Clim. Past Discuss., 6, 63–85, 2010
www.clim-past-discuss.net/6/63/2010/

Climate of the Past Discussions

This discussion paper is/has been under review for the journal Climate of the Past (CP).
Please refer to the corresponding final paper in CP if available.

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

J. D. Carriquiry and J. A. Villaescusa

Instituto de Investigaciones Oceanológicas, Universidad Autónoma de Baja California, Apdo. Postal No. 453. Ensenada, Baja California, México

Received: 25 December 2009 – Accepted: 8 January 2010 – Published: 5 February 2010

Correspondence to: J. D. Carriquiry (jose_carriquiry@msn.com)

Published by Copernicus Publications on behalf of the European Geosciences Union.

Abstract

We analyzed the trace element ratios Cd/Ca and Mn/Ca in three coral colonies (*Pavona gigantea*, *Pavona clivosa* and *Porites panamensis*) 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). The interannual variations in the coral Cd/Ca and Mn/Ca ratios show clear evidence that incorporation of Cd and Mn in the coral skeleton are influenced by ENSO conditions, but the response for each metal is controlled by different process. 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 it was significant ($p<0.05$) only in *P. gigantea*. The decrease in the incorporation of Cd, and the marked increase in Mn during the mature phase of El Niño indicate strongly reduced vertical mixing in the Gulf of California. The oceanic warming during El Niño events produces a relaxation of upwelling and a stabilization of the thermocline which acts 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, which in turn increases the photo-reduction of particulate-Mn and the release of the available Mn into the dissolved phase. These results provide validation for using Mn/Ca and Cd/Ca in biogenic carbonates as tracers of changes in ocean stratification and trade wind weakening and/or collapse in the ETNP during ENSO episodes.

1 Introduction

The El Niño – Southern Oscillation (ENSO) phenomenon is recognized as one of the main sources of global climate variability at inter-annual scale. 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,

CPD

6, 63–85, 2010

Coral Cd/Ca and Mn/Ca records of El Niño

J. D. Carriquiry and J. A. Villaescusa

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 powerful means of reconstructing the environmental conditions with a fidelity that is comparable to instrumental records (Gagan et al., 2000; Correge et al., 2006). 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; etc.). Because the distribution's coefficient (K_D) of the metal/calcium ratio in the coral relative to seawater is known (Shen and Sanford, 1990), the variation of the elemental ratios in the coral skeleton can provide us detailed oceanographic records at different timescales.

Because 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). Because of this, 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). 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 (Linn et al., 1990; Shen et al., 1991; Delaney et al., 1993). Also, but in a different manner, the manifestation of ENSO has been documented in the Mn/Ca ratios of corals from Tarawa atoll. In this region, there is an extensive solubilization of Mn from the lagoonal sediments of the atoll. During the reversal of the trade winds that takes place during ENSO events, the waters enriched with diagenetic-Mn are mobilized into the reef, where corals record these events in their growth bands (Shen et al., 1992a).

While the variation in the Cd/Ca and Mn/Ca ratios along the growth bands of corals seem to record oceanographic conditions that favor its availability in the reef environment, the variability of these trace element ratios among different species of corals growing in the same locality has rarely been assessed (Delaney et al., 1993; Reuer et al., 2003; Matthews et al., 2008). In this study we use the trace element 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 the oceanographic changes occurred during ENSO events.

2 Materials and methods

Characterization of the study area. The Cabo Pulmo reef is located on the east coast of Southern Baja California (23°25′ N and 109°25′ W) (Fig. 1), inside Los Frailes Bay, at a 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 other 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 bottom by differential erosion. Young coral reef development takes place on top of these conglomeratic bars, with a reef framework not larger than 3 m thick, at some points (the average thickness is ∼1 m). Although there is little hydrologic information for the area, during the 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 goes below the lower limit 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 the 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 the 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) water of the California Current (CCW), the saline water (>34.9) 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) and higher temperature >25 °C (e.g., Castro et al., 2006) into the mouth of the Gulf of California. The inter-annual 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 a 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, adversely effecting coastal fisheries in the northwest region of Mexico, where the major fisheries in the Mexican Pacific take place (Lluch-Cota et al., 1999).

2.1 Sample collection

In May 1990 we collected alive coral colonies of *Pavona gigantea*, *Pavona clivosa* and *Porites panamensis clivosa* by scuba diving at Cabo Pulmo reef. In the laboratory, corals were submerged in a 50% (v/v) solution of sodium hypochlorite to remove the coral tissue. The corals were cut using a circular saw, generating slabs of ~7 mm thick. The slabs were later X-rayed on a Picker X-ray G850S. Using the positives of the X-ray images, we established the chronology based on the annual growth bands (growth rates varied between 5 to 10 mm/year for all species). The sampling transect followed the axis of maximum growth.

2.2 Sample treatment and analyses

The analyses of the Cd/Ca and Mg/Ca ratios in the coral skeleton were 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 co-precipitation with an organic complex (APDC) and Co aimed to remove excess-Ca in the solution and to concentrate the metals in the solution. 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 the passage of co-precipitation and diluted in 50 mL of 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 standard fortified with

CPD
6, 63–85, 2010

Cd and Mn was ±91%; the calculated precision of the method was <10%.

2.3 Oceanographic characteristics

The average SST range in the Cabo Pulmo region is ∼8 °C, varying from 21.0 in March to 28.5 °C in September. At inter-annual timescale, 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 and 23′ N; COADS database, Slutz et al., 1985) with the SST anomalies observed in the Niño 3.4 region (Trenberth, 1997). There, it can be seen that with the exception of moderate El Niño event of 1969 and the weak El Niño of 1980, the rest of El Niño events that occurred 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 are synchronous, with the exception of the El Niño event of 1982–1983, where the thermal response in the MGC is 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) displays significant variation among the three coral species studied, as well as within species (Table 1 and Fig. 3a). Comparatively, the mean Cd/Ca ratio (±1 sd) increases from the coral *P. gigantea* (3.28±1.73) to *P. clivosa* (6.94±3.63) to *P. panamensis* (18.0±11.5) (Table 1). Furthermore, the average Cd/Ca ratio (2.76±1.51) in the coral *P. gigantea* sampled at seasonal resolution was very 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.

CPD
6, 63–85, 2010

Similarly to Cd/Ca, in the Mn/Ca ratio (nmol/mol) shows marked differences between species, but variability in each species (i.e., the relative standard deviation) was higher than what was observed in the Cd/Ca ratio (Table 1 and Fig. 3b). The Mn/Ca ratio in the different species increases in the same order as observed for the Cd/Ca ratio: the Mn/Ca ratio was lowest (10.45±5.63) in the coral *P. gigantea*, followed by *P. clivosa* (32.3±31.0), being *P. panamensis* the coral with the highest Mn/Ca ratio (41.6±31). Also, similar to Cd/Ca, the average Mn/Ca ratio sampled at seasonal resolution (10.61±8.9) is practically equal to the Mn/Ca ratio measured at annual resolution (Table 1).

The observed differences in the average trace metal ratios among different species of coral growing in the same locality have also been observed for other proxy tracers, such as $\delta^{18}O$, $\delta^{13}C$ and Sr/Ca ratios (de Villiers et al., 1994; Wellington et al., 1996; Grottoli and Wellington; 1999). However, the few available published records of coral Cd/Ca and Mn/Ca ratios make difficult to reach a general comprehensive conclusion regarding the differences between species observed in this study. For instance, it has been recently shown that the Cd/Ca ratios in the Caribbean coral *Siderastrea siderea* is 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, concluding that these differences could be explained by differences of localities. More recently, Matthews et al. (2008) found that the Cd/Ca ratio decreases in the order *Pavona gigantea*>*P. clavus*>*Porites lobata* from the same locality, concluding that there are three different conditions that could explain the discrepancy in Cd/Ca ratios between species: (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 sample treatment effects could explain the species' differences.

Our results show that in the Gulf of California, the corals of the genus *Porites* concentrate more Cd and Mn, compared with the species of the genus *Pavona*; this is exactly the reverse of the corals from the Gulf of Panama (Mattehws et al., 2008). It is unlikely that species differences observed in this work is a consequence of sample treatment, although it has been proposed that corals can bio-concentrate metals from their diet (e.g., Fallon et al., 2002). The contrast in heterotrophic feeding among the studied species, if exists, should be able to explain the 4.5 time-fold increase in the Cd/Ca ratio and 4 time-fold for the Mn/Ca ratio, between the lowest and the highest trace metal ratios (Table 1). Our results do not show a relationship between growth rate and the Cd/Ca and Mn/Ca ratios within each coral. However, the average growth rate varies inversely with the trace metal ratios between different coral species, i.e., the lower growth rate, the greater are the average Cd/Ca and Mn/Ca ratios, and vice versa (Table 1). The effect of coral growth rate has been assessed through the Sr/Ca ratio, with contrasting results. For instance, de Villiers et al. (1994, 1995) found that high values of the Sr/Ca ratio in the coral skeleton of *P. clavus* are associated with lower skeletal growth rates. In contrast, Allison and Finch (2004) found that the growth rate of *Porites lobata* does not affect the rate of incorporation of Sr in the coral skeleton. Interestingly, both studies were conducted using the same colony but selecting two sampling transects with different growth rate; the contrasting outcomes illustrate the difference in response between species.

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 show a clear inter-annual variability. The behavior of Cd/Ca and Mn/Ca during the 1967–1989 period for the three coral species analyzed is shown in Fig. 3. The trace metal ratios indicate a clear influence of ENSO events in the area, but the effect was more evident in the Mn/Ca than in the Cd/Ca of corals (Fig. 3a and b). This can be better observed by separating the Cd/Ca and Mn/Ca ratios between ENSO and Non-ENSO years (Table 2 and Fig. 4). Statistical *t*-student tests indicate that, with the exception of the coral *P. gigantea* that showed significantly lower Cd/Ca ratios during ENSO years ($p<0.05$) compared to Non-ENSO years, the average Cd/Ca ratio of *P. clivosa* and *P. panamensis* did not vary significantly between the two climatic conditions (Table 2). In contrast to the Cd/Ca, the coral Mn/Ca ratio is significantly higher ($p<0.05$) during ENSO events, compared to the years Non-ENSO, in the three coral species analyzed (Table 2 and Fig. 4).

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 show that the vertical distribution of dissolved Cd depends mainly on two processes: the seasonal cycle of nutrients and organic matter (Delgadillo 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 that takes place in the surface water releasing the Mn from the particles to the dissolved phase, and the dissolution of Mn oxides in the oxygen minimum zone below ~400 m (Delgadillo et al., 2006).

The increase of Cd in surface waters is controlled by vertical mixing. In the southern Gulf this process depends entirely on the seasonal upwelling while in the central Gulf it is caused by year-round turbulent mixing (Delgadillo et al., 2001). In contrast, the atmospheric input of Mn to surface waters of the Gulf of California may be relatively constant throughout the year. Nevertheless, the magnitude of the Mn contributions could 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 et al., 2006). Changing wind patterns can cause a change in the transport of particulate Mn to the surface waters of the Gulf of California, so that, a flow reduction decreases the concentration of dissolved Mn and consequently reduces the availability of Mn to be incorporated in the coral skeletons. In addition, increased vertical mixing, which increases the concentration of dissolved Cd in surface waters may in turn dilute the dissolved Mn and reduce its surface concentration.

These different scenarios partially explain the difference in the oceanic behavior of both elements, as well as the changes in the surficial availability of Cd and Mn under the

CPD

6, 63–85, 2010

two contrasting climatic conditions (ENSO vs. non-ENSO). The interannual variations in the coral Cd/Ca and Mn/Ca ratios show clear evidence that incorporation of Cd and Mn in the coral skeleton are influenced by ENSO conditions, but the response for 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. 4), suggest strongly reduced vertical mixing in the Gulf of California. The 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 that limits the intake of Cd from deeper waters into the surface layer (Delgadillo et al., 2001; Dominguez-Rosas, 2008). In turn, this process can increase the residence time of particulate-Mn in surface waters, which increases the photo-reduction of particulate-Mn and the release of the available Mn into the dissolved phase (Delgadillo 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, the difference in the Cd/Ca ratio between ENSO and non-ENSO years of the three species of corals studied, *P. gigantea* is the one that best responds to changes in the availability of Cd in two contrasting climate conditions (ENSO vs. non-ENSO).

In the other hand, in contrast to the Cd/Ca, the Mn/Ca ratio showed a significant increase during ENSO years in the three species of corals studies. This shows that in the Gulf of California the Mn/Ca coral is much better indicator of oceanographic changes generated by the conditions of the ENSO phenomenon. Several studies have suggested that the Mn/Ca ratios in corals can be used as an "indirect" tracer 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, however, show that the coral Mn/Ca ratios provide a clear and direct manifestation of the environmental conditions produced by El Niño in the mouth of the Gulf of California.

The publication of this article was sponsored by PAGES.

References

Allison, N. and Finch, A. A.: High-resolution Sr/Ca records in modern porites lobata corals: effects of skeletal extension rate and architecture, Geochem. Geophys. Geosyst., 5, Q05001, doi:10.1029/2004GC000696, 2004.

Baumgartner, T. R. and Christensen Jr., N.: Coupling of the Gulf of California to large-scale interannual climatic variability, J. Mar. Res., 43, 825–848, 1985.

Boyle, E. A.: Cadmium: chemical tracer of deepwater paleoceanography, Paleoceanography, 3, 471–489, 1988.

Boyle, E. A., Scatler, F., and Edmond, J. M.: On the marine geochemistry of cadmium, Nature, 263, 42–44, 1976.

Castro, R., Durazo, R., Mascarhenas, A., Collins, C. A., and Transviña, A.: Thermohaline variability and geostrophic circulation in the southern portion of the Gulf of California, Deep-Sea Res. Pt. I, 53, 188–200, 2006.

Correge, T.: Sea surface temperature and salinity reconstruction from coral geochemical tracers, Paleogeogr. Paleoclimatol. Paleoecol., 232, 408–428, 2006

Delaney, M. L., Linn, L. J., and Druffel, E. R. M.: Seasonal cycles of manganese and cadmium in corals from the Galápagos Islands, Geochim. Cosmochim. Ac., 57, 347–354, 1993.

Delgadillo-Hinojosa, F., Macias-Zamora, J. V., Segovia-Zavala, J. A., and Torres-Valdes, S.: X cadmium enrichment in the Gulf of California, Mar. Chem., 75, 109–122, 2001.

Delgadillo-Hinojosa, F., Segovia-Zavala, J. A., Huerta-Díaz, M. A., and Atilano-Silva, H.: Influence of geochemical and physical processes on the vertical distribution of manganese in the Gulf of California, Deep-Sea Res. Pt. I, 53, 1301–1319, 2006.

De Villiers, S., Shen, G. T., and Nelson, B. K.: The Sr/Ca-temperature relationship in coralline

aragonite: influence of variability in (Sr/Ca) seawater and skeletal growth parameters, Geochim. Cosmochim. Ac., 58, 197–208, 1994.
De Villiers, S., Nelson, B. K., and Chivas, A. R.: Biological controls on coral Sr/Ca and δ^{18}O reconstructions of sea surface temperature, Science, 269, 1247–1249, 1995.
Diaz-Rodriguez, G.: Estudio de la distribución vertical de manganeso y cobalto en la región de las grandes islas del Golfo de California, M.Sc. Thesis in Coastal Oceanography, FCM-IIO, UABC. 91 pp., 2008.
Dominguez-Rosas, A.: Distribución vertical y temporal de níquel y cadmio en el Golfo de California, Tesis de Maestría en Oceanografía Costera, FCM-IIO, UABC, 97 pp., 2008.
Fallon, S. J., White, J. C., and McCulloch, M. T.: Porites corals as a recorder of mining and environment impacts: Misima Island, Papua New Guinea, Geochim. Cosmochim. Ac., 66, 45–62, 2002.
Gagan, M. K., Ayliffe, L. K., Beck, J. W., Cole, J. E., Druffel, E. R. M., Dunbar, R. B., and Schrag, D. P.: New view of tropical paleoclimate from corals, Quaternary Sci. Rev., 19, 45–64, 2000.
Grottoli, A. G. and Wellington, G. M.: Effect of light and zooplankton on skeletal δ^{13}C values in the eastern Pacific corals Pavona clavus and Pavona gigantean, Coral Reefs, 18, 29–41, 1999.
Johnson, K. S., Coale, K. H., Berelson, W. M., and Gordon, R. M.: On the formation of the manganese maximum in the oxygen minimum, Geochim. Cosmochim. Ac., 60, 1291–1299, 1996.
Kahru, M., Marinone, S. G., Lluch-Cota, S. E., Parés-Sierra, A., and Mitchell, B. G.: Ocean-color variability in the Gulf of California: scales from days to ENSO, Deep–Sea Res. Pt. II, 51, 139–146, 2004.
Landing, W. M. and Bruland, K. W.: Manganese in the North Pacific, Earth Planet Sc. Lett., 49, 45–56, 1980.
Lavin, M. F. and Marinone, S. G.: An overview of the physical oceanography of the Gulf of California, in: Nonlinear Processes in Geophysical Fluid Dynamics, edited by: Velasco-Fuentes, O. U., Kluwer Academic, The Netherlands, 173–204, 2003.
Linn, L. J., Delaney, M. L., and Druffel, E. R. M.: Trace metals in contemporary and seventeenth-century Galápagos coral: records of seasonal and annual variability, Geochim. Cosmochim. Ac., 54, 387–394, 1990.
Lluch-Cota, S. E.: Coastal upwelling in the eastern Gulf of California, Oceanol. Acta, 23, 731–

740, 2000.
Lluch-Cota, D., Lluch-Belda, D., Lluch-Cota, S., López-Martinez, J., Névares-Martínez, M., Ponce-Díaz, G., Salinas-Zavala, G., Vega-Velázquez, A., Lara-Lara, J. R., Hammann, G., and Morales, J.: Las pesquerías y El Niño, in: Los Impactos del Niño en México, edited by: In: Magaña, V. O., SG-SEP, México, 137–178, 1999.
Matthews, K. A., Grottoli, A. G., McDonough, W. F., and Palardy, J. E.: Upwelling, species, and depth effects on coral skeletal cadmium-to-calcium ratios (Cd/Ca), Geochim. Cosmochim. Ac., 72, 4537–4550, 2008.
Nameroff, T. J., Balistrieri, L. S., and Murray J. W.: Suboxic trace metal geochemistry in the eastern tropical North Pacific, Geochim. Cosmochim. Ac., 66, 1139–1158, 2002.
Reuer, M. K., Boyle, E. A., and Cole, J. E.: A mid-twentieth century reduction inter-tropical upwelling inferred from coralline trace element proxies, Earth Planet. Sc. Lett., 210, 437–452, 2003.
Reyes-Bonilla, H.: Biogeografía y ecología de los corales hermatípicos (Anthozoa: Scleractinia) del Pacífico de México, in: Biodiversidad marina y costera de México, edited by: Salazar-Vallejo, S. I., González, N. E., CONABIO-CIQRO, México D. F., 207–222, 1993a.
Reyes-Bonilla, H.: Coral reef bleaching at Cabo Pulmo Reef, Gulf of California, México, Bull. Mar. Sci. 52, 832–837, 1993b.
Shen, G. T., Boyle, E. A., and Lea, D. W.: Cadmium in corals as trace of historical upwelling and industrial fallout, Nature, 328, 794–795, 1987.
Shen, G. T. and Boyle, E. A.: Determination of lead, cadmium and other trace metals in annually banded corals, Chem. Geol., 67, 47–62, 1988.
Shen, G. T., Campbell, T. M., Dunbar, R. B., Wellington, G. M., Colgan, M. W., and Glynn, P. W.: Paleochemistry of manganese in corals from Galápagos Islands, Coral Reefs, 10, 91–100, 1991.
Shen, G. T., Cole, J. E., Lea, D. W., Linn, L. J., McConnaughey, T. A., and Fairbanks, R. G.: Surface ocean variability at Galápagos from 1936–1982: calibration of geochemical tracers in corals, Paleoceanography, 7, 563–588, 1992a
Shen, G. T., Linn, L. J., Campbell, T. M., Cole, J. E., and Fairbanks, R. G.: A chemical indicator of trade wind reversal in corals from the western tropical Pacific, J. Geophys. Res., 97, 12689–12697, 1992b.
Shen, G. T. and Sanford, C. L.: Trace element indicator of climate variability in reef-building corals, in: Global Ecological Consecuences of the 1982–83 El Niño-Southern Oscillation,

edited by: Glynn, P. W., Elsevier, New York, USA, 255–283, 1990.
Slutz, R. J., Lubker, S. J., Hiscox, J. D., Woodruff, S. D., Jenne, R. L., Joseph, D. H., Steuer, P. M., and Elms, J. D.: Comprehensive Ocean-Atmosphere Data Set: Release 1, number 268 p., 1985.
Trenberth, K. E.: The definition of El Niño, B. Am. Meteorol. Soc., 78, 2771–2777, 1997.
Wellington, G. M., Dunbar, R. B., and Merlen, G.: Calibration of stable oxygen isotope signature in Galpagos corals, Paleoceanography, 11, 467–480, 1996

Table 1. Average (±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

CPD
6, 63–85, 2010

Table 2. Comparison between average (±1 S.D.) Cd/Ca and Mn/Ca (nmol/mol) for El Niño and non-El Niño years in corals collected from Cabo Pulmo reef. The probability values of the t-Student 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 with an asterisk (*).

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*

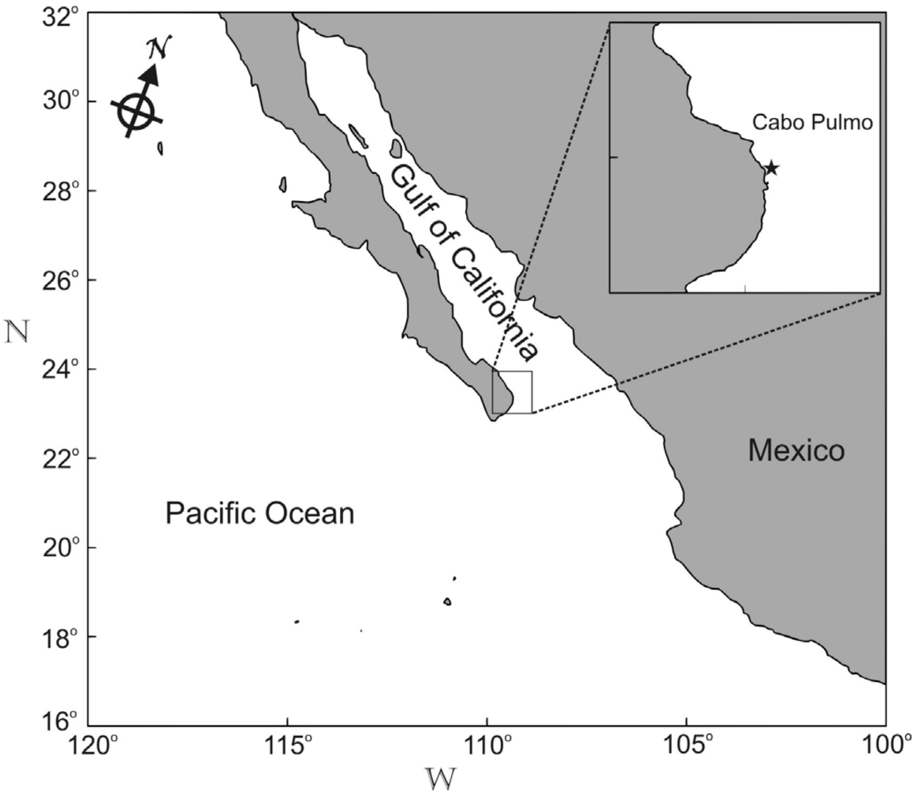

Fig. 1. Study Area. The location of Cabo Pulmo reef, at the mouth of the Gulf of California, Mexico.

CPD
6, 63–85, 2010

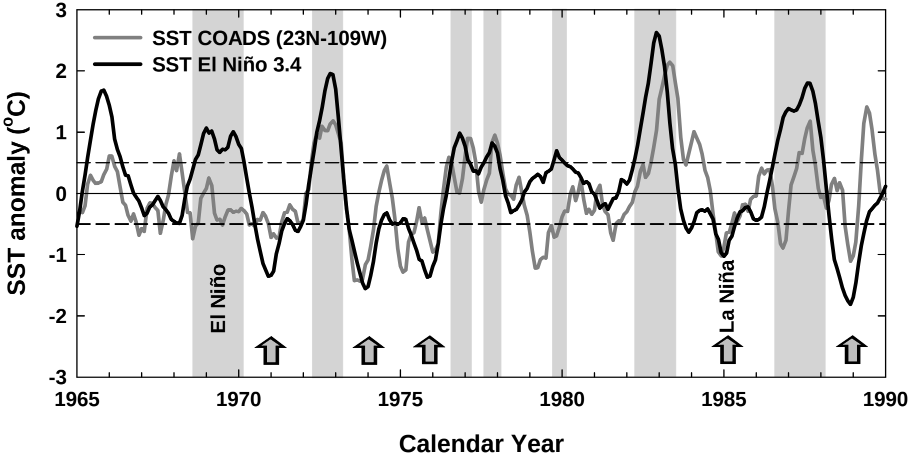

Fig. 2. Comparison of temperature anomalies in the Niño 3.4 region, filtered by a 5-month moving average that define the variability of El Niño (Trenbert, 1997) versus the temperature anomalies (same filtering) in the mouth of the Gulf of California obtained from the COADS database (resolution of 2-nd x 2o, Schultz et al., 1985).

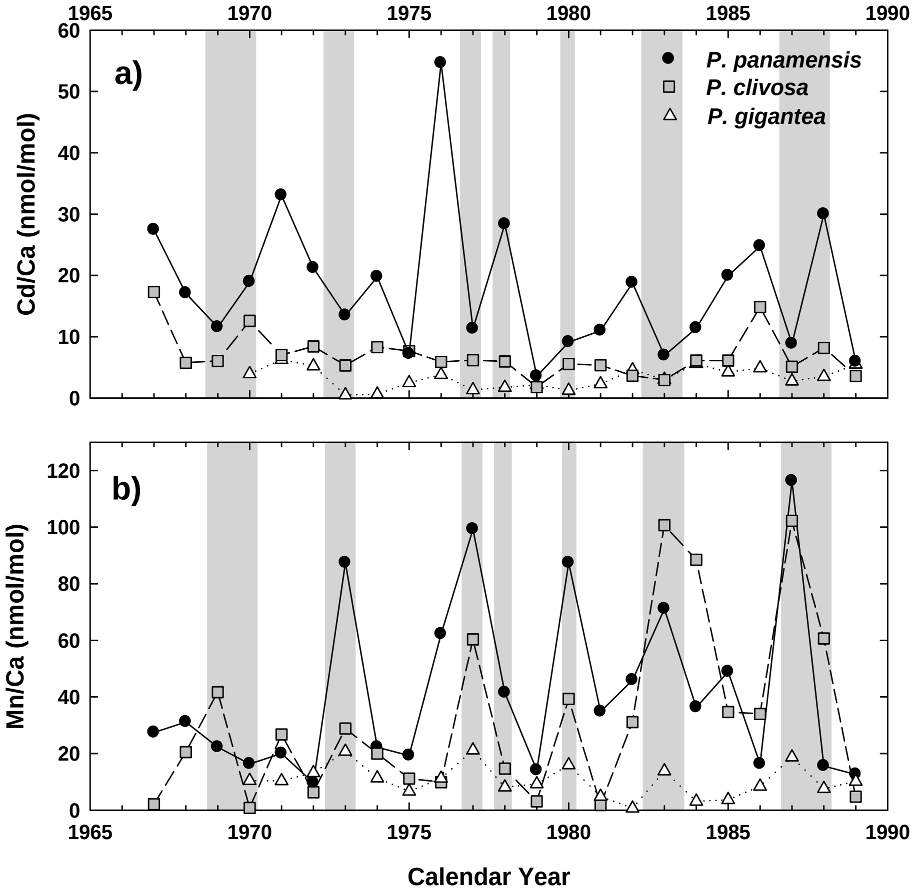

Fig. 3. **(a)** Temporal variation (1967 to 1989) of the annual Cd/Ca ratios of the three coral species used in this study, **(b)** temporal variation of the Mn/Ca ratio in the skeleton of the same coral species.

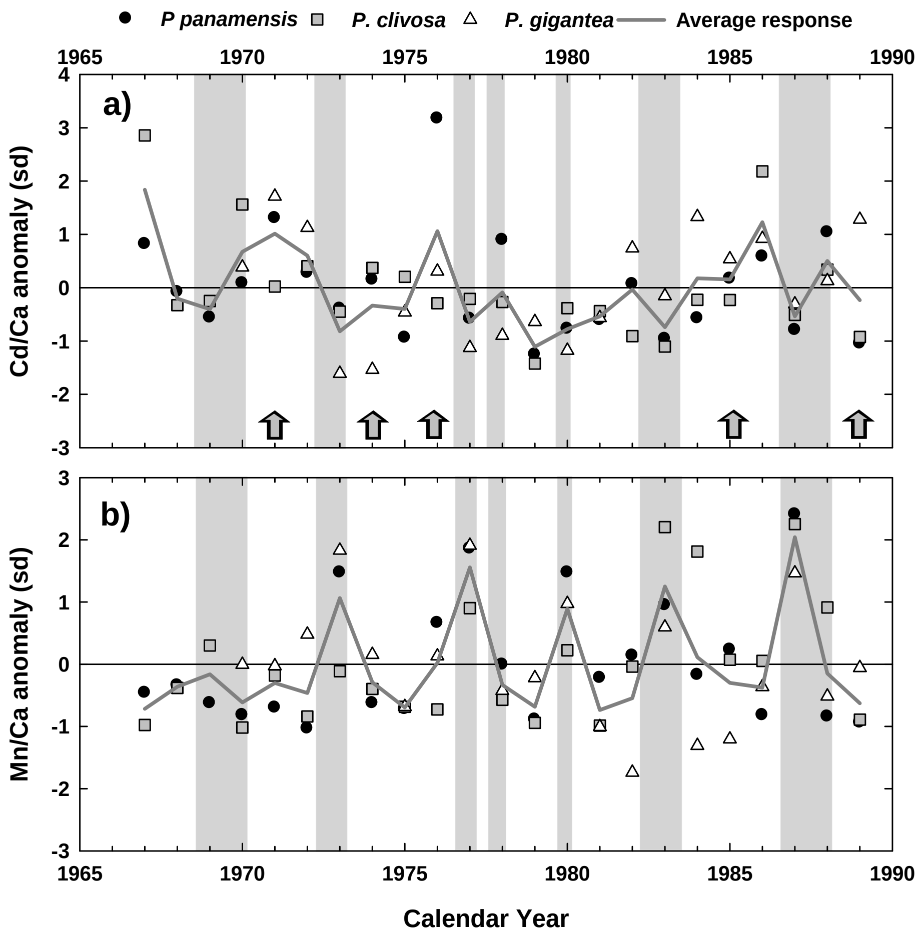

Fig. 4. **(a)** Temporal variation of the normalized anomalies (S.D.) of the Cd/Ca ratio in three species of corals studied, **(b)** temporal variation of the normalized anomalies (S.D.) of the Mn/Ca ratio. The solid line shows the average anomalies for both trace metal ratios.

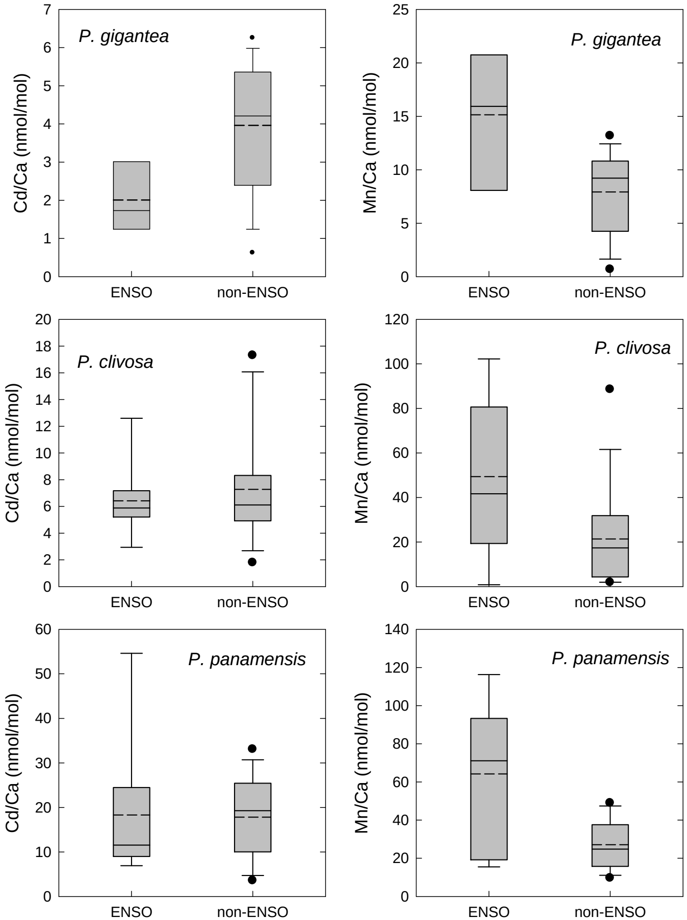

Fig. 5. Box plot separating the Cd/Ca and Mn/Ca ratios between ENSO and Non-ENSO years. The solid line and dashed lines inside the box shows the median and the mean of the distribution, respectively.

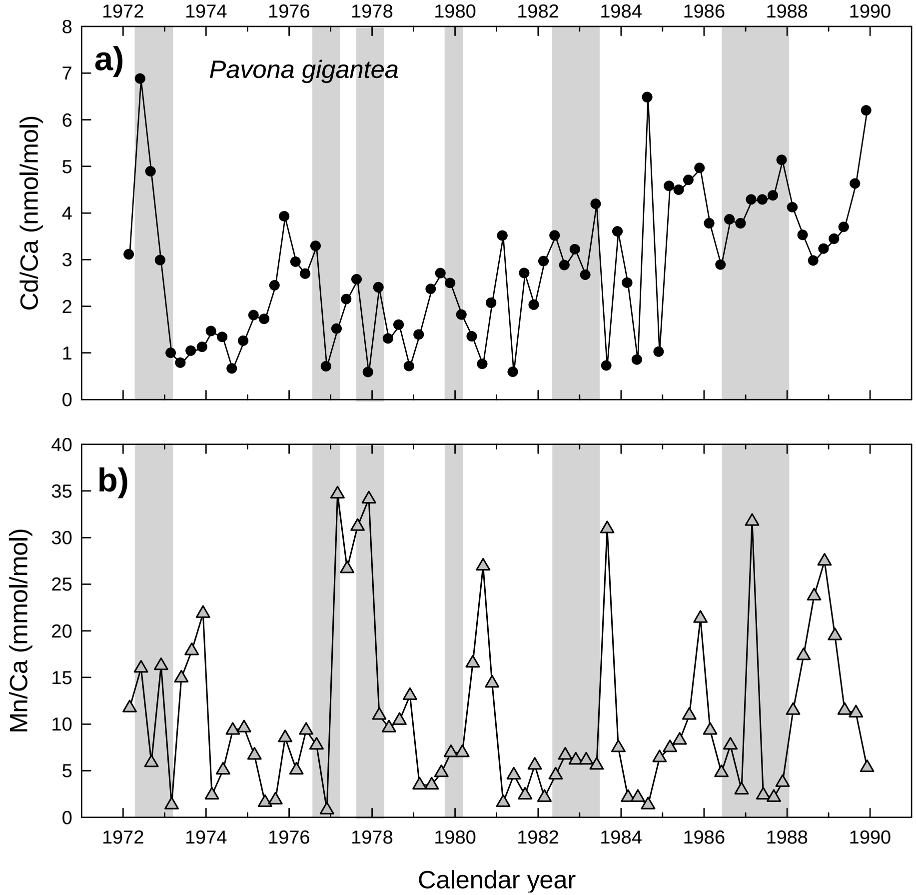

Fig. 6. **(a)** Seasonal variation of the Cd/Ca ratio in the coral *P. gigantea* for the 1972–1990 period, **(b)** seasonal variation of the Mn/Ca ratio in the same coral.

CPD

6, 63–85, 2010

Coral Cd/Ca and Mn/Ca records of El Niño

J. D. Carriquiry and J. A. Villaescusa