Low reservoir ages for the surface ocean from mid-Holocene Florida corals

Ellen R. M. Druffel,1 Laura F. Robinson,2 Sheila Griffin,1 Robert B. Halley,3 John R. Southon,1 and Jess F. Adkins4

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[1] The 14C reservoir age of the surface ocean was determined for two Holocene periods (4908–4955 and 3008–3066 calendar (cal) B.P.) using U/Th-dated corals from Biscayne National Park, Florida, United States. We found that the average reservoir ages for these two time periods (294 ± 33 and 291 ± 27 years, respectively) were lower than the average value between A.D. 1600 and 1900 (390 ± 60 years) from corals. It appears that the surface ocean was closer to isotopic equilibrium with CO2 in the atmosphere during these two time periods than it was during recent times. Seasonal δ18O measurements from the younger coral are similar to modern values, suggesting that mixing with open ocean waters was indeed occurring during this coral’s lifetime. Likely explanations for the lower reservoir age include increased stratification of the surface ocean or increased Δ14C values of subsurface waters that mix into the surface. Our results imply that a more correct reservoir age correction for radiocarbon measurements of marine samples in this location from the time periods ~3040 and ~4930 cal years B.P. is ~292 ± 30 years, less than the canonical value of 404 ± 20 years.


1. Introduction

[2] The reservoir age of the surface ocean is the difference between the conventional 14C ages of samples grown contemporaneously in the atmosphere and that in surface ocean dissolved inorganic carbon (DIC). The reservoir age is maintained primarily by mixing up of deeper waters that have older 14C ages because of 14C decay. Reservoir ages in nonpolar surface regions determined from shells, corals and seawater DIC range from ~300 to 670 years [Stuiver et al., 1986]. Lower values are found in midgyre regions of the ocean where downwelling is dominant, and higher values are found in areas of upwelling (e.g., equator and eastern boundary currents). Atmospheric CO2 Δ14C measured in annual tree rings [Stuiver and Quay, 1980] and in biennial coral bands from the Florida Keys [Druffel and Linick, 1978] and Belize [Druffel, 1980] reveal an average reservoir age for the surface ocean DIC in the Florida Straits of 390 ± 60 years during the past few centuries. Values were higher during the Little Ice Age, when atmospheric Δ14C values were high because of low solar activity.

[3] Little information is available regarding how the reservoir age of the surface ocean has changed prior to A.D. 1600 because of the challenges involved in obtaining pristine carbonates (corals, shells) that can be age dated. This information would help to define changes in mixing patterns over time, e.g., the degree of upwelling or downwelling, and how they have varied in key oceanic regimes.

2. Oceanographic Setting and Collection of the Fossil Corals

[4] Cores of fossil corals (Montastrea annularis) were obtained using an underwater drill from Biscayne National Park, Florida in September 1991 (Figure 1). Both cores were collected from Legare Anchorage, an area of patch reefs centrally located on the SE Florida shelf, off Elliott Key in the upper Florida Keys (25°29′N, 80°08′.5′W). The fossil corals occur buried in sand around the margins of patch reefs. Core A1 (61 cm long) was collected from 7 m water depth, and core C1 (119 cm long) was collected from 8 m water depth. There is a discontinuous shelf edge reef to the east, Triumph Reef, that shoals to 3 m and is less than 2 km in length. The Florida Straits current flows to the east of Triumph Reef, and the patch reefs sampled were well flushed by open ocean waters at the time of collection.

3. Methods

[5] Annual coral samples were cut just below high-density bands (July–September) that were detected from x-radiographs of the slabs [Druffel and Griffin, 1993; Griffin and Druffel, 1985]. Slab A1 had 52 bands and slab C1 had 68 bands. Annual coral bands were precleaned in 3% HCl for 20 s to remove extraneous carbonate, rinsed with milli-Q water and dried. Samples were analyzed for radiocarbon by acidification to CO2 and conversion to graphite on Co
catalyst with H$_2$ gas as the reductant [Vogel et al., 1987]. Radiocarbon was measured at the Center for AMS Research at LLNL. Eleven bands from the A1 coral that had not been precleaned were analyzed for radiocarbon, and no significant differences were found between these results and those from the precleaned samples (Figure 2a).

The C1 coral was also sampled using a dremel drill in 1-mm-sized increments (~8 samples/year) and analyzed for $\delta^{18}O$ and $\delta^{13}C$ at WHOI. Stable isotope results had total uncertainties (1 sigma) of ±0.05‰ for $\delta^{13}C$ and $\delta^{18}O$.

To determine the calendar ages of these corals, four subsections of each coral slab (bands 16–18 from A1 and bands 52–56 from C1) were analyzed to determine the U-Th ages; one visibly dirty piece and three clean pieces were analyzed from each subsample. Three cleaning methods were used on separate aliquots: (1) ultrasonicated in milli-Q water; (2) ultrasonicated sequentially with milli-Q water, an H$_2$O$_2$/NaOH mix, milli-Q water, and finally leached for 3 min in a H$_2$O$_2$/perchloric acid mix; or (3) treated to a full oxidative/reductive cleaning [Cheng et al., 2000]. Samples were dried, weighed and spiked with a mixed $^{229}$Th-$^{230}$U spike calibrated against a Harwell Uraninite solution (HU-1) assumed to be at secular equilibrium. U and Th were then separated and purified by anion-exchange chemistry [Edwards et al., 1986] and measured on a Neptune multi-collector inductively coupled mass spectrometer (MC-ICP-MS) [Robinson et al., 2005]. The $^{232}$Th concentration in each sample was monitored to assess the contribution of $^{230}$Th that is not a product of in-growth [Cheng et al., 2000].

4. Results and Discussion

The $\delta^{234}$U$_{\text{initial}}$ values from all aliquots of both coral samples ranged from 148.2–149.4‰ with an average value of 148.8‰, close to the modern seawater value of 146.0‰ (Table 1). This similarity is consistent with closed system U series chemistry during the postmortem history of the corals, and indicates that the U-Th age is likely to be unbiased by open system behavior [Edwards et al., 1986]. The $^{232}$Th values are low (0.0–307 ppt) except for the C1 visibly dirty aliquot that had 7359 ppt (Table 1). These low values mean that age corrections associated with initial $^{230}$Th are small. A $^{232}_{\text{Th}}$/$^{230}_{\text{Th}}$ atom ratio of 80,000 ± 80,000 was used for this correction since it best corrects the
coral aliquot with the largest $^{232}$Th concentration to the same age as the “cleaner” aliquots, in effect determining the $^{232}$Th/$^{238}$Th as an isochron. This value is a factor of 2 to 3 lower than typical continental ratios, but is higher than observed surface seawater values in the Bahamas that are situated further from the coast [Robinson et al., 2004].

[9] The average corrected age for each coral is based on the three ages that have the lowest $^{232}$Th concentration (Table 1); these values are 4977 ± 63 (1 sigma) and 3070 ± 15 years in 2007 for A1 and C1, respectively. Therefore, the calendar ages (years before A.D. 1950) for the A1 and C1 samples are 4920 ± 62 and 3013 ± 15 calendar (cal) B.P., respectively. Using the IntCal04 calibration curves [Reimer et al., 2004], these calendar ages and 1-sigma uncertainties correspond to atmospheric $^{14}$C ages of 4385 ± 90 and 2900 ± 16 14C years B.P. for the A1 and C1 samples, respectively.

[10] The average of 47 conventional $^{14}$C ages from annual bands in the A1 coral (Figure 2a) was 4674 years. The standard deviation of the average was ±30 years, similar to the uncertainties of the individual ages (±20–36 14C years). For the younger fossil coral (C1), the average of 56 conventional $^{14}$C ages (Figure 3a) averaged 3192 ± 28 years. Two bands (#25 and #27) had significantly older $^{14}$C ages (3280 and 3263 $^{14}$C B.P., respectively) than the average value. Nonetheless, there is remarkably little variability of the $^{14}$C results in both fossil coral sequences.

[11] The averages of seasonal $^{13}$C results from the A1 and C1 samples were −0.4 ± 0.4%o and −0.9 ± 0.4%, respectively (Figures 2b and 3b). These results are similar to those obtained for a recent coral that grew close to our collection site [Swart et al., 1996] (average = −0.33 ± 0.40%).

[12] The $^{18}$O values for seasonal samples from the C1 coral (Figure 3c) averaged −3.56 ± 0.42%o. The annual range was about 1.0–1.5%o, which indicates an SST range of 4–6°C (if $^{18}$O of the water remained constant). There is no apparent correlation between the $^{13}$O and $^{14}$C measurements (Figure 3a). The average $^{18}$O value for the C1 coral is equal to that reported by Swart et al. [Swart et al., 1996] (−3.57 ± 0.25%) for annual $^{18}$O measurements in a coral sequence (M. faveolata) from the same location that grew from 1751 to 1986. The annual range of seasonal $^{18}$O results from this coral (1962–1986) was 0.79%o, somewhat lower than that observed in the C1 coral (1–1.5%o).

4.1. Reservoir Ages During the Mid-Holocene

[13] Reservoir ages for surface waters in which the corals lived are calculated by subtracting the individual coral conventional $^{14}$C ages from the atmosphere conventional $^{14}$C ages from IntCal04 [Reimer et al., 2004]. The reservoir ages for annual bands from the A1 and C1 corals are presented in Figures 4a and 4b. The average reservoir age for the A1 coral that grew from 4908 to 4955 cal years B.P. was 294 ± 33 (n = 47, where n is the number of samples). The average reservoir age from the C1 coral that grew from 3008 to 3066 cal years B.P. was 291 ± 27 years (n = 56). These reservoir ages are somewhat lower than that (390 ± 60 years) obtained for corals that grew in well-flushed regions of the mid-Florida Keys and Glover Reef, Belize from A.D. 1644–1900 [Druffel and Linick, 1978; Druffel, 1980].

4.2. Explanations for Variable Reservoir Ages

[14] Several reasons could explain the low reservoir ages in our fossil corals. First, restricted flow between reef and open ocean surface waters could cause reef surface waters to have had a higher $^{14}$C content because of relatively higher exchange of $^{14}$C-enriched CO$_2$ with the atmosphere. However, since the $^{18}$O values from the C1 coral (Figure 3c) were similar to those reported for recent corals from this well-flushed area [Swart et al., 1996], it seems unlikely that partial isolation of the reef waters had taken place at our mid-Holocene reef location. Additionally, the carbon isotope measurements of the A1 and C1 corals (Figures 2b and 3b) were typical of values for corals presently growing on our mid-Holocene reef location. Furthermore, the radio carbon measurements (Figure 3a) indicate that the surface ocean was likely because the surface ocean takes some time to “catch up” to the drop in the atmosphere. Most of the age-corrected $^{14}$C values shown for the A1 and C1 corals are higher than the calculated Marine04 values (Figure 5), which indicates that this lag effect is insufficient to explain the empirically measured reservoir ages for the Florida Straits.

[15] Finally, reduction of mixing (i.e., stratification) between surface and subsurface waters in the open ocean...
could cause the reservoir ages of surface waters to decrease. Upwelling has been described from the centers of mesoscale gyres off the Tortugas region (southwestern Keys) that move north with the Florida Current [Lee et al., 1995]. When the Yucatan Current is strong, it invades the Gulf of Mexico, forming the Loop Current, inducing a flow south past the Tortugas that initiates gyre formation as the current reenters the Straits of Florida (Figure 1). When the Yucatan

Figure 2. The (a) $\Delta^{14}$C and (b) $\delta^{13}$C results for the annual samples from the A1 coral. Dots with open squares are results from samples that were not acid leached prior to analysis. Annual band numbers increase with coral age.

Table 1. U and Th Isotopic Composition and $^{230}$Th Ages of Samples From the A1 and C1 Corals

<table>
<thead>
<tr>
<th>Lab</th>
<th>Sample</th>
<th>Preparation</th>
<th>$^{238}$U Concentration, ppm</th>
<th>Error, 2 SE</th>
<th>$^{230}$Th Concentration, ppt</th>
<th>Error, 2 SE</th>
<th>$^{232}$Th Concentration, ppb</th>
<th>Error, 2 SE</th>
<th>$^{232}/^{230}$, atom</th>
<th>Error, 2 SE</th>
<th>$\delta^{234}$U Measured, per mil</th>
<th>Error, 2 SE</th>
<th>$\delta^{234}$U Measured, per mil</th>
<th>Error, 2 SE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ed04</td>
<td>LA A1 16-18 H$_2$O-dirty</td>
<td>2.8057</td>
<td>0.0015</td>
<td>2.379</td>
<td>0.024</td>
<td>0.145</td>
<td>0.005</td>
<td>60.29</td>
<td>1.22</td>
<td>146.4</td>
<td>1.2</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Ed03</td>
<td>LA A1 16-18 H$_2$O</td>
<td>2.7990</td>
<td>0.0014</td>
<td>2.302</td>
<td>0.012</td>
<td>0.043</td>
<td>0.003</td>
<td>18.58</td>
<td>0.08</td>
<td>146.4</td>
<td>1.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ed01</td>
<td>LA A1 16-18 Preclean</td>
<td>2.7536</td>
<td>0.0015</td>
<td>2.361</td>
<td>0.013</td>
<td>0.004</td>
<td>0.005</td>
<td>1.69</td>
<td>0.03</td>
<td>147.3</td>
<td>1.3</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Ed02</td>
<td>LA A1 16-18 Full clean</td>
<td>2.8459</td>
<td>0.0018</td>
<td>2.367</td>
<td>0.014</td>
<td>0.006</td>
<td>0.005</td>
<td>2.69</td>
<td>0.08</td>
<td>146.2</td>
<td>1.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ed08</td>
<td>LA C1 52-56 H$_2$O-dirty</td>
<td>2.6687</td>
<td>0.0013</td>
<td>1.477</td>
<td>0.007</td>
<td>7.359</td>
<td>0.033</td>
<td>4939.09</td>
<td>11.08</td>
<td>147.5</td>
<td>1.2</td>
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<tr>
<td>Ed07</td>
<td>LA C1 52-56 H$_2$O</td>
<td>2.6434</td>
<td>0.0013</td>
<td>1.374</td>
<td>0.007</td>
<td>0.307</td>
<td>0.003</td>
<td>221.69</td>
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<tr>
<td>Ed05a</td>
<td>LA C1 52-56 Preclean</td>
<td>2.6097</td>
<td>0.0018</td>
<td>1.373</td>
<td>0.009</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>148.1</td>
<td>1.2</td>
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<tr>
<td>Ed06</td>
<td>LA C1 52-56 Full clean</td>
<td>2.6498</td>
<td>0.0017</td>
<td>1.374</td>
<td>0.009</td>
<td>0.008</td>
<td>0.007</td>
<td>6.02</td>
<td>0.08</td>
<td>148.0</td>
<td>1.3</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

*aThe $^{232}$Th concentrations for Ed05 were lower than bank level.

*bAverage age.

cTwo SD.

dNumber of samples ($n$ in text).

eTwo SE.
Current is weak, it turns sharply eastward south of the Tortugas directly into the Florida Straits and no gyres are formed [Lee et al., 1995]. So there would appear to be a mechanism for turning on and off regional upwelling, which could change the reservoir age of surface waters in our coral region. Perhaps a relatively small climate change, such as that associated with the mid-Holocene warming, could turn this system off for longer periods of time, causing a lower reservoir age.

4.3. Past Changes in Reservoir Age and Implications for Radiocarbon Dating

[18] Using foraminifera from a suite of high-resolution sediment cores in the Florida Straits, Lund et al. [2006] reported that the flow of the Gulf Stream was lower during the Little Ice Age (A.D. ~1200–1850) compared to modern times. This period was also marked by cooler temperatures recorded in foraminifera from the Sargasso Sea [Keigwin, 1996] and corals from the Florida Straits [Druffel, 1982]. Also, the reservoir age of these Florida Straits corals was larger during the Little Ice Age [Druffel, 1982] due in part to increased atmospheric $^{14}$C levels during this period of low solar activity.

[19] Using titanium and iron concentrations measured in sediment layers from the Cariaco Basin (10°N), Haug et al. [2001] found a trend toward drier conditions from 5000 cal years B.P. to the present, with a precipitation minima at 3000 cal years B.P. and during the Little Ice Age. They concluded that these regional changes were indications of southerly displacement of the ITCZ. Whether these changes in the hydrologic cycle are associated with changes in subtropical climate (i.e., in the Florida Straits) are not yet known.

[20] Using deep sea corals, Eltgroth et al. [2006] observed a short time period during the end of the Younger Dryas (11.5 ka) when intermediate water $\Delta^{14}$C values (~1200 m depth) were similar to those in the atmosphere, i.e., the reservoir age of intermediate water was zero. They concluded that there had been large lateral $\Delta^{14}$C gradients in the ocean’s interior. Thus, changes in the intermediate and deep waters of the Atlantic can cause changes in the reservoir age of these water masses.

Figure 3. (a) Annual $\Delta^{14}$C, (b) annual $\delta^{13}$C, and (c) seasonal $\delta^{18}$O results for samples from the C1 coral. Annual band numbers decrease with coral age.
Figure 4. Reservoir ages ($^{14}$C years B.P.) for annual coral bands from the (a) A1 and (b) C1 corals (see text for detail). Lines represent least squares fits of the data.

Figure 5. Age-corrected $\Delta^{14}$C values are shown for atmospheric CO$_2$ (INTCAL04 [Reimer et al., 2004]) and surface ocean DIC (Marine04 [Hughen et al., 2004]). Age-corrected $\Delta^{14}$C values are also shown for the A1 and C1 corals and corals from the Rocks and Pickles coral cores from the mid-Florida Keys, United States [Druiffel and Linick, 1978; Druiffel, 1982], and Glover Reef, Belize [Druiffel, 1980].
We observe low reservoir ages in the surface ocean during two, several decade long periods in the mid- to late Holocene. There are implications for researchers whose radiocarbon dated marine material requires reservoir age correction. Stuiver et al. [1986] specify a reservoir age correction of 404 ± 20 years for the Caribbean region. Our results show that this correction is too high for samples that grew during ~3040 and ~4930 cal years B.P. A more accurate reservoir age correction for radiocarbon measurements of marine samples with similar calendar ages would be 292 ± 30 years.

5. Conclusions

We report that reservoir ages during two, several decade periods ~ 4930 and ~3040 cal years B.P. are lower than those during recent times (390 ± 60 years).

2. The reason for the lower reservoir age during the mid-Holocene cannot be determined with any degree of certainty, though increased stratification and/or higher Δ14C of subsurface waters that mix into the surface are plausible explanations.

3. A more accurate reservoir age correction for radiocarbon measurements of marine samples from this region from the periods ~3040 and ~4930 cal years B.P. is 292 ± 30 years.

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J. F. Atkins, Geological and Planetary Sciences Division, California Institute of Technology, Mail Code 170-25,1200 E. California Boulevard, Pasadena, CA 91125, USA. (jess@gps.caltech.edu)

E. R. M. Druffel, S. Griffin, and J. R. Southon, Earth System Science Department, University of California Irvine, Croul Hall, Irvine, CA 92697-3100, USA. (edruffel@uci.edu)

R. B. Halley, U.S. Geological Survey, 600 Fourth Street South, St. Petersburg, FL 33701, USA. (halley@usgs.gov)

L. F. Robinson, Marine Chemistry and Geochemistry Department, Woods Hole Oceanographic Institution, 266 Woods Hole Road, Woods Hole, MA 02543, USA. (lrobinson@whoi.edu)