

## ***Interactive comment on “Coral Cd/Ca and Mn/Ca records of El Niño variability in the Gulf of California” by J. D. Carriquiry and J. A. Villaescusa***

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We would like to thank very much referee-1's positive and constructive comments and suggestions that served to enhance our paper. We made all the changes requested.

SPECIFIC RESPONSES TO THE REFEREE COMMENTS AND/OR SUGGESTIONS:

1. What is the original source of Mn to this site? I don't believe this is ever really stated in the manuscript. R: The introduction has been modified to include an explanation for the source of Mn in the Gulf of California:

New text: In a different way to cadmium, Mn/Ca ratios have also been used to docu-

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ment 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, 1987; Nameroff et al., 2002). Alike the Pacific Ocean, the vertical distribution of dissolved manganese in the southern Gulf of California (GC) shows a high concentration at the ocean's surface (from 2 to 7 nM, in the upper 50m), 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 GC 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 GC is considered insignificant because most of the rivers that reach the GC have been damned, significantly reducing the flow of fresh water into the Gulf (e.g. Carriquiry et al., 2001; Delgadillo-Hinojosa et al., 2006).

2. Given the relatively weak Cd/Ca signal, particularly in 2 of the 3 coral species, have the authors thought about analyzing Ba since it shows nutrient-like water depth profiles? Is there any water column data that can be used to infer strength of upwelling at the study site? R: There are no measurements of Ba/Ca in corals from the region, but it would be an interesting approach for the future using longer coral records. Nonetheless, the vertical profiles in the GC clearly show that dissolved Cd follows very closely the distribution of nutrients, particularly of phosphates (Delgadillo-Hinojosa et al., 2001). This indicates that Cd is little affected by external sources, as has been shown to affect Ba in other coastal areas of the world (e.g., Shen, 1993). This shows that, in part, Cd should be an effective tracer of changes in the vertical mixing of the water column in the GC. There are no in situ hydrographic data available in the GC that may indicate changes in the upwelling intensity along the east coast of the GC, at the mouth region. The available upwelling indices were derived from wind stress modeling for the East coast of the Central Gulf of California (Lluch-Cota, 2000); the central region of the GC has been much better oceanographically studied than the southern

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GC. Studies here have systematically shown that this region is characterized by very intense vertical mixing during almost all year round (e.g. Lavin and Marinone, 2003), oppositely with what happens at the mouth of the GC where the water column is generally stable. The available hydrographic information of ENSO activity in the southern part of the GC has been derived from large-scale analyses of satellite imagery showing a marked warming of the surface waters during the warm phase of ENSO, which reduces the vertical mixing, for which it is interpreted that productivity decreases during these events, coherently with what happens in most of the Eastern Tropical Pacific (e.g. Kahru et al., 2004, and references therein).

3. Is there any coral  $\delta^{18}\text{O}$  data that would help strengthen the proxy record of ENSO variability given that in the area of study during El Niño episodes, there are SST anomalies of  $4\text{°C}$ ? R: The SST data derived from the COADS database (see Fig.2) show that the SST anomalies during El Niño events are  $\sim 2\text{°C}$  for this region. There are coral- $\delta^{18}\text{O}$  data published for the mouth of the GC (Bernal and Carriquiry, 2001, *Ciencias Marinas*, 27,155-174) and for Sr/Ca (Villaescusa and Carriquiry, 2004, *Ciencias Marinas*, 30,603-618) that show that this area is very sensitive to ENSO activity. These studies have shown that the thermal anomalies of ENSO inside the GC are not very large. The mouth of the GC presents complex circulation patterns where very distinctive water masses (surface Equatorial water, GC water, California Current water) interact at seasonal and inter-annual scale, as we see in this study. Although longer-term climatic records, such as coral proxy records and oceanographic databases show similar temperature anomalies during ENSO events, hydrographic studies published for the mouth of the GC, in area nearby Pulmo reef, show that these anomalies could even be larger ( $>4\text{°C}$ ) (e.g. Castro et al., 2000, 2006). These, however, are probably transient events that are not persistent through time.

4. I feel there should be a greater discussion of why the different coral species yield different trace metal patterns. Are the distribution coefficients different? These values should be clearly stated on page 65. R: We included a new paragraph and a new table

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(Table 3) in section 3.1 of Results and Discussions. In this new part we show that the calculated distribution coefficients (DCd,Mn) are different for the three species studied.

New text: Independently of the factors controlling the differences between species in the Cd/Ca and Mn/Ca ratios, the results obtained in this study indicate that there are differences in the distribution coefficients (D) between the species (Shen, 1993). Using the average dissolved Cd concentration (0.22 nM) and dissolved Mn (3.34 nM) in the upper ocean layer 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 the coral *Porites panamensis*, and the DCd 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, either in the coral skeleton and seawater, very few studies have attempted to calculate D of Cd and Mn in the different coral species (Shen and Sanford, 1990; Shen, 1993). Consequently, it is still unknown the range of D in several coral species, like *Pavona gigantea*. The results obtained in this study suggest that the factors that ultimately determine the concentration of Mn and Cd in the coral skeletons remain somewhat elusive.

4b. It is not clear how the authors conclude that differences in heterotrophic feeding could help explain the 4 to 4.5 time fold for the Mn/Ca and Cd/Ca ratios. There needs to be a reference regarding this interpretation. R: There was probably a misunderstanding: we did not conclude that heterotrophic feeding may explain the 4 - 4.5 times difference in the Mn/Ca and Cd/Ca between species, however, we modified the text to clarify this point: New text: Moreover, because corals can potentially bio-concentrate metals from their diets (Fallon et al., 2002), the difference in the feeding preferences between the species could be an additional factor explaining the differences in metal

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uptake. With regard the species involved in our study, it has been found that heterotrophic feeding in *Porites* is similar or slightly greater than in *Pavona* (e.g. Matthews et al., 2008). Thus, 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), which we find difficult to reconcile.

5. The text on sample collection should be expanded to include information on the following: depth, distance to shore, proximity to the other coral sites, any other site specific information. R: The subsection of 'Sample Collection' was modified and expanded the following new information was included: NEW TEXT: Live coral colonies of *Pavona gigantea* (227 mm high), *Pavona clivosa* (225 mm high) and *Porites panamensis* (154 mm high) were collected at depths between 5 and 10 m from Pulmo reef, southern Baja California, Mexico, in May 1990 (Fig. 1). In the laboratory, the corals were submerged in 50 % (v/v) sodium hypochlorite in order 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 studied. 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 made in each x-rayed coral colony. The observed growth rates were:  $11.3 \pm 2.3$  mm/year (1970 – 1989) for *Pavona gigantea*;  $9.76 \pm 2.5$  mm/year (1967 – 1989) for *Pavona clivosa*, and  $6.67 \pm 1.1$  mm/year (1967 - 1989) for *Porites panamensis*. The annual growth bands traced on the acetate sheets were transferred into 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  $\mu\text{m}$ .

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6. What is the sample resolution for the geochemical measurements? This is never stated on page 68. Were the corals sub-sampled via drilling? Cutting? Since the different coral species exhibit different growth rates, the sample resolution should inherently be different if not then the sampling could bias the geochemistry (see work by Goodkin et al.). What are the statistics behind the authors' conclusion that the growth rate and geochemistry do not show a clear relationship?. The sample resolution and the assigned temporal resolution should be stated in Tables 1 and 2. R: The resolution and sampling details of the coral skeleton were provided in the subsection 2. (Please see the answer to the previous point 5)

7. Why are some El Niño years recorded in the coral trace element data while during other years the signal is weaker? R: This is a consequence that El Niño warming events vary in intensity and duration. For instance, according to the ENSO classification proposed by Ortlieb (2000, in: Diaz, H.H., and Markraf, V (eds). *El Niño and the Southern Oscillation. Multiscale Variability and Global and Regional Impacts.*, Cambridge, p 207-295), the ENSO events occurred during the proxy record studied here (1967 – 1989) are classified as follows: El Niño 1969 -70: Moderate (M-); El Niño 1972-73: Strong (S); El Niño 1976-77 and 77-78: moderate (M) (see also Trenberth, 1997), El Niño 1980-81 (Not defined as El Niño by Ortlieb, but defined as Weak El Niño by Trenberth), El Niño 1982-83: Very Strong (VS); El Niño 1986-89: Moderate (M). This may explain why some El Niño's show strong anomalies while others are weaker by several degrees of intensity

8. How long is the coral core? Is there a hope of extending the trace metal record farther back in time, especially beyond instrumental/historical records? R: The length of the records were specified in the subsection 2.1 Sample Collection (see answer to point 5)

9. What are the grey bars and the arrows in Figures 2, 3, 4, and 6? There is no information in the figure captions. R: The gray bars define the timing and duration (months) of the El Niño events defined by Trenberth (1997). This information is now

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included at the legend of Fig.2.

10. What are the error bars for the Cd/Ca and Mn/Ca measurements? This should be included in the relevant figures as well as in the text. R: Figure 3 was modified, including now the error bars ( $\pm$ sd) calculated from the replicates (n=3) for each annual average

11. I highly suggest the authors plot Cd/Ca and Mn/Ca in Figure 6 on the same plot so that the reader can clearly see when the trace metals behave inversely. R: Figure 6 (which is Figure 7 now) was modified showing now the seasonal measurements of the Cd/Ca and Mn/Ca in the same plot.

12. Suggestion lists the length of the record (i.e., 1967-1989?) in the abstract. R: This information is now included in the abstract.

Typos: 1.Line 16, page 73 comma after 2008) should be a period. R: Corrected 2. Species names should be italicized in reference list R: Corrected

3. Correct reference abbreviation for *Geochimica et Cosmochimica Acta* is *Geochim. Cosmochim. Acta* R: Corrected

4. Trenberth is spelled incorrectly in Figure 2 caption. R: Corrected

5. Capitalize Cadmium in Delgadillo-Hinojosa et al., 2001 ref. R: Corrected

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Interactive comment on *Clim. Past Discuss.*, 6, 63, 2010.