Coral records of central tropical Pacific radiocarbon variability during the last millennium

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[1] The relationship between decadal to centennial changes in ocean circulation and climate is difficult to discern using the sparse and discontinuous instrumental record of climate and, as such, represents a large uncertainty in coupled ocean-atmosphere general circulation models. We present new modern and fossil coral radiocarbon (\(\Delta^{14}C\)) records from Palmyra (6°N, 162°W) and Christmas (2°N, 157°W) islands to constrain central tropical Pacific ocean circulation changes during the last millennium. Seasonally to annually resolved coral \(\Delta^{14}C\) measurements from the 10th, 12th–17th, and 20th centuries do not contain significant interannual to decadal–scale variations, despite large changes in coral \(\delta^{18}O\) on these timescales. A centennial–scale increase in coral radiocarbon from the Medieval Climate Anomaly (~900–1200 AD) to the Little Ice Age (~1500–1800) can be largely explained by changes in the atmospheric \(\Delta^{14}C\), as determined with a box model of Palmyra mixed layer \(\Delta^{14}C\). However, large 12th century depletions in Palmyra coral \(\Delta^{14}C\) may reflect as much as a 100% increase in upwelling rates and/or a significant decrease in the \(\Delta^{14}C\) of higher-latitude source waters reaching the equatorial Pacific during this time. SEM photos reveal evidence for minor dissolution and addition of secondary aragonite in the fossil corals, but our results suggest that coral \(\Delta^{14}C\) is only compromised after moderate to severe diagenesis for these relatively young fossil corals.


1. Introduction

[2] Ocean circulation changes in the tropical Pacific strongly influence global climate, as demonstrated during El Niño–Southern Oscillation (ENSO) extremes. During strong El Niño events, a relaxation of the trade winds results in a large reduction of the equatorial upwelling of cooler subsurface waters and reshapes the wind-driven surface currents in the tropical Pacific [Taft and Kessler, 1991]. This reorganization of equatorial currents causes anomalously warm waters in the eastern and central tropical Pacific, ultimately driving a reorganization of the large-scale global atmospheric circulation. While instrumental data resolve seasonal to interannual variability in tropical Pacific circulation [Picaut and Tournier, 1991; Donguy and Meyers, 1996], the nature of decadal to centennial–scale changes in tropical Pacific circulation remain unknown. Resolving such low-frequency ocean circulation variability and its relationship to low-frequency regional and global climate changes is critical to the improvement of ocean models used for climate prediction.

[3] Radiocarbon (\(^{14}C\)) is a useful tracer of water mass mixing, as deep waters that have been isolated from the atmosphere are depleted in \(^{14}C\) due to radioactive decay, whereas surface waters are relatively enriched. Large surface water \(^{14}C\) gradients arise from horizontal and vertical mixing – upwelling brings relatively depleted \(^{14}C\) waters to the ocean surface whereas prolonged air–sea gas exchange in the mid-ocean gyres drives \(^{14}C\) enrichment in these areas. Thus, regional water masses are ‘tagged’ with a distinct \(^{14}C\) signature depending on the regional oceanographic setting. Changes to regional seawater \(^{14}C\) values through time imply changes in either horizontal or vertical mixing.

[4] Corals are useful tools for the reconstruction of seawater \(^{14}C\) signatures as they incorporate the \(^{14}C\) of the dissolved inorganic carbon of the seawater in which they grow into their skeletal matrix, and can live for decades to centuries [Druffel and Linick, 1978; Dunbar and Cole, 1999; Druffel et al., 2007]. Annual band counting in modern corals and/or U/Th dating in fossil corals ensure accurate, \(^{14}C\)-independent absolute chronologies for the construction of coral-based records of seawater radiocarbon variability through time. Indeed, the incorporation of “bomb \(^{14}C\)”
Examples of postdepositional diagenesis include dissolution into coral paleoclimate reconstructions [Matthews et al., 2007, and references therein]. Tropical Pacific coral 14C into coral skeletal geochemistry and therefore introduce artifacts [Grottoli et al., 2007]. It is important to note that dissolution has no documented effect on coral Δ14C or δ18O, so the primary concern for the fossil corals used in this study is the recrystallization and/or precipitation of secondary aragonite and/or calcite. As the diagenetic history of the beached fossil corals used in this study is unknown, careful diagenetic screening is conducted to characterize the potential effects of diagenesis on the coral 14C records.

3. Oceanographic Setting and Prebomb Δ14C in the Tropical Pacific

Palmyra (6°N, 162°W) and Christmas (2°N, 157°W) Islands are part of the Line Islands in the middle of the tropical Pacific Ocean (Figure 1). Palmyra lies in the path of the Northern Equatorial Counter Current (NECC), which brings warm, fresh waters eastward from the Western Pacific Warm Pool. Located nearer to the equator than Palmyra, Christmas Island is bathed in the cool, salty waters of the westward flowing Southern Equatorial Current (SEC), which carries the signature of equatorial wind-driven upwelling [Reverdin et al., 1994].

Coral 14C records that predate the midcentury bomb testing can be used to map prebomb tropical Pacific seawater 14C gradients (Figure 1). Such records reveal a roughly 20‰ gradient (a large signal given analytical errors of roughly ±3‰) of 14C values ranging from well-equilibrated subtropical gyres at ∼50‰ to more depleted upwelling zones at ∼70‰ (Figure 1 caption and references therein). There is a roughly 20‰ zonal gradient in seawater Δ14C along the
equator, with higher values in the Warm Pool and more depleted values in the eastern Pacific cold tongue. Therefore, the zonal surface currents of the tropical Pacific advect waters with significantly different $^{14}$C values to the Line Island chain. The SEC brings cold, $^{14}$C-depleted waters to Christmas, while the NECC contributes warmer, $^{14}$C-enriched waters to Palmyra. Preliminary runs using the $^{14}$C equipped GFDL MOM4 predict 8–10‰ and 10–14‰ ranges in postbomb interannual variability in radiocarbon at Palmyra and Christmas, respectively (K. Rodgers, personal communication, 2009), although no model-based constraints exist for prebomb seawater $^{14}$C variability.

4. Line Islands Coral Oxygen Isotopic Records

[10] Modern and fossil coral oxygen isotopic ($\delta^{18}$O) records from Palmyra Island have provided detailed reconstructions of ENSO and low-frequency climate variability in the central tropical Pacific during the last millennium [Cobb et al., 2001, 2003b]. The existing 20th century coral $\delta^{18}$O records from Palmyra and Christmas islands are highly correlated to regional SST records ($R = 0.65$ and $R = 0.84$ with NINO3.4, respectively) [Cobb et al., 2001; Evans et al., 1999]. The Palmyra fossil coral $\delta^{18}$O records reveal that during the MCA the tropical Pacific was likely cooler and/or drier than the preindustrial period, with moderate ENSO activity [Cobb et al., 2003b]. The LIA was characterized by more frequent and intense ENSO events, with average climate conditions similar to preindustrial values. Generally speaking, the records reveal prominent low-frequency decadal- to centennial-scale changes in tropical Pacific climate.

[11] By comparing the existing coral $\delta^{18}$O records to newly generated coral $^{14}$C records from Palmyra and Christmas, we can investigate the relationship between surface climate (SST and hydrology) and water mass circulation on interannual to centennial timescales. One would expect that periods of stronger upwelling would be recorded as higher $\delta^{18}$O values (signifying cooler, drier conditions) and more depleted $^{14}$C (signifying the presence of deeper water at the surface). Conversely, periods of reduced upwelling might be recorded as relatively lower $\delta^{18}$O (warmer, wetter conditions) and relatively higher $^{14}$C (isolation of deep waters from surface). As an example, if upwelling increased at Palmyra such that SST and seawater $^{14}$C at Palmyra were equivalent to those values at Galapagos, the change would be roughly $-4^\circ$C in SST (http://www.pmel.noaa.gov/tao/data_deliv/deliv.html) and roughly $-16‰$ in $^{14}$C (Figure 1). The associated changes in coral $\delta^{18}$O and coral $^{14}$C would be $+0.9%o$ [Epstein et al., 1953] and $-16‰$, respectively. However, it is worth noting that the signal to analytical error ratio for coral $\delta^{18}$O in this case is roughly twice that of coral $^{14}$C.

[12] Corals would also be sensitive to changes in the $^{14}$C value of the upwelled waters themselves, which could be caused by changing the depth of upwelling, or by changing the source of equatorial thermocline waters. Therefore, the relationship between surface climate changes (as recorded by coral $\delta^{18}$O) and subsurface ocean circulation change (as recorded by coral $^{14}$C) is potentially complex. Our study provides the first well-reproduced reconstructions of interannual to centennial-scale seawater $^{14}$C variations in the central tropical Pacific – records that can be used to refine our understanding of climate-related changes in Pacific Ocean circulation.

5. Methods

[13] For the most part, the $\delta^{18}$O records and absolute dating constraints for the modern and fossil Porites corals analyzed in this study are previously published. Palmyra ‘ModernB’ is a duplicate core to the Palmyra modern coral record originally published by Cobb et al. [2001]. The Christmas modern coral (PP7–3) was originally published by Evans et al. [1999]. With the exception of Christmas fossil coral M2 and Palmyra fossil corals A27 and SB3B, the relevant $^{14}$C records and U/Th dates for all the fossil corals are reported by Cobb et al. [2003a, 2003b]. SB3B is a duplicate core of the previously published SB3 record from Palmyra [Cobb et al., 2003b], while M2 and A27 will be presented by K. M. Cobb et al. (Fossil coral windows of central tropical Pacific climate over the last millennium, manuscript in preparation, 2010).

5.1. Coral $\delta^{18}$O Measurements

[14] Most of the $^{14}$C sampling was conducted on the exact slab corresponding to the published coral $\delta^{18}$O records, whose climate-related variability guided $^{14}$C sampling. However, in the case of the Palmyra modern coral and a 17th century Palmyra fossil coral (SB3), we generated new $\delta^{18}$O profiles for duplicate slabs (referred to as ‘ModernB’ and ‘SB3B’, respectively) which were subsequently used for $^{14}$C sampling. This was necessary because slab geometries and sample conservation requirements prevented us from drilling the large, closely spaced samples required for $^{14}$C analysis from the original modern and SB3 slabs used by Cobb et al. [2001 and 2003b]. The duplicate coral $\delta^{18}$O profiles were exactly matched to the original Cobb et al. [2001 and 2003b] $\delta^{18}$O profiles (R = 0.80 for the duplicate modern cores and R = 0.64 for the duplicate SB3 cores), allowing for the assignment of firm chronological constraints. Coral powders weighing 60 to 90$\mu$g were drilled every 1mm along the coral axis of maximum growth using a table mounted, low-speed Dremel drill. The powders were analyzed for $\delta^{18}$O on a GV Isoprime Mass Spectrometer at the Georgia Institute of Technology, with an external precision of $\pm0.06‰$ (1$sigma; N = 550$).

5.2. Coral $^{14}$C Measurements

[15] The coral $\delta^{18}$O records were used to target specific time intervals for $^{14}$C analysis. Large amplitude ENSO, decadal, and centennial $\delta^{18}$O variations were targeted as the likeliest periods for major circulation changes and thus the largest $^{14}$C signals.

[16] A 1mm wide diamond-tipped bit was used in a handheld Dremel tool to drill 6–10mg of powder from coral slabs. Subannual $^{14}$C samples were drilled every 1–3mm, corresponding to one sample every 1–2 months (~8 samples/year). Annual $^{14}$C samples were drilled across an entire year of coral growth (10 to 25mm) guided by $\delta^{18}$O chronologies and X-rays of the coral slabs. Coral $^{14}$C samples were analyzed following established protocols outlined by
Coral powders were prepared for analysis by acidification to CO₂ and conversion to graphite using an Fe catalyst and the hydrogen reduction method [Vogel et al., 1984]. Coral Δ¹⁴C was measured on the Keck Carbon Cycle Accelerator Mass Spectrometer (KCCAMS) at the University of California, Irvine [Southon et al., 2004] with a total precision of ±1.8‰ (1σ, N = 129) based on repeat measurements of an in-house coral standard (CSTD). Radiocarbon values are reported as per mil deviation from Radiocarbon values are reported as per mil deviation from a δ¹³C = −25‰ [Stuiver and Polach, 1977]. Correcting the corals’ radiocarbon content using absolute U/Th ages facilitates the comparison of coral Δ¹⁴C of different ages and isolates the variability of radiocarbon in the water mass at the time of coral growth.

Numerous duplicates tested the reproducibility of the graphitization procedure and instrument performance. Of the first 48 samples, 9 were duplicated and all were found to agree within the errors determined by repeat measurements of a coral standard (±1.8‰, 1σ). For the rest of the study, one in ten samples was duplicated.

To test the reproducibility of the University of California Irvine (UCI) coral ¹⁴C measurements, 30 samples from the Palmyra and Christmas corals were measured at the University of Arizona (UA) AMS facility. Subannual samples (1mm wide solid coral slivers) were cut using a band saw from the two modern corals and three fossil corals. Sampling locations were guided by δ¹⁸O chronologies and the UCI coral Δ¹⁴C results to target the largest potential ¹⁴C variability. Coral Δ¹⁴C samples were analyzed following established protocols outlined by Burr et al. [1992]. Coral slivers were prepared for analysis by acidification to CO₂ and conversion to graphite using an Fe catalyst and the zinc reduction method [Sio et al., 1987; Marzaioli et al., 2008]. The total uncertainty for the University of Arizona coral ¹⁴C measurements based on repeated measurements of an in-house coral standard is ±4.0‰ (1σ, N > 1000) [Burr et al., 1998].

### 5.3. Diagenesis Screening by SEM and XRD

A Hitachi S-800 field emission gun Scanning Electron Microscope (SEM) at the Georgia Tech Materials Science and Engineering department was used to investigate microscopic alterations to the coral skeletal morphology. Small pieces of the coral skeleton (<5mm on a side) were chipped off and mounted on SEM studs using double sided carbon tape and sputter coated with ~200Å of gold. Heavily altered coral sections identified by the SEM were ground into fine powder and examined for mineralogical content using a Philips Norelco, water-cooled XRD, type 12045, available at Georgia State University.

### 5.4. Mixed Layer Model of Central Tropical Pacific ¹⁴C Variability

In order to evaluate the potential causes of ¹⁴C variability in the surface waters at Palmyra on interannual to centennial timescales, we modified a mixed layer model originally presented by Druffel [1997] to fit the specifics of the central tropical Pacific. The model represents an effort to quantify the various sources of ¹⁴C to the central tropical Pacific surface waters through time (Figure 2). In this model, the sources of radiocarbon to the central tropical Pacific are horizontal advection, vertical advection, and air-sea CO₂ exchange.

Seawater radiocarbon values in the Palmyra box evolve according to the equation:

\[
P(t + \Delta t) = P(t) + \left[ M(t) - P(t) \right] \Delta t + \left[ k_1 A(t) - k_1 P(t) \right] \Delta t + W_1(t) \times \sum S_i \times \Delta t \times \left[ \sum D_i(t) - P(t) \right]
\]

where \( P(t) \) is the radiocarbon value at Palmyra at time \( t \), \( M(t) \) is the Marine04 global ocean radiocarbon values as modeled by Hughen et al. [2004], \( \Delta t \) is the time step (1 year in this case), \( k_1 \) is the input rate of ¹⁴CO₂ from the air to the sea surface, \( k_1 \) is the output rate of ¹⁴CO₂ from the sea surface to the air, \( A(t) \) is the atmospheric Δ¹⁴C value as reconstructed in INTCAL04 [Reimer et al., 2004], \( W_1(t) \) is the water mass renewal rate (set to 0.17 yr⁻¹ to obtain steady state, prebomb Palmyra surface Δ¹⁴C values of −54‰), \( S_i \) is the mixing constant from the deep to the surface ocean boxes (ranging from \( S_i = 1 \) at the surface to \( S_i = 0.2 \) in the deepest 200m layer), and \( D_i \) is the mixing value in the deep boxes 1 through 7 (ranging from −54‰ at the surface to −100‰ at 200m). We integrate the model from 650 AD to 1950 AD.

Horizontal advection appears to contribute ~30% of the waters entering the Palmyra box, and its radiocarbon content is assumed to follow the evolution of the globally averaged mixed layer ¹⁴C estimated by Hughen et al. [2004]. It is important to note that alternative values for the horizontal advection component are possible, as this is poorly constrained by observations. Alternative choices (20–40%) require changes in the model upwelling rates to match prebomb ¹⁴C at Palmyra. In short, no one combination of horizontal and vertical advection rates is more justifiable than another, and more importantly, changing the relative weight of horizontal versus vertical advection in the model makes little difference in the modeled ¹⁴C over the last millennium. The ¹⁴C value of the horizontally advected seawater tracks Marine04 [Hughen et al., 2004] values for global averaged mixed layer ¹⁴C, as determined by a box diffusion model which converts atmospheric ¹⁴C values from dendrochronologically dated trees rings into marine mixed layer ¹⁴C values. The horizontal advection component in the equatorial Pacific likely represents a combination of the Marine04 globally averaged surface waters (higher ¹⁴C, better equilibrated with atmosphere) and upwelled waters (lower ¹⁴C, poorly equilibrated with atmosphere) that would damp the Marine04 ¹⁴C variability. Therefore, our use of Marine04 as the horizontal advection contribution represents an upper limit on the contribution of atmospheric ¹⁴C variations to surface water ¹⁴C variations at Palmyra through horizontal advection.

Vertical advection is represented by upwelling from seven evenly spaced layers between the surface and 200m...
deep, with $\Delta^{14}C$ values interpolated between $-54\%o$ at the surface (the measured prebomb $\Delta^{14}C$ value at Palmyra) to $-100\%o$ at 200m [Rubin and Key, 2002; Matsumoto and Key, 2004]. The choice of 200m as a maximum depth of upwelling is based on Fine et al. [1983], although some recent studies support a shallower source of upwelled waters ranging from 180m [Bryden and Brady, 1985] to 140m [Weisberg and Qiao, 2000]. In one version of the model, we hold the $\Delta^{14}C$ values of the deep water boxes fixed at the 20th century prebomb values. However, the deep water associated with equatorial upwelling is likely subducted from the extratropics several decades prior, where it experiences air-sea $^{14}CO_2$ exchange. As such, we also create a version of the model in which the deep water $\Delta^{14}C$ values evolve through time, applying the following equation:

$$D_i(t) = D_i(t) + (M_{50} - 56\%o)$$

where $D_i(t)$ is the deep water value at time step $t$, $M_{50}$ is the value of Marine04 averaged from $t_{50}$ years to $t$, years, and $-56\%o$ is the average Marine04 value from 1940 to 1950 AD. With this equation, we essentially add anomalies to each deep water layer whose magnitude is determined by the departure of Marine04 from prebomb $\Delta^{14}C$ differences of $\pm 3\%o$.

Figure 2. Schematic of the mixed layer box model used to estimate Palmyra surface $\Delta^{14}C$ over the last millennium. Horizontal advection is represented by input from box M(t) and varies through time as Marine04 [Hughen et al., 2004]. Air-sea gas exchange occurs via exchange with box A(t) and varies through time as INTCAL04 [Reimer et al., 2004]. Vertical advection contributes $^{14}C$ from deep layers D1 through D7 (20th century prebomb $\Delta^{14}C$ values are labeled), whose $\Delta^{14}C$ values are either held constant through time or are allowed to vary through time by applying Marine04-based anomalies.

Results

6.1. Interannual Coral $\Delta^{14}C$ Variability

We measured Palmyra and Christmas coral $\Delta^{14}C$ across the large 1941–1943 El Niño/La Niña cycle to assess whether seawater $^{14}C$ is affected by ENSO-related changes in upwelling. Christmas coral $\Delta^{14}C$ data measured in 1999 by Warren Beck at UA hint at an ENSO-related signal in ocean $\Delta^{14}C$ variability, with higher $\Delta^{14}C$ during El Niño...
conditions (reduced upwelling) and vice versa during La Niña conditions (Figure 3, top). However, subsequent measurements on the same section of coral performed at both UA and UCI resolve no change in Christmas coral $\Delta^{14}C$ (Figure 3, middle). With the exception of one point circa 1942, the UA and UCI Christmas coral $\Delta^{14}C$ data sets agree within the 2σ analytical errors associated with each lab. At this time there is no satisfactory explanation for the slightly discrepancies between the older UA data and the newer data, which persist despite our repeated analyses of this section of coral.

While the 1999 UA data suggest that there may be interannual seawater $\Delta^{14}C$ anomalies of 5–10‰ at Christmas Island, the bulk of our Christmas Island coral $\Delta^{14}C$ data suggest that these anomalies are likely smaller than 5‰. High-resolution coral $\Delta^{14}C$ measurements from Palmyra spanning the 1941–43 ENSO cycle also reveal insignificant interannual variability. A statistically significant offset (>99.9% as assessed with a student t-test) between $\Delta^{14}C$ values at Palmyra ($-54.8 \pm 1.6$‰ stdev, n = 24) and Christmas ($-58.2 \pm 1.7$‰ stdev, n = 24) reflects the fact that Christmas is closer to the equatorial source of $^{14}C$-depleted upwelling waters, with a smaller influence of more enriched western equatorial Pacific waters. Indeed, previously published coral $\Delta^{14}C$ data from Fanning Island (4°N) fall in between the new
Palmyra and Christmas data, with an average of $\sim -55\%$ [Grottoli et al., 2003].

High-resolution sampling across six additional ENSO cycles recorded in modern and fossil coral $\delta^{18}O$ data from both Palmyra and Christmas reveals similarly low interannual $14^C$ variability (Figure 4). ENSO anomalies in 1917 AD, 1655 AD, 1431–1433 AD, 1421–1422 AD, and 943–945 AD as identified by coral $\delta^{18}O$ anomalies [Cobb et al., 2003b] were analyzed in Palmyra corals and an ENSO cycle in 1537–1538 AD was analyzed in a Christmas fossil coral. We conclude that interannual variations in prebomb seawater $\Delta^{14}C$ in the central tropical Pacific were smaller than the $2\sigma$ analytical error associated with these coral $\Delta^{14}C$ measurements ($\pm 3.6\%$ at UCI).

6.2. Decadal Coral $\Delta^{14}C$ Variability

Large decadal-scale shifts in coral $\delta^{18}O$ were targeted for $\Delta^{14}C$ analysis to investigate lower-frequency changes in surface ocean radiocarbon. Six fossil corals from Palmyra were sampled for annually averaged $\Delta^{14}C$ variations during

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Figure 4. Comparison of Palmyra and Christmas coral $^{14}C$ with coral $\delta^{18}O$. (a) The 10th century Palmyra (sample NB12), (b) 12th century Palmyra (L17), and (c) 13th century Palmyra (A27). The gray shading spans sample horizons which are associated with significant diagenetic alteration including dissolution and the addition of secondary calcite, as evidenced by SEM photos (Figure 9) and XRD analysis (not shown). Here $\Delta^{14}C$ measurements from more pristine portions of the coral represent upper limits on seawater $^{14}C$ during these times. A27 $\delta^{18}O$ reported by Cobb et al. (manuscript in preparation, 2010). (d) The 14th century Palmyra (SB7), (e) 15th century Palmyra (SB5), (f) 16th century Christmas (M2), (g) 17th century Palmyra (SB3B), and (h) Palmyra modern. Error bars are reported as $\pm 1.8\%$ ($1\sigma$) for UCI data and $\pm 4.0\%$ ($1\sigma$) for UA data. Palmyra coral $\delta^{18}O$ data from Cobb et al. [2003b]. All axes have equal scaling. ‘S’ marks the location of sampling horizons for SEM photos presented in Figures 7 and 8.
932–941 AD, 1169–1180 AD, 1344–1356 AD, 1409–1418 AD, 1637–1647 AD, and 1669–1680 AD (Figure 4). The most pronounced feature in the 10th century coral $\delta^{18}O_i$ sa large decadal shift to heavier $\delta^{18}O$ values (cooler/drier) that occurs from 933 to 945 AD. However, coral $\Delta^{14}C$ shows no trend over this time period (Figure 4a). The 12th century annual $\Delta^{14}C$ values are similarly constant, despite a large shift in $\delta^{18}O$ from 1172 to 1180 AD (Figure 4b). Coral $\Delta^{14}C$ values from the 14th and 15th centuries range from $-60.7‰$ in 1409 to $-55.3‰$ in 1413, and do not track a significant decadal-scale change in coral $\delta^{18}O$ centered at 1350 AD (Figures 4d–4e). The mid-17th century $\Delta^{14}C$ values vary from $-52.6‰$ in 1643 to $-46.8‰$ in 1642, and do not correspond to interannual to decadal-scale coral $\delta^{18}O$ variations (Figure 4g). The late 17th century $\Delta^{14}C$ values are relatively constant (Figure 4g). We conclude that seawater $\Delta^{14}C$ at Palmyra did not vary across the large decadal-scale climate anomalies inferred from coral $\delta^{18}O$ during the last millennium. See Table S1 of the auxiliary material for a full list of interannual and annual radiocarbon data.1

6.3. Centennial Coral $\Delta^{14}C$ Variability

[30] The largest signal in the Line Island coral $\Delta^{14}C$ reconstructions is a centennial-scale rise in $\Delta^{14}C$ that occurs from the MCA to the LIA. In comparison to modern pre-bomb $\Delta^{14}C$ values of $-54.8‰ ± 1.6 (n = 3)$, where $n$ is the number of years included in the average, see Table 1) at Palmyra, 12th and 13th centuries are associated with the most depleted radiocarbon values of those sampled during the millennium, averaging $-67.6‰ ± 1.0 (n = 12)$ and $-61.5‰ ± 4.0 (n = 20)$, respectively (Figure 5 and Table 1). It is important to note that the 13th century coral contains appreciable secondary aragonite (see section 6.5), which means that the measured $^{14}C$ values represent an upper limit on seawater radiocarbon during this time. Values during the LIA are higher with respect to the MCA and early 20th century, ranging from $-50.5‰ ± 1.5 (n = 16)$ in the mid-17th century at Palmyra to $-45.0 ± 1.4 (n = 3)$ in the mid 16th century at Christmas (Figure 5 and Table 1). $\Delta^{14}C$ values of Palmyra coral in the 10th, 14th, and 15th centuries $[-60.8 ± 1.2‰ (n = 13), -57.6 ± 1.3‰ (n = 12) and -56.9 ± 1.5‰ (n = 16)$, respectively] are similar to early 20th century $\Delta^{14}C$ values.

Figure 4. (continued)
6.4. Mixed Layer Model Constraints on the Sources of Coral $\Delta^{14}C$ Variability Over the Last Millennium

The Palmyra mixed layer model suggests that atmospheric $\Delta^{14}C$ variations explain most, though not all, of the centennial-scale $\Delta^{14}C$ variability recorded in the Palmyra and Christmas fossil corals (Figure 6).

Twelfth and late 13th century coral $\Delta^{14}C$ values that are significantly lower than the mixed layer model prediction may indicate increased sensitivity to low atmospheric $\Delta^{14}C$ values during this time and/or changes in ocean circulation. It is important to note that the absolute ages of the 12th century coral would have to shift by 50–70 years in order for the $\Delta^{14}C$ data to match the mixed layer model prediction, far beyond the ±10yr chronological errors associated with this coral [Cobb et al., 2003b]. However, the Marine04 curve used in the mixed layer model significantly damps relatively low atmospheric $\Delta^{14}C$ values during this time and/or changes in ocean circulation. In general, the smoothed atmospheric $\Delta^{14}C$ curve overpredicts the observed coral $\Delta^{14}C$ variability over the last millennium (most notably during the 10th and 16th centuries), but is a better match for the 12th century coral data than the Marine04-derived prediction. Therefore, the 12th century coral data may reflect a heightened sensitivity to atmospheric $\Delta^{14}C$ variability during this time (which in turn may be linked to changes in ocean circulation). If the mixed layer model accurately represents the incorporation of atmospheric $\Delta^{14}C$ anomalies into the surface ocean, however, we infer that changes in ocean circulation occurred during the 12th and late 13th centuries.

6.5. Diagenesis in the Line Island Fossil Corals

The majority of the Palmyra coral collection was previously examined for diagenesis using XRD and thin sections [Cobb, 2002], but these techniques cannot resolve subtle diagenesis that could introduce artifacts into coral-based seawater $^{14}C$ reconstructions. A pristine coral skeleton has a smooth, solid surface with easily identifiable dissepiments, and unfilled pore spaces (Figure 7a). Secondary aragonite deposition in corals occurs as tiny needles protruding from the original skeleton into open pore spaces, and is commonly associated with submarine diagenesis [Enmar et al., 2000; Hendy et al., 2007]. SEM photos suggest that the modern Palmyra coral, 10th century coral (NB12), 12th century coral (L17), 14th century coral (SB7), 15th century coral (SB5), and 16th century Christmas coral (M2) all retain relatively
pristine coral skeletons lacking obvious signs of secondary aragonite deposition and/or major dissolution (Figures 7b–7e).

[34] As secondary aragonite precipitation would cause an enrichment in coral $\Delta^{14}C$ values, we used SEM photos to determine whether diagenesis could have caused the relatively large $^{14}C$ enrichments observed in the 16th and 17th century fossil corals. Indeed, SEM photos of 17th century Palmyra coral SB3B reveal areas in the oldest portion of the core that are covered in small secondary aragonite needles (Figure 8a). Radiocarbon values from this horizon average $−50.9^{\pm}0.06^\circ$ (n = 6). However, samples taken from younger sections in the same coral lack any evidence of diagenesis, yet are similarly enriched in $^{14}C$ (averaging $−49.8^{\pm}1.1$, N = 12) (Figure 8b). Furthermore, the late 17th century coral (SB13) is even higher in $\Delta^{14}C$ than SB3B, yet shows no signs of diagenesis (Figure 7d). SEM photos also rule out the influence of diagenesis on the very high $\Delta^{14}C$ values measured in the 16th century Christmas fossil coral M2 ($−45.0^{\pm}1.4$, n = 3). Taken together, these lines of evidence suggest that the minor diagenesis observed in one LIA fossil coral did not significantly affect the $\Delta^{14}C$ values of this coral.

[35] Moderate to severe diagenesis in a 13th century fossil coral (A27) was associated with $\Delta^{14}C$ values as high as $−21^\circ$, far outside the expected range of seawater $\Delta^{14}C$ values in the surface ocean. Such high coral $\Delta^{14}C$ values can only be explained by the addition of relatively young secondary carbonates to the original coral skeleton. In fact, mass balance calculations suggest that portions of this coral must be contaminated with as much as 50% of early 20th century carbonates to obtain values approaching $−21^\circ$. Of course, if thecontaminating material contains bomb radiocarbon, less material would be required to cause the observed enrichments. SEM photos of A27 revealed severe

### Table 1. Absolute Ages, Average Annual $\Delta^{14}C$ Values, and Average $\delta^{18}O$ Values for the Palmyra and Christmas Modern and Fossil Corals

<table>
<thead>
<tr>
<th>Sample</th>
<th>Island</th>
<th>Absolute Age Assignment</th>
<th>AMS</th>
<th>$\Delta^{14}C$ (%)</th>
<th>$\delta^{18}O$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NB12</td>
<td>P</td>
<td>928–961 (±10 yr)</td>
<td>UCI</td>
<td>−60.8 ± 1.19</td>
<td>−4.89</td>
</tr>
<tr>
<td>L17</td>
<td>P</td>
<td>1149–1220 (±10 yr)</td>
<td>UCI</td>
<td>−67.6 ± 1.03</td>
<td>−4.73</td>
</tr>
<tr>
<td>A27</td>
<td>P</td>
<td>1242–1330 (±5 yr)</td>
<td>UCI</td>
<td>−65.6 ± 2.26</td>
<td>−4.86</td>
</tr>
<tr>
<td>SB7</td>
<td>P</td>
<td>1326–1357 (±5 yr)</td>
<td>UCI</td>
<td>−57.6 ± 1.32</td>
<td>−4.83</td>
</tr>
<tr>
<td>SB5</td>
<td>P</td>
<td>1405–1448 (±5 yr)</td>
<td>UCI</td>
<td>−36.9 ± 1.54</td>
<td>−4.78</td>
</tr>
<tr>
<td>M2</td>
<td>C</td>
<td>1515–1561 (±5 yr)</td>
<td>UCI</td>
<td>−45.0 ± 1.36</td>
<td>−4.36</td>
</tr>
<tr>
<td>SB3B</td>
<td>P</td>
<td>1627–1658 (±5 yr)</td>
<td>UCI</td>
<td>−50.5 ± 1.50</td>
<td>−4.85</td>
</tr>
<tr>
<td>SB13</td>
<td>P</td>
<td>1653–1695 (±5 yr)</td>
<td>UCI</td>
<td>−46.4 ± 1.54</td>
<td>−4.90</td>
</tr>
<tr>
<td>Modern</td>
<td>P</td>
<td>1918–1920 (±2 months)</td>
<td>UCI</td>
<td>−53.9 ± 2.14</td>
<td>−4.91</td>
</tr>
<tr>
<td>ModernB</td>
<td>P</td>
<td>1938–1944 (±2 months)</td>
<td>UCI</td>
<td>−54.8 ± 1.07</td>
<td>−4.91</td>
</tr>
<tr>
<td>PP7–3</td>
<td>C</td>
<td>1938–1993 (±2 months)</td>
<td>UCI</td>
<td>−58.0 ± 0.71</td>
<td>−4.51</td>
</tr>
</tbody>
</table>

---

*P, Palmyra Island; C, Christmas Island.

*U/Th dates and uncertainties reported by Cobb et al. [2003a]. Palmyra modern coral age model reported by Cobb et al. [2001]. Christmas modern coral age model reported by Evans et al. [1999].

*Errors represent the 1σ standard deviation of all available coral $\Delta^{14}C$ measurements for a given coral. Analytical error of UCI radiocarbon measurement is ±4.0 ‰. Analytical error for UA radiocarbon measurement is ±4.0 ‰ (1σ). In parentheses, n is the number of years represented in the average, N is the total number of samples, subannual samples were averaged into annual values and included where possible.

*Average coral $\delta^{18}O$. Analytical error for coral $\delta^{18}O$ is ±0.06‰ (1σ).

*Unpublished U/Th ages and $\delta^{18}O$ data for fossil corals A27 and M2 to be reported by Cobb et al. (manuscript in preparation, 2010).

Figure 6. Comparison of Palmyra mixed layer model $\Delta^{14}C$ with measured Palmyra and Christmas coral $\Delta^{14}C$ over the last millennium. Palmyra mixed layer model output for fixed (solid black line) and variable (solid gray line) $\Delta^{14}C$ values for deep water boxes are plotted with Marine04 [Hughen et al., 2004] (dashed line) and average measured coral $\Delta^{14}C$ values for each modern and fossil coral segment. Error bars represent the analytical errors of ±1.8‰ for data generated at UCI, or ±4.0‰ for data generated at UA. The 13th century fossil coral $\Delta^{14}C$ are plotted as maximum values, as secondary carbonates with higher $\Delta^{14}C$ contaminate this coral (downward arrows reflect the fact that the primary coral $\Delta^{14}C$ are likely lower than the $\Delta^{14}C$ values measured).
dissolution in parts of the coral (Figure 9a) in conjunction with smooth, platy crystals that cover large sections of the coral skeleton (Figures 9b–9d). XRD analysis of the most altered portion of A27 revealed the presence of calcite, as sometimes observed in much older, heavily altered fossil corals [e.g., McGregor and Gagan, 2003]. The $\Delta^{14}C$ values obtained for more pristine portions of this coral (Figure 8) are interpreted as upper limits on seawater $\Delta^{14}C$ during this time, as diagenesis may be masking lower $\Delta^{14}C$ during this time.

7. Discussion

7.1. Interannual $\Delta^{14}C$ Variability in the Central Tropical Pacific

[36] Palmyra and Christmas coral $\Delta^{14}C$ values are unchanged throughout multiple large ENSO cycles over the last millennium, including the very large 1941–43 ENSO cycle. The lack of interannual $\Delta^{14}C$ variability indicates that the surface ocean in the central tropical Pacific is relatively well mixed with respect to $^{14}C$, at least to the depth of wind-driven upwelling, and to the limit of current analytical precisions for $\Delta^{14}C$. Indeed, Toggweiler and Carson [1995] use a model of nitrate and carbon concentrations in the surface ocean to demonstrate that the NECC and SEC are not distinguishable in the central tropical Pacific on interannual timescales due to the effective mixing of surface waters in this region, both horizontally and vertically. Indeed, for many geochemical tracers, such as $^{14}C$, the zonal structures of the NECC and the SEC are clear only in multiyear averages. Toggweiler and Carson [1995] find that at this particular site in the central tropical Pacific, seawater $\Delta^{14}C$ is homogenous to depths of 150m, roughly equivalent to the depth of upwelling. If this is correct, then changes in interannual upwelling and/or horizontal advection in the

Figure 7. SEM photos of pristine modern and fossil corals. (a) Palmyra ModernB (sampled at a depth corresponding to ~1942 AD), (b) Palmyra fossil coral NB12 (~930 AD) showing signs of minor dissolution, (c) Palmyra fossil coral SB5 (~1430 AD), (d) Palmyra fossil coral SB13 (~1760 AD), and (e) Christmas fossil coral M2 (~1550 AD). L17 and SB7 photos not shown.
vicinity of Palmyra and Christmas Islands would not be expected to significantly change seawater $\Delta^{14}C$ at these sites. It is important to note that heat is exchanged much more rapidly across the air-sea interface than carbon dioxide (1–2 months versus ~10 years for $^{14}C$ equilibration), meaning that water masses of different heat contents can possess similar $\Delta^{14}C$ signatures. Therefore, ENSO-related upwelling events are associated with changes in SST but not necessarily with changes in seawater $\Delta^{14}C$.

[37] The lack of an interannual $\Delta^{14}C$ signal at Palmyra is supported by a coral $\Delta^{14}C$ reconstruction from nearby Fanning Island (4°N, 154°W), which shows little to no interannual $\Delta^{14}C$ variations [Grottoli et al., 2003]. We are left to conclude that if central equatorial seawater $\Delta^{14}C$ may vary across an ENSO cycle, the associated signal (<5 ‰) is not large enough to be captured using current analytical techniques (i.e., a low signal-to-noise ratio). This can be contrasted with coral $\delta^{18}O$, which can resolve ENSO-related

Figure 8. SEM photos of Palmyra fossil coral SB3B taken (a) from the base of the core, where many secondary aragonite needles cover the original surface of the coral skeleton and (b) midway up the core, where the skeleton is smooth and retains the original skeletal structure. N denotes secondary aragonite needles.

Figure 9. SEM photos of diagenesis in 13th century Palmyra fossil coral A27. (a) Section of coral skeleton characterized by massive dissolution (marked by ‘D’); (b) solid, platy crystals (marked by ‘P’) covering large sections of the original coral skeleton, identified as calcite by XRD (not shown). (c and d) Enlarged views of platy diagenetic crystals in A27.
SST changes of ±1–3°C (±0.2–0.6‰) that occur in this region, given analytical errors of ±0.06‰.

7.2. Decadal to Centennial Δ14C Variability in the Central Tropical Pacific

[38] Large decadal signals in coral δ18O data are not associated with significant coral Δ14C variability, indicating a decoupling between surface climate and seawater Δ14C on decadal timescales. This is somewhat surprising, and cannot be explained by different equilibration times of ocean heat versus 14C, as invoked above to explain the lack of interannual 14C variability. One possibility is that surface climate signals and basin-scale circulation reorganizations are lagged by as much as a decade. In other words, a climate signal that originates at the equator might influence higher-latitude climate fairly quickly, but it might take many years for the changes in high-latitude climate and circulation to make their way into the equatorial thermocline. Such a mechanism has previously been explained to explain Pacific decadal-scale climate variability [e.g., Gu and Philander, 1997], and may underlie the lack of simultaneous changes in coral δ18O and coral Δ14C observed here.

[39] Support for a climate Δ14C delay comes from modeling studies that suggest that variability associated with the relatively 14C-depleted Subantarctic Mode Waters (SAMW) may have a large, but delayed impact on the 14C content of equatorial thermocline waters in the tropical Pacific [Rodgers, 2003]. Indeed, the Rodgers [2003] study indicates that up to 70% of the water reaching the equatorial mixed layer originates in the Southern Hemisphere, where surface radiocarbon values can be as low as ~100‰ [Matsumoto and Key, 2004]. However, it likely takes as long as 30 years for waters subducted as part of the SAMW to reach the equator [Rodgers, 2003], potentially explaining why surface climate changes (as recorded in coral δ18O) and seawater 14C changes (as recorded by coral 14C) in the tropical Pacific could be offset by several decades.

[40] A comparison of the centennial-scale coral δ18O and Δ14C records reveals a poor correlation between reconstructed surface climate and inferred paleocirculation (Figure 10). For example, relatively depleted coral Δ14C anomalies during the 12th century are not associated with positive coral δ18O anomalies, as expected if upwelling variations were responsible for the coral Δ14C shift. The decoupling of δ18O and Δ14C cannot be explained by alterations to the coral skeleton, as the 12th century coral is free of diagenesis. Given the absence of coral δ18O anomalies on these timescales, we infer that changes in high-latitude source water Δ14C signatures caused the observed coral 14C anomalies rather than changes in equatorial Pacific upwelling. Relatively small changes in either the Δ14C of SAMW waters or their relative contribution to the equatorial upwelling could have caused the ~7‰ departures from the atmospheric 14C-driven mixed layer model. In this case, we infer a Δ14C decrease in SAMW (or an increase of SAMW contributions to the EUC) during the 12th century. Likewise, relatively enriched coral radiocarbon during the 16th and 17th centuries could result from a reduction in the amount of SAMW reaching the equatorial mixed layer and/or an increase in the Δ14C of SAMW.

[41] Using the inverse version of the Palmyra mixed layer model, we calculate that a twofold increase in upwelling rates would explain the anomalously depleted 12th century Palmyra coral Δ14C values (not shown). Our simple box model does not constrain the influence of potential changes in high-latitude source water 14C content or circulation that could also account for the observed centennial-scale coral 14C variability. Ultimately, the relationship between low-frequency equatorial climate and high-latitude circulation must be tested with 14C-equipped coupled ocean-atmosphere climate models run for multiple centuries.

7.3. Diagenetic Effects on Coral Δ14C

[42] As discussed previously, the addition of calcite or secondary aragonite to the original coral skeleton introduces younger, relatively 14C-enriched carbonate to the coral skeleton. The magnitude of the diagenetic 14C enrichment depends on the amount of secondary carbonate precipitated, and its age relative to the primary coral skeleton. Diagenetic
altered to 17th century lower section of the core, although these needles do not significantly alter coral Δ14C values relative to pristine portions of the core. However, it is difficult to generate large Δ13C anomalies over a ~400 year period – it would require a 10% addition of modern prebomb carbonate to raise 17th century coral Δ14C values by 4%. A 10% addition of 18th century carbonate to the 17th century coral would result in an undetectable change in coral Δ14C. In agreement with our results, Cohen and Hart [2004] find that secondary aragonite precipitation did not affect the fidelity of their fossil coral radiocarbon ages (~13,500 years old) concluding that the diagenesis must have occurred shortly after skeletal formation. Although many coral paleoclimate proxies can be altered by secondary aragonite precipitation or dissolution [i.e., Hendy et al., 2007], we conclude that the radiocarbon signatures of young (~1000 years old), relatively pristine fossil coral are not significantly affected.

[43] In the case of the 13th century fossil coral that experienced significant diagenesis (both dissolution and secondary calcite precipitation), coral Δ14C values were significantly higher. Previous work indicates that secondary calcite should also cause significant enrichments in coral δ18O [Enmar et al., 2000; Müller et al., 2001; McGregor and Gagan, 2003], which were not observed in this study. This implies a markedly different mechanism of diagenetic alteration than observed in the other fossil corals – one that progressed continuously as the coral lay exposed on the beach over the last seven centuries.

[44] We conclude that the accuracy of modern or fossil coral-based seawater Δ14C reconstructions depends on careful diagentic screening, ideally with SEM photos. As a screening tool, SEM is far preferable to thin sections, as the small needles of secondary aragonite observed in SEM photos of SB3B were not observed in thin section.

8. Conclusions

[45] Despite large variations in interannual to decadal surface climate inferred from modern and fossil coral δ18O, we find no corresponding changes in coral Δ14C, suggesting that these two tracers have markedly different sensitivities and/or response times in the central tropical Pacific. In the case of interannual variability, the relatively long air-sea equilibration time of 14C versus heat means that the horizontal and vertical 14C gradients are generally smaller than they are for SST, which is exacerbated by relatively large error bars for seawater 14C reconstructions. In the case of decadal-scale variations, the potential for changes in the 14C content of extratropical waters that supply the tropical Pacific thermocline waters represents an added complication, as such changes may lead or lag changes in tropical Pacific surface climate by several decades. A centennial-scale increase in coral Δ14C from the MCA to the LIA is largely explained by centennial-scale changes in atmospheric Δ14C. However, 12th and late 13th century coral Δ14C data are more depleted than atmospheric Δ14C-driven mixed layer model estimates. If the mixed layer model accurately represents the incorporation of very low 12th century atmospheric Δ14C values into the Palmyra mixed layer, then the 12th century coral data imply an increase in upwelling during this time and/or a decrease in the 14C content of equatorial source waters, requiring further study with 14C-equipped ocean models. Minor dissolution and addition of secondary aragonite, as observed with SEM photos, has little effect on the accuracy of our coral-based seawater 14C reconstructions. However, moderate to severe diagensis (marked by extensive dissolution and the addition of secondary calcite) is associated with significantly higher Δ14C values.

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