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Radiocarbon and stable isotopes in Palmyra corals during the past century

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Abstract

Annual samples from two Palmyra Atoll corals (*Porites lutea*) that lived during the past 110 years were analyzed for radiocarbon (Δ^{14} C) and δ^{18} O. The Δ^{14} C values decreased 7.6% from 1896 to 1953, similar to other coral records from the tropical and subtropical Pacific. Δ^{14} C values rose from $\sim -60\%$ to $\sim +110\%$ by 1980 due to the input of bomb radiocarbon from the atmosphere. Elevated Δ^{14} C values were observed for the mid- to late-1950s, suggesting early input of bomb radiocarbon, possibly from the largest Marshall Islands bomb tests in 1954. Secondary aragonite precipitation was identified in a portion of one core using scanning electron microscopy and X-radiography, and was responsible for high δ^{18} O and δ^{13} C values and a correlation between them. The Δ^{14} C results were more resistant to alteration, except when contamination was from the bomb era (>1956).

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1. INTRODUCTION

Radiocarbon (¹⁴C) is produced when cosmic rays enter the stratosphere and generate thermal neutrons that react with ¹⁴N. It is oxidized to ¹⁴CO₂, mixes into the troposphere and enters the ocean by air–sea gas exchange. Carbon dioxide is present in oceanic waters as carbonate, bicarbonate and carbonic acid, collectively known as dissolved inorganic carbon (DIC). Δ^{14} C values decrease with depth in the ocean because of decay and isolation from the atmosphere, the source of ^{14}C .

Marine organisms such as corals incorporate DIC into their aragonite skeletons and record the Δ^{14} C value of the seawater DIC at the time of coral formation. Corals produce annual density bands that can be dated and used as proxies of past changes in climate and water mass (Druffel, 1997; Guilderson and Schrag, 1998). δ^{18} O values in corals are influenced by changes in sea surface temperature (SST) and water composition ($\delta^{18}O_{water}$), where cooler waters produce aragonite with a higher δ^{18} O signature (Cole, 1996; Dunbar and Wellington, 1981).

In the tropical Pacific, the trade winds drive surface waters from east to west, forming the North Equatorial Current (NEC) and the South Equatorial Current (SEC). The North Equatorial Countercurrent (NECC) is water redirected from the SEC and NEC that moves eastward, generally between 3 and 10°N. In the SEC, Δ^{14} C values

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are low during normal and La Niña periods, when upwelling is strong. During El Niño events, easterly tradewinds cease or reverse their direction causing eastward flow, resulting in downwelling and the accumulation of high Δ^{14} C surface waters in the eastern tropical Pacific.

Diagenetic features of dissolution, recrystallization and secondary aragonite precipitation were reported by Enmar et al. (2000) in living *Porites* from Elat in the Gulf of Aqaba. These features resulted in significantly higher Sr/Ca ratios than the average ratio in primary coralline aragonite. In a recent study of Palmyra and Christmas Island fossil corals (<1000 years old), the presence of secondary aragonite was found to alter the Δ^{14} C signatures only when the diagenesis was moderate to severe (Zaunbrecher et al., 2010).

Here we report Δ^{14} C and δ^{18} O records in corals from Palmyra Atoll in the central Pacific. A portion of one core showed the presence of secondary aragonite, and in a ~10 year section of this core the Δ^{14} C results were compromised. Analysis of the pristine corals showed a slight increase in Δ^{14} C during the mid-1950s, suggesting the presence of seawater from the western North Pacific that was influenced by early nuclear weapons detonations in the Marshall Islands (Fallon and Guilderson, 2008).

2. METHODS

Coral cores of *Porites lutea* were drilled and collected from two sites at Palmyra Atoll. Core P-2 was collected on 2 June 2005 from a 1.5 m high colony located at 10 m depth near South Beach on the south coast of the atoll (5°51.85'N, 162°06.89'W). The core was 119 cm long and X-rays of 0.7 cm thick slabs revealed that the coral grew from 1930 to 2005. Core P-9 was collected on 4 June 2007 from a 2 m high colony located at 5 m depth near the channel on the western shelf (5°52.015'N, 162°07.092'W). This core was 162 cm long, representing growth from 1896 to 1993. The cores were rinsed with fresh water and air dried in the field.

Corals were slabbed, cleaned, X-rayed, mapped and subsampled using a hand-held Dremel tool with diamond bit according to previously described methods (Griffin and Druffel, 1985). Annual samples were collected from the P-2 and P-9 cores; eight quarter-annual samples were drilled in the P-9 core from the 1955 and 1956 bands. Samples (~8 mg) were acidified to CO_2 and reduced on iron powder with hydrogen gas to produce graphite (Santos et al., 2007). The graphite was analyzed for ¹⁴C at the Keck Carbon Cycle AMS laboratory at UC Irvine. Radiocarbon



Fig. 1. (a) SEM of P-2 coral at the 1954 band showing secondary aragonite precipitation. The secondary aragonite is pictured as needle-like crystals formed on top of the primary aragonite and obscures the original coral. Scale bar is $100 \mu m$; (b) SEM of pristine P-2 coral located at the 1949 band. The image shows pristine coral cavities and no visible signs of secondary aragonite precipitation. Scale bar is $100 \mu m$. (c) X-ray of section of P-2 core with arrows pointing to locations examined using SEM, shown in (a and b).

results are reported as Δ values that are corrected for known age to 1950 according to convention (Stuiver and Polach, 1977). Total uncertainty of Δ^{14} C measurements was $\pm 1.9_{00}^{*}$, determined from multiple analyses of a modern coral standard (CSTD), and duplicate coral analyses over the period of sample analysis.

Distinct white bands were observed via X-ray in the P-2 core (Fig. 1c). We examined four locations on a section of the P-2 core (1949–1955) using SEM. Because these dense bands (hereafter referred to as "white bands") appear to have formed after the original accretion of the coral, care was taken to avoid these high-density features when sampling for isotopic analyses.

Stable oxygen and carbon isotope analyses were performed using a Finnigan MAT252 mass spectrometer coupled to a Kiel III carbonate device at Stanford University. Precision on NIST SRM 8544 (NBS-19) and internal laboratory standards are better than 0.055% and 0.03% for δ^{18} O and δ^{13} C, respectively.

Water samples were taken from four sites at Palmyra Atoll during the two collection periods in 2005 and 2007, poisoned with HgCl₂ stored at room temperature, and analyzed for DIC ¹⁴C at UCI. The water samples were analyzed according to methods previously described (McNichol et al., 1994). Total uncertainty of DIC $\Delta^{14}C$ ($\pm 2.5\%$) measurements was determined from multiple analyses of standard seawater samples.

3. RESULTS

3.1. SEM results

SEM scans of three areas of the P-2 core (1954, 1955 and 1956) that displayed high-density, "white band" features on the X-ray image revealed closely-packed, needle-like crystals, $\sim 10-20 \,\mu\text{m}$ in length (an example is shown in Fig. 1a). Scans of a band (1949) without these high-density features displayed a solid, smooth surface without needle-like crystals (Fig. 1b), and were considered pristine, primary aragonite. Zaunbrecher et al. (2010) used SEM to

determine that secondary aragonite deposition, caused by dissolution and subsequent precipitation, was present on a few of their fossil *Porites* from Palmyra Atoll and Christmas Island. They concluded that minor diagenesis did not change the Δ^{14} C values of the corals, though moderate to severe diagenesis caused significant increase in the Δ^{14} C values of a 13th century fossil coral from Palmyra.

3.2. Coral Δ^{14} C results

Prebomb Δ^{14} C results for annual samples from the P-2 and P-9 cores range from -60.3% in 1949 to -47.7% in 1898 (Fig. 2). Results from both cores are available for 13 samples, and all but two (1930 and 1935) agree within 2σ or 3.8‰; in both cases the P-2 results were higher than the P-9 results. The annually averaged pre-bomb Δ^{14} C results averaged $-54.9 \pm 3.1\%$ (n = 57), however, values were significantly higher from 1911 to 1915 ($-49.8 \pm$ 0.8‰ n = 5) and lower from 1916 to 1918 ($-57.5 \pm 0.5\%$ n = 3).

A least squares fit of the annually averaged Δ^{14} C values reveals a decrease of 7.6% from 1896 to 1953 (Fig. 2). This negative trend is, in part, due to the Suess effect, the decrease of Δ^{14} C in atmospheric CO₂ caused primarily by dilution with ¹⁴C-free CO₂ from fossil fuel burning since the 19th century (Suess, 1953).

The Δ^{14} C values in the P-2 core began to increase in 1955 and reached an initial plateau (-20% to -13%) from 1956 to 1961 (Fig. 3). Values continued to increase in 1961 and rose fastest from 1963 to 1965 (+3% to +46%). Maximum values (+102% to +114%) were reached between 1977 and 1983. From 1984 to 2005, Δ^{14} C values decreased steadily from 110\% to 64\%. Low Δ^{14} C values were apparent in 1978 (102‰) and 1984 (100‰), compared to other values for the 1970s and early 1980s.

Four annual samples from high-density "white bands" in the P-2 core were analyzed and the results are plotted in Fig. 3 as open circles. Three of these Δ^{14} C results were equal to those of pristine aragonite (1930, 1955 and 1962), and one band (1942) was higher by 25.0‰ (Fig. 3).



Fig. 2. Pre-bomb Δ^{14} C measurements of annual coral bands from the P-9 (closed points) and the P-2 cores (open points). Duplicate analyses are averaged and plotted as a single point. The line represents the least squares fit of all of the results.

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Fig. 3. Δ^{14} C measurements of annual coral bands from the P-2 core (closed points). Open points represent results of coral that contained "white bands", or secondary aragonite precipitation.



Fig. 4. Post-1950 Δ^{14} C measurements of annual and quarter-annual coral bands from Palmyra (this work, red points, P-2 open, P-9 closed), Fanning Island (Druffel, 1987), Galapagos Islands (Druffel, 1981) and Makassar Straits, Indonesia (Fallon and Guilderson, 2008). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

These results indicate that "white bands" can contain significant amounts of secondary aragonite that precipitated with Δ^{14} C values significantly higher than that in the primary aragonite, forming some years after primary biogenic precipitation.

We measured Δ^{14} C in samples from annual and quarterannual bands in the P-9 core to determine if there was a difference with those from the P-2 core (see Fig. 4). There is a significant offset between the P-2 and P-9 results in the time period 1955–1961, where the P-9 results are lower. This indicates that the secondary aragonite in the P-2 core caused increased Δ^{14} C values in these bands. Therefore, we eliminated from final analysis and discussion the Δ^{14} C results from these P-2 bands (1955–1962). Quarter-annual Δ^{14} C results in the 1955–1956 bands of the P-9 core ranged from $-53.8\%_{00}$ (in 1955.4) to $-43.4\%_{00}$ (in 1956.9), suggesting that bomb-¹⁴C was present in Palmyra surface waters by 1956.

3.3. Dissolved inorganic carbon Δ^{14} C results

Seawater DIC Δ^{14} C results are reported for four samples (Table 1). The sample taken during June 2005 near the P-2 core had a Δ^{14} C value of +62.8‰, which is within 1 σ of the Δ^{14} C value for the 2005 coral band (+64.4‰) from the P-2 core. Δ^{14} C values of three water samples taken during June 2007 ranged from +52.0‰ to +59.9‰, and were similar to the Δ^{14} C value of a 2006 coral band (+59.6‰) taken from a separate core.

3.4. Stable isotope results

Stable oxygen (δ^{18} O) and carbon (δ^{13} C) isotope records from the Palmyra corals are shown in Fig. 5a. δ^{18} O results for the P-9 core (from 1896 to 1993) ranged from -4.75%to -5.58%, and δ^{13} C values ranged from -0.47% to -2.05%. In contrast, δ^{18} O and δ^{13} C results for the P-2 core

Table 1 Radiocarbon analyses of DIC in seawater samples collected at Palmyra.

Data collected	UCID#	Location	Δ ¹⁴ C (‰)	±
6/2/05	8233	South Beach (core P-2)	62.8	2.5
6/6/07	9488	South Kalua Island	57.8	2.5
6/4/07	9483	Channel, west shelf (core P-9)	52.0	2.5
6/8/07	9461	Northwest terrace	59.9	2.5

were more variable, especially in regions that contained dense "white bands", where values were as high as $-3.6\%_{00}$ and $0.0\%_{00}$, respectively (Fig. 5a). A plot of δ^{13} C vs. δ^{18} O results for the P-2 core showed that the samples from prominent "white bands" (x in Fig. 5b) reveals a direct correlation between the δ^{18} O and δ^{13} C values, whereas

the data from bands with minimal or no "white bands" did not show a correlation. Thus, it appears that "white bands" are evidence of secondary aragonite precipitation causing unusually high values of $\delta^{18}O$ and $\delta^{13}C$ in the P-2 coral.

4. DISCUSSION

4.1. Secondary aragonite precipitation in the P-2 core

Stable isotope results (δ^{18} O and δ^{13} C) from high-density "white bands" in parts of the P-2 core are higher than those from pristine sections. Aragonite formed by the coral polyp is depleted in the heavier isotopes (¹³C and ¹⁸O) due to various processes (e.g., symbiotic algal activity, retention of metabolic CO₂) and is known as the vital effect (McConnaughey, 1989). Inorganic precipitation of aragonite in equilibrium with seawater, on the other hand,



Fig. 5. (a) δ^{13} C (open gray diamond) and δ^{18} O (closed gray diamond) measurements of annual coral bands from the P-9 core (1896–1993). δ^{13} C and δ^{18} O measurements of annual coral bands from the P-2 core are plotted as: filled circles (δ^{18} O) and filled triangles (δ^{13} C) for samples with no "white band" present, open circles (δ^{18} O) and open triangles (δ^{13} C) for samples with minimal "white band" present, and X (δ^{18} O) and $+ (\delta^{13}$ C) for samples with prominent "white band" present; (b) δ^{13} C vs. δ^{18} O measurements for P-2 core, where closed circles are samples with minimal "white band" present, and X (δ^{18} O) and open triangles (δ^{13} C) for samples with prominent "white band" present; (b) δ^{13} C vs. δ^{18} O measurements for P-2 core, where closed circles are samples with no "white band" present, open circles are samples with minimal "white band" present, X are samples with prominent "white band" present and open triangle is inorganic aragonite precipitated at 28 °C. Line is the least squares fit of the X points (y = 0.402x - 3.8426, $R^2 = 0.7980$).

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Fig. 6. Annual δ^{18} O values from the P-9 core (gray diamonds) and monthly δ^{18} O values from a modern coral reported by Cobb et al. (2001) (thin gray line). Thin straight lines are least squares fits of each data set and bold lines are 10-year running means for each data set.

exhibits higher ¹⁸O/¹⁶O and ¹³C/¹²C ratios that can be calculated using known relationships (Epstein and Mayeda, 1953; Tarutani et al., 1969). The δ^{18} O and δ^{13} C values expected for equilibrium inorganic precipitation of aragonite in equatorial surface waters are about -1.2% and +4.4%. respectively, at an SST of 28 °C. These values are plotted in Fig. 5b and are close to the linear relationship (line in Fig. 5b) obtained for the "white bands". This suggests that stable isotopic values of the "white bands" represent a mixture between pristine coral aragonite and inorganic aragonite precipitated in equilibrium with seawater. An estimate of the amount of secondary aragonite present in the most affected bands, e.g., from the 1930s, is calculated using a mass balance equation. If we assume that inorganic aragonite and pristine coral have δ^{18} O values of -1.2% and -5.3%, respectively, and corals with prominent "white bands" have a δ^{18} O value of $-4.0 \pm 0.5\%$ (Fig. 5b), then $32 \pm 12\%$ of the aragonite in the P-2 1930s bands is derived from secondary precipitation of aragonite in equilibrium with seawater at 28 °C.

Most of the P-2 core is free from "white bands", but it is obvious that stable isotopic values are more easily altered than are Δ^{14} C values. The reason for this is that stable isotopes in coralline aragonite are not in equilibrium with seawater, but strongly shifted due to vital effects. This is not the case with Δ^{14} C, because shifts due to fractionation (e.g., vital effects) are corrected for in the calculation of the Δ^{14} C value. However, if the carbon source for the secondary aragonite is from the post-bomb era, then "white bands" produced within pre-bomb aragonite would have significantly higher Δ^{14} C values, such as in the 1942 band in P-2 (Fig. 3). Our results were similar to those of Zaunbrecher et al. (2010) who found that coral Δ^{14} C is only compromised by secondary aragonite after moderate to severe diagenesis for corals <1000 years old. Chiu et al. (2005) used successive acid-leaching experiments to show that enrichment of secondary calcite in very old (>26,000 years old) subaerially exposed, fossil corals occurred because calcite is less soluble than aragonite. Thus, in coral samples affected by secondary

aragonite precipitation (usually submerged in seawater), there is less of an effect on Δ^{14} C results than there is with subaerially-exposed coral samples that are usually affected by secondary calcite.

4.2. Stable isotope records as climate proxies

Despite the evidence of altered stable isotope signals from the presence of "white bands", most of the data from the P-2 core and all of the data from the P-9 core appear to be derived from unaltered coralline aragonite. Two factors control δ^{18} O of corals, SST and δ^{18} O of seawater. Cobb et al. (2003) and Nurhati et al. (2009) determined that approximately half of the $0.34^{o}_{\!\scriptscriptstyle no}$ decrease of monthly δ^{18} O values obtained from 1886 to 1998 in a modern Palmyra coral was from increased SST (~0.8 °C) and the other half was from increased precipitation over the last century. A least squares fit of the P-9 δ^{18} O data show a decrease of 0.29% from 1895 to 1993, approximately equal to that observed by Cobb et al. (2001), though our decline was linear with time and theirs occurred during the later three decades (Fig. 6). The 10-year running mean through the Cobb et al. (2001) δ^{18} O record demonstrate a decadal variability that was reported as coherent with long equatorial Atlantic and Indian Ocean climate records (Cobb et al., 2001). The 10-year running mean through our data shows some similarity with the Cobb et al. (2001) record, though the differences in the sampling frequency (annual vs. monthly) and the uncertainty in the age assignments for the P-9 core $(\pm 2 \text{ years})$ make this comparison difficult.

4.3. Pre-bomb Δ^{14} C record in the Pacific

Pre-bomb Δ^{14} C results in the Palmyra coral decrease from about $-51\%_{00}$ in the late 1890s to $-59\%_{00}$ by 1953 (Fig. 2). The average value in the early 1950s ($-59.3 \pm 0.6\%_{00}$, n = 4) is considerably higher than that for the Galapagos coral (-72.2 ± 2.8 , n = 5), the same as that in a Fanning coral ($3^{\circ}52'$ N, $159^{\circ}23'$ W) ($-59.0 \pm 4.8\%_{00}$, n = 6) and lower than a Kona HI coral ($-52.1 \pm 1.3\%$, n = 3) (Druffel, 1981, 1987; Druffel et al., 2001). These differences reflect the intensity of low Δ^{14} C waters upwelling to the surface at each site, and varies from high in eastern tropical (Galapagos), less in mid-tropical (Fanning and Palmyra), and low in subtropical (Hawaii) regions.

The decreases in Δ^{14} C values during the first half of the 20th century at Makassar Straits (5°02'S, 119°04'E) (8‰) (Fallon and Guilderson, 2008), Hawaii (8%) (Druffel et al., 2001) and Galapagos (0°25'S, 91°W) (7%) (Druffel, 1981) were equal to that at Palmyra (7.6‰). This similarity may appear surprising given that upwelling intensity varies so much at these locations. However, the decrease in $\Delta^{14}C$ observed in the upper ocean is likely, in part, caused by factors other than ¹⁴C-free fossil fuel CO₂ (i.e., Suess effect), such as changes in circulation or climate. For example, Fallon and Guilderson (2008) report that most of the decrease of Δ^{14} C values in the Makassar coral occurred prior to the decrease in atmospheric $CO_2 \Delta^{14}C$ and hypothesized that a change in circulation associated with the Banda Sea was the cause of the Δ^{14} C decline. Another example is found in the absence of a Suess effect in an Australian coral record, attributed to a long-term change in mixing of upper waters that was coincident with a change observed in the nature of ENSO (Druffel and Griffin, 1993).

There appears to be decadal shifts in the Palmyra Δ^{14} C record, with decreases occurring around 1900, 1915, and a smaller shift at 1925 (Fig. 2). Results of spectral analyses (Howell et al., 2006) of the pre-bomb Δ^{14} C record reveals a coherent period at 10 years (95% confidence level), confirming the decadal nature of the Δ^{14} C record. Also revealed in this analysis were coherent periods at 5 and 3.5 years (80% confidence level), which are indicative of ENSO time scales.

4.4. Post-bomb Δ^{14} C record in the Pacific

The post-bomb Palmyra Δ^{14} C results are shown with data from other Pacific coral sites: Galapagos, Fanning and Makassar Straits (Fig. 4). Corals that are influenced by sub-tropical currents (i.e., Makassar) attain their highest Δ^{14} C values in the 1970s, whereas those at tropical sites (Fanning, Galapagos and Palmyra) attain their maximum Δ^{14} C values during the 1980s. Enrichment of bomb ¹⁴C occurs quickly at surface locations with minimal upwelling like the subtropics, whereas tropical sites are diluted with upwelling waters that contain little or no bomb ¹⁴C prior to the 1980s. Therefore, the timing of the maximum bomb ¹⁴C signal is delayed at locations influenced by upwelling, such as Palmyra.

The variability of the Palmyra data is much less than that of the Galapagos (Fig. 4) because the influence of El Niño on the ¹⁴C signal at the Galapagos is strong (Guilderson and Schrag, 1998) and that at Palmyra is minimal (Zaunbrecher et al., 2010).

4.5. Early bomb ¹⁴C peak

Fallon and Guilderson (2008) reported an early Δ^{14} C peak in a Makassar Strait coral beginning in February 1955, where values increased by 40‰ in 3 months (Fig. 7). They attributed this peak to the largest thermonuclear weapons tests at Bikini Atoll (11°35′N, 165°23′E) from March to May 1954 that significantly labeled waters due to fallout around the Marshall Islands and westward. A smaller Δ^{14} C increase (10‰) was noticed in the early 1950s bands of a Fanning Island coral (see Fig. 7) (Druffel, 1987), followed by a decrease in 1955. Strontium-90 was also detected in the early 1950s bands of this Fanning coral (Toggweiler and Trumbore, 1985), which led to the conclusion that the



Fig. 7. Δ^{14} C measurements of annual and quarter-annual coral bands as described in Fig. 4 caption, with the secondary aragonite values for the P-2 core (1954 and 1956–1959) removed (see text for detail).

early peak of bomb-produced isotopes in the tropical Pacific could be attributed to close-in fallout originating from the Marshall Islands tests (Druffel, 1987). Alternatively, 1955 was a La Niña year, which is associated with increased upwelling in the mid- and eastern equatorial Pacific and decreased upwelling in the western Pacific.

In the Palmyra coral, we observe slightly higher Δ^{14} C values (by 5–20‰) during the mid- to late-1950s, indicating that there may be an early bomb ¹⁴C pulse at Palmyra as well (Fig. 7). In particular, the quarter-annual Δ^{14} C results (Fig. 7) showed a seasonal cycle of 8–9‰, unlike previous pre-bomb results that showed no seasonal Δ^{14} C variability (Zaunbrecher et al., 2010). This is consistent with the fact that the NECC is the main source of surface water arriving at Palmyra, and carries western Pacific water labeled with early bomb ¹⁴C (Fallon and Guilderson, 2008).

5. SUMMARY

Elevated Δ^{14} C values, and an enhanced Δ^{14} C seasonal signal, were observed for the mid-1950s at Palmyra Atoll, suggesting early input of bomb ¹⁴C, possibly from the Marshall Islands tests that began in early 1954. Secondary aragonite precipitation was identified in a portion of one core using SEM and X-radiography, which caused changes in the stable oxygen and carbon isotopes, compared to primary aragonite. The effect of secondary aragonite precipitation on the Δ^{14} C signature was significant only for the most prominent "white bands". The δ^{18} O record showed a decrease of values consistent with an increase of SST of up to 0.8 °C during the past century.

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REFERENCES

- Cobb K., Charles C. and Hunter D. (2001) A central tropical Pacific coral demonstrates Pacific, Indian and Atlantic decadal climate connections. *Geophys. Res. Lett.* **28**, 2209–2212.
- Cobb K., Charles C. D., Cheng H. and Edwards R. L. (2003) El Nino/southern oscillation and tropical Pacific climate during the last millennium. *Nature* 424, 271–276.

- Cole J. (1996) Coral records of climate change: understanding past variability in the tropical ocean–atmosphere. In *Climatic* Variations and Forcing Mechanisms of the Last 2000 Years, NATO ASI series, vol. 141 (eds. P. Jones, R. Bradley and J. Jouzel). Springer-Verlag, Berlin, Heidelberg, pp. 331–353.
- Chiu T.-C., Fairbanks R. G., Mortlock R. A. and Bloom A. L. (2005) Extending the radiocarbon calibration beyond 26,000 years before present using fossil corals. *Quatern. Sci. Rev.* 24, 1797–1808.
- Druffel E. (1997) Pulses of rapid ventilation in the North Atlantic surface ocean during the last century. *Science* 275, 1454–1457.
- Druffel E., Griffin S., Guilderson T. P., Kashgarian M., Southon J. and Schrag D. P. (2001) Changes of subtropical North Pacific radiocarbon and correlation with climate variability. *Radiocarbon* 43, 15–25.
- Druffel E. R. M. (1981) Radiocarbon in annual coral rings from the eastern tropical Pacific Ocean. *Geophys. Res. Lett.* 8, 59– 62.
- Druffel E. R. M. (1987) Bomb radiocarbon in the Pacific: annual and seasonal timescale variations. J. Mar. Chem. 45, 667–698.
- Druffel E. R. M. and Griffin S. (1993) Large variations of surface ocean radiocarbon: evidence of circulation changes in the southwestern Pacific. J. Geophys. Res. 98, 20249–20259.
- Dunbar R. B. and Wellington G. M. (1981) Stable isotopes in a branching coral monitor seasonal temperature variation. *Nature* 293, 453–455.
- Enmar R., Stein M., Bar-Matthews M., Sass E., Katz A. and Lazar B. (2000) Diagenesis in live corals from the Gulf of Aqaba. I: The effect on paleo-oceanography tracers. *Geochim. Cosmochim. Acta* 64, 3123–3132.
- Epstein S. and Mayeda I. (1953) Variation of ¹⁸O content of waters from natural sources. *Geochim. Cosmochim. Acta* **4**, 213–224.
- Fallon S. and Guilderson T. (2008) Surface water processes in the Indonesian throughflow as documented by a high-resolution coral D14C record. J. Geophys. Res. 113, doi:10.1029/ 2008JC004722.
- Griffin S. M. and Druffel E. R. M. (1985) Woods hole oceanographic institution radiocarbon laboratory: sample treatment and gas preparation. *Radiocarbon* 27, 43–51.
- Guilderson T. and Schrag D. (1998) Abrupt shift in subsurface temperatures in the tropical Pacific associated with changes in El Nino. Science 281, 240–243.
- Howell P. J., Pisias N., Ballance J., Baughman J. and Ochs L. (2006) ARAND Time-Series Analysis Software, Providence, RI, Brown University.
- McConnaughey T. (1989) ¹³C and ¹⁸O isotopic disequilibrium in biological carbonates. I: Patterns. *Geochim. Cosmochem. Acta* 53, 151–162.
- McNichol A. P., Jones G., Hutton D. and Gagnon A. (1994) The rapid preparation of seawater TCO2 for radiocarbon analysis at the National Ocean Sciences AMS Facility. *Radiocarbon* 36, 237–246.
- Nurhati I. S., Cobb K. M., Charles C. D. and Dunbar R. B. (2009) Late 20th century warming and freshening in the central tropical Pacific. *Geophys. Res. Lett.* 36, 4, doi:10.1029/ 2009GLO40270.
- Santos G., Moore R., Southon J., Griffin S., Hinger E. and Zhang D. (2007) AMS ¹⁴C sample preparation at the KCCAMS/UCI Facility. *Radiocarbon* 49, 255–269.
- Stuiver M. and Polach H. A. (1977) Discussion: reporting of ¹⁴C data. *Radiocarbon* 19, 355–363.
- Suess H. E. (1953) Natural radiocarbon and the rate of exchange of carbon dioxide between the atmosphere and the sea. In: *Proceedings Conference Nuclear Processes in Geological Settings*, vol. 23. pp. 52–56.

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- Tarutani T., Clayton R. and Mayeda T. (1969) The effect of polymorphism and magnesium substitution on oxygen isotope fractionation between calcium carbonate and water. *Geochim. Cosmochim. Acta* 33, 987–996.
- Toggweiler J. R. and Trumbore S. E. (1985) Bomb-test ⁹⁰Sr in Pacific and Indian Ocean surface water as recorded by banded corals. *Earth Planet. Sci. Lett.* **74**, 306–314.
- Zaunbrecher L., Cobb K., Beck W. J., Charles C. D., Druffel E., Griffin S., Fairbanks R. G. and Sayani H. R. (2010) Coral records of central tropical Pacific radiocarbon variability during the last millennium. *Paleoceanography* **25**, PA4212, doi:10.1029/2009PA001788.

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