

The most plausible explanation relates to the occurrence of westerly wind anomalies during the early and mid-phases of ENSO (Luther *et al.*, 1983). These anomalies were persistent enough in 1965 and 1972 to actually reverse the monthly mean zonal wind direction for five consecutive months (Harrison, 1987). Shen *et al.* (1992a) hypothesized that these westerlies, often exceeding speeds of 5 m/sec, generate sufficient wave action to create an aura of diagenetically remobilized Mn from within the shallow westward facing lagoon of Tarawa. If this phenomenon occurs at other atolls in this remote Pacific ENSO rainfall belt, coral drill cores may provide a useful spatial record of historical perturbations in low level trade winds.

7.2.4. Strontium

Strontium is a comparatively abundant constituent of reef corals, occurring at a level of about 8 parts per thousand by weight. The existence of an inverse relationship between skeletal Sr in aragonitic corals and temperature was first documented by Houck *et al.* (1977) and Smith *et al.* (1979). Their analysis of small variations in skeletal Sr/Ca content by atomic absorption, however, limited the precision of this paleothermometer to only $\pm 2^\circ\text{C}$ and the method languished for a decade. Recently, Beck *et al.* (1992) reattacked the problem using high-precision thermal ionization mass spectrometry (TIMS) and demonstrated a Sr/Ca measurement reproducibility of $\pm 0.3\text{‰}$ which translates to a theoretical analytical precision in temperature of $\pm 0.05^\circ\text{C}$. Thus, Sr/Ca measurements in tropical Pacific corals have great potential to delineate historical seasonal temperature progressions as well as ENSO-related thermal anomalies in the surface ocean. At the Galapagos Islands, excellent agreement is found between quarterly measurements of Sr/Ca and SST and between Sr/Ca and $\delta^{18}\text{O}$ (Fig. 10a, 10b). Low Sr/Ca and depleted $\delta^{18}\text{O}$ values reflect periods of warmer temperature. The El Niño events of 1972 and 1976 are manifested similarly in all three of these records.

In a few key respects, the Sr/Ca thermometer may well prove more accurate than $\delta^{18}\text{O}$ (de Villiers *et al.*, submitted). Since Sr and Ca are both highly conservative elements (oceanic residence times $> 10^6$ years) and immune to fractionation by evaporation/precipitation processes, natural hydrographic variability should be small. Even where limited biological uptake of these constituents is observed in the upper ocean, the ratio of Sr to Ca appears to remain highly constant (Fig. 10c). The spread observed in Fig. 10c would in the worst case, introduce a temperature error of 0.5°C due to hydrographic variability. A second factor that may favor Sr/Ca as a temperature sensor is the relative susceptibility of Sr versus $\delta^{18}\text{O}$ to "vital influences". Preliminary studies of Sr/Ca variability along different growth trajectories in a single head coral suggest that precipitation rate effects are also small (de Villiers *et al.*, submitted).

7.3. Radiocarbon

The radiocarbon record in banded corals has provided a wealth of information on preanthropogenic ^{14}C levels on earth and the ventilation of the upper ocean (e.g. Druffel & Linick, 1978; Nozaki *et al.*, 1978; Druffel, 1989). Since pronounced vertical gradients in ^{14}C exist in the oceans, due either to progressive aging of subsurface waters or bomb fallout, corals are well poised to record perturbations to these gradients in tropical waters. In the eastern Pacific, such perturbations have in fact been documented in association with

PUNTA PITT, GALAPAGOS ISLANDS

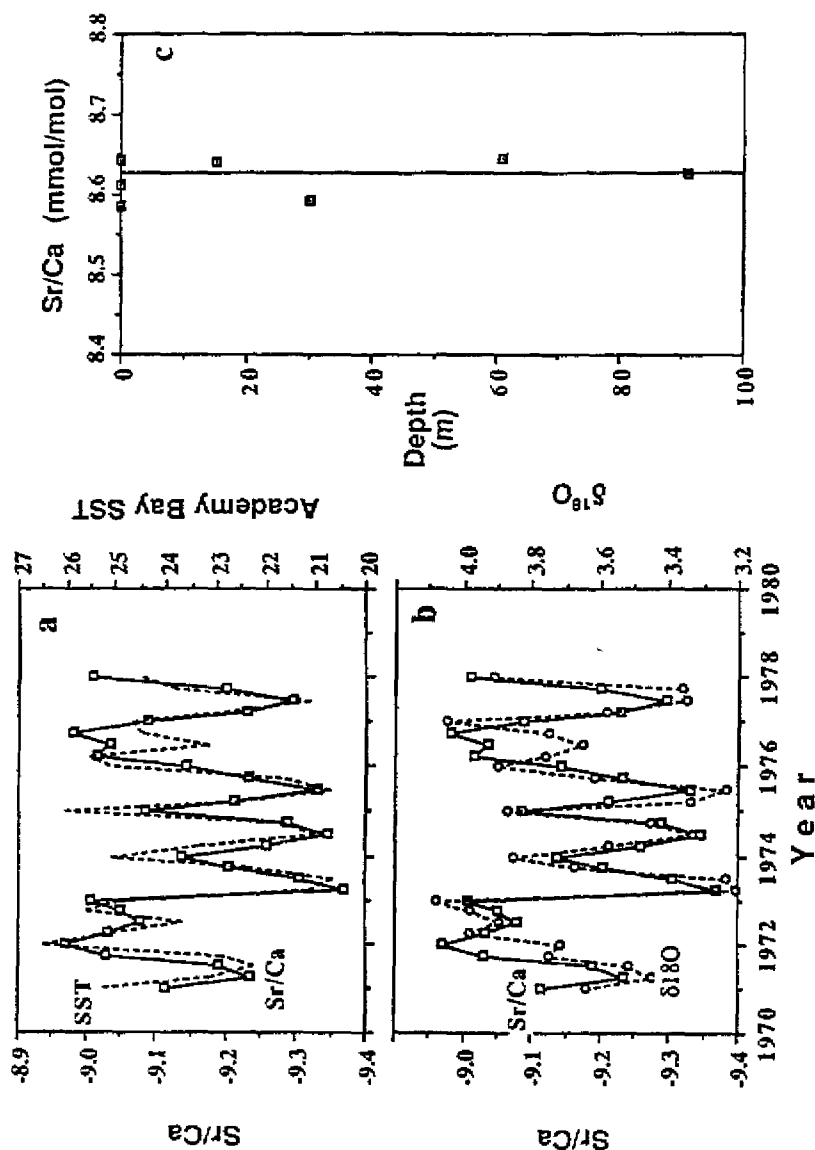


Fig. 10 - a) Sr/Ca measured in quarterly increments of *Pavona clavus* from San Cristobal Island, Galapagos Islands compared with SST at Academy Bay, Santa Cruz Island. b) Sr/Ca and $\delta^{18}\text{O}$ measurements in the same coral subsamples. c) Oceanic dissolved Sr/Ca in the upper 100 m west of San Cristobal Island (from de Villiers *et al.*, submitted).

hydrographic shifts brought about during El Niño. Druffel (1981) observed that radiocarbon levels in Galapagos corals generally increase during El Niño events, presumably due to a deepened thermocline and reduced upwelling of older ^{14}C -depleted waters. In a more recent study (Druffel & Griffin, submitted), the opposite effect has been observed in corals from the southern Great Barrier Reef. Low ^{14}C levels recorded during ENSO events suggest either that upwelling in this corner of the southwestern Pacific is enhanced or that unidentified ^{14}C -depleted waters are advected shoreward during these periods.

7.4. Marine/terrestrial humic and fulvic acids

A review of the geochemical tracers covered to this point quickly reveals a bias toward inorganic constituents thought to reside as integral parts of the mineral structure of corals. Isdale (1984) demonstrated, however, that certain components of dissolved organic matter may also be useful as runoff tracers. Although humic and fulvic acids are among the most poorly characterized of all compounds, those that are derived from land can be readily distinguished from those of marine origin through their fluorescence spectra (Boto & Isdale, 1985; Coble *et al.* 1990). In this manner, detailed reconstructions of fluvial discharge can be obtained from strategically-positioned corals in coastal environments (Isdale, 1984; Smith *et al.*, 1989). Humic and fulvic residues are apparently long-lived, as fluorescent banding has been observed in reef terraces of 100-250 kyr age in the Sinai Peninsula (Klein *et al.*, 1990). As for the case of the fluvial tracer, Ba, fluorescence banding may find particular use throughout Australasia where precipitation anomalies are the premier manifestation of ENSO. Both of these tracers, however, must be used with care as their river sources can be highly localized. Spatial variability in coral fluorescence has been observed on 25 km distance scales in the Java Sea (Scoffin *et al.*, 1989).

8. CALIBRATION OF GEOCHEMICAL PROXIES

Although each of the examples discussed previously can be viewed as a test of particular tracer of a specific environmental parameters in a particular coral species, few directed studies have been carried out to calibrate the performance of multiple tracers in a single coral colony. The results of one such effort are summarized in Fig. 11 and Table 3 (Shen *et al.*, 1992b). Here, the temporal variability of five geochemical tracers in a 47-year coral growth interval from the Galapagos Islands is compared against the SST record at Puerto Chicama, Peru. Linear least squares regressions for four of these tracers ($\delta^{18}\text{O}$, $\delta^{13}\text{C}$, Ba/Ca, and Cd/Ca) show highly significant correlations with Peruvian SST. Over specific frequency bands (annual, biennial, and ENSO (3.8 yrs)), cross-spectral comparisons show even stronger coherency, with Peruvian SST commonly accounting for 70-90% of the variance in these tracers. Judging from the performance of Sr/Ca in the limited seven-year analysis of the same coral (Fig. 10), we would expect this tracer to compare with the best in Fig. 11. These results can be viewed as high marks for the performance of these tracers, particularly when one considers the distance separating proxy from instrumental record, uncertainties in sampling/dating/analysis, and basic differences in tracer dynamics. The temperature correlation with $\delta^{18}\text{O}$, Sr/Ca, and the nutrient analogues Ba and Cd appears principally controlled by seasonal and interannual upwelling cycles. High SSTs which occur during both the normal warm season and during El Niño periods, are reflected by depleted values

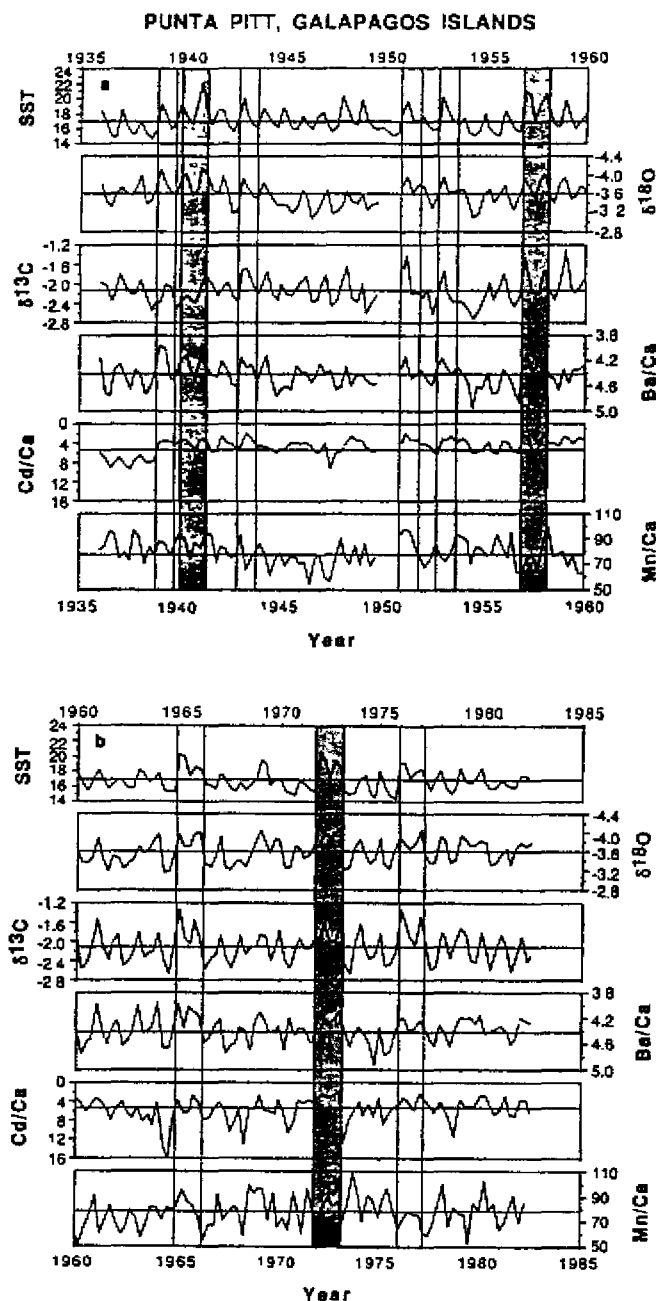


Fig. 11 - Quarterly SST at Puerto Chicama, Peru and coral geochemical tracer data from Punta Pitt, San Cristobal Island, Galapagos Islands for the period 1936-1982. Peruvian SST is plotted positive upward. Tracers are plotted such that El Niño conditions appear as positive deviations ($\delta^{18}\text{O}$, Ba/Ca, Cd/Ca are reversed; $\delta^{13}\text{C}$ and Mn/Ca are normal). Nine El Niño events of "moderate" to "strong" intensity (Quinn *et al.*, 1987) are indicated (from Shen *et al.*, 1992b).

	$\delta^{18}\text{O}$	$\delta^{13}\text{C}$	Ba/Ca	Cd/Ca	Mn/Ca	PC SST
$\delta^{18}\text{O}$		-69 (.0001)	+72 (.0001)	+51 (.0001)	-32 (.0001)	-65 (.0001)
$\delta^{13}\text{C}$			-60 (.0001)	-45 (.0001)	+14 (.06)	+61 (.0001)
Ba/Ca				+39 (.0001)	-10 (.17)	-64 (.0001)
Cd/Ca					-08 (.28)	-51 (.0001)
Mn/Ca						+09 (.23)

Table 3 - Least squares correlation coefficients (R) for 1936-1982 quarterly raw data series. Significance levels are indicated parenthetically (PC = Puerto Chicama; SST quarters defined as FMA-MJJ-ASO-NDJ).

of $\delta^{18}\text{O}$, Sr/Ca, Ba/Ca, and Cd/Ca. The inverse relationship between SST and $\delta^{13}\text{C}$ most likely derives from the coexistence of warm ocean conditions and high irradiance in the Galapagos archipelago as discussed earlier. Thus, the warm season and El Niño are both manifested by depleted $\delta^{13}\text{C}$. Phase relationships derived from spectral analysis of the data confirm each of the above dynamic associations.

The fifth tracer in Fig. 11, the transition metal Mn, exhibits more complex variability. Throughout most of 1936-1982, Mn/Ca cycles appear approximately 6 months out-of-phase with respect to $\delta^{18}\text{O}$, Ba, and Cd (in-phase as plotted in Fig. 11). This has been attributed to the existence of a surface maximum of dissolved Mn which is found in most open ocean settings (Shen *et al.*, 1991; 1992b). Periodically, however, Mn/Ca shifts into phase with $\delta^{18}\text{O}$, Ba, and Cd (out-of-phase as plotted in Fig. 11) for periods of 1-2 years. This behavior as well as recent observations by Delaney *et al.* (in press) suggests that the surface Mn maximum may not a stable feature near Galapagos and that regional differences in trace element cycling may exist within the archipelago.

Proxy records such as those shown in Fig. 11 may also find use from the standpoint of identifying specific historical El Niño events and describing the surface ocean conditions which accompanied them. In the eastern Pacific, extremes in temperature, upwelling, and isolation can be categorized either as warm phase (El Niño) or cool phase ("anti-El Niño" or "La Niña") events. In Table 4, we consider the significance of the 12 greatest minima or maxima in the annually-averaged SST, isotopic, Ba, and Cd anomaly series which occurred in an El Niño sense (high-temperature, high-insolation, low-nutrient). Quinn *et al.* (1987) identify nine events of "moderate" to "strong" intensity over the 47-year period of interest. Three of these straddled two consecutive years, hence the specification of 12 minima/maxima. Extrema in the four tracers $\delta^{18}\text{O}$, $\delta^{13}\text{C}$, Ba/Ca and Cd/Ca coincide with recognized El Niño events 73% of the time. For comparison, the dozen warmest anomalies in the annually averaged Puerto Chicama SST data set match known events 83% of the time. Thus, the geochemical tracers are nearly as successful as the instrumental temperature record in

ENSO	intensity rating	identification by 12 minima/maxima:				
		max SST	min $\delta^{18}\text{O}$	max $\delta^{13}\text{C}$	min Ba/Ca	min Cd/Ca
1939	M+		x		x	x
1940-1941	S	xx	xx	x	xx	x
1943	M+	x		x	x	x
1951	W/M	x	x	x		x
1953	M+	x	x		x	x
1957-1958	S	xx	xx	xx	x	xx
1965	M+	x	x	x	x	
1972-1973	S	x	x	x	x	x
1976	M	x	x	x	x	
Tracer-Niño match rate:		10/12	10/12	8/12	9/12	8/12
Matches incl. weak Niños:		12/12	11/12	8/12	11/12	9/12

* Scores include "weak" El Niño events of 1944, 1946, 1948, 1951, 1963, 1969, and 1975.

Table 4 - Correspondence between annually averaged SST and tracer anomalies and known "moderate-to-strong" (Quinn *et al.*, 1987) ENSO activity. Events marked by xx are identified by minima/maxima during both designated years.

identifying major events that have been historically indexed. Inclusion of lesser events catalogued as "very weak" to "weak" (i.e. events of 1944, 1946, 1948, 1951, 1963, 1969 and 1975; Quinn *et al.*, 1978) further improves the identification rate (81%), suggesting that even minor warming events can be detected in the proxy records.

9. LONG-TERM ENSO RECORDS TO DATE

Relatively few century-length records of ENSO activity have yet been produced from massive corals. More typically, short modern records have been generated as pilot studies or tracer calibrations as discussed earlier. Cole and coworkers (1992) have synthesized several contemporary studies from locations spanning the Pacific (Galapagos, Tarawa, Bali) to illustrate the feasibility of reconstructing spatial patterns of ENSO evolution. The longest coral record to date is a 350-year record of stable isotope, extension rate, and Mn variability at Urvin Bay, Isabela Island, Galapagos Islands (Dunbar *et al.*, 1991, and Shen *et al.*, 1991). Records of this length will ultimately improve our understanding of the frequency and intensity of ENSO events which predate the modern record (Enfield, 1989). The importance of longer records, however, transcends ocean-climate variation in the ENSO frequency band. The question of ocean variability on decadal and century scales is a fundamental one which remains poorly understood as long instrumental records are scarce and the record from deep-sea sediments cannot resolve this window. Close scrutiny of available climatic indices reveals that decadal shifts in Pacific climate have occurred recently; for example, from 1937-1946 and from 1977-1988 (Cooper *et al.*, 1989; Trenberth, 1990). Longer proxy records will allow us to evaluate the nature of these shifts during different periods in Earth's history.

The first clues from the coral record as to longer term oceanic changes are seen in annual growth band thickness variations and annual $\delta^{18}\text{O}$ measurements from western Galapagos (Fig. 12). Taken as a pure temperature signal, the $\delta^{18}\text{O}$ record suggests that at Urvina Bay, the period of the Little Ice Age was not uniformly cold as was the case in many continental areas, but instead was punctuated by warmer-than-average intervals at 1650-1670 and 1700-1800. Variance spectra for the Urvina Bay $\delta^{18}\text{O}$ (Dunbar *et al.*, 1991) and Mn/Ca (Shen *et al.*, 1991) records closely resemble each other over the period 1826-1954 and reveal

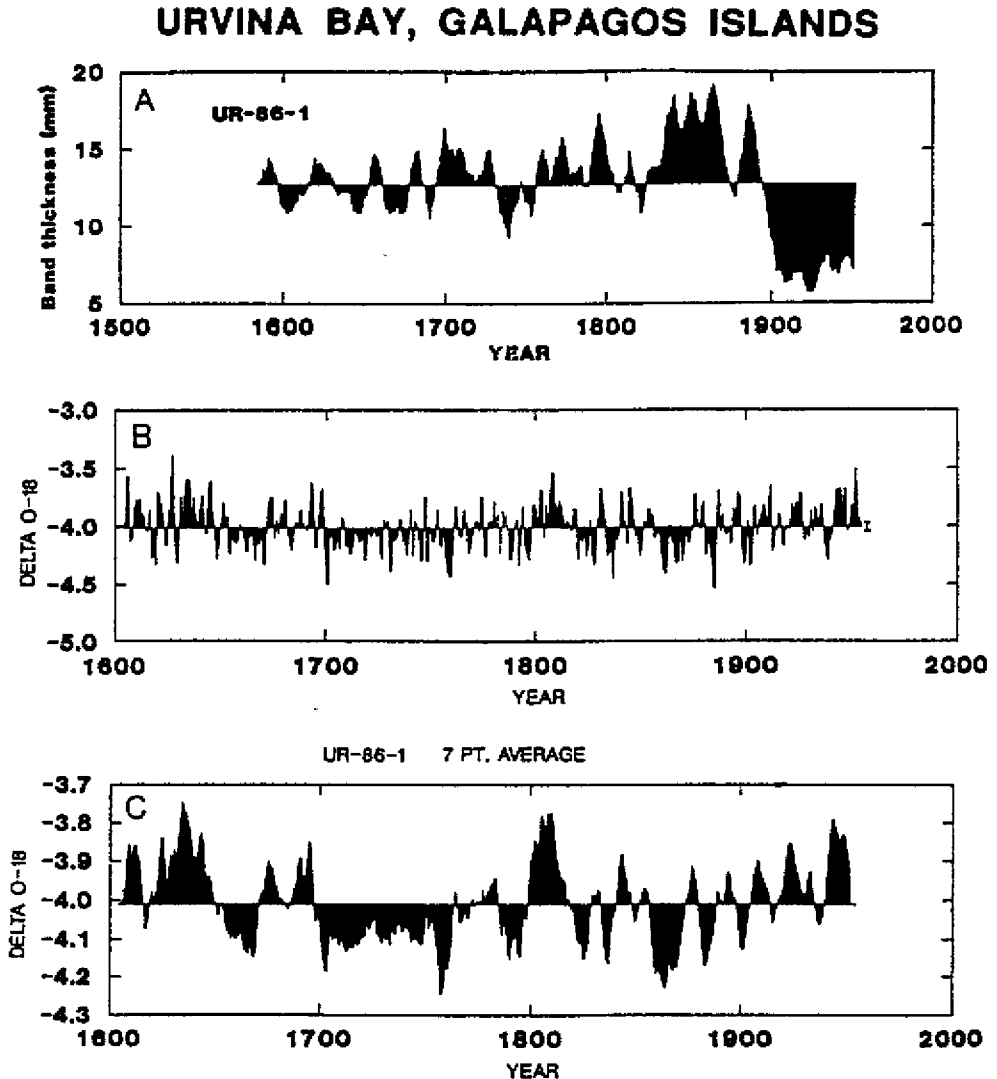


Fig. 12 - Time series records from Urvina Bay uplift coral (ca. 1600-1954), Isabela Island, Galapagos Islands (*Pavona clavus*). A) growth band thickness (7-point moving average); B) annually measured $\delta^{18}\text{O}$; C) annual $\delta^{18}\text{O}$ smoothed by a 7-point moving average filter (from Dunbar *et al.*, 1991).

a concentration of variance near 20 years. Dunbar *et al.* (1991) have also noted the existence of lower frequency periods near 30 and 50 years over the entire $\delta^{18}\text{O}$ record length. Corresponding growth band thickness (Dunbar *et al.*, 1991) and skeletal Mn/Ca spectra for the period 1600-1954 also show peaks near 11 and 20 years. A bi-decadal oscillation in surface temperatures has also been detected in instrumental records of surface temperature (Newell *et al.*, 1989; Chil & Vautard, 1991), however, its origin is uncertain and its persistence spatially and temporally is poorly documented (Eisner & Tsonis, 1991). Suggestions that solar forcing may influence climate have been made on the basis of tree ring, coral and varved sediment studies (e.g. Sonnett & Suess, 1984; Dunbar *et al.*, 1991; Anderson, 1992), however, mechanisms by which relatively small changes in irradiance might be amplified remain unclear. Longer records of SSTs from a variety of locales would be useful in establishing the significance this low-frequency mode.

Preliminary results from a second high resolution reconstruction from Galapagos show visible decadal variations which are mirrored by all three trace metal indicators - Cd/Ca, Ba/Ca, and Mn/Ca (Fig. 13). The colony under study, *Pavona gigantea*, was collected dead

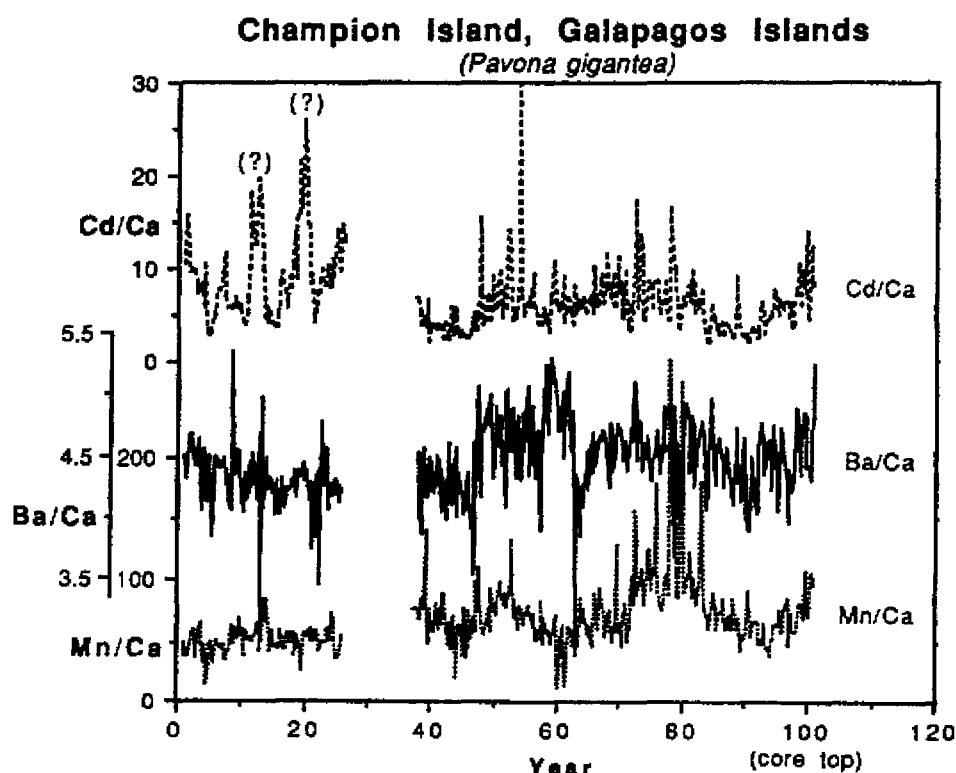


Fig. 13 - Preliminary trace element data (Cd/Ca, Ba/Ca, and Mn/Ca) from *P. gigantea* collected from Champion Island, Galapagos Islands. The interval shown is estimated to be 101 years in length (total colony length approx. 165 yrs), ending at the core top (right) which was dead at time of collection. Absolute chronology awaits analysis of U-Th by high-precision mass spectrometry (Dr. Bruno Hamelin - Université d'Aix-Marseille). Note the existence of low frequency changes in these century length records and similarities between the geochemical tracers.

from Champion Island, therefore, an absolute chronology will require U-Th mass spectrometric dating. The oscillations seen in Fig. 13 likely reflect long period variations in the upper ocean, on top of which are superimposed high frequency El Niño perturbations. Curiously, these low frequency oscillations are not apparent in the 47-year calibration record from Punta Pitt (Fig. 11). This implies that there may exist local hydrographic variations in the eastern archipelago, or that the Champion record predates that at Punta Pitt and reflects hydrographic characteristics not evident in the latter twentieth century.

10. SUMMARY

In the last two decades, our understanding of the biological and geochemical properties of reef corals has advanced remarkably. Today, we recognize the annual nature of coral growth bands to define time as we play back this natural recording device. In colonies which lack clear bands, radiometric means are at hand to date samples with excellent precision. Many trace constituents have been quantified and their environmental controls delineated with the result that we now possess the means to reconstruct the history of the tropical surface ocean in great detail far into the past. Because of the accessibility of living and fossil corals, their high-resolution data storage, and the unique geochemistry of aragonite precipitated in seawater, one may expect increasing focus on this natural recording system on the part of scientists from many disciplines. El Niño has been a catalyst and remains a perfect focal point for continued progress in the use of corals as a paleoceanographic/paleoclimate archive.

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