

UC Irvine

UC Irvine Previously Published Works

Title

Trace metals in contemporary and seventeenth-century Galapagos coral: Records of seasonal and annual variations

Permalink

<https://escholarship.org/uc/item/17b8t31s>

Journal

Geochimica et Cosmochimica Acta, 54(2)

ISSN

0016-7037

Authors

Linn, LJ
Delaney, ML
Druffel, ERM

Publication Date

1990

DOI

10.1016/0016-7037(90)90327-H

Copyright Information

This work is made available under the terms of a Creative Commons Attribution License, available at <https://creativecommons.org/licenses/by/4.0/>

Peer reviewed

Trace metals in contemporary and seventeenth-century Galapagos coral: Records of seasonal and annual variations

L. J. LINN,^{1*} M. L. DELANEY,¹ and E. R. M. DRUFFEL²

¹Institute of Marine Sciences, University of California, Santa Cruz, CA 95064, USA

²Woods Hole Oceanographic Institution, Woods Hole, MA 02543, USA

(Received July 31, 1989; accepted in revised form November 22, 1989)

Abstract—We report trace element/calcium ratios for modern (Cu/Ca, Mn/Ca, Cd/Ca, and Pb/Ca) and seventeenth-century (Cu/Ca, Mn/Ca, and Pb/Ca) specimens of *Pavona clavus* collected in the Galapagos Islands. These data include the first reliable measurements of Cu/Ca ratios in coralline aragonite. We estimate that the ratio of Cu/Ca in the lattice to that in seawater (i.e., the effective distribution coefficient) is ~ 0.3 , lower than the value of 1 observed for several other divalent elements; we estimate the effective distribution coefficient for Mn is ~ 1 . Distribution coefficients in coral aragonite for 8 divalent metals are near unity despite different ionic radii and chemical speciation in seawater. Investigation of where these substituents are incorporated in the aragonite lattice is clearly warranted. In a modern Hood Island coral, quarter-annually sampled from 1964–73, Cu/Ca ratios decrease twofold from the late 1960s to early 1970s. Mn/Ca and Cd/Ca ratios vary seasonally with upwelling and the generic El Niño. The El Niño Southern Oscillation (ENSO) events of 1965, 1969, and 1972 are marked by suppression of Cd/Ca ratios by about 2.5 nmol/mol, while the Mn/Ca ratio is highest during the strong 1972 ENSO. Pb/Ca ratios were relatively constant throughout this period. From the Cu/Ca record of a seventeenth-century Urquina Bay coral annually sampled from 1600–1725 and the estimated Cu distribution coefficient, surface seawater Cu concentrations at Galapagos during the seventeenth century were similar to present day at 0.7–1.4 nmol/kg. Estimated Pb concentrations were lower at 5–20 pmol/kg, and Mn concentrations were slightly higher at 1.6–2.8 nmol/kg.

INTRODUCTION

TRACE METAL CONCENTRATIONS in coral skeletal aragonite have been suggested to reflect concentrations in surface seawater (AMIEL et al., 1973; SCHNEIDER and SMITH, 1982; HOWARD and BROWN, 1984; SHEN, 1986; SHEN and BOYLE, 1988). Banded aragonitic corals have been useful recorders of surface water composition changes over time because annual and sub-annual sections can be assigned ages based on growth patterns. Temporal changes in metal/Ca ratios recorded in corals were attributed to changing regional oceanographic circulation patterns and to temporal variations in surface metal concentrations as the result of natural or anthropogenic perturbations (OOMORI et al., 1982; SCHNEIDER and SMITH, 1982; SHEN and BOYLE, 1987).

Several divalent trace metals (e.g., Cd, Ba, Ra, Nd, Sr, and Co) appear to be incorporated into coral aragonite with a distribution coefficient, K_D , of 1 (SHEN, 1986; SHEN and BOYLE, 1988), where

$$K_D = \frac{[\text{Me}]/[\text{Ca}]_{\text{coral}}}{[\text{Me}]/[\text{Ca}]_{\text{seawater}}}$$

Previous reports of 300–8000 nmol/mol Cu/Ca levels in coral aragonite (LIVINGSTON and THOMPSON, 1971; ST. JOHN, 1974; HOWARD and BROWN, 1984) represent unreasonably high surface water Cu concentrations (i.e., ~ 3 –80 nmol/kg) if the Cu K_D is ~ 1 . In addition, coral Cu concentrations in

these studies did not vary systematically with coral age or environment. SHEN and BOYLE (1988) attempted to resolve this apparent problem for some trace metals by developing techniques to isolate lattice-bound trace metals incorporated in coralline aragonite. These procedures removed trace metals associated with contaminants other than the aragonite matrix (e.g., authigenic and organic coatings) as demonstrated by decreases in trace metal levels with successive treatment steps, then constant skeletal concentrations of Pb, Cd, and Zn relative to Ca with increasing severity of treatment.

We investigated Cu, Mn, Cd, and Pb concentrations in two Galapagos corals to determine how these trace metals may serve as indicators of the substantial seasonal and annual circulation changes in this region. Primary currents affecting the Galapagos region are the South Equatorial Current (SEC), the Equatorial Undercurrent (Cromwell Current), and the seasonally variable Panama, or El Niño, Current (Fig. 1a). Throughout much of the year, SEC waters, derived from the nutrient-rich Peru current and driven by the southeast trade-winds, dominate in the Galapagos region (HOUVENAGHEL, 1984); mixed-layer depths are typically 20–50 m depending on season. The Cromwell Current, an eastward-flowing, subsurface, nutrient-rich current between 2°N–3°S, is generally at depths of 30–300 m and shoals as it approaches the western Galapagos (LUKAS, 1986). From December–March, the El Niño Current, which consists of warm, low salinity, nutrient-depleted waters from the Panama Basin, flows southward replacing the normally nutrient-rich, cool, upwelled waters at the Galapagos. This seasonal shift in circulation of the “generic” El Niño is due to southward shift of the intertropical

* Present address: School of Oceanography, WB-10, University of Washington, Seattle, WA 98195, USA.

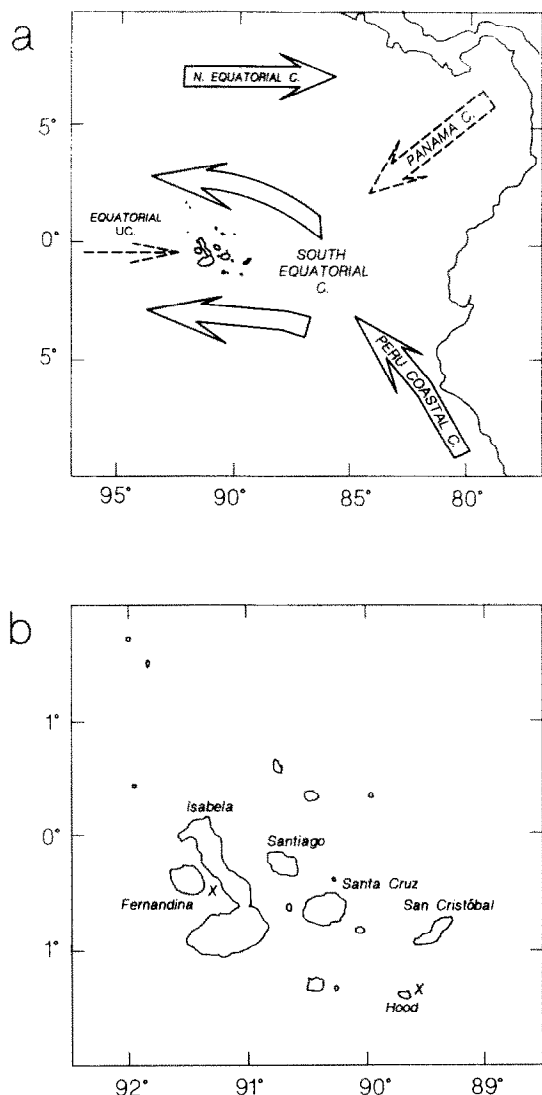


FIG. 1. a) Primary current systems affecting the Galapagos region. b) Collection sites (X) of corals analyzed in this work (both adapted from GLYNN et al., 1983).

convergence zone during the relaxation of the southeast tradewinds (GLYNN et al., 1983).

At intervals, the Galapagos is affected by El Niño Southern Oscillation (ENSO) events, large scale circulation perturbations throughout the Pacific Ocean which generally last 6–18 months (KOGELSCHATZ et al., 1985). Tradewind anomalies during ENSO events result in the depression of the normally shallow thermocline at the Galapagos (WYRTKI, 1975; KOGELSCHATZ et al., 1985). The Galapagos Front, the boundary between the cool, upwelled, nutrient-rich waters at the Galapagos and the more oligotrophic surface waters to the north, moves southward and the Galapagos region is bathed with nutrient-poor waters. Thus, both the seasonally occurring generic El Niño and occasional, longer duration ENSO events result in warmer, more nutrient-depleted Galapagos surface waters.

Trace metals such as Cd, Mn, and Cu may be sensitive proxies for these circulation shifts based on their observed

water column and geographic distributions which may reflect nutrient cycles (e.g., Cd) or aeolian and fluvial sources (e.g., Mn). The surface water concentration ranges expected in the Galapagos region for these trace metals and for dissolved Pb are given in Table 1, along with expected directions of change at the Galapagos with ENSO events. Table 1 also lists estimated distribution coefficients in coral aragonite and effective ionic radii for these metals.

Cd concentrations in surface waters and with depth are strongly correlated with the nutrients phosphate and nitrate (BOYLE et al., 1976; MARTIN et al., 1976; BRULAND et al., 1978; BRULAND, 1980). For example, typical surface water Cd concentrations in the central North Pacific oligotrophic gyre were 2 pmol/kg, while concentrations in the California Current and eutrophic coastal upwelling zones ranged from ~50–150 pmol/kg (BRULAND, 1980). Thus, generic El Niño currents and ENSO events should both be marked by lower surface water Cd concentrations at the Galapagos.

Mn typically has a surface concentration maximum, reflecting the importance of aeolian and fluvial sources, decreasing concentrations with depth, and a mid-depth maximum coincident with the oxygen minimum from reduction of particulate Mn. KLINKHAMMER and BENDER (1980) reported relatively high dissolved Mn concentrations of 2.5–3.0 nmol/kg in the surface mixed-layer of the Panama Basin region, consistent with the observations of LANDING and BRULAND (1987) of high dissolved Mn in mixed layers near shore in the North Pacific. BOYLE and HUESTED (1983) observed surface dissolved Mn concentrations ~5–10 nmol/kg in the Gulf of Panama. However, normal Galapagos surface waters should have lower Mn concentrations, both because upwelling brings lower Mn waters to the surface and because open ocean, surface water Mn concentrations are typically lower than those in coastal regions. For example,

Table 1. Elements studied, surface seawater concentrations, expected ENSO signals at the Galapagos, distribution coefficients in coral aragonite, and ionic radii

Element	Concentration ^a range (nmol/kg)	Expected ENSO change	K_D ^b	Effective ^c ionic radius, Å
Cu	0.5–2.0	none/small	0.3	0.73
Mn	0.5–3.0	increase	1.0	0.96
Cd	0.01–0.1	decrease	1.0	1.10
Pb	0.02–0.05	none	2.3	0.94
Ca	10.3×10^6	none	-	1.12

a. References: Cu, BRULAND (1980) and BOYLE and HUESTED (1983); Cd, BRULAND (1980); Mn, KLINKHAMMER and BENDER (1980), BOYLE and HUESTED (1983), and LANDING and BRULAND (1987); Pb, FLEGAL (1986).

b. References: Cu and Mn, this work; Cd, SHEN (1986), SHEN et al. (1987); Pb, SHEN (1986), SHEN and BOYLE (1987, 1988).

c. SHANNON (1976) ionic radii for divalent cations in octahedral coordination, except for Cu with octahedral coordination not listed; Cu value given is that for coordination number VI.

LANDING and BRULAND (1987) reported surface water Mn concentrations of 0.5 nmol/kg for a central Pacific station (0°S, 160°W). The generic El Niño current and ENSO events should therefore be recorded as maxima in Mn/Ca ratios due to the increased influence of Panama Basin waters with high Mn replacing upwelling and open ocean waters with low Mn.

Cu profiles are characterized by surface minima and increasing concentrations with depth. Typical Cu surface water concentrations range from 0.5 nmol/kg in open ocean stations to >1 nmol/kg in near-shore regions off the US west coast (BRULAND, 1980). High Cu concentrations (>2 nmol/kg) and a covariation of Cu and Mn enrichments in Panama Basin surface waters (BOYLE and HUESTED, 1983) suggested that Cu levels at Galapagos would be elevated with the appearance of the El Niño Current and ENSO events. However, Mn enrichments in Panama Basin surface waters were greater than those for Cu, and detection of enrichments at the Galapagos would depend on the relative transport of both elements. Thus, Cu concentrations in Galapagos surface waters may or may not vary seasonally or during ENSO events with the changing influence of Panama Basin waters.

Dissolved Pb profiles have a subsurface maximum and decreasing concentrations with depth to relatively constant values; this pattern arises from aeolian sources for Pb in conjunction with biological scavenging (FLEGAL and PATTERSON, 1983). Pb concentrations in Peru surface waters (~5°S, 75°W) were ~20–50 pmol/kg, with typical open ocean values ~20 pmol/kg (FLEGAL, 1986). Pb/Ca ratios are not expected to change with the occurrence of the generic El Niño or ENSO in the Galapagos.

Previous studies have documented that Cd/Ca ratios in banded corals record ENSO events (SHEN et al., 1987) and seasonal upwelling variations (LEA et al., 1989) as relative minima. SHEN (pers. commun., 1989) found seasonal peaks in Mn/Ca ratios in an Urquina Bay coral from the 1600s. Pb, typically a difficult element to determine, has also been measured in Galapagos corals (SHEN and BOYLE, 1987). Reliable Pb determinations serve as quality controls here on sample handling and potentially may yield information on patterns of aeolian input.

SAMPLES AND METHODS

Cu/Ca, Mn/Ca, Cd/Ca, and Pb/Ca results reported here are from two colonies of *Pavona clavus*, one of the species studied by SHEN and BOYLE (1987, 1988; SHEN et al., 1987). A contemporary coral from Hood (Española) Island (HI-6), collected live from a depth of 4 m at Gardner Bay, was sampled quarter-annually from mid-1964 through 1973. An older coral (UR-1-86) sectioned annually from A.D. 1600–1725, grew at ~5 m depth (COLGAN, pers. commun., 1989) and was collected in 1986 from the Urquina Bay uplift site. Although the coral head was sub-aerially exposed from the rapid uplift in 1954 (RICHARDS, 1954) until sampling in 1986, there was no visible indication of diagenetic alteration, nor do oxygen isotope data indicate any alteration (DUNBAR, pers. commun., 1989). However, Cd/Ca ratios measured in a second, nearby Urquina Bay coral do not have peaks corresponding to those from the Urquina Bay coral analyzed here in the time range of their overlap (~1850–1900; SHEN, pers. commun., 1989). Thus, at least the Cd/Ca results from this coral may represent changing microenvironments or diagenetic alteration. Oceanographic interpretations of the other trace element records in this coral must also be viewed with caution until these discrepancies are resolved.

X-radiographs of coral slabs taken along axes of corallite growth were used to assign ages of band pairs. Confirmation of annual band-

ing in the Hood Island coral (HI-6) was provided by bomb radiocarbon measurements made previously (DRUFFEL, 1981). Samples were cut from the slabs with a coping saw, crushed with an agate mortar and pestle, and sieved to a size fraction (290–710 μm) found to be effectively treated by the cleaning procedure. The fine fraction (<290 μm) was used for stable oxygen and carbon isotopic analyses. Samples were roasted under vacuum at 375°C for one hour to remove organic carbon. They were acidified in orthophosphoric acid at 50°C, and the resultant carbon dioxide was measured on a VG Micromass 602E mass spectrometer in the laboratory of L. D. Keigwin at WHOI.

Weighed subsamples (75 \pm 1 mg) of sieved coral (290–710 μm) were subjected to a series of oxidative, reductive, and weak acid treatments (see SHEN, 1986, and SHEN and BOYLE, 1988, for details). Cu/Ca ratios measured after strictly following the reported protocol resulted in poor agreement among replicates and in sporadically high results (LINN et al., 1987). We modified these methods by using a final series of more dilute acid rinses with larger volumes (500 μl of 0.001N HNO₃ rather than 250 μl of 0.15N) for more effective cleaning of the surfaces with lower total dissolution. We tested these modified conditions with a sequential cleaning experiment using replicate aliquants of a coral sample and with partial dissolution results. The results of these experiments, and improved precision for Cu/Ca sample replicates, indicated these procedures were adequate for ensuring accurate Cu/Ca results. They did not affect the accuracy or precision of Mn/Ca, Cd/Ca, or Pb/Ca determinations and were used for all results reported here.

After dissolution of the treated coral with 520 μl 2.8N HNO₃, the resulting solution (500 μl) was co-precipitated by a modification of the Co-APDC method first reported by BOYLE and EDMOND (1975) for seawater analysis. Consistency standards, 1M Ca solutions with known concentrations of Cu, Mn, Cd, and Pb representative of typical dissolved coral samples, provided measures of trace metal recoveries with co-precipitation. Reagent blanks were co-precipitated in triplicate with each analytical run. Precipitates were digested with 16N sub-boiling quartz distilled (Q) HNO₃ and diluted to appropriate concentrations for graphite furnace atomic absorption spectrophotometry (GFAAS). Mechanical loss of precipitate (during siphoning) was accounted for by determination of Co concentrations in the final solutions.

All reagents were carefully cleaned and checked for trace metal blanks prior to use with coral samples; details of solution preparation are available elsewhere (LINN, 1988). Sample and reagent containers were leached with hot acid before use. Sample siphoning, transfer, and washes were performed in a class 100 laminar flow bench, except those requiring use of a chemical fume hood.

Trace metal determinations used a Perkin Elmer 5000 atomic absorption spectrophotometer (continuum source background correction) equipped with a Perkin Elmer heated graphite analyzer model 500 and an AS-1 autosampler. Sample analysis was based on duplicate injections of 20 μl . Mn and Pb were analyzed by atomization from a L'vov platform. Ca and Co were analyzed by flame atomic absorption spectrophotometry. Results are reported as molar ratios to Ca in coralline aragonite.

Detection limits, defined as 3 times the 1 σ standard deviation of reagent blanks, are equivalent in typical coral samples to ratios of Cu/Ca 6.4 nmol/mol, Mn/Ca 1.3 nmol/mol, Cd/Ca 0.3 nmol/mol, and Pb/Ca 0.5 nmol/mol. Generally, blanks for individual solutions used in sample treatment and co-precipitation were at or below trace metal detection limits by GFAAS after purification. Total reagent blanks, close to GFAAS detection limits (also expressed as equivalent ratios in typical coral samples), are Cu/Ca 6.9 nmol/mol, 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 4 times the detection limit absorbance. All reported results are corrected for blanks and for co-precipitation recoveries measured with each analytical run.

Hood Island coral samples were processed in triplicate, while Urquina Bay coral samples were processed at least in duplicate. Results for the Hood Island coral are presented as mean values \pm 1 σ standard deviations, while the Urquina Bay results are presented as mean values of replicates for annual bands. Reproducibility of measured ratios, estimated as the average relative standard deviation of individual samples, are Cu/Ca \pm 14%, Mn/Ca \pm 6%, Cd/Ca \pm 13%, Pb/Ca \pm 19%.

RESULTS

Cu/Ca ratios in coral aragonite

Initial attempts to measure Cu/Ca ratios in coral samples according to the methods developed by SHEN (1986) resulted in poor agreement between sample replicates and occasional nonreproducible high ratios. However, measured Cd/Ca and Pb/Ca ratios agreed with results reported by SHEN (1986) for splits of the same coral samples. An experiment designed to check the effectiveness of the different sample treatments using replicates of an Urvina Bay *P. clavus* "coral consistency standard" revealed that Cu/Ca ratios, higher in untreated samples, decreased with each successive treatment up to the final acid rinses (Fig. 2a). Samples treated with the acid strength (0.15N HNO₃) used by SHEN (1986) had widely scattered Cu/Ca ratios (25–75 nmol/mol). Samples treated with larger volume, weaker acid rinses (0.001N HNO₃) as the final step had better agreement among replicates and a slightly lower average Cu/Ca. This experiment also confirmed that a second oxidizing treatment was unnecessary for these coral samples.

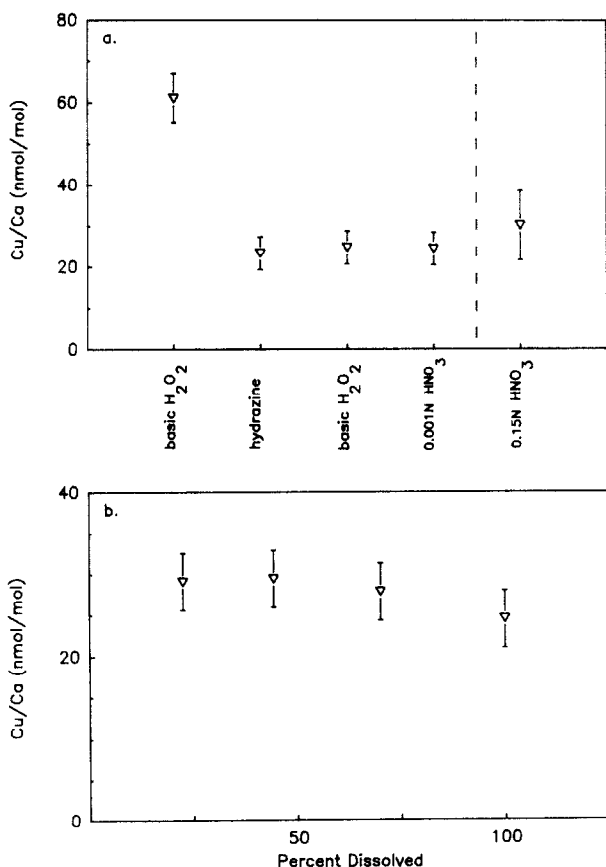


FIG. 2. a) Effect of successive sample treatments on Cu/Ca ratios of coralline aragonite. Cu/Ca ratios of coral samples processed through treatment step indicated on horizontal axis. Cu/Ca ratios decrease to a steady value with successive treatments. The rightmost point is Cu/Ca for coral sample with identical treatment as preceding point except for stronger acid for final acid rinses. b) Partial dissolution results. Cu/Ca ratios of a coral sample processed with the full treatment procedure using weak acid for final rinses vs. percent dissolved. Cu/Ca ratios remain constant with increasing percent coral dissolved.

Partial dissolution results from a split of the coral sample which had undergone the modified treatment regime are presented in Fig. 2b. These data show no increase or decrease in Cu/Ca with increasing percent coral dissolved, indicating that the modified procedure effectively removes extraneous (non-lattice bound) Cu from the coral. These modified procedures did not affect Cd, Mn, or Pb results.

Hood Island coral (1964–1973) quarter-annual samples

Cu/Ca ratios in this coral range from 20 to 70 nmol/mol and show no apparent seasonal pattern (Fig. 3a). In a given year Cu/Ca ratios fluctuate by approximately 10–20 nmol/mol, although there is less variation in the latter half of the record (1969–74). A long-term shift in Cu/Ca ratios (from ~50 to ~25 nmol/mol) is evident in the late 1960s and early 1970s.

Mn/Ca ratios range from 50–150 nmol/mol (Fig. 3b), similar to values reported by SHEN (pers. commun., 1988) in a different Urvina Bay coral (UR-87-3, Mn/Ca range 70–170 nmol/mol for annual samples from 1969–1978). Hood Island Mn/Ca ratios display seasonality, with high values in the early part of the year, coincident with the timing of the generic El Niño current, and a total seasonal variation of ~30 nmol/mol. Seasonal oscillation in Mn/Ca ratios is nearly absent during ENSO events of 1965 and 1969. The strong ENSO event of 1972 is represented by the highest Mn/Ca ratio (~150 nmol/mol) in this record.

Cd/Ca ratios in this coral vary from 1–8 nmol/mol (Fig. 3c); these results agree in range and seasonal variation with those of SHEN et al. (1987) for a coral from San Cristobal in the Galapagos Islands. Seasonally, Cd/Ca ratios range from low values during the first part of the year (El Niño current influence) to a peak coinciding with increased upwelling during the latter half of the year as expected. ENSO events (1965, 1969, and 1972) are characterized by suppression of Cd/Ca ratios by approximately 2–3 nmol/mol. Known periods of intense upwelling (1964, 1967 and 1973) are reflected by the highest Cd/Ca ratios. Stable isotope results confirm seasonal age assignments, with more negative values in the beginning of years coincident with generic El Niño and more positive values mid-year marking seasonal upwelling.

Pb/Ca ratios are 6–9 nmol/mol and are relatively constant throughout the record (Fig. 3d). SHEN and BOYLE (1987) reported Pb/Ca ratios for a San Cristobal coral between 10–15 nmol/mol for 1963–1982. Our quarter-annual data generally agree in pattern with their annually sampled results, with the exception of two years (1969 and 1970) for which they suspected their samples were contaminated, resulting in erroneously high Pb/Ca ratios.

Urvina Bay coral (1604–1725) annual samples

Cu/Ca ratios range from 20–40 nmol/mol (Fig. 4a). There is lower variability in the early (~1600–1620) and late (~1694–1725) sections of this record, with average Cu/Ca ratios ~30 nmol/mol. The central portion of the record (~1625–1690) has periods of higher Cu/Ca variability. Specifically, two intervals circa 1630 and 1675 are marked by elevated Cu/Ca ratios. Both events have relatively low Cu/

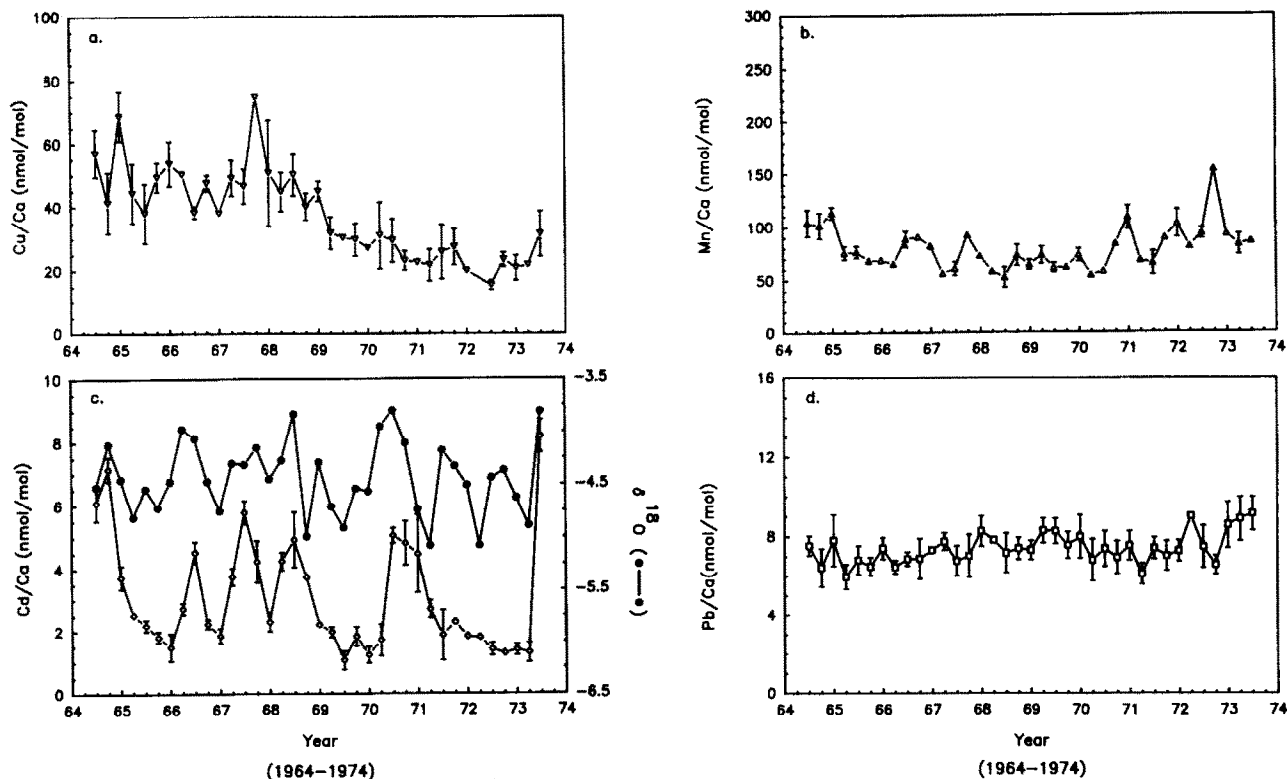


FIG. 3. Quarter-annual trace metal/calcium ratios for a modern Hood Island coral (1964–1973). Results are plotted as means $\pm 1\sigma$ error vs. assigned band age. a) Cu/Ca ratios; b) Mn/Ca ratios; c) Cd/Ca ratios and $\delta^{18}\text{O}$; d) Pb/Ca ratios.

Ca ratios before and after their peaks, with a total change in Cu/Ca ratios of 15–20 nmol/mol. The interval between these two Cu/Ca peaks is marked by minor fluctuations of around 10 nmol/mol, comparable to annual Cu/Ca fluctuations in the modern coral records.

Mn/Ca ratios generally range between 160–270 nmol/mol (Fig. 4b), higher than those of the modern coral. Periods of elevated Mn/Ca ratios range from 5 to 10 years in length with highest Mn/Ca events generally the shortest in duration. Mn/Ca ratios toward the end of this record (post-1715) are the lowest and approach levels found in contemporary corals.

Cd/Ca ratios display a wide range from 5–35 nmol/mol (LINN, 1988). These data are in excellent agreement for both range and pattern with those reported by SHEN (pers. commun., 1988) for subsample replicates of coral samples. The Cd/Ca record differs from the Cu/Ca and Mn/Ca records of this coral in that periods of elevated Cd/Ca ratios are significantly longer in duration. Three periods of elevated Cd/Ca ratios (20–35 nmol/mol) occurred circa 1605–1615, 1660–1680, and 1700–1715. In between episodes of high Cd/Ca, ratios range between 4–15 nmol/mol, similar to the range for non-ENSO years found in the Hood Island contemporary coral.

Pb/Ca ratios generally range from 1–5 nmol/mol (Fig. 4c), excluding data prior to 1618, with high variability and elevated Pb/Ca ratios (>10 nmol/mol). The elevated ratios at the beginning of this record are most likely due to incomplete removal of authigenic phases in samples near the base of the coral head. Contamination is not expected to be significant for the other metals, due to their higher natural levels in the

coralline aragonite relative to those in potential contaminant phases. Pb/Ca ratios show aperiodic maxima, roughly correlated with Cd/Ca ratios.

DISCUSSION

Copper

Using a representative Cu/Ca ratio for the Hood Island record of 25 nmol/mol and a seawater concentration for Cu of 1 nmol/kg (BRULAND, 1980), the estimated Cu coral:seawater K_D is 0.25. Previous determinations of Cu in contemporary Galapagos corals using the unmodified Shen technique (LINN et al., 1987) implied a K_D of 0.35 (average Cu/Ca = 35 nmol/mol, dissolved [Cu] = 1 nmol/kg); because of the analytical uncertainties for these earlier results, this is probably an upper limit. Thus, the best estimate of the coral:seawater Cu K_D for contemporary *P. clavus* is 0.3 ± 0.1 . This value is lower than those for other trace metals in coralline aragonite, but may in part result from Cu's small effective ionic radius (Table 1). Mg, another divalent element with a small effective ionic radius (0.89 Å), has been measured in corals at levels which imply a K_D of ~ 0.003 (AMIEL et al., 1973). Mg is also discriminated against in *Mytilus edulis* aragonite; LORENS and BENDER (1980) reported that the aragonite:solution Mg K_D for the mussel is 0.0035.

With a range in Cu/Ca ratios for the older Urquina Bay coral of 20–40 nmol/mol and a K_D of 0.3, the implied range in Cu concentration in surface waters is 0.7–1.4 nmol/kg for the 1600s and early 1700s, similar to estimated present-day concentrations.

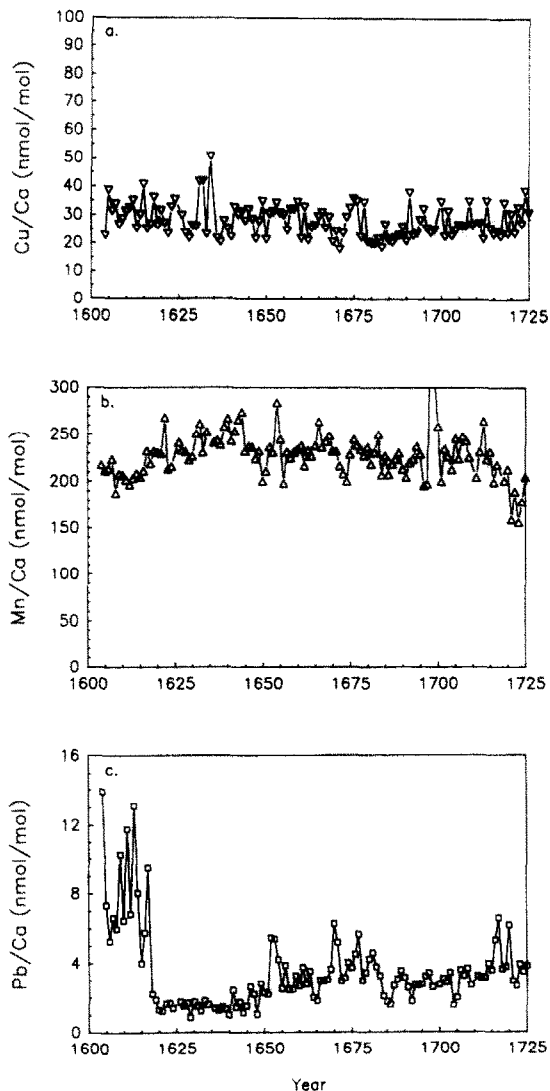


FIG. 4. Annually sampled trace metal/calcium ratios for a seventeenth-century Urvina Bay coral (1600–1725). Results are plotted as mean values of annual replicate samples. a) Cu/Ca ratios; b) Mn/Ca ratios; c) Pb/Ca ratios.

Manganese

Using the high coral Mn/Ca ratio associated with the 1972 ENSO (~ 150 nmol/mol) and a Mn concentration of 2 nmol/kg as estimate of the Mn concentration in an ENSO water mass originating in the Panama Basin, the estimated K_D is ~ 0.8 . In contrast, coral Mn/Ca ratios for normal upwelling times and a Mn concentration of 0.6 nmol/kg for upwelling water yield an estimated K_D of 1.0. Mn/Ca ratios of a contemporary Urvina Bay coral (LINN et al., 1987) had a range of 100–170 nmol/mol, which also implied a K_D of ~ 1 (assuming seawater [Mn] = 1 nmol/kg). We therefore estimate that K_D for Mn in coralline aragonite is approximately 1, similar to those observed for other divalent trace metals of size similar to Ca (SHEN and BOYLE, 1987, 1988).

Using a value of unity (1.0) for the Mn K_D and the observed range of Mn/Ca for the older Urvina Bay record (160–270 nmol/mol), the inferred range in surface seawater Mn is 1.6–

2.8 nmol/kg at this location during the 1600s and early 1700s. Although these are slightly higher than contemporary Mn concentrations in the Galapagos region, higher Mn/Ca ratios, and thus a higher aeolian source function, may also be evidence of more intense tradewinds during the Little Ice Age.

Cadmium

For the Hood Island coral, using an average Cd/Ca ratio for non-ENSO type samples (6.9 nmol/mol) and estimating surface Cd concentrations of 0.1 nmol/kg, an estimate of K_D is 0.7, similar to the Cd K_D of 1 reported by SHEN et al. (1987) for *P. clavus*. Similarly, Cd/Ca ratios of a contemporary Urvina Bay coral implied K_D of 1 (LINN et al., 1987).

The decadal Cd/Ca elevations observed in the Urvina Bay coral record may not represent oceanographic processes, but instead changing microenvironments or diagenetic alteration for this coral as discussed earlier. The Cu, Mn, and Pb records presented here and the stable isotope data (DUNBAR, pers. commun., 1989) do not show clear evidence of changing microenvironments or of diagenetic alteration. Interpretation of these data is as yet unclear.

Lead

Using a Pb/Ca ratio of 9 nmol/mol for the Hood Island coral and an estimated surface water Pb concentration of 50 pmol/kg, we calculate a Pb $K_D = 1.8$. This estimate is in reasonable agreement with the value reported by SHEN and BOYLE (1987) of 2.3 given our uncertainties in estimating surface-water Pb concentrations.

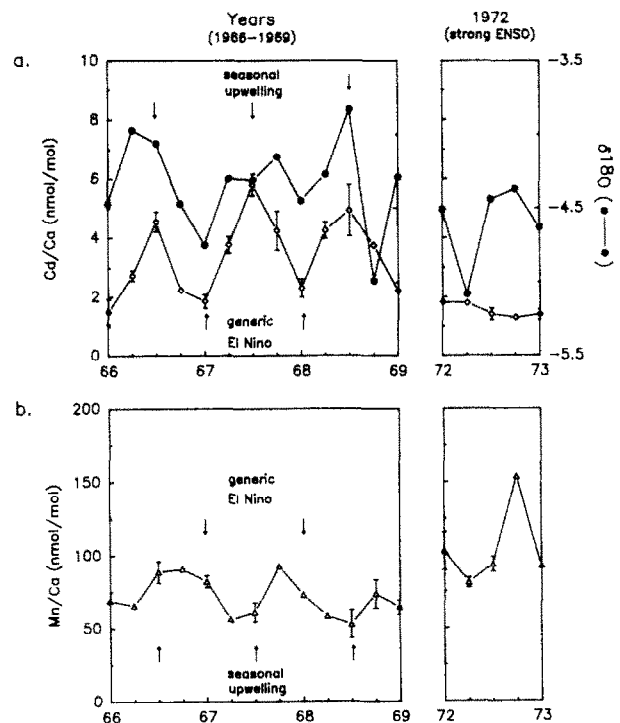


FIG. 5. Three normal years (1966–68) and one ENSO year (1972) for a Hood Island coral. Seasonal upwelling and generic El Niño are marked by arrows. a) Cd/Ca ratios and $\delta^{18}\text{O}$; b) Mn/Ca ratios.

Assuming the Pb/Ca K_D is 2.0, the range in Pb/Ca ratios for the older Urvina Bay coral (1–4 nmol/mol) implies a range in the concentration of Pb in surface seawater of 5–20 pmol/kg during the 1600s. The low end of the range is in line with the predicted preindustrial Pb concentration of 3.9 pmol/kg in the central South Pacific (FLEGAL and PATTERSON, 1983).

Thus, distribution coefficients in coral aragonite are near unity for a range of elements, despite different sizes and chemical speciation in seawater. Thermodynamic predictions of distribution coefficients for 8 divalent metals bracketing Ca in ionic radius span 3 orders of magnitude, while observed values are all close to 1 (SHEN and BOYLE, 1988; SHEN and SANFORD, 1990). As discussed by SHEN, this suggests kinetic, rather than thermodynamic, control of incorporation of elements from seawater into coral aragonite. It is possible that this reflects “trapping” of seawater and the retention of elements on surfaces of growing aragonite crystals, rather than direct incorporation in lattice sites. This remains an area for future research.

Seasonality and ENSO events

Since Cd has a nutrient-like distribution in seawater, both the generic El Niño and ENSO events should produce records in the coral lattice of relatively depleted ratios. Mn, enriched in Panama Basin waters, should be elevated in the coral lattice when this water mass moves into the Galapagos region during ENSO events. Cu is also enriched in Panama Basin waters, but not to the same degree as Mn. Cu may also be more rapidly removed than Mn from surface waters and thus may not yield a detectable signal at the Galapagos with either generic El Niño or ENSO. Pb should have no significant variations.

Cd/Ca ratios of the Hood Island coral have an annual cycle with elevated values occurring mid-year corresponding with periods of upwelling during non-ENSO years (Fig. 5a). This seasonal upwelling signal is interrupted during the ENSO years of 1965, 1969, and 1972 (Figs. 3c and 5a). Cd/Ca ratios appear to be inversely correlated with $\delta^{18}\text{O}$, as would be expected, but $\delta^{18}\text{O}$ appears to lag slightly behind Cd/Ca.

Mn/Ca ratios of the Hood Island coral also have an annual cycle, with elevated ratios during the early part of the year (Fig. 5b). During ENSO this seasonality appears to be damped out. The very strong ENSO event of 1972 is marked by the highest Mn/Ca ratio of this record. Cu/Ca ratios have no corresponding signals. These data suggest that the influence of Panama Basin waters (with elevated Mn) is only recorded by corals at Hood Island during strong or very strong ENSO events; during weaker events the Galapagos Front is too far to the north of Hood Island for the elevated Mn signal to be recorded there.

CONCLUSIONS

Determinations of lattice-bound trace metals Cu, Mn, Cd, and Pb in coralline aragonite were carried out using a modification of the treatment of SHEN (1986; SHEN and BOYLE, 1988). We have shown that Cu/Ca can be reproducibly measured in coralline aragonite, suggesting these levels may reflect Cu concentrations in seawater. We calculated a Cu coral:

seawater distribution coefficient of 0.3, different from the K_D of 1 estimated for several other divalent metals, and estimated a Mn distribution coefficient of approximately 1. We have also confirmed the results of SHEN (1986; SHEN and BOYLE, 1987; SHEN et al., 1987) showing that Cd/Ca and Pb/Ca ratios of Galapagos corals are apparently representative of their surface seawater concentrations.

Mn/Ca ratios of the Hood Island coral (1964–1973) display a regular seasonal pattern in normal years with elevated values in the early part of the year. Unlike contemporary, quarter-annual, Urvina Bay Mn/Ca ratios (LINN et al., 1987), these data suggest that Mn/Ca ratios are elevated during strong ENSO events. Cd/Ca ratios in this coral also have a clear seasonal signal, with lower ratios coinciding with the timing of the generic El Niño current. The annual peak in Cd/Ca ratios is damped during ENSO events. Cu/Ca and Pb/Ca ratios do not demonstrate much seasonal variation.

Cu/Ca ratios of the Hood Island coral decrease by a factor of ~ 2 from the early (1960s) to late (1970s) portions of this record. This long-term shift may reflect an increase in the scavenging of Cu from surface waters, although a similar trend is not seen in the other trace metal records. The speciation of Cu should play a role in its incorporation in the coralline aragonite (e.g., only incorporation of free Cu^{2+} or organically complexed copper). The twofold change in the data could be explained by a change in the relative abundance of chemically available Cu. The fact that a similar decrease is not seen for the other trace metal ratios examined in this coral implies that any mechanism for complexing Cu more strongly affects Cu than the other trace metals determined here; this is consistent with the differing complexation characteristics of these metals.

The trace metal/calcium ratios of the seventeenth-century Urvina Bay coral (1604–1725) provide a record of surface seawater concentrations of these elements in the Galapagos, although questions remain about the integrity of this coral from the comparison of its Cd/Ca record to that of a nearby coral. Generally, Cu concentrations appear similar to present-day levels. Mn concentrations were somewhat higher than present-day, but could reflect either more influence from Panama Basin waters or possibly increased aeolian input with more intense tradewinds. Pb concentrations were lower than present-day, consistent with estimates for prehistoric Pb levels.

As demonstrated by the contemporary coral record, both Mn/Ca and Cd/Ca ratios of Galapagos corals are tracers of historical ENSO events. Mn/Ca ratios increase with a southward shift of the Galapagos Front, while Cd/Ca ratios are depleted with a damping of the normal upwelling signal. A direction for further use of Mn/Ca ratios in Galapagos corals as an ENSO indicator lies in obtaining a coral core from one of the islands in the north end of the Archipelago. This area is likely to be more sensitive to the shifting of the Galapagos Front and would probably have a stronger seasonal variability in Mn, and possibly Cu, concentrations than Hood Island, the southernmost island in the Archipelago.

Acknowledgments—We would like to acknowledge support of this work by NSF Visiting Professorship for Women RII-8620256 (to ERMD) and partial support by NSF OCE-8614027 (to MLD). We would especially like to thank Dr. G. T. Shen for his advice, assistance, and encouragement throughout this work and Dr. E. Boyle for his

thoughtful and helpful advice. Dr. K. Bruland's comments on versions of the manuscript were appreciated. We would also like to thank Drs. M. Colgan, R. Dunbar, and P. Glynn for making coral samples available to us. We thank S. Griffin for the isotopic analyses, C. Low for many hours of FAAS analyses, and G. Smith for help in establishing our techniques. Thanks to R. Franks and the Marine Analytical Lab, Institute of Marine Sciences, for chemicals, advice, and technical expertise and to W. Graham for editing and general support. Helpful and insightful comments by Drs. E. A. Boyle, A. R. Flegal, and R. A. Schmitt are gratefully acknowledged.

Editorial handling: R. A. Schmitt

REFERENCES

- AMIEL A. J., FRIEDMAN G. M., and MILLER D. S. (1973) Distribution and nature of incorporation of trace elements in modern aragonitic corals. *Sedimentology* **20**, 47–64.
- BOYLE E. A. and EDMOND J. M. (1975) Determination of trace metals in aqueous solution by APDC chelate coprecipitation. *Adv. Chem.* **147**, 44–55.
- BOYLE E. A. and HUESTED S. (1983) Aspects of the surface distributions of copper, nickel, cadmium, and lead in the North Atlantic and North Pacific. In *Trace Metals in Sea Water* (eds. C. S. WONG et al.), pp. 379–394. Plenum Press.
- BOYLE E. A., SCLATER F., and EDMOND J. M. (1976) On the marine geochemistry of cadmium. *Nature* **263**, 42–44.
- BRULAND K. W. (1980) Oceanographic distributions of cadmium, zinc, nickel, and copper in the North Pacific Ocean. *Earth Planet. Sci. Lett.* **47**, 176–198.
- BRULAND K. W., KNAUER G. A., and MARTIN J. H. (1978) Cadmium in Northeast Pacific Waters. *Limnol. Oceanogr.* **23**, 618–625.
- DRUFFEL E. M. (1981) Radiocarbon in annual coral rings from the eastern tropical Pacific Ocean. *Geophys. Res. Lett.* **8**, 59–62.
- FLEGAL A. R. (1986) Lead in tropical marine systems: a review. *Sci. Total Envir.* **58**, 1–8.
- FLEGAL A. R. and PATTERSON C. C. (1983) Vertical concentration profiles of lead in the Central Pacific at 15°N and 20°S. *Earth Planet. Sci. Lett.* **64**, 19–32.
- GLYNN P. W., WELLINGTON G. M., and WELLS J. W. (1983) *Corals and Coral Reefs of the Galapagos*. University of California Press.
- HOUVENAGHEL G. T. (1984) Oceanographic setting of the Galapagos Islands. In *Key Environments-Galapagos* (ed. R. PERRY), pp. 55–69. Pergamon Press.
- HOWARD L. S. and BROWN B. E. (1984) Heavy metals and reef corals. *Oceanogr. Mar. Biol. Ann. Rev.* **22**, 195–210.
- KLINKHAMMER G. P. and BENDER M. L. (1980) The distribution of manganese in the Pacific Ocean. *Earth Planet. Sci. Lett.* **46**, 361–384.
- KOGELSCHATZ J., SOLORZANO L., BARBER R., and MENDOZA P. (1985) Oceanographic conditions in the Galapagos Islands during the 1982/1983 El Niño. In *El Niño en las Islas Galapagos: El Evento de 1982-1983* (eds. G. ROBINSON and E. M. DEL PIÑO), pp. 91–123. Charles Darwin Foundation.
- LANDING W. M. and BRULAND K. B. (1987) The contrasting biogeochemistry of iron and manganese in the Pacific Ocean. *Geochim. Cosmochim. Acta* **51**, 29–43.
- LEA D. W., SHEN G. T., and BOYLE E. A. (1989) Coralline barium records temporal variability in equatorial Pacific upwelling. *Nature* **340**, 373–376.
- LINN L. J. (1988) Trace metals in Galapagos corals: quarter-annual and annual cycles of copper, manganese, cadmium, and lead. Master's thesis, Univ. California, Santa Cruz.
- LINN L. J., DRUFFEL E. R. M., and DELANEY M. L. (1987) Trace metal concentrations in a Galapagos coral: an ENSO indicator? (abstr.). *Eos* **68**, 1743–1744.
- LIVINGSTON H. D. and THOMPSON G. (1971) Trace element concentrations in some modern corals. *Limnol. Oceanogr.* **16**, 786–796.
- LORENS R. B. and BENDER M. L. (1980) The impact of solution chemistry on *Mytilus edulis* calcite and aragonite. *Geochim. Cosmochim. Acta* **44**, 1265–1278.
- LUKAS R. (1986) The termination of the equatorial undercurrent in the Eastern Pacific. *Prog. Oceanogr.* **16**, 63–90.
- MARTIN J. H., BRULAND K. B., and BROENKOW W. W. (1976) Cadmium transport in the California Current. In *Marine Pollutant Transfer* (eds. H. L. WINDOM and R. A. DUCE), pp. 159–184. Heath.
- OOMORI T., KANESHIMA K., NAKAMURA Y., and KITANO Y. (1982) Seasonal variations of minor elements in coral skeletons. *Galaxea* **1**, 77–86.
- RICHARDS A. F. (1954) Volcanism in Eastern Pacific Ocean Basin: 1945–1955. In *International Geological Congress session—Ciudad de Mexico, 1965: seccion-Volcanologia Del Cenozoico Mexico. D.F. 1957*, 19–31.
- SCHNEIDER R. C. and SMITH S. V. (1982) Skeletal Sr content and density in *Porites* spp. in relation to environmental factors. *Mar. Biol.* **66**, 121–131.
- SHANNON R. D. (1976) Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Cryst. A* **32**, 751–767.
- SHEN G. T. (1986) Lead and cadmium geochemistry of corals: reconstruction of historic perturbations in the upper ocean. Ph.D. dissertation, MIT/WHOI.
- SHEN G. T. and BOYLE E. A. (1987) Lead in corals: reconstruction of historical industrial fluxes to the surface ocean. *Earth Planet. Sci. Lett.* **82**, 289–304.
- 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. and SANFORD C. L. (1990) Trace element indicators of climate variability in reef-building corals. In *Global Ecological Consequences of the 1982–83 El Niño* (ed. P. GLYNN). Elsevier (in press).
- 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**, 794–796.
- ST. JOHN B. E. (1974) Heavy metals in the skeletal carbonate of scleractinian corals. *Proc. 2nd Intl. Coral Reef Symp. Brisbane* **2**, 461–469.
- WYRTKI K. (1975) El Niño—the dynamic response of the equatorial Pacific Ocean to atmospheric forcing. *J. Phys. Oceanogr.* **5**, 572–584.