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Seasonal cycles of manganese and cadmium in coral from the Galapagos Islands

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Abstract—Manganese-to-calcium ratios in corals from the eastern and western Galapagos demonstrate regional differences in seasonal trace metal cycling. The variability of trace metal-to-calcium ratios within the Galapagos Islands points to their unique geographic setting as a major factor. This region is influenced by several major oceanic currents (e.g., the South Equatorial Current, the Equatorial Undercurrent, and the Panama, or El Niño, Current) and by extremely intense upwelling. Manganese-to-calcium ratios in a banded coral *Pavona clavus* from Isabela Island, the westernmost island in the Galapagos, have distinct seasonal cycles for the non-El Niño Southern Oscillation (ENSO) years 1946–50, with lower ratios following intensified seasonal upwelling. Cadmium/calcium ratios show less distinct seasonal cycles. The near-moderate ENSO event in 1951 is marked by the disruption of seasonal cycles in Mn/Ca and Cd/Ca ratios. In contrast, corals from islands further east in the Galapagos (Hood Island, 1964–73, LINN et al., 1990; San Cristobal, 1965–79, SHEN and SANFORD, 1990), have stronger seasonal Cd/Ca signals, with higher ratios following seasonal upwelling, and less distinct seasonal cycles in Mn/Ca ratios one-half year out of phase with Cd/Ca variations. Average Mn/Ca ratios are lower for these corals from locations further east, indicating that Urvina Bay appears to have an additional localized source of Mn (SHEN and SANFORD, 1990). In general, these regional variations in seasonal trace metal cycling are consistent with coral stable isotope signals and with their geographic locations. These variations are important to consider in using coral records to reconstruct and interpret oceanographic events occurring prior to historical records.

INTRODUCTION

TRACE METAL CONCENTRATIONS in the aragonite of banded corals reflect those in surface waters of the ocean, thus incorporating a record of ocean history otherwise difficult to obtain (e.g., SHEN, 1986; SHEN and BOYLE, 1988). These trace metal-to-calcium ratios are thus proving useful for studying seasonal and interannual surface water variability and its links to oceanic and climatic processes. This can prove particularly useful in regions of complex seasonality like the Galapagos.

The primary currents affecting the Galapagos Islands, the study area for this paper, are shown in Fig. 1. Three features of their influence, as discussed in LINN et al. (1990), are of significance for trace metal records in corals. First, the influence of the nutrient-poor Panama, or El Niño, Current is seasonally variable. In typical years, due to the seasonal shift of the intertropical convergence zone, this current flows southward from approximately December–March, replacing the normally nutrient-rich, cool, upwelled waters in the Galapagos. We refer to this seasonal occurrence as "generic" El Niño. Second, at intervals the Galapagos region is affected by large-scale circulation perturbations throughout the Pacific Ocean, generally lasting 6–18 months, known as El Niño-Southern Oscillation (ENSO) events. During ENSO events, the normally shallow thermocline at the Galapagos is depressed, and the Galapagos Front, the boundary between the cool, upwelled, nutrient-rich waters influencing the Galapagos for much of a normal (i.e., non-ENSO) year and the more oligotrophic surface waters to the north, moves southward. During both the generic El Niño, of seasonal duration in non-ENSO years, and the longer duration ENSO events, Galapagos waters are more nutrient-depleted. Third, we note that the influence of the Equatorial Undercurrent (or Cromwell Current) is most intense in the western Galapagos, and less seasonality in surface waters is anticipated there.

Cadmium, with a nutrient-like oceanic distribution, is enriched in upwelling waters and depleted in oligotrophic oceanic surface waters (BOYLE et al., 1976; MARTIN et al., 1976). In contrast, Mn is enriched in oceanic mixed layers. This surface enrichment is due generally to atmospheric dust inputs and to the effects of sunlight on the microbially mediated redox cycles of Mn (SUNDA and HUNTSMAN, 1988); in near-shore environments, Mn-rich continental sources, presumably reducing sediments, contribute to the surface enrichment as well. Manganese is depleted with increasing depth in surface waters and with increasing distance offshore (KLINKHAMMER and BENDER, 1980; LANDING and BRULAND, 1987). Cd/Ca ratios in corals from the Galapagos Islands are thus expected to be higher during seasonal upwelling, typically occurring mid-year in non-ENSO years. Elevated Mn/Ca ratios are expected during suppression of upwelling, as occurs during the generic El Niño or in the more extended ENSO events. Manganese enrichment could result from input of warmer surface waters influenced by reduced sediment sources intruding from the Panama Basin (KLINKHAMMER and BENDER, 1980) or from other localized shelf sources, for example, at Isabela Island (SHEN and SANFORD, 1990).

Observations of coral trace metal ratios in the Galapagos have confirmed these initial expectations about seasonal variations in Cd/Ca and Mn/Ca ratios. SHEN and SANFORD

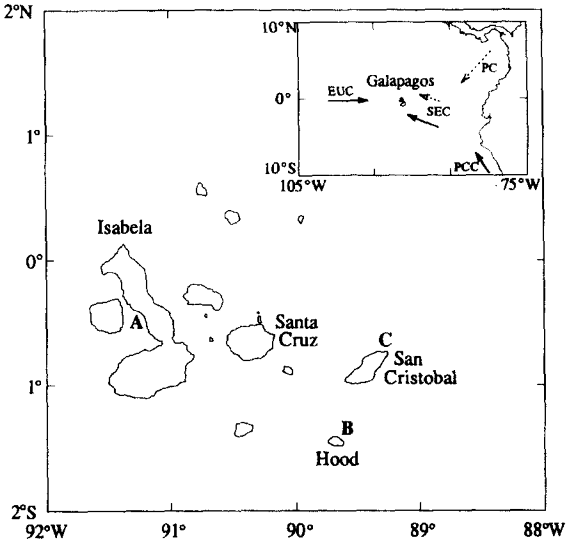

FIG. 1. Map of the Galapagos archipelago (adapted from GLYNN et al., 1983) showing collection sites of corals discussed in this study: (A) Urvina Bay, Isabela Island (this study and SHEN and SANFORD, 1990); (B) Gardner Bay, Hood Island (LINN et al., 1990); and (C) Punta Pitt, San Cristobal (SHEN and SANFORD, 1990). The inset map shows the primary surface and near-surface currents affecting this region. The South Equatorial Current (SEC), derived from the nutrient-rich Peru Coastal Current (PCC or Humboldt Current) and driven by the southeast trade winds, dominates the Galapagos region throughout much of the year. The Equatorial Undercurrent (EUC or Cromwell Current), a subsurface nutrient-rich current between 2°N and 3°S and generally at depths of 30–300 m, shoals as it approaches the western Galapagos where its influence is particularly intense. The Panama Current (PC or El Niño Current) consists of warm, low-salinity, nutrient-depleted waters from the Panama Basin which seasonally (typically December–March, referred to here as the generic El Niño) influence the Galapagos.

(1990) found a distinct seasonal pattern in Cd/Ca ratios for a *Pavona clavus* (1965–79) from San Cristobal Island in the eastern Galapagos (Fig. 1), with higher Cd/Ca ratios generally corresponding to colder regional sea surface temperatures (SST). A seasonal cycle of Mn/Ca ratios at San Cristobal, by contrast, was not present. For a *P. clavus* (1964–73) from Hood Island, south of San Cristobal, LINN et al. (1990) found pronounced seasonal variability in Cd/Ca ratios, and again no clear seasonal pattern in Mn/Ca ratios, concluding that Hood Island may be too far south to be strongly influenced by Mn-enriched Panama Basin waters. By contrast, for a *P. clavus* (UR-3-86; 1969–78) from Urvina Bay, Isabela Island in the western Galapagos, SHEN and SANFORD (1990) found that Cd/Ca ratios had a poor correspondence to regional SST anomalies, but Mn/Ca ratios had pronounced seasonal cycles in phase with SST (high SST, high Mn/Ca).

We present seasonal trace metal and stable isotope data from an older *P. clavus* coral (UR-LL-86; 1946–53) from Urvina Bay, Isabela Island and contrast these results to those from the corals discussed above from both the eastern and western Galapagos (Table 1). These data demonstrate strong Mn/Ca seasonal patterns and less distinct Cd/Ca patterns in the western Galapagos, thus supplying additional evidence for significant regional variations in trace metal concentration variability in surface waters. We also discuss the relationship of trace metal variability to stable isotope signals in both areas. Regional variation in the Galapagos is important to consider when using trace metal signatures in corals to study seasonal cycles and ENSO events in coral records on long time scales. It is also important for the determination of past metal cycling in a remote region that is complicated by volcanic activity and equatorial upwelling.

MATERIALS AND METHODS

A sample of *P. clavus* (designated UR-LL-86), with an original water depth of ~5 m (M. Colgan, pers. commun., 1988), was collected in 1986 from the Urvina Bay, Isabela Island (Galapagos) 1954 uplift site (COLGAN and MALMQUIST, 1987). Although the coral head was subaerially exposed from the rapid, early 1954 uplift (RICHARDS, 1954) until sampling in 1986, there was no visible evidence of alteration from aragonite to calcite. Our previous visual estimates of severity of alteration have shown good correlation with mineralogy determined by X-ray diffraction.

The coral was slabbed along the axis of corallite growth and sectioned quarter-annually based on an X-radiograph that displayed distinct high- and low-density bands, with each year represented by a high-density/low-density band pair. Seasonal warming in the Galapagos starts as early as October/November and reaches its maximum in February/April; seasonal upwelling begins in June/July and reaches its peak in August/September, as indicated by coldest mean temperatures (HOUVENAGHEL, 1984). Based on observations of coral banding relative to collection date, high-density bands in Galapagos corals are thought to form primarily during the warm season, although $\delta^{18}O$ results from coarse resolution sampling of an Urvina Bay coral did not display a consistent correlation of most negative values with high-density bands (GLYNN and WELLINGTON, 1983). The coral was uplifted in early 1954, during the warm season, and the outer band had high density. We do not report metal/calcium ratios for the outer two bands as trace metal results from coral edges often appear anomalous; although the causes for this effect are not clear, it may be due to higher amounts of organic carbon near growth edges.

We took two samples from each high- and each low-density band, resulting in four samples per year. We designated those from the high-density band as $(y - 1).75$ and $y.00$, where y represents the assigned year, and those from the following low-density band, $y.25$ and $y.50$. (Note that this represents a shift of +0.25 y in the chronology as given in LINN et al., 1990, for the Hood Island coral also discussed in this paper.) With this chronology, generic El Niño intervals should be recorded in high-density bands, and seasonal upwelling intervals, in low-density bands. Although corals do not strictly follow the calendar year nor its seasonal increments in band formation, this gave a reasonable correspondence between presumed timing of band formation and known seasonal temperature (and thus $\delta^{18}O$) patterns.

Trace metal ratios were determined for coral samples following sample processing and cleaning procedures described in LINN et al. (1990) as modified from SHEN (1986) and SHEN and BOYLE (1988). Coral samples were crushed to a specified size fraction (290–710 μm), then treated with a series of oxidative, reductive, and weak acid rinses to remove trace metals extraneous to those lattice-bound within the aragonite matrix. Samples were then dissolved and trace metals coprecipitated with cobalt-APDC to isolate them from Ca, which when present reduces graphite tube life as well as sensitivity of metal determinations.

Trace metal determinations were carried out on a Perkin Elmer 5000 atomic absorption spectrophotometer (continuum source background corrector) equipped with a Perkin Elmer Heated Graphite Analyzer Model 500 and an AS-1 autosampler (referred to as GFAAS). Results are reported as molar ratios to Ca in coralline aragonite. Detection limits, defined as three times the one σ standard deviation of reagent blanks, were equivalent in typical coral samples to Mn/Ca ratios of 1.3 nmol/mol; Cd/Ca, 0.3 nmol/mol; and Pb/Ca 0.5 nmol/mol. Blanks for individual solutions used in sample treatment and processing were generally at or below trace metal detection limits by GFAAS after purification. Total reagent blanks, close to GFAAS detection limits (expressed as equivalent ratios in

Table 1. Seasonal Observations in Galapagos *Pavona Clavus*

Location	Years	Mn/Ca seasonal contrast[1]	Cd/Ca seasonal contrast	Reference
WESTERN GALAPAGOS				
Urvina Bay, Isabela Island (uplift site) (UR-LL-86)	1946-53	+	–	THIS STUDY
Urvina Bay, Isabela Island (offshore near uplift site) (UR-3-86)	1969-78	+	–	SHEN and SANFORD (1990)
EASTERN GALAPAGOS				
Gardner Bay, Hood Island (HI-6)	1964-73	–	+	LINN et al. (1990)
Punta Pitt, San Cristobal	1965-79	–	+	SHEN and SANFORD (1990)[2]

1. Seasonality characterized: (+), strong seasonality observed, (–) seasonal cycles not distinct.

2. Quarter-annually sampled record for Punta Pitt coral extends to 1936 (G. SHEN, pers. comm., 1990).

typical coral samples) were Mn/Ca, 1.8 nmol/mol; Cd/Ca, 0.6 nmol/mol; and Pb/Ca, 0.4 nmol/mol. Sample absorbances were typically at least four times detection limit absorbances. All reported results were corrected for blanks and for coprecipitation recoveries measured with each analytical run. Samples were generally processed in triplicate. Reproducibility of measured ratios, estimated as the average relative 1σ standard deviation of individual samples, were Mn/Ca, ±6%; Cd/Ca, ±13%; and Pb/Ca, ±19%.

Stable carbon and oxygen isotopes were measured on the fine fraction (<290 μm). Samples were roasted at 375°C under vacuum for one hour and measured on a V.G. Micromass 602E isotope ratio mass spectrometer in the laboratory of L. D. Keigwin at Woods Hole Oceanographic Institution (Woods Hole, MA, USA). Errors of the $\delta^{18}O$ and $\delta^{13}C$ measurements were ±0.10 parts per mil.

RESULTS AND DISCUSSION

Trace element and stable isotope data (1946–53) for the Urvina Bay *P. clavus* (UR-LL-86) are listed in Table 2 and plotted vs. age in Fig. 2. Mn/Ca ratios range from 100–175 nmol/mol (Fig. 2a). There is a distinct seasonality in Mn/Ca ratios, with lowest values in the first half of the high-density bands, and the highest values in the first half of the low-density bands. The chronology we assigned place these low Mn/Ca values in the coral increment following the upwelling season. Assuming similar banding intervals represent equivalent time intervals throughout the Galapagos, this timing is similar to the weaker Mn/Ca seasonal cycles observed in the Hood Island coral (HI-6) samples from 1964–73, although mean Mn/Ca ratios were lower for that coral, typically 50–150 nmol/mol (LINN et al., 1990). The seasonal cycle in Mn/Ca ratios is disrupted by the weak/moderate ENSO event that occurred during 1951 (QUINN et al., 1987).

There is only weak seasonality apparent in the $\delta^{18}O$ record (Fig. 2a). More negative $\delta^{18}O$ values, corresponding to warmer temperatures and/or lower surface salinities, are sometimes coincident with higher Mn/Ca ratios as expected from known Mn sources. Previous studies have documented that the primary factor affecting $\delta^{18}O$ in Galapagos corals is SST (DRUFFEL, 1985; DRUFFEL et al., 1990). Strong seasonality in the $\delta^{18}O$ signal for this coral is not expected, as the range of SST in Urvina Bay is attenuated due to the influence of the Equatorial Undercurrent. The Hood Island coral record presented by LINN et al. (1990), by contrast, showed more distinct seasonal $\delta^{18}O$ cycles, with most negative values corresponding to higher Mn/Ca ratios.

Cd/Ca ratios are in the range of 12–25 nmol/mol (Fig. 2b). Using quarter-annual sampling, the seasonal pattern is less consistent from year to year than for Mn/Ca ratios, and was also disrupted during the 1951 ENSO event. Cd/Ca ratios for samples from later in 1952, although consistent with the range observed in an older Urvina Bay coral (LINN et al., 1990), may be high due to proximity to the growth edge, which was exposed from uplift in 1954 until collection in 1986. The Hood Island coral (Table 1; LINN et al., 1990), with lower average Cd/Ca ratios, had very distinct Cd/Ca seasonal cycles, with higher Cd/Ca ratios corresponding to lower Mn/Ca ratios.

The $\delta^{13}C$ record shows more consistent variations with season than does $\delta^{18}O$ (Fig. 2b). The most negative $\delta^{13}C$ values generally occur with lower Cd/Ca ratios and higher Mn/Ca ratios, suggesting these represent lower productivity intervals. However, compared to Mn/Ca, $\delta^{13}C$ does not have a consistent seasonal pattern, with a stronger resemblance to

Table 2. Trace element and stable isotope results for *Pavona clavus* UR-LL-86 from Urvina Bay, Isabela Island

Sample[1]	n[2]	Mn/Ca nmol/mol mean	sd[3]	Cd/Ca nmol/mol mean	sd	Pb/Ca nmol/mol mean	sd	$\delta^{18}O$ per mil (PDB)	$\delta^{13}C$ per mil (PDB)
1945.75	2(3,2)	129	22	15.0	1.0	1.70	0.02	-4.15	-1.31
1946.00	2	139	3	17.2	2.3	2.04	0.40	-4.14	-1.48
.25	2	159	1	17.1	2.0	1.19	0.01	-4.06	-1.34
.50	2(3,3)	147	1	16.4	0.8	1.09	0.37	-4.20	-1.38
.75	3	118	21	15.6	2.8	1.31	0.34	-4.20	-1.44
1947.00	3	142	10	14.7	0.5	1.98	0.08	-4.21	-1.22
.25	3	172	14	13.1	0.7	2.75	0.72	-4.66	-2.08
.50	2(3,3)	148	7	12.4	1.5	1.38	0.33	-4.50	-1.74
.75	3(3,2)	112	4	20.0	0.9	1.38	0.56	-4.27	-1.54
1948.00	1(2,2)	126	-	20.9	1.0	1.96	0.89	-4.24	-1.38
.25	2	145	23	15.3	0.6	1.35	0.02	-4.31	-2.04
.50	1(1,2)	143	-	16.2	-	1.73	0.37	-4.36	-2.00
.75	3	111	3	16.4	0.2	2.03	1.14	-4.14	-1.61
1949.00	3	127	11	16.9	0.6	2.04	1.11	-4.12	-1.55
.25	2(2,1)	145	10	14.2	0.3	1.45	-	-4.25	-1.72
.50	2(2,1)	129	27	12.5	1.6	2.26	-	-4.31	-1.93
.75	1	98	-	13.0	-	2.54	-	-3.87	-1.96
1950.00	2	126	23	20.3	1.6	1.68	0.43	-3.93	-1.03
.25	1	151	-	17.4	-	1.70	-	-3.78	-1.30
.50	1	157	-	15.9	-	1.09	-	-3.82	-1.94
.75	3	129	9	18.4	2.2	1.32	0.64	-4.15	-1.46
[4]1951.00	1	136	-	18.3	-	1.30	-	-3.93	-1.77
.25	1	102	-	18.0	-	1.84	-	-4.22	-1.60
.50	2	134	7	17.9	0.5	0.94	0.14	-3.95	-1.40
.75	2(3,3)	129	4	18.9	2.6	1.14	0.35	-4.43	-1.77
1952.00	3	122	7	17.9	0.7	0.95	0.23	-4.16	-1.66
.25	2	126	3	17.6	0.9	1.17	0.07	-4.27	-1.19
.50	2(2,1)	120	6	23.1	1.5	1.59	-	-	-
.75	1	112	-	24.4	-	0.90	-	-4.16	-1.40
1953.00	1	137	-	25.8	-	1.41	-	-4.09	-1.50

1. Quarter-annual samples were taken based on banding observed in X-radiographs of coral slab. (y-1).75 and y.00 are subsamples of the high density band for year y, and y.50 and y.75 are subsamples of the low density band.

2. Number of replicates included in mean trace element ratios. For samples where number of replicates for Cd/Ca and/or Pb/Ca were different from those for Mn/Ca, the respective numbers are given in parentheses.

3. Standard deviations given are $\pm 1\sigma$.

4. Moderate ENSO (QUINN et al., 1987).

the Cd/Ca record, nor do the relative amplitudes of signals in the records agree well. In addition, $\delta^{13}C$ changes may lag or lead Mn/Ca changes by a quarter-annual increment.

The factors controlling (or complicating) $\delta^{13}C$ in corals are the $\delta^{13}C$ signature in dissolved inorganic carbon (DIC) in seawater *and* the ambient light as a function of coral depth (WEBER and WOODHEAD, 1972; MCCONNAUGHEY, 1989), cloud cover (FAIRBANKS and DODGE, 1979), position on the coral community (MCCONNAUGHEY, 1989; WEFER and PATZOLD, 1985), and shading from adjacent coral colonies. Lower algal activity is expected during periods of lower ambient light (e.g., the generic El Niño), thus causing the DIC pool within the calcioblastic layer in the coral to be less depleted in ^{12}C and resulting in lower overall $\delta^{13}C$ values for skeletal carbonate. Given the nature of this record, it appears that ambient light is a major, though not the only, factor controlling $\delta^{13}C$ in this coral.

Pb/Ca ratios in this Urvina Bay coral range from 1–3 nmol/mol; the variation does not appear to be seasonally driven, nor is it large relative to analytical reproducibility

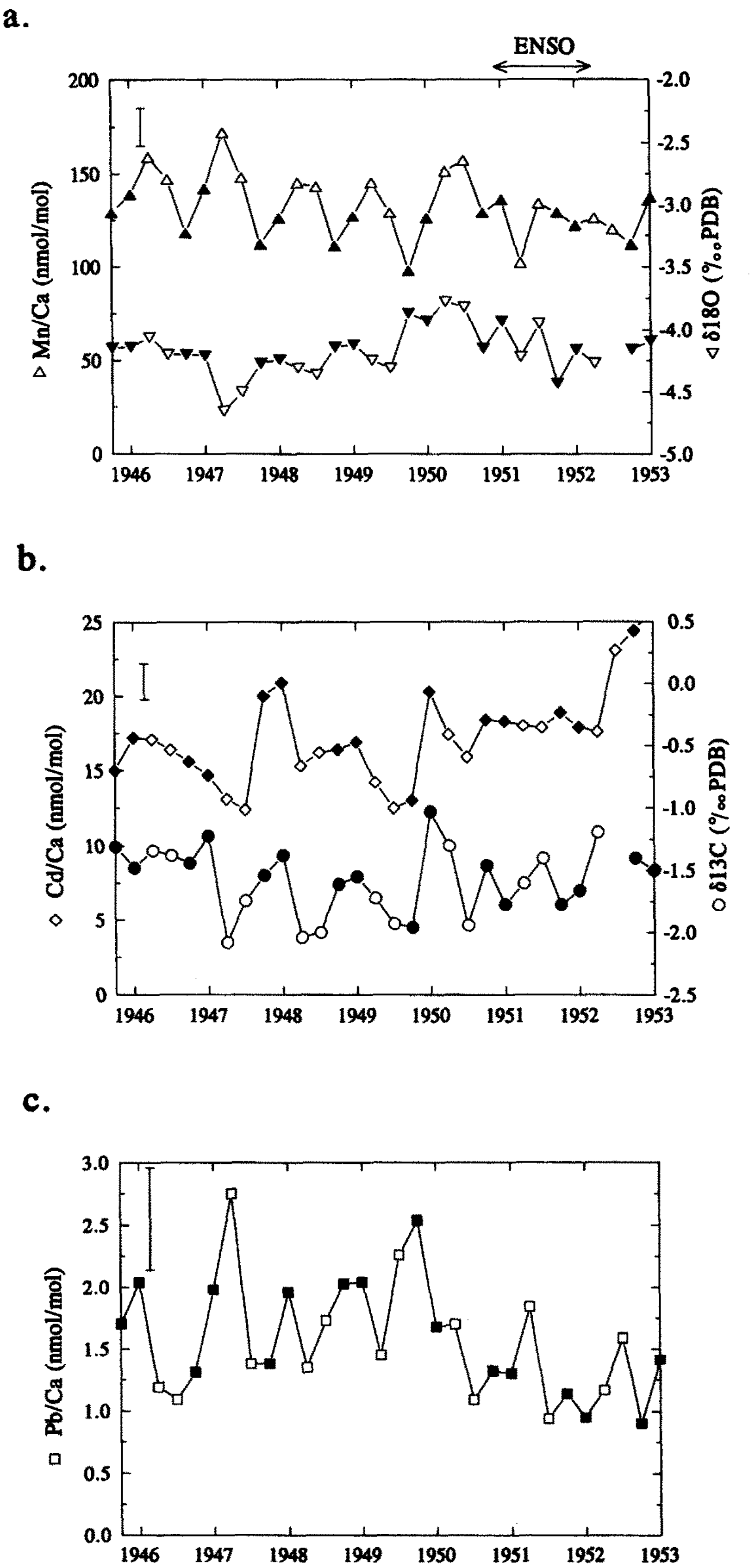

FIG. 2. Trace element and stable isotope data vs. assigned sample band age for a *Pavona clavus* (UR-LL-86) from the Urvina Bay uplift site, Isabela Island. Samples from high- and low-density bands are represented by filled and open symbols, respectively. Error bars represent typical analytical reproducibility ($\pm 1\sigma$) for trace element ratios. (a) Mn/Ca ratios and $\delta^{18}O$. (b) Cd/Ca ratios and $\delta^{13}C$. (c) Pb/Ca ratios.

(Fig. 2c). These results are similar to the Pb/Ca ratios reported for an older Urvina Bay uplift coral (UR-1-86, LINN et al., 1990). Pb/Ca ratios in the Hood Island coral (LINN et al., 1990) were 6–9 pmol/mol with no significant seasonality, similar to results for a San Cristobal coral (SHEN and BOYLE, 1987). These Pb/Ca ratios are reasonable considering surface water Pb concentrations expected in this region (for example, Peru surface waters ~5°S, 75°W, 20–50 pmol/kg; open ocean surface waters, ~20 pmol/kg; FLEGAL, 1986) and the effective partition coefficient for Pb in coral aragonite of approximately 2 (SHEN and BOYLE, 1987).

The range of Cd/Ca ratios observed for this *P. clavus* (UR-LL-86) from the Urvina Bay uplift site is consistent with the range of 5–35 nmol/mol observed over several centuries for a large *P. clavus* also from the uplift site (UR-1-86) as established by results from two laboratories (A.D. 1604–1725, LINN, 1988; A.D. 1604–1850, G. Shen, pers. commun. 1990). Some caution is advised in paleoceanographic interpretation of the UR-1-86 results, however, since the contemporary coral previously discussed reported by SHEN and SANFORD (1990; UR-3-86) and a third large coral from the uplift site (UR-2-86, original water depth ~4–5 m; A.D. 1583–1954) have lower Cd/Ca ratios, typically 2–7 nmol/mol (SHEN and SANFORD, 1990; G. Shen, pers. commun., 1990). The offset observed in baseline Cd/Ca ratios for these adjacent corals, two giving relatively high ratios (UR-LL-86, UR-1-86) and two relatively low ones (UR-2-86, UR-3-86), may be due to: 1) Cd contamination not removed by sample treatment procedures (unlikely given the consistent results for two labs on a large number of sample splits from UR-1-86), 2) diagenetic alteration (not substantiated by any other observation in the trace metal or stable isotope results), or 3) consistent differences in the microenvironments of precipitation over long time intervals. Whatever the mechanism, it must have acted in such a way as to affect Cd/Ca ratios without affecting Mn/Ca or Pb/Ca ratios, stable isotope values, or their observed seasonality. We are thus cautious in extrapolating surface water Cd concentrations from the coral Cd/Ca record, but conclude that the observations of relative intensity of seasonal cycling based on these records are still warranted.

As a means of evaluating relationships between various trace metals and stable isotope ratios, we tested for correlations between various result pairs for the non-ENSO samples of 1945.75–1950.50 from this Urvina Bay coral (UR-LL-86). We also tested correlations with a lag or lead of one quarter-annual increment between variables. We evaluated the significance of the r values for these linear correlations using the number of points in the regression. This approach ignores the possibly autocorrelated nature of seasonal records (BAUMGARTNER and CHRISTENSEN, 1985), and therefore may tend to overestimate the significance of the observed correlations; it is, however, a reasonable first approach for raw data records such as these. The highest correlation coefficient ($r = 0.591$; significant at the 99% confidence level) was found between Cd/Ca ratios and $\delta^{13}C$. The correlation was not significant with either a quarter-annual lag or lead between the two records, as would be expected for two seasonally driven cycles. Although the correlation is modest, it suggests that periods of increased upwelling, when seawater Cd/Ca ratios are higher, are marked by higher $\delta^{13}C$ in coral. Higher ambient light and primary productivity are also concurrent with these periods. The correlation of Mn/Ca ratios with $\delta^{13}C$ was not significant ($r = 0.156$), but higher Mn/Ca ratios were correlated with more positive $\delta^{13}C$ values in the preceding quarter-annual sample ($r = 0.533$; significant at the 95% confidence level) and more negative $\delta^{13}C$ values in the subsequent quarter-annual sample ($r = 0.419$; significant at the 90% confidence level). These suggest that intervals of high Mn/Ca ratios follow the end of higher productivity upwelling seasons as expected, and that lower productivity continues as Mn levels decrease. $\delta^{18}O$ and $\delta^{13}C$ were weakly correlated ($r = 0.388$; significant at the 90% confidence level), suggesting that low SST/high-salinity water (high $\delta^{18}O$) occurs during periods of high $\delta^{13}C$. We also tested correlations between result pairs after removing long-term trends by fitting linear regressions to the data and using the residual differences from these long-term trends in calculations. The nature of the observed correlations did not change, although, as expected, the correlation coefficients generally increased slightly.

To summarize the contrast in the nature of the seasonal cycles for Mn at Urvina Bay and Hood Island (Table 1), mean trace metal ratios for each quarter-annual increment from non-ENSO years (LINN et al., 1990) are plotted vs. seasonal increment (Fig. 3). This comparison makes the assumption that similar banding patterns represent equivalent time intervals throughout the Galapagos (GLYNN and WELLINGTON, 1983). Although this neglects year-to-year variability and the different temporal intervals covered by each record, it is a useful method for depicting overall patterns and for contrasting the two locations.

Mean seasonal Mn/Ca ratios at Urvina Bay increase during the time of the generic El Niño and are highest in the first quarter-annual sample in the low-density band (designated *y*.25; Fig. 3a). They decrease to their lowest values in the first half of the high-density band (designated *y*.75), after the seasonal upwelling season. The total range in mean Mn/Ca ratios is 37 ± 18 nmol/mol (1σ standard deviation), from 113 ± 10 to 150 ± 15 nmol/mol. Mean Mn/Ca ratios in the Hood Island coral (Fig. 3a) are consistently lower than those from Urvina Bay, with a total range of 21 ± 17 nmol/mol which overlaps within error limits that for Urvina Bay, with values from 60 ± 6 to 81 ± 16 nmol/mol. The pattern with season is less distinct at Hood Island, and may tend to lead the Urvina Bay pattern by a quarter-year increment. Hood Island may be too far south in the eastern Galapagos to be strongly affected by higher Mn from intruding Panama Basin waters because of the propensity of Mn to be scavenged and Hood Island's distance from the source. Surprisingly, Mn/Ca ratios and presumably Mn concentrations are higher in surface waters at Urvina Bay, Isabela Island, suggesting that the shelf there must contain an additional reduced Mn source (SHEN and SANFORD, 1990) as open ocean surface Mn concentrations are presumably low (LANDING and BRULAND, 1987).

Mean $\delta^{18}O$ values do not vary significantly with quarter-annual increment for the Urvina Bay coral, with larger standard deviations on the slightly more negative mean values representing the low-density bands (Fig. 3b). Seasonal variations in $\delta^{18}O$ are pronounced for the Hood Island coral, with a total range of 0.56 ± 0.26 parts per mil. If this were due solely to SST variation, this range would be equivalent to about 2.5°C; this is reasonable considering the coarse na-

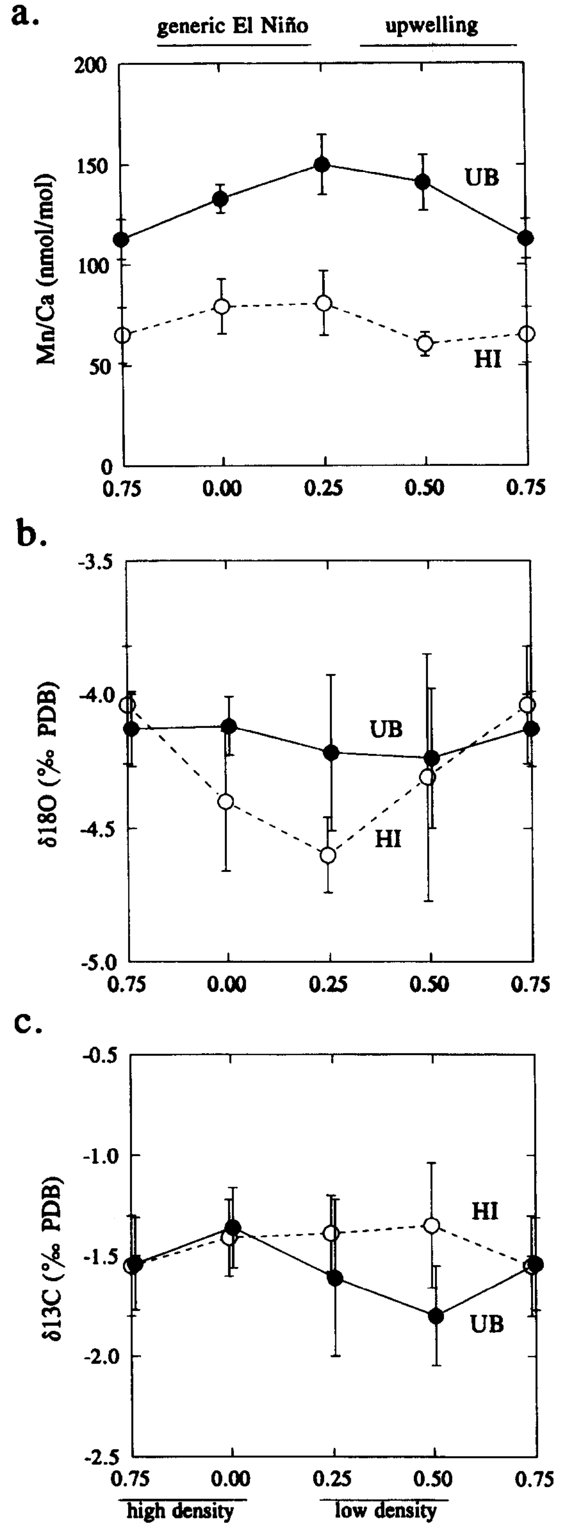

FIG. 3. Mean trace element ratios and stable isotope results ($\pm 1\sigma$ standard deviation) for quarter-annual increments of *Pavona clavus* for non-ENSO years from eastern and western Galapagos. Solid circles, Urvina Bay, Isabela Island (western Galapagos) coral, 1945.75–1950.50 and 1952.25–1953.00 (last 4 values excluded for Cd/Ca means), this study. Open circles, Hood Island (eastern Galapagos) coral, 1966.00–1968.75 and 1970.00–1971.75, LINN et al. (1990). Subsamples of the high-density band are designated 0.75 and 0.00; those of the low-density bands, 0.25 and 0.50. Labels at the top of the figure indicate the correspondence of band intervals to seasonal events (generic El Niño and seasonal upwelling) in the Galapagos as discussed in the text. (a) Mn/Ca ratios, (b) $\delta^{18}O$, (c) $\delta^{13}C$.

ture of our sampling (four increments per year) and the expected SST range, typically 4–5°C (DRUFFEL et al., 1990). The first sample in the low-density band has the most negative mean value, although this overlaps within error those for the two neighboring samples. Mean $\delta^{13}C$ values, for which ambient light levels may be a significant control, also show no strong variation with season in either location, although there is a suggestion of seasonality at Urvina Bay (Fig. 3c). The total range in mean $\delta^{13}C$ for the Urvina Bay coral is 0.44 ± 0.32 parts per mil, with values becoming more negative in the low-density bands and more positive in the high-density bands.

CONCLUSIONS

Studies of the trace metal ratios and stable isotope values for a coral from Urvina Bay in the western Galapagos, along with comparisons to other records from eastern and western Galapagos locations, provide evidence of regional differences in seasonal patterns of these tracers. Corals from Urvina Bay show strong seasonal variations in Mn/Ca ratios and somewhat weaker $\delta^{13}C$ seasonal patterns; there is no consistent variation in Cd/Ca ratios and $\delta^{18}O$ values with season. By contrast, corals from two eastern Galapagos sites have pronounced seasonal variations in Cd/Ca ratios and $\delta^{18}O$, with much less distinct Mn/Ca and $\delta^{13}C$ patterns. These trace metal and stable isotope variations are generally consistent with the geographic range of influence of the various currents and with the relative intensity of upwelling at these locations. This indicates that different tracers in corals contribute independent evidence about environmental variations, as well as that these environmental influences can have regional variations. These points are important to consider when using coral records to interpret oceanographic history, and demonstrate the importance of using multiple tracers on a single record and multiple records from a given region.

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