RADIOCARBON IN ANNUAL CORAL RINGS OF FLORIDA

Ellen M. Druffel and Timothy W. Linick

Mount Soledad Radiocarbon Laboratory, Department of Chemistry
University of California, San Diego, La Jolla, California 92093

Abstract. Radiocarbon measurements on a 175-year (A.D. 1800 to 1974) growth of the coral Montastrea annularis from The Rocks reef off the Florida Keys reveal the rate of local uptake of fossil fuel CO_2 and bomb ^{14}C by surface ocean waters of the Gulf Stream. In the nineteenth century, the pre-bomb, pre-industrial $\Delta^{14}C$ value of surface ocean waters as seen in these corals of the Gulf Stream in the Florida Straits was $-51 \pm 2‰$. By 1955, uptake of industrial CO_2 by these waters had lowered the $\Delta^{14}C$ values to about $-61‰$. The results can be used to make predictions regarding anthropogenic CO_2 that can be expected to enter the oceans in future decades. Bomb-produced ^{14}C is found to be present in the corals in comparable concentrations to that found in the dissolved inorganic carbon (DIOC) of the North Pacific and North Atlantic Oceans.

Introduction

Radiocarbon measurements of dissolved inorganic carbon (DIOC) in ocean waters began in the mid-1950's (*Bien, et al.*, 1960; *Broecker, et al.*, 1960; *Rafter*, 1968; *Rafter and Fergusson*, 1958; *Rubin and Alexander*, 1958). They were used to identify water masses and to trace their general circulation patterns within the world's oceans. With the introduction of bomb-produced ^{14}C to the ocean waters, ^{14}C measurements of DIOC (*Linick and Suess*, 1972; *Linick*, 1975; *Ostlund, et al.*, 1974; *Ostlund, et al.*, 1976; *Broecker, et al.*, in press) revealed useful information about upwelling in equatorial and polar regions. Pre-industrial $\Delta^{14}C$ values for equatorial surface waters of the Pacific and the Atlantic (*Broecker, et al.*, 1960; *Rafter and Fergusson*, 1958; *Rafter*, 1968; *Rubin and Alexander*, 1958; *Linick and Suess*, 1972; *Linick*, 1975) can be estimated to average about 5 to 10‰ lower than their respective mid-gyre values. Radiocarbon values for Antarctic surface water were 60 to 70‰ lower than those of the gyres (*Broecker, et al.*, 1960; *Linick*, 1975).

Combustion of fossil fuel since the turn of the century is generally assumed to have caused, by 1978, an 11 to 15% rise of the CO_2 content of the atmosphere (*Keeling*, 1973). According to Keeling, this rise represents a little over half of the CO_2 actually released into the atmosphere by coal and oil burning. The other half of this anthropogenic CO_2 is believed to have been mostly taken up by the oceans, although some of it may have gone into the land biota. The results of the radiocarbon measurements of coral carbonate, listed in Table I (on microfiche), show quantitatively the amounts of fossil fuel CO_2 that have entered the surface waters of the Gulf Stream. The fate of fossil fuel CO_2 is of utmost importance because it may cause a rise in global temperature as a result of the so-called "greenhouse effect" (*United Nations Department of Economic and Social Affairs*, 1956).

Radiocarbon measurements on this coral also demonstrates the rise in $\Delta^{14}C$ during and after the time of input of bomb ^{14}C into the atmosphere. This rise can be compared to that obtained in measurements of radiocarbon in DIOC of surface waters of the North Pacific (*Linick*, 1975) and North Atlantic Oceans (*Ostlund, et al.*, 1974; *Ostlund, et al.*, 1976). A simple three-box model appears to fit the data reported here for the uptake of fossil fuel CO_2 as well as that of bomb ^{14}C by the surface waters.

Pre-anthropogenic concentrations of ^{14}C in atmospheric CO_2 are well investigated (*Cain and Suess*, 1976; *Suess*, 1970; *Lerman, et al.*, 1970), while corresponding data for marine DIOC are almost absent. We can show now from the data represented here that during the time from A.D. 1800 to 1900 coral skeletons had an average value of $\Delta^{14}C$ equal to $-51 \pm 2‰$ with no significant variation from this value.

Coral Samples

Knutson, et al. (1972), were the first to conclusively demonstrate that the banding of reef-building corals is annual. Both radiochemical methods (*Emiliani*, in press) and field observations (*Hudson, et al.*, 1976) show that Montastrea annularis off the Florida coast produce high-density aragonitic skeletons during the warm summer months of June through September and thicker, less dense bands, during the cooler months of October through May.

The collection site of the coral head at The Rocks (24°57'N, 80°33'W) is located on a reef tract approximately one km offshore from Plantation Key in four meters of water (see Figure 1). The Florida Current, a part of the Gulf Stream System, is located four km to the south. The water on the reef tract has an average salinity of 36.0‰ (*Smith, et al.*, 1950). It is supplied mainly by Florida Current surface water of salinity 36.6‰ (*Siewell*, 1938), admixed with a small amount of Florida Bay water from north of the Keys. As there is no reason to believe that DIOC ^{14}C levels in the bay are significantly different from those of surface waters of the Florida Current, radiocarbon levels on the reef tract should be nearly the same as those of the surface water of the Florida Current. Upwelling is non-existent in this area (J.H. Hudson, personal communication). Dissolution of carbonate sediments on the reef tract does not occur, as the sediment is 80-90% aragonite (E.A. Shinn, personal communication). Aragonite does not exchange its CO_2 with other carbonates, nor does it dissolve in surface waters to any significant degree.

A 3.1-meter core of continuous Montastrea annularis growth was slabbed (4 mm thick) in the direction of coralite growth and x-rayed (see Figure 2) as described by *Knutson, et al.* (1972). Radiocarbon data from the last 1.5 meters of the core, spanning the time period from A.D. 1800 to 1974, are reported here. The results from the remaining 1.6 meters will be published in a subsequent paper. As shown in Figure 2, annual rings can be clearly recognized. The core was sectioned into yearly growth rings. Radiocarbon analyses on samples consisting of five annual rings each were used for coral that had grown from 1800 to 1935. For the time period 1936 to 1974, samples representing one year of growth each were used. Each sample was dissolved in hydrochloric acid. The evolved CO_2 was converted to acetylene gas, via lithium carbide, and this acetylene was aged at least three weeks to allow for the decay of ^{222}Rn (3.8-day half life). All samples more recent than 1935 were counted for two days in each of two stainless steel gas proportional beta counters with volumes of 1.0 liter and 400 cc, respectively. Two quartz gas proportional beta counters with volumes of 2.4 and 2.8 liters were used for two-day countings of the five-year samples (older than 1936). Mass spectrometric $\delta^{13}C$ determinations were made on all samples for correction of isotope fractionation. The $\delta^{13}C$ of all the samples is close to that of DIOC in sea water (averages 0 to + 2‰), because the origin of the coral's calcium carbonate skeleton is mostly marine DIOC which is in equilibrium with atmospheric CO_2. Metabolic CO_2 incorporated into the skeleton from the coral polyp itself does not have any significant effect upon the $\Delta^{14}C$ values because the radiocarbon content of the coral's food (zooplankton) is approximately the same as that of DIOC of the ocean water (*Williams and Linick*, 1975). Once the aragonitic skeleton is accreted, it does not exchange with carbonate from the sea water and thus remains a permanent record of past radiocarbon levels.

The Pre-Anthropogenic $\Delta^{14}C$ Values

Table I (on microfiche) lists the results of radiocarbon measurements for Montastrea annularis growth from A.D. 1800 to 1974[1] The $\Delta^{14}C$ values are reported in per mille (*Broecker and Olson*, 1961) based on a 0.95 NBS oxalic acid standard. All $\Delta^{14}C$ values are normalized to a $\delta^{13}C$ of $-25‰$ and for ^{14}C decay from the time of ring formation to A.D. 1950. The

[1] Table 1 is available on microfiche. Order from American Geophysical Union, 1909 K Street, N. W., Washington, D. C. 20006. Document L78-004; $1.00. Payment must accompany order.

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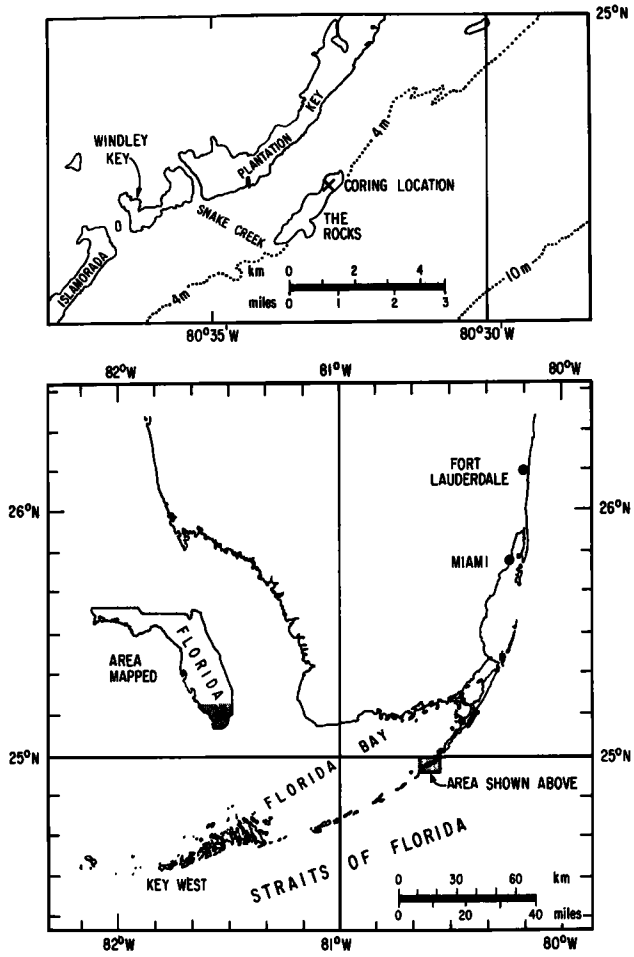

Fig. 1. Map of southern Florida and the Florida Keys. Upper portion shows the area where The Rocks coral reef grows.

results show that $\Delta^{14}C$ for pre-bomb, pre-industrial surface ocean waters off the south Florida coast was constant throughout the 1800's, averaging $-51 \pm 2‰$. This value corresponds to an apparent age of 420 years. It can be compared with the $-38‰$ value calculated by *Broecker* (1960) for the pre-bomb, pre-fossil fuel value for the DIOC of the western North Atlantic mid-gyre waters. A least squares analysis of these coral data yields no significant slope. As seen from tree ring analyses, the atmospheric $\Delta^{14}C$ during this period has been found to be 0‰ (*Cain and Suess*, 1976; *Suess*, 1970; *Lerman, et al.*, 1970). This 5% depletion in ^{14}C concentration of surface waters is the result of two mechanisms: (1) Diffusion of older waters from intermediate depths, with an apparent age of approximately 600 to 900 years, dilutes the radiocarbon levels in the ocean's surface layer; (2) Small rate constants delay the establishment of equilibrium between the troposphere and surface ocean.

Fossil Fuel CO_2

The combustion of fossil fuel since the late nineteenth century had by 1955 increased the CO_2 content of the atmosphere by 6% (*Revelle and Suess*, 1957). Carbon dioxide originating from the burning of fossil fuels contains no measurable ^{14}C. As a result, this "dead" gas has diluted the existing atmospheric CO_2 and has lowered the atmospheric ^{14}C concentration. This decrease (the Suess effect) was first observed in tree rings. It was found to be $33 \pm 10‰$ by 1955 in the northern hemisphere (*Revelle and Suess*, 1957; *Münnich and Vogel*, 1958; *Brannon, et al.*, 1957; *Houtermans, et al.*, 1967). The Suess effect can also be expected to decrease surface ocean ^{14}C levels. Indeed, Figure 4 shows a decrease of $\Delta^{14}C$ in coral from 1900 to 1955. Note that the four points for 1938, 1943, 1948 and 1953 are averages of five $\Delta^{14}C$ measurements each, and error bars are standard deviations of those five points.

An exponential curve, fitted through the experimental values from 1900 to 1955, is shown in Figure 4 as a solid line. This type of fit is used because the input of fossil fuel CO_2 to the atmosphere has been nearly exponential since its onset in the late 1800's (*Revelle and Suess*, 1957; *Brannon, et al.*, 1957). In this way, an 11‰ decrease in DIOC radiocarbon from 1900 to 1955 is apparent.

Bomb ^{14}C

The testing of thermonuclear devices during the late 1950's and early 1960's released large amounts of neutrons, which reacted with ^{14}N in the atmosphere to form ^{14}C. After rapid oxidation of the ^{14}C atoms to $^{14}CO_2$, the ^{14}C concentration of tropospheric CO_2 in the northern hemisphere temporarily reached values a factor of two above normal (Figure 3). This ^{14}C "bomb spike" decreased during the following years, primarily by isotope exchange with the DIOC of the oceans. The coral data reported here (Figure 4) show that, as early as 1959, bomb ^{14}C was present in observable amounts in Gulf Stream surface waters. Its maximum $\Delta^{14}C$ value of 152‰ was reached around 1969. This time delay between the atmospheric and oceanic $\Delta^{14}C$ maxima shows that several years are required for the atmosphere and the surface ocean to approach a steady state. Similar $\Delta^{14}C$ values were obtained by GEOSECS in 1972-73 for DIOC in the surface waters of the Atlantic Ocean; in the mid-North Atlantic $\Delta^{14}C$ values of about 150 to 185‰ prevailed during that time (*Ostlund, et al.*, 1974; *Ostlund, et al.*, 1976).

In the northern mid-Pacific, $\Delta^{14}C$ values for DIOC in surface waters (*Linick*, 1975) were similar to those for the corals shown in Figures 3 and

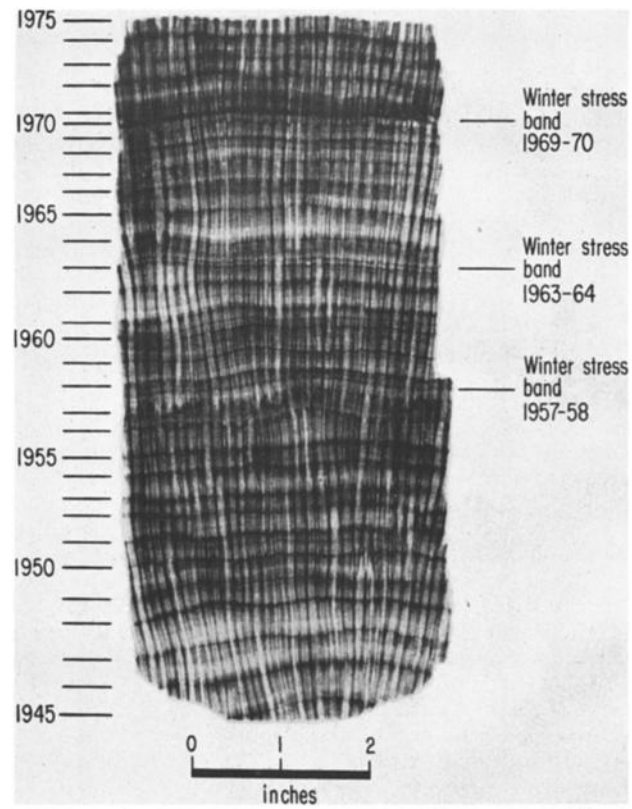

Fig. 2. X-radiograph of part of the Montastrea annularis coral core used for radiocarbon measurements. It was collected at The Rocks coral reef off the Florida Keys. The coral was cored in the direction of growth. A 4mm thick slab was cut and x-rayed as described by *Knutson, et al.* (1972). High density (dark) bands represent coral accretion during warm water months (June through September), low density bands during cold months (October through May) (*Hudson, et al.*, 1976). Additional dark bands, otherwise known as "stress bands" interrupting normal winter growth, represent accretion during an unusually cold winter. These "stress bands" are apparent for the winters of 1957-58, 1963-64 and 1969-70. They are less pronounced for the winter of 1960-61.

4. Bomb ^{14}C was first detected there in the late 1950's. Its maximum of 160‰ was reached around 1970. Bomb ^{14}C in equatorial surface waters is considerably diluted due to the upwelling of subsurface waters having diminished ^{14}C concentrations.

The origin of Gulf Stream waters in the Florida Straits is mainly the southwestern Sargasso Sea and the North Equatorial Current (*Iselin*, 1936; *Stommel*, 1965). Less than one-third of the water originates in the South Atlantic. Therefore, as we might expect, Gulf Stream waters responded to atmospheric bomb ^{14}C somewhat like the North Pacific and North Atlantic mid-oceanic gyre surface waters, but dissimilar to equatorial surface waters where significant upwelling occurs.

Conclusions

The coral data presented here give the first accurate information on pre-fossil fuel concentrations of ^{14}C in surface water DIOC. $\Delta^{14}C$ values of -51 ± 2‰ prevailed with no significant variation during the time period from A.D. 1800 to 1900.

The presence of both fossil fuel CO_2 and bomb ^{14}C in annual coral rings from the Gulf Stream near the Florida coast can be recognized. The bomb ^{14}C observed by us for the Gulf Stream is in some ways similar to that of mid-gyre surface waters in the oceans of the world. If one applies a simple three-box model to the situation where the three boxes are the troposphere, the surface ocean (to about 100m depth where total inorganic carbon of the troposphere equals that of the surface ocean) and the deep ocean, then one can make the following statement. Using known atmospheric $\Delta^{14}C$ values (*Nydal*, in press), a close fit of the bomb $\Delta^{14}C$ measurements in coral growth from 1959 to 1974 requires apparent residence

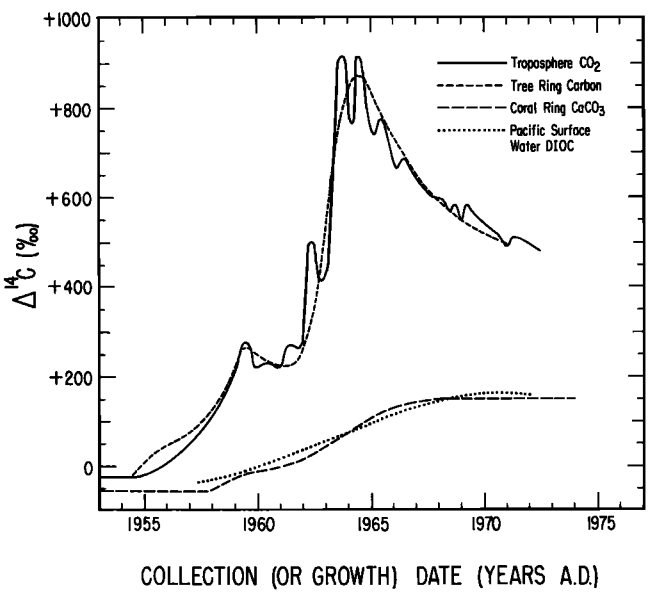

Fig. 3. The $\Delta^{14}C$ trends for troposphere, surface oceans and land biota during the period affected by bomb ^{14}C. (a) The $\Delta^{14}C$ measurements by *Nydal* (in press) for tropospheric carbon dioxide. Monthly averages for numerous stations in the northern hemisphere (average latitude 28°N) were used to obtain a smoothed curve (after *Linick*, 1975). Annual peaks in $\Delta^{14}C$ represent the yearly "spring leaks" with increased exchange between stratosphere and troposphere; (b) The $\Delta^{14}C$ measurements by *Cain and Suess* (1976) for annual tree rings of a Bear Mountain Oak from rural New York state. The wood was treated with acetone, then with heated alkali and acid. The originally published $\Delta^{14}C$ values (*Cain and Suess*, 1976) were recalculated with 0.95 NBS oxalic acid as standard. The slight elevation of about 50‰ during 1954 to 1957 is caused by the "heartwood effect" i.e. the transfer of lignin to earlier rings; (c) $\Delta^{14}C$ for annual Montastrea annularis coral rings from The Rocks coral reef off the Florida Keys (Figure 4); (d) The $\Delta^{14}C$ of dissolved inorganic carbon (DIOC) in the surface waters of the North Pacific gyre (*Linick*, 1975). Radiocarbon measurements were averaged for a latitude range of 15°N to 27°N, and a longitude range of 140°E to 120°W.

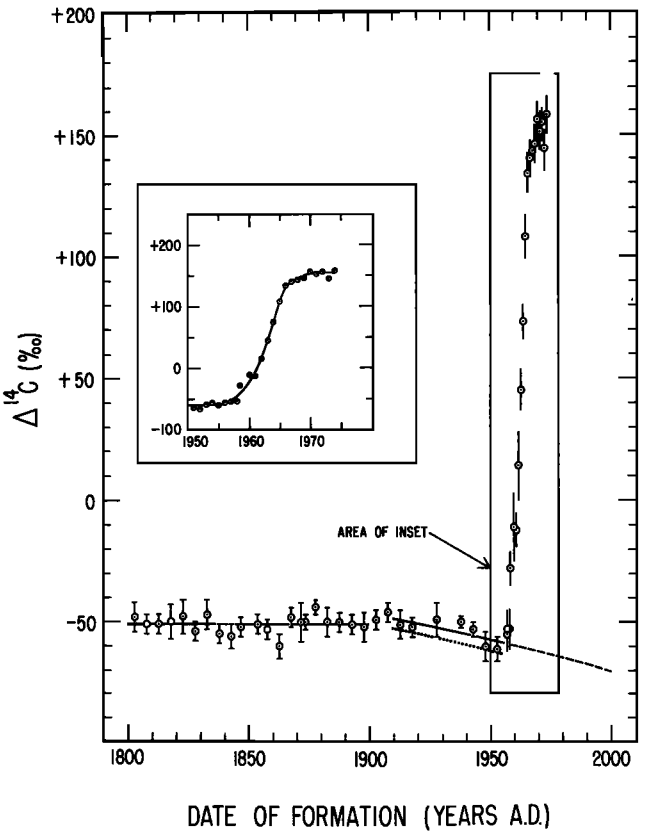

Fig. 4. The $\Delta^{14}C$ for Montastrea annularis collected from The Rocks during its growth period from 1800 to 1974. Measurements for 1800 to 1935 were made on 5-year samples, for 1936 to 1974 on individual year samples. Points for 1938, 1943, 1948 and 1953 are averages obtained from five individual measurements (see Table I, on microfiche); error bars for these four points represent the standard deviations of the five $\Delta^{14}C$ values. Error bars for all other measurements represent one-sigma counting errors. The solid line through points from 1800 to 1900 represents the average $\Delta^{14}C$ of the coral (thus for surface ocean waters of the Gulf Stream) in the nineteenth century, viz. -51 ± 2‰. The solid line through points from 1900 to 1955 represents an exponential curve fitted through the experimental $\Delta^{14}C$ values for the time during which fossil fuel CO_2 was present in the atmosphere. The dashed line is an extrapolation of the exponential curve indicating the future uptake of fossil fuel CO_2. The dotted line represents the calculated $\Delta^{14}C$ values using a simple three-box model (see text) for the uptake of fossil fuel CO_2 by surface ocean waters in this area.

times for carbon dioxide in the atmosphere (with respect to transfer to the surface ocean) and in the surface ocean (with respect to transfer to the deep ocean) of 14 and 8.5 years, respectively. Using these values, the predicted drop by 1955 in the radiocarbon of Gulf Stream surface waters due to the input of fossil fuel CO_2 (dotted line, Figure 4) is 12‰. This agrees with the experimentally determined decrease of 11‰ found in this work.

Extrapolation of the exponential curve fitted to the experimental $\Delta^{14}C$ values between 1900 and 1955 predicts future uptake of excess CO_2 from fossil fuel combustion (dashed line, Figure 4). If the input of fossil fuel CO_2 to the atmosphere continues to grow exponentially, then an additional $\Delta^{14}C$ decrease of 12‰ can be expected by the year A.D. 2000 (from 1955) for the DIOC of Gulf Stream waters.

^{14}C concentrations in the DIOC of the surface layers of the northern Pacific and Atlantic Oceans are slightly higher than that of the corals in the Florida Straits. This may be a result of some North Equatorial Current water (subject to upwelling) entering the Gulf Stream System.

It must be pointed out that this one set of $\Delta^{14}C$ measurements is by no means sufficient for the purpose of examining the uptake of industrial CO_2 and bomb ^{14}C by the surface waters of the world's oceans. Many more coral series from varying localities must be analyzed in order to obtain a firm handle on this problem.

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