



Evidence for preindustrial variations in the marine surface water carbonate system from coralline sponges

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[1] Coralline sponge skeletons are excellent tools for reconstructing the carbon isotope history of dissolved inorganic carbon (DIC) in tropical surface waters. Carbon isotope records from coralline sponges clearly reflect the industrial ^{12}C increase in atmospheric CO_2 with a precision that permits quantitative interpretations. We find from a set of $\delta^{13}\text{C}$ records of four Caribbean sponge specimens that the isotopic response of surface water DIC to the changing isotopic composition of atmospheric CO_2 varied dynamically during the last century, depending on the rate of atmospheric change. Three of our sponges provide 600 year long $\delta^{13}\text{C}$ records. For the first time, we can reconstruct surface water $\delta^{13}\text{C}_{\text{DIC}}$ for the full history of the industrial CO_2 release as well as the preceding preindustrial period back to the beginning of the Little Ice Age. This provides a well-founded estimate of the anthropogenically uninfluenced, preindustrial background level of surface water $^{13}\text{C}/^{12}\text{C}$ ratios. Our records show small but systematic variations that appear to be linked to the climate fluctuations of the Little Ice Age.

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1. Introduction

[2] We investigate stable carbon isotope records of aragonitic skeletons of the coralline sponge *Ceratoporella nicholsoni* (Figure 1), which lives in surface and upper thermocline waters of the Caribbean. These sponges precipitate aragonite very close to isotopic equilibrium with ambient sea water [Druffel and Benavides, 1986; Böhm *et al.*, 1996; Reitner, 1992]. Carbon isotope histories recorded by the sponges display the anthropogenic carbon isotope shift of the 19th and 20th century [Druffel and Benavides, 1986; Böhm *et al.*, 1996; Swart *et al.*, 1998; Lazareth *et al.*, 2000; Moore *et al.*, 2000; Nozaki *et al.*, 1978] as well as variations prior to the 19th century. These preindustrial variations provide evidence for natural variations in the atmosphere/surface ocean CO₂ inventory.

[3] On the basis of ice core analyses [Etheridge *et al.*, 1996], it has been shown that the atmospheric CO₂ mixing ratio ($p\text{CO}_2$) varied by 6 ppm before the onset of industrial influences. Carbon isotope data of these ice core inclusions vary in concert with $p\text{CO}_2$ [Francey *et al.*, 1999]. These variations have been linked to climatic variations known as “Medieval Warm Period” and “Little Ice Age.” Combined with the ice core record, our data provide further constraints on the modeling of global climate changes during this period and support the notion that the Little Ice Age had a measurable, global impact on the carbon cycle.

2. Material and Setting

[4] We collected living sponges (Figure 1) in 1993 and 1996 at Jamaica (Rio Bueno and Montego Bay) in reef caves in ~20 m of water and at the northwestern slope of Pedro Bank in 125 m of water (78°57'W 17°32'N). The sites are well exposed to the open sea. The Jamaican sites are situated within the mixed layer of the “Caribbean Surface Water,” while the Pedro Bank site is positioned below a barrier layer [Sprintall and Tomczak, 1992] near the top of the “Subtropical Underwater” [Morrison and Nowlin, 1982].

Whereas the Caribbean Surface Water is mainly derived from the tropical South Atlantic, the Subtropical Underwater forms in the tropical and subtropical North Atlantic from where it is transported southwest into the Caribbean [Schmitz and Richardson, 1991]. Thus the shallow water sponges formed their skeletons in waters that predominantly equilibrated with atmospheric CO₂ southeast of the Caribbean, while the deeper water sponges lived in waters that mainly reflect the atmosphere-surface water equilibration in the southwest flowing part of the North Atlantic subtropical gyre [Schmitz and McCartney, 1993].

[5] As the deeper water site is positioned near the transition from Subtropical Underwater to Caribbean Surface Water, a varying degree of mixing between the two water masses can be expected at this water depth. Upwelling of Subtropical Underwater in the southern parts of the Caribbean [Gordon, 1967] leads to further mixing of the two water masses. It should also be noted that the surface water stratification pattern of the Caribbean may have been different during the Little Ice Age.

3. Methods

[6] Microsamples for isotope analysis were collected with a 0.5 mm dental drill and processed using standard procedures as described by Böhm *et al.* [1996]. Analyses were carried out at the isotope lab of the Geological Institute, University of Erlangen, with a Finnigan Mat 252. Temporal resolutions of individual samples range from 2 to 4 years/sample, depending on the growth rates varying from 0.19 to 0.43 mm/year. External precision (2σ) of $\delta^{13}\text{C}$ measurements based on multiple analyses ($N = 87$) of standards NBS 19 and IAEA CO1 is $\pm 0.04\%$. All carbon isotope ratios are given in the common delta notation, relative to V-PDB (Vienna Pee Dee Belemnite).

[7] Growth rates derive from U/Th dates in three specimens (measured at GEOMAR and at Göttingen University) and fits of ^{14}C AMS data (Figure 2) to the radiocarbon “bomb spike” [Benavides and

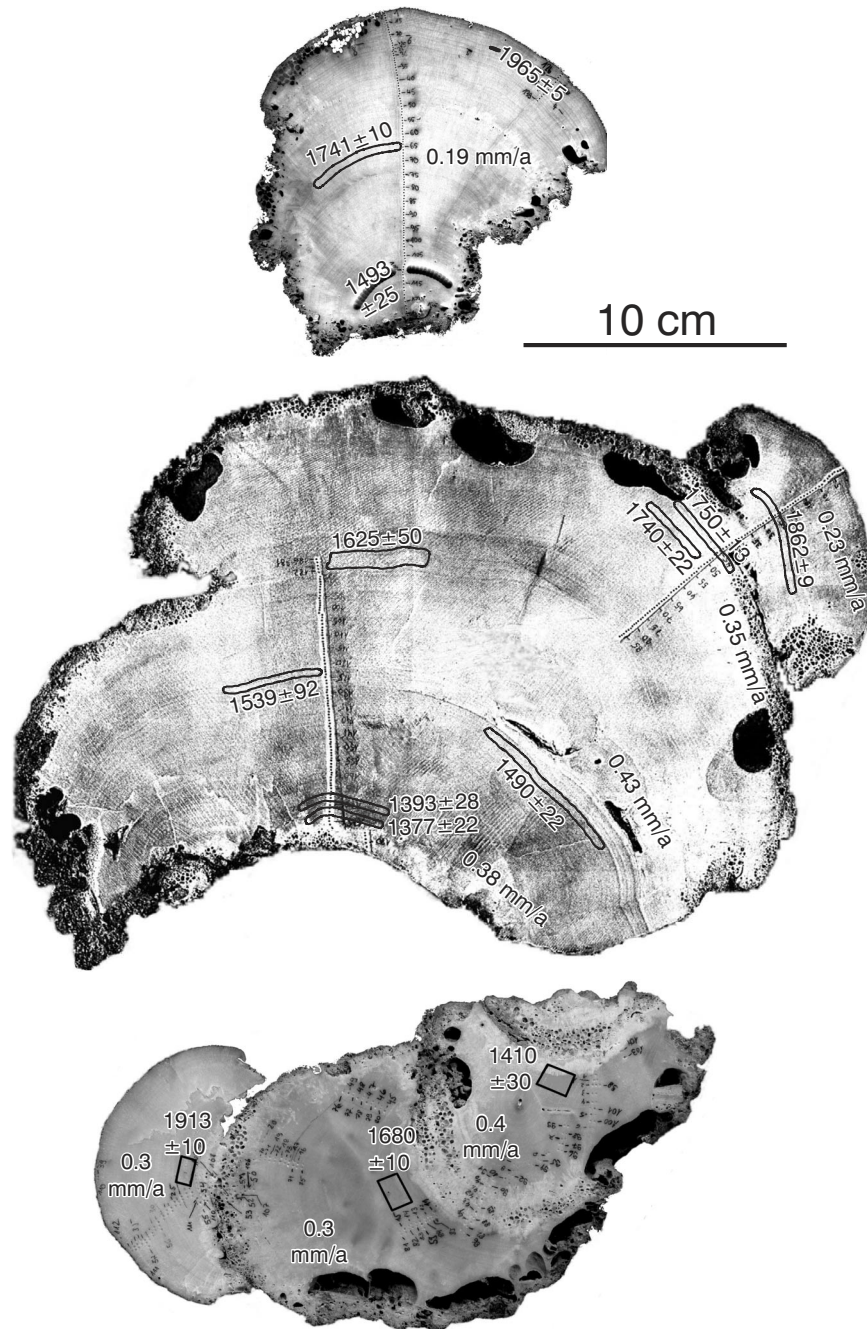


Figure 1. Polished slabs of the investigated *Ceratoporella nicholsoni* specimens (from top 392-19, Ce96-1 and Ce95-2) with sample transects (dotted lines). Uranium/Thorium ages are given as years of formation (A.D.) of the respective layers together with standard errors (2σ). The 1965 datum of the top specimen is the radiocarbon bomb spike. The sampling spots of the U/Th datings and the radiocarbon sample that was assigned to the year 1965 A.D. are marked with bold black lines. Average growth rates are calculated from U/Th ages and the age of the surface, i.e., the years of collection (1996 A.D. for Ce96-1 and 392-19 and 1995 A.D. for Ce95-2).

Druffel, 1986; Druffel, 1989] in specimen Ce145 [Böhm *et al.*, 1996] and specimen 392-19 (measured at the Leibniz-Labor, Kiel University). For the latter we assume that the timing of the radiocarbon

increase at 125 m depth was similar to the timing in surface waters of that region because the amplitude of change in $\Delta^{14}\text{C}$ is similar to the surface water change (Figure 2).

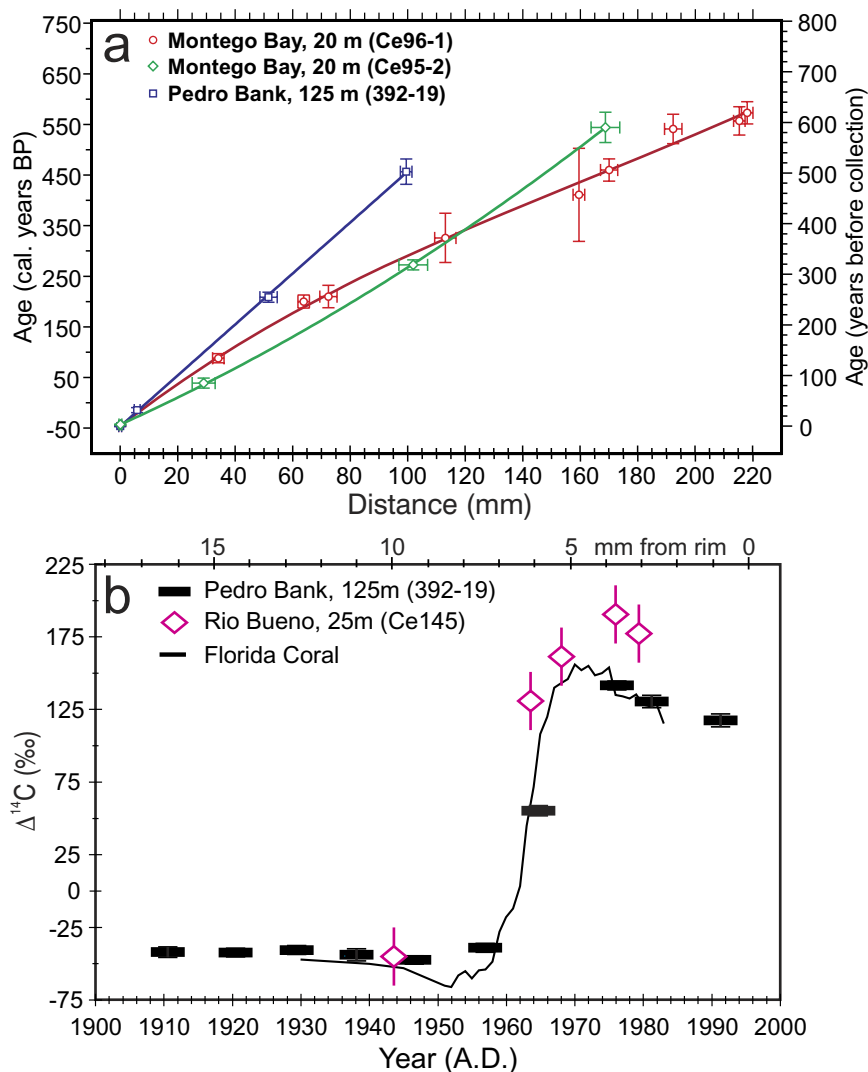


Figure 2. (a) Age depth curves of the three investigated sponge specimens. Depth is measured along the isotope sample transects. The data points at 0 mm represent the top surfaces of the sponges. Horizontal error bars represent the sample width (measured parallel to growth axis). BP, before present (i.e. before 1950 A.D.). The data points are fitted by polynomials. (b) Fit of the measured radiocarbon values of specimens 392-19 and Ce145 to the coral $\Delta^{14}\text{C}$ curve for Atlantic Ocean surface waters east of southern Florida [Druffel, 1989]. Error bars are smaller than symbols except where shown. The width of the symbols is equivalent to the width of the samples. The lower x axis corresponds to the Florida coral $\Delta^{14}\text{C}$ curve. The upper x axis shows the sample distance from the top of the sponge skeleton along the growth axis. We take the value intermediate between the prebomb and postbomb levels to represent the year 1964 ± 5 A.D. in both sponge skeletons. Spacing of the sponge radiocarbon samples is scaled to the lower x axis (time) by assuming a growth rate of 0.19 mm/a. Specimen Ce145 probably grew slightly faster (0.22 mm/a [Böhm et al., 1996]) than specimen 392-19.

[8] On the basis of these data, we rely on steady growth rates to estimate the ages of individual sampled skeleton layers. Constant growth seems to be the rule, as growth rates calculated from U/Th dated sections of a single specimen show little variation, as long as homogeneous parts of a skeleton are considered (Figure 1). We use linear

regression to fit growth curves to the radiometrically dated tie points (Figure 2). A linear growth model provides an optimal fit to the age data of specimen 392-19. We used a second-order polynomial for specimen Ce95-2 and a third order polynomial for specimen Ce96-1. Details of the dating methods will be given elsewhere (A.

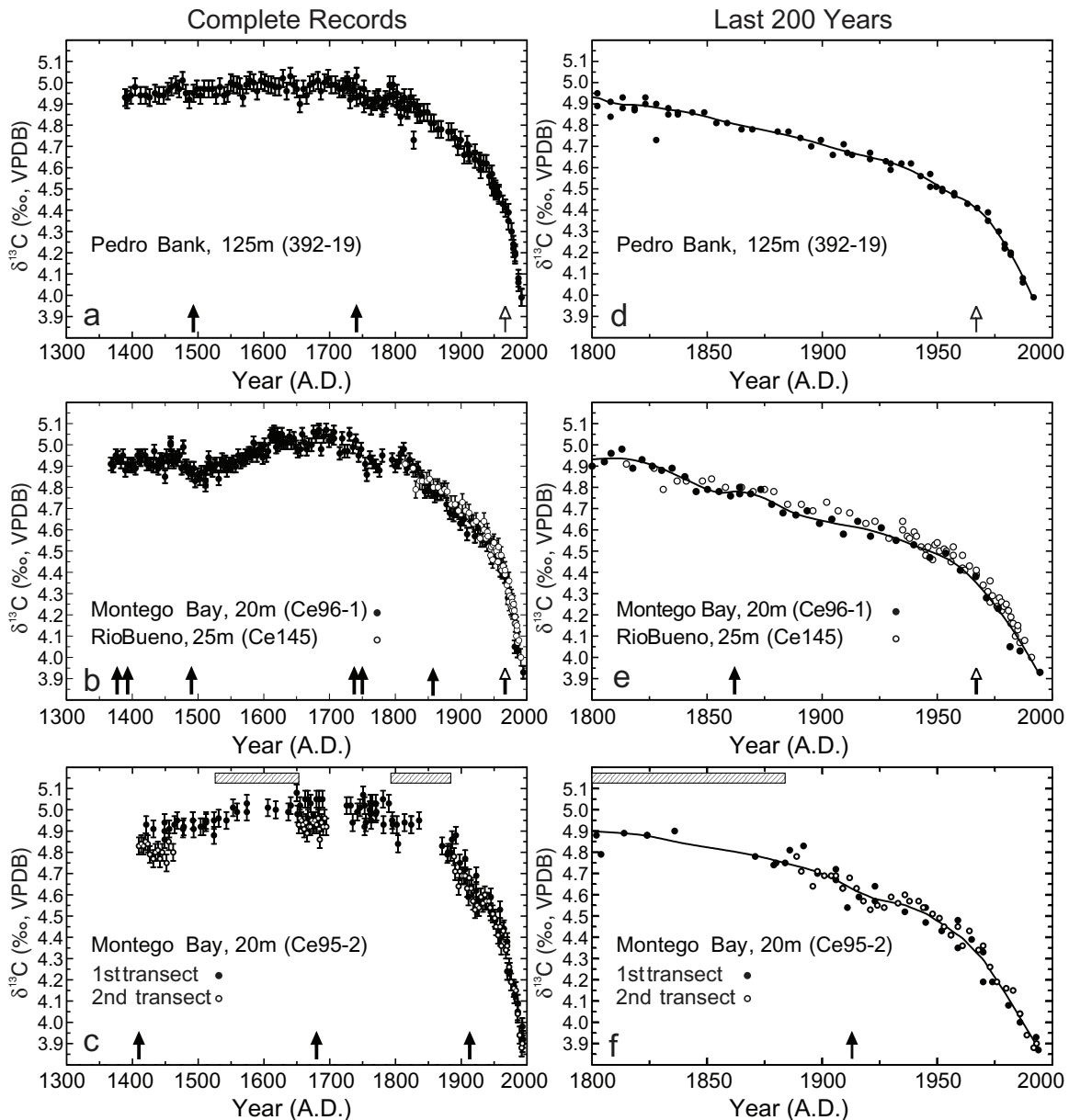


Figure 3. Stable carbon isotope records of the *Ceratoporella* skeletons. Error bars are $\pm 2\sigma$ (standard deviation). The lines are locally weighted linear regressions (LOWESS, 10% window). Black arrows mark U/Th dates as shown in Figure 1. Open arrows mark positions of the bomb spike in samples Ce145 [Böhm *et al.*, 1996] and 392-19. Hatched bars in Figures 3c and 3f mark the positions of the bleached and bored zones in sample Ce95-2. Values from these bands may be slightly altered. Sample Ce145 is plotted with sample Ce96-1 for comparison.

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4. Results

[9] All $\delta^{13}\text{C}$ records (appendix A) show the full extent of the industrial decline (Figure 3) caused by the anthropogenic addition of ^{12}C -enriched CO_2 to the atmosphere [Druffel and Benavides, 1986;

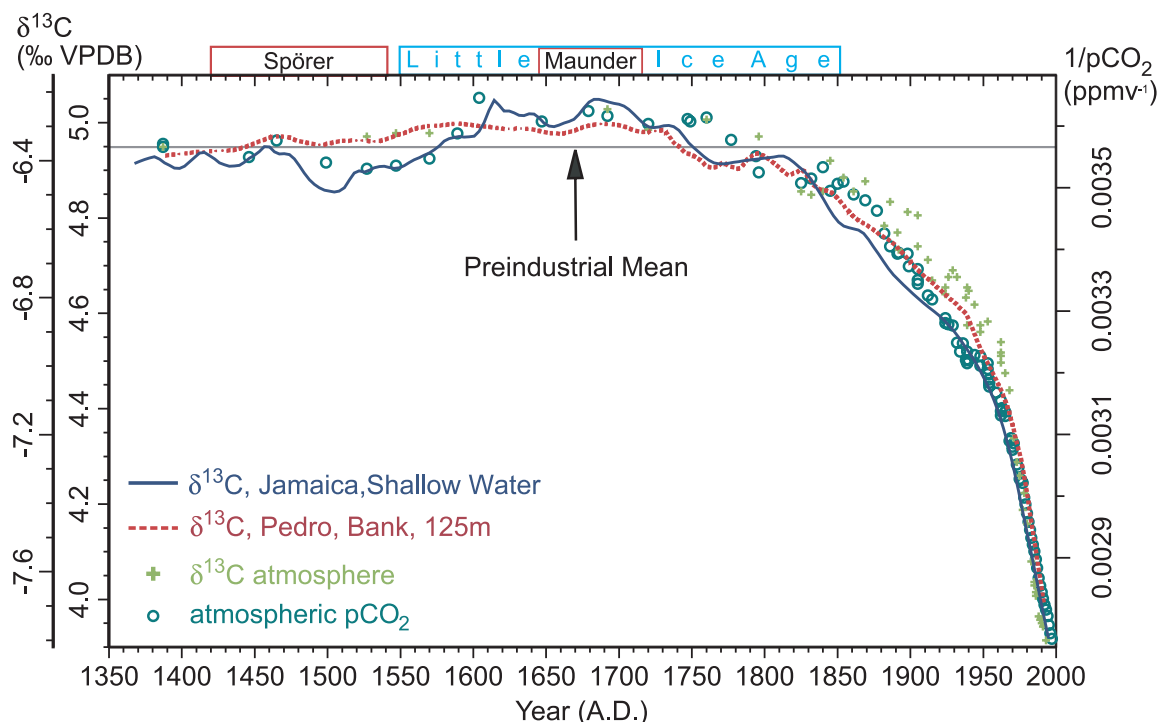


Figure 4. Comparison between Caribbean shallow (blue solid line) and deeper water (red dotted line) sponge $\delta^{13}\text{C}$ records (inner left y axis), $\delta^{13}\text{C}$ of atmospheric CO_2 (green crosses, outer left y axis) and atmospheric $p\text{CO}_2$ (circles, right y axis, reciprocal scale). Atmosphere data are derived from Antarctic ice core and firm air inclusions [Etheridge *et al.*, 1996; Francey *et al.*, 1999] and air measurements [Keeling and Whorf, 2001]. The atmospheric $\delta^{13}\text{C}$ record is scaled for its preindustrial mean and minimum values to fit the shallow water sponge record. The $\delta^{13}\text{C}$ curves are smoothed by locally weighted linear regressions (9% window). The horizontal line marks the preindustrial (1400–1850 A.D.) means (280.5 ppm, -6.37‰ , 4.95‰ VPDB, respectively). Slight offsets in the timing between atmosphere and sponge records can be artefacts of the dating methods. Blue bar at the top shows the approximate duration of the Little Ice Age [Grove, 1988]. Red bars mark the Spörer (ca. 1420–1540 A.D.) and Maunder (1645–1715 A.D.) sunspot minima.

Keeling *et al.*, 1979; Friedli *et al.*, 1986; Francey *et al.*, 1999; Quay *et al.*, 1992; Laube-Lenfant and Pierre, 1994; Bacastow *et al.*, 1996]. In all records the industrial period shows an older segment of slowly declining $\delta^{13}\text{C}$ values. In contrast, the younger segment, starting about 1960 A.D., exhibits rapidly declining values (Figures 3d–3f). This parallels the records of atmospheric $p\text{CO}_2$ and its ^{12}C content, measured in ice core inclusions and air, which started to increase at higher rates between 1950 and 1960 A.D. [Friedli *et al.*, 1986; Etheridge *et al.*, 1996; Francey *et al.*, 1999] (Figure 4).

[10] The industrial decline in $\delta^{13}\text{C}$ started in the first half of the 19th century after a short period of stable values around 1800 A.D. This late preindustrial plateau shows nearly constant values in all

measured sponges (Figure 3). The stable period was preceded by a slight decline in $\delta^{13}\text{C}$ in the middle of the 18th century. The highest measured $\delta^{13}\text{C}$ values of both shallow water records occur during the 17th and early 18th century (Figure 3b and 3c). Before that period, i.e., before about 1600 A.D., values were in the same range as in the early 19th century. In the shallow water sponge records the mean $\delta^{13}\text{C}$ of the 1400–1500 A.D. interval is significantly lower ($p < 0.01$) than the 1620–1720 A.D. mean (Table 1).

[11] Specimen Ce95-2 has two bio-eroded zones interrupting the isotope record (Figure 3c). It shows a relatively high scatter in the preindustrial part of the record. Two parallel isotope transects were sampled at a distance of $\sim 1\text{cm}$. We find an offset of $\sim 0.1\text{‰}$ between corresponding values of the

Table 1. Mean $\delta^{13}\text{C}$ for Certain Time Intervals Calculated From the Measured Values^a

Sample Depth	Mean $\delta^{13}\text{C}$ (‰ VPDB $\pm 2\sigma/\sqrt{n}$) of specified intervals (A.D.)					$\Delta\delta^{13}\text{C}_s$		$\Delta\delta^{13}\text{C}_s/\Delta\delta^{13}\text{C}_a$	
	1400–1500	1620–1720	1400–1850	1960–1970	1980–1990	pi to 1960s	1960s–1980s	pi to 1960s	1960s–1980s
Ce96-1	4.92 \pm 0.01 <i>n</i> = 39	5.02 \pm 0.01 <i>n</i> = 34	4.95 \pm 0.01 <i>n</i> = 147 (4.95)	4.37 \pm 0.03 <i>n</i> = 2	4.06 \pm 0.13 <i>n</i> = 3	–0.58 \pm 0.03	–0.31 \pm 0.13	0.9 \pm 0.09	0.5 \pm 0.22
20 m	–	–	–	4.41 \pm 0.03 <i>n</i> = 7	4.12 \pm 0.04 <i>n</i> = 12	–0.54 \pm 0.03	–0.29 \pm 0.05	0.8 \pm 0.08	0.5 \pm 0.10
Ce145	–	–	–	4.39 \pm 0.05 <i>n</i> = 7	4.07 \pm 0.06 <i>n</i> = 7	–0.59 \pm 0.05	–0.32 \pm 0.08	0.9 \pm 0.11	0.5 \pm 0.13
25 m	4.92 \pm 0.01 <i>n</i> = 13	5.03 \pm 0.02 <i>n</i> = 16	4.98 \pm 0.01 <i>n</i> = 71	4.42 \pm 0.04 <i>n</i> = 4	4.12 \pm 0.07 <i>n</i> = 4	–0.53 \pm 0.04	–0.30 \pm 0.08	0.8 \pm 0.09	0.5 \pm 0.14
392-19	4.96 \pm 0.01 <i>n</i> = 17	4.98 \pm 0.01 <i>n</i> = 20	4.95 \pm 0.01 <i>n</i> = 107	–	–	–	–	–	–
125 m	–	–	–	–	–	–	–	–	–

^a For sample Ce95-2, only data from the first transect are used. Here 1400–1850 means are calculated from the smoothed data sets interpolated to 1 year intervals. Decadal means are read from linear regression lines through respective decadal data. Preindustrial record of sample Ce95-2 is fragmentary; therefore the preindustrial mean may be slightly biased. Last four columns show measured marine decrease ($\Delta\delta^{13}\text{C}_s$) from preindustrial mean (pi) until 1960s and from 1960s to 1980s. Preindustrial mean for Ce145 is copied from Ce96-1. Last two columns give ratios between these values and the respective atmospheric carbon isotopic decline ($\Delta\delta^{13}\text{C}_a$, ice core, and firn air inclusion data [Francey *et al.*, 1999]), which is pi to 1960s: -0.67‰ , 1960s to 1980s: -0.59‰ .

two transects in the preindustrial part (Figure 3c). The second transect was sampled almost 3 years after the first one; therefore the observed $\delta^{13}\text{C}$ offset may represent a similar ageing effect as previously described for sponge aragonite [Druffel and Benavides, 1986]. Nevertheless, the means of the 1400–1500 A.D. interval (transect 1: 4.92‰; transect 2: 4.81‰) and of the 1620–1720 A.D. interval (transect 1: 5.03‰; transect 2: 4.93‰) are again significantly different ($p \ll 0.01$) for both transects respectively. Furthermore, the means of the respective intervals from the first transect and sample Ce96-1 are identical (Table 1).

[12] The deeper water sample from Pedro Bank shows no obvious $\delta^{13}\text{C}$ maximum during the 17th or 18th century but rather very constant values in most of the preindustrial interval (Figure 3a). However, even in this sample we find a 1400–1500 A.D. mean that is slightly lower than the 1620–1720 A.D. mean (Table 1). The difference is significant at a 95% probability level.

5. Discussion

5.1. Preindustrial Variations

[13] The sponge records provide the first preindustrial marine $\delta^{13}\text{C}$ data with decadal resolution. Additionally, they cover the entire industrial period with higher accuracy, better temporal resolution and better timing constraints than previous records [Druffel and Benavides, 1986; Böhm *et al.*, 1996]. The excellent reproducibility between records from different sites of similar water depth (Figure 3b and 3e) shows that sponge skeletons can reliably register regional environmental signals. The great similarity between the Jamaica and Pedro Bank records indicates that the measured carbon isotope signal is representative for open sea surface waters of the central Caribbean and of the equatorial to tropical/subtropical Atlantic Ocean.

[14] Surface water studies [Bacastow *et al.*, 1996; McNichol and Druffel, 1992; Gruber *et al.*, 1998] show a high $\delta^{13}\text{C}_{\text{DIC}}$ variability at timescales of days to months with amplitudes significantly greater than 0.1‰. Variations with periods of 3–5 years and amplitudes of $\sim 0.1\text{‰}$ have been

observed on interannual timescales [Bacastow *et al.*, 1996]. Also, $\Delta^{14}\text{C}$ in subtropical surface waters may vary significantly on subdecadal to decadal timescales while lacking the expected Suess effect long-term trend [Druffel, 1997]. Such subdecadal variations are explained by advection, vertical mixing, and productivity changes. Longer surface water $\delta^{13}\text{C}_{\text{DIC}}$ time series have not been available up to now. With the precision and resolution of our records (sample spacing $\sim 2\text{--}6$ years), we can reliably detect $\delta^{13}\text{C}$ variations $> 0.05\text{‰}$ on interdecadal and centennial timescales ($> 15\text{--}20$ years). Our records (Figure 3) demonstrate that variations in this time band are very small in the Caribbean. This is most obvious for the deeper water setting at Pedro Bank, where the preindustrial (A.D. 1400–1850) $\delta^{13}\text{C}$ variation is only $\pm 0.07\text{‰}$. Most of this variability is caused by a decrease of roughly 0.1‰ between A.D. 1730 and 1760 (Figure 4).

[15] The most prominent feature of the preindustrial shallow water record (Figure 3b) is the 50 years long 0.1‰ increase in $\delta^{13}\text{C}$ from about 1550 to 1600 A.D. and the subsequent decrease until about 1770 A.D. (Figure 4). The $\delta^{13}\text{C}$ of atmospheric CO_2 increased by ~ 0.05 to 0.10‰ [Francey *et al.*, 1999] and atmospheric $p\text{CO}_2$ decreased by ~ 6 ppm [Etheridge *et al.*, 1996] during the same period (Figure 4). Unfortunately, the coarse resolution and limited dating accuracy of both the sponge and ice core records currently prohibit conclusions about the precise temporal relation between the atmospheric and marine records.

[16] The $\delta^{13}\text{C}$ of atmospheric or marine dissolved total CO_2 is expected to correlate with $1/p\text{CO}_2$ [Keeling *et al.*, 1979] as long as CO_2 is sequestered by or released from organic carbon. This is due to the strong ^{13}C depletion of organic carbon. Addition of such isotopically light carbon to the atmosphere/ocean inorganic carbon pool will in parallel increase the CO_2 and its ^{12}C content. There are, of course, other mechanisms to change atmospheric $p\text{CO}_2$ and the isotopic composition of CO_2 or DIC independently, for example, changes in the ocean salinity or in the deepwater carbonate ion content will affect atmospheric $p\text{CO}_2$ without isotopic effects [Broecker, 1995].

[17] The period of $p\text{CO}_2$ reduction and $\delta^{13}\text{C}$ increase (1550–1700 A.D.) starts after the Spörer sunspot minimum and coincides with the Maunder sunspot minimum (approximately 1420–1540 and 1645–1715 A.D.; Figure 4). These are periods of reduced solar activity [Stuiver and Quay, 1980; Lean *et al.*, 1995]. Moreover, the period between 1550 and 1850 A.D. was an interval of intermittent cool periods, called “Little Ice Age” [Grove, 1988; Jones *et al.*, 2001]. Thus global cooling may have been the cause of the parallel $p\text{CO}_2$ reduction and atmospheric/marine $\delta^{13}\text{C}$ increase [Trudinger *et al.*, 1999]. Increased solubility of CO_2 in colder surface waters or carbon sequestration in the terrestrial biosphere was discussed previously [Etheridge *et al.*, 1996; Trudinger *et al.*, 1999; Joos *et al.*, 1999]. Only the latter can explain the parallel atmospheric and marine $\delta^{13}\text{C}$ increase.

[18] Global cooling of sea surface temperatures would sequester atmospheric CO_2 due to its higher solubility by ~ 10 ppm/K. Models show that on timescales of some decades about half of this amount will be taken up by the oceans [Bacastow, 1996]. Thus global sea surface temperature cooling alone could explain the $p\text{CO}_2$ decrease, if the globally averaged cooling during the Little Ice Age was ~ 1 K [Grove, 1988; Trudinger *et al.*, 1999; Keigwin, 1996; Kitagawa and Matsumoto, 1995; Watanabe *et al.*, 2001]. However, a global 1 K cooling of sea surface temperatures would increase the isotopic equilibrium fractionation between air and water by $\sim 0.1\text{‰}$ [Zhang *et al.*, 1995] and this would only lower the $\delta^{13}\text{C}$ of atmospheric CO_2 and leave the marine $\delta^{13}\text{C}_{\text{DIC}}$ almost unchanged. This is because on a multi-decadal timescale the exchangeable carbon mass in the ocean is much larger than the mass of carbon in the atmosphere [Keir *et al.*, 1998]. Therefore the observed parallel increase of $\delta^{13}\text{C}_{\text{DIC}}$ and of atmospheric $\delta^{13}\text{C}$ during the period of lower $p\text{CO}_2$ requires an alternative explanation.

[19] The observed close correlation of our data with atmospheric $p\text{CO}_2$ indicates a common and therefore global cause. The most likely common cause of all observed carbon cycle changes is an increase in the global biogenic carbon mass during the Little Ice Age [Trudinger *et al.*, 1999; Joos *et al.*, 1999].

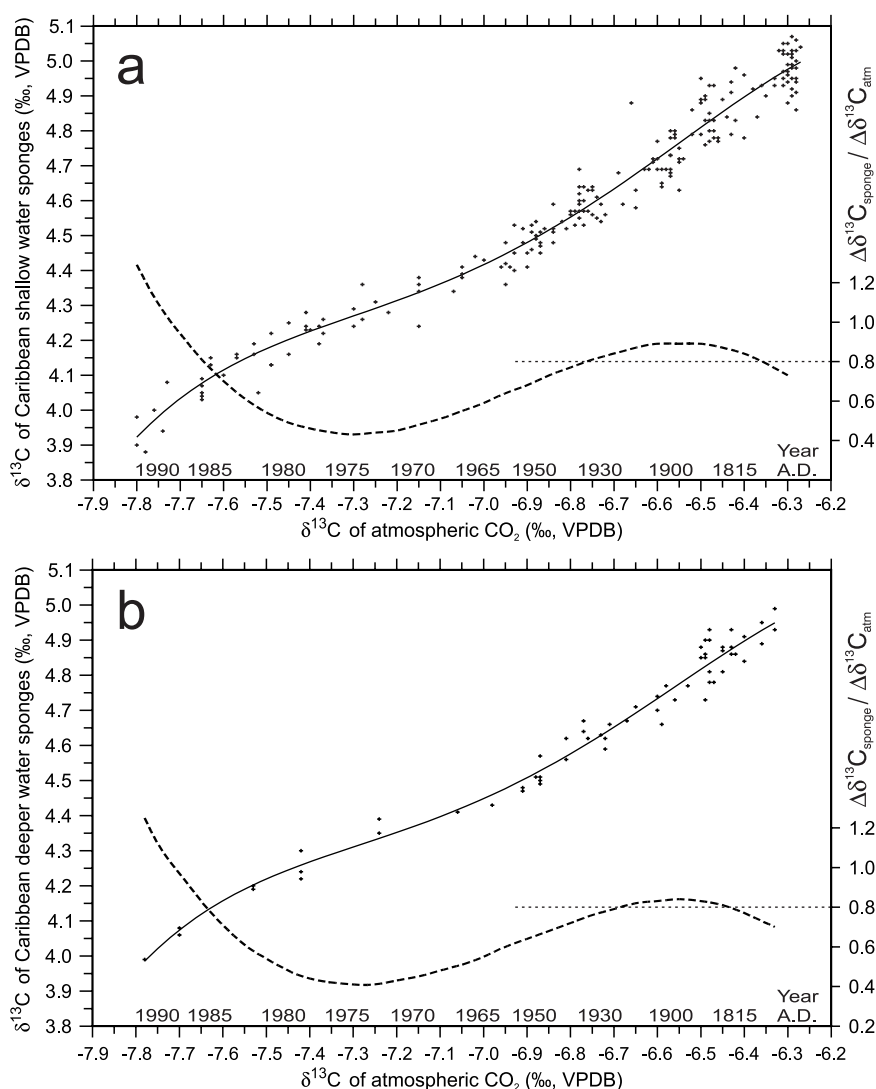


Figure 5. Cross plot of carbon isotope values of Caribbean shallow water sponge aragonite and atmospheric CO₂ [Francey *et al.*, 1999]. Age increases from left to right with increasing atmospheric values. The continuous line is a fourth-order polynomial fit to the data. The dashed line (right y axis) is the first derivative of the polynomial fit. It represents the ratio of carbon isotopic change between Caribbean surface water DIC and atmospheric CO₂. This ratio varied around an average value of 0.8 before 1960, declined significantly during the 1960s and 1970s and reached its highest values near 1 in the 1990s. (a) Shallow water specimens from Jamaica. (b) Deeper water specimen from Pedro Bank.

At the same time, the combined atmospheric and marine data allow for only minor global cooling of the ocean surface.

[20] It is unknown whether sequestration of organic carbon to the deep sea by increased oceanic productivity or rather increased storage of organic matter in terrestrial environments caused the observed changes in the earth's carbon budget during the Little Ice Age. Changes in the large-

scale ocean circulation [Broecker, 2000] but also increased wind induced upwelling in the southern Caribbean and subtropical North Atlantic [Black *et al.*, 1999; deMenocal *et al.*, 2000] may additionally have contributed to the observed variation of Caribbean $\delta^{13}\text{C}_{\text{DIC}}$ during the Little Ice Age. Only additional long-term records of $\delta^{13}\text{C}_{\text{DIC}}$ from other oceans will help to find out whether our observations represent a purely global signal. The only published Pacific Ocean carbon isotope record

reaching back to the Little Ice Age of a coralline sponge from the Great Barrier Reef [Wörheide *et al.*, 1997] shows slightly higher values ($\sim 0.05\%$) during the 17th century, which is in accord with a global nature of the observed marine variations.

5.2. Industrial Period

[21] The sharp contrast between the almost invariant preindustrial record and the strong decline in $\delta^{13}\text{C}$ since 1850 A.D. underlines the exceptional quality of this recent anthropogenic disturbance of the global carbon cycle. Comparing the observed decrease of $\delta^{13}\text{C}$ in Caribbean surface water and in the atmosphere [Francey *et al.*, 1999], we find a consistent and significant decline in the ratio of the marine to the atmospheric change ($\Delta\delta^{13}\text{C}_{\text{DIC}}/\Delta\delta^{13}\text{C}_{\text{Atm}}$) from the pre-1960 period to the 1970s and 1980s (Table 1, Figure 5): The marine $\delta^{13}\text{C}$ decrease from preindustrial times to the 1960s was $\sim 80\%$ of the atmospheric change. The marine $\delta^{13}\text{C}$ decrease from the 1960s to the 1980s, however, was only half the atmospheric change. This decline in the apparent isotopic equilibration between atmosphere and surface waters is evident in all four sponge records. Therefore it is unlikely that this observation represents just an artefact of insufficient dating control and unnoticed decadal growth rate variations of our sponges.

[22] In contrast to our observation of a reduced isotopic ocean-atmosphere equilibration after the 1960s, Gruber *et al.* [1999] report a $\delta^{13}\text{C}_{\text{DIC}}$ decrease during the decade from 1983 to 1995 in the Sargasso Sea that equals or possibly exceeds the contemporary atmospheric $\delta^{13}\text{C}$ decline. However, the youngest part of our isotope record from Specimen Ce95-2 points to a decrease of $\sim 0.2 \pm 0.07\%$ from the 1980s until 1995 (Figure 3f). This decrease is compatible with the observations of Gruber *et al.* [1999]. Obviously, after the minimum of the 1970s (Figure 5), the isotopic ocean-atmosphere equilibration increased again to the very high values of the 1990s reported by Gruber *et al.* [1999] and indicated by the youngest portion of our sponge records.

[23] These variations of the isotopic ocean-atmosphere disequilibrium in the Caribbean Sea can be explained by the history of the atmospheric $\delta^{13}\text{C}$.

The rate of decline of atmospheric $\delta^{13}\text{C}$ increased during the 1950s and 1960s, remained high until the late 1980s, and was low during the 1990s [Francey *et al.*, 1999; Gruber *et al.*, 1999]. During the first half of the 20th century the carbon isotopic decline of the atmosphere was slow enough for the tropical surface ocean DIC to follow closely ($\sim 80\%$ “equilibration”, i.e., $\Delta\delta^{13}\text{C}_{\text{DIC}}/\Delta\delta^{13}\text{C}_{\text{Atm}}$, in Caribbean and tropical North Atlantic surface waters, Table 1, Figure 5). However, with the finite carbon isotopic equilibration time between atmosphere and surface waters, the faster atmospheric $\delta^{13}\text{C}$ decrease during the 1960s and 1970s led to a lower degree of equilibration ($\sim 50\%$). The subsequent slow down of the 1990s allowed the oceans to start catching up on the isotopic equilibrium (100–125% equilibration [Gruber *et al.*, 1999]; $\sim 100\%$ in Figure 5). This varying degree of isotopic equilibration between atmospheric CO_2 and surface water DIC clearly reflects the current state of the global carbon cycle, far from steady state due to the serious anthropogenic interference of the last 200 years.

6. Conclusions

[24] This study shows that the coralline sponge *Ceratoporella nicholsoni* is a very accurate recorder of $\delta^{13}\text{C}_{\text{DIC}}$. Coralline sponges are very useful in providing long-term, high-resolution $\delta^{13}\text{C}$ records. These provide useful information for estimating ocean uptake of anthropogenic CO_2 [Quay *et al.*, 1992; Bacastow *et al.*, 1996; Sonnerup *et al.*, 1999, 2000] and the terrestrial biota turnover times [Keir *et al.*, 1998].

[25] Our data shows a period of higher values during the Little Ice Age. These preindustrial variations are in concert with changes in the atmospheric carbon reservoir. Our data provide an independent evidence for variations in the global carbon reservoirs prior to the onset of anthropogenic perturbations.

[26] Varying degrees of carbon isotopic equilibration between atmospheric CO_2 and surface water DIC during the industrial increase of atmospheric $p\text{CO}_2$ reflect the dynamic response of the carbon cycle to human interference with magnitudes and



Appendix A. Carbon Isotope Values From Caribbean Sponge Specimens Used in This Study^a [The full Appendix A is available in ASCII tab-delimited format at <http://www.g-cubed.org>.]

Ce145, 25 m			Ce96-1, 20 m			Ce95-2, 20 m, First Transect			Ce95-2, 20 m, Second Transect			392-19, 125 m		
Year A.D.	d ¹³ C		Year A.D.	d ¹³ C		Year A.D.	d ¹³ C		Year A.D.	d ¹³ C		Year A.D.	d ¹³ C	
1886	4.07		1995	3.93	1612	1994	3.92	1993	1993	3.90	1992	1992	3.99	1758
1885	4.13		1986	4.03	1610	1993	3.98	1992	1992	3.88	1992	1992	3.99	1758
1885	4.15		1982	4.05	1606	1986	4.09	1989	1989	3.94	1987	1987	4.06	1752
1884	4.10		1977	4.23	1604	1986	4.05	1986	1986	4.04	1987	1987	4.08	1752
1883	4.16		1971	4.28	1601	1981	4.13	1983	1983	4.15	1982	1982	4.19	1746
1882	4.19		1967	4.38	1598	1974	4.24	1980	1980	4.16	1982	1982	4.20	1746
1881	4.22		1960	4.41	1595	1970	4.38	1976	1976	4.19	1979	1979	4.22	1741
1880	4.25		1954	4.49	1593	1970	4.24	1973	1973	4.26	1979	1979	4.24	1741
1979	4.24		1947	4.47	1590	1965	4.44	1970	1970	4.36	1977	1977	4.30	1736
1978	4.22		1940	4.53	1587	1959	4.53	1968	1968	4.34	1972	1972	4.35	1736
1977	4.23		1932	4.55	1585	1959	4.40	1964	1964	4.43	1972	1972	4.39	1731
1977	4.28		1926	4.61	1582	1952	4.48	1961	1961	4.36	1967	1967	4.41	1731
1976	4.24		1921	4.57	1580	1945	4.52	1959	1959	4.45	1963	1963	4.43	1727
1974	4.29		1915	4.64	1577	1945	4.59	1956	1956	4.41	1957	1957	4.48	1727
1973	4.26		1909	4.58	1575	1936	4.57	1953	1953	4.45	1957	1957	4.47	1721
1972	4.31		1904	4.65	1572	1923	4.69	1951	1951	4.49	1952	1952	4.50	1721
1970	4.34		1899	4.63	1570	1923	4.62	1948	1948	4.51	1952	1952	4.49	1715
1967	4.41		1894	4.69	1568	1916	4.64	1944	1944	4.54	1950	1950	4.51	1709
1964	4.43		1889	4.67	1565	1911	4.59	1942	1942	4.57	1947	1947	4.57	1703
1962	4.41		1883	4.68	1561	1906	4.77	1938	1938	4.57	1947	1947	4.51	1698
1961	4.42		1878	4.72	1557	1906	4.72	1936	1936	4.60	1943	1943	4.56	1693
1957	4.48		1873	4.79	1554	1898	4.75	1933	1933	4.56	1939	1939	4.62	1687
1956	4.45		1869	4.77	1552	1892	4.88	1930	1930	4.59	1934	1934	4.62	1682
1954	4.50		1864	4.77	1550	1886	4.86	1927	1927	4.54	1930	1930	4.62	1675
1953	4.51		1860	4.80	1547	1884	4.80	1924	1924	4.55	1930	1930	4.59	1670
1951	4.50		1860	4.76	1544	1880	4.80	1921	1921	4.53	1928	1928	4.63	1665
1949	4.53		1855	4.78	1542	1879	4.79	1918	1918	4.57	1928	1928	4.63	1660
1948	4.46		1850	4.79	1539	1871	4.83	1915	1915	4.63	1921	1921	4.67	1655
1946	4.52		1845	4.78	1537	1836	4.95	1912	1912	4.68	1921	1921	4.64	1650
1945	4.51		1840	4.85	1534	1824	4.93	1909	1909	4.63	1913	1913	4.66	1646
1943	4.52		1835	4.89	1531	1824	4.94	1906	1906	4.69	1911	1911	4.67	1640
1941	4.57		1830	4.88	1528	1814	4.94	1904	1904	4.69	1909	1909	4.71	1635
1938	4.56		1826	4.90	1525	1804	4.84	1901	1901	4.69	1905	1905	4.66	1629
1937	4.57		1822	4.93	1522	1802	4.93	1898	1898	4.71	1899	1899	4.73	1623
1935	4.64		1818	4.89	1519	1796	4.93	1896	1896	4.64	1895	1895	4.70	1617
1991	4.00		1813	4.98	1519	1795	4.95	1891	1891	4.71	1891	1891	4.74	1612
1988	4.08		1808	4.96	1516	1790	5.03	1889	1889	4.78	1885	1885	4.77	1607

^a Note that the ages given are only approximate estimates based on interpolations of U/Th dated layers! Carbon isotope values are given in ‰ VPDB.

rates of change that are unprecedented for the last 600 years and probably for the whole Holocene.

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References

- Bacastow, R. B., The effect of temperature change of the warm surface waters of the oceans on atmospheric CO₂, *Global Biogeochem. Cycles*, 10, 319–333, 1996.
- Bacastow, R. B., C. D. Keeling, T. J. Lueker, and M. Wahlen, The ¹³C Suess effect in the world surface oceans and its implications for oceanic uptake of CO₂: Analysis of observations at Bermuda, *Global Biogeochem. Cycles*, 10, 335–346, 1996.
- Benavides, L. M., and E. R. M. Druffel, Sclerosponge growth rate as determined by ²¹⁰Pb and Δ¹⁴C chronologies, *Coral Reefs*, 4, 221–224, 1986.
- Black, D. E., L. C. Peterson, J. T. Overpeck, A. Kaplan, M. N. Evans, and M. Kashgarian, Eight centuries of North Atlantic Ocean atmosphere variability, *Science*, 286, 1709–1713, 1999.
- Böhm, F., M. M. Joachimski, H. Lehnert, G. Morgenroth, W. Kretschmer, J. Vacelet, and W.-C. Dullo, Carbon isotope records from extant Caribbean and South Pacific sponges: Evolution of δ¹³C in surface water DIC, *Earth Planet. Sci. Lett.*, 139, 291–303, 1996.
- Broecker, W. S., *The Glacial World According to Wally*, 318 pp., Lamont-Doherty Earth Observatory, Palisades, N. Y., 1995.
- Broecker, W. S., Was a change in thermohaline circulation responsible for the Little Ice Age?, *Proc. Natl. Acad. Sci. U. S. A.*, 97, 1339–1342, 2000.
- deMenocal, P., J. Ortiz, T. Guilderson, and M. Sarnthein, Coherent high- and low-latitude climate variability during the holocene warm period, *Science*, 288, 2198–2202, 2000.
- Druffel, E. R. M., Decade timescale variability of ventilation in the North Atlantic: high precision measurements of bomb radiocarbon in banded corals, *J. Geophys. Res.*, 94, 3271–3285, 1989.
- Druffel, E. R. M., Pulses of rapid ventilation in the North Atlantic surface ocean during the past century, *Science*, 275, 1454–1457, 1997.
- Druffel, E. M., and L. M. Benavides, Input of excess CO₂ to the surface ocean based on ¹³C/¹²C ratios in a banded Jamaican sclerosponge, *Nature*, 321, 58–61, 1986.
- Etheridge, D. M., L. P. Steele, R. L. Langenfelds, R. J. Francey, J. M. Barnola, and V. I. Morgan, Natural and anthropogenic changes in atmospheric CO₂ over the last 1000 years from air in Antarctic ice and firn, *J. Geophys. Res.*, 101, 4115–4128, 1996.
- Francey, R. J., C. E. Allison, D. M. Etheridge, C. M. Trudinger, I. G. Enting, M. Leuenberger, R. L. Langenfelds, E. Michel, and L. P. Steele, A 1000 year high precision record of δ¹³C in atmospheric CO₂, *Tellus, Ser. B*, 51B, 170–193, 1999.
- Friedli, H., H. Löffler, H. Oeschger, U. Siegenthaler, and B. Stauffer, Ice core record of the ¹³C/¹²C ratio of atmospheric CO₂ in the past two centuries, *Nature*, 324, 237–238, 1986.
- Gordon, A. L., Circulation of the Caribbean Sea, *J. Geophys. Res.*, 72, 6207–6223, 1967.
- Grove, J. M., *The Little Ice Age*, 498 pp., Methuen, New York, 1988.
- Gruber, N., C. D. Keeling, and T. F. Stocker, Carbon-13 constraints on the seasonal inorganic carbon budget at the BATS site in the northwestern Sargasso Sea, *Deep Sea Res.*, 45, 673–717, 1998.
- Gruber, N., C. D. Keeling, R. B. Bacastow, P. R. Guenther, T. J. Lueker, M. Wahlen, H. A. J. Meijer, W. G. Mook, and T. F. Stocker, Spatiotemporal patterns of carbon-13 in the global surface oceans and the oceanic Suess effect, *Global Biogeochem. Cycles*, 13, 307–335, 1999.
- Jones, P. D., T. J. Osborn, and K. R. Briffa, The evolution of climate over the last millennium, *Science*, 292, 662–667, 2001.
- Joos, F., R. Meyer, M. Bruno, and M. Leuenberger, The variability in the carbon sinks as reconstructed for the last 1000 years, *Geophys. Res. Lett.*, 26, 1437–1440, 1999.
- Keeling, C. D., and T. P. Whorf, Atmospheric CO₂ records from sites in the SIO air sampling network, in *Trends: A Compendium of Data on Global Change*, Carbon Dioxide Info. Anal. Cent., Oak Ridge Natl. Lab., Oak Ridge, Tenn., 2001. (Available at <http://cdiac.esd.ornl.gov/trends/co2/sio-spl.htm>)
- Keeling, C. D., W. G. Mook, and P. P. Tans, Recent trends in the ¹³C/¹²C ratio of atmospheric carbon dioxide, *Nature*, 277, 121–123, 1979.
- Keigwin, L. D., The little ice age and medieval warm period in the Sargasso Sea, *Science*, 274, 1504–1508, 1996.
- Keir, R., G. Rehder, E. Suess, and H. Erlenkeuser, The δ¹³C anomaly in the northeastern Atlantic, *Global Biogeochem. Cycles*, 12, 467–477, 1998.
- Kitagawa, H., and E. Matsumoto, Climatic implications of the δ¹³C variations in a Japanese cedar (*Cryptomeria japonica*) during the last two millennia, *Geophys. Res. Lett.*, 22, 2155–2158, 1995.
- Laube-Lenfant, E., and C. Pierre, Variability of δ¹³C of ΣCO₂ in ocean waters of the Equatorial Pacific, *Oceanol. Acta*, 17, 633–641, 1994.
- Lazareth, C. E., P. Willenz, J. Navez, E. Keppens, F. Dehaers, and L. André, Sclerosponges as a new potential recorder of environmental changes: Lead in *Ceratoporella nicholsoni*, *Geology*, 28, 515–518, 2000.
- Lean, J. L., O. R. White, and A. Skumanich, On the solar ultraviolet spectral irradiance during the Maunder Minimum, *Global Biogeochem. Cycles*, 9, 171–182, 1995.
- McNichol, A. P., and E. R. Druffel, Variability of the δ¹³C of

- dissolved inorganic carbon at a site in the north Pacific Ocean, *Geochim. Cosmochim. Acta*, 56, 3589–3592, 1992.
- Moore, M. D., C. D. Charles, J. L. Rubenstone, and R. G. Fairbanks, U/Th-dated sclerosponges from the Indonesian Seaway record subsurface adjustments to west Pacific winds, *Paleoceanography*, 15, 404–416, 2000.
- Morrison, J. M., and W. D. Nowlin, General distribution of water masses within the Eastern Caribbean Sea during the winter of 1972 and fall of 1973, *J. Geophys. Res.*, 87, 4207–4229, 1982.
- Nozaki, Y., D. M. Rye, K. K. Turekian, and R. E. Dodge, A 200 year record of carbon-13 and carbon-14 variations in a Bermuda coral, *Geophys. Res. Lett.*, 5, 826–828, 1978.
- Quay, P. D., B. Tilbrook, and C. S. Wong, Oceanic uptake of fossil fuel CO₂: Carbon-13 evidence, *Science*, 256, 74–79, 1992.
- Reitner, J., “Coralline Spongien”. Der Versuch einer phylogenetisch-taxonomischen Analyse, *Berliner Geowiss. Abh., Reihe E*, 1, 1–352, 1992.
- Schmitz, W. J., and M. S. McCartney, On the North Atlantic circulation, *Rev. Geophys.*, 31, 29–49, 1993.
- Schmitz, W. J., and P. L. Richardson, On the sources of the Florida Current, *Deep Sea Res.*, 38, suppl. 1, S379–S409, 1991.
- Sonnerup, R. E., P. D. Quay, A. McNichol, J. L. Bullister, T. A. Westby, and H. L. Anderson, Reconstructing the oceanic ¹³C Suess effect, *Global Biogeochem. Cycles*, 13, 857–872, 1999.
- Sonnerup, R. E., P. D. Quay, and A. McNichol, The Indian Ocean ¹³C Suess effect, *Global Biogeochem. Cycles*, 14, 903–916, 2000.
- Sprintall, J., and M. Tomczak, Evidence of the barrier layer in the surface layer of the tropics, *J. Geophys. Res.*, 97, 7305–7316, 1992.
- Tuiver, M., and P. D. Quay, Changes in atmospheric carbon-14 attributed to a variable Sun, *Science*, 207, 11–19, 1980.
- Swart, P. K., M. Moore, C. Charles, and F. Böhm, Sclerosponges may hold new keys to marine paleoclimate, *EOS, Trans. AGU*, 79, 636–638, 1998.
- Trudinger, C. M., I. G. Enting, R. J. Francey, D. M. Etheridge, and P. J. Rayner, Long-term variability in the global carbon cycle inferred from a high precision CO₂ and δ¹³C ice core record, *Tellus Ser. B*, 51B, 233–248, 1999.
- Watanabe, T., A. Winter, and T. Oba, Seasonal changes in sea surface temperature and salinity during the Little Ice Age in the Caribbean Sea deduced from Mg/Ca and ¹⁸O/¹⁶O ratios in corals, *Marine Geol.*, 173, 21–35, 2001.
- Wörheide, G., P. Gautret, J. Reitner, F. Böhm, M. M. Joachimski, V. Thiel, W. Michaelis, and M. Massault, Basal skeletal formation, role and preservation of intracrystalline organic matrices, and isotopic record in the coralline sponge *Astroclera willeyana* LISTER, 1900, *Bol. R. Soc. Esp. Hist. Nat. (Sec. Geol.)*, 91, 355–374, 1997.
- Zhang, J., P. D. Quay, and D. O. Wilbur, Carbon isotope fractionation during gas-water exchange and dissolution of CO₂, *Geochim. Cosmochim. Acta*, 59, 107–114, 1995.