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RECONSTRUCTION OF EL NIÑO HISTORY FROM REEF CORALS

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Abstract

Of all the mineral phases found in the marine environment, carbonates of various biological origins have proven to be the richest repository of paleoceanographic/ paleoclimatic information. Over the last two decades, a process framework has evolved to permit the interpretation of such information in aragonitic reef corals. Corals comprise a particularly useful archive in that they are widely distributed, temporally banded, and geochemically well-suited to record environmental information. This paper reviews these attributes from the perspective of historical El Niño-Southern Oscillation influences on the tropical Pacific Ocean.

Key words: *El Niño - Southern Oscillation, corals, paleoclimate, carbonate geochemistry, stable isotopes, trace elements*

RECONSTRUCCIÓN DE LA HISTORIA DE EL NIÑO A PARTIR DE ARRECIFES CORALINOS

Resumen

De todas las fases minerales encontradas en el ambiente marino, los carbonatos de varios orígenes biológicos han demostrado ser el repositorio más rico de información paleoceanográfica y paleoclimática. Durante las dos últimas décadas, se ha desarrollado un método de trabajo para permitir la interpretación de la información en los arrecifes de corales aragoníticos. Estos corales proveen un archivo especialmente útil por su amplia distribución, su bandeado temporal y su geoquímica apropiada para registrar información sobre el medio ambiente. Este artículo revisa estos atributos desde la perspectiva de las influencias históricas de El Niño-Oscilación Austral sobre el océano Pacífico tropical.

Palabras claves: *El Niño- Oscilación del Sur, corales, paleoclima, geoquímica de carbonatos, isótopos estables, elementos traza.*

RECONSTRUCTION DE L'HISTOIRE DE EL NIÑO À PARTIR DES RÉCIFS DE CORAUX

Résumé

Parmi toutes les phases trouvées en milieu marin, les carbonates de diverses origines biologiques se sont révélés être la source la plus riche en information paléo-océanographique et plaéo-climatique. Au cours des 20 dernières années, une méthode de travail s'est développée pour permettre l'interprétation de l'information sur les coraux des récifs d'aragonite. Ces coraux fournissent une information particulièremet utile pour leur large distribution, leur rubanement en fonction du temps et leur géochimie apropriée pour enregistrer l'information du milieu ambiant. Cet article rend compte de ces caractéristiques depuis la perspective des iunfluences historiques du El Niño-Oscillation Austral sur l'Océan Pacifique Tropical.

Mots clés : *EL Niño-Oscillation du sud, coraux, paléo-climat, géochimie de carbonates, isotopes stables, éléments trace.*

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1. INTRODUCTION

In contrast to most retrospective studies of El Niño which have origins along the continental margin of the Americas, this paper explores the El Niño record from the open waters of the tropical Pacific Ocean. Continental records, examples of which may be found in this issue, are particularly useful in the tropical eastern Pacific where El Niño air-sea perturbations are the dominant interannual signal. At higher latitudes or toward the interior of the continents, however, the quality of such records depends on the nature of the teleconnection (*e.g.* Ropelewski & Halpert, 1987; Hamilton, 1988). Tree ring records from western North America, for example, exhibit strong correlations with the Southern Oscillation Index (Lough & Fritts, 1985; Lough, 1992). Andean ice cores, though closer to the main locus of ocean warming, do not record a pure El Niño signal, but show influence from mixed transport processes (*i.e.* dust from the west and water vapor from the east) (Thompson & Mosley-Thompson, 1987). In principle, oceanic records of El Niño and the basin-scale El Niño-Southern Oscillation (ENSO) phenomenon should show the greatest regionality and least contamination of all geologic records.

Marine-based records are available from two natural archives: sediments and marine biogenic deposits. Retention of interannual information in marine sediments is generally limited to areas of rapid accumulation and anoxia (Souta & Crill, 1977). In the eastern Pacific, the Santa Barbara Basin and Gulf of California are two of the more prominent locations that have been studied in a paleo-ENSO context using a variety of markers (Baumgartner *et al.*, 1985; Schrader & Baumgartner, 1987; Schimmelmann *et al.*, 1990; Lange *et al.*, 1990; Kennedy & Brassell, 1992). More widespread in occurrence are calcareous organisms such as molluscs and corals which are capable of continuously recording environmental information on time scales of years to centuries (Hudson *et al.*, 1976; Jones, 1983). Shell middens have proven useful in identifying large scale temperature transitions over the last 10,000 years (Rollins *et al.*, 1986; DeVries, 1987), however, few attempts have been made to delineate El Niño-related climate change geochemically using mollusk valves.

In recent years, numerous efforts have been made to utilize physical growth indices and geochemical properties of aragonitic reef corals as paleoenvironmental markers. The diversity of skeletal tracers that has been identified is probably unsurpassed by any other biogeological medium (Table 1). Here I review the use of corals from the perspective of building an El Niño timeline which transcends the modern record.

2. ENSO MANIFESTATIONS IN THE TROPICAL PACIFIC

The large scale oscillation of the tropical ocean-atmosphere system that is ENSO varies in space as well as time. Although each El Niño event has its own unique characteristics, a composite description of the general phenomenon has emerged (Wyrtki, 1975; Rasmusson & Carpenter, 1982; Cane, 1986). A summary of the main points follows in the terminology of Cane (1986). The *"prelude"* phase of the basin scale ENSO phenomenon is marked by a strengthening of easterly trade winds in the western basin causing unusually high sea level toward Indonesia. Sea surface temperatures (SSTs) are slightly elevated in the west and depressed in the east. During the *"onset"* stage beginning in northern fall of the year

Indicators\Processes			Upwelling/	Anthropogenic		Terrestrial			Environmental	Sediment fluxes
	SST	Salinity	Nutrients	Inputs	ENSO	Runoff	Rainfall	Light	Stress	Volcanic inputs
$^{18}O/^{16}O$	xx	xx			xx		x			
$^{13}C/^{12}C$			x	x	x			x		
Sr/Ca	xx				x					
Ba/Ca	x	x	xx		x	x				
Cd/Ca	x		xx	x	x					
Mn/Ca			x							x
Pb/Ca				xx						
Bomb radionuclides			x	xx	x					
UV Fluorescence						xx				
Extension rate/hiatuses			x	x	x	x		x	xx	
Band density			x				x		x	
Crystallography			x						x	

Table 1 - Coral-based indicators of environmental change: (xx) indicates strong signals with know wide geographic variability; (x) indicates signal strongly correlated with processes at some sites, with strong events at many sites, or requiring further development (adapted from Workshop on Coral Bleaching, Coral Reef Ecosystems, and Global Change: Report of proceedings, NSF/EPA/NOAA, Miami, FL, June 17-21, 1991)

before the event, the easterly trades diminish and occasionally reverse causing the east-west slope in sea level to relax. Positive SST and precipitation anomalies develop in the western basin as the Indonesian Low migrates toward the dateline. In the *"event"* stage, the well-known warming off South America begins near the start of the calendar year, the thermocline deepens, and equatorial rainfall increases from South America to at least 165°E. Parts of Indonesia are stricken by drought. Westerly wind anomalies become more common in the vicinity of the dateline and sea level continues to fall in the west and build in the east. Warm temperatures in the eastern Pacific peak near May and the warm pool then spreads westward, eventually merging with the warm water anomaly in the central Pacific. By the fall, SST in the east has cooled to nearly normal temperatures. The final *"mature"* phase is marked by attenuation of the temperature anomalies and overshooting of the mean state in the latter half of the year following the event. Trade winds are stronger and eastern Pacific temperatures slightly cooler than normal. Rainfall over the northwest and southwest Pacific remains weak.

From this synopsis of a "canonical" ENSO, it is apparent that the range of possible expressions in surface-dwelling corals is very broad. Certainly direct indicators of temperature, salinity, insolation change, ocean mixing (*e.g.* upwelling), rainfall, and surface winds would be very useful. Such markers have actually been identified for each of these ocean properties and processes (Table 1); a description of their use as ENSO tracers follows.

3. DISTRIBUTION OF CORALS IN THE TROPICAL PACIFIC

From the standpoint of ENSO history, the most important aspect of the modern distribution of coral reefs is the broad coverage afforded throughout the entire tropical Pacific basin (Fig. 1). High and low limits of reef coral diversity are approached on either side of the tropical Pacific, with genera commonly numbering above 50 in the western basin to about 5 in the east (Rosen, 1971; Glynn & Wellington, 1983). Wells (1957) ascribes the high species abundance in the Indo-Pacific region to the optimal temperatures there which extend into the central Pacific. Toward the eastern margin, reef development is limited by cool temperatures caused by equatorial and coastal upwelling and a paucity of suitable substrata. The north-south boundaries of coral reefs, roughly coinciding with the Tropics of Cancer and Capricorn (23°30'N and S), generally follow the 20°C (annual minimum) surface isotherm. Subtropical reefs do occur, but as limited outposts as in the case of the northwest portion of the Hawaiian Island chain. The existence of western boundary currents such as the Kuroshio allows the poleward extent of reef development to be wider in the western Pacific than in the east.

The existence of reefs in a given locale, however, does not ensure that a useful record of climate change can be extracted. Success depends on the nature of the climate signal at a particular site and the availability of a physical or geochemical tracer that can capture and retain this signal. Thus, in the eastern tropical Pacific where ENSO sea surface temperature (SST) anomalies are largest, a coral index of temperature change would be of great value. At least two such temperature indices have been identified in coral aragonite. In western Pacific waters, a record of precipitation anomalies might prove of greater use. Several rainfall/runoff tracers are in development as will be described. Still in other regions where the manifestation of ENSO is not so obvious (but potentially very important as in event precursor areas), the utility of the coral record remains to be seen.

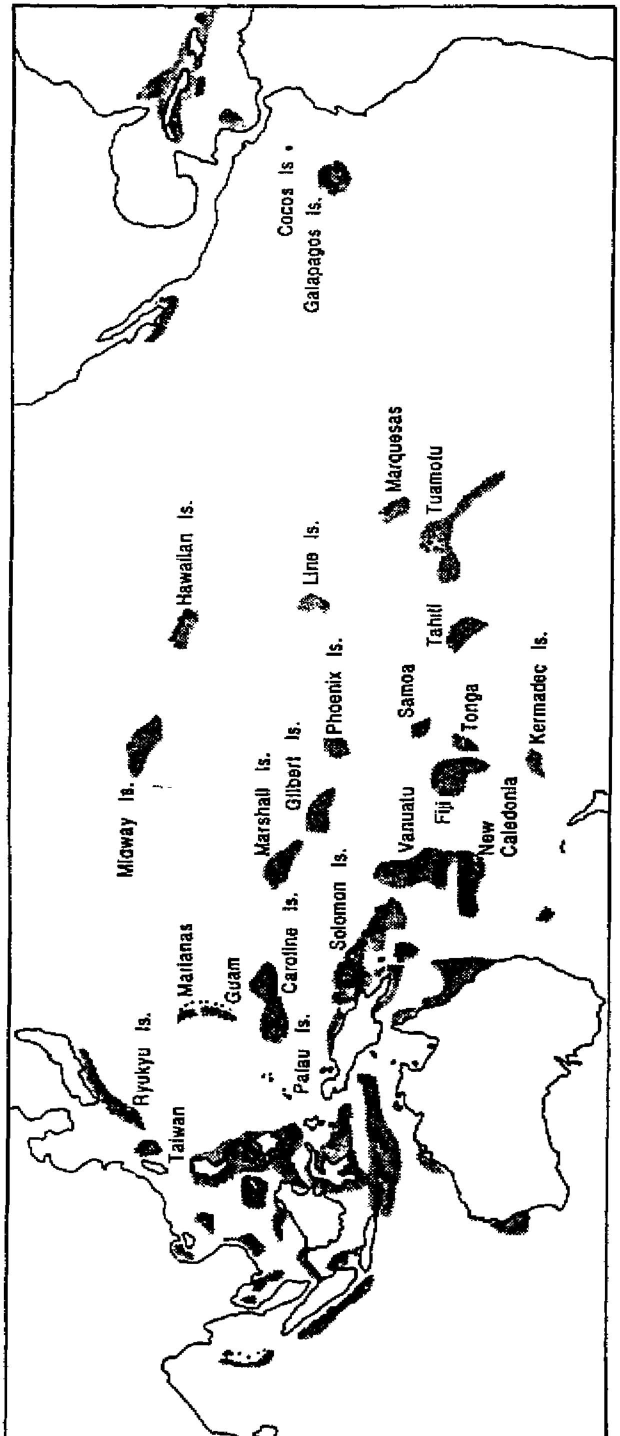

Fig. 1 - Distribution of Pacific coral reefs (adapted from Veron, 1986).

4. CORAL SAMPLING

Sampling techniques for reef corals depend largely on the record length of interest. Short modern records can be extracted from small head or branching corals taken live by hammer and chisel on scuba or snorkel. Drill cores are the most efficient means of obtaining longer growth intervals from massive corals. Hydraulic or pneumatic coring also eliminates the need to sacrifice entire colonies - an important concern in underwater parks and stressed reefs. Cores of 2.5 cm diameter and 30 cm" length can be taken on scuba using a standard pneumatic hand drill connected to a spare diving tank (a 90 ft^3 tank will power such a drill for about 10-15 minutes). At a typical tropical growth rate of 1 cm/yr, such a coral core will provide a record length of roughly 30 years. Wider, longer cores from massive corals require higher power drills, a few of which have been described in the literature (Macintyre, 1975; Hudson, 1981). The hydraulic drill we currently use (fabricated by E. Wheeler, Round Rock, TX) cuts a 3" diameter core in increments of 30" with maximum possible recovery of several meters. The 220 rpm drill is powered overhead by a 2200 psi hydraulic compressor run by an 11 h.p. gasoline engine. The gasoline engine also powers a small pump which delivers water via a separate hose through the diamond core bit to flush away carbonate cuttings. The drill can be operated by divers at any depth, however, the need to dive repetitively and risk of decompression sickness limits most practical drilling to 15 meters. A well-designed air-powered coral drilling system has also been described by Isdale & Daniel (1988).

One of the limitations to sampling by coring stems from the tendency of some massive coral species (*e.g.* Porites *lobata*) to change their growth orientation over time. Since a drill core follows a straight line, a 3-meter core will only be useful if the coring axis remains parallel to the growth axis. For this reason, multiple cores are commonly taken from individual colonies, thus increasing the chances of full recovery. In some cases, it may be advantageous to recover whole portions of specimens or to break off entire columns in the case of more lobate forms. These can then be sectioned on a large masonry saw and growth axes carefully identified through x-radiography or possibly Computerized-Axial Tomagraphy (*i.e.* CAT-scan) (R.B. Dunbar, personal communication 11/1992).

Beyond individual massive colonies, longer records through deceased reef framework and drowned terraces can be drilled by more sophisticated means from a floating platform. In this manner, Fairbanks (1989) penetrated 30,000 years of reef development in a semi-continuous manner off south Barbados, the result of which is the most detailed glacio-eustatic sea level curve ever produced.

As far as sample cleaning, slabbing, x-radiography, and other preparative protocols, handling requirements may vary depending on application (*e.g* densitometry, stable isotope analysis, trace element assay). A general treatment is given by Buddemeier (1978), however, readers are advised to consult the literature specific to their analytical interest.

5. GROWTH CHARACTERISTICS AS TEMPORAL AND ENVIRONMENTAL MARKERS

The principal attribute of scleractinian corals as recording systems is their continuous accretion for periods up to several hundred years. In many corals, this mineral accretion occurs in discrete annual layers (Knutson *et al.*, 1972; Dodge & Thompson, 1974) which permits rapid and accurate dating. The exact triggers for deposition of annual high and low-density aragonite band pairs are as yet unclear. Seasonal environmental cues in the tropics can be very subtle. Most models have proposed that temperature or light intensity, or a combination of the two, mediate zooxanthellar/reproductive activity and hence, Ca CO_3 precipitation (Highsmith, 1979; Wellington & Glynn, 1983). In clearly banded samples taken from live corals (thus fixing the date of the topmost band), dating of horizons through x-radiography can be very accurate, encompassing hundreds of years if there are no growth hiatuses. In other cases, absence of banding or existence of multiple band pairs can render band counts ambiguous. Geochemical means of time control are then needed. A recent study of skeletal structure using reflectance optical microscopy suggests that daily growth increments of the order of 10 mm can be detected in certain reef corals (Risk & Pearce, 1992), thus introducing the possibility of ultra-high resolution environmental reconstructions.

It would seem that analagous to dendrochronology, measurement of coral band widths and density would be a useful means of identifying environmental change. Certainly, seasonal and interannual differences in these properties are evident in most corals. The link between changes in these physical growth parameters and specific environmental controls, however, can be ambiguous and reef specific. For example, growth rates as measured by skeletal linear extension and mass deposition have been correlated with temperature, depth, sedimentation, light, and wave energy (see Buddemeier & Kinze, 1976; Dodge & Vaisnys, 1980; Lough & Barnes, 1990). All of these environmental parameters are interdependent, thus making it difficult to isolate the dominant controls.

One impediment to applying continuous growth records to identify El Niño episodes is the disturbance of reef corals during severe events. For example, Glynn (1990) documented up to 70-90% coral mortality in Costa Rica, Panama, and Columbia, and >95% mortality in the Galapagos Islands as a result of the 1982-1983 El Niño. Glynn hypothesizes that in the Galapagos, an event of this proportion has not occurred for 400-500 years. The large-scale mortality experienced during the 1982-1983 event was most likely induced by prolonged warming throughout the eastern tropical basin. During disturbances like this, irreparable damage to coral reefs may occur wherein deceased massive structures are undermined by boring molluscs and eroded away. Following lesser events where heads are recolonized, a hiatus will appear in the growth record, thus introducing uncertainty in the age of band horizons below. Even when there is no reef mortality in response to stressful conditions, coral bleaching (expulsion of symbiotic zooxanthellae) may result in reduced accretion rates and altered physiology, thus physically and chemically distorting the environmental signal left behind in the skeleton.

6. RADIOMETRIC DATING TECHNIQUES

The geochronology of coral reefs is most widely understood in the context of Pleistocene glacial-interglacial sea level changes. The use of uranium and thorium series isotopes to date fossil terraces ranging in age from thousands to a million years has been practiced for several decades (see reviews by Veeh & Green, 1977, and Schwarcz, 1989).

On much shorter timescales, there are several radiochemical alternatives to band counting. ^{228}Ra and ^{210}Pb, isotopes with respective half-lives of 6.7 and 22.5 years, can be used to establish approximate chronologies on modern samples of up to 100 years age (Moore & Krishnaswami, 1973; Dodge & Thomson, 1974). An example of the close agreement attainable

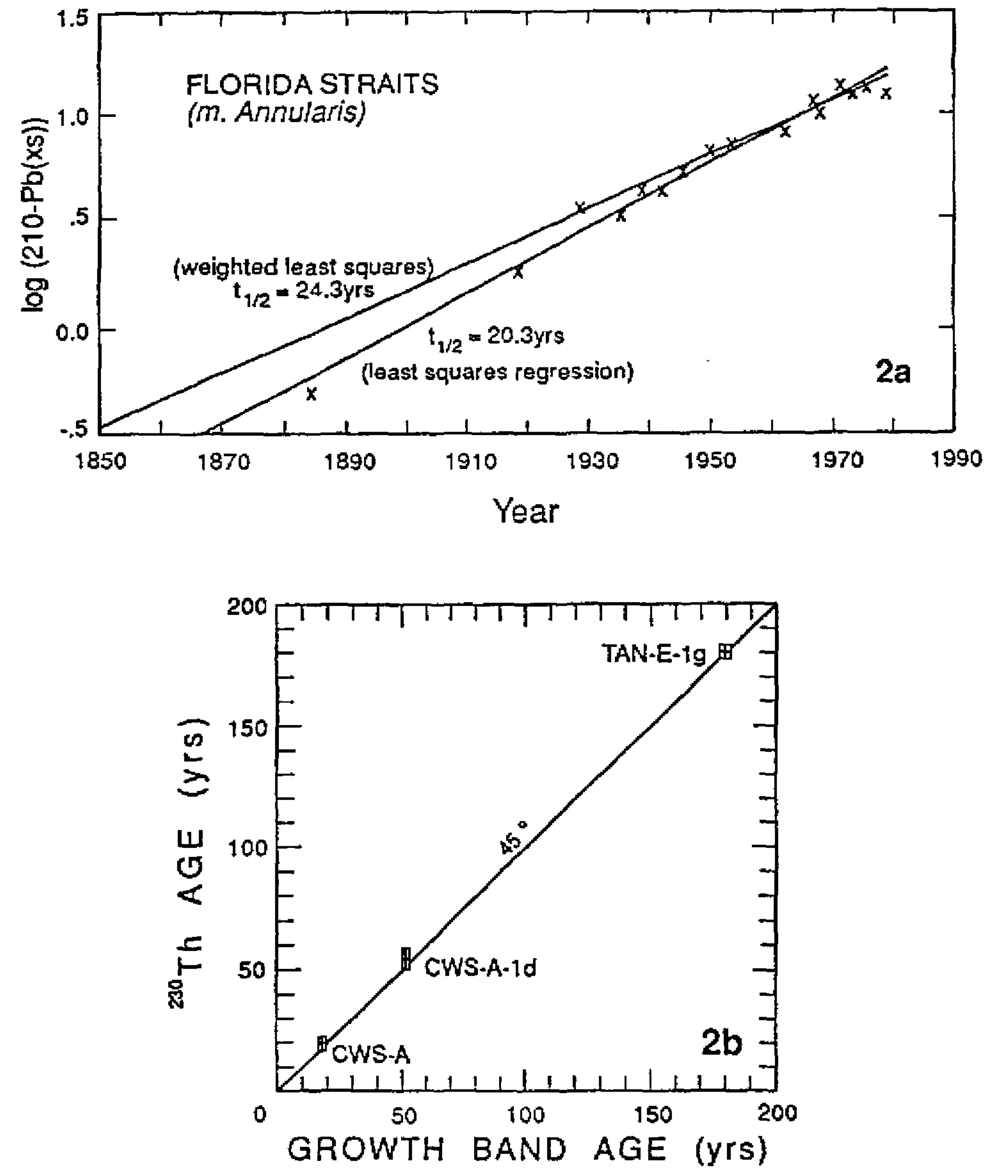

Fig. 2 - a) Skeletal ^{210}Pb concentrations (dpm/100 g coral in excess of that supported by skeletal ^{226}Ra assumed = 7.4 dpm/100 g coral) *versus* band counted age in *Montastrea annularis* from the Florida Straits (from Shen & Boyle, 1988). Based on the half-life of ^{210}Pb, the predicted slope of the log $^{210}Pb_{xs}$ *vs* time plot should be 22.5 years. The experimentally determined slope is within 10% of this value. b) ^{230}Th *versus* band counted age for three modern corals from Vanuatu (from Edwards, 1988). All three determinations intersect the 45° line indicating that within the errors of the measurement, the ^{230}Th ages are identical to the growth band ages. The error about sample CWS-1-A-1d is ±3 yrs.

between ^{210}Pb and band counted age is shown in Fig. 2. A few studies of ^{210}Pb in corals, however, have yielded results inconsistent with simple exponential decay (*e.g.* Moore & Krishnaswami, 1973; Benninger & Dodge, 1986). Since lead is quickly scavenged from the dissolved phase in the marine environment, a possible source of such inconsistencies is ^{210}Pb uptake into skeletal host phases other than the actual Ca CO_3 lattice (*i.e.* organic, interstitial, and adsorbed phases). The existence of non-lattice ^{210}Pb in corals and its removal are discussed at length in Delaney *et al.* (1989) and Shen (1986). Use can also be made of pulse imputs of artificial radionuclides from bomb testing (^{90}Sr, $^{239,240}Pu$, ^{14}C) to identify specific growth horizons in slabbed corals, thus allowing definition of annual couplets or estimation of an average growth rate over a known period of several decades (Knutson *et al.*, 1972; Moore & Krishnaswami, 1973; Benninger & Dodge, 1986). Since the confirmation of the annual nature of coral bands, studies of artificial radionuclides in corals have mostly adopted the opposite approach, relying upon band counted ages to precisely reconstruct deposition histories of bomb fallout to the surface ocean (*e.g.* Druffel & Linick, 1978; Toggweiler & Trumbore, 1985).

On century timescales, the dating tool of choice has historically been radiocarbon, ^{14}C ($t_{1/2}$ = 5568 yrs - Stuiver & Polach, 1977). The reason, however, has less to do with the accuracy of this technique than it does with the fact that there are few alternative dating schemes in this age range. Owing to natural variations in the specific activity of ^{14}C in the atmosphere and surface oceans, empirically determined calibration curves are necessary to convert radiocarbon ages to calendar years (Stuiver *et al.*, 1986). For marine samples, a reservoir age correction (typically about 400 yrs) must also be made to account for the difference in ^{14}C activity between atmosphere and surface ocean. For these reasons, minimum uncertainties of ±50 years are common in the several hundred year age range. Additionally the marine radiocarbon calibration curve occasionally displays zones of nonsingularity, particularly in the last 500 years, which could cause greater uncertainites (Stuiver *et al.*, 1986).

The most remarkable breakthrough in coral dating resulted from an analytical reevaluation of the familiar ^{234}U-^{230}Th technique. In spite of the long half-lives of these isotopes (^{234}U $t_{1/2}$= 244,000 yrs, ^{230}Th $t_{1/2}$ = 75, 400 yrs), the working range of this parent-daughter system has recently been extended to include marine aragonites as young as a few decades (Edwards *et al*, 1987 - Fig. 2b). This extension of the applicable ^{234}U-^{230}Th age range is made possible by precise mass spectrometric atom counting of ingrown ^{230}Th in the presence of very little background ^{230}Th. Corals only decades old can now be dated to ±3 yrs using only a few grams of sample.

Given a few reference horizons established radiometrically or by other means, dating of poorly banded corals can also be accomplished geochemically by identifying markers that vary seasonally (*e.g.* $\delta^{18}O$, $\delta^{13}C$, Cd/Ca) in response to a regular environmental stimulus and producing detailed time series measurements of these markers. Produced for the sake of time control alone, this technique might prove too laborious to be practical, however, in a detailed reconstruction of ENSO history, stable isotopic and trace element measurements are often already the focus. Cole & Fairbanks (1990) and Cole (1992) have successfully developed age models in poorly banded corals from Tarawa based on the response of coralline $\delta^{13}C$ to seasonal insolation changes.

7. GEOCHEMICAL MARKERS IN CORALS

Numerous skeletal constituents in corals have been found to covary with one or more environmental parameters. In fact, the array of geochemical tracers in corals presently exceeds that developed in any other biogenic mineral phase, including marine biogenic calcite (*i.e.* foraminifera, radiolaria). And the list will probably grow as hybrid analytical techniques such as inductively-coupled plasma mass spectrometry (ICP-MS) improve and the search for tracers expands to include constituents that are not integral parts of the mineral phase, but are occluded. In the following discussions, the present state of understanding of coral tracers is reviewed and examples selected from the literature.

7.1. Stable isotopes

Of all the geochemical constituents studied in marine biogenic carbonates, the most familiar is $\delta^{18}O$. The applicability of oxygen isotope paleothemometry in marine organisms was first demonstrated by Epstein *et al.* (1953) using mollusks. Weber & Woodhead (1970; 1972) established that the temperature dependence for $^{18}O/^{16}O$ fractionation in reef corals is similar to that observed in inorganic calcite and mollusks, with the main complication being that different genera exhibit near-constant offsets in their paleotemperature equations. Generally, coral aragonite is depleted in the heavier isotope, ^{18}O, relative to equilibrium by 3-4°/$_{oo}$. Physiologic influences on oxygen isotope fractionation have been described by Swart (1983) and McConnaughey (1989a; 1989b). According to the more recent interpretation, the overall depletion in $\delta^{18}O$ is thought to result from kinetic isotopic fractionation during CO_2 hydration and hydroxylation. Skeletal carbonate is derived chiefly from this fractionated CO_2 which leaks from cells of the coral's skeletogenic epithelium (McConnaughey, 1989b).

There is an an abundance of literature which addresses the caveats of using oxygen isotopic ratios as a temperature sensor. Many of these describe the dependence of $\delta^{18}O$ on salinity which ultimately derives from fractionation induced by air-sea evaporation/precipitation cycles (*e.g.* Swart & Coleman, 1980; Dunbar & Wellington, 1981). Skeletal growth has also been found to influence oxygen isotope fractionation in the sense that rapid precipitation rates lead to higher kinetic disequilibria (Land *et al.*, 1975; Erez, 1978; Weil *et al.*, 1981; McConnaughey, 1989a). This effect, however, appears most pronounced at very slow growth rates and thus can be minimized by sampling along major growth axes. In spite of these complex linkages, $\delta^{18}O$ has been used successfully to estimate ENSO-related changes in Pacific SSTs. For example, Druffel (1985) and Druffel *et al.* (1990) produced a number of brief $\delta^{18}O$ time series from regularly banded corals situated away from strong salinity gradients in the Galapagos Islands and the mid-Pacific islands of Canton and Fanning (Fig. 3). The attenuation of the seasonal temperature cycle (and ENSO signal) is apparent as one moves westward from Galapagos. The clarity with which corals can record seasonal upwelling and El Niño temperature anomalies is best seen in the Galapagos $\delta^{18}O$ reconstructions of McConnaughey (1986) (Fig. 4). On the far eastern margin of the Pacific off Costa Rica, the 1982-1983 El Niño $\delta^{18}O$ signature has been captured in another brief record (Carriquiry *et al.*, 1988).

Since the partitioning of oxygen isotopes between ocean and atmosphere is influenced by evaporation and precipitation, an alternative possibility exists to use $\delta^{18}O$ in corals not as a thermometer, but as a rainfall/runoff gauge. Cole & Fairbanks (1990) and

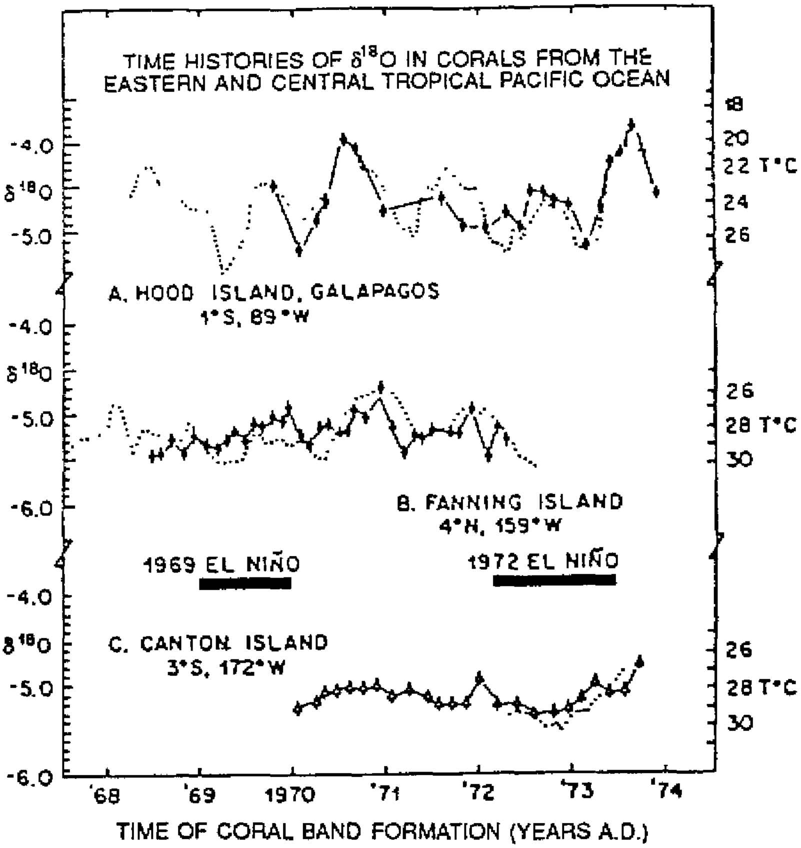

Fig. 3 - Subannual measurements of $d^{18}O$ (°/$_{oo}$ units) in corals from the eastern and central tropical Pacific during 1968-1974. Sea surface temperatures are shown in dotted lines (Fanning SST is actually from Christmas Is.). The analyzed period encompasses one "strong" (1972) and one "weak" (1969) El Niño (intensity scale according to Quinn *et al.*, 1987) (from Druffel, 1985).

Cole *et al.* (submitted) successfully adapted $\delta^{18}O$ in this manner at Tarawa, an atoll in the western Pacific subject to intense precipitation anomalies during ENSO events. Here, depleted rains (estimated -8 - -10°/$_{oo}$ $\delta^{18}O$ content) actually alter the isotopic composition of Tarawa surface waters during ENSO years when the Indonesian Low migrates to this vicinity (Fig. 5). The use of oxygen isotopes in this manner in continental margin reefs is largely untested, however, controls on the isotopic content of coastal water masses are potentially much more complex than in a remote atoll (Swart *et al.*, 1989).

The use of stable carbon isotopes is more complicated than that of $\delta^{18}O$, primarily due to extensive involvement of metabolic processes in carbon isotope fractionation. Corals are generally depleted of the heavier carbon isotope, ^{13}C, relative to thermodynamic equilibrium due to the same kinetic fractionations described for $\delta^{18}O$ (McConnaughey, 1989b). Here, however, the similarity ends. As temperature induced fractionation of carbon isotopes is small (-0.035°/$_{oo}$/°C - Rubinson & Clayton, 1969), skeletal $\delta^{13}C$ deviations beyond the kinetic effect derive from photosynthesis and respiration. These vital processes exert opposite

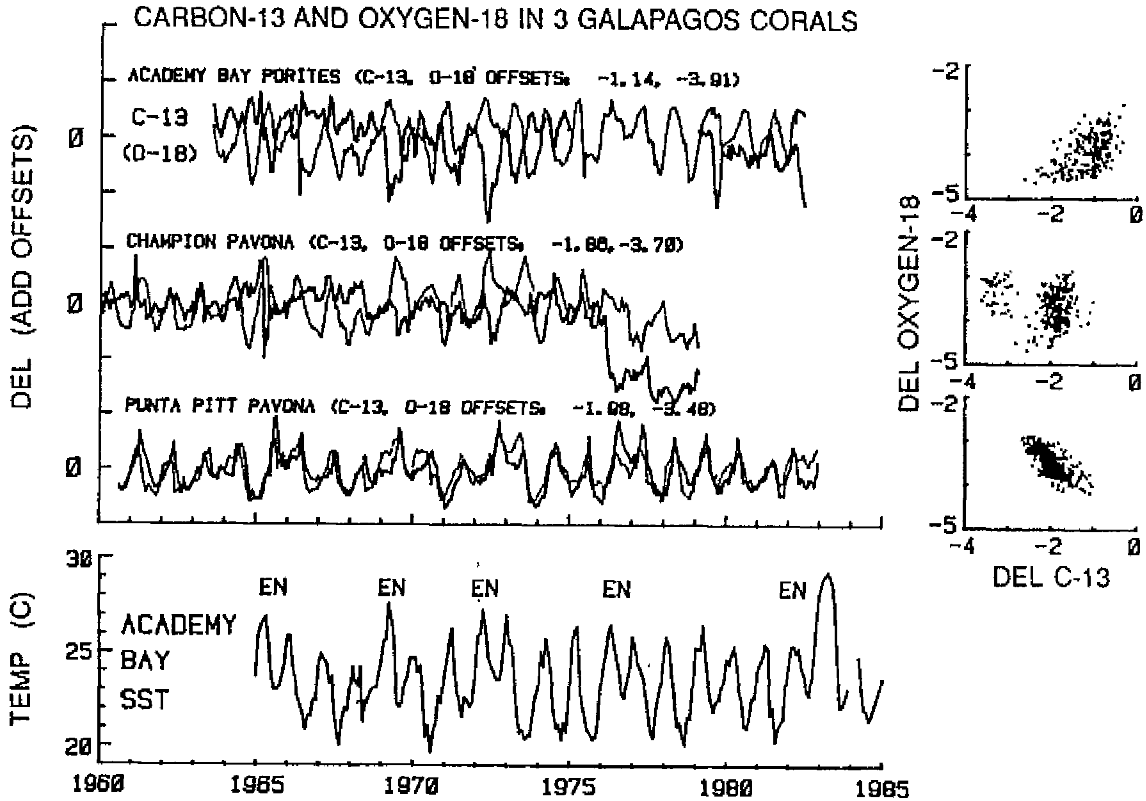

Fig. 4 - Isotopic records of three Galapagos corals, collected from three different reefs at approximately the low tide line (top), 3-4m (middle), and 14 m (bottom). In each panel, coral $\delta^{18}O$ (dark lines, positive downward) and $\delta^{13}C$ (light lines, positive upward) records are shown as deviations from mean values, given in parentheses. In all three corals, skeletal $\delta^{18}O$ varies inversely with temperature (bottom panel) and provides a consistent proxy for sea surface temperature. Skeletal $\delta^{13}C$ fluctuations apparently reflect ambient light levels, modulated by cloudiness. The sense of correlation is, however, opposite in deep and shallow corals. In the deep coral, skeletal $\delta^{13}C$ is highest during the warmest, generally least cloudy time of the year, presumably due to preferential use of ^{12}C by increased photosynthesis. The opposite result in shallow corals may reflect decreased coral photosynthesis in response to bright light at the sea surface (from McConnaughey, 1986).

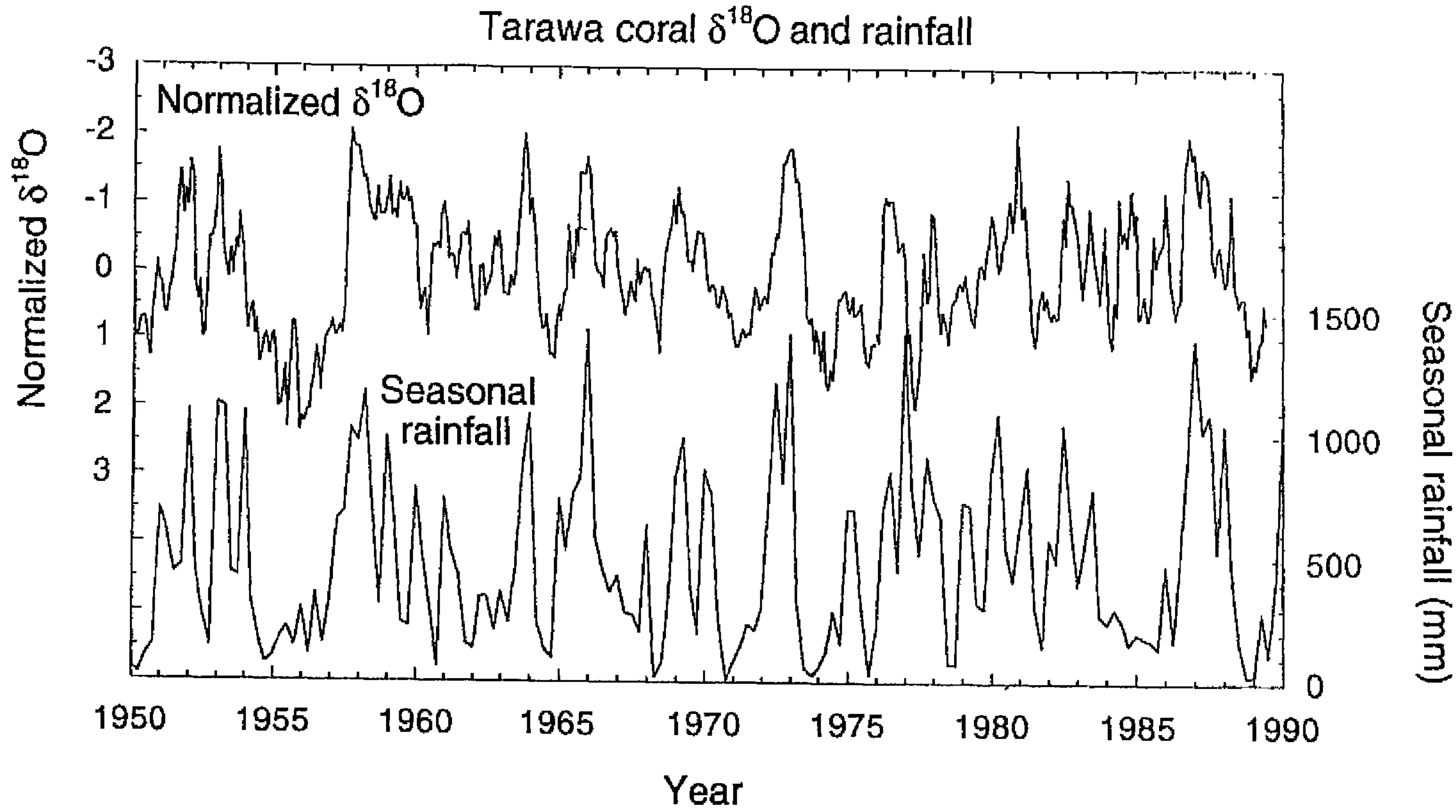

Fig. 5 - Comparison of normalized $\delta^{18}O$ in *Hydnophora microconos* and seasonal rainfall at Tarawa, Republic of Kiribati (1°N, 172°E). Large peaks (depleted $\delta^{18}O$, high rainfall) correspond to ENSO periods (*e.g.* 1951, 1953, 1957-58, 1963, 1965, 1972, 1976, 1987). The isotopic response is primarily caused by changes in surface ocean $\delta^{18}O$ resulting from seasonal rainfall and extremely intense precipitation during ENSO years (from Cole & Fairbanks, 1990, and Cole *et al.*, 1991).

influences on skeletal $\delta^{13}C$: photosynthesis preferentially fixes light carbon into coral tissues, thereby enriching the calcification reservoir in ^{13}C, whereas respiration adds back depleted carbon (Goreau, 1977; Swart, 1983; McConnaughey, 1989a; Muscatine *et al.*, 1989). Observed correlations between $\delta^{13}C$ and seasonal changes in light intensity (Fairbanks & Dodge 1979; Patzold, 1984) derive from the balance between these metabolic controls. An example of the positive modulation of skeletal $\delta^{13}C$ by photosynthesis in a deep-dwelling (14 m) coral is shown in the third panel of Fig. 4. At Punta Pitt, a negative correlation between $\delta^{18}O$ and $\delta^{13}C$ is the expected result given that high SSTs coincide with high light levels at Galapagos. Past attempts to couple carbon and oxygen isotope fractionation mechanisms in corals have been confused by the existence of different SST - insolation relationships in different locales (Fairbanks & Dodge, 1979) as well as light saturation effects (also explained in Fig. 4) which may influence corals residing in shallow waters (McConnaughey, 1989a). Changes in the isotopic content of reef waters due to photosynthetic removal of $^{12}CO_2$ can also influence the isotopic state of coral skeletons, but often the largest of these variations occur diurnally (Weber & Woodhead, 1971; Smith & Kroopnick, 1981) and little trace of this effect is seen in coral subsamples that integrate longer growth periods. Seasonal water mass shifts in $\delta^{13}C$ are a more likely possibility in coastal zones subject to runoff or in strong upwelling areas. Temporal records of $\delta^{13}C$ from such locales must be interpreted with these influences in mind.

7.2. Minor and trace elements

In parallel with the development of stable isotopic tracers in corals, investigators have addressed the feasibility of using alkali, alkaline earth, and transition metals as environmental and physiological indicators. A major difficulty in this effort has been identifying cations that reside in a well-behaved host phase. For example, cations that physically replace Ca^{2+} in the octahedral lattice of aragonite would be expected to comprise a more permanent and reproducibly analyzed elemental population than adsorbed or organically-bound cations. The alkali metals are generally too small to effectively substitute for Ca^{2+}, and their monovalent charge poses problems with coordination (Amiel *et al.*, 1973). Measured levels of these metals in corals show wide variations and incorporation mechanisms are poorly understood. Near-neighbor alkaline earth metals are among the most promising of candidates, and indeed relationships between skeletal and aquatic chemistry have been identified for the larger alkaline earths Sr, Ba, and Ra. Oomori *et al.* (1983) have measured variations in Mg content in *P. lutea* (up to 30%) which they ascribe to temperature and growth rate changes, however, several earlier studies found no relationship between skeletal and dissolved concentrations nor evidence of temperature/ growth rate dependences for this small radius group II element (Swart, 1981; Weber, 1974). Variable background levels and interpretation of distributions of scarcer elements has resulted in much confusion as to uptake mechanisms and utility of many other metals (Howard & Brown, 1984).

Analytical advances have more recently enabled quantification of a variety of trace elements in corals, many of which appear to be compatible in the aragonite lattice. Some of these concentration measurements are summarized in Table 2. For the most part, abundances of these trace constituents are very low (0.4-1000 ppb) and difficult to measure. Table 2 also presents estimates of distribution coefficients (D) based on measured coral metal/calcium ratios and

Cation	Effective ionic radius[1] (A)	Measured abundance in coral*	Estimated D
Ra^{2+}	1.48	6 dpm ^{226}Ra/100 g [2]	0.8 [6]
Ba^{2+}	1.42	$4\text{-}6 \times 10^{-6}$	1.0-1.5 [7]
Pb^{2+}	1.29	$4\text{-}60 \times 10^{-9}$	2.3 [8]
Nd^{2+}	1.29	$0.3\text{-}6.6 \times 10^{-9}$ [3]	1.0-1.9 [9]
Sm^{2+}	1.27	$0.1\text{-}2.3 \times 10^{-9}$ [3]	1.6-3.8 [9]
Sr^{2+}	1.26	$7.5\text{-}9.8 \times 10^{-3}$ [4]	1.0 [4]
Ca^{2+}	1.12	0.40	
Cd^{2+}	1.10	$0.4\text{-}7 \times 10^{-9}$	0.9-2.0 [10]
Mn^{2+}	0.96	$15\text{-}1000 \times 10^{-9}$	0.1-0.6 [11,12]
Fe^{2+}	0.92	$100\text{-}1500 \times 10^{-9}$	6-30 (?) [13]
Co^{2+}	0.90	$1\text{-}10 \times 10^{-9}$ [5]	0.2-2.0 [14]
Zn^{2+}	0.90	$30\text{-}100 \times 10^{-9}$	7-13 (?) [15]
Cu^{2+}	0.81 (*extrapol.*)	$10\text{-}300 \times 10^{-9}$	0.1-3.0 (?) [10]

* expressed as mole ratios relative to calcium.

? denotes measurements with high susceptibility to contamination.

References for oceanic metal concentrations: (1) Shannon (1976); (2) Dodge & Thompson (1974); (3) Shaw & Wasserburg (1985); (4) deVilliers *et al.* (1992); (5) Weber (1974); (6) Broecker *et al.* (1976); (7) Chan *et al.* (1977); (8) Boyle *et al.* (1987); (9) Klinkhammer *et al.* (1983); (10) Bruland & Franks (1983); (11) Landing & Bruland (1987); (12) Yeats & Bewers (1985); (13) Landing & Bruland (1987); (14) Boyle *et al.* (1987).

Table 2 - Cations with effective ionic radii, measured abundances in corals, and estimated distribution coefficents (*uncited data based on published and unpublished work of this author*).

estimated seawater concentrations of the respective metals at given sites. Interestingly, nearly all of the estimated D's lie within an order of magnitude of unity. This is suggestive of an overall kinetic control mechanism since thermodynamic D's would be expected to show a wider range (Shen & Sanford, 1990). Little is actually known about the physiological transport processes between seawater and skeleton, however, McConnaughey (1989b, 1989c) has suggested that the dominant cation, Ca^{2+}, may enter chiefly through fluid connections rather than enzymatic transport. If contaminant cations behave similarly, the overall influence of vital processes on metal uptake would be appreciably smaller than that observed for oxygen and carbon isotopes.

7.2.1. Cadmium

A close resemblance between oceanic dissolved cadmium and nutrients forms the basis for cadmium's use as an ENSO tracer. Like dissolved phosphate or nitrate, Cd exhibits a steep concentration gradient in the upper ocean as a result of biological fixation in surface waters and remineralization in deeper waters (Boyle *et al.*, 1981). In most tropical waters, this vertical fractionation remains relatively constant seasonally and interannually. In the eastern equatorial Pacific, however, the upper ocean is highly dynamic. Seasonal upwelling enhances levels of nutrients and nutrient-like elements in the surface layer. In the opposite season, this upward flux of regenerated nutrients is diminished. As corals reside in the surface layer, they form a permanent Cd archive and hence, a continuous record of upwelling intensity at locations like the Galapagos Islands (Fig. 6a) (Shen *et al.*, 1987; Linn *et al.*, 1990; Shen & Sanford, 1990).

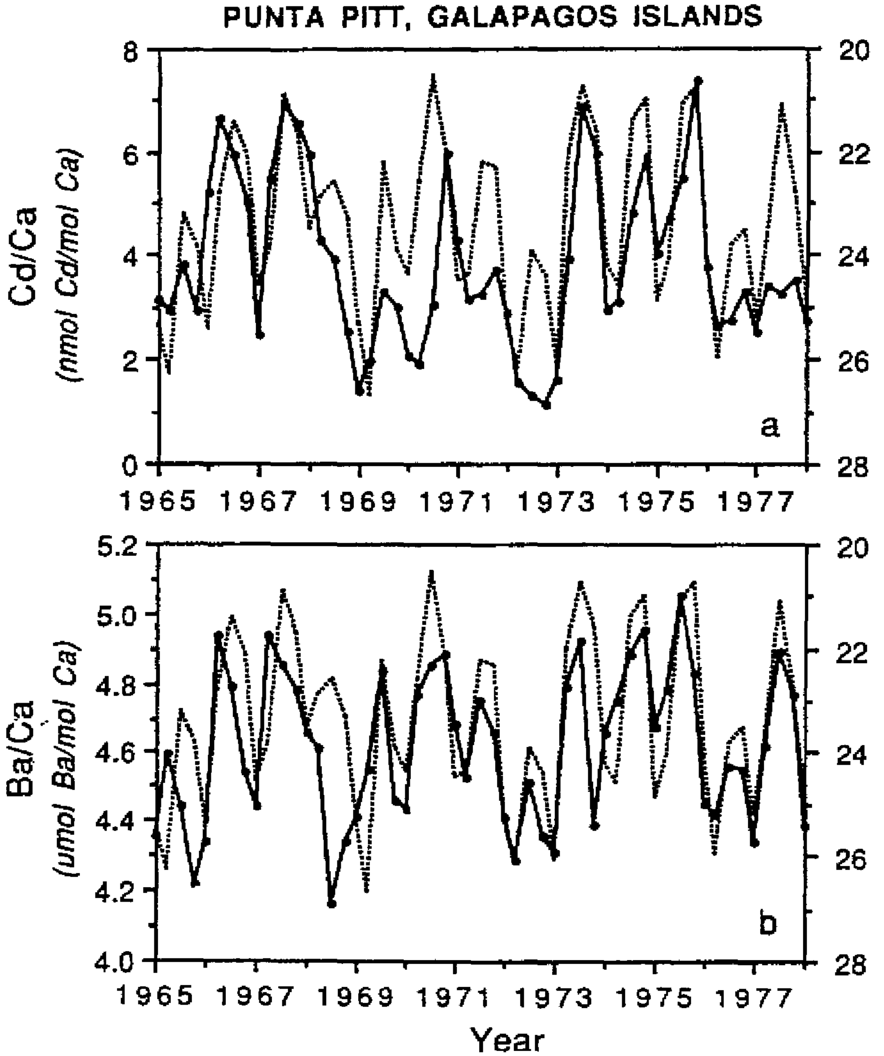

Fig. 6 - a) Cd/Ca (solid lines) measured at quarterly intervals in *Pavona clavus* collected from San Cristobal Island, Galapagos Islands. Note the inverse relationship to SST (broken line-axis is reversed) as measured at Santa Cruz Island (Charles Darwin Research Station). The most prominent El Niño during this period, the 1972 event, is marked by an attentuated cool phase, overall warm temperatures, and low Cd/Ca (data from Cole *et al.*, 1992). b) same as (a) but for coralline Ba/Ca (data from Lea *et al.*, 1989).

ENSO events are recorded either as intervals lacking a normal 6-month cool phase or sometimes as anomalously low-Cd growth intervals. By establishing relationships between dissolved Cd, nutrients, and SST, the coral record can be used to quantitatively infer historical environmental fluctuations (Shen *et al.*, 1992b).

7.2.2. Barium

Barium has the potential to be used as an ENSO marker in several ways. Most obviously, Ba is also fractionated biologically in the oceans (Chan *et al.*, 1977) and thus can be used in a similar manner to Cd in upwelling areas (Fig. 6b) (Lea *et al.*, 1989). The main difference between these two nutrient proxies lies in barium's longer residence time in surface waters (Lea & Boyle, 1991) and tendency to regenerate deeper in the ocean than Cd.

There is also a possibility that Ba precipitation in aragonite is temperature dependent. The magnitude of such an effect is presently unknown, however, assuming a dependence similar to that of Sr, Lea *et al.* (1989) suggested that 20% of the Ba/Ca variation they observed in a Galapagos coral may be due to temperature. If both a hydrographic and temperature control exists in the eastern Pacific for Ba uptake in corals, their effects are additive; *i.e.* increased upwelling adds skeletal Ba via vertical advection and higher partitioning under colder conditions.

Another geochemical property of Ba which may find use in ENSO reconstruction is this element's enrichment in rivers and estuaries (Edmond *et al.*, 1978). The combination of a strong weathering flux and estuarine desorption from suspended particles makes dissolved Ba a potentially sensitive runoff indicator (Shen & Sanford, 1990). In areas which experience large positive or negative rainfall anomalies such as the western tropical Pacific, this signal may prove to be a reliable fingerprint of historical ENSO activity. A pilot study of Porites lobata growing in the Gulf of Papua, south of New Guinea, shows preliminary evidence of this hypothesized effect (Fig. 7). Seasonal and interannual Ba/Ca variations in a coral collected off Darnley Island exceed those previously measured in corals from either the Galapagos or Caribbean (Lea *et al.*, 1989; Shen & Sanford, 1990 - note D also appears smaller for *Porites*). These variations are likely modulated by discharge of the Fly River (14th largest river in sediment load draining 76,000 km^2 of New Guinea - Milliman & Syvitski, 1992) into the Gulf of Papua approximately 130 km to the north. Comparison of the Darnley Island Ba/Ca data to sea level pressure (SLP) at Darwin, Australia (Fig. 7) shows an expected antithetical relation over the earlier part of the record (1963-1975), however, this inverse correlation weakens in the more recent period. The cause of the variable response is unclear, but may stem from competing circulation effects over the Great Barrier Reef Shelf (Wolanski *et al.*, 1984). Recovery of additional drill cores near this and other large Australasian estuaries may eventually provide useful measures of regional rainfall variability associated with ENSO.

7.2.3. Manganese

Manganese is another example of an element with possible uses on both sides of the Pacific in coral-based ENSO reconstruction. In the upwelling region of the eastern Pacific, its use is again based on the existence of a vertical concentration gradient. The sense and the origin of this gradient, however, differs markedly from that of Cd and Ba. An omnipresent

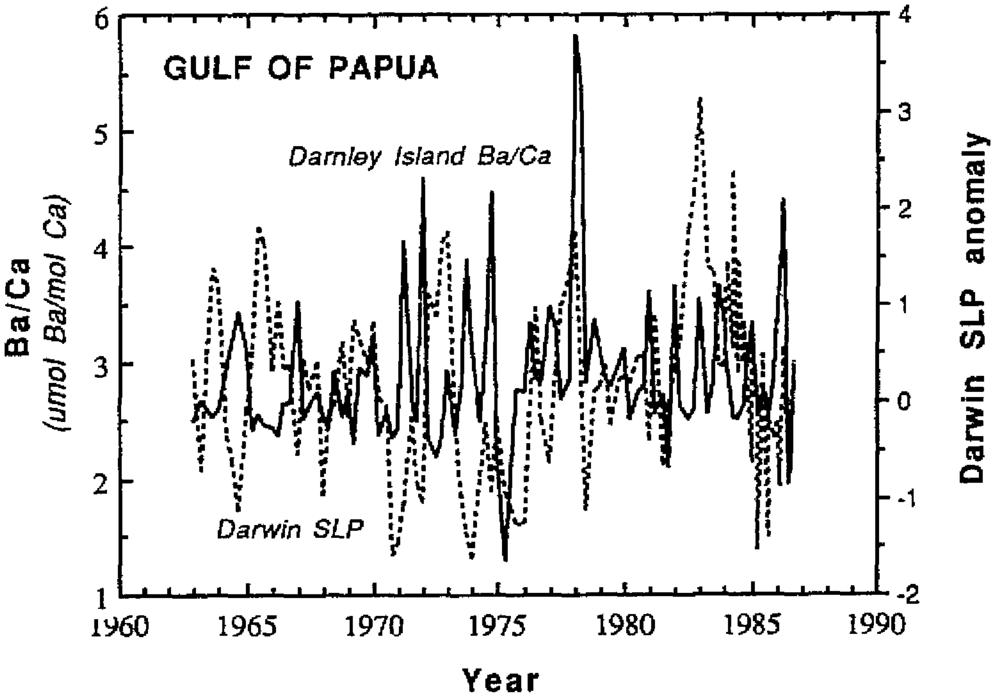

Fig. 7 - Preliminary Ba/Ca measurements in *Porites lobata* (solid line) from Darnley Island, Gulf of Papua for the period 1963-1987 compared with Darwin sea level pressure (SLP) anomaly (dashed line). Low pressure at Darwin is associated with heavy rainfall over Australasia, which should be indexed as high Ba/Ca at Darnley Island (see text). *(Coral data courtesy of D. LeBel of U. Washington; sample collected and processed by P. Isdale and G. Brunskill of AIMS).*

surface maximum in dissolved Mn in the eastern Pacific reflects inputs from laterally advecting continental shelf waters, rivers, and atmospheric dust (Klinkhammer & Bender, 1980; Martin *et al.*, 1985; Landing & Bruland, 1987). Since the Mn gradient is the opposite of that of Cd or Ba, a consistent skeletal signal should be temporally out-of-phase with the signals generated by the nutrient analogues (or in-phase with SST) (Shen & Sanford, 1990; Linn *et al.*, 1990; Shen *et al*, 1991). This pattern is generally what is observed at Urvina Bay in the Galapagos Islands (Fig. 8). A closer analysis of Mn variability in waters of the Galapagos archipelago is given by Shen *et al.* (1992b) and Delaney *et al.* (in press) and some discussion follows in section VIII.

The most recent development in the use of Mn as an ENSO indicator relates to the western Pacific basin (Shen *et al.*, 1992a). Chemical variability in the surface ocean here is expected to be minimal as vertical mixing is mild relative to the eastern basin. Yet, in an examination of Mn levels in a colony of *H. microconos* from Tarawa (1°N, 173°E), dramatic interannual changes have been observed (Fig. 9). Specifically, Mn/Ca ratios are highly perturbed during three El Niño - Southern Oscillation events (1965, 1972, 1976) which occurred within the growth period 1960-1977. These features co-occur with negative $\delta^{18}O$ pulses recorded in the same coral which are the result of torrential rainfall (Cole & Fairbanks, 1990).

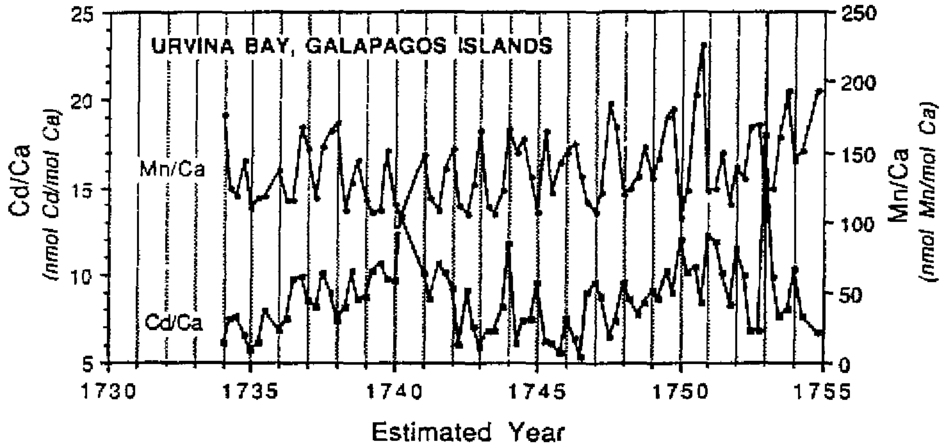

Fig. 8 - Quarterly measurements of Cd/Ca and Mn/Ca in *Pavona clavus* from Urvina Bay, Isabela Island, Galapagos Islands. The age of this section is based on band counting of this tectonically uplifted coral (from Shen *et al.*, 1991).

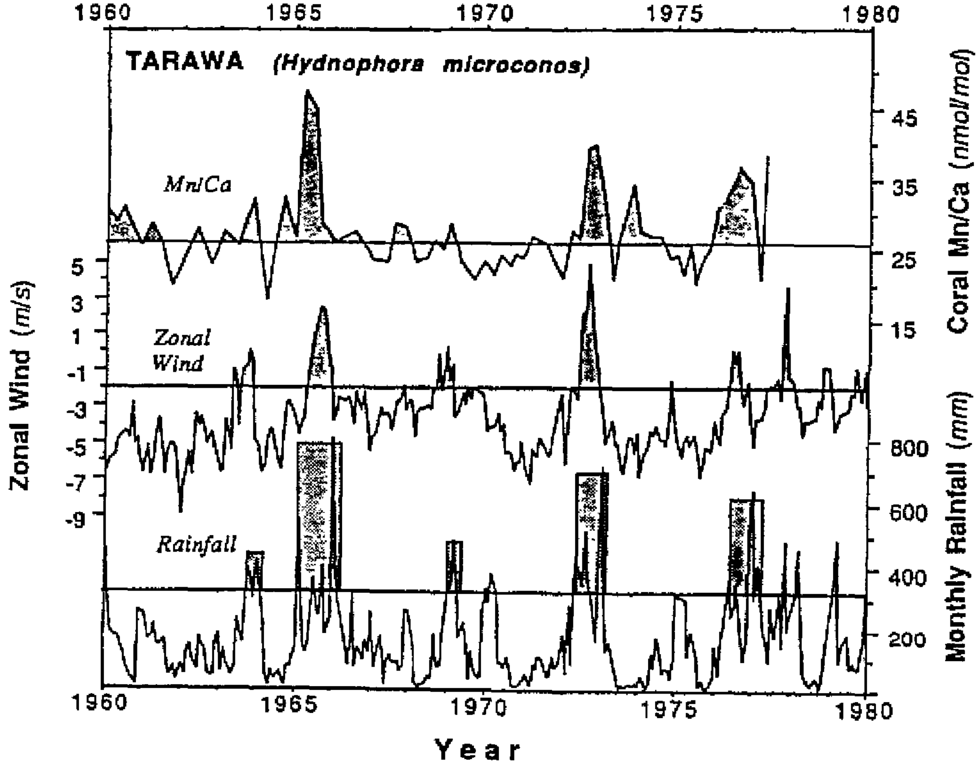

Fig. 9 - Mn/Ca measurements in *Hydnophora microconos* compared with monthly zonal winds and monthly mean rainfall at Tarawa for the period 1960-1977. Reference lines are arbitrarily chosen to highlight five ENSO events indexed over this time interval (1963: *very weak*, 1965: *moderate*, 1969: *weak*, 1972-1973: *strong*, and 1976: *moderate* - intensities according to Quinn *et al.*, 1978 and 1987) (from Shen *et al.*, 1992a).