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PRE-BOMB SURFACE WATER RADIOCARBON OF THE GULF OF MEXICO AND CARIBBEAN AS RECORDED IN HERMATYPIC CORALS

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ABSTRACT. Radiocarbon measurements of hermatypic corals from 4 sites in the Gulf of Mexico (GOM) and Caribbean Sea were made to estimate the marine ^{14}C reservoir age (R) and the marine regional correction (ΔR) for this region. Coral skeletal material from the Flower Garden Banks (northern GOM continental shelf), Veracruz, Mexico, and 2 reefs from the Cariaco Basin, Venezuela, were analyzed. Annual and subannual samples from 1945–1955 were milled and ^{14}C composition was determined. In the Gulf of Mexico, average coral $\Delta^{14}C$ is –52.6 ± 0.7‰ and average $\Delta^{14}C$ for the Cariaco Basin corals is –53.4 ± 0.8‰. Average values for the marine reservoir age and ΔR are computed with this data and compared with results derived from previous measurements made in the same regions. These values are important in calibrating the ^{14}C ages of carbonate samples from the area.

INTRODUCTION

Due to the rapid mixing rates in the atmosphere, terrestrial organisms typically exhibit $^{14}C/^{12}C$ concentrations in equilibrium with that of the atmosphere (once corrected for mass dependent fractionation). Alternately, marine organisms generally deposit their carbonate shells close to isotopic equilibrium with the seawater in which they are living (deriving carbon from the DIC of the surrounding water). Because of the large carbon reservoir of the oceans and the rates in which carbon mixes across the ocean-atmosphere boundary and across the interface between the ocean's surface mixed layer and underlying waters, the surface mixed layer of the ocean is depleted in ^{14}C relative to the atmosphere. This causes marine organisms to exhibit an apparent ^{14}C age greater than their contemporaneous terrestrial counterparts. It is therefore necessary to apply a correction in order to compare marine and terrestrial samples. This correction is termed the marine reservoir age, R, (Stuiver et al. 1986) and is the difference in years between the measured ^{14}C age of a marine organism's carbonate shell and the atmospheric ^{14}C age at the time as reported in the terrestrial calibration curve, IntCal04 (Reimer et al. 2004). Additionally, a regional correction designated as ΔR (Stuiver and Braziunas 1993) is needed to adjust for the difference between the regional reservoir age and the nominal average global marine reservoir age for surface ocean waters based on a one-dimensional marine box model (Oeschger et al. 1975). The marine model is forced with a prescribed atmospheric $\Delta^{14}C$ and pCO^2 based on an average air-sea exchange coefficient, which causes regional excursions from the global average. Due to temporally and spatially varying oceanographic processes that can influence surface water ^{14}C, the regional reservoir age can differ greatly from the global marine average. Therefore, it is important to know the regional correction (ΔR) when calibrating marine samples with the internationally ratified marine calibration curve, Marine04 (Hughen et al. 2004a). At present, only a few studies have computed the reservoir age and ΔR in the Caribbean, and there have been no studies within the Gulf of Mexico (Figure 1). Here, we present ^{14}C reservoir age and ΔR corrections based on marine carbonates from 4 locations in the Caribbean and Gulf of Mexico.

GENERAL OCEANOGRAPHY

The 2 regions of focus in this study are the Gulf of Mexico and Caribbean Sea (Figure 1). The main surface currents in the Caribbean region are the Caribbean Current, Yucatan Current, Loop Current

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(Gulf of Mexico), and the Florida Current (Centurioni and Niiler 2003). Water entering the Caribbean originates from both the North and South Atlantic oceans (Wilson and Johns 1997). Water flows into the Caribbean Sea in the southeast and flows westward as the Caribbean Current. Surface current velocities, as high as 70 cm s^{-1}, are highest along the coast of Venezuela and the Netherland Antilles. The Caribbean Current then turns northwest past the Colombian Basin (80°W, 12°N). It is channeled through a trough southwest of Jamaica and then through the Yucatan Channel as the Yucatan Current (Fratantoni 2001).

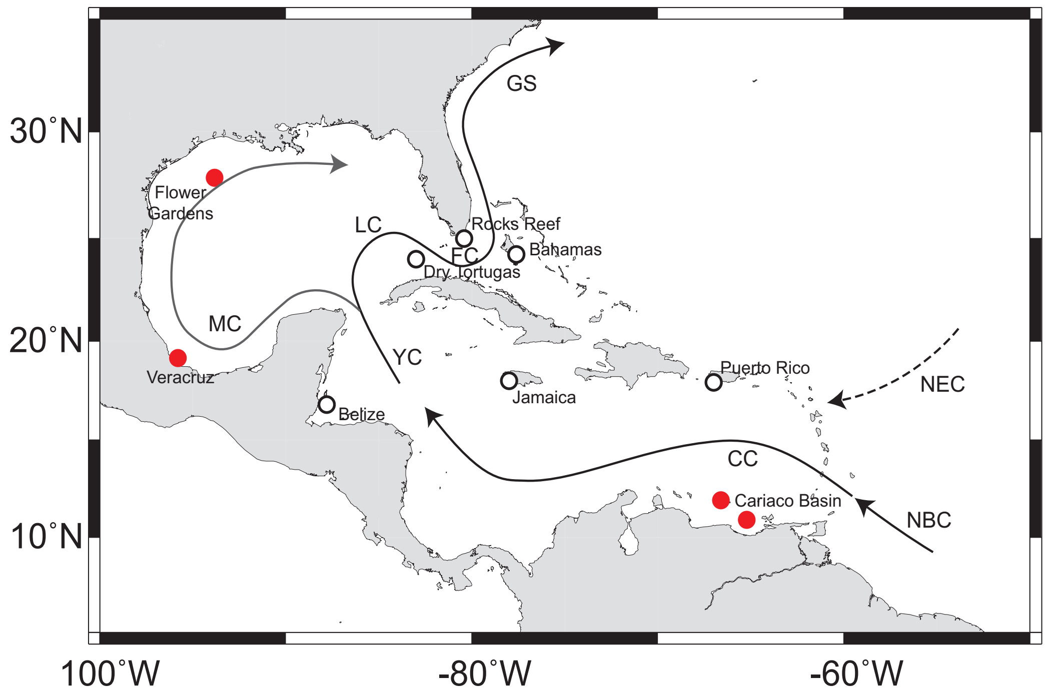

Figure 1 Existing ^{14}C sites in the Caribbean and Gulf of Mexico shown as open circles. New sites from this study indicated by closed circles. Some major surface currents are labeled (CC - Caribbean Current, FC - Florida Current, GS - Gulf Stream, LC - Loop Current, MC - Mexican Current, NBC - North Brazil Current, NEC - North Equatorial Current, and YC - Yucatan Current).

Once in the Gulf of Mexico, the Yucatan Current initially follows the continental shelf break from 21°N to 24.5°N and then changes direction to a northwesterly direction around 23.5°N, 87°W (Molinari and Cochrane 1972). There is a clockwise flow that extends northward into the Gulf of Mexico and joins the Yucatan Current and the Florida Current, which is known as the Loop Current. The position of the Loop Current is variable and can intrude into the Gulf of Mexico as an intense clockwise flow as far north as 29.1°N or it can flow in an almost direct path to the Florida Current (Molinari et al. 1977; Sturges and Evans 1983). The Yucatan and Florida currents have been shown to be within 10% of each other's volume at any given time (Molinari and Morrison 1988). Therefore, variabilities in the Loop and Yucatan currents are expected to have a strong impact on the Florida Current. In addition to the Loop Current, Sturges and Blaha (1976) have suggested a western boundary current in the far western Gulf of Mexico that stems from the Yucatan Current as it enters the Gulf of Mexico.

Considering the rate (24–30 Sv) at which the surface water is entering the Gulf of Mexico through the Yucatan Channel and leaving through the Florida Straits, the residence time within the mixed layer is relatively short (on the order of 2 to 3 months). The corals in this study from the Gulf of Mexico are from the upper 20 m and are therefore typically bathed in surface water from the Caribbean Sea. This suggests that the reservoir age of carbonates from the Gulf of Mexico should be similar to that of carbonates in the Caribbean Sea.

METHODS

Coral cores were collected from live corals using diver-operated underwater hydraulic drilling equipment. All specimens are of the species *Montastraea faveolata*, a common Caribbean reef-building hermatypic coral that exhibits regular annular banding (Goreau 1959; Hudson et al. 1976; Fairbanks and Dodge 1979; Dodge and Lang 1983). Two coral cores each from the Gulf of Mexico and the Cariaco Basin were used in this study (Figure 2). The first was collected in May 1990 from the Flower Garden Banks National Marine Sanctuary (93°50′W, 27°52′N) in approximately 20 m of water. The Flower Garden Banks are located approximately 180 km south of the Texas/Louisiana border on the continental shelf of the northern Gulf of Mexico. The second specimen from the Gulf of Mexico is from Santiaguillo Reef (95°48.5′W, 19°08.3′N), which is located about 20 km off the coast of Veracruz, Mexico, in the western Gulf of Mexico. The coral grew in ~6 m of water and was drilled in 1991. The 2 coral cores from the Cariaco Basin used in this study are from Boca de Medio Island (66°36′W, 11°55′N) and Isla Tortuga (65°21′W, 10°53′N). Boca de Medio is located in the Los Roques archipelago, outside of the Cariaco Basin proper. The sample was drilled in July 1998 in water depth of ~2 m. Isla Tortuga is located at the northern margin of the Cariaco Basin. The coral core was collected from the southern coast of the island in March 1996 in water depth of ~2 m.

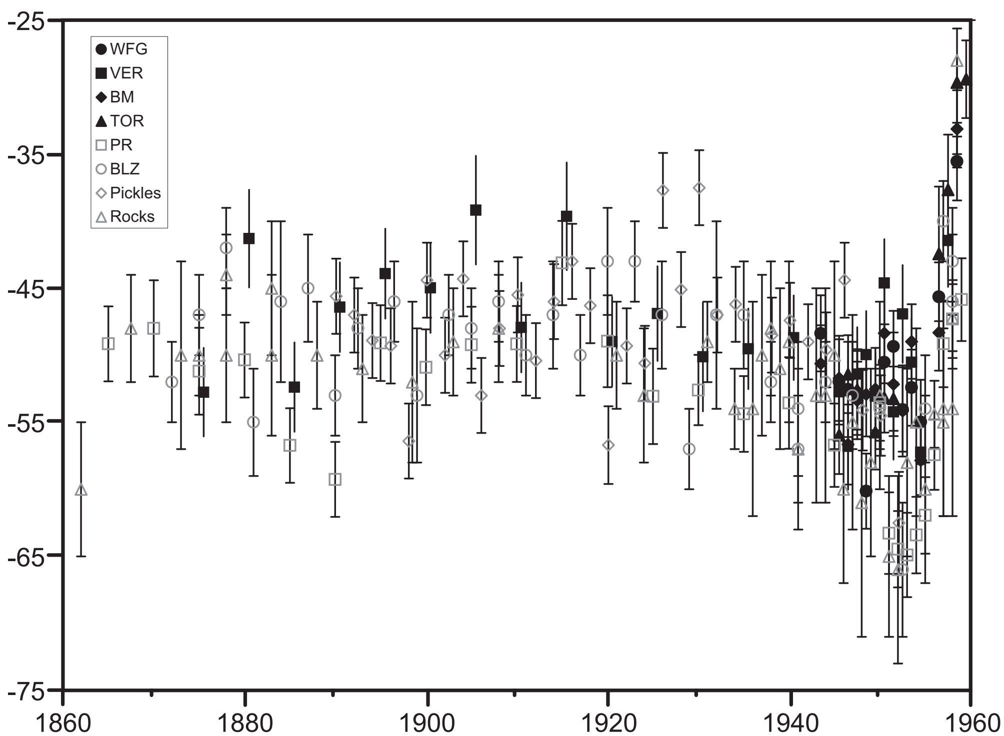

Figure 2 Caribbean and Gulf of Mexico coral $\Delta^{14}C$ records. New data are shown as solid black symbols (WFG - West Flower Gardens, Gulf of Mexico; VER - Veracruz, Mexico; BM - Boca de Medio, Cariaco Basin; TOR - Isla Tortugas, Cariaco Basin). Data previously published are shown as open gray symbols (PR - Puerto Rico; BLZ - Gulf of Honduras, Belize; Pickles - Pickles Reef, Florida; Rocks - Rocks Reef, Florida). Error bars indicate 1 standard deviation.

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The cores were cut into ~10-mm slabs, cleaned, and air-dried. Coral slabs were X-rayed to determine the high- and low-density band couplet. Ages were then assigned using the density bands and counting back from the top of the core. Based on published literature, we assumed the high-density bands were formed during the Northern Hemisphere summer season (e.g. Hudson et al. 1976). Samples were micromilled from the respective slabs to obtain calcium carbonate from the corals for ^{14}C analysis. Annual samples for years 1945–1954 were chosen for analysis in this study because of the years of overlap between the individual coral cores prior to atmospheric nuclear weapons testing. ^{14}C measurements were made at the Center for Accelerator Mass Spectrometry (CAMS) at the Lawrence Livermore National Laboratory (Davis et al. 1990). Annual samples of ~10 mg were placed in individual vacutainers, evacuated, heated, and acidified with orthophosphoric acid at 90 °C. The resultant CO_2 was then converted to graphite in the presence of an iron catalyst (Vogel et al. 1987). ^{14}C results are reported as age-corrected $\Delta^{14}C$ (‰) as defined by Stuiver and Polach (1977) and include a background and $\delta^{13}C$ correction. Reproducibility of results is better than ±3.5‰ (1 σ) based on an in-house coral process standard.

RESULTS

Individual analytical results are presented in Table 1. We do not make any attempt to correct for the Suess effect as there is no noticeable trend in our samples. During the years that the records overlap (1945–1954) and prior to the atmospheric nuclear weapons testing, all 4 records show similar $\Delta^{14}C$ values (Table 2). The mean Flower Garden Banks $\Delta^{14}C$ is –53.2 ± 1.0‰ (n = 9); the Veracruz, Mexico, average $\Delta^{14}C$ is –51.9 ± 1.1‰ (n = 10); the average Boca de Medio $\Delta^{14}C$ is –53.2 ± 1.0‰ (n = 10); and the Isla Tortuga mean $\Delta^{14}C$ is –53.9 ± 1.5‰ (n = 3). The 2 Gulf of Mexico records combined have an average $\Delta^{14}C$ of –52.6 ± 0.7‰ (n = 19) and the 2 Cariaco Basin records have an average $\Delta^{14}C$ of –53.4 ± 0.8‰ (n = 13).

The $\Delta^{14}C$ of the Northern Hemisphere atmosphere in 1950 as recorded in tree rings is –24.5 ± 1.1‰ (Reimer et al. 2004) and the $\Delta^{14}C$ of the global ocean as derived from the Marine04 model is –56.7 ± 2.8‰. These results yield average reservoir ages of 235 ± 11 yr (ΔR of –36 ± 25 yr) and 242 ± 12 yr (ΔR of –28 ± 25 yr) in the Gulf of Mexico and Cariaco Basin, respectively.

Because of the surface circulation of the region (discussed above) it is reasonable to consider the Caribbean and Gulf of Mexico data together to obtain values representative of the entire region. The average $\Delta^{14}C$ of all 4 records is –52.9 ± 0.5‰ (n = 32). These results yield an average reservoir age of 238 ± 10 yr and a ΔR of –32 ± 25 yr.

The sample from Veracruz, Mexico, extended before the time of significant industrialization and therefore lacks the Suess effect in its earliest years. The average $\Delta^{14}C$ for the pre-industrial time period 1875–1895 is –47.6 ± 1.5‰ (n = 5), which yields a reservoir age of 354 ± 15 yr and a ΔR of –13 ± 27 yr.

DISCUSSION

Coral $\Delta^{14}C$ pre-bomb values are nearly indistinguishable among all sites. The average Gulf of Mexico reservoir age is 235 ± 11 yr and a ΔR of –35 ± 25 yr. This compares well to an average of 280 ± 44 yr and ΔR of 10 ± 49 yr for all previously published data from the region (Table 3). The average reservoir age and ΔR for the Cariaco Basin results is 242 ± 12 yr and –28 ± 25 yr, respectively. Surface water $\Delta^{14}C$ in the Gulf of Mexico and Cariaco Basin are so similar due to the rapid transport between the basins with relatively little modification of the water masses.

Table 1 Raw data from this study.

Site	Year	^{14}C age (conventional)	Fraction modern (absolute)	$\Delta^{14}C$ (‰) (age-corrected)
West Flower Gardens				
	1954.5	450 ± 30	0.9450 ± 0.0031	–55.0 ± 3.1
	1953.5	430 ± 25	0.9476 ± 0.0028	–52.4 ± 2.8
	1952.5	445 ± 30	0.9460 ± 0.0031	–54.0 ± 3.1
	1951.5	405 ± 25	0.9506 ± 0.0027	–49.4 ± 2.7
	1950.5	415 ± 25	0.9495 ± 0.0028	–50.5 ± 2.8
	1948.5	500 ± 25	0.9399 ± 0.0028	–60.1 ± 2.8
	1947.5	440 ± 30	0.9472 ± 0.0031	–52.8 ± 3.1
	1946.5	435 ± 35	0.9475 ± 0.0036	–52.5 ± 3.6
	1945.5	435 ± 30	0.9480 ± 0.0032	–52.0 ± 3.2
Veracruz, Mexico				
	1954.5	470 ± 30	0.9428 ± 0.0032	–57.2 ± 3.2
	1953.5	415 ± 30	0.9495 ± 0.0033	–50.5 ± 3.3
	1952.5	385 ± 35	0.9531 ± 0.0036	–46.9 ± 3.6
	1951.5	445 ± 35	0.9458 ± 0.0036	–54.2 ± 3.6
	1950.5	365 ± 30	0.9554 ± 0.0033	–44.6 ± 3.3
	1949.5	440 ± 30	0.9469 ± 0.0032	–53.1 ± 3.2
	1948.5	415 ± 30	0.9500 ± 0.0033	–50.0 ± 3.3
	1947.5	425 ± 30	0.9486 ± 0.0035	–51.4 ± 3.5
	1946.5	475 ± 30	0.9432 ± 0.0032	–56.8 ± 3.2
	1945.5	440 ± 30	0.9473 ± 0.0032	–52.7 ± 3.2
	1895.5	415 ± 30	0.9561 ± 0.0034	–43.9 ± 3.4
	1890.5	440 ± 30	0.9536 ± 0.0033	–46.4 ± 3.3
	1885.5	495 ± 30	0.9476 ± 0.0033	–52.4 ± 3.3
	1880.5	405 ± 35	0.9587 ± 0.0036	–41.3 ± 3.6
	1875.5	510 ± 30	0.9472 ± 0.0033	–52.8 ± 3.3
Boca de Medio				
	1954.5	475 ± 25	0.9421 ± 0.0026	–57.9 ± 2.6
	1953.5	400 ± 25	0.9510 ± 0.0028	–49.0 ± 2.8
	1952.5	445 ± 30	0.9458 ± 0.0034	–54.2 ± 3.4
	1951.5	430 ± 35	0.9478 ± 0.0039	–52.2 ± 3.9
	1950.5	400 ± 35	0.9516 ± 0.0037	–48.4 ± 3.7
	1949.5	435 ± 30	0.9475 ± 0.0031	–52.5 ± 3.1
	1948.5	440 ± 30	0.9471 ± 0.0031	–52.9 ± 3.1
	1947.5	445 ± 25	0.9466 ± 0.0029	–53.4 ± 2.9
	1946.5	470 ± 30	0.9433 ± 0.0030	–56.7 ± 3.0
	1945.5	430 ± 30	0.9483 ± 0.0032	–51.7 ± 3.2
Isla Tortugas				
	1951.5	440 ± 25	0.9468 ± 0.0024	–53.2 ± 2.4
	1950.5	440 ± 25	0.9468 ± 0.0026	–53.2 ± 2.6
	1949.5	460 ± 25	0.9443 ± 0.0028	–55.7 ± 2.8
	1947.5	435 ± 30	0.9475 ± 0.0030	–52.5 ± 3.0
	1946.5	425 ± 25	0.9486 ± 0.0029	–51.4 ± 2.9
	1945.5	465 ± 25	0.9440 ± 0.0029	–56.0 ± 2.9

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Table 2 Age-corrected $\Delta^{14}C$, conventional ^{14}C age of sample, computed reservoir age, and computed ΔR for coral samples used in this study. $\Delta^{14}C$ and ^{14}C ages are calculated using weighted average of individual data points. Variance is weighted mean measurement error.

Site	Midpoint (year)	$\Delta^{14}C$ (‰) (age-corrected)	^{14}C age (conventional)	Reservoir age (yr)	ΔR (yr)
Flower Garden Banks	1950 (n = 9)	–53.2 ± 1.0	439 ± 9	240 ± 13	–30 ± 26
Veracruz, Mexico	1950 (n = 10)	–51.9 ± 1.1	428 ± 10	229 ± 13	–41 ± 26
Gulf of Mexico Avg	1950 (n = 19)	–52.6 ± 0.7	434 ± 7	235 ± 11	–36 ± 25
Boca de Medio	1950 (n = 10)	–53.2 ± 1.0	438 ± 9	239 ± 13	–31 ± 26
Isla Tortugas	1950 (n = 3)	–53.9 ± 1.5	447 ± 14	248 ± 17	–22 ± 28
Caribbean Avg	1950 (n = 13)	–53.4 ± 0.8	441 ± 8	242 ± 12	–28 ± 25
Veracruz, Mexico	1885 (n = 5)	–47.6 ± 1.5	456 ± 14	354 ± 15	–13 ± 27

Table 3 Previously published $\Delta^{14}C$ data from the Caribbean Sea and Gulf of Mexico.

Site	Year	Reservoir age	ΔR	Reference	Material
Bahamas	1950	229 ± 43	–40 ± 42	Broecker and Olson 1961	Gastropod
Bahamas	1885	423 ± 59	56 ± 59	Broecker and Olson 1961	Gastropod
The Rocks, FL Keys	1950	281 ± 21	11 ± 31	Druffel 1980	Coral
The Rocks, FL Keys	1850	405 ± 18	33 ± 16	Druffel and Linick 1978; Druffel 1982	Coral
Tortugas, FL	1884	482 ± 52	114 ± 51	Lighty et al. 1982	Coral
Golden Cay, Bahamas	1912	493 ± 66	146 ± 66	Lighty et al. 1982	Coral
Gulf of Honduras, Belize	1950	259 ± 20	–11 ± 30	Druffel 1980	Coral
Jamaica	1884	323 ± 42	–44 ± 41	Broecker and Olson 1961	Gastropod
Jamaica	1930	273 ± 43	–30 ± 42	Broecker and Olson 1961	Gastropod
La Parguera, Puerto Rico	1950	306 ± 14	36 ± 26	Kilbourne et al. 2007	Coral
La Parguera, Puerto Rico	1885	402 ± 13	35 ± 26	Kilbourne et al. 2007	Coral
Cariaco Basin, Venezuela	1935	336 ± 61	33 ± 60	Hughen et al. 2004b	Foraminifera
Cariaco Basin, Venezuela	1910	361 ± 50	12 ± 50	Hughen et al. 2004b	Foraminifera
Isla Tortuga, Venezuela	1941	264 ± 41	–22 ± 40	Guilderson et al. 2005	Coral
Isla Tortuga, Venezuela	1906	290 ± 41	–70 ± 40	Guilderson et al. 2005	Coral
Boca de Medio, Venezuela	1945	256 ± 42	–18 ± 41	Guilderson et al. 2005	Coral
Los Testigos, Venezuela	1940	285 ± 43	–1 ± 42	Guilderson et al. 2005	Coral

The small ΔR values for the Caribbean and Gulf of Mexico region imply good agreement with the one-dimensional marine model and the atmospheric curve used to derive the Marine04 curve and estimate the global marine ^{14}C age. This implies common source waters and short residence times and indicates the rate of air-sea exchange of CO_2 in this region is close to the global average. Therefore, for the pre-bomb period the global marine model can be used to provide a reasonable estimate of the ^{14}C age of marine samples for the Caribbean and Gulf of Mexico for modern times (i.e. when boundary conditions in the area are as they are today).

At times in the past when different climatic/oceanographic regimes existed, one cannot make this same assumption. For example, a change in the relative proportions of surface water from the North and South Atlantic would have an impact on the reservoir and ΔR ages of the region. The ΔR calculated from a coral off southern Puerto Rico is 36 ± 26 yr (Kilbourne et al. 2007) compared to –32 ±

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25 yr for the Caribbean. The difference between the values is due to the difference in source water to the areas (Northern Atlantic via the North Equatorial Current versus equatorial waters via the Northern Boundary Current).

CONCLUSIONS

We present estimates of the surface water $\Delta^{14}C$ concentration in the Caribbean Sea and Gulf of Mexico. The average ^{14}C for the region is –52.9 ± 0.5‰. This yields an average reservoir age of 238 ± 10 yr and ΔR of –32 ± 25 yr. These values are close to previously published reservoir ages and ΔR ages for the Caribbean. The relatively small ΔR ages compared to the marine 1-D model suggest the Marine04 curve is a reasonable approximation for this region for the modern oceanographic regime. This may not be the case during the past when significantly different oceanographic and climatic regimes existed. The smaller reservoir age compared to the marine model is consistent with short residence times in the Caribbean and Gulf of Mexico and high rates of air-sea exchange of CO_2. There is little to no Suess effect apparent in the Gulf of Mexico $\Delta^{14}C$ values, which implies a relatively small amount of ^{14}C-depleted atmospheric CO_2 being mixed into the surface waters.

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