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T.P. Guilderson, J.E. Cole, and J.R. Southon

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Thomas P. Guilderson[1]

Center for Accelerator Mass Spectrometry, Lawrence Livermore National Laboratory, Livermore, California 94551, USA

Julia E. Cole

Department of Geosciences, University of Arizona, Tucscon, Arizona 85721, USA

and

John R. Southon [2]

Center for Accelerator Mass Spectrometry, Lawrence Livermore National Laboratory, Livermore, California 94551, USA

1. Also at Department of Ocean Sciences, University of California – Santa Cruz, Santa Cruz CA 94056

2. now at Department of Earth System Science, University of California – Irvine, Irvine, CA 92697 USA

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Abstract

The $\Delta^{14}C$ content of surface waters in and around the Cariaco Basin were reconstructed from ^{14}C measurements on sub-annually sampled coral skeletal material. During the late 1930s – early 1940s surface waters within and outside of the Cariaco Basin are similar. Within the Cariaco Basin at Islas Tortugas coral $\Delta^{14}C$ averages -51.9 ±3.3‰. Corals collected outside of the basin at Boca de Medio and Los Testigos have $\Delta^{14}C$ values of -53.4 ± 3.3‰ and -54.3 ±2.6 respectively. Additional ^{14}C analyses on the Isla Tortugas coral document an ~11‰ decrease between ~1905 (-40.9±4.5‰) and ~1940. The implied Suess Effect trend (-3‰/decade) is nearly as large as that observed in the atmosphere over the same time period. If we assume that there is little to no fossil fuel $^{14}CO_2$ signature in Cariaco surface waters in ~1905, the waters have an equivalent reservoir age of ~312 years.

Introduction

The Cariaco Basin is a small, shallow silled (~140m) basin located on the northwest Venezuelan margin. Detailed records of past climate variability spanning nearly 600,000 years are preserved in the basin's rapidly accumulating sediments (Peterson *et al.*, 2000). The sedimentary record is comparably undisturbed by bioturbation due to anoxic conditions at depth. The combination of a lack of bioturbation and seasonally distinct sedimentary input components (terrigenous vs. biogenic) conspire to provide an environment that promotes the formation and preservation of distinct annual laminae or varves. Variations in biogeochemical, geochemical, and sedimentological proxies in these sediments have been interpreted to reflect variations in regional sediment discharge, the strength of the trade-winds and the position of the inter-tropical convergence zone (e.g., Black *et al.*, 1999; Hughen *et al.*, 1998, 2000; Peterson *et al.*, 1991, 2000).

Although numerous paleoceanographic studies have taken advantage of the unique records preserved in the marine sediments including detailed ^{14}C-calendar calibrations (*eg*., Hughen *et al.*, 2000) a detailed assessment of the natural-^{14}C or pre-bomb variability has not previously been made. We use annually banded corals from several sites within and around the basin to determine the seasonal variability in pre-bomb $\Delta^{14}C$ as it relates to air-sea exchange, surface water dynamics and the potential influence of the Orinoco River and local fluvial input.

General Oceanography

Sea surface temperatures in the Cariaco Basin vary in response to both radiative forcing and ocean dynamics. The sea surface temperature minimum in the Cariaco Basin follows the local upwelling regime, with lowest temperatures occurring in April/May. Upwelling in the basin occurs in response to both direct or local wind forcing in relation to the seasonal migration of the inter-tropical convergence zone (ITCZ) and the replacement of warm, less saline surface waters with subsurface cooler, salty waters through lateral advection and mesocale eddies (Astor *et al.*, 2003). The seasonal sea surface temperature maximum occurs during late boreal summer and early fall during the time of minimum wind speed. Salinity varies seasonally in direct response to the passage of the ITCZ and regional fluvial input from the Rio Unare and Rio Tuy. The salinity minimum occurs during the August-October rainy season.

The shallow sill inhibits advection of interior waters; thus the characteristics of the surface waters are primarily controlled by surface waters of the Caribbean and subtropical underwater. Waters shallower than the sill depth interact with surface waters from the outside of the basin. Vertical mixing between upper well ventilated waters and those at depth is inhibited by the presence of a strong pycnocline. The boundary between oxic and anoxic waters varies in conjunction with the strength and duration of the upwelling season. This boundary averaged 280±40 meters between 1996 and 1998. (Astor *et al.*, 2003; Muller-Karger *et al.*, 2001).

Methods

Several cores from long-lived coral colonies were collected in 1996 and 1998, using diver-operated hydraulic drilling gear. For this study, three cores were utilized. A *Siderastrea siderea* was cored in March 1996 from the Arquipelago Los Testigos (11°23'N, 63°08'W) to the northeast of the Cariaco Basin (Figure 1). Also in March of 1996, a *Montastrea annularis* was drilled on the southwestern side of Isla Tortuga (10° 54'N, 65°14'W) opening on the Cariaco Basin. The final specimen that we have worked on is a *Montastrea annularis* drilled in July 1998 from Boca de Medio (11°55' N, 66°36'W) in the Los Roques archipelago. The Los Roques archipelago is outside of the Cariaco Basin proper and should represent a well-mixed non-upwelling site. The Los Testigos site is also outside of the Cariaco proper but is influenced by the same water masses in conjunction with coastal upwelling. In addition, Los Testigos undergoes a pronounced seasonal cycle in salinity as a consequence of Orinoco River discharge.

The cores (9 cm diameter) were cut into ~5mm slabs, ultrasonically cleaned in distilled water, and air-dried. None of the sampled regions were infiltrated with boring filamentous algae or other organisms. After identifying the major vertical growth axis, pre-bomb levels were identified using density banding, and the coral was sequentially sampled at 1 mm increments in the time period of interest with a low-speed drill. The coral age-models were derived using a combination of sclerochronology (*e.g.*, Dodge and Vaisnys, 1980) and the seasonal cycle recorded in the carbon and oxygen isotopic composition of the coral skeleton (Cole *et al.,* 1993; Guilderson and Schrag, 1999 among others). For the Boca de Medio and Testigos samples, ages were assigned using annual density bands and counting back from the top of the coral core. We assumed, based on published literature (*e.g.*, Fairbanks and Dodge 1979), that dense bands formed in the warmest season and assigned the month of September to the samples that coincided with dense bands. Years were determined by counting bands back from the known date of collection. In these samples, density banding was reasonably clear and we assume no more than one year possible age error. Our isotopic results from the intervals sampled confirm the annual nature of these bands. In the Tortuga sample, density banding was less clear, particularly in the oldest regions. We analyzed stable oxygen and carbon isotopes at 1mm resolution throughout the core and developed an age model using the seasonal cycle of $\delta^{18}O$. We assumed that the most positive values of $\delta^{18}O$ correspond with the coolest month, and assigned seasonal positive extremes to March of each year (the coolest month, on average, in the COADS SST data from 11°N, 64°W). Linear interpolation between annual tie points provide the subannual chronology. We assume a slightly larger age uncertainty in the Tortuga core, on the order of ±1-2 years at the base.

All drilled samples were analyzed for $\delta^{18}O$ and $\delta^{13}C$ at the University of Arizona, using a Micromass Optima stable isotope ratio mass spectrometer with an Isocarb (common acid bath) automated preparation device. Analytical error, based on replicate analyses of an in-house standard, is approximately ±0.07‰ for $\delta^{18}O$ and ±0.04‰ for $\delta^{13}C$. Values are presented relative to PDB.

Radiocarbon sampling focused on samples spanning the late 1930s and 1940s. In specimens that had a faster growth rate (*M. annularis* from Tortuga and Boca de Medio) we analyzed every other 1 mm increment whereas every sample from the slower growing colony (*S. siderea* from Testigos) was analyzed. Individual samples (8-10mg) were placed in individual vacutainers, evacuated, heated, and then acidified with orthophosphoric acid at 90°C. The evolved CO_2 was purified, trapped, and converted to graphite in the presence of iron catalyst in individual reactors similar to the method described by Vogel *et al.*, (1987). Graphite targets were measured at the Center for Accelerator Mass Spectrometry, Lawrence Livermore National Laboratory (Davis *et al.*, 1990). Radiocarbon results are reported as age-corrected $\Delta^{14}C$ (‰) as defined by Stuiver and Polach (1977) and include a background subtraction and the $\delta^{13}C$ correction obtained from the stable isotope results. Analytical precision and accuracy of the radiocarbon measurements is ±3.5‰ (1σ) as monitored with an in-house homogenized coral standard and officially distributed secondary and tertiary radiocarbon standards.

Results

Over the time-frame of overlap (late 1930s through early 1940s), $\Delta^{14}C$ values at all three locations are very similar (Table 1). The mean Isla Tortuga $\Delta^{14}C$ is -51.9‰ (n=40), the Boca de Medio $\Delta^{14}C$ averages -53.4‰ (n=42), and the Los Testigos sample mean is -54.4‰ (n=53). All three locations experience similar range in $\Delta^{14}C$. $\Delta^{14}C$ is not very well correlated with $\delta^{18}O$ (Figure 2) in the sense that there is not a consistent or strong seasonal cycle (in $\Delta^{14}C$). Between 1905 and 1908 $\Delta^{14}C$ values as recorded in the

Islas Tortugas coral average -40.9‰ (n=41; Figure 3). When compared to the Northern hemisphere atmosphere in 1905 (-4.2‰) these results yield an equivalent reservoir age of 312 years. The equivalent rate of change between ~1906 to ~1940 is -3‰ per decade.

Table 1
Cariaco Coral $\Delta^{14}C$

		Abs Fm	$\Delta^{14}C$		n
Isla Tortugas					
1937.68	1943.29	0.9481	-51.9	±3.3	40
1905.07	1907.71	0.9591	-40.9	±4.5	41
Boca de Medio					
1942.48	1948.33	0.94660	-53.4	±3.3	42
Los Testigos					
1934.21	1946.21	0.9457	-54.3	±2.6	53

Table 1. Weighted average of the absolute fraction modern and age-corrected $\Delta^{14}C$ (Stuiver and Polach, 1977) from corals in the Cariaco region for four time windows .

Discussion

In the late 1930s-1940s, the three locations have similar absolute fraction modern or age-corrected $\Delta^{14}C$. No strong correlation between upwelling season and $\Delta^{14}C$ is observed. Over the respective sampling intervals a z-score normalization (in which the mean is subtracted from the data and the result is divided by the std dev.) of the individual $\delta^{18}O$ and $\Delta^{14}C$ shows no correlation (Figure 4). This is not surprising given the relatively shallow water that is the source for upwelling in the Cariaco Basin and along the Venezuelan margin. In general upwelling in this region taps subtropical underwater, a recently ventilated water mass that during formation undergoes significant air-sea exchange. Thus, in contrast to the conventional view of the influence of upwelling on $\Delta^{14}C$, very little depletion occurs. This indicates that there is very little difference in the ^{14}C character of the upwelled water and surface waters of the Caribbean, in stark contrast to the observations provided by nutrients (Astor *et al.*, 2003; Thunell pers. comm). This observation reinforces the concept that ^{14}C in DIC is primarily a water-mass tracer whereas nutrient content is a combination of pre-formed nutrient concentration (if applicable) and remineralization of recently exported particulates.

It is instructive to assess the effect of ^{14}C-barren fossil fuel burning on atmospheric CO_2 and the subsequent effect observed in the ocean. The $\Delta^{14}C$ of ocean DIC oceanic response integrates air-sea CO_2 exchange and ocean dynamics. Over the length of the post-industrial period, atmospheric $^{14}CO_2$ has decreased from ~ -4‰ in 1880 (pentad centered on 1880) with similar values in 1900 (~ -3‰) to ~-25‰ in 1950 prior to the advent of atmospheric nuclear weapons testing, yielding a rate of about -3‰ per decade. The Cariaco Basin's decrease in $\Delta^{14}C$ ("Suess Effect") is also about 3‰/decade determined between ~1905 and ~1940 and is similar to that predicted in a simple 1-D diffusion model (Table 2). Although it is possible that the observed decrease in $\Delta^{14}C$ observed at Cariaco is the result of ocean dynamics (*e.g.*, changes in the water mass feeding the upwelling), the interpretation of least astonishment is that the decrease is a consequence of air-sea exchange and the carbon isotopic signature of fossil fuel CO_2 entering the surface ocean.

Our value is in general agreement with that determined by Druffel (1980) on a coral from Belize/Honduras but not in exact agreement with the coral-based records from the Florida Keys (Druffel, 1982; Druffel 1997) and Bermuda (Druffel, 1997). Over the respective overlapping post-industrial period (~1880 – 1940) there is no significant linear trend in $\Delta^{14}C$ in the Bermuda and Florida Keys records, nor over the interval of common overlap (Figure 5). The Florida Keys records exhibit a strong $\Delta^{14}C$ decrease between ~1940 and the mid 1950s whereas the Bermuda record exhibits no decrease in $\Delta^{14}C$ over the length of the "Suess" interval. The subtle differences in the timing and amplitude of the "Suess Effect" between the various records reinforces the potentially competing influences of air-sea exchange and ocean dynamics on the radiocarbon isotopic signature of surface waters.

Conclusion

We have reconstructed the $\Delta^{14}C$ of late 1930s early 1940s surface waters in, and around the Cariaco Basin from hermatypic corals. We do not see a significant difference in values from within (Isla Tortugas -51.9 ±3.3‰) and outside (Boca de Medio -53.4 ± 3.3‰; Los Testigos -54.3 ±2.6) of the basin. These values are similar to those of subtropical surface waters and indicate a shallow, well-ventilated source that feeds upwelling in the basin.

Samples from Isla Tortugas demark an ~11‰ decrease between ~1905 and ~1940. The implied Suess Effect trend (-3‰/decade between 1905 and 1940) is nearly as large as that observed in the atmosphere (-4‰/decade) and larger than that estimated from other circum-Atlantic corals spanning the same time-range.

If we assume that there is little to no fossil fuel $^{14}CO_2$ signature in Cariaco surface waters in ~1905, the waters have an equivalent reservoir age of ~312 years. This is slightly younger than the ~420 year reservoir age derived from measurements on mid-19th century planktonic foraminifera recovered from sediment cores (Black *et al.*, 1999). The difference reflects natural variability related to stratification and the extent of air-sea isotopic equilibration in the basin and the formation regions of the subtropical underwaters.

Table 2. "**Suess Effect $\Delta^{14}C$**"

	$\Delta^{14}C$ (‰)	"Suess" ^{14}C ‰/decade
North Rock Bermuda (*Druffel,* 1997)		
1905	-46	--
1940	-44	
Honduras (*Druffel,* 1980)		
1905	-47	-2.0
1940	-54	
Pickles Reef, Florida (*Druffel,* 1997)		
1905	-49	--
1940	-48	
Plantation Key, Florida (*Druffel, 1982*)		
1905	-49	--
1940	-52	
Islas Tortugas, *this study*		
1905	-42	-3.0
1940	-52	
1-D Model (*Stuiver et al.,* 1998)		-1.5
Atmosphere		-3.8

Table 2. "Suess" effect depletion of age-corrected $\Delta^{14}C$ recorded in circum-Atlantic surface water time-series. For comparison we also present the synthetic marine response in a 1-D advection-diffusion model, and as recorded in the atmosphere (Stuiver *et al.*, 1998). Coral and model data were averaged on the pentad centered on 1905 and 1940. -- = no Suess effect within uncertainty of measurements.

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Figure Captions.

Figure 1. Map of the Cariaco basin and locations (crosses) of the coral samples discussed. Contors are depths (meters) along the main Venezuelan continental margin.

Figure 2. Coral $\Delta^{14}C$ (solid symbol) and $\delta^{18}O$ (open symbol) from A) Islas Tortugas, B) Boca de Medio and C) Los Testigos. Data are plotted such that warmer sea surface temperatures (more negative $\delta^{18}O$) are upward. For clarity we have plotted a representative 1-sigma $\Delta^{14}C$ error bar to the right of each panel. D) The three coral-based ^{14}C time-series on a common time frame: Los Testigos (star), Boca de Medio (open symbol) and Islas Tortugas (closed symbol).

Figure 3. Turn of the century coral $\Delta^{14}C$ at Isla Tortugas (solid symbols) and $\delta^{18}O$ (open symbols). Note slightly different scales relative to Figure 2.

Figure 4. Z-score normalized $\delta^{18}O$ versus $\Delta^{14}C$ for the respective time-windows. Symbols as in figure 2D.

Figure 5. $\Delta^{14}C$ time histories (1880-1950 AD) of the atmosphere and the surface ocean as recorded in circum-Caribbean/Atlantic corals. Atmosphere data (dash dot) from Stuiver et al., (1998). Coral data are presented from Bermuda (thin solid line; Druffel, 1997), Florida Keys (thick solid line; Druffel, 1997), Belize (dashed; Druffel, 1980) and Cariaco basin (hatchured boxes, this study). Coral data from Druffel are presented as pentad averages derived from annual linear interpolations to the original annual and biannual data. Representative 1-sigma error bar for the Druffel data is in the lower left corner of the figure. Note left and right vertical axes correspond to surface water (coral) and atmosphere data respectively.

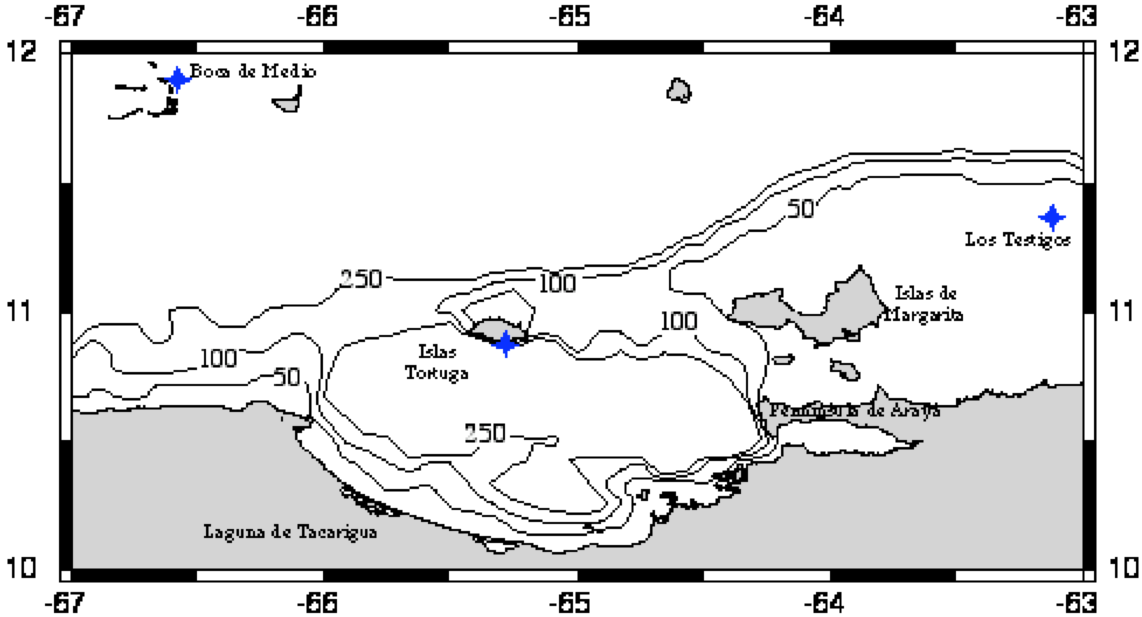

-67
-66
-65
-64
-63
12
11
10
Boca de Medio
50
100
250
Los Testigos
Islas de Margarita
Islas Tortuga
Peninsula de Araya
Laguna de Tacarigua

Figure 2 A-C

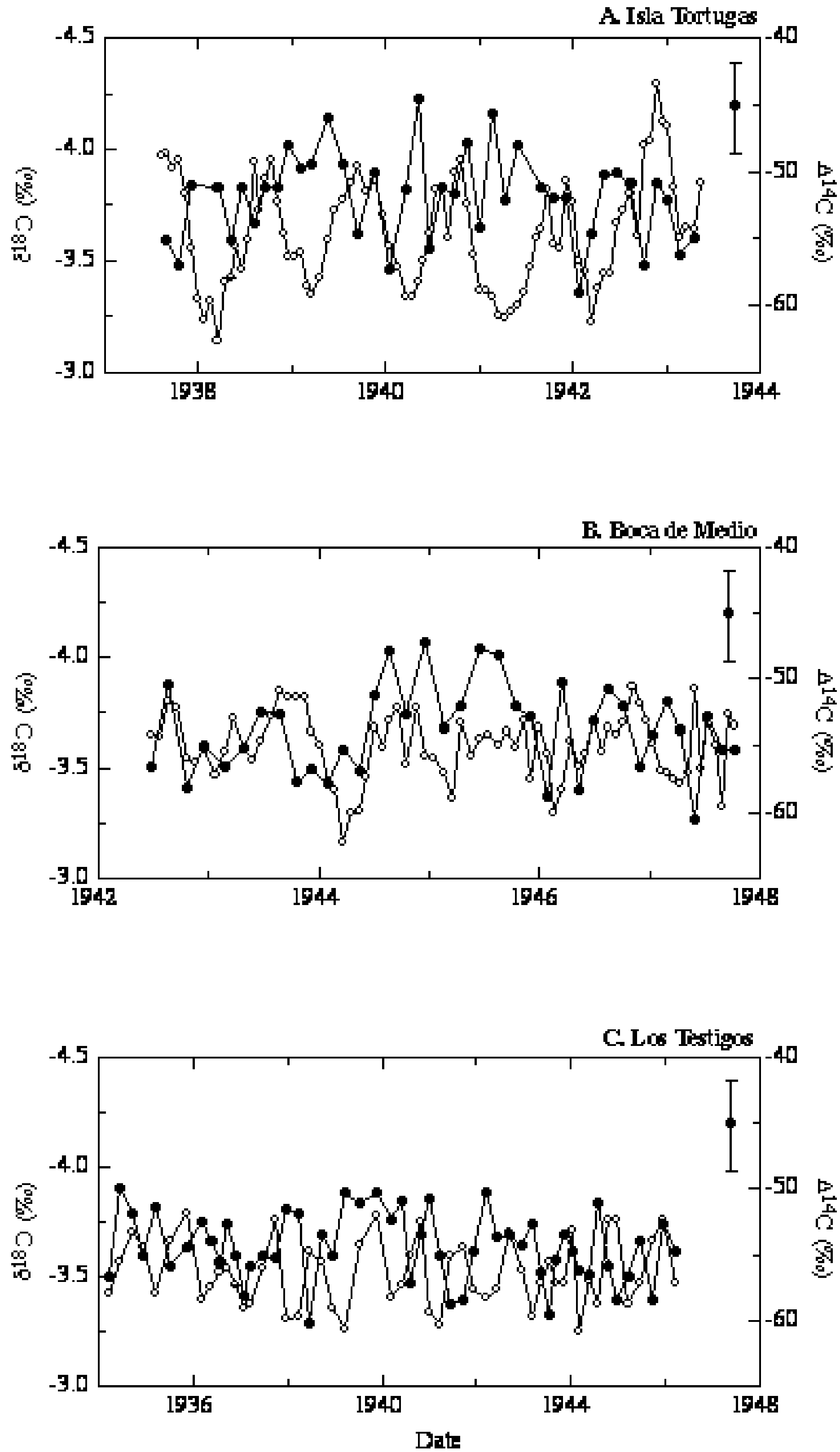

A. Isla Tortugas
-4.5
-4.0
-3.5
-3.0
δ18O (‰)
-40
-50
-60
Δ14C (‰)
1938
1940
1942
1944
B. Boca de Medio
-4.5
-4.0
-3.5
-3.0
δ18O (‰)
-40
-50
-60
Δ14C (‰)
1942
1944
1946
1948
C. Los Testigos
-4.5
-4.0
-3.5
-3.0
δ18O (‰)
-40
-50
-60
Δ14C (‰)
1936
1940
1944
1948
Date

Figure 2D

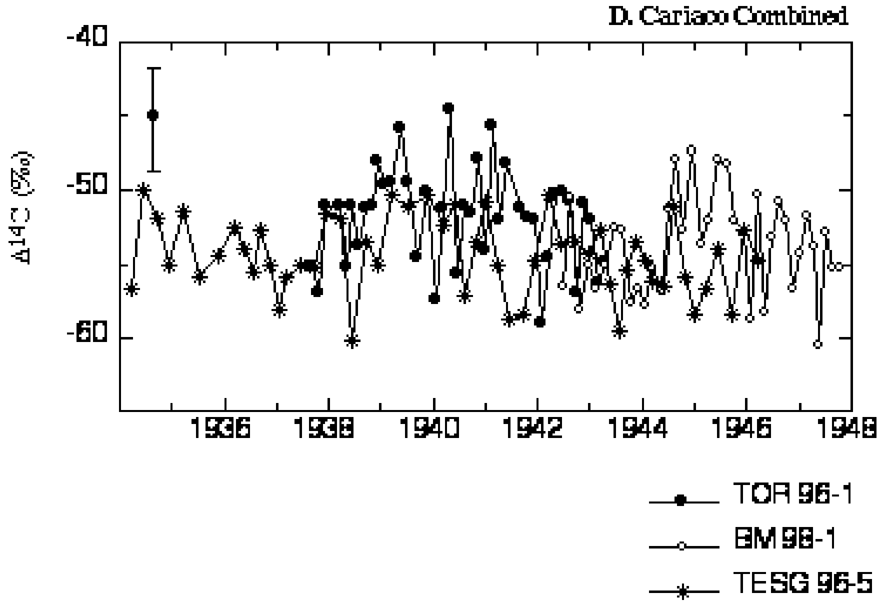

D. Cariaco Combined
-40
-50
-60
Δ14C (‰)
1936
1938
1940
1942
1944
1946
1948
TOR 96-1
BM 98-1
TESG 96-5

Figure 3

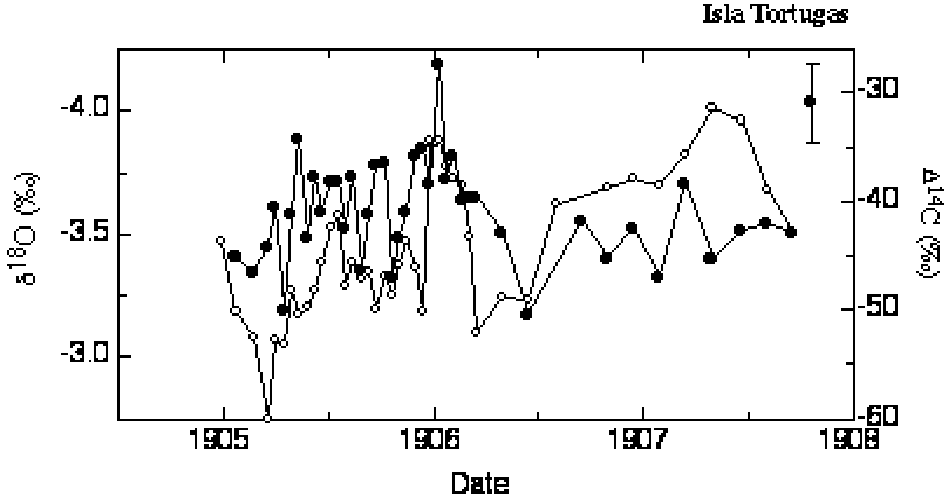

Isla Tortugas
-4.0
-3.5
-3.0
δ18O (‰)
-30
-40
-50
-60
Δ14C (‰)
1905
1906
1907
1908
Date

Figure 4

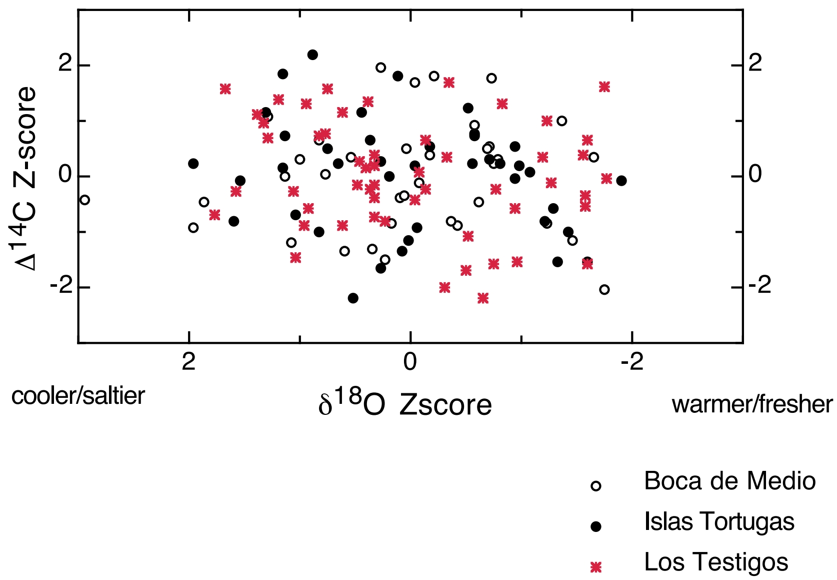
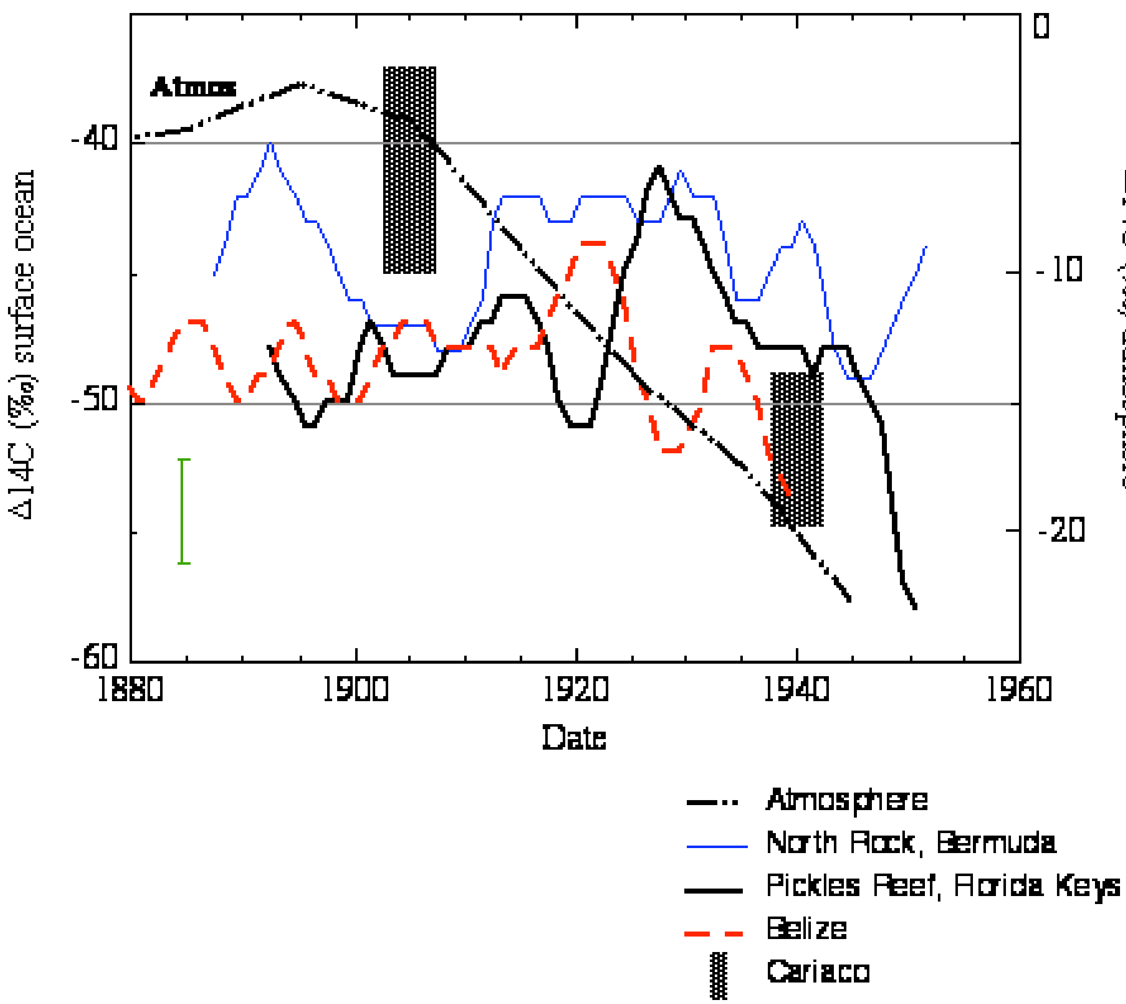

2
0
-2
2
0
-2
Δ^{14}C Z-score
2
0
-2
cooler/saltier
δ^{18}O Zscore
warmer/fresher
Boca de Medio
Islas Tortugas
Los Testigos

Figure 5


Atmos
-40
-50
-60
Δ14C (‰) surface ocean
0
-10
-20
Δ14C (‰) atmosphere
1880
1900
1920
1940
1960
Date
Atmosphere
North Rock, Bermuda
Pickles Reef, Florida Keys
Belize
Cariaco