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PALEOCHEMISTRY OF REEF CORALS: HISTORICAL VARIABILITY OF THE TROPICAL PACIFIC

Glen T. SHEN, Laura J. LINN and Mary T. PRICE
School of Oceanography, WB-10, University of Washington
Seattle, WA 98195 USA
Julia E. COLE and Richard G. FAIRBANKS
Lamont-Doherty Geological Observatory of Columbia University
Palisades, NY 10964
David W. LEA
Department of Geological Sciences, University of California
Santa Barbara, CA 93106
Ted A. McCONNAUGHEY
Water Resources Division, U.S. Geological Survey,
Denver, CO 80225

Abstract

A variety of chemical tracers have been developed in corals on either side of the equatorial Pacific Ocean for the purposes of establishing the natural variability of the surface ocean on annual to century timescales. Over a recent 50-year historical period, time series measurements of $\delta^{18}O$, $\delta^{13}C$, Ba/Ca, and Cd/Ca at the Galapagos Islands exhibit highly significant correlations with sea surface temperature, one of the few instrumental records readily available for calibration over the last several decades. $\delta^{18}O$ is the most direct proxy recorder of temperature; $\delta^{13}C$ responds primarily to changes in insolation while the nutrient analogues Cd and Ba reflect changes in the extent of vertical mixing (i.e. upwelling) near Galapagos. The Mn/Ca tracer is complicated by lateral water mass movements which occur during the normal annual and El Niño cycles. In the western Pacific, several new skeletal indicators exhibit the potential to track other manifestations of the El Niño - Southern Oscillation phenomenon. Mn/Ca variations in a coral record at Tarawa respond to dramatic changes in trade wind flow that can be paired with $\delta^{18}O$ as a precipitation index. In the far western basin, Ba/Ca ratios could signal fluctuations in river discharge associated with migration of the Indonesian low pressure system.

Introduction

Recently, efforts have been directed toward establishing an approach to paleoclimate research using reef corals that parallels the development of carbonate paleochemistry in ocean sediments. Corals can be used to examine high-frequency changes which have occurred in the surface ocean over wide ranging time and space scales. On Pleistocene timescales, the key contribution of coral studies has been the delineation of sea level change (Chappell, 1974; Fairbanks, 1989). A subset of recent coral studies has explored the chemistry of contemporary growth bands to describe recent oceanographic and climatic changes. Decadal length temperature reconstructions based on aragonite oxygen isotope thermometry (Weber and Woodhead (1972)) have been produced in various tropical Pacific reef settings (e.g. Dunbar, 1981; McConnaughey, 1989). A second high-resolution paleothermometer appears to be resurrected in the form of high-precision determination of Sr/Ca in coral aragonite (Smith et al., 1983; Beck et al. 1991). In specific locales where temperature changes are small and precipitation anomalies large, $\delta^{18}O$ can also be used to trace historical changes in rainfall (Cole and Fairbanks, 1990). Photosynthetic influences on the carbon isotopic content of corals can be pronounced as algal symbionts deplete the carbon pool for skeletogenesis of the light isotope, ^{12}C (e.g. Fairbanks and Dodge, 1979; Patzold, 1984). A newer class of chemical tracers in corals is based upon lattice uptake of trace substituents in seawater. Thus far, three trace elements, Cd, Ba, and Mn have been identified as probable lattice substituents of coral skeletons whose abundances reflect natural changes in specific reef environments. Skeletal Cd and Ba permanently fingerprint changes in historical nutrient levels brought about by oceanographic changes in the upper thermocline and mixed layer (Shen et al., 1987; Lea et al., 1989; Linn et al., 1990). Manganese exhibits fractionation in the surface ocean in the reverse sense of the nutrients (due to atmospheric and coastal inputs), and thus also serves as a mixing tracer (Shen et al., 1991).

This abstract focuses mainly on a calibration of five geochemical tracers in a coral from the Galapagos Islands in the eastern Equatorial Pacific Ocean. Quarterly 47-year time series of $\delta^{18}O$, $\delta^{13}C$, Ba/Cd, Cd/Ca, and Mn/Ca are compared with one another, as well as against instrumental records of sea surface temperature (SST) from the Galapagos Islands and coastal Peru. As efforts to describe historical basin scale effects of ENSO are ongoing, the potential of coral tracers in the western Pacific basin is also considered.

Calibration of geochemical tracers in a Galapagos coral

To compare the usefulness of various coral tracers, measurements were made on homogenized sample splits from a 47-year growth interval of *Pavona clavus* from Punta Pitt, San Cristobal Island in the Galapagos Islands. The study coral grew in an open exposure at a depth of 14 m. Raw data for each of five chemical determinations are plotted as time series along with SST at Puerto Chicama, Peru in **Fig. 1**. Linear least squares regression coefficients for the various data series are shown in **Table 1a**. The correlations are also calculated against SST at Academy Bay, Santa Cruz Island in the Galapagos for the period 1965-1982 (**Table 1b**).

environmental controls

In spite of relatively low sampling frequency, the oxygen isotope tracer displays strong seasonality in *P. clavus*. As expected, an inverse relationship with Peruvian SST (same for Academy Bay SST) can be seen with depleted values reflecting periods of warm temperature. The carbon isotopic record seen in Fig. 1 is remarkably similar to both $\delta^{18}O$ and SST. While there are many possible environmental controls on $\delta^{13}C$, in this particular case there are probably only two dominant mechanisms at work (McConnaughey, 1989). The first, like the disequilibrium $\delta^{18}O$ offset observed in all corals, is likely due to kinetic fractionation. The second effect, superimposed on the kinetic bias toward a lighter skeleton, can be explained in terms of the photosynthetic response of algal symbionts. The positive correlation between $\delta^{13}C$ and SST suggests that skeletal $\delta^{13}C$ maxima occur during the warm season. Curiously, the warm season at Galapagos (also the rainier season) experiences less low stratocumulus cloud cover and hence greater insolation than the cold season. Water mass influences on coralline $\delta^{13}C$ are thought to be comparatively small since corals growing at shallower depths (0-4 m) in the Galapagos have been observed to exhibit little $\delta^{13}C$ seasonality or phasing in the opposite sense to the normal insolation response due to photoinhibition (McConnaughey, 1989).

The nutrient tracers Ba and Cd display negative correlations with SST according to the upwelling mechanism previously described in Shen et al. (1987) and Lea et al. (1989). The origin of this indirect relationship is straightforward enough as higher nutrients are usually accompanied by colder temperatures (deeper source waters), however, the precise nature of these relationships is not obvious. In considering the hydrography (Cd-PO_4-T relationships) in the Galapagos archipelago, a first order case can be argued for linear metal-SST relationships up to a temperature limit of 24.5°C. The poorest of correlations can be qualitatively witnessed in the case of Mn/Ca versus SST. On the basis of surface water maxima in dissolved Mn observed in the eastern Pacific (Klinkhammer and Bender, 1980; Shen et al., 1991), skeletal Mn/Ca is anticipated to behave in the reverse sense of a nutrient (or $\delta^{18}O$). This behavior indeed exists in segments of the raw Mn time series , however, it fails to apply consistently. We hypothesize that irregular Mn cycling is a result of advection of differing water masses into and out of the Galapagos region. Halpern (1987) has monitored a prominent east-west seasonal oscillation in zonal surface flow over a period of 5 years at 110° and 95° west of Galapagos. The significance of these reversals with respect to the normal Mn annual cycle is that variability promoted by upwelling may be opposed by lateral transport processes of surface waters that are enriched (to the east) or depleted (to the west) in Mn. As a result of these competing sources, interpretation of the Mn

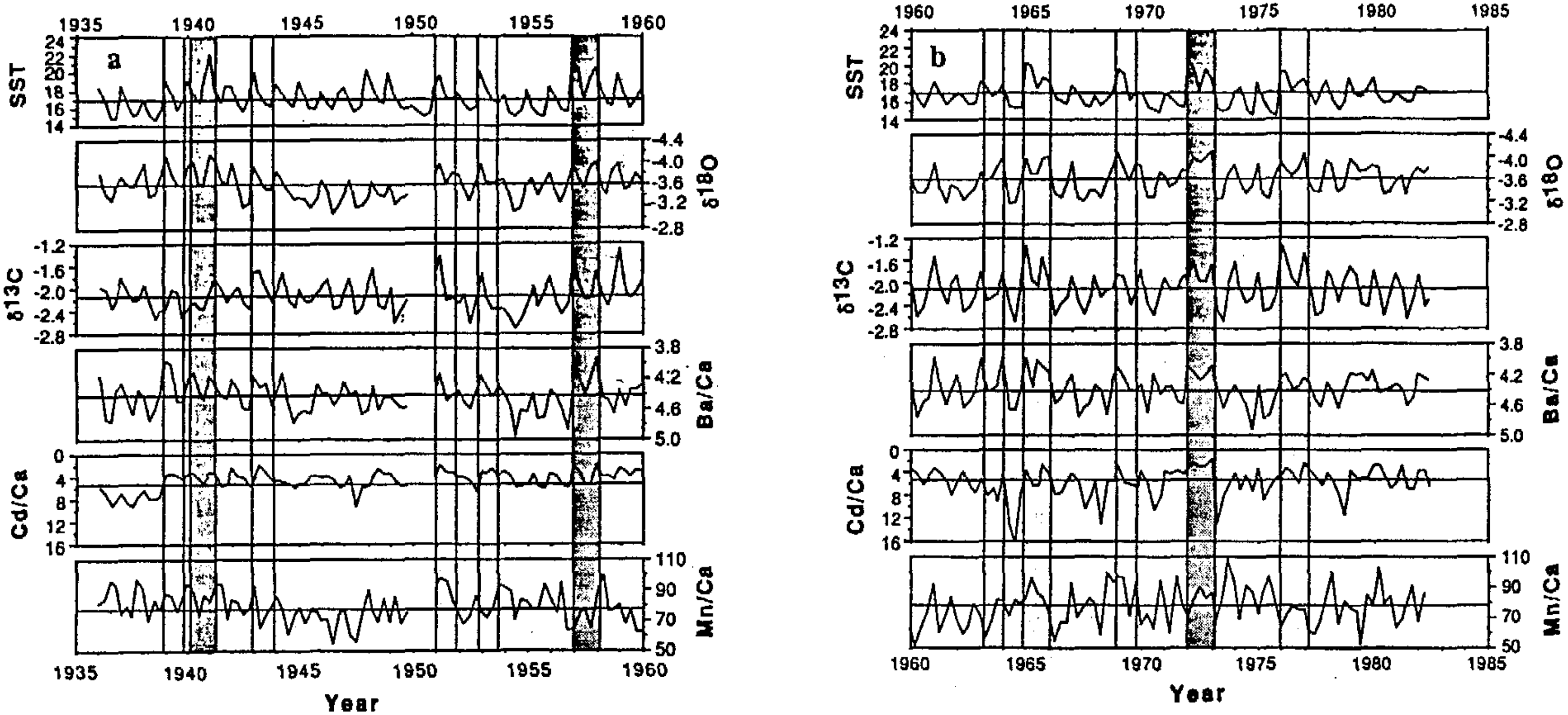

Fig. 1 Quarterly SST at Puerto Chicama, Peru and raw coral tracer data series from Punta Pitt, San Cristobal Island, Galapagos Islands. (a) 1935-1960; is plotted positive upward. Tracers are plotted such that El Niño conditions appear as positive deviations ($\delta^{18}O$, Ba/Ca, Cd/Ca are reversed; $\delta^{13}C$ normal). Nine El Niño events of "moderate" (light stipple) to "strong" (darker stipple) intensity (Quinn et al., 1987) are indicated.

Table 1 a. Least squares correlation coefficients (R) for 1936-1982 quarterly raw data series *(PC = Puerto Chicama; SST quarters defined as FMA-MJJ-ASO-NDJ).*

	$\delta^{18}O$	$\delta^{13}C$	Ba/Ca	Cd/Ca	Mn/Ca	PC SST
$\delta^{18}O$		-.69	+.72	+.51	-.32	-.65
$\delta^{13}C$			-.60	-.45	+.14	+.61
Ba/Ca				+.39	-.10	-.64
Cd/Ca					-.08	-.51
Mn/Ca						+.09

b. Least squares correlation coefficients (R) for 1965-1982 quarterly raw data series *(PC = Puerto Chicama; AB = Academy Bay; SST quarters defined as FMA-MJJ-ASO-NDJ).*

	$\delta^{18}O$	$\delta^{13}C$	Ba/Ca	Cd/Ca	Mn/Ca	PC SST	AB SST
$\delta^{18}O$		-.78	+.71	+.69	-.29	-.71	-.79
$\delta^{13}C$			-.62	-.56	+.14	+.69	+.78
Ba/Ca				+.43	+.07	-.72	-.68
Cd/Ca					-.18	-.55	-.57
Mn/Ca						+.03	+.03
PC SST							+.87

Table 2. Correspondence between tracer extrema and known ENSO activity.

ENSO event	intensity rating[1]	identification by 10 extrema: min $\delta^{18}O$	max $\delta^{13}C$	min Ba/Ca	min Cd/Ca	Event score
1939	S	xx		xx		2/4
1940-41	M+	xxxx				1/4
1943	M+				x	1/4
1951	W/M		x		x	2/4
1953	M+				x	1/4
1957-58	S	x	x	x	xx	4/4
1965	M+	x	xx	xxx		3/4
1972-73	S		x	x	xx	3/4
1976	M	x	xxx		x	3/4
tracer scores		9/10	8/10	7/10	8/10	(80% overall)

tracer is complex; the influence of water mass intrusions appears substantially more important than in the cases of the stable isotopic and other metal tracers.

tracer-SST relationships

The three chemical tracers $\delta^{18}O$, $\delta^{13}C$, and Ba/Ca all show relatively high degrees of correlation with both instrumental temperature records. Values of R^2 lie between 0.37-0.62, indicating that 37-62% of the total variance of proxy and SST is explained by a linear relationship. Cd/Ca also correlates with SST with lower R^2 values of 0.26-0.32. The poorer performance of Cd/Ca is likely related to the relatively large measurement error associated with this tracer which resides in the coral skeleton at parts-per-billion levels. Cross correlations show these tracers to be highly coherent with SST over periods of around 2 years. The Mn/Ca chemical tracer fails to show a consistent relationship with SST due to the variable phasing of the observed annual cycle. The overall correspondence between chemical tracers is variable, but highly significant, with the exception of comparisons with Mn/Ca. In general, the isotopic records agree closely (R^2 = 0.48-0.61), there is good agreement between isotopes and trace elements (R^2 = 0.20-0.52), and unexpectedly low correspondence between the two trace element records, Ba/Ca and Cd/Ca (R^2 = 0.15-0.18). The signs of the linear regressions are always as predicted, with the exception of the 1965-82 Mn/Ca-Ba/Ca comparison. The marked decline in the performance of the chemical tracers in going from the shorter 1965-1982 time series to the complete 1936-1982 data set is most likely due to the fact that the coral core quality declines with age. Slightly poorer overall statistics result when the tracer data are expressed as seasonal anomalies.

In regressing tracer signals recorded in individual seasons against SST, it emerges that the best correlations exist for the period May-October. The latter three months, Aug-Sept-Oct, in particular, show high correlation coefficients for PC SST against $\delta^{18}O$ (R=0.67), $\delta^{13}C$ (0.62), Ba/Ca (0.63), and Cd/Ca (0.50). Correlations are virtually absent in the months November-April. Coincidentally, May-November is the phase of the year when the Galapagos front is at its strongest, with temperature differences of 5°C and salinity changes of $1^{o}/_{oo}$ across (Hayes, 1985). It is also noteworthy that SST also compares most favorably to the Southern Oscillation Index during Aug-Sept-Oct (and on into Jan). It would appear that the transition toward and early phase of the upwelling cycle are accompanied by the most distinct physical and chemical changes recorded by the coral tracers.

Interannual variability and El Niño

To gain an appreciation of how well the tracers hindcast particular historical anomalies, we consider the significance of the 10 largest extrema in the isotopic and Ba and Cd data series which occurred in a warming (El Niño) sense **(Table 2)**. We focus on warm anomalies simply because these have been better catalogued and characterized than cool phase anomalies. Quinn et al., (1987) identify nine events of "moderate" to "strong" intensity over the 47-year period of interest. The number 10 has no statistical basis other than that divided into 47, it represents close to the average El Niño period and in fact, resembles the number of indexed events. We note that individual extrema are certainly not the only means of identifying discrete events. For example, it is often the persistence and not the absolute magnitude of an anomaly that signals a major environmental perturbation. 80% of the extrema in the raw data coincide with indexed El Niño events. As might be hoped, there is near-unanimous recording by all four tracers of the two strongest episodes of 1957-58 and 1972 (the 11th and 12th largest $\delta^{18}O$ anomalies both fall in 1972). The Niños of 1965 (M+) and 1976 (M) are also signaled vividly. At other moderate and weak rating levels, event recognition is not always proportional to the event intensities. In addition to events being recorded by multiple tracers, they are also frequently marked by clusters of individual tracer extrema (e.g. 1939, 1940-41, 1965, 1976). This explains partly why none of the tracers successfully identified all nine El Niño events. Manganese hindcasts less ably by this method with a 40% recognition rate.

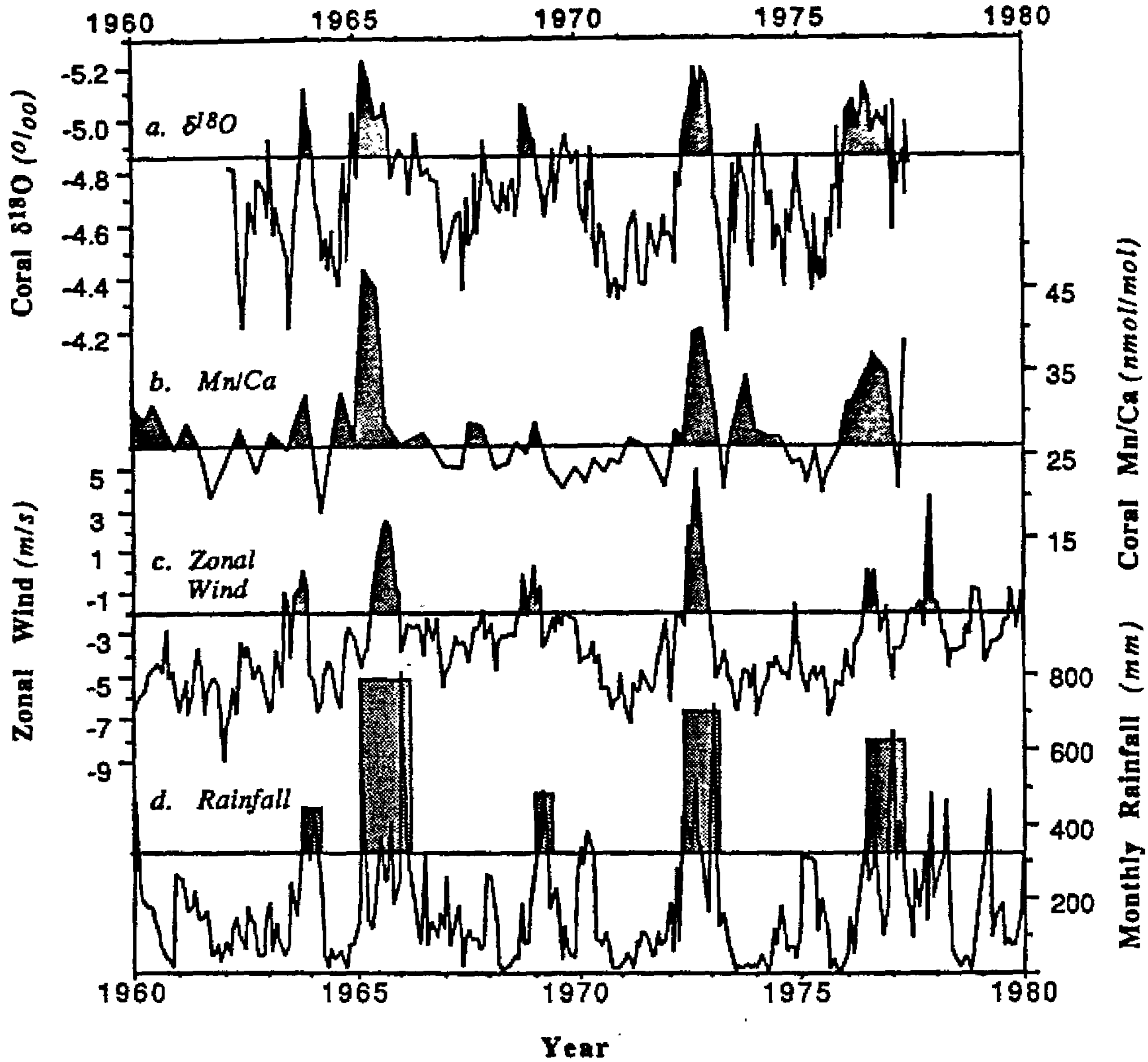

Fig. 2 a. $\delta^{18}O$ of *H. microconos* drilled at approximate 1 mm increments and assigned ages based on seasonal $\delta^{13}C$ behavior (see Cole and Fairbanks, 1990). Arbitrarily chosen reference lines for $\delta^{18}O$ and accompanying tracers highlight 5 ENSO events known to have occurred over this time interval [1963 (very weak); 1965 (moderate); 1969 (weak); 1972-73 (strong); 1976 (moderate) – Quinn et al., 1987 and 1977].

b. Time series Mn/Ca measurements for the period 1960-1977. Samples were cut in approximate trimonthly increments according to band structure as seen on the X-radiograph of Fig. 2. Ages are based on locations of cut increments relative to $\delta^{13}C$ samples and the associated age model.

c. Monthly mean rainfall recorded at Tarawa (New Zealand Met. Service unpublished data (1987), Taylor (1973), and Monthly Climatic Data for the World)

d. Monthly zonal surface wind measurements at Tarawa. Westerly winds are denoted by positive values (data furnished by D. E. Harrison).

Coral tracers in the Western Pacific

Manifestation of ENSO conditions in the western Pacific varies widely from what is observed near Galapagos. A very useful tracer of anomalously heavy precipitation has recently been described for a narrow equatorial band centered near the International Dateline (Cole and Fairbanks, 1990). A second chemical constituent shows promise as an indicator of trade wind reversals along a similar equatorial swath. As seen from **Fig. 2**, Mn/Ca ratios are highly perturbed in a coral from Tarawa (1°N, 173°E) during three El Niño - Southern Oscillation events (1965, 1972, 1976) that occurred within the growth period 1960-1977. For approximately 6 months during each of these events, Mn/Ca ratios increase by 50-80% from a background of 27 nmol Mn/mol Ca. These features co-occur with negative $\delta^{18}O$ pulses recorded in the same coral by Cole and Fairbanks which result from anomalously abundant rainfall. The most plausible explanation has to do with the transient appearance of westerly winds along the equator during ENSO periods. Particularly vigorous westerly wind "bursts" (sometimes averaging 10 m/sec or more over 16 hrs - Luther et al., 1983) during the above years may have generated wind waves of sufficient strength to create an aura of particulate and diagenetically remobilized Mn from within the shallow westward facing lagoon of Tarawa. This interpretation is supported by relatively high Mn concentrations measured in pore waters of Tarawa lagoon sediments.

Closer to the Indonesian land masses, another possibility exists for tracing variations in monsoonal rainfall. We have identified subtle oscillations in the Ba content of corals at Barbados which are caused by the advection of Ba-rich Amazon estuarine waters over a 2,000 km path. This tracer could in principle be used in conjunction with $\delta^{18}O$ and fluorescence markers (Isdale, 1983) to isolate local fluvial and precipitation effects in coral cores from the Indonesian archipelago.

Conclusions

While the number of available long-term coral data bases is presently small, the means are at hand to describe a variety of paleoenvironmental conditions in wide-ranging reef locales (see Cole et al., in press). As progress in precise radiometric dating (Edwards et al., 1987) and drilling technology (Fairbanks, 1989) continues, the potential grows to improve our understanding of paleoclimatic perturbations as familiar as the El Niño - Southern Oscillation and as distant as Earth's ice ages.

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THE FOSSIL DIATOMS OF LAKE YAMBO, ECUADOR. A 2500 YEAR RECORD ON INTENSE EL NIÑO EVENTS.

Miriam STEINITZ-KANNAN, Mark A. NIENABER and Melanie A. RIEDINGER
Department of Biological Sciences
Northern Kentucky University, Highland Heights, Kentucky 41099, U.S.A.

Diatomeas fósiles de la Laguna de Yambo, Ecuador: Un posible record de 2500 años de intensos fenómenos de "El Niño".

Resumen: Estudios limnológicos se han realizado cada año desde 1975 en la Laguna de Yambo, una laguna ubicada en una parte árida de la región interandina del Ecuador. Estos estudios indican que el agua de esta laguna tiene una alta concentración de sales disueltas y una flora de diatomeas rica en Navicula halophila, especie característica de lagunas salobres. En 1982-1983 uno de los fenómenos de "El Niño" más inesperados, intensos y catastróficos azotó la costa sudamericana del Pacífico y causó un aumento considerable en la precipitación de la región de la laguna. Este aumento hizo que la conductividad del agua sea reducida en un 30%. La comunidad de diatomeas respondió a este cambio en la química del agua, y observamos un aumento en la abundancia de la diatomea Melosira italica, y una reducción en la abundancia de Navicula halophila (Figura 1). Análisis de diatomeas fósiles en sedimentos de la laguna de Yambo revelan estas mismas fluctuaciones en estas dos especies (Figura 2). Debido a que la laguna se encuentra en una región muy árida, y que cambios en salubridad del agua pueden resultar solamente como consecuencia de cambios dramáticos en precipitación, en el record de cambios en la comunidad de diatomeas de la Laguna de Yambo debe existir una historia de los fenómenos de "El Niño" más intensos ocurridos durante los 2500 años de existencia de la laguna.

We present here the preliminary results of the analyses of fossil diatoms from the sediment core of Lake Yambo (1°05' S, 78°35' W, 2600 m elevation), an endorheic and highly eutrophic lake in the Inter-Andean desert of Ecuador. A 7.5 meter core, radiocarbon dated to 2540 ± 170 B.P., was retrieved from this basin and subsampled for diatoms and pollen. Analyses of the diatom communities throughout the core revealed fluctuations in the abundance of two taxa, *Melosira italica* and *Navicula halophila*. We interpret these changes as evidence for fluctuations in lake conductivity and water level, and suggest that they may hold a record of past precipitation anomalies for this region.

We have extensively studied Lake Yambo since 1975, and seasonal information on its water chemistry and algal flora exists (Steinitz-Kannan 1979, Steinitz-Kannan *et. al.* 1983, Colinvaux *et. al.* 1988). The present lake has a very high concentration of dissolved ions, and a diatom flora rich in *Navicula halophila*, which is characteristic of this high salinity. During the 1982-1983 El Niño, the interAndean plateau of Ecuador experienced a significant increase in precipitation. This caused water levels to rise in Lake Yambo, and resulted in a 30% drop in conductivity (Steinitz-Kannan 1979, Steinitz-Kannan *et al.* 1983, Nienaber and Steinitz-Kannan 1989). The change in water chemistry caused a shift in the diatom flora, with a decline in the population of *N. halophila* and dramatic increase in the frequency of *Melosira italica* (Figure 1).

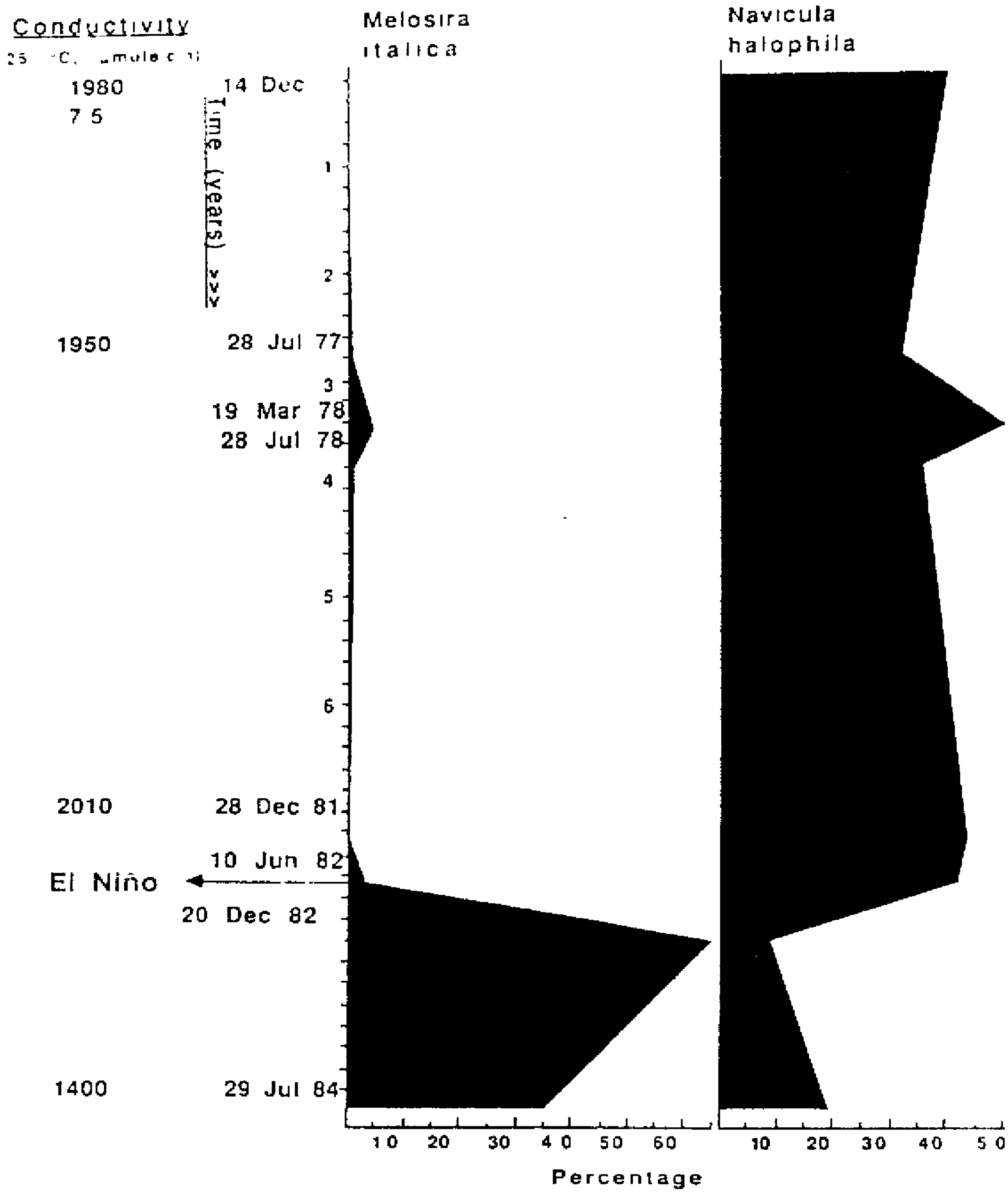

Figure 1: The effect of the 1982-83 El Niño on Lake Yambo

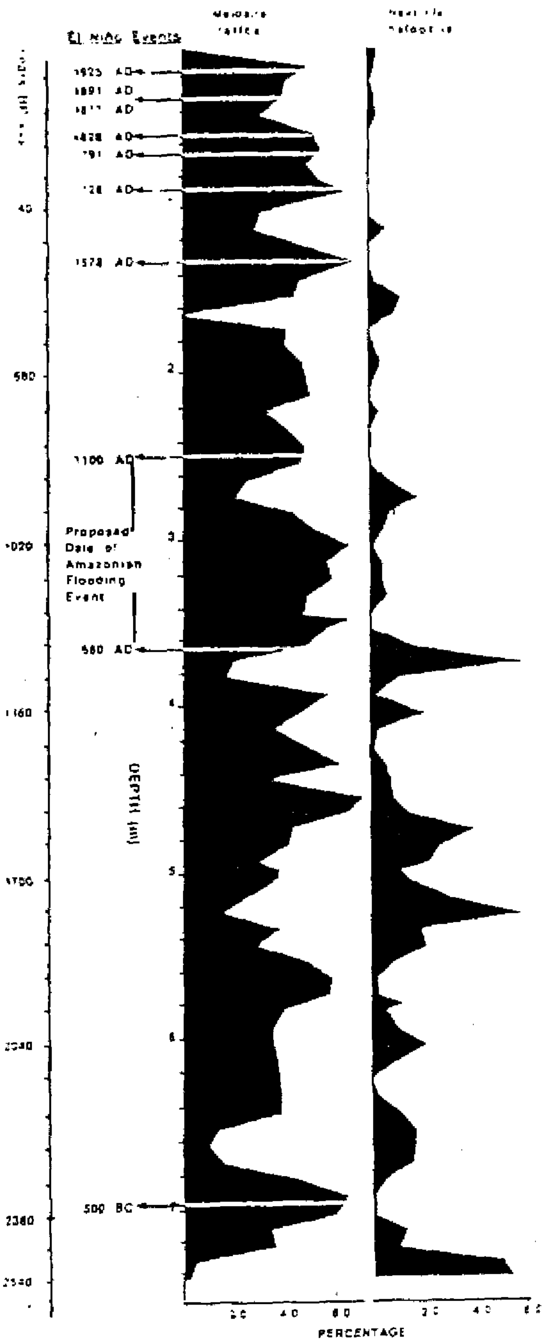

Figure 2: A Record of Ancient Precipitation Events in the Inter-Andean Plateau, as revealed by changes in the fossil diatom communities of Lake Yambo. All dates except those represented by an * are extrapolated dates.