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# Carbon isotope constraints on vertical mixing and air-sea $CO_2$ exchange

Stewart J. Fallon,[1] Thomas P. Guilderson,[1,3] and Ken Caldeira[2]

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[1] We have developed a ~45 year carbon isotope record ($\delta^{13}C$, $\Delta^{14}C$) from the coralline sponge *Acanthochaetetes wellsi* from Vanuatu in an effort to examine air-sea $CO_2$ exchange using both the $\delta^{13}C$ Suess effect and the bomb-$^{14}C$ transient. From 1953 to 1999 $\delta^{13}C$ decreased by 0.9‰. Pre-bomb $\Delta^{14}C$ is -59‰, consistent with coral based estimates from the same region and the post-bomb maximum (+121‰) is achieved in 1973. A 1-D box-diffusion model was employed to quantify vertical diffusivity and air-sea exchange rates. The model suggests that a low vertical diffusion rate (0.1 $cm^2$ $s^{-1}$) coupled with a moderate $CO_2$ exchange rate produces the overall observed shape of the pre-post bomb $\Delta^{14}C$ record and the general large scale features of the $\delta^{13}C$ time series. These parameters are on the low end of values used in ocean-carbon GCMs but are consistent with microscale tracer experiments. *INDEX TERMS:* 4504 Oceanography: Physical: Air/sea interactions (0312); 3339 Meteorology and Atmospheric Dynamics: Ocean/atmosphere interactions (0312, 4504); 4842 Oceanography: Biological and Chemical: Modeling. **Citation:** Fallon, S. J., T. P. Guilderson, and K. Caldeira, Carbon isotope constraints on vertical mixing and air-sea $CO_2$ exchange, *Geophys. Res. Lett.*, *30*(24), 2289, doi:10.1029/2003GL018049, 2003.

## 1. Introduction

[2] One of the strongest constraints on the exchange and uptake of anthropogenic carbon dioxide ($CO_2$) by the ocean is derived from systematic and secular variations of the carbon isotopic signature of the dissolved inorganic carbon (DIC) pool as a consequence of the burning of $^{13}C$ and $^{14}C$ depleted fossil fuel $CO_2$ [*Broecker et al.*, 1985; *Quay et al.*, 1992]. The time-history of $^{14}C$ is complicated by atmospheric nuclear weapons testing in the late 1950s and early 1960s when the amount of radiocarbon ($^{14}C$) in the atmosphere doubled. The different time-histories of oceanic $^{13}CO_2$ and $^{14}CO_2$ are a potential tool to study the rates of $CO_2$ uptake.

[3] Observations of spatial and temporal variations in both $\delta^{13}C$ and $\Delta^{14}C$ of DIC are sparse, and are primarily from samples taken during GEOSECS in the 1970s, TTO/SAVE (1985) and the World Ocean Circulation Experiment (WOCE) of the 1990s. These discrete snap-shots are augmented by $\Delta^{14}C$ time-series in biogenic archives (corals) that have been shown to be equivalent to DIC when corrected for mass-dependent fractionation using coralline $\delta^{13}C$ [*Druffel*, 1987; *Guilderson et al.*, 1998; *Nozaki et al.*, 1978]. Unfortunately, the $\delta^{13}C$ time-history in coral skeletons is complicated by vital-effects [e.g., *Guilderson and Schrag*, 1999; *Swart et al.*, 1996] such that we can not use a dual-tracer approach to reconstruct both the $^{13}C$ and $^{14}C$ history from hermatypic reef-building corals.

[4] Estimates of the current ocean $CO_2$ uptake are derived from a combination of data-based estimates [e.g., *Broecker et al.*, 1985; *Quay et al.*, 1992] and ocean general circulation models [*Orr et al.*, 2001]. Estimates based upon $\delta^{13}C$ measurements are hampered due to the large natural DIC spatial and seasonal to interannual variability, and the lack of high quality historical data. Carbon-based measurements can be used to evaluate ocean GCMs used to predict future ocean $CO_2$ uptake [e.g., *Duffy and Caldeira*, 1995; *Orr et al.*, 2001].

[5] We have resolved the time varying $\delta^{13}C$ and $\Delta^{14}C$ surface water history recorded in the skeleton of a calcareous sponge *Acanthochaetetes wellsi*, from Vanua Lava, Vanuatu in the southwest Pacific. The $pCO_2$ difference method [*Takahashi et al.*, 2002; *Tans et al.*, 1990] implies that this region is a sink for atmospheric $CO_2$. Unlike their coral cousins, sclerosponges deposit their skeletons in $\delta^{18}O$ and $\delta^{13}C$ isotopic equilibrium [*Bohm et al.*, 1996; *Druffel and Benavides*, 1986]. We compare the time varying response of $\delta^{13}C$ and $\Delta^{14}C$ resolved in this record with that simulated in a one-dimensional box diffusion model in an effort to constrain the most parsimonious solution utilizing three parameters: air-sea exchange, vertical diffusivity, and upwelling rates.

## 2. Methods

[6] A 75 mm diameter sclerosponge (*Acanthochaetetes wellsi*) was collected off Vanua Lava, Vanuatu (13.8 S, 167.5 E) in July 1999 (Figure 1a) at a depth of 10 m. The basal skeleton of this sponge is constructed of high Mg-calcite. The sample was cut into a 5-mm thick slab, cleaned in Milli-Q water and dried at 40°C. Samples were milled sequentially in 0.5 mm increments and every fifth sample was analyzed. Subsamples (~150 μg) were analyzed on a Finnigan MAT 251 with a Kiel carbonate device using 105% $H_3PO_4$ at 90°C [*Gagan et al.*, 1994]. Stable isotope data is reported relative to V-PDB with an average analytical precision of ±0.03‰. $^{14}C$ sample splits (~7 mg) were evacuated, heated and acidified in individual chambers with orthophosphoric acid at 90°C [*Guilderson et al.*, 1998]. The $CO_2$ was purified, trapped, and converted to graphite using an iron catalyst following a method similar to that described by *Vogel et al.* [1987]. The $^{14}C$ results are reported as age-

[1]Center for Accelerator Mass Spectrometry, Lawrence Livermore National Laboratory, Livermore, California, USA.

[2]Climate and Carbon Cycle Modeling Group, Lawrence Livermore National Laboratory, Livermore, California, USA.

[3]Also at Department of Ocean Sciences and Institute of Marine Sciences, University of California, Santa Cruz, California, USA


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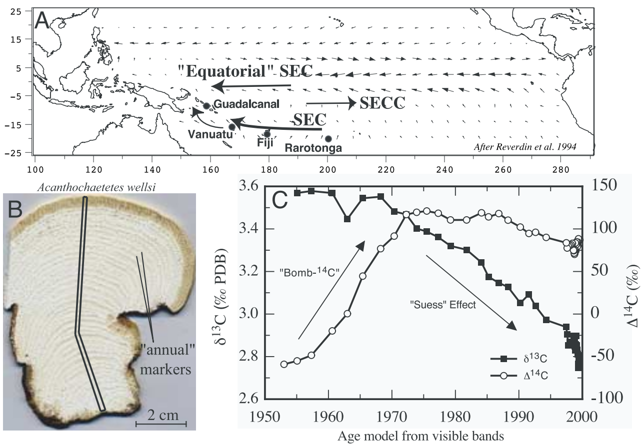


**Figure 1.** (a) Map of sample location, current vectors and major surface currents are after [*Reverdin et al.*, 1994]. (b) Picture of coralline sponge showing "annual" markers. Sample transect shown on sponge sample. (c) Vanuatu sclerosponge $\delta^{13}C$ and $\Delta^{14}C$.

corrected $\Delta^{14}C$ (‰) as defined by *Stuiver and Polach* [1977] and include a $\delta^{13}C$ correction and a blank subtraction based on $^{14}C$-free calcite. Radiocarbon accuracy and precision is ±3.5‰ (1σ) based on replicate analyses of a homogenous in-house coral standard (n = 69).

[7] X-ray and visual analysis reveal density variations in some biogenic carbonates that can be used for sclerochronology [*Buddemeier et al.*, 1974; *Dodge and Vaisnys*, 1975]. Our specimen exhibits clear density variations (Figure 1b), which we used to construct our age-model. The distance from the top of the sample to each horizontal "tabulae" was measured and a date corresponding to June of the year was then assigned to that distance. Using this method the growth rate varied from 0.8 to 2.6 mm $yr^{-1}$ with an average extension of 1.5 ± 0.5 mm $yr^{-1}$, resulting in an age model error of ±1–2 years. To explore the relative importance of vertical diffusivity, air-sea exchange (piston velocity), and upwelling rate on the carbon isotope time-history an "Oeschgeresque" 1-D box-diffusion model was constructed. The box model contains 20 layers each of 20m to a final depth of 500m. Isotopes were handled individually following the Ocean Carbon Modeling Comparison Protocol [*Orr et al.*, 2001] and air-sea exchange was parameterized as a piston-velocity. Based upon hydrographic observations we set the bottom boundary condition to be 4°C, 1.3‰ $\delta^{13}C$, and -100‰ for $\Delta^{14}C$. Starting with steady-state conditions under a pre-industrial atmosphere (280 ppm, -6.5‰ $\delta^{13}C$, 0‰ $\Delta^{14}C$) the model was forced with evolving atmospheric $CO_2$ concentrations and carbon isotopes starting in 1750 as documented by archives and observational networks [*Boden et al.*, 1994; *Francey et al.*, 1999; Steele and Francey, pers. comm.]. Vertical diffusivity, air-sea exchange, and upwelling rates were varied systematically as shown in the legend of Figure 3.

## 3. Results

[8] The $\delta^{13}C$ values range from 3.6‰ in 1953 and decrease to a value of 2.7‰ in 1999 (Figure 1c). The rate of change is accelerated in the late 1990s. This decrease in $\delta^{13}C$ corresponds to the outer edge (tissue zone) of the sample (Figure 1b) and would be hard to explain by variable DIC. A small vital fractionation in the tissue layer has been observed in other sclerosponges [*Reitner and Gautret*, 1996] Pre-bomb $\Delta^{14}C$ is -59‰ and values begin to rise by 1958. The largest increase (+45‰) occurs between 1963 and 1965 reaching the post-bomb maximum (+121‰) in 1973 (Figure 1c). The $\Delta^{14}C$ values hover around +112‰ until ~1980 when they begin decreasing to the 1999 value of +87‰ (Figure 1c).

## 4. Discussion

### 4.1. Regional $\Delta^{14}C$ Records

[9] The Vanuatu sponge radiocarbon record is similar to published coral $^{14}C$ records from the south Pacific (Figure 2). The Vanuatu pre-bomb value of -59‰ (reservoir age of 510 ± 30) is identical within error to the pre-bomb estimate of 494 ± 10yrs given by [*Burr et al.*, 1998]. These two independent results are similar to values derived from a Fijian coral [*Toggweiler et al.*, 1991] but are ~7‰ lower than the open southern hemisphere subtropical surface water as documented in a coral from Raratonga [*Guilderson et al.*, 2000b], and within error to a Solomon Sea coral record to the north [*Guilderson et al.*, 2003]. The lower pre-bomb value at Vanuatu most likely indicates increased mixing with subsurface (lower $^{14}C$) water compared to Raratonga, consistent with the delta-p$CO_2$ observations [*Takahashi et al.*, 2002].

[10] The amplitude and timing of the post-bomb $\Delta^{14}C$ peak is influenced by dilution (mixing) with subsurface $^{14}C$-depleted waters and by dynamic processes [*Guilderson et al.*, 2000b; *Guilderson et al.*, 1998]. The post-bomb $^{14}C$ peaks at Vanuatu (+121‰), Fiji (+133‰) and Rarotonga (+153‰) occur between 1973 and 1975 [Figure 2 *Guilderson et al.*, 2000b; *Toggweiler et al.*, 1991]. At Vanuatu $\Delta^{14}C$ values remain relatively constant from 1975 to 1990 and decrease at a rate of ~4‰/year thereafter (Figure 2). The sustained post-bomb post-peak $^{14}C$ level at Vanuatu can be attributed to mixing with subsurface waters that, after penetration of bomb-$^{14}C$ into the subthermocline, are higher in $^{14}C$ than

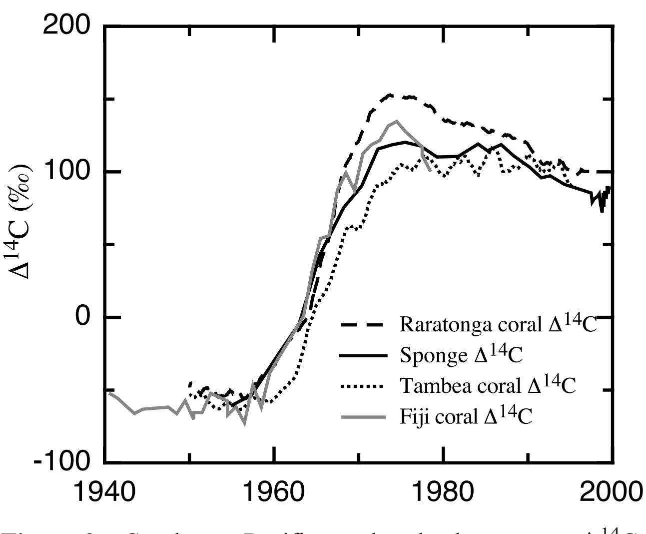


**Figure 2.** Southwest Pacific coral and sclerosponge $\Delta^{14}C$ records to time. Fiji coral from [*Toggweiler et al.*, 1991], Raratonga coral data from [*Guilderson et al.*, 2000b] and Tambea coral data from [*Guilderson et al.*, 2003].

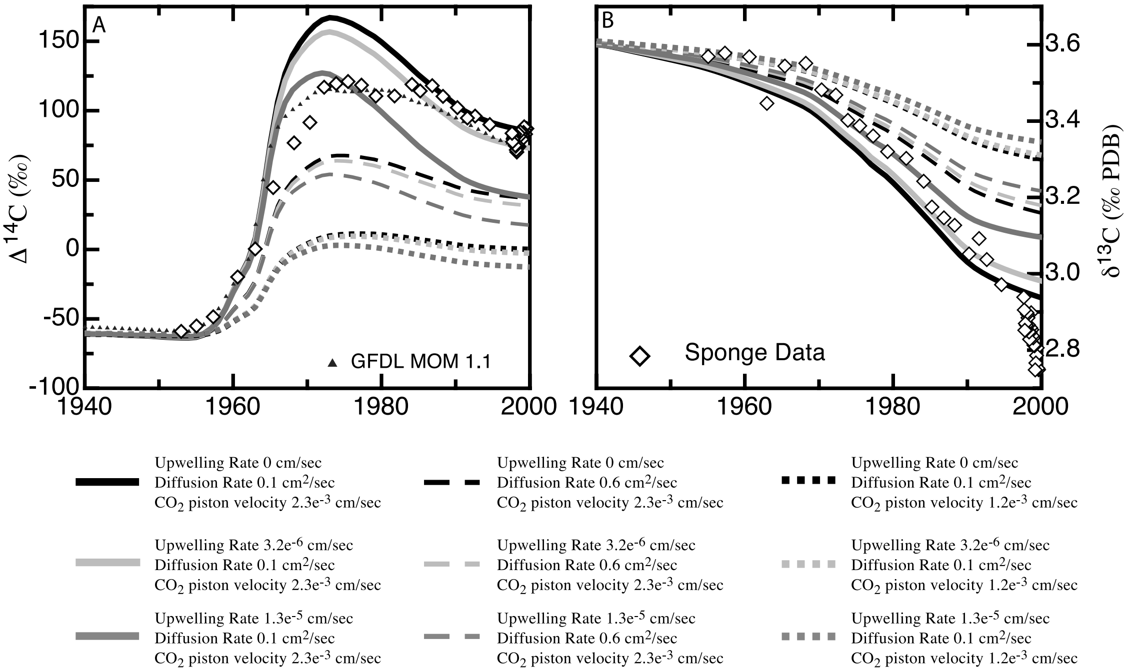


**Figure 3.** Model and sclerosponge $\Delta^{14}C$ and $\delta^{13}C$ to time. To remove absolute value offsets as a consequence of the model's boundary conditions, we have "tied" or adjusted the model $\Delta^{14}C$ and $\delta^{13}C$ results to the sclerosponge data in 1953.

the surface water [*Guilderson et al.*, 2000b; *Key et al.*, 1996; *Quay et al.*, 1983]. This low rate of $^{14}C$ decrease after the post-bomb maximum is a general reflection of the overall shallow meridional overturning circulation of the Pacific and ventilation of the tropical thermocline [*Gu and Philander*, 1997; *Guilderson and Schrag*, 1999; *Quay et al.*, 1983; *Wyrtki and Kilonsky*, 1984].

### 4.2. 1-D Modeling

[11] Atmosphere-ocean $CO_2$ transfer and the transport of carbon to deeper waters via the solubility and biologic pumps are the two dominant steps in determining ocean uptake of atmospheric $CO_2$. The ability to determine the time history of past oceanic $\Delta^{14}C$ and $\delta^{13}C$ variations in response to atmospheric forcing (Suess and/or bomb-$\Delta^{14}C$ and Suess effect $\delta^{13}C$) provides a strong constraint on the rate of exchange of anthropogenic $CO_2$ between the atmosphere and ocean and, implicitly our ability to model and predict future exchange. Because the initial boundary conditions and spin-up determine the model's pre-bomb $^{14}C$ value we adjusted the model $\Delta^{14}C$ and $\delta^{13}C$ to reflect the sponge value in 1953, i.e., shifted the curve in absolute space and "fixed" it to observations in 1953. We examined the sensitivity of the carbon isotope time series in a 1-D box diffusion model where we varied air-sea exchange, vertical diffusivity, and upwelling rates (Figure 3). Combinations of these parameters encompassed upwelling rates of 0, $3.2e^{-6}$ or $1.3e^{-5}$ cm $s^{-1}$ (global mean); the vertical diffusion rate was either 0.6 or 0.1 $cm^2\ s^{-1}$; and the $CO_2$ exchange rate (portrayed as the $CO_2$ piston velocity) was $2.3e^{-3}$ (global mean) or $1.2e^{-3}$ cm $s^{-1}$ and yielded three families of curves. The most realistic representation of the carbon isotope time-history in the 1-D model was accomplished with low vertical diffusivity (0.1 $cm^2\ s^{-1}$) in combination with a moderate $CO_2$ exchange rate (piston velocity) and moderate upwelling rates ($1.3^{-5}$ cm $s^{-1}$). This configuration best reproduced the general shape of the pre- to post-bomb $\Delta^{14}C$ transition and the same general shape of the sponge $\delta^{13}C$ record (Figure 3).

[12] The 1-D model fails to precisely recreate the carbon isotope histories due to the fixed input values at 500 m and the lack of allowing for lateral mixing and the penetration of the bomb-$^{14}C$ transient. The model $\Delta^{14}C$ decreases steadily after the post-bomb peak whereas the sponge record flattens from 1975–1990. The strength for $^{14}C$ in this 1-D model is during the initial bomb-$^{14}C$ rise whereas due to the small dynamic range of Suess effect and background $\delta^{13}C$ the model is useful for the whole $\delta^{13}C$ timeseries. The "most representative" model vertical diffusion rate (0.1 $cm^2\ s^{-1}$) is on the low end of values used in ocean GCMs [0.2–2 $cm^2 s^{-1}$ *Guilderson et al.*, 2000a; *Mahadevan*, 2001; *Toggweiler et al.*, 1991] but consistent with that determined by deliberate microscale (SF6) tracer experiments [*Ledwell et al.*, 1993].

[13] Additionally, we compare our $\Delta^{14}C$ data to that predicted in a fully coupled ocean general circulation model (Figure 3a) forced with observed winds and using OCMIP protocols. GCM results are from the LLNL enhanced version of the GFDL modular ocean model [*Pacanowski et al.*, 1991] generated in a similarly configured a-biotic run as presented in *Guilderson et al.* [2000a]. GCM results indicate that in the post-$^{14}C$ maximum era lateral advection at Vanuatu is important to reconstruct the $\Delta^{14}C$ history. Similar to other model/data comparisons, the response of $^{14}C$ occurs too early implying an inaccurate coupling between surface and interior waters [*Guilderson et al.*, 2000a; *Mahadavan*, 2001; *Rodgers et al.*, 2000].

## 5. Conclusions

[14] The ~45 year long Vanuatu sponge carbon isotope ($\delta^{13}C$, $\Delta^{14}C$) record is one of the few long ocean dual-

carbon isotope records that can be utilized to explore air-sea $CO_2$ exchange reflecting both the Suess $\delta^{13}C$ effect and the bomb-$^{14}C$ transient. Our modeling efforts suggest that a low vertical diffusion rate (0.1 $cm^2\ s^{-1}$) coupled with a moderate $CO_2$ exchange rate produces the observed shape of the pre- to post-bomb $\Delta^{14}C$ transition of the sponge record, and the general large-scale features in the $\delta^{13}C$ time-series. These parameters are on the low end of values used in many ocean GCMs but are consistent with microscale tracer experiments.

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S. J. Fallon and T. P. Guilderson, Center for Accelerator Mass Spectrometry, Lawrence Livermore National Laboratory, Livermore, CA, USA. (fallon4@lnll.gov)

K. Caldeira, Climate and Carbon Cycle Modeling Group, Lawrence Livermore National Laboratory, Livermore, CA, USA.