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► **To cite this version:**

Martine Paterne, Nathalie Feuillet, Guy Cabioch, Elsa Cortijo, Dominique Blamart, et al.. Reservoir Ages in the Western Tropical North Atlantic from One Coral off Martinique Island (Lesser Antilles). Radiocarbon, 2018, 60 (2), pp.639 - 652. 10.1017/RDC.2017.118 . hal-01806834

HAL Id: hal-01806834

<https://hal.science/hal-01806834>

Submitted on 18 Jun 2021

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RESERVOIR AGES IN THE WESTERN TROPICAL NORTH ATLANTIC FROM ONE CORAL OFF MARTINIQUE ISLAND (LESSER ANTILLES)

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ABSTRACT. Sea surface reservoir ages (R) are reported from radiocarbon (¹⁴C) measurements of the annual growth bands of coral *Siderastrea siderea* collected on the Atlantic coast off Martinique Island, in the Lesser Antilles volcanic arc. Mean values of R are similar between 1835 and 1845 during pre-anthropogenic times at 385 ± 30 yr and between 1895 and 1905 at 382 ± 20 yr when there was a huge eruption from the Montagne Pelée volcano in 1902–1903. Limited ¹⁴C aging of sea surface (~40 yr) may be due to enhanced volcanic activity. Variability of R is slightly greater during 1835–1845 than during 1895–1905. It is linked to a moderate increase of $\Delta^{14}\text{C}$ of 5‰, strengthened by a clear increase of $\delta^{18}\text{O}$ of 0.4‰. This is attributed to a decrease of the northward advection of the South Atlantic Waters into the western tropical North Atlantic and Caribbean Sea and relative enhanced westward flux of the tropical North Atlantic surface waters, the southern waters having lower values of ¹⁴C and $\delta^{18}\text{O}$ than the North Atlantic ones. From 1835 to 1845, the fraction of the South Atlantic Waters transported up to Martinique Island was reduced from 25% to 15%.

KEYWORDS: coral, Lesser Antilles, marine reservoir ages, Martinique, stable isotopes, volcanic effects.

INTRODUCTION

Quantification of the sea surface reservoir ages (R), a measure of the difference between the marine and atmospheric radiocarbon (¹⁴C) ages at the same time, contributes substantially to a better understanding of ocean dynamics and climate. This difference is due to the isolation of subsurface seawater from the atmosphere and to ¹⁴C decay. It reflects the balance between the ¹⁴C production and the ocean–atmosphere exchange of ¹⁴CO₂ as well as mixing between the surface and subsurface waters by vertical convection and horizontal advection due to changes of wind strength and oceanic currents. Values of R can be measured from biogenic carbonates, the ¹⁴C of which representing that of the dissolved inorganic carbon (DIC) in seawater in which they grow.

Numerous estimates of R from corals were obtained in the subtropical western North Atlantic (Druffel and Linick 1978; Druffel 1980, 1982, 1997; Druffel and Suess 1983; Goodkin et al. 2012; Fernandez et al. 2015), the Caribbean Sea (Druffel 1980; Druffel and Suess 1983; Guilderson et al. 2005; Kilbourne et al. 2007), and the Gulf of Mexico (Wagner et al. 2009). No values of R were acquired within the Atlantic inflow, which penetrates into the eastern Caribbean Sea through the sill passages along the Lesser Antilles volcanic arc. Here we report values of R for the eastern Caribbean Sea and the western tropical North Atlantic region from ¹⁴C measurements of an annually banded coral *Siderastrea siderea* collected alive in early 2008 at îlet Chancel off the eastern coast of Martinique Island in the Lesser Antilles arc (14°70'N; 60°90'W; 1.50 m water depth) (Figure 1A).

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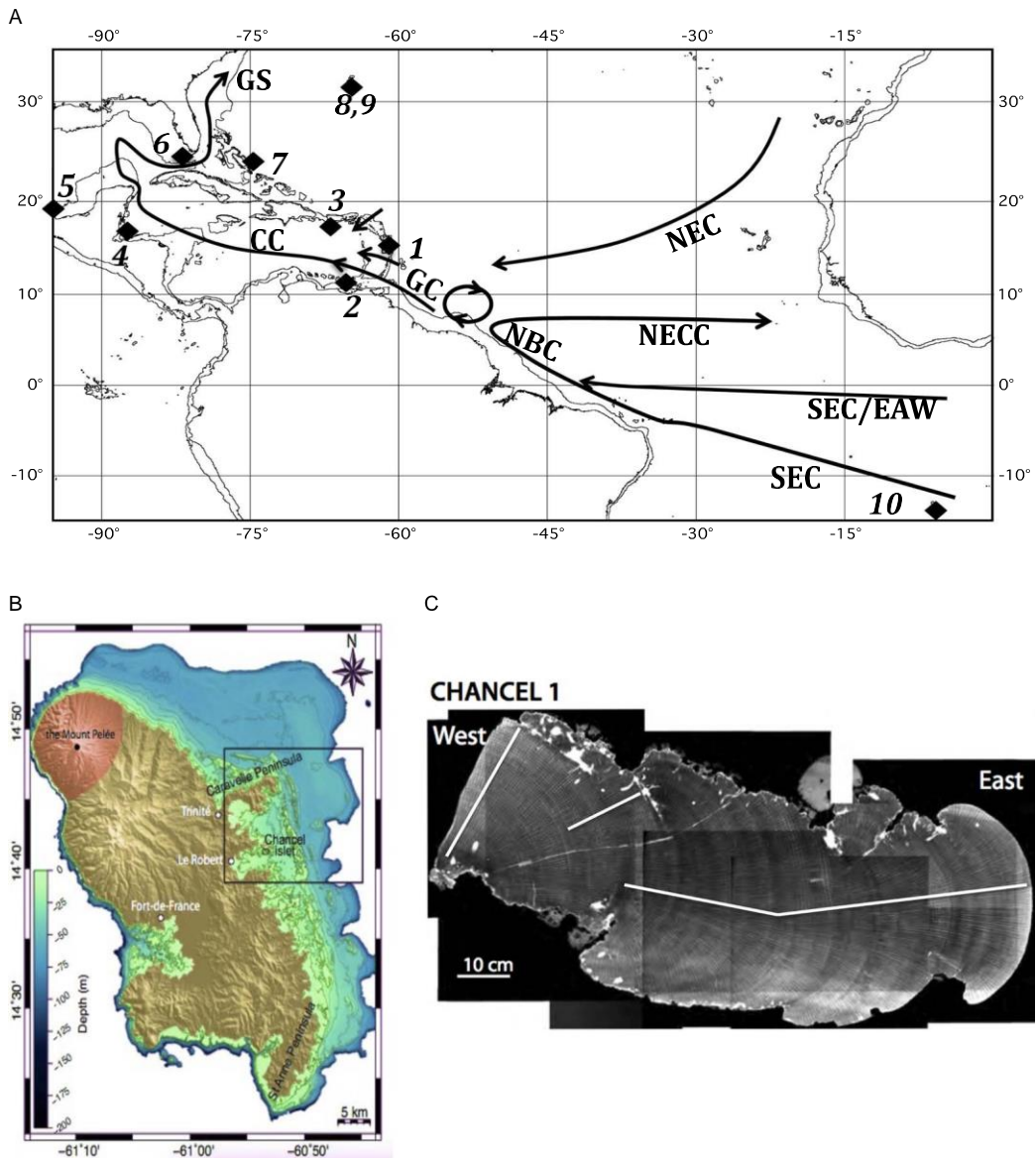


Figure 1 (A) Location of corals, sclerobiontes, and mollusk shells cited in the text and schematic patterns of the oceanic currents. 1: Martinique; 2: Cariaco basin (Guilderson et al. 2005); 3: Puerto-Rico (Kilbourne et al. 2007); 4: Belize (Druffel 1980); 5: Gulf of Mexico (Wagner et al. 2005); 6: Florida (Druffel and Linick 1978; Druffel 1980, 1982); 7: Bahamas (Fernandez et al. 2012); 8: Bermuda north shore (Druffel 1989; 1997); 9: Bermuda south shore (Goodkin et al. 2012); 10: Santa Helena (Lewis et al. 2008). NEC: North Equatorial current; NECC: North Equatorial undercurrent; NBC: North Brazil current; GC: Guiana current; SEC: South Equatorial current; EAW: East Atlantic current; CC: Caribbean current; GS: Gulf Stream. The 1000-m isobath is represented: (B) location and (C) radiography of coral Chancel 1. White thick lines represent sampling plates.

Martinique Island is located alongside one of the main passages of the Atlantic inflow (Wilson and Johns 1997; Johns et al. 1999, 2002; Cherubin and Richardson 2007). This island is characterized by sustained volcanic activity with widespread hydrothermal and geothermal fields and diffuse degassing of CO₂ from shallow magma chambers. This old mantle-derived CO₂

dissolves into shallow aquifers and rivers (Rivé et al. 2011) and in coastal seawater from submarine gas vents, mainly located offshore the western coast of Martinique (Gadalia et al. 2015). Residence time of waters in the hydrothermal and geothermal systems may be extremely short (<10 yr), but it is mostly of some hundred years up to ten thousand years (Sanjuan et al. 2005; Rad et al. 2011). In Martinique, river discharges are very small (<1 m³/s) so that sea surface aging by freshwater runoff is unlikely. Only massive destabilization of shallow aquifers as well as active submarine CO₂ degassing from geothermal fields, such as during an eruption, may potentially drive local aging of sea surface in coastal areas near coral reefs.

The values of R are established during two decades marked by a quasi-stable atmospheric ¹⁴C content (Stuiver et al. 1998) and by either quiescent or active volcanism between 1835 and 1845 and between 1895 and 1905, respectively. One devastating 2-yr-long eruption of Montagne Pelée volcano, killing 28,000 people, occurred in 1902–1903 on Martinique Island (Lacroix 1904). Values of R from coral Chancel 1 in Martinique were compared to previous data from corals and sclerophytes collected in the subtropical and tropical western North Atlantic (Druffel and Linick 1978; Druffel 1980, 1982, 1997; Druffel and Suess 1983; Guilderson et al. 2005; Kilbourne et al. 2007; Wagner et al. 2009; Goodkin et al. 2012; Fernandez et al. 2015). We analyzed the variability of R during each decade and a potential effect of volcanic activity on the ¹⁴C ages. Oxygen isotope analyses were performed to account for changes of local hydrology, ocean dynamics and volcanism.

MATERIAL AND METHODS

The full description of coral Chancel 1, which was collected alive in January 2008 at a water depth of ~1.50 m on the Atlantic coast of Martinique Island, is reported elsewhere (Weil-Accardo et al. 2016) (Figure 1B). The coral slab extends over a ~1-m length, and X-radiographs were taken to display the annual density bands (Figure 1C). Chronology is based on the counting of annual bands of growth, Th/U dating and on the correlation of die down surfaces of a series of corals from microatolls sampled south of the Caravelle Peninsula (Weil-Accardo et al. 2016). In addition, U/Th dating was performed on the growth band years 1849–1851 in coral Chancel 1 with a MC-ICPMS-Neptune following previously described procedure (Pons-Branchu et al. 2014) (Table 3). Annual bands were drawn on a tracing overlay of the radiography digitized at the scale of the coral allowing a precise sampling along growth axes using a diamond saw.

X-ray diffraction of random samples was performed using a PANalytical X'Pert Pro diffractometer at the GEOPS Laboratory to infer presence of calcite (Table 1). Oxygen and carbon isotopes were analyzed at the LSCE using an Optima-VG mass spectrometer (isotope ratio mass spectrometer) coupled with a common acid bath and an automated preparation line to produce CO₂. The isotope compositions were calibrated against the NBS 18 and 19 standards. Oxygen and carbon isotopic compositions are reported in the classical notation δ expressed in per mil (‰) versus PDB (Pee Dee Belemnite). The external precision is 0.02 and 0.04‰ (1 σ) for carbon and oxygen respectively. The method for radiocarbon analyses of carbonates was described elsewhere (Tisnerat-Laborde et al. 2001). Chemical pretreatment of coral powder was done using HNO₃ (0.01N) and rinsed in distilled water. Carbonate hydrolyzes with H₃PO₄ in a semi-automatic vacuum line were performed at the Gif-LSCE Radiocarbon Laboratory. Graphite targets were prepared and measured at the French National AMS-ARTEMIS- LMC14 facility (Cottreau et al. 2007). Results are expressed in conventional years BP and the $\Delta^{14}\text{C}$ ‰ is the deviations in parts per thousand (‰) of a sample's ¹⁴C/¹²C ratio of known age from that of the absolute standard activity in 1950 (Stuiver and Polach 1977). Reservoir age, R, is the difference at the date of coral growth between the measured ¹⁴C age and the atmospheric

^{14}C age using the calibration record single-year IntCal98 (Stuiver et al. 1998), which takes more account of the variability of the atmospheric ^{14}C ages than the calibration record IntCal13 (Reimer et al. 2013). ΔR is the difference between the measured ^{14}C age and the modeled global sea surface age from a global box-diffusion carbon model (Stuiver et al. 1986; Stuiver and Braziunas 1993) using the marine calibration dataset IntCal 04 (Hughen et al. 2004), which is equivalent to the marine IntCal13 over the considered time interval (Reimer et al. 2013).

HYDROLOGIC SETTING AND SEA SURFACE DIC $\Delta^{14}\text{C}$

The water masses in the western tropical North Atlantic and the eastern Caribbean Sea were previously described in detail (Morrison and Nowlin 1982; Wilson et al. 1994; Stramma and Schott 1999; Stramma et al. 2005; Rhein et al. 2005) and the following description is summarized for the upper water masses (~500 m) near the Lesser Antilles (Rhein et al. 2005; Kirchner et al. 2009). The tropical surface waters (TSW) at 27°C form the mixed layer which are influenced by the freshwater plumes of the Amazon and Orinoco Rivers. These are transported equatorward by the North Brazil Current (NBC) and the Guiana Current (GC) (Figure 1A) into the western tropical North Atlantic and the Caribbean Sea where they spread extensively (Pailler et al. 1999; Hellweger and Gordon 2002; Field 2005, 2006). Below TSW is the underlying salinity maximum water (SMW) formed by subduction of surface waters at the northern and southern Atlantic tropics/subtropics transitions (Wilson et al. 1994; Stramma et al. 1999; Stramma et al. 2005; Rhein et al. 2005; Kirchner et al. 2009). The northern surface waters flow westward from the North Atlantic subtropical gyre along the North Equatorial Current (NEC). Surface waters from the South Atlantic gyre and from the east South Atlantic (EAW) flow along the South Equatorial Current (SEC) then the NBC and GC (Wilson et al. 1994; Bourles et al. 1999; Stramma and Schott 1999; Stramma et al. 2005). Anticyclonic rings form at the retroflexion of NBC near ~6°N feeding the eastward flowing North Equatorial Counter-current (NECC). They transport the South Atlantic waters as far as 15–18°N along the Atlantic side of the Lesser Antilles islands, where they decay (Hu et al. 2004; Fratantoni and Richardson 2006; Field 2005). Below SMW down to ~400–500 m water-depth are found the central waters (CW) (Rhein et al. 2005) which originate from both the South Atlantic Central water (SACW) and the North Atlantic Central water (NACW), zonally separated across the North Atlantic at around 15°N (Stramma et al. 2005). SMW from the southern origin are fresher than SMW from the North (Bourles et al. 1999) as well as NACW are saltier and warmer than SACW (Stramma et al. 2005).

The Atlantic inflow into the Caribbean Sea penetrates through the sill passages of the Lesser Antilles, the main ones located to the south of 14°N in the Grenada (11°N) and the St Lucia-Martinique (14°N) passages and to the north in the Antigua and Anegada-Jungfern (17°N) passages (Morrison and Nowlin 1982; Wilson and Johns 1997; Johns et al. 2002; Cherubin and Richardson 2007). These inflows feed the Caribbean Current flowing westward and northward through the Yucatan strait to feed the Florida Current then the Gulf Stream (Figure 1A).

In the Caribbean region and western tropical North Atlantic, two main hydrologic features will have an impact on the variability of the sea surface $\delta^{18}\text{O}$ and $\Delta^{14}\text{C}$. First, the Martinique Island is exposed all the year round to the E-NE Trade Winds so that sea surface waters will pile up along the roughly northwest/southeast coast of the island, and significant local upwelling cannot form. Second, the well-marked salinity gradient between the fresh buoyant surface waters TSW and the underlying SMW causes a strong pycnocline and a stable barrier layer (BL) in density (Sprintall and Tomczak 1992; Pailler et al. 1999; de Boyer Montégut et al. 2004). It is almost permanent all the year round (de Boyer Montégut et al. 2004, 2007; Mignot et al. 2007)

and it may be episodically eroded or suppressed by strong winds such as those generated by hurricanes (Grodsky et al. 2012). As the evaporation minus precipitation budget is positive in the region between 10°N and 20°N (Schmitt et al. 1989; Dessier and Donguy 1994; Hellweger and Gordon 2002), the BL was linked to advective processes and runoff from the Amazon and Orinoco Rivers (Pailler et al. 1999; Mignot et al. 2007; Balaguru et al. 2012). This stable BL separates the density based mixed layer from the thermocline and inhibits wind induced turbulent vertical mixing of the thermocline waters into the surface mixed layer (Pailler et al. 1999; Ffield 2005, 2006; de Boyer Montégut et al. 2007; Mignot et al. 2007).

The sea surface ^{14}C content in the tropical Atlantic and Caribbean Sea was measured in the years 1955–1957 before the huge ^{14}C input into the atmosphere due to the nuclear tests in the 1960s (Broecker et al. 1960). The values of $\Delta^{14}\text{C}$, corrected from the small bomb ^{14}C input (Broecker et al. 1960), are more depleted in surface waters of SEC due to upwelling than in the NEC ones at -63% and -52% , respectively. In the Caribbean Sea, the sea surface $\Delta^{14}\text{C}$ is around -56% .

RESULTS

Results are reported in Tables 1 and 2. Negligible crystallization of calcite ($<1\%$) is documented from X-ray diffraction measurements (Table 1). Chancel 1 grew continuously over a time span of ~ 230 yr (Weil-Accardo et al. 2016). The thickness of the annual bands does not vary greatly at an average of $\sim 6 \pm 1$ mm along the growth axis except prior to ~ 1830 AD when it varies between ~ 3 and 4 mm. The uncertainty at 1σ on the counting is estimated at ± 1 yr, except prior

to 1830 AD at ± 2 yr. Values of $\delta^{234}\text{U}$ are in the accepted range for modern seawater at $\sim 146\%$ (Delanghe et al. 2002; Robinson et al. 2004; Andersen et al. 2010) (Table 3). The mean Th/U age of 1853 ± 12 (2σ) AD is in close agreement with the counting of the growth band years at 1849–1851 AD (Weill-Accardo et al. 2016).

Between 1835 and 1845, and 1895 and 1905, the arithmetic means of R at 1σ are similarly centered at 385 ± 30 yr BP and 382 ± 20 yr BP, respectively (Figure 2, Table 1). Mean value of ΔR in the western tropical Atlantic is close to zero during the two decades. The variability of R is larger during the oldest decade than during the youngest one, when the Montagne Pelée eruption occurred. Values of R vary from 331 ± 32 yr up to 443 ± 33 yr during the older decade and from 351 ± 32 yr up to 415 ± 31 yr during the younger decade.

Values of $\delta^{18}\text{O}$ vary similarly by 0.5 – 0.6% around the mean of -3.9% during the two decades. However they exhibit a well-marked increase of $\sim 0.4\%$ during the older decade (Figure 3A) while no trend exists during the younger one (Figure 3B). During the older decade, values of $\delta^{18}\text{O}$ and $\Delta^{14}\text{C}$ are significantly correlated at the 95% confidence level ($r = 0.65$). At the time of the eruption of Montagne Pelée in 1902–1903, a well-marked $\delta^{18}\text{O}$ high is recorded and it coincides with slightly depleted $\Delta^{14}\text{C}$ values although in the range of uncertainties (Table 1).

DISCUSSION

There is no large regional departure of the sea surface ^{14}C near Martinique from the modeled global mixed layer value (Hughen et al. 2004) ($\Delta R \approx 0$) and values of R are identical at an average of 384 ± 25 yr between 1935 and 1845 and between 1895 and 1905. The sea surface variations of ^{14}C off Martinique reproduce mainly the atmospheric ^{14}C changes at steady state in the western tropical North Atlantic/Eastern Caribbean and the ocean–atmosphere $^{14}\text{CO}_2$ exchange and ocean dynamics do not vary greatly when comparing the two decades. Nevertheless, the oldest decade records a large range of variations in $\Delta^{14}\text{C}$ and $\delta^{18}\text{O}$ characterized by

Table 1 Lab codes and values of ^{14}C , stable oxygen and carbon isotopes, and calcite content in % in annual growth bands in coral Chancel 1. ^{14}C ages are expressed in conventional yr BP. See text for R, ΔR , and $\Delta^{14}\text{C}$ calculations.

Lab code	Lab code	Coral growth	^{14}C age $\pm 1\sigma$	$\Delta^{14}\text{C} \pm 1\sigma$	R $\pm 1\sigma$	$\Delta\text{R} \pm 1\sigma$	$\delta^{18}\text{O}$	$\delta^{13}\text{C}$	Calcite
	GifA	year (AD)	(yr BP)	(‰)	(yr)	(yr)	(PDB)	(PDB)	(%)
37882	14387	1835	555 \pm 30	-53.7 \pm 3.5	443 \pm 33	64 \pm 42	-4.02	-0.20	—
39852	14452	1836	510 \pm 30	-48.5 \pm 3.6	401 \pm 31	19 \pm 40	-3.88	0.25	—
37883	14388	1837	510 \pm 30	-48.6 \pm 3.6	373 \pm 31	19 \pm 40	-3.81	-0.24	—
39854	14454	1838	505 \pm 30	-48.1 \pm 3.6	376 \pm 31	15 \pm 39	-3.70	0.15	—
37885	14390	1839	500 \pm 20	-47.6 \pm 3.6	383 \pm 33	10 \pm 43	-3.69	0.34	—
39855	14455	1840	485 \pm 30	-46.0 \pm 3.6	370 \pm 33	-5 \pm 43	-3.73	0.51	—
37886	14391	1841	510 \pm 30	-49.1 \pm 3.6	367 \pm 33	20 \pm 43	-3.86	0.56	—
39856	14456	1842	535 \pm 30	-52.1 \pm 3.5	420 \pm 32	46 \pm 41	-3.68	0.65	—
37887	14392	1843	490 \pm 30	-46.9 \pm 3.6	370 \pm 31	1 \pm 40	-3.70	0.58	—
39858	14458	1844	440 \pm 30	-41.1 \pm 3.6	331 \pm 32	-48 \pm 40	-3.39	0.86	—
37889	14459	1845	520 \pm 30	-50.7 \pm 3.5	398 \pm 36	32 \pm 48	-3.56	0.61	—
<i>Mean (STDV)</i>			505 \pm 29	-48.4 \pm 3.3	385 \pm 30	16 \pm 29			
37903	14408	1895	460 \pm 30	-49.4 \pm 3.6	389 \pm 32	0 \pm 40	-4.07	-0.80	—
37904	14409	1896	460 \pm 30	-49.5 \pm 3.6	397 \pm 31	1 \pm 40	-3.88	-0.10	—
43943	15542	1897	430 \pm 30	-46.0 \pm 3.6	351 \pm 32	-28 \pm 41	-3.86	-0.49	—
32686	13058	1898	445 \pm 30	-47.9 \pm 3.6	367 \pm 32	-11 \pm 41	-3.87	-0.71	0.57
32687	13059	1899	450 \pm 30	-48.6 \pm 3.6	364 \pm 32	-5 \pm 41	-3.80	-0.32	0.18
32688	13060	1900	450 \pm 30	-48.7 \pm 3.6	378 \pm 32	-4 \pm 42	-3.82	-0.03	0.06
32689	13061	1901	445 \pm 30	-48.3 \pm 3.6	407 \pm 31	-8 \pm 40	-4.06	-0.57	0.07
32691	13063	1902	485 \pm 30	-53.1 \pm 3.5	415 \pm 31	33 \pm 40	-3.60	0.14	0.06
32692	13064	1903	470 \pm 30	-51.5 \pm 3.5	390 \pm 32	19 \pm 41	-3.75	0.09	0.39
32693	13065	1904	440 \pm 30	-48.0 \pm 3.6	361 \pm 32	-10 \pm 41	-4.13	-0.36	0.18
32695	13067	1905	475 \pm 30	-52.3 \pm 3.5	387 \pm 32	26 \pm 41	-4.06	-1.20	0.02
<i>Mean (STDV)</i>			455 \pm 15	-49.4 \pm 2.1	382 \pm 20	1 \pm 18			
<i>Total (STDV)</i>			480 \pm 35	-49 \pm 3	384 \pm 25	6 \pm 20			

a moderate increase of $\Delta^{14}\text{C}$ and a well-marked increase of $\delta^{18}\text{O}$ of $\sim 0.4\text{‰}$, which is not observed during the youngest decade (Figure 3).

The variations of $\delta^{18}\text{O}$ reflect the changes of the sea surface temperatures (SST) and sea surface salinities (SSS), due to changes in the evaporation-precipitation budget and runoff. In addition, in the eastern Caribbean Sea, SSS also depend on the oceanic current patterns (Hellwegger and Gordon 2002) and they may be punctually related to changes in volcanic activity. Although in this region rainfalls play a minor role in changing the sea surface salinities (Schmitt et al. 1989; Dessier and Donguy 1994; Hellwegger and Gordon 2002), we analyzed their local influence by comparing the records of $\delta^{18}\text{O}$ and precipitation on Martinique Island. The fluctuations of $\delta^{18}\text{O}$ in coral Chancel 1 are analyzed using available records of SST (ersst.v3 at ncdc.noaa.gov/data-access/marineocean-data; Xue et al. 2000; Smith et al. 2006), the precipitation records (www.climexp.knmi.nl; van Oldenborgh and Burgers 2005) as well as the values of $\delta^{18}\text{O}$ of seawater near volcanic gas vents and in groundwaters (McCarthy et al. 2005; Sanjuan et al. 2005; Jones et al. 2011; Hemmings et al. 2015; Sanjuan and Brach 2015). We first compared the sea surface ^{14}C values in coral Chancel 1 with previous data from the tropical and subtropical North

Table 2 Mean values of $\Delta^{14}\text{C}$, R, and number (nr) of values between 1835 and 1845 and between 1895 and 1905. * refers to values in IntCal98 (Stuiver et al. 1998) and numbers in parentheses to coral sites cited in the text. Same legends as in Figure 1.

	1835-1845			1895-1905		
	$\Delta^{14}\text{C} \pm 1\sigma$ (‰)	R $\pm 1\sigma$ (yr)	Nr	$\Delta^{14}\text{C} \pm 1\sigma$ (‰)	R $\pm 1\sigma$ (yr)	Nr
Atmosphere*	-2 ± 1	121 ± 11	11	-3 ± 2	73 ± 14	11
Bermuda-North (9)				-45.4 ± 2.4	348 ± 32	8
Bermuda-South (8)	-39 ± 2	298 ± 21	6	-41.0 ± 1.9	311 ± 32	6
Bahamas (7)				-54.2 ± 2.8	408 ± 20	2
Florida (6)	-55.5 ± 3	448 ± 30	2	-49.0 ± 5.0	381 ± 40	6
Gulf Mexico (5)				-43.9 ± 3.4	344 ± 32	1
Belize (4)				-48.5 ± 3.1	371 ± 21	4
Puerto Rico (3)	-51.9 ± 4.2	418 ± 45	3	-49.7 ± 1.0	381 ± 19	3
Martinique (1)	-48.4 ± 3.3	385 ± 30	11	-49.4 ± 2.1	382 ± 20	11
Islas Tortugas (2)				-42.2 ± 4.6	306 ± 38	1

Table 3 Results of uranium-thorium dating of two aliquots of the growth year bands 1849-1851. The Th/U ages are expressed as years before 1950 (yr BP) or in calendar years (AD). "Age cor" are corrected for detrital thorium using a mean marine $^{230}\text{Th}/^{232}\text{Th}$ activity ratio of 10 ± 4 (Frank et al. 2004), close to the estimated correction of the non-radiogenic ^{230}Th in one Haitian coral (Weil-Accardo et al. 2016). Errors are propagated and are given at the 2σ confidence level.

Lab	^{238}U	^{232}Th			$\delta^{234}\text{U}_0$	Age	Age cor.	Age cor.
sample	(ppb)	(ppb)	$^{230}\text{Th}/^{238}\text{U}$	$^{230}\text{Th}/^{232}\text{Th}$	(‰)	(yr BP)	(yr BP)	(AD)
6261	3073 ± 5	0.3260 ± 0.0002	0.00218 ± 0.00002	63.74 ± 1.10	145.9 ± 0.8	144 ± 2	111 ± 15	1839 ± 15
6392	2916 ± 17	0.4054 ± 0.0018	0.00198 ± 0.00002	45.36 ± 0.47	146.7 ± 1.2	124 ± 2	82.5 ± 18.5	1867.5 ± 18.5

Atlantic (Druffel and Linick 1978; Druffel 1980; Druffel and Suess 1983; Druffel 1982 1997; Guilderson et al. 2005; Kilbourne et al. 2007; Wagner et al. 2009; Goodkin et al. 2012; Fernandez et al. 2015). We then analyzed the variability of $\delta^{18}\text{O}$ and $\Delta^{14}\text{C}$, linked to local hydrology, ocean dynamics, and volcanism.

COMPARISON OF R AND $\Delta^{14}\text{C}$ IN CHANCEL 1 AND IN CORALS AND SCLEROPONGES OF THE TROPICAL AND SUBTROPICAL WESTERN NORTH ATLANTIC

The mean values of R and $\Delta^{14}\text{C}$ near Martinique compare well with previous ones (Table 2): in Puerto Rico (Kilbourne et al. 2007), Belize (Druffel 1980; Druffel and Suess 1983), the Gulf of Mexico (Wagner et al. 2009), the Florida Strait within the Gulf Stream (Druffel and Linick 1978; Druffel 1980, 1982, 1997; Druffel and Suess 1983), and the Bahamas (Fernandez et al. 2015). In one instance, slightly higher $\Delta^{14}\text{C}$ than observed in the whole Caribbean Sea is observed from one coral near Islas Tortugas in the Cariaco basin, but it is based only on a one-year average (Guilderson et al. 2005). No gradient in the mean $\Delta^{14}\text{C}$ is observed between the Atlantic inflow east off Martinique Island and the Caribbean Sea and Gulf Stream.

Values off Martinique are older than the subtropical North Atlantic ones considering coral records from either the northern or the southern shorelines off Bermuda (Druffel 1989, 1997; Goodkin et al. 2012). Compared to values of R and $\Delta^{14}\text{C}$ from the southern coral, which

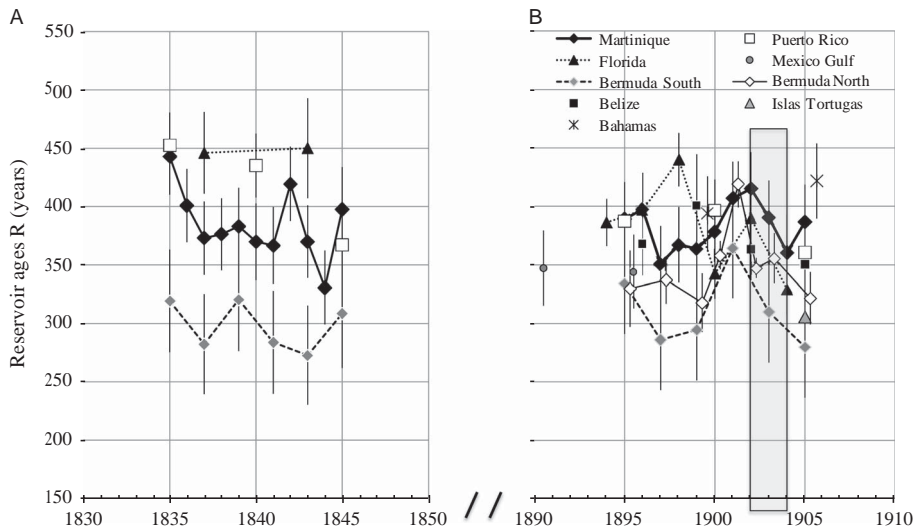


Figure 2 Values of sea surface reservoir ages R (yr) off Martinique and at the sites located in Figure 1A as a function of calendar years (AD) between years (A) 1835–1845 and (B) 1895–1905. The gray box in (B) marks the 2-yr-long eruption of Montagne Pelée. The legend in (B) also pertains to (A).

characterizes open ocean conditions in the subtropical gyre (Goodkin et al. 2012), they differ by 70–90 yr and 8–9‰ in Chancel 1, respectively, over the two decades (Figure 2). The difference in $\Delta^{14}\text{C}$ compares well with the $\sim 11\%$ offset between the SEC and NEC DIC $\Delta^{14}\text{C}$, the southern waters having the most ^{14}C -depleted values (Broecker et al. 1960). The aging of the tropical sea surface off Martinique Island reflects the imprint of the South Atlantic Waters transported by the SEC/NBC/GC along the Lesser Antilles arc and into the Caribbean Sea.

Fluctuations of $\delta^{18}\text{O}$ and $\Delta^{14}\text{C}$ in Coral Chancel 1

Changes in $\delta^{18}\text{O}$ between 1835 and 1845

The $\delta^{18}\text{O}$ and SST in carbonates are commonly negatively correlated, the more depleted the $\delta^{18}\text{O}$, the warmer the SST, and vice versa (Weber and Woodhead 1972). The correlation between available SST between 1895 and 1905 (Xue et al. 2000; Smith et al. 2006) and $\delta^{18}\text{O}$ is positive (Figures 4A, 4B). This implies that the variations of $\delta^{18}\text{O}$ are dominated by sea surface salinity changes (SSS), the low salinities corresponding to depleted $\delta^{18}\text{O}$ values, and vice versa. The mean annual precipitation on Martinique Island are very similar between 1835 and 1945 (2270 mm/yr) and between 1895 and 1905 (2200 mm/yr) (van Oldenborgh and Burgers 2005) (Figures 4C, 4D). The changes of the salinity-dependent $\delta^{18}\text{O}$ are not correlated to the variations in the mean annual precipitation on Martinique Island in agreement with previous findings (Dessier and Donguy 1994; Hellweger and Gordon 2002; Folz et al. 2004). Furthermore, the annual and interannual variations of evaporation are weak in the Caribbean region (Yoo and Carton 1990; Dessier and Donguy 1994; Hellweger and Gordon 2002; Folz et al. 2004) so that the increase of $\delta^{18}\text{O}$ between 1835 and 1845 cannot be due to evaporation processes. As the density BL prevents vertical mixing in this region (Pailler et al. 1999; Sprintall and Tomczak 1992; de Boyer Montégut et al. 2004), the changes of the salinity-dependent $\delta^{18}\text{O}$ near Martinique are therefore related to advective processes, as previously stated (Dessier and Donguy 1994; Hellweger and Gordon 2002). In the southeast Caribbean Sea, the SSS changes are highly

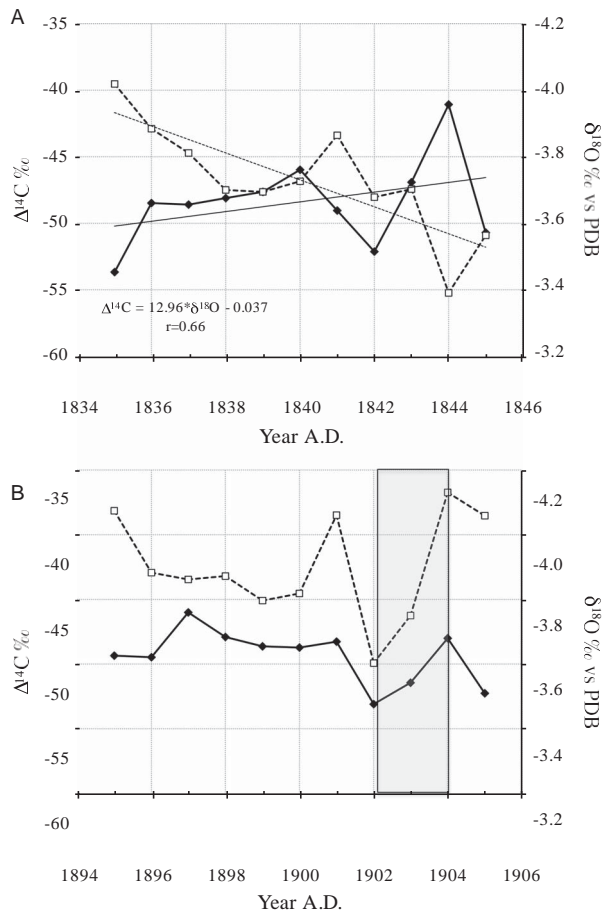


Figure 3 Variations of $\Delta^{14}\text{C}$ (‰) (left axis, black diamonds) and $\delta^{18}\text{O}$ (‰ PDB) (right axis, open squares) between (A) 1835 and 1845 and (B) 1895 and 1905. The gray box in (B) marks the 2-yr-long eruption of Montagne Pelée.

correlated to the Amazon River freshwater discharges (Hellwegger and Gordon 2002), the influence of which was felt far from the river mouth by depleted $\delta^{18}\text{O}$ (Karr and Showers 2002) and low SSS (Field 2005). Changes of $\delta^{18}\text{O}$ between 1835 and 1845 are thus attributed to variations in either the magnitude of the Amazon and Orinoco runoff or in the current strength of the SEC/NBC/GC, which transport the South Atlantic Waters (SAW) into the western tropical North Atlantic and Caribbean Sea, or both.

Changes in Oceanic Water Masses Advection off Martinique Island between 1835 and 1845

The South Atlantic Waters (SAW), transported northward into the Caribbean Sea, are characterized by low SSS, related to the Amazon River discharges (Hellwegger and Gordon 2002) and by low $\Delta^{14}\text{C}$ (Broecker et al. 1960). Thus the increase of both $\delta^{18}\text{O}$ and $\Delta^{14}\text{C}$ off Martinique between 1835 and 1845 requires a decrease in the strength of the SEC/NBC/GC and thus in the freshwater advection. Changes in SAW advection into the eastern Caribbean across the sills were previously pointed out from repeated hydrographic surveys (Wilson and Johns 1997; Johns et al. 2002; Rhein et al. 2005). Similarly, variations in the northward extent of equatorial water masses was also evidenced in the northern Caribbean Sea at Puerto Rico from a post-1963 coral record of $\Delta^{14}\text{C}$ (Kilbourne et al. 2007).

The fraction of SAW in TSW is not well assessed and it is estimated in SMW at 20–30% along the Lesser Antilles arc up to $\sim 15^\circ\text{N}$ (Rhein et al. 2005; Kirchner et al. 2009). Using a 25% SAW fraction in TSW, similarly as in SMW, and NEC $\Delta^{14}\text{C}$ at $\sim -39\text{‰}$ in ~ 1835 (Goodkin et al. 2012) (Table 2), one may calculate a $\Delta^{14}\text{C}$ value of the SEC at -85‰ when $\Delta^{14}\text{C}$ is $\sim -50\text{‰}$ in 1835 off Martinique. This calculated value is identical to the one determined at $\sim -85\text{‰}$ in AD 1815–1835 at Santa Helena located within the southern branch of the SEC (Lewis et al. 2008). To augment the $\Delta^{14}\text{C}$ near Martinique by $\sim 5\text{‰}$ such as from 1835 to 1845, the SAW fraction might be reduced from 25% to 15%.

Changes of $\delta^{18}\text{O}$ during the 1902–1903 Eruption of Montagne Pelée

Warm and salty surface waters prevailed at the time of the eruption (Figure 4A). The values of $\delta^{18}\text{O}$ from hydrothermal and geothermal fluids are mainly depleted with respect to those of seawater in the Lesser Antilles volcanic arc. Hydrothermal fluids from aquifers and groundwaters have very depleted $\delta^{18}\text{O}$ varying between about 0‰ and -4‰ versus SMOW (Jones et al. 2011; Hemmings et al. 2015; Sanjuan and Brach 2015), compared to the seawater value ($\sim -1\text{‰}$ versus SMOW; McCarthy et al. 2005; Sanjuan and Brach 2015). Similarly, $\delta^{18}\text{O}$ from CO_2 degassing in submarine gas vents vary between values of seawater and those of the $\delta^{18}\text{O}$ -depleted meteoritic waters ($\sim -2\text{‰}$ /SMOW) and the largest vents of highest flow rate have $\delta^{18}\text{O}$ values closer to the meteoritic ones (McCarthy et al. 2005). However few positive values of

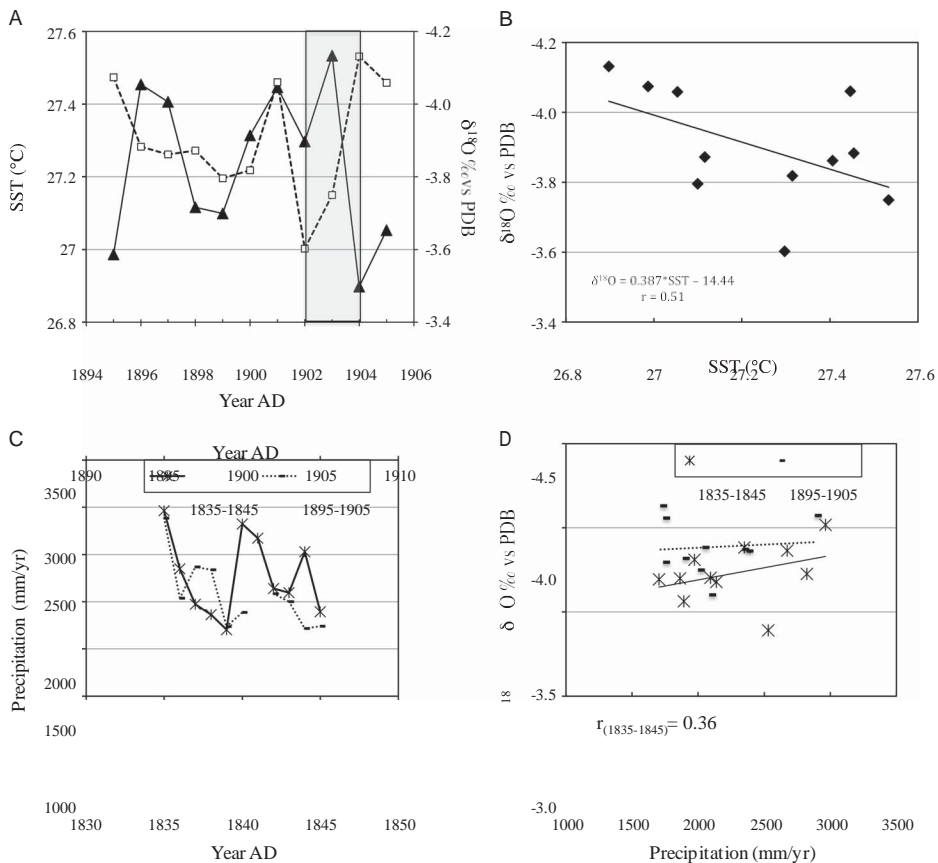


Figure 4 (A) Variations of the mean annual SST ($^\circ\text{C}$) (left axis, black triangles) at $\sim 16^\circ\text{N}$; 61°W (Xue et al. 2000; Smith et al. 2006) and $\delta^{18}\text{O}$ (‰ versus PDB) (right axis, open squares) and (B) variations of $\delta^{18}\text{O}$ as a function of the mean annual SST ($^\circ\text{C}$) between 1895 and 1905; (C) variations of the mean annual precipitation (in mm/year) on Martinique Island (van Oldenborgh and Burgers 2005) and (D) variations of $\delta^{18}\text{O}$ as a function of the mean annual precipitation between 1835 and 1845 and between 1895 and 1905.

$\delta^{18}\text{O}$, higher than the seawater one, were measured at +2.5‰ in geothermal fluids from hot water ponds on the southern seashore on Montserrat Island (Hemmings et al. 2015) and at ~+2‰ on the western seashore of Martinique (Sanjuan et al. 2005). Thus, the observed increase of $\delta^{18}\text{O}$ in Chancel 1 could be linked to enhanced seaward discharge of geothermal fluids when the eruption occurred, although volcanic fluids are statistically characterized by $\delta^{18}\text{O}$ -depleted values and hot water ponds are mainly located on the western coast of Martinique (Sanjuan et al. 2005; Gadhia et al. 2015). This feature, *if it exists*, would account for a slight $\Delta^{14}\text{C}$ decrease of 5‰, that is in the range of uncertainties (Table 1).

CONCLUSION

Values of R and $\Delta^{14}\text{C}$ for the eastern Caribbean Sea and the western tropical North Atlantic are quantified from one annually banded coral Chancel 1 collected on the eastern coast of Martinique Island.

The mean values of R and $\Delta^{14}\text{C}$ are similar between 1835 and 1845 and between 1895 and 1905 with an average of 385 ± 25 yr and -49 ± 3 ‰ respectively for the two decades. No gradient in the mean values of R and $\Delta^{14}\text{C}$ is observed along the Caribbean Current from the eastern Caribbean Sea to the Florida Straits. A positive gradient of about ~70–90 yr and 8–9‰, respectively, is observed between the tropical and subtropical regions of the North Atlantic in agreement with the advection of the old South Atlantic Waters by the SEC/NBC/GC into the Caribbean Sea and the northwestern tropical Atlantic.

Sea surface aging due to enhanced volcanic activity such as during the 2-yr-long eruption of Montagne Pelée cannot be completely excluded. It could amount to some ~40 yr ($\Delta^{14}\text{C}$ ~5‰), which is in the range of dating uncertainties.

Between 1835 and 1845, a reduced northward advection of the South Atlantic Waters, characterized by low SSS and low $\Delta^{14}\text{C}$, towards the Martinique Island is inferred from the well-correlated increase of both $\delta^{18}\text{O}$ and $\Delta^{14}\text{C}$. Using modern estimates of the SAW fraction around the Lesser Antilles (Kirchner et al. 2009) and values of $\Delta^{14}\text{C}$ in the South Atlantic (Lewis et al. 2008) and subtropical North Atlantic (Goodkin et al., 2012), we calculated that the SAW fraction off Martinique Island was reduced from 25% to 15% from 1835 to 1845. Thus, although the sea surface $\Delta^{14}\text{C}$ compare well between the two decadal records in the western tropical North Atlantic, their variability indicates changes in ocean dynamics.

ACKNOWLEDGMENTS

This work received the financial support of the CEA-CNRS-UVSQ, the CNRS/INSU programs: OA/Leffe-ARRA, ST/PERSEIS; the ACI-FNS Risques Naturels et Changement climatique and the ANR SUBSISMANTI. Thanks are due to E. Kaltnecker, C. Noury, L. Foliot, and F. Manssouri for technical support and the LMC14 team for graphite targets preparation and AMS- ^{14}C measurements. M. Fontugne and P. Lacey are thanked for their helpful discussions and suggestions.

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