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REPORT

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# Assessing between-colony oxygen isotope variability in the coral *Porites lobata* at Clipperton Atoll

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**Abstract** The eastern Pacific warm tongue is a region of stable and elevated sea surface temperature (SST) located just north of the equator in the eastern Pacific. This warm water mass is thought to influence the position of the Intertropical Convergence Zone (ITCZ) in the eastern Pacific and to directly influence climate in Central America. To assess the use of corals in the development of paleoclimatic reconstructions in this region, we have developed oxygen isotope ($\delta^{18}O$) time-series from multiple specimens of the massive coral *Porites lobata* collected at Clipperton Atoll (10°18′N, 109°13′ W). Six near-monthly $\delta^{18}O$ records from different sized (age) colonies where produced for the interval 1986–1994, and three of these were extended back to 1969. All corals sampled were found to contain numerous fish-grazing skeletal scars ( ~ 0.5 mm deep scallop shaped hiatuses). Samples collected at 1 mm intervals showed anomalous $^{18}O/^{16}O$ in the area of a bite scar, with 2 to 2.5 mm sampling intervals (10–12/year) minimizing these effects. Our results show that the average $\delta^{18}O$ disequilibrium offset (vital effect) from equilibrium seawater composition for individual corals can vary by up to 0.4‰. However all $\delta^{18}O$ results suggest that the vital effect offset is constant over time. Similar "offsets" are observed in the tops of old (age = ~ 100 y) and young (age = ~ 10 y) colonies, further suggesting that the biologically mediated vital effect offset does not change as a *Porites* colony ages. A 6-coral average composite $\delta^{18}O$ record was constructed from 1985–1994 and a 3-coral average $\delta^{18}O_{anomaly}$ record was constructed from 1969–1994. Regression analysis between monthly SST and the 6 coral average $\delta^{18}O$ records yields an $r^2$ correlation of 0.54 (individual $r^2$-values ranged from 0.27–0.55). The 3 coral $\delta^{18}O_{anomaly}$ average record has an even lower correlation to SST, with an $r^2$ of 0.40. Potential causes of the only moderate correlation to SST are explored and we find that inferred salinity effects, fish grazing scars, and slight chronology imperfections have all contributed to a reduced correlation to SST. Nevertheless, all El Niño events in this time period appear to be recorded by coral skeletal $\delta^{18}O$.

**Key words** Corals · Oxygen isotopes · *Porites lobata* · Paleodimatology · Clipperton Atoll · Eastern Pacific

## Introduction

In the eastern tropical Pacific the highest mean annual sea surface temperature (SST) occurs not at the equator, but in an east-west elongated region between 5–10°N that is coincident with the average position of the Intertropical Convergence Zone (ITCZ) (Fig. 1). This warm water tongue is related to the eastward-flowing North Equatorial Counter Current, strong meridional wind stress, and is known to have a direct influence on the position of the ITCZ and climatic processes in the eastern Pacific and western America (PACS 1994; Philander 1990; Philander et al. 1996). In the first step of the development a 100 + year paleorecord of climatic variations in this region we have analyzed the oxygen isotopic ($\delta^{18}O$) composition of 4 short coral cores and of 2 small specimens of the massive hermatypic coral *Porites lobata* from Clipperton Atoll (10°18′N, 109°13′W) in order to examine between-colony $\delta^{18}O$ variability and the climatic significance of the isotopic signal.

Massive hermatypic coral skeletons are one potential source of tropical paleoclimatic information.

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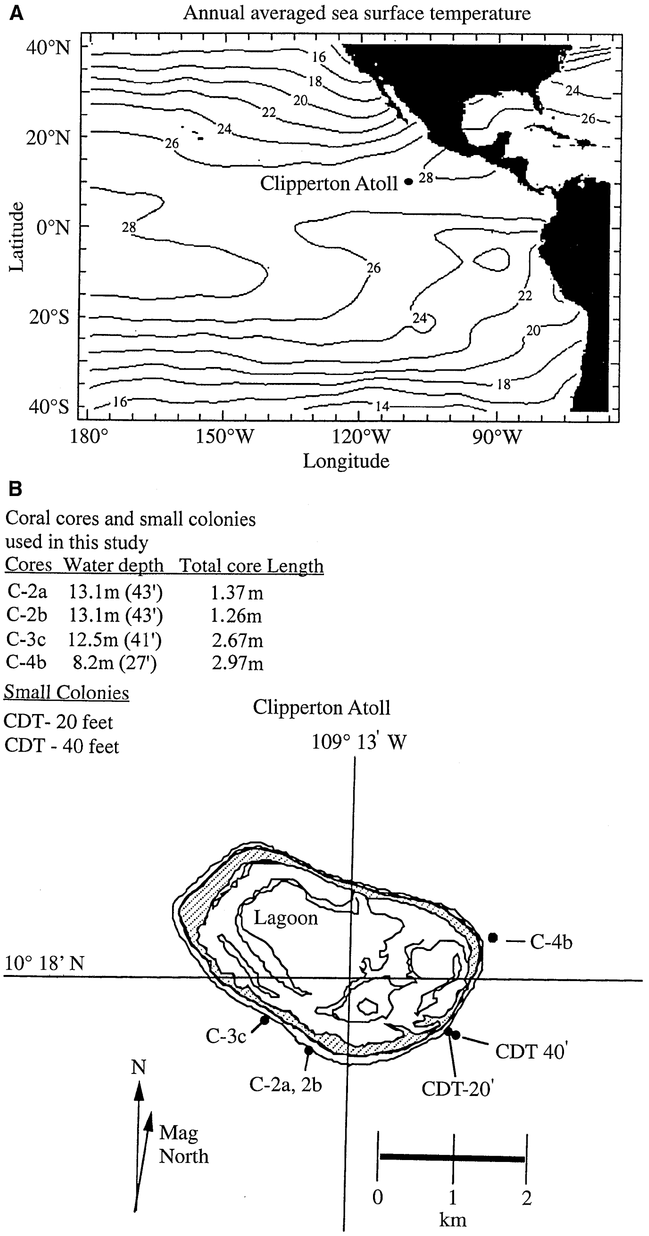
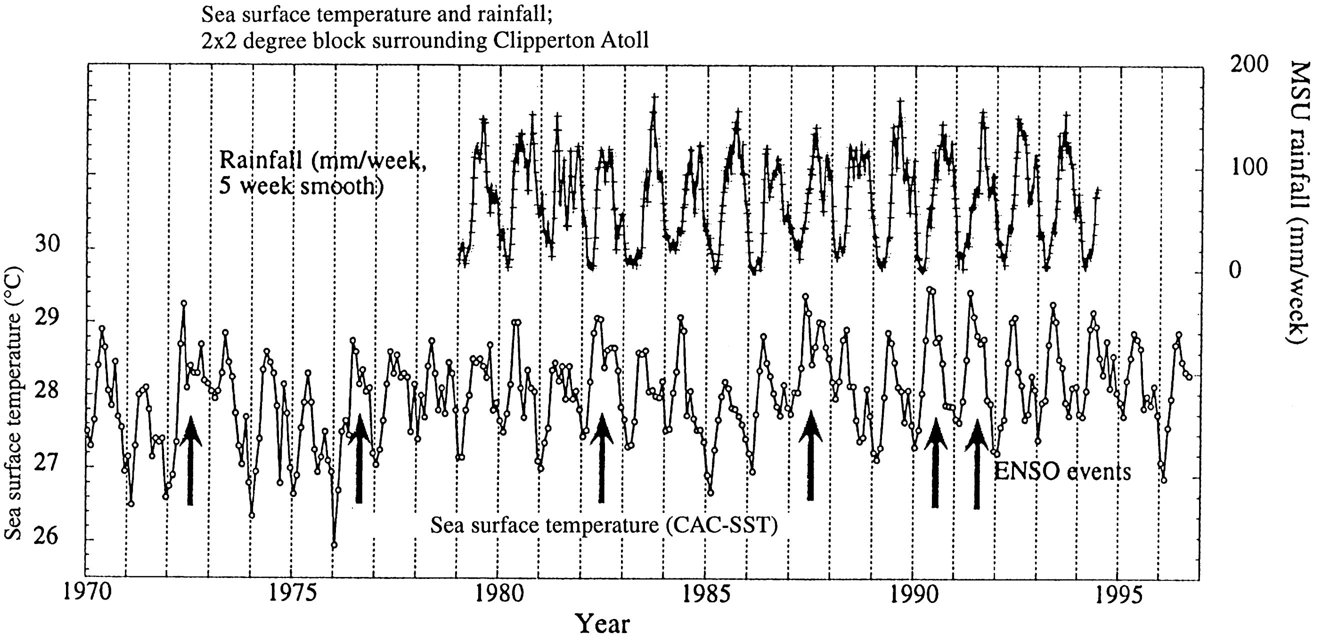


**Fig. 1A** Annually averaged sea surface temperature in the eastern Pacific (Levitus and Boyer 1994). Note the location of Clipperton in the east-west elongated region of elevated water temperature. **B** Enlargement of Clipperton Atoll showing locations of corals used in this study

Corals of this type live in the surface-ocean mixed layer, grow continuously at rates of several millimeters to several centimeters per year, and in many cases deposit annual skeletal density bands that have proven useful for development of annually resolved chronologies. The $\delta^{18}O$ composition of hermatypic corals has been utilized in numerous reconstructions of past SST, salinity, and seawater $\delta^{18}O$ composition (for example; Charles et al. 1997; Cole and Fairbanks 1990; Cole et al. 1993; Dunbar and Wellington 1981; Dunbar et al. 1994; Linsley et al. 1994; Quinn et al. 1993; Schrag et al. 1997; Swart et al. 1996a, b; Tudhope et al. 1996). Because the $\delta^{18}O$ composition of coral skeleton can be a function of both temperature and/or $\delta^{18}O$ of seawater, the use of this tracer in concert with independent measures of temperature such as Sr/Ca; (Alibert and McMulloch 1997; Beck et al. 1992) and Mg/Ca (Mitsuguchi et al. 1996) appears highly promising for de-convolving temperature and salinity at sites with large variations in both parameters.

The $\delta^{18}O$ of scleractinian coral skeletons is several parts per miL(‰) more depleted in $^{18}O$ than predicted for aragonite precipitated in $\delta^{18}O$ equilibrium with sea water (McConnaughey 1989; Weber and Woodhead 1970). Although this departure from equilibrium ("disequilibrium offset" or vital effect) appears to be constant in the axis of maximum coral growth (Land et al. 1975; McConnaughey 1989; Wellington et al. 1996), Barnes and Lough (1992) and Barnes et al. (1995) propose that the vital effect offset may not be constant over the life of a long-lived coral colony. Concerns have also been raised regarding the possible influence of metabolic and growth rate effects on the $\delta^{18}O$ signal (Allison et al. 1996; Barnes et al. 1995; Cohen and Hart 1997; de Villiers et al. 1995; Land et al. 1975; Lough et al. 1996; McConnaughey 1989; Taylor et al. 1995). Seasonal variation in coral skeletal extension rate and/or calcification rate have been proposed as possible sources of oxygen isotope fractionation which could mask or mimic the effect of temperature, salinity or other external environmental control (Allison et al. 1996; Barnes et al. 1995; Cohen and Hart 1997; de Villiers et al. 1995; Land et al. 1975; Lough et al. 1996). The amount or fraction of calcification that occurs within the tissue layer away from the outermost 1 to 2 mm of growing skeleton has also been proposed as a potential source of smoothing of the environmental record (Barnes and Lough 1992; Barnes et al. 1995; Taylor et al. 1995; Tudhope et al. 1996; Wellington et al. 1996). Finally, while the reproducibility of coral $\delta^{18}O$ records has been examined at several sites (Cole and Fairbanks 1990; Linsley et al. 1994; Tudhope et al. 1995; Wellington et al. 1996), questions still remain regarding the reproducibility of coral records and their regional significance. As part of this study we have assessed the impact of several of these potential problems on *P. lobata* at Clipperton Atoll.

Clipperton Atoll is the easternmost atoll in the Pacific lying 5700 km east of the Line Islands and 1000 km west from coastal Mexico (Fig. 1A, B). Clipperton lies within the North Equatorial Counter Current (NECC) in an area of relatively stable SST where temperature varies less than 2 °C annually (Reynolds 1988; Reynolds and Marsico 1993; Reynolds and Smith 1994) (Fig. 2). The island is one of only a few in this region, and in fact there are no islands between Clipperton and the Line Islands at 160°W. Over the last decade SST in



the 2° × 2° grid box surrounding Clipperton has averaged ∼ 28.5 °C and surface salinity has averaged ∼ 33.7‰ around Clipperton (Levitus et al. 1994; Reynolds and Smith 1994). SST maxima occur in May and average 29 °C and SST minima occur in January-February and average ∼ 27 °C. During El Niño Southern Oscillation (ENSO) warm-phase (El Niño) events, the surface ocean in the region of Clipperton warms between 0.5 °C (e.g. 1982–1983 and 1990–1994 events) and ∼ 1 °C (e.g., 1972–1973 and 1986–1987 events) (Reynolds 1988; Reynolds and Marsico 1993). During some ENSO events, SST minima at Clipperton reach only 28 °C (see Fig. 2). The climate near Clipperton is also seasonally effected by the ITCZ with a pronounced wet season lasting from May/June through November (Mitchell and Wallace 1990; Spencer 1993). Precipitation maxima lag SST maxima by at least 1 month and occasionally up to 2 months (see Fig. 2). Salinity in the 2.5 × 2.5 degree grid box that includes Clipperton is seasonally uniform from the surface ocean down to ∼ 30 m (Levitus et al. 1994), probably the result of surface water mixing enhanced by the prevailing northeasterly winds and large ocean swell (Fig. 3). Average surface salinity varies by < 0.8‰ annually, ranging from 33.3‰ in September-December to 34.1‰ in January-March (see Fig. 3), (Levitus et al. 1994). During ENSO warm-phase events, Clipperton is located at the boundary between a zone of high rainfall along the equator and a latitudinal belt of anomalously drier conditions just to the north (Deser and Wallace 1990; Hoerling and Ting 1994; Yulaeva and Wallace 1994; and others). This effect is most pronounced during large El Niños like the 1982/83 and 1997/98 events. Consequently, salinity of surface waters near Clipperton can be affected in opposite directions by different ENSO events.

**Fig. 2** Sea surface temperature (Climate Analysis Center, CAC, SST, 2° × 2° grid box; Reynolds 1988; Reynolds and Smith 1994), and MSU (Microwave Sounding Unit, 2.5° × 2.5° grid box) satellite estimated rainfall (Spencer 1993) in the vicinity of Clipperton Atoll. Years in which El Niño Southern Oscillation (ENSO) warm-phase (El Niño) events occurred are marked with arrows

## Methods

In April 1994 coral cores and specimens were collected from multiple heads of *P. lobata* at Clipperton (Fig. 1B). The colonies grew within 2 km of each other near the outer edge of a carbonate terrace surrounding the atoll. Water depths of individual colony tops

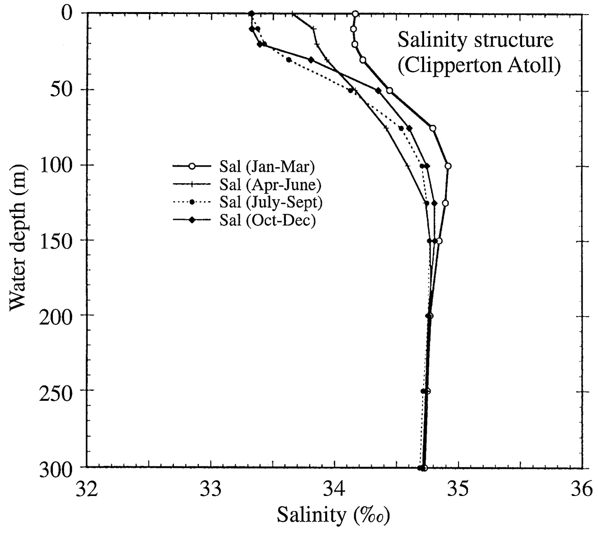
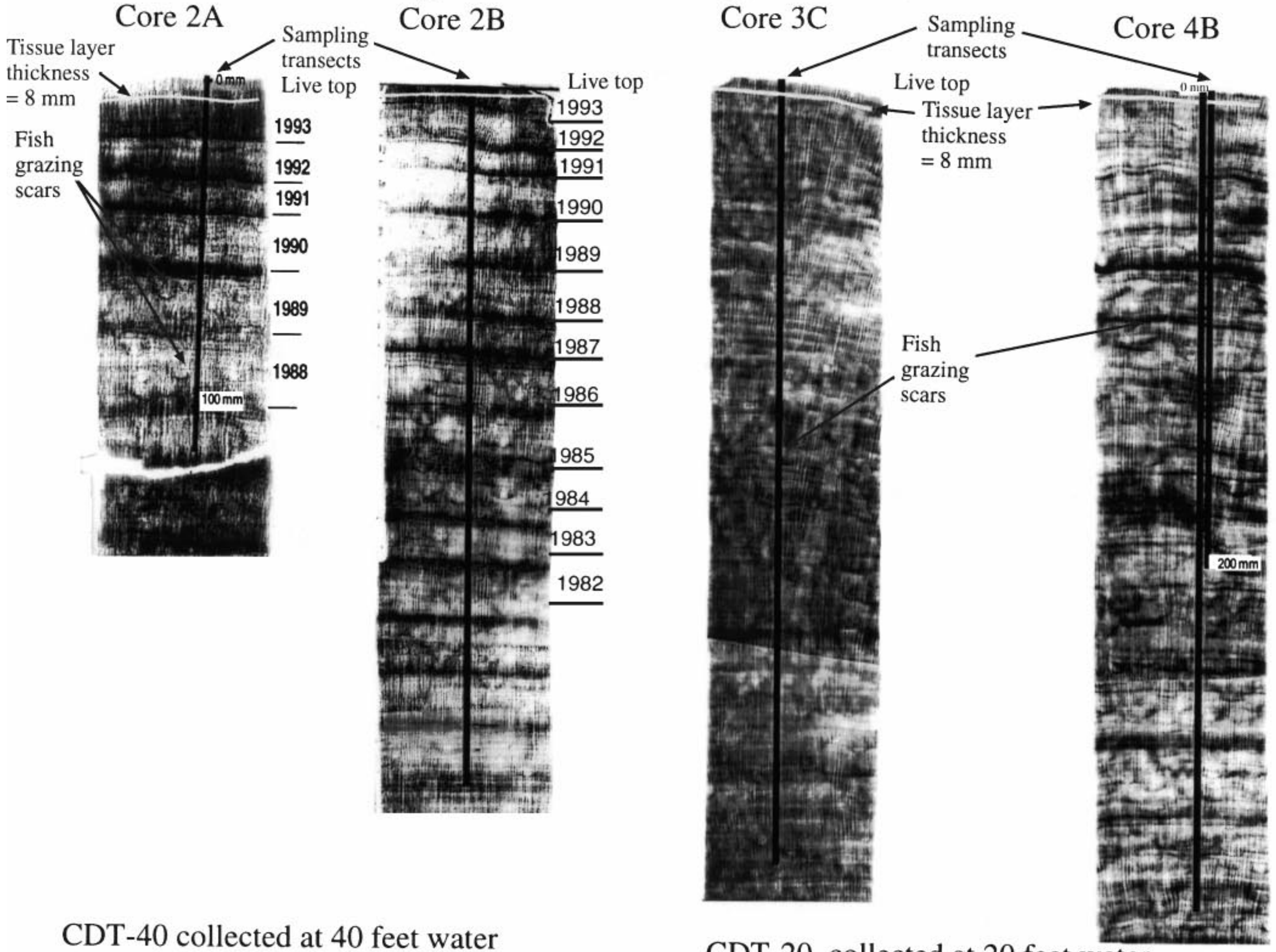
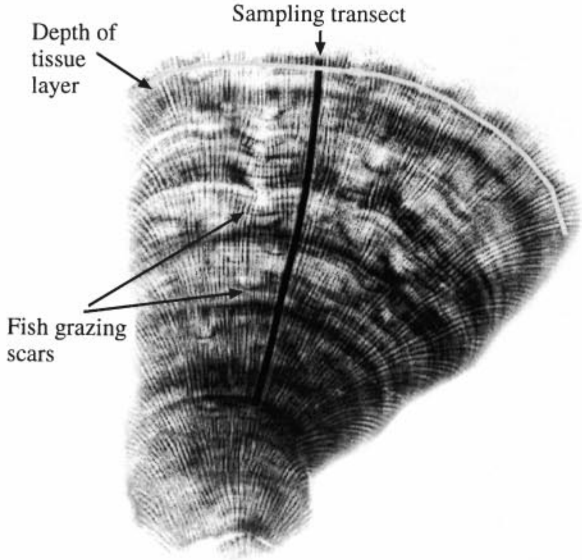


**Fig. 3** Average seasonal vertical salinity profiles in the upper 300 m in the 5° × 5° grid box surrounding Clipperton (data from Levitus et al. 1994). Note the 0.9‰ reduction in surface salinity during the wet months of July-December

**Clipperton Corals used in the study** (all *Porites lobata*)



CDT-40 collected at 40 feet water depth (12.2m), SE side of atoll



CDT-20, collected at 20 feet water depth (6.1m), SE side of atoll

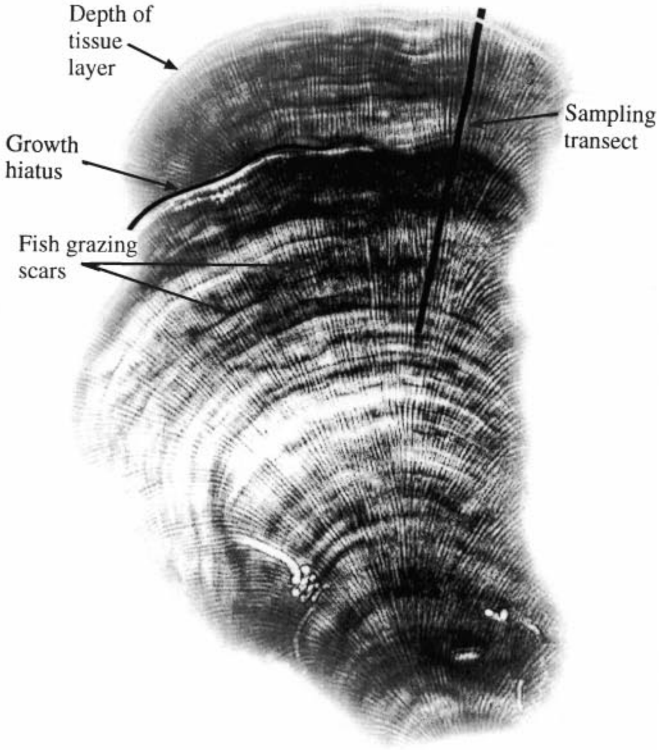


**Table 1** Coral samples used in this study

| Sample Number | Water depth | Sampling interval | Tissue layer thickness | Notes |
|---|---|---|---|---|
| *Cores from tops of medium to large colonies* | | | | |
| 2A<br>Colony age = 55 y | 13.1 m (43 feet) | 1 mm; 1–60 mm<br>2 mm; 60–110 mm | 8 mm | Distinct banding |
| 2B<br>Colony age = 55 y | 13.1 m (43 feet) | 1 mm; 1–60 mm<br>2 mm; 60–521 mm | 8 mm | Distinct banding |
| 4B<br>Colony age = ~ 120 y | 8.2 m (27 feet) | 1 mm; 1–120 mm<br>2.5 mm 0–640 mm | 5–6 mm | Poor banding |
| 3C<br>Colony age = ~ 100 y | 12.5 m (41 feet) | 2 mm; 1–552 mm | 5–6 mm | Poor banding |
| *Small colonies* | | | | |
| CDT 20 (12 y) | 6.1 m (20 feet) | 1 mm; 1–100 mm | 5–6 mm | Poor banding |
| CDT 40 (9 y) | 12.2 m (40 feet) | 1 mm; 1–100 mm | 5–6 mm | Faint banding |

ranged from 6.1 to 13.1 m. Although water depths varied, we observed no vertical SST gradient on this exposed terrace during field work and noted that all corals were in areas of heavy swell breaking on the atoll. None of the corals was observed to be influenced by shading or other micro-environmental factors. Upon collection, all corals were washed with fresh water, air dried, and then sectioned with a low-speed band saw into 7 mm thick slabs. X-ray positives of the corals used in this study are shown in Fig. 4. *Porites lobata* at Clipperton do not have a lobate surface topography typical of many *P. lobata*, but have smooth upper growth surfaces and flat lying (non-wavy) growth bands. X-radiographs reveal the presence of numerous fish bite scars. Puffer and Parrot fish where observed grazing on *Porites* colonies in the field (Glynn et al. 1996). Individual bites do not kill polyps (as the individual corallites continue across bite scars), but remove ~ 0.5 mm of tissue and skeleton on the growing outer edge and result in a skeletal scar observable in X-ray positives.

For isotopic analysis slabs of coral were cleaned in deionized water in an elongate ultrasonic bath for 15 minutes to remove saw-cuttings and were then oven dried at 40 °C. Dry slabs were sampled under a binocular microscope with a low-speed micro-drill along tracks parallel to corallite traces as identified in X-ray positives. Sampling transects are shown in Fig. 4. A 1 mm round diamond drill bit was used to removed homogenized skeletal powder at discrete intervals along the sampling transects. Skeletal material from the entire interval was extracted and stored in individual plastic snap-top vials. The excavated groove in all cases was 1 mm deep and 2 mm wide, which corresponds to the approximate diameter of 2 corallites. Table 1 lists the sampling intervals for the corals used in this study. As the corals were growing at an average rate of ~ 18 mm per year, 2 mm sampling results in ~ 9 samples per year and 1 mm sampling results in ~ 18 samples year. A total of 150–300 µg samples were dissolved in 100% $H_3PO_4$ at 90 °C in a Multiprep carbonate inlet system and the resulting $CO_2$ gas was analyzed with a Micromass Optima triple-collecting mass spectrometer in the University at Albany, State University of New York stable isotope facility. For the samples analyzed during this study the average standard deviation of the NBS-19 standards analyzed was 0.018‰ $\delta^{13}C$ and 0.038‰ for $\delta^{18}O$ ($n = 238$). The average standard deviation of the replicate samples analyzed was 0.041‰ for $\delta^{13}C$ and 0.036‰ $\delta^{18}O$ ($n = 124$). There was no difference between the standard deviations of replicate analyses of samples collected at 1 mm or 2 mm sampling intervals. The upper six years of growth in core 3C was analyzed at Rice University where 500 to 800 µg samples were analyzed with a semi-automated VG Micromass 602 E mass spectrometer. The Rice University $\delta^{18}O$ data have been adjusted by − 0.2‰ to account for an offset between the replicate analyses run at each laboratory. In the Rice laboratory the standard deviation of the NBS-19 standards analyzed over the time of these analyses was 0.06‰ for $\delta^{18}O$ and 0.05‰ for $\delta^{13}C$. The average standard deviation of the replicate samples analyzed was 0.08‰ for $\delta^{18}O$ and 0.07‰ for $\delta^{13}C$. All data are reported relative to V-PDB (See Epstein et al. 1953).

◄

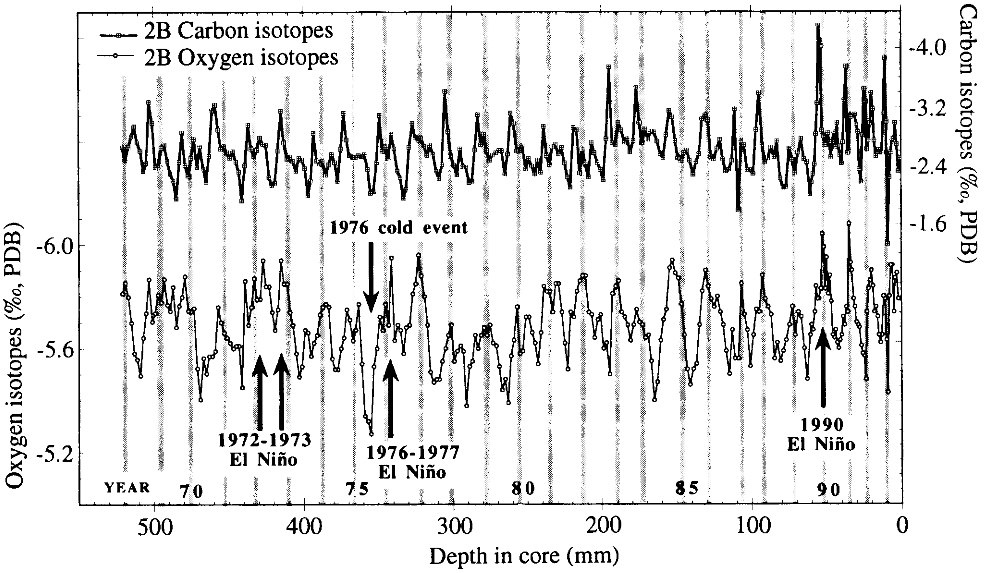
**Fig. 4** X-ray positives of coral skeletons used in the study showing the location of mm-scale sampling transects. Cores 2A and 2B are from the same colony. Note the numerous occurrences of fish grazing skeletal scars

In the results and discussion section we have applied two different treatments to the $\delta^{18}O$ results. "Centered" $\delta^{18}O$ data had been de-meaned by subtraction of the mean. This treatment centers the results around 0.0‰ and allows for the averaging of $\delta^{18}O$ records with different disequilibrium "vital effect" offsets. For the 1969–1994 results and the 6 core average (1985–1994) we have also de-seasonalized the data by subtracting the average oxygen isotopic year from each record. In this paper we will refer to data de-seasonalized in this way as $\delta^{18}O_{anomaly}$. By this method $\delta^{18}O_{anomaly}$ is in units of per miL(‰).

## Chronology development

Only cores 2A and 2B (same colony) had well-defined annual density bands (see Fig. 4). To develop chronologies for the isotopic results, we first determined that the density banding observed in core 2B was annual. A simple chronology where each density band in 2B was assumed to be annual, temporally aligned anomalously $^{18}O$ depleted years precisely during the 1972–1973, 1976–1977, and 1990 El Niño events when there were noted positive SST anomalies at Clipperton (see Figs. 2 and 5). With this chronology the 1976 cold event is also clearly identified in the 2B $\delta^{18}O$ record. There is also a pronounced annual cycle in $\delta^{13}C$ with the lowest $\delta^{13}C$ values generally occurring just prior to the base of each dense band in the most rapidly extending part of the coral skeleton (see Fig. 5). This annual cycle in $\delta^{13}C$ agrees with our age model. Because the average annual $\delta^{18}O$ range in core 2B of 0.45‰ (and all corals analyzed in this study) is approximately equal to the $\delta^{18}O$ range expected if water temperature was the dominant influence on coral $\delta^{18}O$ using either $\Delta\delta^{18}O$ = 0.18‰/°C (Gagan et al. 1994) or $\Delta\delta^{18}O$ = 0.22‰/°C (Dunbar and Wellington 1981; Epstein et al. 1953; Wellington et al. 1996), we refined this chronology by re-tuning the 2B $\delta^{18}O$ data to the monthly SST record shown in Fig. 2. The density bands in core 2A agreed with this chronology (Fig. 4). We developed chronologies for all other corals with non-distinct banding by tuning $\delta^{18}O$ results to monthly SST and core 2B $\delta^{18}O$. We are aware of the potentially circular nature of this chronologic development method, but as we demonstrate in the next section, the observed general agreement of

**Fig. 5** Oxygen and carbon isotopic data in the core 2B plotted vs. depth in the core. Position of skeletal density bands are shown by vertical shaded bars. Arrows denote years in which noted sea surface temperature changes occurred that correlate with isotopic shifts if it is assumed that the bands are annual (see Fig. 2). This simple age-model provided justification for re-tuning the age model for the oxygen isotopic results to monthly sea surface temperature



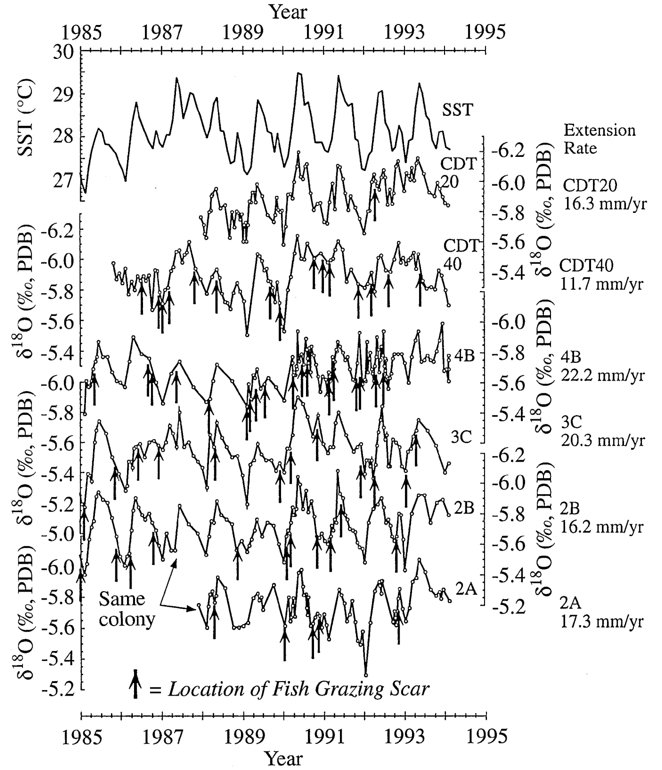


**Fig. 6** Oxygen isotopic results for cores 2A, 2B, 3C, 4B, and specimens CDT-20 and CDT-40. Scales have been offset for visual display. The position of fish bite scars observed in X-ray positives are indicated by arrows. Monthly sea surface temperature (CAC SST) is shown along the top

interannual peak heights in both the multi-coral average $\delta^{18}O$ and SST and the lack of a similar correlation with rainfall provides justification for this method. It should be noted that where we tuned the chronology to monthly rainfall, the interannual and annual maximum and minimum variations in $\delta^{18}O_{coral}$ and rainfall did not align like they do when tuned to water temperature.

## Results

### Years 1985–1994

Oxygen isotopic results for the 6 corals analyzed are presented in Fig. 6 along with monthly SST for the 2 × 2 degree latitude-longitude block surrounding Clipperton (Reynolds and Smith 1994). Individual $\delta^{18}O$ profiles have been offset for visual comparison. In these corals average skeletal extension rates ranged from 11.7 to 22.2 mm/year. In Fig. 6 the location of identified fish grazing scars are indicated by arrows. Although sampling transects were designed to minimize intersection with fish grazing scars and to stay in the maximum growth axis, not all scars could be avoided, and as the X-ray images of scar location were taken through a 7 mm thick slab it is also possible that faint scars were not observed or that we did not actually sample through imaged scars. Unusually heavy scarring of sample CDT-40 and core 4B was observed over the interval from 1990–1993.

To facilitate comparison to measured environmental parameters, all coral $\delta^{18}O$ records were interpolated to equal time increments of 1 month and plotted on the same $\delta^{18}O$ scale (Fig. 7A). This comparison also

**Fig. 7A** Oxygen isotope time-series for the six corals analyzed plotted on the same scale (PDB) and interpolated to equal time increments of 1 month. See text for discussion of "offset" observed. **B** Upper curve; oxygen isotope time-series for the six corals with the mean removed (centered). Lower curve; average oxygen isotopic series showing standard deviation. Also shown is the effect on the average of removing the most heavily fish bitten corals. **C** Comparison of average oxygen isotope series to monthly CAC SST (Reynolds and Smith 1994). The effects of removing the two most heavily fish-grazed corals (4B and CDT-40) from the average are also shown

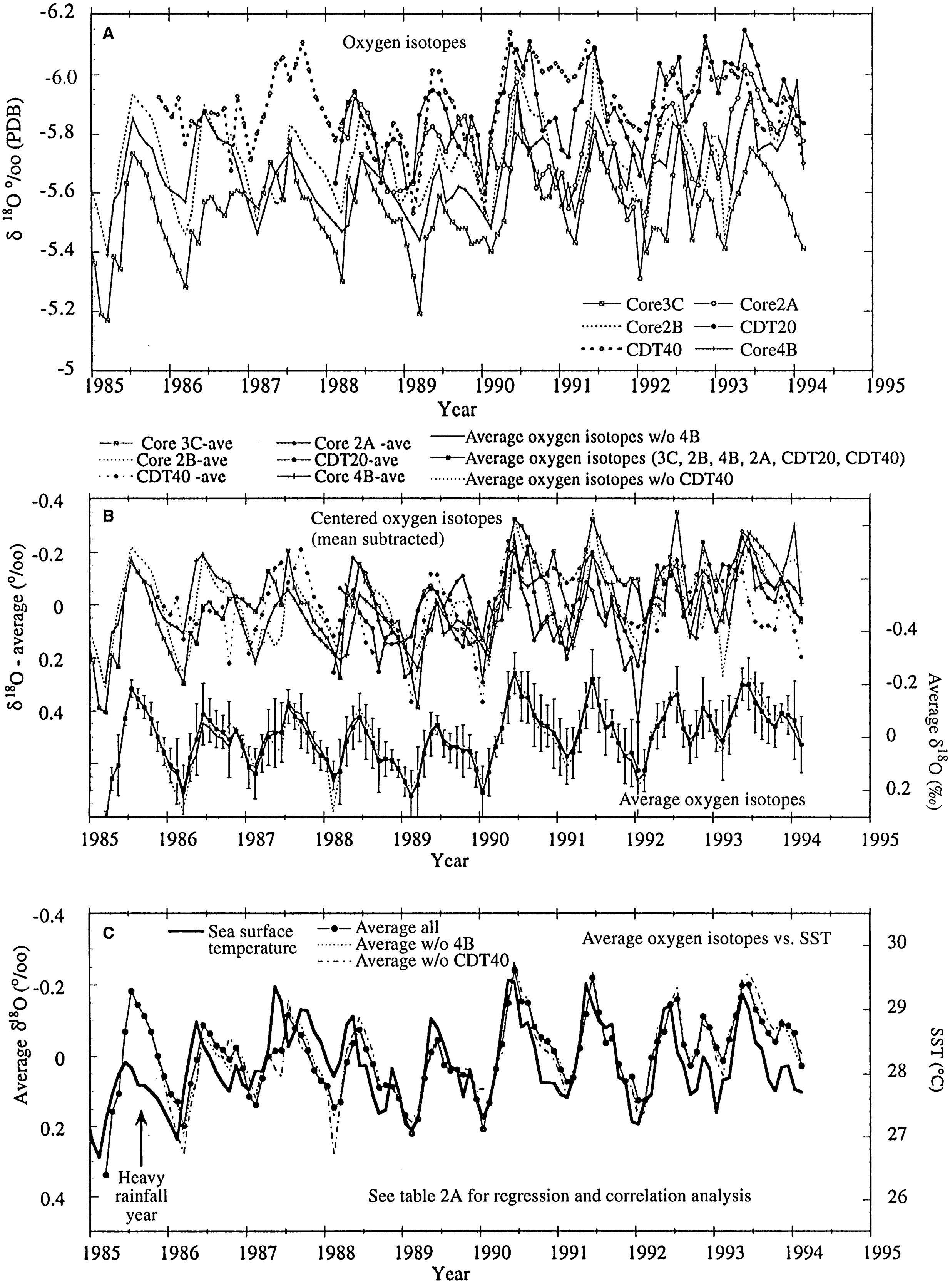

A
Oxygen isotopes
δ ¹⁸O °/oo (PDB)
-6.2
-6.0
-5.8
-5.6
-5.4
-5.2
-5
Core3C
Core2A
Core2B
CDT20
CDT40
Core4B
1985
1986
1987
1988
1989
1990
1991
1992
1993
1994
1995
Year
Core 3C-ave
Core 2B-ave
CDT40 -ave
Core 2A -ave
CDT20-ave
Core 4B-ave
Average oxygen isotopes w/o 4B
Average oxygen isotopes (3C, 2B, 4B, 2A, CDT20, CDT40)
Average oxygen isotopes w/o CDT40
B
Centered oxygen isotopes
(mean subtracted)
δ¹⁸O - average (°/oo)
-0.4
-0.2
0
0.2
0.4
Average oxygen isotopes
Average δ¹⁸O (‰)
-0.4
-0.2
0
0.2
1985
1986
1987
1988
1989
1990
1991
1992
1993
1994
1995
Year
C
Sea surface temperature
Average all
Average w/o 4B
Average w/o CDT40
Average oxygen isotopes vs. SST
Average δ¹⁸O (°/oo)
-0.4
-0.2
0
0.2
0.4
Heavy rainfall year
See table 2A for regression and correlation analysis
SST (°C)
30
29
28
27
26
1985
1986
1987
1988
1989
1990
1991
1992
1993
1994
1995
Year

**Table 2A** (Top) Pearson Product-Moment Correlation matrix between CAC SST, Clipperton 6 coral average, and corals 3C, 2B, 2A, CDT-40, CDT-20, 4B, for the period 1985–1994. (Bottom) linear regression relationships between centered oxygen isotope results, annual minimum-maximum $\delta^{18}O$, and 6 coral average $\delta^{18}O_{anomaly}$, against CAC SST for the period 1985–1994. Annual minimum-maximum SST and CAC SST anomaly were used for comparison to annual minimum-maximum $\delta^{18}O$ and $\delta^{18}O_{anomaly}$, respectively

| | SST | average | 3C | 2B | 2A | CDT-40 | CDT-20 | 4B-mm | 4B-2.5 |
|---|---|---|---|---|---|---|---|---|---|
| SST | 1 | | | | | | | | |
| 6 coral average | – 0.734 | 1 | | | | | | | |
| 3C | – 0.566 | 0.835 | 1 | | | | | | |
| 2B | – 0.481 | 0.795 | 0.721 | 1 | | | | | |
| 2A | – 0.646 | 0.677 | 0.29 | 0.525 | 1 | | | | |
| CDT-40 | – 0.626 | 0.699 | 0.526 | 0.287 | 0.22 | 1 | | | |
| CDT-20 | – 0.743 | 0.878 | 0.604 | 0.521 | 0.639 | 0.688 | 1 | | |
| 4B; 1 mm intervals | – 0.388 | 0.689 | 0.68 | 0.763 | 0.355 | 0.368 | 0.574 | 1 | |
| 4B 2.5 mm intervals | – 0.496 | 0.633 | 0.697 | 0.652 | 0.168 | 0.419 | 0.505 | 0.653 | 1 |

Linear regression, oxygen isotopes versus SST (SST dependent variable)

| Coral | Equation | $r^2$ | $n$ | slope (per miL/°C) |
|---|---|---|---|---|
| 6 coral average | $SST = 28.15–4.28(\delta^{18}O_{coral})$ | 0.54 | 72 | 0.23 |
| 3C | $SST = 28.08–2.18(\delta^{18}O_{coral})$ | 0.32 | 110 | 0.45 |
| 2B | $SST = 28.0–2.55(\delta^{18}O_{coral})$ | 0.29 | 110 | 0.39 |
| 2A | $SST = 28.1–2.97(\delta^{18}O_{coral})$ | 0.42 | 72 | 0.34 |
| CDT-40 | $SST = 28.12–3.02(\delta^{18}O_{coral})$ | 0.39 | 100 | 0.33 |
| CDT-20 | $SST = 28.15–3.34(\delta^{18}O_{coral})$ | 0.55 | 73 | 0.30 |
| 4B; 1 mm | $SST = 28.15–1.89(\delta^{18}O_{coral})$ | 0.15 | 110 | 0.53 |
| 4B 2.5 | $SST = 28.04–2.57(\delta^{18}O_{coral})$ | 0.27 | 110 | 0.39 |
| Annual $\delta^{18}O$ max-min<br>SST max-min | $SST = 28.22–4.95(\delta^{18}O_{coral})$ | 0.83 | 22 | 0.20 |
| Average $\delta^{18}O$ anomaly<br>versus SST anomaly | $SST = 0.3–2.83(\delta^{18}O_{anomaly})$ | 0.32 | 72 | 0.35 |

**Table 2B** Pearson Product-Moment Correlation matrix as in Table 2A except all data filtered with 3 month running average

| | SST | average | 3C | 2B | 2A | CDT-40 | CDT-20 | 4B-mm | 4B-2.5 |
|---|---|---|---|---|---|---|---|---|---|
| SST | 1 | | | | | | | | |
| 6 coral average | – 0.771 | 1 | | | | | | | |
| 3C | – 0.617 | 0.859 | 1 | | | | | | |
| 2B | – 0.599 | 0.836 | 0.755 | 1 | | | | | |
| 2A | – 0.659 | 0.68 | 0.308 | 0.614 | 1 | | | | |
| CDT-40 | – 0.642 | 0.717 | 0.598 | 0.359 | 0.175 | 1 | | | |
| CDT-20 | – 0.77 | 0.903 | 0.649 | 0.616 | 0.663 | 0.708 | 1 | | |
| 4B; 1 mm intervals | – 0.381 | 0.73 | 0.701 | 0.784 | 0.393 | 0.424 | 0.692 | 1 | |
| 4B; 2.5 mm intervals | – 0.62 | 0.74 | 0.721 | 0.481 | 0.209 | 0.551 | 0.646 | 0.729 | 1 |

Linear regression, oxygen isotopes (3 month smooth) versus SST (3 month smooth) (SST dependent variable)

| Coral | Equation | $r^2$ | $n$ | slope (per miL/°C) |
|---|---|---|---|---|
| 6 coral average | $SST = 28.16–4.31(\delta^{18}O_{coral})$ | 0.60 | 70 | 0.23 |
| 3C | $SST = 28.08–2.34(\delta^{18}O_{coral})$ | 0.29 | 108 | 0.43 |
| 2B | $SST = 28.04–2.55(\delta^{18}O_{coral})$ | 0.29 | 108 | 0.39 |
| 2A | $SST = 28.16–2.97(\delta^{18}O_{coral})$ | 0.43 | 70 | 0.34 |
| CDT-40 | $SST = 28.17–3.02(\delta^{18}O_{coral})$ | 0.41 | 98 | 0.33 |
| CDT-20 | $SST = 28.15–3.47(\delta^{18}O_{coral})$ | 0.59 | 71 | 0.29 |
| 4B; 1 mm intervals | $SST = 28.16–1.88(\delta^{18}O_{coral})$ | 0.15 | 108 | 0.53 |
| 4B; 2.5 mm intervals | $SST = 27.94–2.90(\delta^{18}O_{coral})$ | 0.38 | 108 | 0.35 |

highlights differences in the average disequilibrium "offset" or vital effect. Although we do not have isotopic data for water samples from Clipperton, the $\delta^{18}O$ composition of surface water in the eastern Pacific is near 0.0‰ (SMOW), ranging from ~ + 0.4‰ to – 0.5‰ (Craig and Gordon 1965; McConnaughey 1989). From Fig. 7A it is apparent that the $\delta^{18}O$ disequilibrium offset for Clipperton *Porites* varies by as much as 0.4‰ (– 5.4‰ to – 5.8‰ PDB or 25.29‰ to 24.88‰ SMOW using $\delta^{18}O_{calcite(SMOW)} = 1.03086 \ \delta^{18}O_{calcite(PDB)} + 30.86$). A small difference in offset is also observed within an individual colony (cores 2A and 2B). The offset shows no consistent relationship to water depth and appears constant over the length of all 6 $\delta^{18}O$

records assuming no trend in annual average $\delta^{18}O_{seawater}$. The $\delta^{18}O$ offsets for the small and medium sized colonies (CDT-20; ~ 12 y, CDT-40; ~ 9 y, and colony 2; ~ 55 y) are in the same range as the "offsets" for the older colonies ( 3C; ~ 100 y, and 4B; ~ 120 y), suggesting little long-term drift of the biologically-mediated $\delta^{18}O$ vital effect of the older coral colonies sampled here. To assess more accurately the common variance in each time series, the mean was subtracted from each $\delta^{18}O$ series (time-series were centered) and all six records were plotted on the same scale along with an average of all 6 $\delta^{18}O$ records (Fig. 7B). Here the common variance is more apparent. If the fish grazing scars were introducing a random error into each $\delta^{18}O$ time-series, an average of all six records would tend to minimize this random error. In Fig. 7C we compare the 6-coral average $\delta^{18}O$ record to monthly SST (Reynolds and Smith 1994). The effects of removing the two most heavily fish grazed records (core 4B and CDT-40) from the average are also shown (Fig. 7B lower curves, and Fig. 7C).

Table 2A summarizes Pearson Product-Moment correlation coefficients between these coral $\delta^{18}O$ time-series and monthly SST. Linear least-squares regression equations describing the $\delta^{18}O$ vs. SST relationship are also given, along with the relationship between annual maximum-minimum $\delta^{18}O$ and SST, and average 6-coral $\delta^{18}O_{anomaly}$ and $SST_{anomaly}$. In Table 2B correlation coefficients and regression equations for 3-month running average versions of $\delta^{18}O$ and SST are presented. The Pearson correlation matrix reveals that with the exception of CDT-20, the average $\delta^{18}O$ record is more highly correlated to SST than individual records, with correlation coefficients ranging from $-0.48$ to $-0.74$ (excluding the heavily fish grazed 1 mm sampled core 4B series). The correlations improve slightly when all data are smoothed with a three month running average (compare Table 2A and 2B). Least squares linear regression indicates that monthly SST and average monthly $\delta^{18}O$ are moderately correlated with an $r^2$ value of 0.54. Individual $r^2$ values range from 0.27 to 0.55, again excluding the 1 mm interval sampled core 4B. The correlation between the average $\delta^{18}O$ record and SST improves to an $r^2$ of 0.83 if only annual minima and maxima are used, but decreases to $r^2 = 0.32$ if average coral $\delta^{18}O_{anomaly}$ and $SST_{anomaly}$ are compared (see Table 2A). Because the correlation decreases when the annual cycle is removed, this suggests that additional factors other than SST are influencing coral skeletal $\delta^{18}O$ in Clipperton *Porites* over the period from 1985 to 1994. The slope of the average monthly coral $\delta^{18}O$ and monthly SST regression yields a $\Delta\delta^{18}O = 0.23‰/°C$, however the relationship ranges from 0.23 to 0.53‰/°C for individual $\delta^{18}O$ records. It should be noted that the coral with the least amount of fish grazing (CDT-20) has the highest correlation to SST and that the most heavily grazed coral (core 4B) has the lowest correlation to SST. Removal of the two most heavily grazed corals (4B and CDT-40) from the average results in only small changes in the overall average and does not change the degree of correlation to monthly SST (Fig. 7B, C). The lowest correlation occurs during the 1987 El Niño event when SST shows two distinct maxima and average $\delta^{18}O$ only records one maxima, and also during 1985 when average $\delta^{18}O$ is 0.3‰ less than expected (Fig. 7C). The month to month correlations could be improved with further slight refinements of the individual $\delta^{18}O$ chronologies but our opinion is that this level of chronology tuning is unjustifiable and would not change our primary conclusions.

### Years 1969–1994

To assess the longer period stability of the $\delta^{18}O$ "offset" over a 25 y period, near-monthly $\delta^{18}O$ records were generated for cores 2B, 3C, and 4B, back to 1969 (Fig. 8A). Cores 2B and 3C were sampled at 2 mm intervals and core 4B was sampled at 2.5 mm intervals. In the lower half of Fig. 8A the $\delta^{18}O_{anomaly}$ data are displayed for each core. The $\delta^{18}O_{anomaly}$ was calculated by subtracting the average isotopic year for each core. The raw $\delta^{18}O_{anomaly}$ was then filtered with a three month running mean to minimize the effects of fish grazing scars and month-to-month chronology uncertainties.

The carbon isotope data ($\delta^{13}C$) for cores 3C, 2B and 4B are presented in Fig. 8b. We observe more discordance between the individual $\delta^{13}C$ time-series from each core than in $\delta^{18}O$. There is a positive relationship between $\delta^{13}C$ and $\delta^{18}O$ in individual time series (highest $\delta^{13}C$ values correlate with the highest $\delta^{18}O$ values). Thus the highest $\delta^{13}C$ values occur during the times of lowest SST when there is low cloud cover and most likely the highest rates of photosynthesis (see Fig. 2). This pattern is in agreement with the idea that the $\delta^{13}C$ of a coral skeleton reflects the level of photosynthetic activity of symbiotic zooxanthellae in coral tissue with maximum annual photosynthetic activity coincident with the most $^{13}C$ enriched portions of the skeleton (Erez 1978; Fairbanks and Dodge 1979; Goreau 1977; McConnaughey 1989; Patzold 1984; Swart 1983). Further interpretation of the $\delta^{13}C$ data is beyond the scope of this study.

In Fig. 9 the average $\delta^{18}O_{anomaly}$ of cores 3C, 4B, and 2B is compared to SST anomaly from the CAC SST database for the 2° × 2° latitude-longitude block surrounding Clipperton (Climate Analysis Center; Reynolds and Smith 1994), and to the OS SST anomaly data for the 5° × 5° area surrounding the island (Kaplan et al. 1998). The last five El Niño events are also indicated and are recorded in the average $\delta^{18}O_{anomaly}$ composite. Table 3A summarizes Pearson Product-Moment correlation coefficients between the core 3C, 4B, and 2B $\delta^{18}O$ time-series and monthly

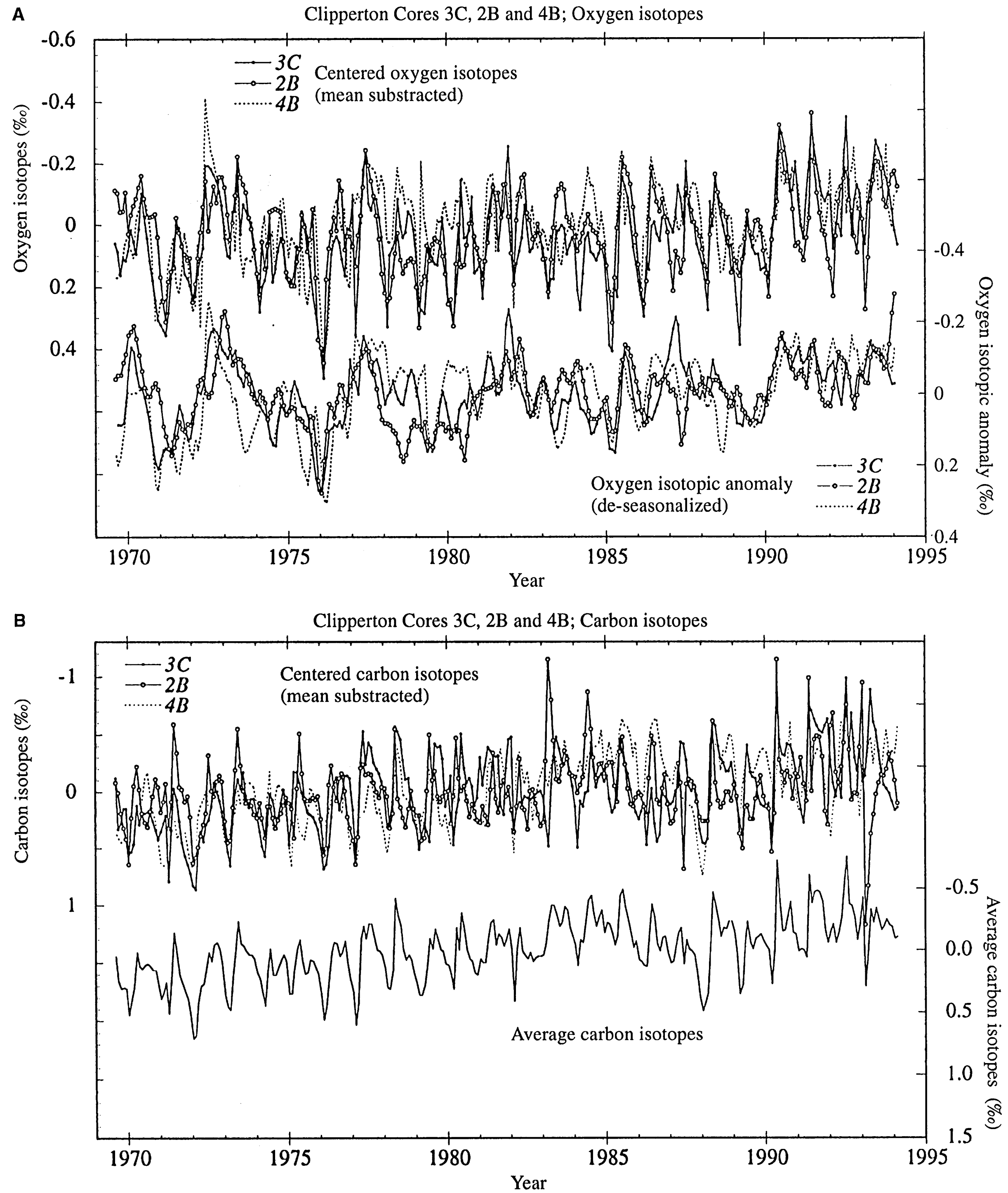


**Fig. 8A** Oxygen isotopic and anomaly (de-seasonalized) results for cores 3C, 2B, and 4B extended back to 1969. Oxygen isotopic anomaly has been smoothed with a 3 month running mean to minimize effects of fish grazing scars and month-to-month chronology uncertainties. **B** Carbon isotopic results for cores 3C, 2B, and 4B

CAC SST, and Table 3B summarizes correlation coefficients between coral $\delta^{18}O_{anomaly}$ (smoothed with 3 month running mean) and CAC SST anomaly. Linear least-squares regression equations describing the $\delta^{18}O$ versus SST relationship are also given in both tables. The 2° x 2° CAC SST data was selected for correlation and regression analysis as it is thought to be more representative of conditions near Clipperton. Correlation coefficients between individual coral $\delta^{18}O$ and SST range from $-0.52$ to $-0.54$, with the three core average having the highest coefficient at –0.61. Correlation coefficients between $\delta^{18}O_{anomaly}$ and SST anomaly range from $-0.44$ to $-0.59$, with the three core average having the highest coefficient at $-0.64$. The

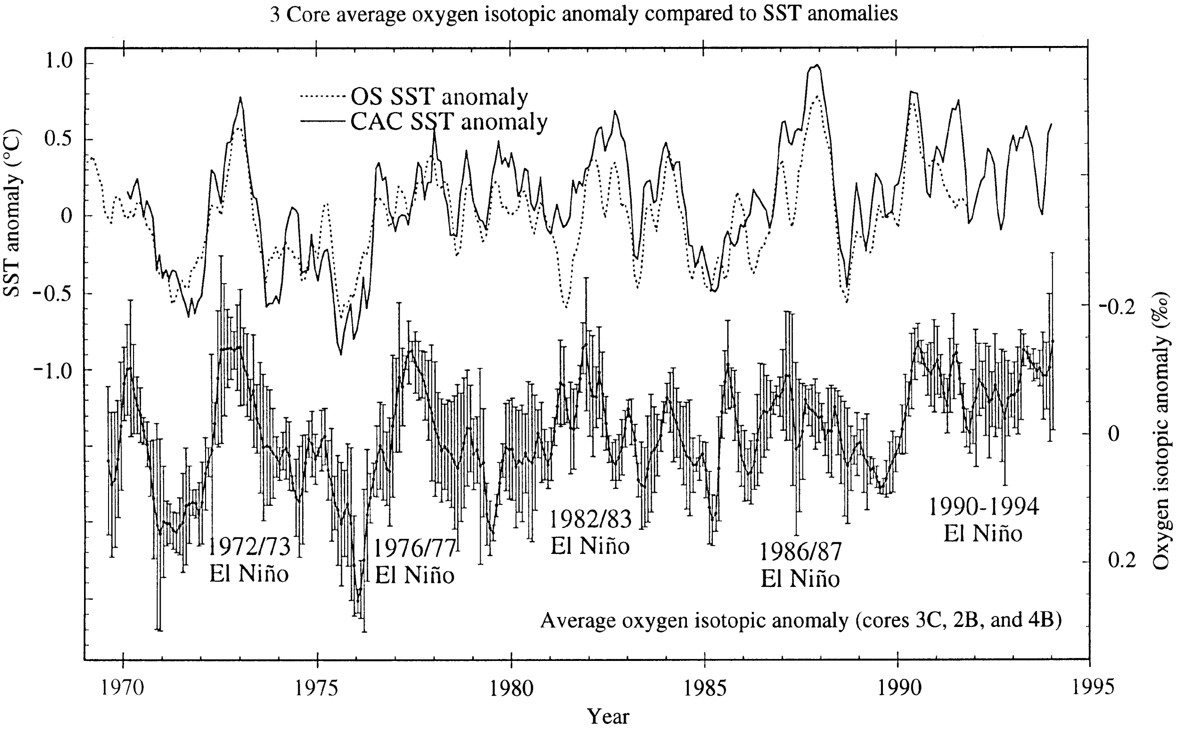


**Fig. 9** Average oxygen isotopic anomaly for cores 3C, 2B, and 4B with standard deviation (using results displayed in lower half of Fig. 8A), and sea surface temperature anomaly from the 2° × 2° degree block (CAC SSTa, Reynolds and Smith 1994), and 5° × 5° degree block (OS SSTa, Kaplan et al. 1998) surrounding Clipperton

slope of the $\delta^{18}O$ vs. SST relationship for both the monthly and anomaly cases is 0.31 per miL/°C.

## Discussion

This reproducibility study shows that the degree of $\delta^{18}O$ disequilibrium offset in massive coral colonies that are thought to be the same species and are living in nearly identical environments within 2 km of each other can vary by up to 0.4‰. We suspect that the observed 0.4‰ variation in disequilibrium offset is primarily the result of sampling location on the dome shaped colony. McConnaughey (1989) and Patzold (1984) have shown that $\delta^{18}O$ composition of skeletal aragonite varies across the uppermost living surface depending on shading and position relative to the maximum growth axis. It is possible that core position within the maximum growth axis has led to this small change in disequilibrium vital effect offset.

After removing the $\delta^{18}O$ mean from each time-series, the common variance in each record is apparent, but significant differences are also observed. Some of this disagreement can be explained by chronology imperfections. In addition, at Clipperton fish grazing scars also reduce the fidelity of the oxygen isotopic records. Averaging of multiple $\delta^{18}O$ coral time-series at Clipperton appears to minimize chronology imperfections, and results in a composite $\delta^{18}O$ record that is moderately correlated to SST and also records all El Niño events over the time period of this study. The implications of this result is that the paleoclimatic significance of an individual coral $\delta^{18}O$ record can be improved by averaging multiple records and that, if possible, the selection of additional coral material with minimal skeletal grazing hiatuses for analysis is critical. However, at Clipperton even with averaging of multiple $\delta^{18}O$ records, there is still a significant amount of variance not explained by SST variability.

To explain the other sources of variance for Clipperton coral $\delta^{18}O$ that are not related to SST, the potential effects of salinity-precipitation and tissue layer thickness were evaluated. The 0.8‰ annual salinity range in the region of Clipperton was expected to result in a ~ 0.09‰ to 0.22‰ annual $\delta^{18}O$ range in the coral depending on whether you assume the relationship between $\delta^{18}O_{seawater}$ and salinity is 0.12‰ $\delta^{18}O$ per‰ salinity (Craig and Gordon 1965; Dunbar and Wellington 1981; Wellington et al. 1996) or 0.27‰ $\delta^{18}O$ per‰ salinity (Fairbanks et al. 1997). As the relationship determined by Fairbanks et al. (1997) is from samples collected within convective regions in the tropical Pacific, this relationship might be more applicable to Clipperton which is within the ITCZ. At Clipperton, seasonally low salinity correlates with the season of maximum ITCZ related rainfall. In addition, hydrocast salinity data collected along the TAO Array north-south transect at 110°W indicates that rainfall does influence the salinity of upper thermocline waters in the region of Clipperton during some years (*NOAA PMEL TAO array* 1997 *personal communication*, http://www.pmel.noaa.gov/toga-tao/realtime.html). The additive influence of an annual 0.8‰ salinity change and an annual SST range of 2 °C suggests we should have found a larger annual coral $\delta^{18}O$ range than observed. However, the time of maximum rainfall lags maximum SST by 1–2 months. This would tend to minimize the additive effect and could explain both the moderate correlation between coral $\delta^{18}O$ and SST and the average 0.4 per ml $\delta^{18}O$ annual range.

In an attempt to isolate the salinity effect in the coral $\delta^{18}O$ signal, we calculated the difference between the average three core $\delta^{18}O$ anomaly (1970–1994) and SST anomaly records after first adjusting the SST anomaly data using a factor of 0.22 per mil/°C. This $\delta^{18}O$-SST difference (for both OS SSTa and CAC SSTa) is shown in Fig. 10, along with precipitation anomaly for the period 1979–1994. We interpret more negative $\delta^{18}O$-SST difference values as times of lower salinity (more rainfall) and more positive $\delta^{18}O$-SST difference values as times of higher salinity (less rainfall). This comparison suggests that rainfall-induced lowering of surface salinity has affected coral $\delta^{18}O$ in certain years, particularly in the early to mid-1980s. For example, 1985 was an anomalously wet year and also a year in which coral $\delta^{18}O$ does not correlate well with SST (see Fig. 7C). Thus it appears that poorly constrained salinity effects are preserved in coral $\delta^{18}O$ from Clipperton, with the effect being more pronounced in certain years.

Another scenario for years of anomalously low $\delta^{18}O$ not due to SST is westward propagation of coastal low-salinity eastern Pacific water. It is possible, although not provable here, that changes in NECC movement and/or westward propagating anticyclonic eddies may have altered the $\delta^{18}O$ of seawater at Clipperton in certain years. Such large-scale eddies have been documented in the eastern Pacific (Hansen and Maul 1991) and have been shown to affect sea level at Clipperton by up to 30 cm (Maul et al. 1992). Depending on location of ring formation, they can transport coastally modified water offshore (Hansen and Maul 1991). Anticyclonic rings generally occur once each year and take approximately six months to dissipate. The rings are analogous with the familiar warm-core rings associated with the Gulf Stream and other western boundary currents. However in the eastern Pacific, these rings form in a particularly warm region of the ocean and there is little or no evidence of their presence in sea surface temperature. Although little long term information exists about the conditions needed for ring formation, it appears that these eddies originate in a region of the eastern Pacific where surface salinity as low as 32–33‰ is typical (Bennett 1966; Levitus et al. 1994). The passage of coastal water entrapped in an anticyclonic ring past Clipperton would be a potential mechanism to explain $^{18}O$-depleted water during certain years.

Another potential complication of interpreting a coralline skeletal $\delta^{18}O$ signal is a possible smoothing effect induced by calcification that occurs throughout the thickness of the coral tissue layer (Barnes and Lough 1992; Barnes et al. 1995; Taylor et al. 1995). This type of skeletogenesis may distort the geochemical record of both sudden pulse events and annual climate cycles (Barnes et al. 1995; Taylor et al. 1995). Since tissue layer thickness can be an appreciable portion of an annual growth band, thickening of skeletal elements throughout the tissue layer will reduce the amplitude of annual climate cycles as recorded by geochemical tracers such as $\delta^{18}O$. However, in corals from the Galápagos which grow faster than 10 mm per year, no effect of tissue layer thickness on skeletal $\delta^{18}O$ has been found (Wellington et al. 1996).

Table 1 shows measured tissue layer thickness of the corals used in this study. Tissue thickness averaged 5–6mm and are all essentially identical with the exception of colony 2 (cores 2A and 2B) which had a tissue layer thickness of 8 mm. Contrary to the findings of Barnes and Lough (1992), we find no difference in tissue layer thickness in old versus young colonies at Clipperton. Under the models developed by Barnes et al. (1995) and Taylor et al. (1995) this average tissue layer thickness coupled with an average extension rate of 18 mm per (ratio of tissue layer thickness to extension = 0.33) would result in a three month smoothing effect (1/4 year). Although our results cannot rule out some smoothing effect, the preservation of subseasonal SST variability in some of the 1 mm sampled corals suggests that the smoothing effect is minimal and certainly allows the preservation of monthly changes in SST (see $\delta^{18}O$ of minimally fish grazed corals in Fig. 6; e.g.: CDT-20). In addition the thicker tissue layer in cores 2 A and 2B has not reduced the amplitude of the seasonal $\delta^{18}O$ changes as would be expected if the tissue layer was in fact having a pronounced smoothing effect on $\delta^{18}O$ (see Figs. 6 and 8 A). In their coral growth model Barnes et al. (1995) assumed that 50% of the mass of skeleton was added within the tissue layer after the skeletal architecture was in place. For Clipperton *Porites* this estimate seems high and our results are more in-line with the suggestion of Wellington et al. (1996) that 80–90% of eventual skeletal mass forms within 1 mm of the outer margin. This is also in agreement with Alibert and McCulloch (1997) who viewed Great Barrier Reef *Porites* under Scanning Electron Spectroscopy and could find no evidence of skeletal element thickening within the tissue layer.

**Table 3A** (Top) Pearson Product-Moment Correlation matrix for centered oxygen isotope results for 3 core average, and cores 4B, 2B, and 3C for period 1970–1994. (Bottom) linear regression relationships between centered oxygen isotope results and CAC SST for period 1970–1994

| | SST | 3 core average | 4B $\delta^{18}O$ | 2B $\delta^{18}O$ | 3C $\delta^{18}O$ |
|---|---|---|---|---|---|
| SST | 1 | | | | |
| 3 core average | – 0.612 | 1 | | | |
| 4B $\delta^{18}O$ | – 0.522 | 0.809 | 1 | | |
| 2B $\delta^{18}O$ | – 0.536 | 0.836 | 0.454 | 1 | |
| 3C $\delta^{18}O$ | – 0.539 | 0.917 | 0.639 | 0.714 | 1 |

Linear regression (SST dependent variable)

| Coral | Equation | $r^2$ | $n$ | slope (per miL/°C) |
|---|---|---|---|---|
| 3 core average | $SST = 28.0–3.18(\delta^{18}O_{coral})$ | 0.38 | 290 | 0.31 |
| 4B | $SST = 27.96–2.43(\delta^{18}O_{coral})$ | 0.27 | 290 | 0.41 |
| 2B | $SST = 28.0–2.55(\delta^{18}O_{coral})$ | 0.29 | 290 | 0.39 |
| 3C | $SST = 28.08–2.24(\delta^{18}O_{coral})$ | 0.29 | 290 | 0.45 |

**Table 3B** (Top) Pearson Product-Moment Correlation matrix for oxygen isotope anomaly (de-seasonalized) results for 3 core average, and cores 4B, 2B, and 3 C for period 1970–1994, and CAC SST anomaly. Oxygen isotope anomalies filtered with 3 month running mean (see text). (Bottom) linear regression relationships between oxygen isotope anomaly results and CAC SST anomaly for period 1970–1994

| | SSTa | 3 core average | 4B $\delta^{18}Oa$ | 2B $\delta^{18}Oa$ | 3C $\delta^{18}Oa$ |
|---|---|---|---|---|---|
| SSTa | 1 | | | | |
| 3 core average | – 0.635 | 1 | | | |
| 4B $\delta^{18}O_{anomaly}$ | – 0.593 | 0.811 | 1 | | |
| 2B $\delta^{18}O_{anomaly}$ | – 0.443 | 0.756 | 0.317 | 1 | |
| 3C $\delta^{18}O_{anomaly}$ | – 0.54 | 0.894 | 0.627 | 0.623 | 1 |

Linear regression (SST dependent variable)

| Coral | Equation | $r^2$ | $n$ | slope (per miL/°C) |
|---|---|---|---|---|
| 3 core average | $SST = 0.1–3.05(\delta^{18}O_{coral})$ | 0.40 | 290 | 0.31 |
| 4B | $SST = 0.1–2.17(\delta^{18}O_{coral})$ | 0.35 | 290 | 0.41 |
| 2B | $SST = 0.1–1.94(\delta^{18}O_{coral})$ | 0.19 | 290 | 0.39 |
| 3C | $SST = 0.1–2.20(\delta^{18}O_{coral})$ | 0.29 | 290 | 0.45 |

## Summary and conclusions

Although the disequilibrium vital effect $\delta^{18}O$ offset can vary between corals by 0.4‰ even in corals in close proximity, when $\delta^{18}O$ time-series are centered (mean removed) seasonal coral $\delta^{18}O$ variability from different colonies is coherent and significantly correlated. We observe similar disequilibrium $\delta^{18}O$ offsets in corals of different sizes and ages at Clipperton which suggests little long-term drift of the biologically mediated $\delta^{18}O$ "vital effect" as *P. lobata* ages. Twenty-five years of subseasonal $\delta^{18}O$ measurements in three cores from different colonies shows that the $\delta^{18}O$ disequilibrium offset has remained constant over this interval of time.

Fish grazing on the outermost edge of the tissue layer can remove a small amount of skeleton. Accretion of new skeleton to replace the damaged area results in a scar which in many cases is resolvable in X-rays. If the grazing scar is in the plain of the sampling transect, the area of the scar can have anomalous $\delta^{18}O$ which can be a problem when interpreting coral-derived isotopic records. These scars induce chronology hiatuses and contain possible $^{18}O$ depleted skeleton. Fish grazing scars have also been observed by the authors in X-rays of corals from the genera *Porites* and *Pavona* from other locations. This result indicates that close attention to the position of grazing scars in corals from other areas will improve the climatic reconstructions and reduce the error that bite scars can induce.

Coral skeletal $\delta^{18}O$ composition in Clipperton *Porites* is primarily controlled by the complex interacting effects of sea surface temperature (SST) and surface salinity (SSS). Averaging of multiple $\delta^{18}O$ records improves the correlation to water temperature. We lack a comparable time series record for determining the exact relationship between coral $\delta^{18}O$ and salinity.

We view this reproducibility study as a near worst-case scenario for addressing reproducibility and calibration issues in *P. lobata.* This is due to the complex relationship between a small annual SST signal and a comparatively large ITCZ salinity signal at Clipperton, and the resulting small annual coral $\delta^{18}O$ signal coupled with the complicating effect of fish grazing scars. Even under these non-ideal conditions, the coral $\delta^{18}O$ records analyzed all suggest that the corals have recorded the prevalent external environmental signals at Clipperton and have also preserved a record of past

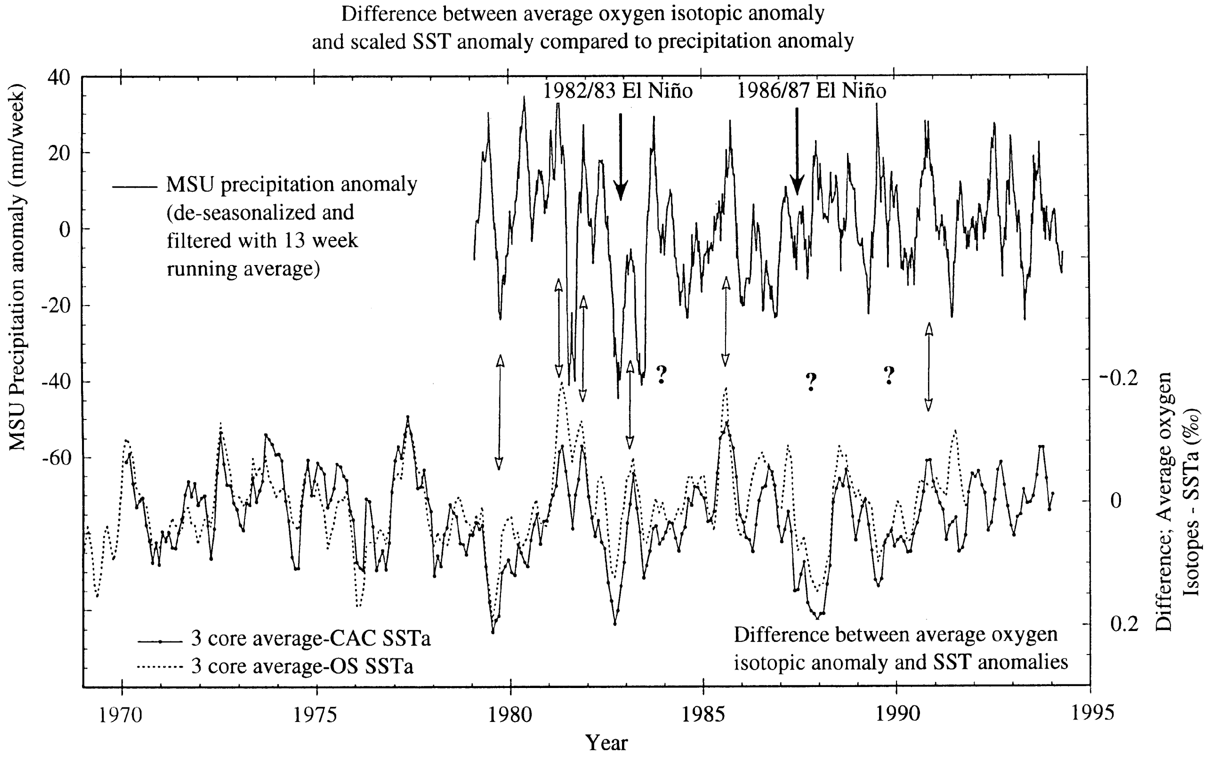


**Fig. 10** The $\delta^{18}$O-SST difference (average $\delta^{18}O_{anomaly}$ minus scaled SST anomaly, SSTa, for both OS SSTa and CAC SSTa; see text) along with precipitation anomaly (filtered with 13 week running average) for the period 1979–1994. We interpret more negative $\delta^{18}$O-SST difference values as times of lower salinity (more rainfall) and more positive $\delta^{18}$O-SST values as times of higher salinity (less rainfall)

El Ninõ events. Although our test of the stability of the disequilibrium $\delta^{18}$O offset only extends back 25 y, we find the results encouraging for the utility of $\delta^{18}$O as a paleoclimatic tracer in corals from Clipperton.

The implications of the observed range in vital effect disequilibrium $\delta^{18}$O offsets between coral colonies in close proximity indicates that the PDB value may not be as significant for paleoclimatic reconstructions as the seasonal, interannual, and long-term $\delta^{18}$O ranges and trends. Thus, the comparison of centered (mean removed) coral-based $\delta^{18}$O time series may result in more accurate interpretations of oxygen isotopic data. Additional studies examining inter- and intra-colony $\delta^{18}$O variability in hermatypic corals from other regions are needed to continue assessment of this widely used tracer.

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