

Deglacial sea surface temperatures of the western tropical Pacific: A new look at old coral

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[1] Using Secondary Ion Mass Spectrometry (SIMS) ion microprobe techniques, we generated annual Sr/Ca cycles with subweekly resolution from chunks of *Porites* coral retrieved from a Tahiti barrier reef drill core (149°W, 17°S), representing the period 13,650 to 13,100 years B.P. The centers of pristine skeletal septa were selectively targeted with a 10 μm diameter ion beam spot, avoiding adjacent pore spaces occupied by secondary aragonite needles. Applying a Sr/Ca–sea surface temperature (SST) calibration equation derived from modern Tahiti *Porites* having the same low growth rate as the fossil specimens, we obtained SSTs $\sim 0.5^\circ\text{--}1.5^\circ\text{C}$ cooler during the Bølling-Allerød relative to the present day, with no significant change in seasonality. On the contrary, we estimate that analysis of bulk samples would yield excessively cool Sr/Ca-based SST estimates due to the occupation by secondary aragonite crystals of up to 50% of the skeletal pore space in the ancient samples. We find that growth rate effects on coral Sr/Ca further depress the apparent mean annual derived SSTs (by $>3^\circ\text{C}$) and amplify the apparent seasonality by selectively enhancing wintertime cooling. Our microscale analysis of pristine skeleton and application of an appropriate growth-dependent calibration yield Sr/Ca-derived SSTs that are in good agreement with those derived from Mg/Ca ratios of calcitic foraminifera which indicate a continuous postglacial warming of the western tropical Pacific, in phase with the warming of the tropical Atlantic. *INDEX TERMS*: 4267 Oceanography: General: Paleooceanography; 4294 Oceanography: General: Instruments and techniques; 4875 Oceanography: Biological and Chemical: Trace elements; *KEYWORDS*: tropical Pacific, sea surface temperature, Bølling-Allerød, coral Sr/Ca, ion microprobe, diagenesis

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1. Introduction

[2] The Sr/Ca ratio of coral skeleton decreases with increasing seawater temperature and is widely used as a paleothermometer. However, Sr/Ca measurements of fossil coral from both submerged and uplifted reefs have yielded paleosea surface temperatures (SSTs) several degrees colder than those based on other marine proxies [e.g., Guilderson *et al.*, 1994; Beck *et al.*, 1997; McCulloch *et al.*, 1999; Corregge *et al.*, 2004], and their accuracy has been questioned [Crowley, 2000]. Empirically derived coral Sr/Ca–SST equations may fail to predict paleoSSTs for two reasons. First, the Sr/Ca–SST calibration may be sensitive to coral growth rate. At a given temperature, the Sr/Ca content of slow-growing skeleton tends to be higher than that of fast-growing skeleton, yielding apparently cooler Sr/Ca-derived SSTs [Weber, 1973; de Villiers *et al.*, 1995; Alibert and McCulloch, 1997; Goodkin *et al.*, 2004]. Second, abiogenic or secondary (2°) aragonite needles may grow into the skeletal pore spaces of submerged corals [Bar-Matthews *et al.*, 1993; Enmar *et al.*, 2000; Ribaud-Laurenti *et al.*, 2001; Lazar *et al.*, 2004]. The Sr/Ca ratio of abiogenic aragonite precipitated from seawater is higher than that of aragonite accreted by living corals [Kinsman and Holland, 1969; Bar-Matthews *et al.*,

1993; Enmar *et al.*, 2000; Gaetani and Cohen, 2004]. Thus the presence of 2° aragonite crystals in a bulk sample of fossil coral may shift Sr/Ca-derived SSTs toward cooler temperatures [Ribaud-Laurenti *et al.*, 2001].

[3] We used SIMS ion microprobe to analyze Sr/Ca ratios of two small chunks of coral retrieved from a *Porites*-dominated bed at 69–82 m depth in the Tahiti barrier reef drill core P7 (149°W, 17°S) [Bard *et al.*, 1996; Montaggioni *et al.*, 1997]. U/Th measurements place the bed between 12,875 years B.P. and 13,775 years B.P. [Bard *et al.*, 1996, 1998], coincident with the timing of the Bølling-Allerød deglacial warm period ($\sim 14,600\text{--}12,800$ years B.P.) in the GISP2 ice core [Stuiver *et al.*, 1995]. The absence of diagenetic alteration in the form of calcite was strongly indicated by triplicate XRD analyses [Bard *et al.*, 1996] although boron isotope measurements indicate that some recrystallization might have occurred [Gaillardet and Allegre, 1995].

2. Microstructural Features of Modern and Ancient *Porites*

[4] Examination of the polished sections with an Olympus BHSP polarizing microscope at 10–50 X magnification revealed the fossil skeletons to be largely well preserved, based on several telltale microstructural features (Figures 1a and 1b). The centers of septa are occupied by vertical lines of discrete, dark, oval-shaped calcification centers, 15–20 μm long and ~ 10 μm at their widest point. The length of the

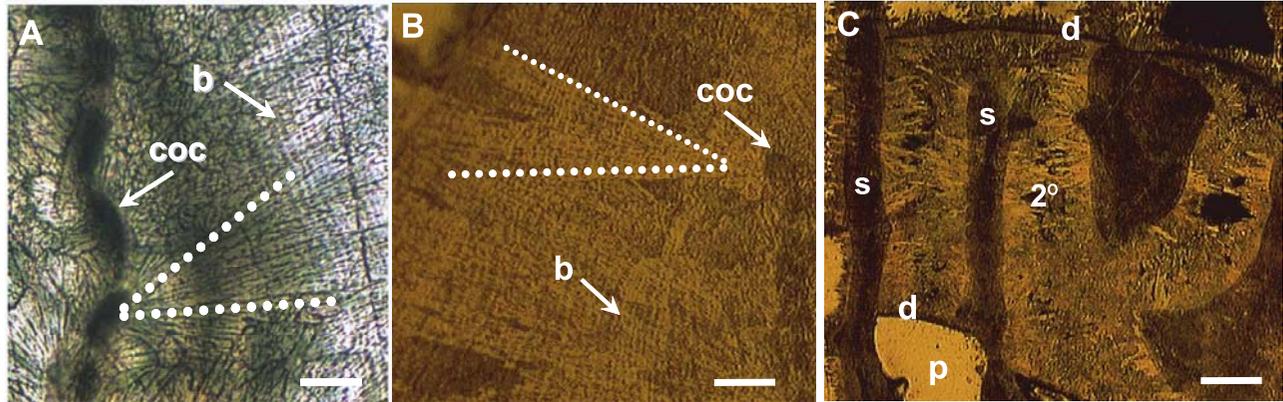


Figure 1. (a) Centers of calcification (coc) and fine growth bands (b) are features of modern *Porites* skeleton visible in thin section viewed in polarized, transmitted light. Fan-shaped crystal bundle enclosed within broken lines is one of many fasciculi that originate from a single calcification center. (b) The same features in a polished, gold-coated, thick-section of ancient *Porites* indicate well-preserved areas for ion microprobe analysis. (c) Pore spaces between adjacent dissepiments (d) and septa (s) of the same ancient specimen shown in Figure 1b are heavily infilled with secondary aragonite needles (2°). Some pore spaces (p) in the sample are unoccupied. Scale bar is $30\ \mu\text{m}$ in Figure 1a, $20\ \mu\text{m}$ in Figure 1b, and $100\ \mu\text{m}$ in Figure 1c.

calcification centers, accreted daily [Cohen *et al.*, 2001], indicates an annual growth rate of $\sim 6.5\ \text{mm}$ per year. Bundles of fine ($\sim 1\ \mu\text{m}$ thick) needle crystals radiating out from the calcification centers are bisected at regular ($\sim 2\ \mu\text{m}$) intervals by fine bands oriented perpendicular to the axis of fiber growth (Figure 1b). Thin horizontal sheets, the dissepiments, are intact and spaced $\sim 0.5\ \text{mm}$ apart. These are ultrastructural features and dimensions of pristine *Porites* skeleton (Figure 1a) [Cohen *et al.*, 2001]. The fine-scale sampling capabilities of the ion microprobe, typically $10\ \mu\text{m}$ diameter, $5\ \mu\text{m}$ depth, allowed us to selectively analyze pristine regions of the primary skeleton while avoiding areas where the clarity of these features was reduced.

[5] Of greater significance is the presence of large aragonite crystals, visible neither to the naked eye nor to XRD, within skeletal pore spaces once occupied by gastrovascular canals and tissue (Figure 1c). These crystals are not features of pristine coral skeleton but are secondary precipitates, grown abiogenically in the absence of coral tissue. Elongated along their *c* axes, they are distinguished from coral fibers in their size (up to $10\ \mu\text{m}$ thick), shape and orientation. Growth occurs from the distal edges of fiber bundles that define the boundary between the skeletal elements and the pore spaces. In some sections the entire pore space between adjacent dissepimental sheets is filled with secondary crystals (Figure 1c). Here we estimate that approximately one half of the sample volume is contributed by 2° aragonite.

3. Age Determination

[6] Using a Minimet handheld microdrill, we selectively removed $\sim 50\ \text{mg}$ of pristine skeleton from each of the fossil corals (TA8 and TA9) and submitted these for ^{14}C dates along with a section of TA9 that was heavily infested with 2° aragonite crystals (WHOI NOSAMS 43999, 44000, 44001). Radiocarbon ages of the pristine samples are $11,900 \pm 70$ (TA9) and $11,450 \pm 65$ (TA8) ^{14}C years B.P.

Applying a 300 year reservoir age correction [Bard *et al.*, 1998] and the INTCAL age calibration [Hughen *et al.*, 2000] places the corals at $13,650 \pm 70$ years B.P. and $13,100 \pm 65$ years B.P., respectively, coincident with later, cooler Allerod stage spanning $\sim 14,000$ years B.P. through 12,800 years B.P. in the GRIP ice core [Seierstad *et al.*, 2004]. TA9 with 2° aragonite infilling dated to $13,530 \pm 65$ years B.P. in agreement, within 1-sigma, with the age obtained from pristine TA9. While the younger mean age (by ~ 100 years) probably reflects the presence of younger 2° needles within the coral skeleton, the difference cannot be considered significant given the measurement and other sources of error such as short term variability of the reservoir age [e.g., Brown *et al.*, 1993]. The closeness in age between the pristine and altered sections indicates that growth of the 2° crystals in these particular samples probably occurred within 200 years after the primary skeleton was accreted and the intervening pore spaces were evacuated by coral tissue. The apparent rapidity of 2° growth in our fossil corals is in agreement with field evidence suggesting that this process is initiated while massive corals are alive [Enmar *et al.*, 2000; Lazar *et al.*, 2004].

4. Sr/Ca Analyses by Ion Microprobe

[7] Measurements of the skeletal composition of modern and ancient specimens were made with a Cameca 3f Ion Microprobe employing a $4\ \text{nA}\ \text{O}^-$ primary ion beam accelerated at $12.5\ \text{keV}$ [Hart and Cohen, 1996; Cohen *et al.*, 2001]. Secondary ion intensities for ^{88}Sr and ^{42}Ca were measured using a $-80\ \text{eV}$ (± 30) energy filter and converted to molar ratios using a standard (OKA) of known composition [Cohen *et al.*, 2001]. Replicate analyses of the standard within each ion microprobe session are reproducible to within 0.5%. The 20 mm long sections were epoxy-mounted in a 1" diameter Al ring, final polished with $0.3\ \mu\text{m}$ alumina suspension and gold-coated.

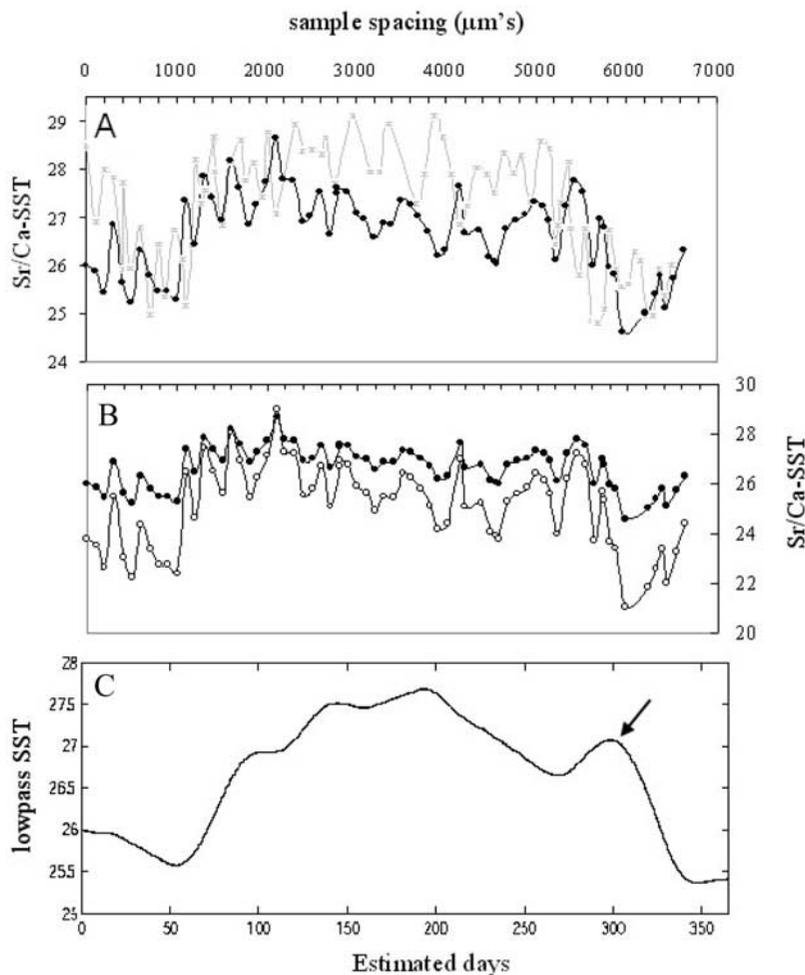


Figure 2. (a) Sr/Ca-SSTs derived from modern (asterisks) and ancient (TA8, solid circles) *Porites* from Tahiti plotted against sampling distance (microns). The extended summertime plateaus in the Sr/Ca annual cycles from both corals are caused by the skeleton extending more rapidly in the summertime than it does in the winter. (b) TA8 data shown in Figure 2a (solid circles) compared against SSTs derived from application of fast-growth equation to TA8's Sr/Ca ratios (open circles). Application of a fast-growth calibration decreases the mean derived SST and increases the amplitude of the seasonal cycle relative to the slow-growth calibration. The high-frequency oscillations captured here have approximately monthly and biweekly periodicity and are removed by low-pass filter to calculate the amplitude of the annual SST cycle (c). Microns are converted to days by assuming maximum Sr/Ca coincides with minimum NCDC SSTs and vice versa. Also in Figure 2c, the filtered Sr/Ca-SSTs from TA8 derived using the slow-growth calibration reveal a distinct double-hump in the annual cycle (arrow), indicative of the shallow depth at which the coral grew [Cohen and Sohn, 2004].

A modern *Porites* sample collected live on the Tahitian island of Moorea in 1973, and monthly averaged SSTs for the corresponding time period (NOAA NCDC extended SSTs [Smith and Reynolds, 2004]) were used to derive a Sr/Ca-SST calibration.

[8] Annual Sr/Ca cycles were generated at subweekly resolution using a 10 μm diameter spot to selectively analyze the centers of pristine skeletal septa, avoiding the edges of skeletal elements and adjacent pore spaces filled with secondary crystals. High-amplitude Sr/Ca cycles occurring with periodicities of 1 week to 1 month are superimposed upon the annual Sr/Ca cycles (Figure 2a). Such high-frequency oscillations are characteristic of high-

resolution coral Sr/Ca records [Hart and Cohen, 1996; Cohen et al., 2001; Meibom et al., 2003; Cohen and Sohn, 2004] and are thought to be driven by tidal modulation of zooxanthellate photosynthesis [Cohen and Sohn, 2004]. Their presence in the fossil samples supports our inference based on structural characteristics that the Sr/Ca profiles we generated were originally emplaced within the live skeletons as they grew.

[9] Unfiltered Sr/Ca ratios obtained from pristine skeleton of the modern and fossil corals range from 9.7 mmol/mol through 8.3 mmol/mol (Figure 2a). By contrast, discrete measurements of the 2° aragonite crystals occupying pore spaces within the fossil skeleton yielded Sr/Ca ratios rang-

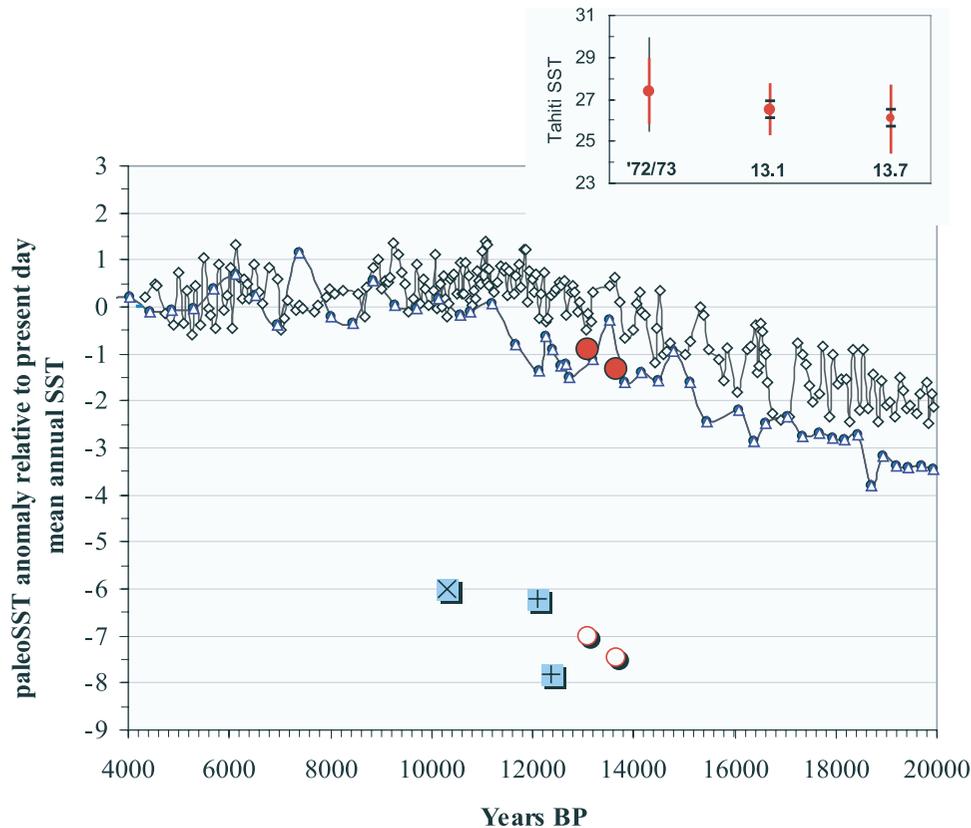


Figure 3. Reconstructed paleoSST anomaly relative to the mean annual present-day SSTs in the western tropical Pacific 4–20 kyr B.P. Mg/Ca-based SSTs from calcite foraminifera from the Sulu Sea (diamonds [Rosenthal *et al.*, 2003]) and Makassar Strait (triangles [Visser *et al.*, 2003]). Sr/Ca-based SSTs from corals on Tahiti (solid circles, this study) and Vanuatu (squares with a plus sign [Correge *et al.*, 2004]; square with a cross [Beck *et al.*, 1997]). Vanuatu data shown here are the minimum Sr/Ca-derived SSTs in each record. Also shown are Sr/Ca-based SSTs expected from bulk sample analyses of Tahiti coral containing 50% secondary aragonite derived using a fast-growth Sr/Ca-SST calibration (open circles). Inset shows annual range of Sr/Ca-derived SSTs obtained from ancient coral (13.1 and 13.7 kyr B.P.) compared with present-day recorded SSTs on Tahiti. Maximum, minimum, and mean Tahiti SSTs for 1972/1973 (NCDC data set) are indicated by the thick vertical line; maximum (29.9°C) and minimum (25.28°C) satellite (IGOSS NMC) SSTs for Tahiti 1981–2000 AD are indicated with the thin vertical line. Measurement error on Sr/Ca-derived SSTs, based on multiple successive analyses of the standard OKA, is indicated by horizontal black bars.

ing from 10.5 through 10.2 mmol/mol, consistent with observations of higher Sr/Ca ratios of abiogenic aragonites relative to reef coral aragonite [Kinsman and Holland, 1969; Enmar *et al.*, 2000; Gaetani and Cohen, 2004].

[10] A four-pole, zero-phase, low-pass Butterworth digital filter with corner period of 60 days was used to remove Sr/Ca oscillations at periods less than 2 months and reveal the annual Sr/Ca cycle. The width of the annual cycles generated from all three samples indicates comparable annual growth rates of 6–7 mm. A distinct “double hump” in the filtered annual Sr/Ca cycle of TA8 suggests that this was a shallow water coral, growing just a few feet from the sea surface (Figure 2c) [Cohen and Sohn, 2004].

5. Derivation of Sr/Ca-SST Calibration

[11] Annual Sr/Ca ratios in the modern Tahiti coral range from ~8.6 mmol/mol (summer) to ~9.3 mmol/mol (winter)

over an annual SST cycle of 28.9°C in the summer and 25.9°C in the winter recorded in 1972/1973. The linear least squares (LLS) spectral transfer function that describes the relationship between the annual SST and annual Sr/Ca cycles is: $SST = -3.582 \cdot Sr/Ca + 58.928$ (equation (1)). Wintertime SSTs within the atoll lagoon may be cooler than are indicated by the NCDC SSTs (T. Correge, IRD, personal communication, 2004). The lowest wintertime IGOS NMC satellite-derived SST since 1981, for a $1 \times 1^\circ$ grid square centered on Tahiti, is 25.28°C (Figure 3 inset). Using this minimum SST to derive the Sr/Ca-SST calibration yields the following equation: $SST = -4.330 \cdot Sr/Ca + 65.481$ (equation (2)).

[12] By comparison, a faster-growing (15 mm/year) *Porites* coral analyzed by the same technique yielded lower Sr/Ca ratios, consistent with independent observations of a growth rate dependence of coral Sr/Ca [Weber, 1973; de Villiers *et al.*, 1995; Correge *et al.*, 2004;

Goodkin *et al.*, 2004] and a shallower slope for the Sr/Ca-SST relationship. The LLS spectral transfer function derived for this coral is $SST = -6.978 * Sr/Ca + 87.939$ (equation (3)).

[13] The difference in slope of the Sr/Ca-SST relationships between the fast and slow-growing *Porites* occurs because the difference in skeletal calcification rate is manifest at low temperatures. Wintertime skeleton of the slow-growing colony yielded higher Sr/Ca ratios than the wintertime skeleton of the fast-growing colony at the same temperature. At summertime temperatures, the skeletal Sr/Ca ratios of both colonies are the same and the regressions converge at $\sim 28^{\circ}\text{C}$. Sr/Ca-SST calibrations derived using bulk sampling techniques might exaggerate this effect further by failing to capture the full amplitude of the wintertime Sr/Ca peak. For example, the even shallower slope of the *Porites* Sr/Ca-SST relationship derived by Beck *et al.* [1992]), corrected by Beck [1994] to $SST = -16.013 * Sr/Ca + 167.8$, is caused by lower wintertime Sr/Ca ratios than were captured in our corals using ion microprobe, while the summertime Sr/Ca ratios are comparable.

6. Derivation of Sr/Ca-Based PaleoSSTs

[14] Applying our slow-growth Tahiti Sr/Ca-SST calibrations to the slow growing fossil coral Sr/Ca data yields an annual SST range of $24.5^{\circ}\text{C} - 27.6^{\circ}\text{C}$ at 13,650 years B.P. and $25.3^{\circ}\text{C} - 27.7^{\circ}\text{C}$ at 13,100 years B.P. (equation (1)) (Figures 2b and 2c). PaleoSSTs derived using equation (2) are similar: $24.0^{\circ}\text{C} - 27.6^{\circ}\text{C}$ and $25.0^{\circ}\text{C} - 27.7^{\circ}\text{C}$, respectively. Because summer and winter SSTs are differentially reflected in the annual Sr/Ca cycle, a result of seasonal extension rates (Figure 2a), we report the average annual SSTs as the average between the maximum and minimum SSTs rather than averaging the entire data set. From this we deduce that Tahiti SSTs during the Bølling-Allerød were $0.5^{\circ} - 1.5^{\circ}\text{C}$ cooler than the average annual SSTs at this site today in agreement with paleoSSTs derived from Mg/Ca ratios of calcitic foraminifera (Figure 3) [Rosenthal *et al.*, 2003; Visser *et al.*, 2003].

[15] Application of our fast-growth calibration (equation (3)) to the Sr/Ca data obtained from the slow-growing fossil *Porites* yields Sr/Ca-derived SSTs that are on average 3°C cooler than today (Figure 2b). By lowering wintertime SSTs, this calibration also increases the apparent seasonal range to $4^{\circ} - 5^{\circ}\text{C}$ relative to today's range of $\sim 3^{\circ}\text{C}$ (Figure 2b). Furthermore, the higher Sr/Ca content of the 2° aragonite crystals yield lower Sr/Ca-derived SSTs, an average of 21.8°C (equation (1)). On the basis of these calculations, we predict that Sr/Ca-based SSTs derived through bulk analysis of corals containing 50% secondary aragonite by volume, using a fast-growth calibration would be $>6^{\circ}\text{C}$ cooler than today (Figure 3).

7. Discussion

[16] Our results indicate that growth rate effects and/or the presence of secondary aragonite crystals within

skeletal pore spaces of ancient corals may produce colder Sr/Ca-derived SSTs than were experienced by the living coral. While the impacts of growth and calcification rate on coral Sr/Ca ratios are not always apparent [e.g., Allison and Finch, 2004] and may be complicated by differences in seasonal growth rates amongst different colonies, our data support experimental and field evidence that links high calcification rates to lower skeletal Sr/Ca ratios [Ip and Krishnaveni, 1991; de Villiers *et al.*, 1995; Alibert and McCulloch, 1997; Ferrier-Pages *et al.*, 2002; Cohen *et al.*, 2002; Goodkin *et al.*, 2004]. Increases in skeletal Sr/Ca ratios coincident with decreases in growth and calcification rate have been observed both within colonies when comparing fast and slow-growing axes [e.g., de Villiers *et al.*, 1995; Alibert and McCulloch, 1997], and along the axis of maximum growth where interannual changes in growth rate have occurred [Goodkin *et al.*, 2004].

[17] The impact of 2° aragonite on the ^{14}C - and derived calendar ages of the ancient corals used in this study was not statistically significant relative to measurement error. However, it would be premature to apply this specific case observation to all ancient corals until we know more about the kinetics of 2° crystal growth within coral skeletons and the conditions under which growth of 2° crystals is initiated or enhanced. In our samples, the small age discrepancy between primary skeleton and 2° crystals indicates that growth of the abiogenic aragonite may have occurred very soon after the skeletal pore spaces were evacuated by tissue. Tissue uplift is an integral part of the process of skeletal extension in living corals [Barnes and Lough, 1993]. Therefore massive living corals and calcite-free fossils retrieved from uplifted reefs are also likely to host 2° crystals in their skeletal pore spaces.

[18] Interpretation of our results in terms of their implications for the evolution of deglacial SSTs of the western tropical Pacific must take into account the small number of samples and years represented in our data set. Nevertheless, the excellent agreement amongst our Sr/Ca-derived SSTs from fossil corals and those derived from Mg/Ca ratios in calcitic foraminifera for the corresponding time period increases our confidence in the interpretation of both paleoclimate archives. The Mg/Ca-based records indicate a continuous postglacial warming of the western tropical Pacific unpunctuated by the Bølling-Allerød warming or abrupt Younger Dryas cooling events that are prominent deglacial features of North Atlantic and terrestrial records. On the contrary, our data do not support the hypothesis based on coral Sr/Ca data from Vanuatu (167°E , 15.5°S), located west of Tahiti, that post-LGM warming of the southwest equatorial Pacific lagged that of the tropical Atlantic by several thousand years [Beck *et al.*, 1997].

[19] While this work does not exclude the possibility of remarkably cold tropical SSTs during the LGM and last deglaciation [Guilderson *et al.*, 1994; Beck *et al.*, 1997; Correge *et al.*, 2004], it does suggest that those data should be confirmed with future analyses. With a combination of appropriate Sr/Ca-SST calibrations and employment of microanalytical techniques capable of selective analysis of pristine skeleton, continuous, seasonally resolved SST

records for the tropical open ocean can be extracted from fossil corals with accuracy and precision.

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