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Climate of the Past

Coral Cd/Ca and Mn/Ca records of ENSO variability in the Gulf of California

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Abstract. We analyzed the trace element ratios Cd/Ca and Mn/Ca in three coral colonies (*Porites panamensis* (1967–1989), *Pavona clivosa* (1967–1989) and *Pavona gigantea* (1979–1989)) from Cabo Pulmo reef, Southern Gulf of California, Mexico, to assess the oceanographic changes caused by El Niño – Southern Oscillation (ENSO) events in the Eastern Tropical North Pacific (ETNP). Interannual variations in the coral Cd/Ca and Mn/Ca ratios showed clear evidence that incorporation of Cd and Mn in the coral skeleton was influenced by ENSO conditions, but the response for each metal was controlled by different processes. The Mn/Ca ratios were significantly higher during ENSO years ($p < 0.05$) relative to non-ENSO years for the three species of coral. In contrast, the Cd/Ca was systematically lower during ENSO years, but the difference was significant ($p < 0.05$) only in *Pavona gigantea*. A decrease in the incorporation of Cd and a marked increase in Mn indicated strongly reduced vertical mixing in the Gulf of California during the mature phase of El Niño. The oceanic warming during El Niño events produces a relaxation of upwelling and a stabilization of the thermocline, which may act as a physical barrier limiting the transport of Cd from deeper waters into the surface layer. In turn, this oceanic condition can increase the residence time of particulate-Mn in surface waters, allowing an increase in the photo-reduction of particulate-Mn and the release of available Mn into the dissolved phase. These results support the use of Mn/Ca and Cd/Ca ratios in biogenic carbonates as tracers of increases in ocean stratification and trade wind weakening and/or collapse in the ETNP during ENSO episodes.

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1 Introduction

The El Niño – Southern Oscillation (ENSO) phenomenon is one of the main sources of global climate variability at interannual time scales. The region of the mouth of the Gulf of California is characterized by a strong response to ENSO activity. During the El Niño episodes, this area experiences sea-surface temperature anomalies of 4 °C, a dramatic submergence of the thermocline down to 50 m from its normal depth, and a decrease in salinity (0.1–0.2 psu) that results from the invasion of tropical surface waters (Lavin and Marinone, 2003; Castro et al., 2006). Although the Gulf of California has been studied widely, the regional oceanographic anomalies produced by ENSO have only been derived from synoptic studies; hence, continuous long-term studies of oceanographic variability have been missing.

Corals offer significant advantages as paleoceanographic recorders because they contain annual skeletal growth bands that provide a very precise annual chronology. Their widespread presence throughout the tropical seas of the world, and the geochemical signals contained in their skeletons provide a powerful means of reconstructing environmental conditions with a fidelity that is comparable to instrumental records (Gagan et al., 2000). With regard to trace metals, it is now widely known that the ocean distribution of certain trace elements, such as cadmium (Cd) and manganese (Mn), are sensitive to oceanographic processes such as vertical mixing, upwelling and lateral advection (Boyle et al., 1976; Landing and Bruland, 1980; Boyle, 1988; Delgadillo-Hinojosa et al., 2001). Because the distribution coefficient (D) of Cd/Ca and Mn/Ca ratios in the coral relative to seawater is known (Shen and Sanford, 1990), their variation in the coral skeleton can provide us with detailed oceanographic records on different time scales.

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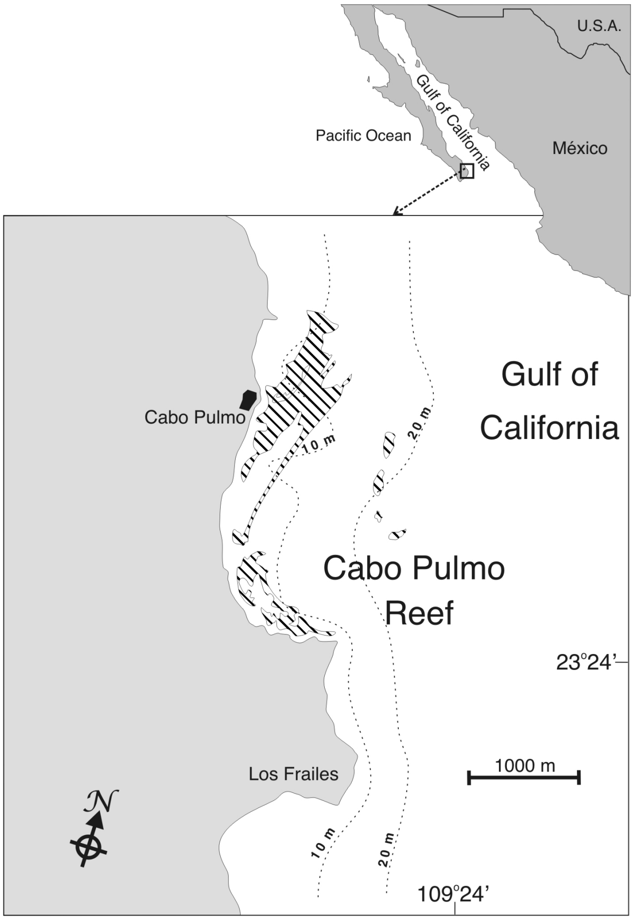

Fig. 1. Location of Cabo Pulmo reef (hatched area), at the mouth of the Gulf of California, Mexico.

Because of its geochemistry and nutrient-type distribution in the ocean, Cd is a direct tracer of upwelling and vertical mixing (Boyle et al., 1976; Boyle, 1988). During upwelling events, subsurface water rich in nutrients is carried to the surface exposing the reef areas to seawater enriched with Cd, and corals are able to record these changes in their skeleton (Shen et al., 1987, 1992a; Linn et al., 1990; Delaney et al., 1993; Reuer et al., 2003). The variability of Cd in the coral skeleton has been correlated with large oceanographic processes, such as ENSO, that efficiently modulates upwelling activity in the eastern tropical Pacific (Shen et al., 1987, 1992a).

In a different way to cadmium, Mn/Ca ratios have also been used to document changes in the dynamics of the ocean surface. In the Pacific Ocean, dissolved-Mn in the water column shows a subsurface maximum, due to dissolution of Mn oxides (Landing and Bruland, 1980; Nameroff et al., 2002). As in the Pacific Ocean, the vertical distribution of dissolved manganese in the southern Gulf of California shows a high concentration at the ocean's surface (from 2 to 7 nM, in the upper 50 m), a rapid decrease in subsurficial waters (to <2 nM), probably due to oxidative removal and by adsorption of dissolved-Mn by suspended particles, and finally a slight increase in deep waters where the oxygen minimum zone occurs (Delgadillo-Hinojosa et al., 2006). The surface maximum of dissolved-Mn in the Gulf of California has been explained mainly by atmospheric supply of particulate Mn and by the photoreduction of manganese oxides (Delgadillo-Hinojosa et al., 2006). The potential supply of Mn by fluvial discharge into the Gulf of California is considered insignificant because most of the rivers that reach the Gulf of California have been damned, significantly reducing the flow of freshwater (e.g. Carriquiry et al., 2001).

Coral Mn/Ca records have been shown to record periodic advective pulses of dissolved-Mn originating from the dissolution of Mn oxides that are present in the coastal shelf of the Galapagos Islands (Linn et al., 1990; Shen et al., 1991; Delaney et al., 1993). Also, but in a different manner, the ENSO variability has been documented in the Mn/Ca ratios of corals from Tarawa atoll, in the central Pacific Ocean (Shen et al., 1992b). In this region, as a consequence of Trade wind reversal (development of intense Westerlies) that takes place during ENSO years, bottom lagoonal sediments become resuspended, enriching the water column with diagenetic-Mn; corals record these Mn-pulse events in their growth bands (Shen et al., 1992b).

Variation in the Cd/Ca and Mn/Ca ratios along the growth bands of corals seem to record oceanographic conditions that favor the Cd and Mn availability in the reef environment, but whether of these trace element ratios vary among species of corals in the same locality has rarely been assessed (Delaney et al., 1993; Reuer et al., 2003; Matthews et al., 2008). In this study, we examine the ratios of Cd/Ca and Mn/Ca in three species of massive corals (*Pavona gigantea*, *Pavona clivosa* and *Porites panamensis*) from Cabo Pulmo reef, Southern Gulf of California, Mexico, to assess oceanographic changes during ENSO events.

2 Materials and methods

2.1 Characterization of the study area

The Cabo Pulmo reef is located on the east coast of southern Baja California (23°25′ N, 109°25′ W) (Fig. 1), inside Los Frailes Bay, at a water depth between 5 and 18 m. The shallow reef flats are dominated by species of the branching coral *Pocillopora*, while in the deeper reef zones, species of massive corals thrive, such as *Porites panamensis, Pavona gigantea and Pavona clivosa*, and to a lesser extent *Porites porosa*, *Tubastraea tenuilamellosa*, *Tubastrae coccinea*, *Psammocora stellata*, *Psammocora brighami* and *Madracis sp*. (Reyes-Bonilla, 1993a). Structurally, the reef is composed of well-cemented conglomerate bars that have been exposed above the sea floor by differential erosion (Carriquiry, personal observation). Young coral reef development takes place on top of these conglomeratic bars, with a reef framework of up to 3 m thick in some locations (the average thickness is ~1 m). Although there is little hydrologic information for the area, during spring a thermocline develops at ~10 m depth, while in summer, autumn and winter, the water column from 0 to 30 m is well mixed. SST varies between 19 and 30 °C, but occasionally is lower than this during the upwelling period (see Fig. 2) causing sporadic cold-water bleaching events (e.g., Reyes-Bonilla, 1993b).

In the absence of any physical barrier that could separate Cabo Pulmo reef from the open ocean, and the lack of a continental shelf in the area, the hydrological characteristics in the reef are the same as to those of the Gulf of California. Geographically, the reef site is located in the Eastern Tropical North Pacific (ETNP) in a hydrographic region known as Transitional Pacific of Mexico. The oceanography of the area is complex because it is affected by the large-scale circulation of the Eastern Tropical Pacific. This region seasonally receives the arrival of the cold (18–20 °C) and low salinity (<34.5 psu) water of the California Current (CCW), the saline water (>34.9 psu) of the Gulf of California water (GCW) and the water of the Coastal Current of Costa Rica (CCCRW) that later turns into the West Mexican Current (WMC) transporting equatorial waters of low-salinity (34 to 34.8 psu) and higher temperature>25 °C (e.g. Castro et al., 2006) into the mouth of the Gulf of California. The interannual climatic and oceanographic variability in this region is modulated by El Niño events that significantly affect the circulation patterns in the ETNP (Baumgartner and Christensen, 1985; Lavin and Marinone, 2003; Castro et al., 2006). Although the normal seasonal SST cycle in this region shows an 8 °C range, during the El Niño years there have been positive SST anomalies of 3–4 °C (Castro et al., 2006). This anomalous warming associated with ENSO episodes produces a deepening of the thermocline, which significantly limits the supply of nutrients to the surface and their availability for primary organic productivity. This situation adversely affects coastal fisheries in northwest Mexico, where the major fisheries in the Mexican Pacific take place (Lluch-Cota et al., 1999).

2.2 Sample collection

Live colonies of *Pavona gigantea* (227 mm high), *Pavona clivosa* (225 mm high) and *Porites panamensis* (154 mm high) were collected at water depths between 5 and 10 m from Cabo Pulmo reef, in May 1990. In the laboratory, the corals were submerged in 50% (v/v) sodium hypochlorite to remove the organic tissue. The coral colonies were slabbed using a circular saw (MK Diamond Products, Inc.) equipped with a 14″ diameter diamond blade. The resulting 7 mm-thick coral slabs were x-rayed (Picker X-ray G850S) to reveal the annual growth bands that were used to develop the age model of each coral colony. From the positive impressions of x-ray images, each annual growth band was traced using acetate sheets over the positive prints. The annual skeletal growth rates were calculated from three different transects in each x-rayed coral colony. The observed growth rates were: 11.3±2.3 mm/year (1970–1989) for *Pavona gigantea*; 9.76±2.5 mm/year (1967–1989) for *Pavona clivosa*, and 6.67±1.1 mm/year (1967–1989) for *Porites panamensis*. The annual growth bands traced on the acetate sheets were transferred to the coral slabs to later cut each annual growth band using a mini-drill (Dremel, Moto-Tool 395) equipped with a flexible shaft (Dremel 225T1) and a circular mini-saw (Dremel 409). Prior to sample treatment and analyses, coral samples were crushed in an agate mortar to a size range of 250–600 µm.

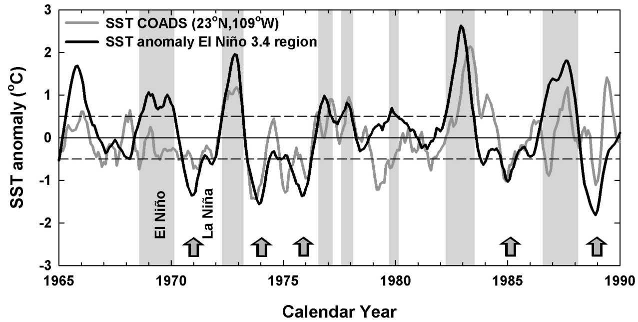

Fig. 2. Comparison of temperature anomalies in the Niño 3.4 region, filtered by a 5-month moving average that define the variability of El Niño (Trenberth, 1997) versus the temperature anomalies (same filtering) in the mouth of the Gulf of California obtained from the COADS database (resolution of 2° × 2°, Slutz et al., 1985). The gray bars define the timing and duration (months) of the El Niño events and the arrows indicate the cold events of La Niña defined by Trentberth (1997).

2.3 Sample treatment and analyses

Analyses of the Cd/Ca and Mg/Ca ratios in the coral skeleton was performed using the Shen and Boyle (1988) method, with the modifications proposed by Linn et al. (1990). This procedure uses a sequence of successive oxidative and reductive steps designed to remove the metals adsorbed to the surface of coral, the metals associated with Fe- and Mn-oxides, and the metals incorporated into the organic matter fraction commonly present in the skeletons. The final step includes coprecipitation with an ammonium pyrrolidine dithiocarbamate (APDC) and Co complex, aimed at removing excess-Ca in the solution and to concentrate the metals. This procedure is designed to only measure the metals that are part of the crystal lattice of the calcium carbonate coral skeleton. The analysis of Cd and Mn was performed in an atomic absorption spectrophotometer, Thermo Jarrell Ash (TJA), SH12 model, equipped with a graphite furnace CTF-188 and a correction system developed by Smith-Hieftje. The Ca concentration of each sample was obtained from an aliquot of 40 µL obtained prior to co-precipitation and diluted in 50 mL of

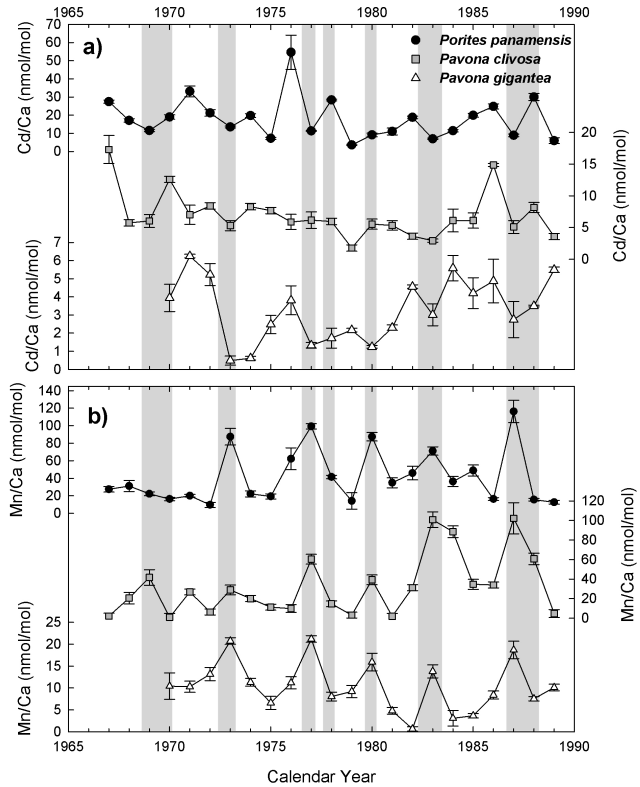

Fig. 3. Temporal variation (1967 to 1989) of the annual Cd/Ca ratios of the three coral species used in this study **(a)**, and temporal variation of the Mn/Ca ratio in the skeleton of the same coral species **(b)**. The error bars (±1 s.d.) were obtained from the replicates (n=3) used to calculate the annual average. The gray bars define the timing and duration (months) of the El Niño events and the arrows indicate the cold events of La Niña defined by Trentberth (1997).

nitric acid 2 M. The solution was analyzed by atomic absorption using a nitrous oxide/acetylene flame. For quality control, a laboratory standard was prepared from a coral powder homogenate that was treated and analyzed in the same way as the samples. The calculated recovery percentage of the coral standard, spiked with Cd and Mn was ±91% (the Cd/Ca and Mn/Ca data were corrected by the recovery). The calculated precision of the method was better than 10% (n=16).

2.4 Oceanographic characteristics

The average SST range in the Cabo Pulmo region is ∼8 °C, varying from 21.0 °C in March to 28.5 °C in September. At interannual time scales, SST variability at the mouth of the Gulf of California is controlled by El Niño. Figure 2 compares the SST-anomaly in the mouth of the Gulf of California region (MGC) (2×2 degrees resolution centered at 109° W, 23° N; COADS database, Slutz et al., 1985) with the SST anomalies observed in the Niño 3.4 region (Trenberth, 1997). With the exception of the moderate El Niño event of 1969 and the weak El Niño of 1980, the rest of the El Niño events in the 1965 to 1990 period (i.e., ENSO years 1972–1973, 1976 and 1977, 1982–1983 and 1986–1988) were characterized in this region by a significant positive anomaly in SST. SST anomalies between the two regions were synchronous, with the exception of the El Niño event of 1982–1983, where the thermal response in the mouth of the Gulf of California was of similar intensity but delayed by ∼3 months (Fig. 2).

3 Results and discussion

3.1 Interspecific differences in the Cd /Ca and Mn/Ca ratios of corals

The skeletal ratio of Cd/Ca (nmol/mol) displayed significant variation among the three coral species studied (Table 1 and Fig. 3a). The mean Cd/Ca ratio (±1 s.d.) increased from the coral *Pavona gigantea* (3.28±1.73) to *Pavona clivosa* (6.94±3.63) to *Porites panamensis* (18.0±11.5) (Table 1). Furthermore, the average Cd/Ca ratio (2.76±1.51) in the coral *Pavona gigantea* sampled at seasonal resolution was similar to average Cd/Ca ratios sampled at annual resolution, indicating that the annual resolution adequately reflects the incorporation of Cd in this species throughout the year.

Similar to the Cd/Ca ratio, the Mn/Ca ratio (nmol/mol) showed marked differences between species, but variability within each species (i.e., the relative standard deviation) was higher than in the Cd/Ca ratio (Table 1 and Fig. 3b). The Mn/Ca ratio among the different species increased in the same order as observed for the Cd/Ca ratio: the Mn/Ca ratio was lowest in *Pavona gigantea* (10.45±5.63), moderate in *Pavona clivosa* (32.3±31.0), and highest in *Porites panamensis* (41.6±31). Also, similar to the Cd/Ca ratio, the average Mn/Ca ratio sampled at seasonal resolution (10.61±8.9) was practically equal to that measured at annual resolution (Table 1).

Concentration differences of several geochemical proxies have also been described from different coral species growing in the same locality, such as δ^{18}O, δ^{13}C and Sr/Ca ratios (de Villiers et al., 1994; Wellington et al., 1996; Grottoli and Wellington; 1999). However, the lack of information about Cd/Ca and Mn/Ca ratios among different coral species makes it difficult to interpret the observed interspecific geochemical differences of this study. For instance, it has been shown that the Cd/Ca ratios in the Caribbean coral *Siderastrea siderea* are greater than those measured in *Montastrea annularis* collected at the same site (Reuer et al., 2003). In the Pacific, Shen and Sanford (1990) found that the Cd/Ca ratio in *Pavona clavus* from the Galapagos was slightly lower than that measured in *Pavona gigantea* from Panama and concluded that these differences were caused by locality differences. Matthews et al. (2008) found that the Cd/Ca ratio was highest in *Pavona gigantean*, moderate in *Pavona clavus*, and low in *Porites lobata* from the same locality,

Table 1. Average (±1 s.d.) of the growth rate (GR mm/yr) and the Cd/Ca and Mn/Ca ratios (nmol/mol) measured in the corals collected from Cabo Pulmo reef, Gulf of California, Mexico.

Coral	GR (mm/yr)	Cd/Ca	Mn/Ca
Pavona gigantea	11.28±2.34	3.28±1.73	10.45±5.63
Pavona clivosa	9.76±2.42	6.94±3.63	32.34±31.02
Porites panamensis	6.68±1.06	18.00±11.54	41.64±31.01
Pavona gigantea (seasonal sampling)	11.40±2.28	2.76±1.51	10.61±8.90

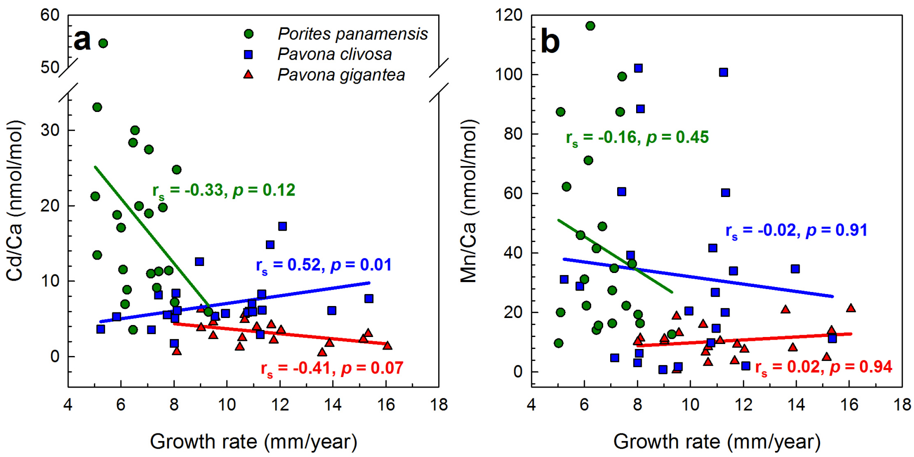

Fig. 4. Relationship between skeletal growth rate and Cd/Ca **(a)** and Mg/Ca **(b)** for *Porites panamensis*, *Pavona clivosa* and *Pavona gigantea*. Spearman rank correlation value (r_s) and statistical probability (p) are provided.

and they proposed three possible explanations for the differences: (1) differences in the plankton feeding rate (heterotrophy), (2) kinetic effects controlled by the differences in growth rate, and (3) an artifact related to the cleaning procedure. The authors did not find a relationship between growth rate and the Cd/Ca ratio, nor an effect due to heterotrophy; concluding that, in their study, sample treatment effects explained the species' differences. According to these authors, the skeletal structure of *Porites* is more delicate relative to that of *Pavona*, favoring a larger loss of *Porites* samples in their procedures; the losses they observed could explain the differences in the Cd/Ca ratios among species. We did not measured the sample loss among species, but our results indicate that in the Gulf of California, corals of the genus *Porites* concentrate more Cd and Mn, compared with species of the genus *Pavona*. This result the opposite conclusion reached for the Gulf of Panama (Mattehws et al., 2008). Consequently, it is highly unlikely that a larger sample loss during the cleaning protocol of *Porites* samples could explain why *Porites* had higher Cd/Ca and Mn/Ca ratios than the two species of *Pavona* studied here.

Because corals potentially bioconcentrate metals from their diets (Fallon et al., 2002), the feeding preferences among species could also explain the differences in metal uptake. For instance, it has been found that heterotrophic feeding by *Porites* is similar or slightly greater than that *Pavona* (e.g. Matthews et al., 2008). Thus, the contrast in heterotrophic feeding among the studied species, if it exists, would have to explain the remarkable 4.5 fold increase in the Cd/Ca ratio and 4 fold increase for the Mn/Ca ratio between the lowest and highest ratios (Table 1), which seems unlikely to us.

Concerning the effects of growth rate on metal uptake, we found that, except for the significant correlation between the Cd/Ca ratios and the skeletal growth rate of *Pavona* (Spearman rank correlation, r_s=0.52, p=0.012), other coral species showed no relationship between growth rate and Cd/Ca and Mn/Ca ratios (Fig. 4). The effect of coral growth rate has been assessed elsewhere through the Sr/Ca ratio, with contradictory results. For instance, de Villiers et al. (1994, 1995) found that high values of the Sr/Ca ratio in the coral skeleton of *Pavona clavus* were associated with lower skeletal growth rates. High Sr/Ca ratios in the coral *Diploria labyrinthiformis* from Bermuda were inversely correlated with low temperatures and low rates of skeletal growth, and vice versa (Goodkin et al., 2005). In contrast, Allison and Finch (2004) found that the growth rate of *Porites lobata* did not affect the rate of incorporation of Sr in the coral skeleton. Interestingly, these studies were conducted on one coral colony along two sampling transects with different growth rates, and

Table 2. Distribution coefficients (D) calculated (±1 s.d.) for the Cd/Ca and Mn/Ca ratios of the coral species studied, considering the average Cd and Mn concentration in the surface layer of the southern Gulf of California (station 19, Delgadillo-Hinojosa et al., 2001, 2006) and the average Ca concentration in seawater (of 10.3 mM, Bruland, 1983).

Coral species/(Me/Ca) ratio	Calculated D (±1 s.d.)	Estimated D (Shen et al., 1993)
Porites panamensis		
Cd/Ca	0.83±0.53	0.9–2.0
Mn/Ca	0.13±0.10	0.1–0.6
Pavona clivosa		
Cd/Ca	0.32±0.17	
Mn/Ca	0.10±0.10	
Pavona gigantea		
Cd/Ca	0.15±0.08	
Mn/Ca	0.03±0.02	

Table 3. Comparison between average (±1 s.d.) Cd/Ca and Mn/Ca ratios (nmol/mol) for ENSO and non-ENSO years in corals collected from Cabo Pulmo reef. The probability values of the two sample student's t-tests are included. The trace metal ratios for the years that are statistically different ($p \leq 0.05$) between ENSO and non-ENSO conditions are marked in bold.

Coral	ENSO vs. Non-ENSO	Cd/Ca	Mn/Ca
Pavona gigantea	ENSO (n=7)	**2.01±1.10**	**15.14±5.64**
	Non-ENSO (n=13)	**3.96±1.64**	**7.93±3.81**
	Probability (p)	**0.0028**	**0.0070**
Pavona clivosa	ENSO (n=9)	6.42±2.68	**49.37±35.67**
	Non-ENSO (n=14)	7.27±4.19	**21.39±22.71**
	Probability (p)	0.2783	**0.0288**
Porites panamensis	ENSO (n=9)	18.30±15.31	**64.20±37.91**
	Non-ENSO (n=14)	17.81±8.99	**27.14±12.81**
	Probability (p)	0.4661	**0.0097**

the contrasting results of these studies illustrate differences in response among the coral species and localities.

Independent of the factors controlling Cd/Ca and Mn/Ca ratios in the coral skeleton, the results obtained in this study indicate differences in the distribution coefficients (D) among the species. Using the average dissolved Cd concentration (0.22 nM) and dissolved Mn (3.34 nM) in the surface ocean of the southern Gulf of California (Delgadillo-Hinojosa et al., 2001, 2006) and the ocean average Ca concentration (10.3 mM, Bruland, 1983), we calculated the distribution coefficients for Cd and Mn of the different species studied (Table 3). These results show that the distribution coefficient for Mn and Cd in *Porites panamensis* and the D_{Cd} for *Pavona clivosa* are within the ranges published by Shen (1993), while the distribution coefficient values for Cd in *Pavona clivosa*, and for Cd and Mn in *Pavona gigantea* are smaller than the previously estimated ones (Table 3). Because of the analytical difficulties involved in measuring extremely low concentrations of Cd and Mn, in both coral skeleton and seawater, very few studies have attempted to calculate D of Cd and Mn in different coral species (Shen and Sanford, 1990; Shen, 1993). Consequently, the range of D for several coral species, like *Pavona gigantea*, is still unknown. The results of this study suggest that the factors that ultimately determine the concentration of Mn and Cd in the coral skeletons remain somewhat elusive.

3.2 Interannual variations of the Cd/Ca and Mn/Ca ratio and ENSO

The annually-resolved Cd/Ca and Mn/Ca ratios obtained from coral skeletons from the Gulf of California showed significant interannual variability. The Cd/Ca and Mn/Ca variability during the 1967–1989 period for the three coral species is shown in Fig. 3, and the normalized anomalies of the average Cd/Ca and Mn/Ca ratios are shown in Fig. 5. The ratios indicate a clear influence of ENSO events, although the average normalized anomalies of the three coral species show that the effect is more evident in the Mn/Ca ratio than in the Cd/Ca ratio. This can be better observed by separating the Cd/Ca and Mn/Ca ratios between ENSO and Non-ENSO years (Table 2 and Fig. 6). Statistical student's

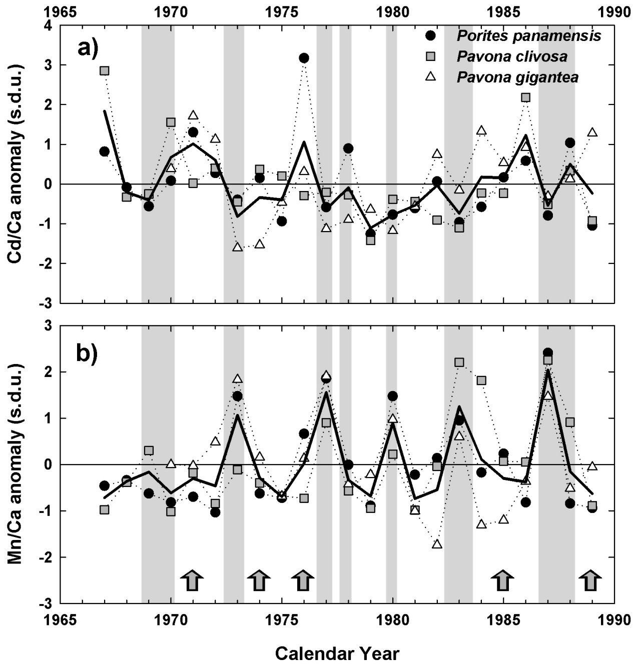

Fig. 5. Temporal variation for the 1967–1990 period of the normalized anomalies in standard deviation units (s.d.u.) of the Cd/Ca ratio in three species of corals studied **(a)** and temporal variation of the normalized anomalies (s.d.u.) of the Mn/Ca ratio **(b)**. The solid line represents the average anomalies for both trace metal ratios. The gray bars define the timing and duration (months) of the El Niño events and the arrows indicate the cold events of La Niña defined by Trentberth (1997).

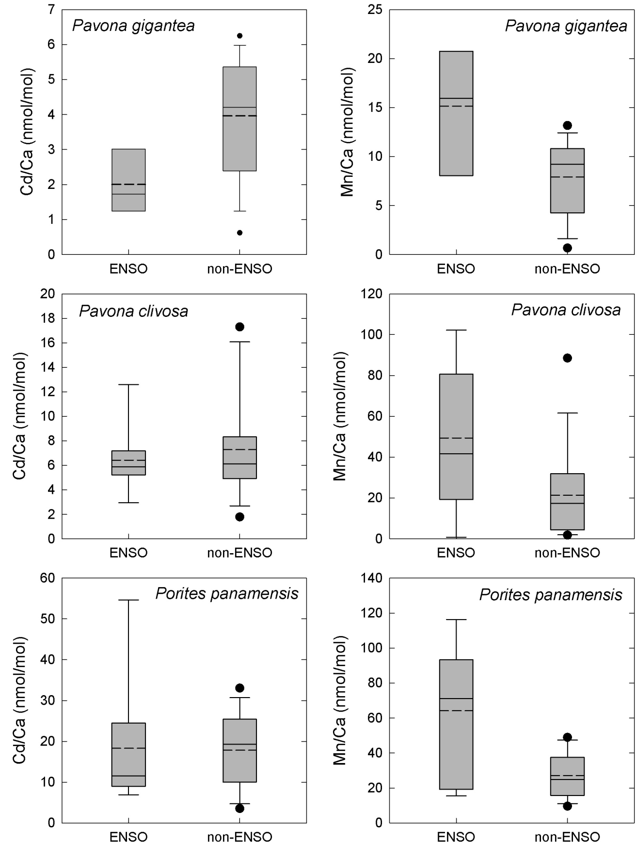

Fig. 6. Box plot separating the Cd/Ca and Mn/Ca ratios between ENSO and Non-ENSO years. The solid line and dashed lines inside the box shows the median and the mean of the distribution, respectively.

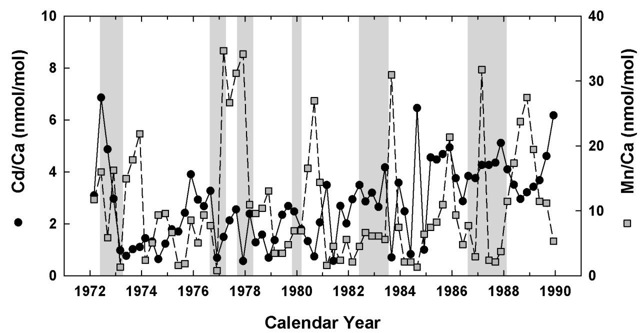

Fig. 7. Seasonal variation of the Cd/Ca ratio in *Pavona gigantea* for the 1972–1990 period **(a)** and seasonal variation of the Mn/Ca ratio in the same coral **(b)**.

t-tests indicate that, with the exception of *Pavona gigantea*, wich showed significantly lower Cd/Ca ratios during ENSO years ($p < 0.05$) compared with Non-ENSO years, the average Cd/Ca ratio of *Pavona clivosa* and *Porites panamensis* did not vary significantly between the two climatic conditions (Table 2 and Fig. 6). In contrast to the Cd/Ca ratio, the Mn/Ca ratio was significantly higher ($p < 0.05$) during ENSO events, compared to the Non-ENSO years, in the three coral species (Table 2 and Fig. 6).

The Cd/Ca and Mn/Ca ratios that were analyzed at seasonal resolution in the *Pavona gigantea* (Fig. 7) showed variability associated with ENSO, that was similar to the annual Cd/Ca and Mn/Ca ratios (Fig. 3). Similarly to the annual Cd/Ca records, the variability of the Cd/Ca sampled at seasonal resolution in *Pavona gigantea* was less responsive to ENSO events (Fig. 7). In contrast, the seasonal and annual Mn/Ca ratios in *Pavona gigantea* showed a clear increase during ENSO events. It is interesting to note from the seasonal-resolution record that the maximum Mn/Ca values occured during the final phase of the El Niño warming events, particularly during the El Niño events of 1972–1973, 1980–1981, 1982–1983 (Fig. 7). This apparent delay in the response of the seasonal Mn/Ca series indicates that the hydrographic conditions that favor an increase in dissolved Mn concentration in the surface waters of the Gulf of California occur shortly after the El Niño reaches its mature phase of maximum warming.

In accordance with Boyle et al. (1976), Boyle (1988), Landing and Bruland (1980), Johnson et al. (1996), and

Nameroff et al. (2002), biogeochemical studies in the Gulf of California suggest that the vertical distribution of dissolved Cd depends mainly on two processes: the seasonal cycle of nutrients and organic matter (Delgadillo-Hinojosa et al., 2001). In contrast to Cd, the behavior of dissolved Mn appears to be controlled by physical processes such as atmospheric input, photo-reduction of manganese oxides in the surface water, which releases Mn from the particles to the dissolved phase, and the dissolution of Mn oxides in the oxygen minimum zone below ∼400 m water depth (Delgadillo-Hinojosa et al., 2006).

The increase of Cd in surface waters is generally controlled by vertical mixing. In the southern Gulf of California this process depends entirely on the seasonal upwelling, whereas in the central Gulf, it is caused by year-round turbulent mixing (Delgadillo-Hinojosa et al., 2001). In contrast, atmospheric input of Mn to the surface waters of the Gulf may be relatively constant throughout the year. The magnitude of the Mn contribution may change due to seasonal changes in wind direction and interannual changes in the direction and intensity of winds associated with the onset of ENSO (Delgadillo-Hinojosa et al., 2006). Changing wind patterns would alter the transport of particulate Mn to the surface waters of the Gulf, decreasing the concentration of dissolved Mn and consequently the incorporation of Mn in coral skeletons. In addition, increased vertical mixing, which would increase the concentration of dissolved Cd in surface waters, may in turn dilute the dissolved Mn at the surface.

These different scenarios may partially explain differences in the oceanic behavior of both elements, as well as the changes in surface availability of Cd and Mn under ENSO vs non-ENSO conditions. The interannual variations in coral Cd/Ca and Mn/Ca ratios show clear evidence that the incorporation of Cd and Mn in coral skeleton is influenced by ENSO conditions, but the intake of each metal is controlled by different process. The decrease in the incorporation of Cd and the marked increase in Mn during the mature phase of El Niño (Fig. 5) suggest strongly reduced vertical mixing in the Gulf of California. SST data for the area near the mouth of the Gulf of California (obtained from COADS, $2^\circ \times 2^\circ$ resolution, centered at 23° N, 109° W) show temperature anomalies of $\sim 2\,^\circ$C (Fig. 2) during El Niño events. Notwithstanding, in situ measurements of temperature during El Niño warming can reach $>4\,^\circ$C in this region (Castro et al., 2000).

Oceanic warming during El Niño events produces a relaxation of upwelling and a stabilization of the thermocline (e.g., Lluch-Cota, 2000; Kahru et al., 2004), which acts as a physical barrier to intake of Cd from deeper waters into the surface layer (Delgadillo-Hinojosa et al., 2001; Dominguez-Rosas, 2008). In turn, this process increases the residence time of particulate-Mn in surface waters, allowing an increase in the photo-reduction of particulate-Mn and the release of the available Mn into the dissolved phase (Delgadillo-Hinojosa et al., 2006; Diaz-Rodriguez, 2008).

When comparing upwelling periods (non-ENSO conditions) with non-upwelling periods (ENSO conditions), the behavior of the coral Cd/Ca ratios in the Gulf of California is similar to that observed in the Gulf of Panama (Matthews et al., 2008). Moreover, *Pavona gigantea* was the most sensitive to changes in the availability of Cd between ENSO and non-ENSO conditions.

In contrast to the Cd/Ca, the Mn/Ca ratio showed a significant increase during ENSO years in the three species of corals. This result indicates that in the Gulf of California the Mn/Ca ratio in coral is a better indicator of oceanographic changes generated by the El Niño phenomenon. Several studies suggest that the Mn/Ca ratios in corals can be used as an “indirect” tracers of ENSO events in the Galapagos Islands (Linn et al., 1990; Shen and Sanford, 1990; Shen et al., 1991; Delaney et al., 1993). The results of this study indicate that coral Mn/Ca ratios also provide a clear ENSO signal in the mouth of the Gulf of California.

4 Conclusions

The Cd/Ca and Mn/Ca ratios in the corals *Pavona clivosa*, *Porites panamensis* and *Pavona gigantea* display clear evidence of El Niño activity at the mouth of the Gulf of California, although the effect is stronger in the Mn/Ca than in the Cd/Ca ratios. The seasonal-resolution Cd/Ca and Mn/Ca ratios in *Pavona gigantea* showed interannual variability related to ENSO that was very similar to that observed in the annually-resolved records. Mn/Ca values were highest at the end of the warming phase of El Niño episodes, indicating that the oceanographic conditions that increase the concentration of dissolved Mn develop immediately after the El Niño warming event reaches its mature phase. Our results show that in the Gulf of California, the Mn/Ca ratio in corals reflects better the oceanographic changes generated by ENSO activity than Cd/Ca ratios.

The average Cd/Ca and Mn/Ca ratios were greatest in *Porites panamensis* and lowest in *Pavona gigantea.* The seasonal records of Cd/Ca and Mn/Ca ratios in *Pavona gigantea* were similar to the annually-resolved records, suggesting that an annual sampling resolution adequately reflects the variability of these elemental ratios through the year. No evidence was found to support recent suggestions that the incorporation of Cd and Mn in the coral skeletons is affected by sample treatment, heterotrophic feeding rates, or by skeletal growth rate. However, the distribution coefficients of Cd (D_{Cd}) and Mn (D_{Mn}) varied among the coral species. The D_{Cd} and D_{Mn} in *Porites panamensis*, and D_{Cd} for *Pavona clivosa*, were within the published ranges. The D_{Cd} in *Pavona clivosa*, and D_{Cd} and D_{Mn} in *Pavona gigantea* were smaller than previous estimates, suggesting that more factors may control D in the coral skeletons than previously thought.

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