $\delta^{18}O_{sw}$ and downwelling light intensity on the reef relative to the nonupwelling interval (Table 1). Like SSS, $\delta^{18}O_{sw}$ varies due to evaporation, precipitation and water mass mixing (Epstein and Mayeda, 1953; Criss, 1999). The increases in precipitation and cloud cover during the nonupwelling interval were most likely the main drivers for the observed decreases in $\delta^{18}O_{sw}$. Downwelling light

Table 4
Results of a three-way Model I ANOVA assessing species, depth (1 and 7 m), and interval (upwelling and nonupwelling) effects on maximum linear skeletal extension (MLSE), $\delta^{13}C$ and $\delta^{18}O$ in *Pavona clavus*, *Pavona gigantea*, and *Porites lobata* at Contadora Island, Panama ($n = 56$)

Source	df	MLSE		$\delta^{13}C$		$\delta^{18}O$	
		SS	Pr > F	SS	Pr > F	SS	Pr > F
Model	11	27.3	0.0018*	9.0	0.0923	20.9	<0.0001*
Species	2	0.5	0.7151	0.6	0.5516	1.9	0.0008*
Depth	1	3.6	0.0311*	5.2	0.0017*	1.2	<0.0001*
Interval	1	10.2	0.0005*	0.9	0.1606	18.3	<0.0001*
Species × depth	2	6.5	0.0169*	1.2	0.2807	<0.1	0.7325
Species × interval	2	3.2	0.1222	0.5	0.5950	0.1	0.3811
Depth × interval	1	0.3	0.5500	0.4	0.3413	<0.1	0.7129
Species × depth × interval	1	1.4	0.3961	0.4	0.6800	0.1	0.6617
Error	44	30.2		19.9		2.7	

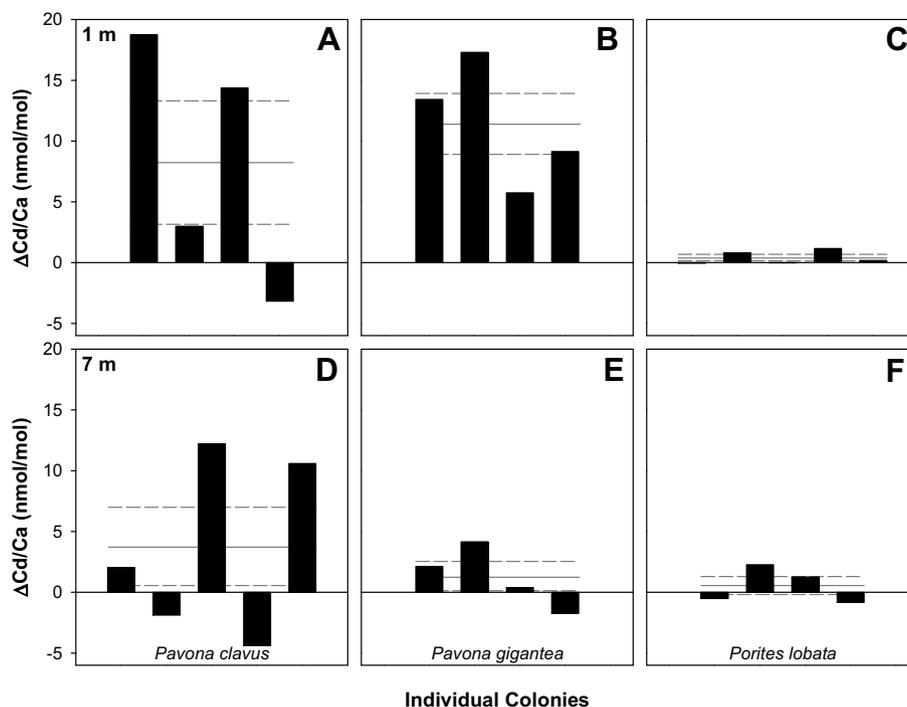Significant *p* values are marked with a * symbol.

Fig. 6. Difference in Cd/Ca between upwelling and nonupwelling samples in each colony of *Pavona clavus* (A,D), *Pavona gigantea* (B,E) and *Porites lobata* (C,F) ($\Delta Cd/Ca = Cd/Ca_{upwelling} - Cd/Ca_{nonupwelling}$). The data in the top panels (A–C) are from 1 m depth, and the bottom panels (D–F) from 7 m depth. The solid horizontal grey line marks the average value in each panel, and the dashed lines mark ±1 standard error.

Table 5
Probability results generated using the Monte Carlo procedure for $\Delta Cd/Ca$ ($\Delta Cd/Ca = Cd/Ca_{upwelling} - Cd/Ca_{nonupwelling}$) from all *Pavona clavus*, *Pavona gigantea* and *Porites lobata* samples

	P. clavus (1 m)	*P. clavus* (7 m)	*P. gigantea* (1 m)	*P. gigantea* (7 m)	*P. lobata* (1 m)	*P. lobata* (7 m)
Probability that the experimental mean $\Delta Cd/Ca$ is within 1 standard deviation of the randomized mean $\Delta Cd/Ca$						
$n = 1$	n/a	n/a	n/a	n/a	n/a	n/a
$n = 2$	0.506	0.483	0.507	0.376	0.490	0.565
$n = 3$	0.754	0.725	0.748	0.560	0.727	0.748
$n = 4$	0.880	0.797	0.874	0.665	0.842	0.819
$n = 5$	0.926	0.892	0.911	0.748	0.898	0.891
Probability that the randomized mean $\Delta Cd/Ca$ is within 1 standard deviation of the experimental mean $\Delta Cd/Ca$						
$n = 1$	0.506	0.593	0.501	0.757	0.795	0.602
$n = 2$	0.876	0.843	0.878	0.941	0.880	0.918
$n = 3$	0.971	0.936	0.967	0.986	0.968	0.939
$n = 4$	0.993	0.975	0.990	0.984	0.983	0.976
$n = 5$	0.992	0.990	0.993	0.992	0.994	0.991

intensity on the reef was primarily a function of two competing factors: water turbidity which was highest during upwelling due to enhanced algal and zooplankton concentrations, and cloud cover which was highest during nonupwelling as this was also the rainy season. Due to a near total lack of cloud cover and despite high turbidity, average downwelling light intensity during upwelling was twice that measured during nonupwelling (Table 1; see also Glynn, 1977).

Since Contadora is a small island composed of siliciclastic material, the influence of surface runoff on $\delta^{13}C_{DIC}$ during the nonupwelling (rainy) season was not expected to be

significant. As such, the primary forcing mechanism for any change in $\delta^{13}C_{DIC}$ was variation in ocean water composition. The mean $\delta^{13}C_{DIC}$ values for upwelling and nonupwelling intervals did not vary significantly; however the slight depletion found during upwelling is consistent with the lower $\delta^{13}C_{DIC}$ typically observed in deep water (Kroopnick, 1985).

$[Cd]_{sw}$ and $[Cd]_{zp}$ did not significantly differ between upwelling and nonupwelling periods. Although not previously measured during a tropical upwelling event, $[Cd]_{sw}$ was expected to be significantly higher during the upwelling interval given the high dissolved phosphate concentrations

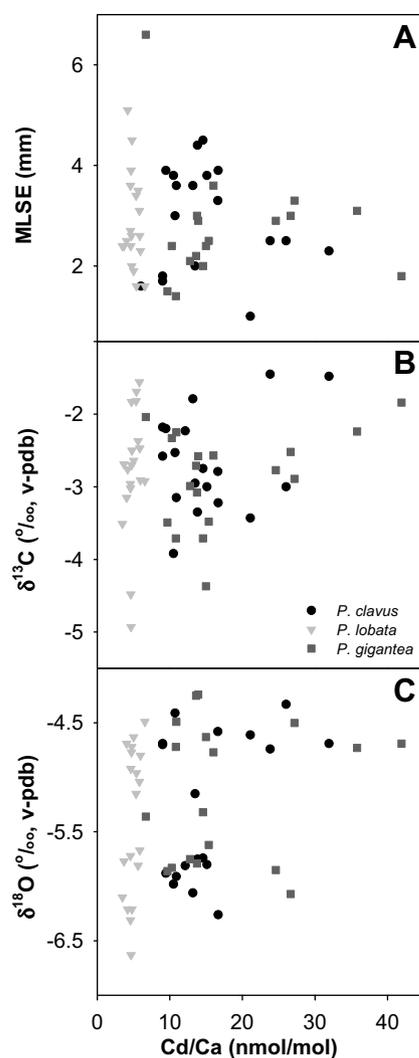Fig. 7. Scatter plots of coral Cd/Ca versus maximum linear skeletal extension (MLSE) (A), $\delta^{13}C$ (B) and $\delta^{18}O$ (C) for each species (*Pavona clavus*, *Pavona gigantea* and *Porites lobata*). The results of the correlation analyses are in Table 6.

Table 6
Results of correlation analyses of Cd/Ca versus maximum linear skeletal extension (MLSE), $\delta^{13}C$, and $\delta^{18}O$ for all *Pavona clavus*, *Pavona gigantea*, *Porites lobata* samples

Correlation			r	p
Cd/Ca		Parameter		
Pavona spp.	vs.	MLSE	0.14	0.410
P. clavus	vs.	MLSE	0.14	0.574
P. gigantea	vs.	MLSE	0.14	0.641
P. lobata	vs.	MLSE	0.22	0.351
Pavona spp.	vs.	$\delta^{13}C$	0.30	0.075
P. clavus	vs.	$\delta^{13}C$	0.28	0.257
P. gigantea	vs.	$\delta^{13}C$	0.37	0.128
P.lobata	vs.	$\delta^{13}C$	0.36	0.132
Pavona spp.	vs.	$\delta^{18}O$	0.26	0.118
P. clavus	vs.	$\delta^{18}O$	0.41	0.086
P. gigantea	vs.	$\delta^{18}O$	0.14	0.556
P.lobata	vs.	$\delta^{18}O$	0.42	0.071

Scatter plots are shown in Fig. 7.

sured in the Gulf of Panama (D'Croz and O'Dea, 2007 and references therein) would not have the same timing in concentration maxima as seen in $[Cd]_{sw}$. Although not significant at this small sample size, $[Cd]_{zp}$ was slightly higher during upwelling, providing further support the hypothesis of initial rapid uptake of bio-active Cd by organisms (Lea et al., 1989). High resolution sampling of seawater (particulate and dissolved), phytoplankton, zooplankton and coral tissue throughout the upwelling season would further illuminate this $[Cd]_{sw}$ scavenging process.

4.2. Cadmium in coral

4.2.1. Species effect

Cd/Ca and $[Cd]_{coral}$ significantly differed among species (Table 3 and Fig. 4). Grottoli and Wellington (1999) also found species-specific differences in $\delta^{13}C$ between *P. clavus* and *P. gigantea* at this site. Researchers have also identified species-specific offsets for other paleoceanographic tracers, such as $\delta^{18}O$ and Sr/Ca (e.g., Dunbar et al., 1994; de Villiers et al., 1994; Wellington et al., 1996). Due to the very limited number of colonies and species for which Cd/Ca data are available, a broader discussion of species effects is not possible. However, previously published works appear to qualitatively illustrate these differences among species. Reuer et al. (2003) reported that the range of Cd/Ca values in a single Caribbean *Siderastrea siderea* colony was greater than in a single *Montastrea annularis* colony collected at the same site. In the Pacific, average *P. clavus* (Galápagos) ratios were somewhat lower than average *P. gigantea* (Panama) ratios (Linn et al., 1990; Shen et al., 1992; Shen and Sanford, 1990). This disparity was originally noted in Shen and Sanford (1990), and a "location" effect was postulated. However results from the current study indicate that *P. clavus* has lower Cd/Ca values than *P. gigantea* at the same site, suggesting that species, in addition to location, must be considered as a source of Cd/Ca variability.

Cd/Ca levels in *P. lobata* corals showed the smallest response to upwelling, irrespective of depth and interval

measured during upwelling events in the region (e.g., D'Croz and O'Dea, 2007), and the positive correlation between dissolved phosphate and $[Cd]_{sw}$ in the global ocean (Boyle et al., 1976; de Baar et al., 1994). Instead, the data presented here suggest that $[Cd]_{sw}$ is highly bio-active and rapidly scavenged at the beginning of upwelling at a pace similar to its supply rate, keeping $[Cd]_{sw}$ low during early stages of upwelling. Lea et al. (1989) also noted the high bio-activity and scavenging rate for Cd, suggesting that its concentration would remain low during weak upwelling and increase only when supply exceeds uptake. This possibility is further supported by a closer examination of time series data from our study, which indicates that the $[Cd]_{sw}$ maximum lagged the SST minimum by ~4 weeks (Matthews, 2007).

Furthermore, the Cd in surface seawater appears to be preferentially removed compared to phosphate (de Baar et al., 1994), suggesting that the phosphate records mea-

(Fig. 4C). Possible reasons for the lack of Cd variability in *P. lobata* (and, potentially in other species) include: (1) low rates of feeding on plankton, (2) effects of growth-related kinetics and/or (3) an artifact of the cleaning process. First, species-specific differences in feeding behavior could produce a wide range of Cd/Ca if metals from consumed zooplankton were incorporated into the coral skeleton. Fallon et al. (2002) suggested that coral heterotrophy may affect trace metal concentrations if there was a distinct difference in the quality (e.g., zooplankton versus bacteria or particulates) or quantity of feeding. Recent findings by Palardy et al. (2005, 2006) and Grottoli et al. (2006) suggested that the rate of feeding exhibited by the Pavonids is somewhat less than, or equal to, the rate measured for *P. lobata*. If, as suggested by Fallon et al. (2002), coral might bio-concentrate trace metals from their food, then it would be *P. lobata*, with a slightly higher feeding rate, that would record higher skeletal Cd/Ca values, not lower values as reported here. As such, feeding on zooplankton is unlikely to be the primary cause of this large genus-specific difference.

Variation in skeletal growth rates, in particular calcification, could also explain the large differences in Cd/Ca between the *Porites* and *Pavona* genera as has been shown for Sr/Ca ratios (e.g., Allison and Finch, 2004; de Villiers et al., 1994). Yet the lack of a relationship between Cd/Ca and δ^{13}C (i.e., a measure of coral metabolic processes), coupled with the lack of a relationship between Cd/Ca and MLSE (Table 6 and Fig. 7), suggests that Cd/Ca is independent of skeletal calcification at the scale measured here. This finding does not preclude, however, the possibility of a genus-specific difference in the manner of Cd–Ca substitution during skeletogenesis.

A third possible explanation stems from the cleaning procedure used on the powdered coral. Previous research has shown that Sr/Ca can vary at the micron scale with ratio ranges far greater than those due to environmental effects (Cohen and McConnaughey, 2003 and references therein). If a similarly scaled variation is present in Cd/Ca then the effects of the cleaning procedure could alter the bulk Cd/Ca value. Although all samples were ground and cleaned using the same method, the *P. lobata* samples experienced a significantly greater loss of mass during the process (41% loss) than *P. clavus* (23%) or *P. gigantea* (19%). The skeletal structure of *P. lobata* is much more delicate than the Pavonid corals, a property still apparent even after the drilled samples were ground to a coarse powder. As such, there was heightened sample loss due to (1) static adhesion of fine dust to the container sides during transfers (e.g., mortar to cleaning vial, cleaning vial to dissolution beaker), (2) suspended particulate removal during aspiration of cleaning solutions and (3) increased sample dissolution during the multiple weak acid leaches due to the higher surface area-to-mass ratio of the *P. lobata* powder. If the Cd present in the *P. lobata* skeleton was concentrated in the coral dust and/or the outer surface of the fine structural elements, then it may have been preferentially removed prior to dissolution. It should also be noted that a similar, but not significant, pattern can be seen in the Pavonid corals. The average *P. clavus* Cd/Ca ratio was slightly lower than the *P. gigantea* ratio (15.2 ± 2.8 nmol/mol versus

18.2 ± 2.9 nmol/mol), mirroring their respective sample losses (23% versus 19%). Thus, feeding and growth are not likely factors controlling Cd/Ca at the seasonal scale, but cleaning methods may preferentially remove Cd-enriched coral skeletal elements. Since this cleaning of surface contaminants is necessary for measuring low abundance elements in corals, the *P. lobata* species is not an ideal choice for Cd/Ca paleoupwelling reconstructions.

4.2.2. Depth effect

Likely sources of depth-related coral skeletal Cd/Ca variation include differences in MLSE, [Cd]$_{sw}$ and temperature. MLSE has already been shown (Section 3.2.) to have no significant relationship to Cd/Ca via correlation analysis. The lack of any difference in [Cd]$_{sw}$ between 1 and 5 m depths indicates that disparities in Cd/Ca are not due to differences in [Cd]$_{sw}$. Yet temperature at 7 m depth was significantly cooler than at 1 m (Table 1 and Fig. 3), suggesting that the lower Cd/Ca values at depth may have been affected by the reduced temperatures. This influence may have been indirect (e.g., light- or temperature-induced physiological changes) or direct (e.g., slower kinetics of Cd^{2+} substitution). Although no specific research exists on coral Cd uptake, work on light and temperature effects on foraminiferal Cd reveal partition coefficients varying from <0.1 to >4 (e.g., Mashiotta et al., 1997; Marchitto, 2004). Given the large differences between corals and foraminifera in phylogeny, growth environment, morphology, life history traits and, in some cases, mineralogy, it is difficult to apply such findings to these coral results.

In eastern Pacific corals, MLSE and skeletal δ^{18}O are both directly affected by temperature (Wellington, 1982, Wellington et al., 1996) and δ^{13}C is a reliable recorder of coral photosynthesis and heterotrophy (Grottoli and Wellington, 1999). Although depth was the only significant effect shared by Cd/Ca, MLSE, δ^{13}C and δ^{18}O (Tables 3 and 4), attempts to identify a connection between the latter variables and Cd/Ca using correlation analysis found no significant relationships (see Section 4.3 for further discussion). This suggests that physiological changes are not likely the cause of reduced Cd/Ca at depth. Thus, we propose that Cd^{2+} substitution decreases as ambient temperature decreases, an effect that could dampen the upwelling-derived Cd signal due to the associated low temperatures. Additional laboratory experiments are needed to confirm this hypothesis.

4.2.3. Interval effect

Average Cd/Ca ratios were higher in the coral skeleton deposited during upwelling (January–April 2003) than during nonupwelling (April–July 2003) (Table 3 and Fig. 4). This effect was most pronounced in the shallow Pavonid corals, especially *P. gigantea*. It should be noted, however, that there was a great deal of variability within a given species and depth. For example, individual bulk Cd/Ca results ranged from 9.0 to 31.9 nmol/mol among the upwelling/shallow/*P. clavus* colonies (Fig. 4A, black symbols). Nonupwelling values for the same depth and species had minimum and maximum ratios of 6.0 and 16.7 nmol/mol, respectively (Fig. 4A, black symbols). This suggests that,

while Cd/Ca averages from multiple colonies of a species track upwelling conditions, direct comparison of a record from one colony to the record from another may not be possible. Unlike the Pavonids, the *P. lobata* Cd/Ca values were much lower and their variability very small. The difference between their upwelling and nonupwelling averages were so minute that reconstructing an upwelling record from *P. lobata* would be highly challenging, if not impossible, given the precision of presently available methodologies.

4.2.3.1. Comparison to existing Cd/Ca-derived upwelling records. The large range of Cd/Ca seen in multi-year records from several individual colonies across the Galápagos was similar to the range measured in multiple fragments from a single year at Contadora Island. Linn et al. (1990) reported Cd/Ca results from several *P. clavus* colonies in the Galápagos. An Española (Hood) Island record (4 samples/year) displayed a clear seasonality with a range of 1–8 nmol/mol; however another *P. clavus* from Urvina Bay sampled at the same frequency exhibited a somewhat larger range and a much higher concentration (~11–26 nmol/mol) and, when present, a dampened seasonality. Additional records from the *P. clavus* species in the Galápagos had ranges of <1–7 nmol/mol (Punta Pitt, Shen and Sanford, 1990), 2–17 nmol/mol (Española Island, Shen et al., 1992), and 2–7 nmol/mol (Urvina Bay, Shen et al., 1991). Overall, some but not all records exhibited clear seasonality, and Cd/Ca ranges varied widely as well. These Cd/Ca data from other Pacific corals support the current study's conclusion of high within-species Cd/Ca variability.

The only previously published Cd/Ca record from the Gulf of Panama is from a *P. gigantea* (1967–1979) core from Contadora Island (Shen and Sanford, 1990). A wide range in the Cd/Ca values (9–20 nmol/mol) was still measurable despite the coarse sampling resolution (2 samples/year), although significant changes in upwelling due to El Niño-Southern Oscillation (ENSO) events were difficult to identify. Any skeleton deposited during the ~3-month upwelling period would have also been sampled with an additional 3 months of skeleton deposited during nonupwelling, so peak Cd/Ca values would have been attenuated. As such, the range reported for *P. gigantea* in this study (6.7–41.9 nmol/mol) highlights the improvement in signal resolution given the smaller sample size permitted with ID-ICP-MS analysis. This larger range also indicates that the previously reported Cd/Ca results did not adequately reflect the true spread of coral Cd/Ca values. These previously published results from Galápagos and Contadora Island support this study's conclusion that single coral cores from the same site cannot be quantitatively compared. Thus, to yield reproducible results with clear environmental implications, the use of averaged Cd/Ca values from multiple cores at a sample site appears necessary.

4.2.4. ΔCd/Ca: individual colony response to upwelling

The large majority of coral paleoceanographic records are constructed using a single coral core, not pooled averages from multiple colonies. To isolate the response of individual coral colonies to upwelling, ΔCd/Ca for each colony

was calculated (Fig. 6). The average ΔCd/Ca was positive (i.e., $Cd/Ca_{upw} > Cd/Ca_{nonupw}$), with the Pavonid corals showing a much larger response to upwelling than *P. lobata* (~5.8 nmol/mol versus 0.3 nmol/mol). Pavonid corals from 1 m depth also had a greater ΔCd/Ca than those at 7 m (6.2 nmol/mol versus 1.5 nmol/mol). Although these are encouraging results for the application of Cd/Ca for upwelling reconstruction, caution is warranted, as 23% of the colonies had negative ΔCd/Ca values. These unexpected responses might explain why Cd/Ca records in the Galápagos can appear to "miss" or have a dampened response to some upwelling seasons (e.g., 1978–1979 in Punta Pitt core, Shen and Sanford, 1990). Overall, these results strongly indicate that shallow Pavonid corals have the largest and most consistent response to oceanic upwelling.

Even among that group, use of replicate cores would reduce the influence of anomalous responses by individual colonies to environmental conditions (i.e., Fig. 6A). This finding is reinforced by the results of the Monte Carlo tests (Table 5). For example, the mean Cd/Ca value of three colonies has a ~75% chance of falling within 1SD of the "true" Cd/Ca value in all groups except deep *P. gigantea*. When the Cd/Ca mean from only two coral fragments is used, the probability drops to between 38% and 57%, depending on the depth and species used. Even for the shallow Pavonids, which appear to be the most faithful recorders of upwelling, using the average Cd/Ca value from two colonies results in only a 50% chance of falling within 1SD of the "true" Cd/Ca ratio. These differences among Cd/Ca responses to upwelling highlight the limitations of single core reconstructions, and raise the possibility of similar behavior in other trace metal records.

4.3. Relationship to other proxies

4.3.1. Skeletal growth

Coral growth has been correlated to Sr/Ca in genera such as *Diploria* (Goodkin et al., 2005), *Acropora* (Reynaud et al., 2007) and *Pavona* (de Villiers et al., 1995; de Villiers et al., 1994), although no effect was found in *Porites* (Mitsuguchi et al., 2003). In this study, the lack of any significant relationship between Cd/Ca and MLSE suggests that Cd/Ca is decoupled from skeletal extension rate at the seasonal scale (Table 6 and Fig. 7). This lack of relationship, especially when compared to Sr/Ca, may be explained by the difference in sampling resolution or thermodynamics (e.g., as relating to ionic radii) between these substituting elements. The radius of Cd^{2+} more closely resembles that of Ca^{2+} than does Sr^{2+} (Shen and Sanford, 1990). The rate limiting step during skeletogenesis may be mediated by ionic radii size and thus have a greater impact on Sr^{2+} incorporation than on Cd^{2+} incorporation. Additional research incorporating finer scale measurements and calcification rate data (e.g., via the buoyant weight technique) would further illuminate any role of growth processes on coral Cd uptake.

4.3.2. $\delta^{13}C$

During upwelling increased light due to decreased cloud cover (see Table 1) would lead to increased photosynthesis.

In addition, recent work shows that despite increases in zooplankton abundance during these cold upwelling events, feeding is suppressed (Palardy et al., 2005). Thus, both increased light and decreased feeding should increase Pavonid skeletal $\delta^{13}C$ during upwelling. Indeed, a time series of a single *P. clavus* from Contadora Island (from 1979) did show more positive $\delta^{13}C$ values during upwelling months (Grottoli and Wellington, 1999). However this research found that average coral skeletal $\delta^{13}C$ was only nonsignificantly higher during upwelling. The lack of significant correlation between Cd/Ca and $\delta^{13}C$ (Table 6 and Fig. 7) indicates a decoupled relationship between coral metabolic processes and Cd incorporation at the seasonal scale.

4.3.3. $\delta^{18}O$

The $\delta^{18}O$ data in this study clearly reflected the environmental conditions, with more positive values during upwelling (low SST, high SSS) and more negative values during nonupwelling (Fig. 5). Since upwelling events are always linked with those two variables, one would expect to see a clear, direct relationship between Cd/Ca and $\delta^{18}O$ data. Here, the Cd/Ca–$\delta^{18}O$ relationship was not statistically significant (Table 6). This suggests that although both $\delta^{18}O$ and Cd/Ca have significant interval effects, they are decoupled from each other. This conclusion is supported by high-resolution (sub-monthly) measurements of $[Cd]_{coral}$ that show a lag between changes in SST (and $\delta^{18}O$) and $[Cd]_{coral}$ (Matthews, 2007).

4.4. Summary

Results of this research have broad implications for the use and interpretation of coral Cd as an upwelling proxy. The use of tightly constrained growth intervals, *in situ* measurements of several environmental parameters, and multiple coral replicates, species and depths allowed for statistically rigorous findings on the qualities of natural variability in Cd/Ca. Overall, *P. lobata* at this locality has a very small range and consistently low Cd/Ca (and $[Cd]_{coral}$) values. Shallow *Pavona* spp. corals have the strongest Cd response to upwelling, making this genus a good choice for paleoupwelling reconstruction. The generally high natural variability found among colonies of the same species, coupled with the finding of "inverse" responses among some colonies, indicates that records from single coral cores should not be relied upon. Indeed, at least three coral individuals should be sampled for an accurate reconstruction of upwelling conditions via Cd/Ca. Field experiments of longer duration and finer sampling resolution, with concurrent seawater, zooplankton, coral zooxanthellae, tissue and skeletal sampling, would further improve our understanding of Cd fluxes in the reef environment and its behavior as an upwelling proxy.

No significant correlation was observed between Cd/Ca and MLSE, $\delta^{13}C$ or $\delta^{18}O$, suggesting that Cd/Ca is decoupled from extension rate, coral metabolism, and ocean temperature/salinity. These are surprising findings, as both MLSE and $\delta^{18}O$ are significantly affected by the presence of upwelling. Thus we conclude that, at seasonal resolution, Cd incorporation into the coral skeleton is independent of

growth rate, although it may be dampened by low temperatures. Researchers should consider these findings in their constructions, interpretations and comparisons of multiproxy records from upwelling regions.

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