3-12-2010

The 13C Suess Effect in Scleractinian Corals Mirror Changes in the Anthropogenic CO2 Inventory of the Surface Oceans

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Recommended Citation

Swart, Peter K., Lisa Greer, Brad E. Rosenheim, Chris S. Moses, Amanda J. Waite, A. Winter, Richard E. Dodge, and Kevin Helmle. "The 13C Suess effect in scleractinian corals mirror changes in the anthropogenic CO2 inventory of the surface oceans." Geophysical Research Letters 37, no. 5 (2010).

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GEOPHYSICAL RESEARCH LETTERS, VOL. 37, L05604, doi:10.1029/2009GL041397, 2010

The ^{13}C Suess effect in scleractinian corals mirror changes in the anthropogenic CO_2 inventory of the surface oceans

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Received 4 November 2009; revised 4 January 2010; accepted 20 January 2010; published 12 March 2010.

[1] New $\delta^{13}C$ data are presented from 10 coral skeletons collected from Florida and elsewhere in the Caribbean (Dominica, Dominican Republic, Puerto Rico, and Belize). These corals range from 96 to 200 years in age and were collected between 1976 and 2002. The change in the $\delta^{13}C$ of the skeletons from these corals between 1900 and 1990 has been compared with 27 other published coral records from the Atlantic, Pacific, and Indian Oceans. The new data presented here make possible, for the first time, a global comparison of rates of change in the $\delta^{13}C$ value of coral skeletons. Of these records, 64% show a statistically significant ($p < 0.05$) decrease in $\delta^{13}C$ towards the modern day (23 out of 37). This decrease is attributable to the addition of anthropogenically derived CO_2 (^{13}C Suess effect) to the atmosphere. Between 1900 and 1990, the average rate of change of the $\delta^{13}C$ in all the coral skeletons living under open oceanic conditions is approximately -0.01‰ yr^{-1}. In the Atlantic Ocean the magnitude of the decrease since 1960,-0.019 yr^{-1} ±0.015‰, is essentially the same as the decrease in the $\delta^{13}C$ of atmospheric CO_2 and the $\delta^{13}C$ of the oceanic dissolved inorganic carbon (-0.023 to -0.029‰ yr^{-1}), while in the Pacific and Indian Oceans the rate is more variable and significantly reduced (-0.007‰ yr^{-1} ±0.013). These data strongly support the notion that (i) the $\delta^{13}C$ of the atmosphere controls ambient $\delta^{13}C$ of the dissolved inorganic carbon which in turn is reflected in the coral skeletons, (ii) the rate of decline in the coral skeletons is higher in oceans with a greater anthropogenic CO_2 inventory in the surface oceans, (iii) the rate of $\delta^{13}C$ decline is accelerating. Superimposed on these secular variations are controls on the $\delta^{13}C$ in the skeleton governed by growth rate, insolation, and local water masses. **Citation:** Swart, P. K., L. Greer, B. E. Rosenheim, C. S. Moses, A. J. Waite, A. Winter, R. E. Dodge, and K. Helmle (2010), The ^{13}C Suess effect in scleractinian corals mirror changes in the anthropogenic CO_2 inventory of the surface oceans, *Geophys. Res. Lett.*, *37*, L05604, doi:10.1029/2009GL041397.

1. Introduction

[2] The interpretation of the $\delta^{13}C$ of coral skeletons has principally focused on factors which control the annual variation in the amount of inorganic carbon derived from respiration and influenced by photosynthesis in the internal pool from which calcification takes place [*Swart*, 1983]. The most widely accepted idea is that the $\delta^{13}C$ is controlled by a combination of physiological mechanisms [*Grottoli and Wellington*, 1999], kinetic effects [*McConnaughey*, 1989; *McConnaughey et al.*, 1997], and pH [*Adkins et al.*, 2003]. Moderate increases in the rate of photosynthesis, related to increases in light intensity, appear to increase the $\delta^{13}C$ of the skeleton, while decreases in light result in reduced $\delta^{13}C$ values in the skeleton [*Weber*, 1970]. It has been suggested that $\delta^{13}C$ variations in the skeleton might also be related to changes in growth rate, insolation or other factors affecting the symbiotic relationship between the corals and their zooxanthellae. In addition to the annual variation in $\delta^{13}C$, several workers have remarked upon long term trends towards lower $\delta^{13}C$ values within coral skeletons and attributed these declines to the ^{13}C Suess effect [*Druffel and Benavides*, 1986]. The first paper to make this observation in coral skeletons [*Nozaki et al.*, 1978] noted an approximate 0.4‰ decrease in the $\delta^{13}C$ from 1900 to 1950, about the same amount as had been observed in tree rings [*Damon et al.*, 1978]. Although the conclusions of *Nozaki et al.* [1978] were disputed [*Weil et al.*, 1981], long term decreases in the $\delta^{13}C$ of coral skeletons are well documented [*Asami et al.*, 2005; *Bagnato et al.*, 2004; *Chakraborty and Ramesh*, 1998; *Halley et al.*, 1994; *Kilbourne et al.*, 2007, 2004; *Kuhnert et al.*, 1999, 2000; *Linsley et al.*, 1999; *Moses et al.*, 2006; *Quinn et al.*, 1998; *Schmidt et al.*, 2004; *Swart et al.*, 1996a, 1996b; *Wei et al.*, 2009].

2. Data

[3] The new $\delta^{13}C$ data presented here are from coral skeletons collected in the Atlantic and Caribbean (Table 1 and Figure 1). These corals were mainly taken from water depths of 3 m or less. The samples from the new locations were analyzed in a similar manner to previous specimens [*Swart et al.*, 1996a, 1996b, 1998]. These data have been compared with data archived in the NOAA paleoclimate database (http://www.ncdc.noaa.gov/paleo/paleo.html) (Figure 1 and Table S1).[8] As the data in these studies were collected over

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0094-8276/10/2009GL041397

[8] Auxiliary materials are available in the HTML. doi:10.1029/2009GL041397.

Table 1. Carbon Isotopic Data Reported in This Paper[a]

Species	Location and Depth	1960–19xx[b]	19xx–19xx[c]	Period of Record
Siderastrea siderea	Cheeca Rocks, Florida Keys (3 m)	**−.0274 (.43)**	**−.0093 (.41)**	1777–1994
Siderastrea siderea	Caloosa Rocks, Florida Keys (3 m)	**−.0289 (.41)**	**−.0048 (.26)**	1817–1994
Montastraea faveolata	Crocker Reef, Florida Keys (8 m)	**−.0377 (.49)**	**−.0094 (.32)**	1874–1998
Montastraea faveolata[b]	Elliot Key, Florida Keys (3 m)	**−.0250 (.33)**	**−.0039 (.06)**	1856–1985
Siderastrea sidereal[c]	Dominica (8 m)	**−.0217 (.52)**	**−.0158 (.54)**	1942–2000
Solenastrea bournoni	East Key, Florida Bay (2 m)	**−.0654 (.85)**	**−.0123 (.31)**	1897–1996
Montastraea faveolata[c]	Dominican Republic (3 m)	−.0152 (.19)	**−.0118 (.29)**	1934–1995
Montastraea faveolata[b]	Belize, Glovers Reef (3 m)	+.0087 (.04)	+.0033 (.07)	1822–1976
Montastraea faveolata[c,d]	Belize, Wee Wee Reef (3 m)	**−.0343 (.67)**	**−.0108 (.23)**	1936–2002
Montastraea faveolata	La Paguera (3 m)	**−.0167 (.19)**	−.0022 (.03)	1740–1991

[a] The r^2 value for the regression between age and δ^{13}C is given in brackets and bolded values are statistically significant at the 95% confidence limits.

[b] If the coral does not extend to 1990, then the period of correlation is between 1960 and the end of the record.

[c] If the age of the coral does not extend to 1900, then the period of correlation only extends from oldest age to 1990.

[d] This coral was analyzed at Pennsylvania State University.

a range of different sampling intervals, all data have been interpolated to annual average values using a rectangular interpolation method. For comparative purposes the data have been separated into two time periods, 1960–1990 and 1900–1990. In those corals in which the record did not start at or prior to 1900 the actual period of record has been used. In the following text comparison of trends are considered to be statistically significant at the 95% confidence limits

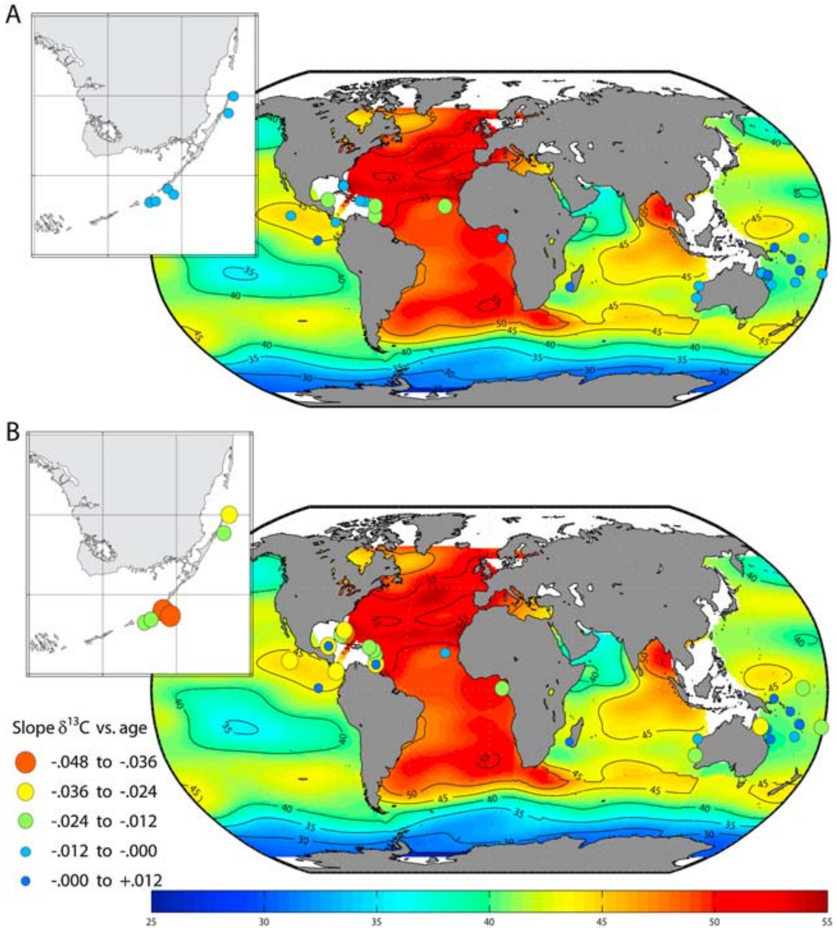

Figure 1. (a) The slope of the relationship between δ^{13}C and age over the time period 1900–1990 superimposed on a map of the inventory of anthropogenic CO_2 (μmol CO_2/kg seawater) in the surface waters [*Key et al.*, 2004; *Sabine et al.*, 2004] similar to the approach used previously [*Grottoli and Eakin*, 2007]. The size of the symbols and the color relates to the magnitude of the slope between the δ^{13}C and age. Large symbols and warmer colors indicate a more negative slope. Insert shows changes in corals from South Florida; corals from enclosed basins such as Florida Bay, Gulf of Kutch and the Red Sea have not been shown. (b) Similar to (a) but for the period 1960–1990. The changes in the CO_2 are greater in the Atlantic compared to the Pacific, particularly for the 1960–1990 period. The larger changes are located in oceans which possess the largest inventory of anthropogenic CO_2 in the surface oceans. See Tables 1 and S1 for all coral data.

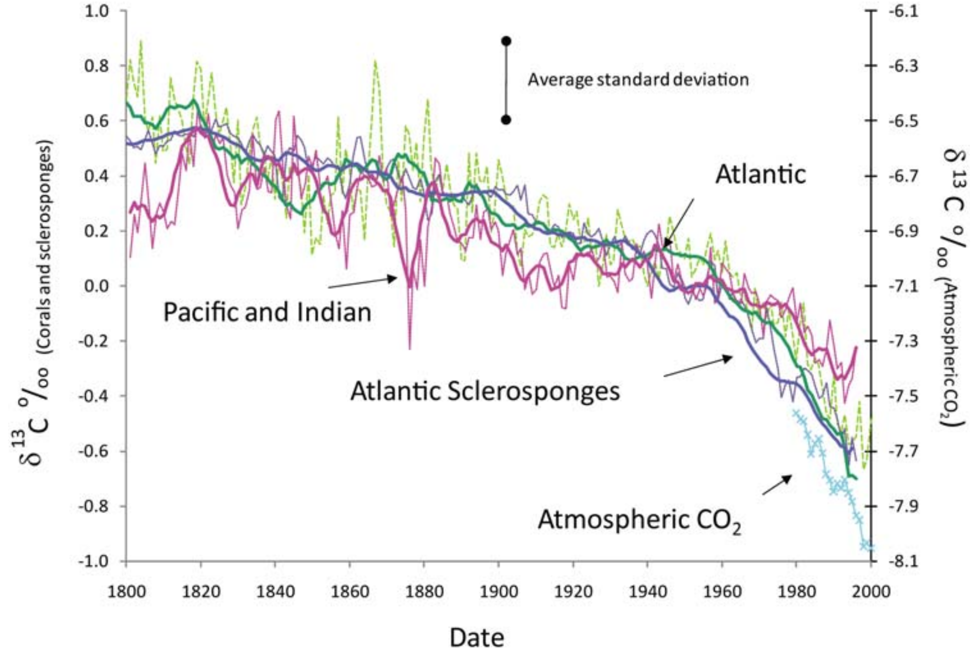

Figure 2. Changes in the δ^{13}C with respect to age for corals from the Atlantic and the Pacific/Indian Oceans compared to published data from sclerosponges [*Böhm et al.*, 1996; *Swart et al.*, 2002; *Waite et al.*, 2007] as shown in Figure 1. All data have been averaged after removing the mean δ^{13}C value of the coral skeleton from 1900 to the present day. The solid lines represent a five year running mean of the data while the dashed lines show the original data. Corals from the isolated basins are not included. The error bar represents an average standard deviation of 0.4‰. The average standard deviation is approximately 0.3 ‰ in the indo-Pacific corals and 0.4‰ in the Atlantic corals. Data on the changes of the δ^{13}C in the atmosphere since 1980 [*Keeling et al.*, 1980] are shown for comparison and indicate similar decreases to those seen in the corals and sclerosponges.

[*Fisher*, 1958]. Comparisons between the means of slopes between oceans were tested using a Student's t-test and considered to be statistically significant at the 95% confidence limits.

3. Results

[4] Of the 37 corals included in this study, 28 (78%) show an inverse correlation between δ^{13}C and age and 23 have statistically significant negative correlations with respect to time over the period 1900-end of the record (the corals had varying collection dates and hence the period of the record varies) (see Table S1). Over the time period 1960–1990, 19 of the corals have statistically significant negative correlations with respect to age and the slopes are significantly steeper than over the period 1900–1990. Separating the corals into different oceans (and ignoring the corals from enclosed basins such as Florida Bay, Gulf of Kutch and the Gulf of Aquaba), those from the Atlantic Ocean have much steeper slopes (−0.0074 ± 0.0065‰ yr^{-1}) between δ^{13}C and age and more significant correlations compared to those from the Pacific (−0.0027‰ yr^{-1} ±0.0052) and Indian Oceans (−0.0024‰ yr^{-1} ±0.0047) (Table S1) over the time period 1900–1990. The average slope for the Atlantic corals is statistically significantly different from the Pacific corals at the 95% confidence limits. There is no significant difference between the rate of decrease in the δ^{13}C in corals in the Pacific and Indian Oceans. The significant difference in the relationship between δ^{13}C and age between the Atlantic and Pacific corals is also evident over the interval 1960–1990 (Figure 2).

4. Discussion

[5] The decrease in the δ^{13}C of the coral skeleton normally might be interpreted as a reduction in the amount of insolation over time. Since there is no evidence of such a global decrease in insolation this explanation can probably be ruled out. Another explanation might be that more negative values are associated with faster rates of skeleton formation. While the growth rates for many of the previously published studies have not been published (Table S1), those for which data are available show no evidence of an increase in extension rate coupled with a decrease in δ^{13}C towards the present day. Another pattern which might be evident in large coral colonies as they grow towards the water surface would reflect an increase in insolation and therefore an increase in δ^{13}C. This is the opposite trend to that observed in most of the corals. Changes in the δ^{13}C of some calcareous organisms have been linked to ontogeny with more depleted values evident in older organisms. This possibility was discarded as there was no relationship between the overall age of each colony and the eventual decrease in the δ^{13}C. For example, the same trends were seen in colonies ~100 and ~300 years old.

[6] A final explanation for the relatively consistent trends in coral δ^{13}C, and one preferred in this paper, is that the δ^{13}C of the corals is driven by the anthropogenic addition of $^{12}CO_2$ to the oceans. This change is known as the ^{13}C Suess

effect [*Druffel and Benavides*, 1986]. The difference in the magnitude of the slope of the δ^{13}C with respect to time between the Atlantic and Pacific generally reflects the fact that CO_2 is being recharged into the oceans in the Atlantic [*Key et al.*, 2004; *Sabine et al.*, 2004], while in the Pacific Ocean, more deep water is being returned to the surface (Figure 1). This is evident in the fact that the slope in the corals in the Atlantic (−0.019‰ yr^{-1} ±0.015), between the δ^{13}C and age over the time interval 1960 and 1990, is essentially identical to that of the δ^{13}C of atmospheric CO_2 (−0.023 to −0.029‰ yr^{-1}) [*Keeling et al.*, 2005] and the δ^{13}C of the oceanic dissolved inorganic carbon (DIC) [*Gruber et al.*, 1999] (Figure 2). This compares to minimal average changes of between only −0.0066 and −0.0057‰ yr^{-1} in the corals from the Pacific and Indian Oceans respectively.

[7] Anthropogenic carbon exchange between the atmosphere and the ocean has also been recorded in Δ^{14}C of coral skeletons. Using age-corrected radiocarbon records from corals, *Grottoli and Eakin* [2007] showed that uptake of ^{14}C has been greatest in the ocean gyres, supporting conclusions reached by *Quay et al.* [1992] that anthropogenic CO_2 uptake was higher there. Between 1960 and 1970, trends in coral Δ^{14}C qualitatively resemble trends in anthropogenic CO_2 uptake rates of the oceans. The correlation of the δ^{13}C records presented here and the anthropogenic CO_2 inventory in the surface oceans indicates that corals are recording the anthropogenic CO_2 uptake by the oceans and that this signal often outweighs the physiological signals recorded in δ^{13}C records.

[8] The changes over time in the δ^{13}C of corals are similar to variations in the δ^{13}C measured in the skeletons of sclerosponges reported by various other workers, both in the Atlantic and the Pacific [*Böhm et al.*, 1996; *Druffel and Benavides*, 1986; *Swart et al.*, 2002; *Wörheide*, 1998; *Waite et al.*, 2007]. In the first study on sclerosponges, a change of about 0.5‰ in the δ^{13}C of the skeleton was measured from pre-industrial times to 1970 [*Druffel and Benavides*, 1986]. Later work determined that a further 0.4‰ change occurred between 1970 and 1990 [*Böhm et al.*, 1996], giving a mean change of −0.01‰ yr^{-1} over the period 1900–1990 for sclerosponges from the Caribbean. This change is similar to that observed in another study in the Bahamas [*Swart et al.*, 2002] on sclerosponges between 1900–1992 (−0.0093 ‰ yr^{-1}) and the average change for corals over the same period presented in this study (−0.0085 ‰ yr^{-1} ± 0.0060). The δ^{13}C changes in sclerosponges from Pacific locations, like the Coral Sea [*Böhm et al.*, 2000] and the Great Barrier Reef [*Wörheide*, 1998] (−0.0070 and −0.0039 ‰ yr^{-1}), are also significantly less than those observed in the Atlantic and similar to the mean change observed for the Pacific corals in this study (−0.0037 ‰ yr^{-1} ± 0.0049) (Figure 2). *Böhm et al.* [1996] pointed out that the change in the δ^{13}C of the sclerosponges was significantly less than the estimated 1.4‰ decrease based on HCO_3 equilibrium with air CO_2. This discrepancy was postulated to be a result of incomplete equilibrium between the surface oceans and the atmosphere. However, as measurements of direct changes in the δ^{13}C of atmospheric CO_2 have only been available since approximately 1980, the estimate of a 1.4‰ change may be incorrect. The change in the δ^{13}C of atmospheric CO_2 from 1980–2000 is approximately 0.0235 ‰ yr^{-1} which is not only similar to the change in the δ^{13}C of sclerosponges over that interval, but also similar to the record observed in Atlantic corals (−0.027‰ yr^{-1}) for the same period.

[9] One problem associated with using the δ^{13}C of coral skeletons as records of the δ^{13}C of atmospheric CO_2 is that while most corals seem to exhibit the decrease, there are exceptions. These include instances in which (i) there is either an increase or no significant change in the δ^{13}C, (ii) there are decadal increases and decreases in the δ^{13}C which bear no relationship to the known changes in the δ^{13}C of atmospheric CO_2, and (iii) the decrease in the coral δ^{13}C is greater than that observed in atmospheric CO_2. Perhaps the easiest of these to explain is when the decrease in the skeleton is greater than expected. These instances all occur in restricted environments such as Florida Bay, where enhanced input of organic material is oxidized to release isotopically depleted CO_2. Corals that show increases in the δ^{13}C were observed at several locations. There is no definitive explanation for these anomalies, but one possibility is that these corals received a greater amount of light as they grew towards the surface. The decadal variations seen in many of the corals are perhaps the most puzzling of the deviations from the negative trend as the timing of these variations is not consistent even between corals which are closely located. For example, records from five sites in South Florida representing two different species all show the decrease in δ^{13}C towards the present day, but superimposed on this decrease are decadal variations of up to 0.5‰. Although these higher order variations in δ^{13}C are similar, they do not appear to correlate between the records. As these sites receive more or less similar amounts of insolation and experience similar temperatures, variations in the δ^{13}C of the skeleton might be related to a number of factors such as specific physiological differences between the colonies, shading of a colony by another coral or organism for an extended period, local differences in the nutrient concentration in the water, variations in growth rate or skeletal density or some combination of all of these or other unknown factors.

5. Conclusions

[10] This paper has shown that most corals exhibit a decrease in the δ^{13}C of the skeletons towards the present day, a change which can be attributed to the addition of anthropogenic CO_2. The magnitude of this decrease is greater in the Atlantic compared to the Indian and Pacific Oceans and can be modified by local bathymetric conditions and the physiological activity of the corals. If this pattern is truly a global signal then these trends can be used to correct the δ^{13}C records and reveal the true regional and physiological controls on the δ^{13}C in the coral skeleton.

[11] **Acknowledgments.** The authors wish to thank Harold Hudson who cored the corals from Biscayne National Park, the Peterson Keys, and Glovers Reef, John Halas who cored the coral from East Key, Otto Rutten who helped core the corals from Cheeca, Caloosa, and Crocker reefs, Lila Gerald who obtained the core from Wee Wee Cay, and Phil Kramer and Jim Leder who helped core corals from Tobago. Collection of cores and geochemical analyses were supported by grants from NOAA, NURC, NCORE, SFWMD, and the University of Miami. We especially thank Mark Eakin for funding from the NOAA Coral Reef Watch Program.

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