# UC Irvine
## UC Irvine Previously Published Works

**Title**
Input of excess CO2 to the surface ocean based on 13C/12C ratios in a banded Jamaican sclerosponge

**Permalink**
https://escholarship.org/uc/item/162995j0

**Journal**
Nature, 321(6065)

**ISSN**
0028-0836

**Authors**
Druffel, Ellen RM
Benavides, Livia M

**Publication Date**
1986-05-01

**DOI**
10.1038/321058a0

Peer reviewed

1. Hamilton, P. J. et al. Nature 279, 298-300 (1979).
2. Jahn, B. M., Gruau, G. & Glikson, A. Y. Contr. Miner. Petrol. 80, 25-40 (1982).
3. Jahn, B. M. & Shih, C. Geochim. cosmochim. Acta 38, 611-627 (1974).
4. Van Niekirk, C. B. & Burger, A. J. Trans. geol. Soc. S. Afr. 72, 9-25 (1969).
5. Hurley, P. M., Nagy, B. & Pinson, W. H. Jr Earth planet. Sci. Lett. 14, 360 (1972).
6. De Wit, M. J. et al. Econ. Geol. 77, 1783-1802 (1982).
7. York, D. et al. Eos 62, 429 (1981).
8. Martinez, M. L. et al. Nature 307, 352-354 (1984).
9. Viljoen, M. J. & Viljoen, R. P. Spec. Pub. geol. Soc. S. Afr. 2, 9-151 (1969).
10. Tankard, A. J. et al. Crustal Evolution of Southern Africa (Springer, New York, 1982).
11. Viljoen, M. J. & Viljoen, R. P. in African Magmatism and Tectonics (eds Clifford, T. N. & Gass, I. G.) 27-49 (Oliver and Boyd, Edinburgh, 1970).
12. Williams, D. & Furnell, R. G. Precamb. Res. 9, 325-347 (1979).
13. De Wit, M. J. J. struct. Geol. 4, 117-136 (1982).
14. De Wit, M. J. Spec. Pub. geol. Soc. S. Afr. 9, 185-187 (1983).
15. De Wit, M. J., Fripp, R. E. P. & Stanistreet, I. G. Spec. Pub. geol. Soc. S. Afr. 9, 21-29 (1983).
16. De Wit, M. J. & Stern, C. R. 2nd int. Archaean Symp., Perth 85-87 (Geological Society of Australia, 1980).
17. Taylor, H. P. Jr & Epstein, S. Geol. Soc. Am. Bull. 73, 461-480 (1962).
18. Clayton, R. N. & Mayeda, T. K. Geochim. cosmochim. Acta 27, 43-52 (1963).
19. Coplen, T. B., Kendall, C. & Hopple, J. Nature 302, 236-238 (1983).
20. Gregory, R. T. & Taylor, H. P. Jr J. geophys. Res. 86(B4), 2737-2755 (1981).
21. Cocker, J. D., Griffin, B. J. & Muehlenbachs, K. Earth planet. Sci. Lett. 61, 112-122 (1976).
22. Stern, C. R., De Wit, M. J. & Lawrence, J. R. J. geophys. Res. 81, 4370-4380 (1976).
23. Hoffman, S. E. thesis, Oregon State Univ. College of Oceanography (1985).
24. Stakes, D. S. & O'Neil, J. R. Earth planet. Sci. Lett. 57, 285-304 (1982).
25. Taylor, H. P. Jr in Hydrothermal Processes at Seafloor Spreading Centers (eds Rona, P. A. et al.) 83-139 (Plenum, New York, 1983).
26. Muehlenbachs, K. & Clayton, R. N. Can. J. Earth Sci. 9, 471-478 (1972).
27. Beaty, D. W. thesis, California Institute of Technology (1980).
28. Beaty, D. W. & Taylor, H. P. Jr Econ. Geol. 77, 95-108 (1982).
29. Hein, J. R. & Yeh, H.-W. Init. Rep. DSDP 62, 749-758 (1981).
30. Perry, E. C., Jr & Tan, F. C. Geol. Soc. Amer. Bull. 83, 647-664 (1972).
31. Heinrichs, T. Precamb. Res. 24, 237-283 (1984).
32. Lowe, D. R. & Knauth, L. P. J. Geol. 85, 699-723 (1977).
33. Muehlenbachs, K. & Clayton, R. N. J. geophys. Res. 81, 4365-4369 (1976).
34. Abbott, D. H. & Hoffman, S. E. Tectonics 3, 439-440 (1984).
35. Taylor, H. P. Jr J. geol. Soc. Lond. 133, 509-558 (1977).
36. Beaty, D. W. & Taylor, H. P. Jr in Komatiites (ed Arndt, N. T. & Nisbet, E. G.), 267-280 (Allen & Unwin, London, 1982).

# Input of excess CO₂ to the surface ocean based on ¹³C/¹²C ratios in a banded Jamaican sclerosponge

## Ellen R. M. Druffel & Livia M. Benavides*†

Department of Chemistry, Woods Hole Oceanographic Institution, Woods Hole, Massachusetts 02543, USA
* Department of Civil Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA

The CO₂ content of the atmosphere has increased during the past two centuries as a result of the combustion of fossil fuels for energy[1] and the reduction of forest and soil carbon reservoirs on land[2]. The amount of CO₂ added to the atmosphere from fossil-fuel burning is known from historical records[1] (±10%), but the contribution from reduction of the terrestrial biosphere is far less certain. Several authors have estimated the relative contributions from the two sources by measuring the change in the $^{13}C/^{12}C$ ratio in atmospheric CO₂ as revealed in tree rings[3-8] (CO₂ derived from these two sources is depleted in $^{13}C$ with respect to that in the atmosphere). Using trees in the Northern Hemisphere, recent estimates of the integrated CO₂ release from the terrestrial biosphere since AD 1800 ranged from 70% (ref. 5) to 90% (ref. 9) of that released from fossil fuels. Here we present surface ocean $\delta^{13}C$ and $\delta^{18}O$ records measured in the skeleton of a living sclerosponge (Ceratoporella nicholsoni), which accretes aragonite in isotopic equilibrium with the surrounding sea water/dissolved inorganic carbon (DIC) system. The $\delta^{13}C$ record reveals a decrease

Fig. 1 Schematic diagram showing the sampling intervals for stable isotopes along profile D (0.5-mm drill holes) and for ²¹⁰Pb and ¹⁴C analyses (0.5–1.0 mm bands)[19]. The $\delta^{18}O$ and $\delta^{13}C$ measurements obtained from the profile with the highest resolution are discussed in the text. Data obtained from three other profiles are not reported because an unexpected ageing effect after drilling was observed for these samples. Although it is standard practice to store aragonitic CaCO₃ samples indefinitely, we found that the $\delta^{18}O$ values of these drilled samples were lower by 0.3–0.4‰ after storage periods of a few months; most of the $\delta^{13}C$ results were decreased by 0.1–0.15‰. When samples were stored for a period of months after baking this effect was even greater. The effect of baking was observed previously by Land et al.[17], but these workers did not mention storage effects. We suspect that high-speed drilling of dense aragonite heats up the material sufficiently to cause partial conversion to calcite, a mineral that can exchange its $CO_3^{2-}$ with other sources of CO₂. The results reported here are for samples that were analysed within 48 h of drilling, thus ensuring the smallest possible ageing effect.

of 0.50‰ from 1820 to 1972. Using a model of the world carbon cycle and a deconvolution of our $\delta^{13}C$ data, we estimate that the amount of excess CO₂ derived from the terrestrial biosphere is ~38% of that from fossil-fuel sources. Our model calculations support a preindustrial CO₂ concentration in the atmosphere of 280 p.p.m.v. (parts per million by volume), in agreement with direct measurements of air occluded in Antarctic ice cores[10].

Tree-ring records may not accurately reflect changes in atmospheric $\delta^{13}C$ with time because of kinetic isotope fractionation during the diffusion of CO₂ through the leaf stomata and during carboxylation of ribulose diphosphate during photosynthesis[11,12]. Small variations of the fractionation associated with these and other[11,12] processes may alter the tree-ring $\delta^{13}C$ record, rendering it unrepresentative of the actual change in the atmosphere due to excess CO₂ input.

Another approach for determining the relative contributions of fossil-fuel and forest/soil CO₂ is to examine $\delta^{13}C$ records obtained from the surface waters of the oceans. Nozaki et al.[13] found a reduction in $\delta^{13}C$ of 0.50‰ from 1900 to 1974 in a banded coral (Diploria) from Bermuda. However, other authors have found changes in coral $\delta^{13}C$ for this period that are too large to be attributed solely to the input of excess CO₂ from the atmosphere (ref. 14 and E.R.M.D., unpublished data). Corals contain symbiotic algae (zooxanthellae) whose photosynthetic activities fractionate the DIC pool from which the coral accretes its aragonite. This and other processes constitute the 'vital effect' which, as in trees, might vary with time masking the actual $\delta^{13}C$ change in sea water. Isotopic studies of corals devoid of symbiotic algae reveal a $\delta^{13}C$ record more representative of the ambient DIC in sea water, as that part of the vital effect associated with photosynthesis is absent[15,16]. However, Land et al.[17] found a direct correlation between the $\delta^{13}C$ and $\delta^{18}O$ in several shallow-water ahermatypic corals, indicating a common effect on both stable isotope ratios. Land et al. proposed that this was caused by variable retention rates of metabolic CO₂ in the internal DIC pool, another process contributing to the vital effect.

In the present study, we used the sclerosponge Ceratoporella nicholsoni as a recorder of ¹³C/¹²C and ¹⁸O/¹⁶O ratios in sea water. This animal has no symbiotic algae and appears to precipitate aragonite without a vital effect. The sclerosponge was
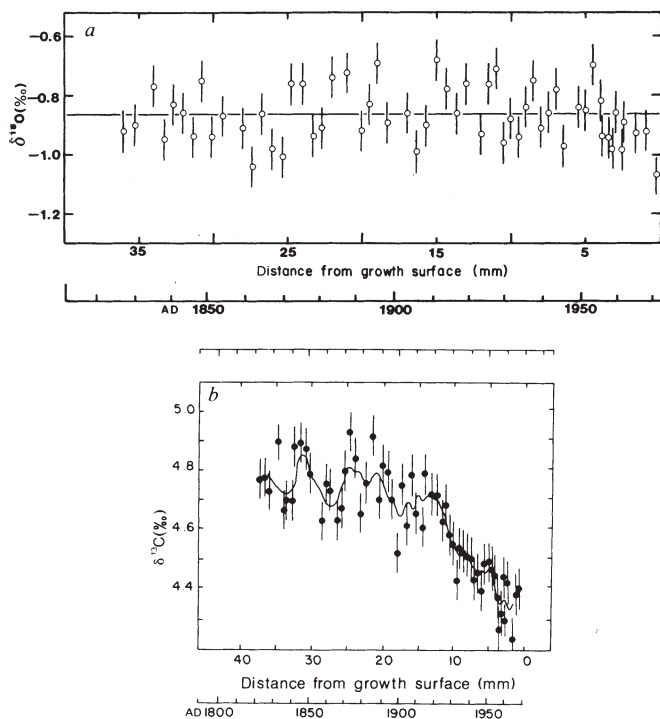
**Fig. 2** *a*, $\delta^{18}O$ measurements for drilled samples along profile D. There is no apparent trend in these data, suggesting that there was no significant change in the long-term averaged SST, salinity and water composition from 1820 to 1972 on the reef. The solid line represents a least-squares fit of the data. Error bars represent $1\sigma$ error of $\pm0.07‰$, determined from numerous triplicate analyses. *b*, $\delta^{13}C$ measurements for drilled samples along profile D. A decrease of $0.50‰$ from the mid-1800s to 1972 is apparent. The solid line represents a cubic spline function fitted to the data (with 4-point smoothing). The error bars represent a $1\sigma$ error of $\pm0.07‰$.

collected in 1972 in the fore-reef zone of Chalet Caribe Reef from the north-west coast of Jamaica at a depth of 26 m. This area is laved by open ocean waters. The major current system influencing this western Caribbean location is the precursor to the Gulf Stream.

The sclerosponge ($\sim7$ cm in diameter) was cut into slabs 3–4 mm wide which were studied using a dissecting microscope to ensure that they had been cut parallel to the growth axis. The slabs were cleaned ultrasonically to eliminate remnants of worm tubes and dust from cutting. A thin slab (1 mm) was X-rayed in an attempt to discern growth bands of varying density; however, despite the use of high-contrast film, no bands were detected. Dark-light band pairs, approximately 1 mm wide, were visible to the naked eye. These bands were identified by Hartman and Goreau[18] as a part of the organic matrix of the sclerosponge. The slabs were mapped using these organic bands (a total of 26) and sectioned for radioacarbon and $^{210}Pb$ analyses[19]. To obtain higher resolution of the stable isotope records, samples were drilled along a profile on a single slab (see Fig. 1). The profiles were drilled at intervals of 0.5 to 1.0-mm. For stable isotope analyses, the samples were baked at 375 °C for 1 h and converted to $CO_2$ by acidification with 100% orthophosphoric acid under vacuum at 50 °C. A VG Micromass 602E mass spectrometer was used to make the measurements.

The growth rate of this Jamaican sclerosponge was determined[19] using $^{210}Pb$ and bomb $^{14}C$ distributions in growth layers near the active growing surface. From these measurements and from the pre-bomb $^{14}C$ distributions in the sclerosponge bands, the specimen was estimated to have lived from $\sim$ AD 1700 to 1972; the average growth rate was $0.25\pm0.05$ mm yr$^{-1}$ using the two methods. This gives an uncertainty of $\pm30$ yr for our oldest year assignment (AD 1825).

Figure 2*a* and *b* shows the $\delta^{18}O$ and $\delta^{13}C$ results, plotted against distance from the growing surface and also against date of formation based on the bomb $^{14}C$ chronology[19].

The $\delta^{18}O$ measurements in Fig. 2*a* show no obvious trends. The entire data set gives an average $\delta^{18}O$ value of $-0.87‰$ (s.d. $= 0.07‰$). These data suggest that there was no significant long term variation in any of the factors controlling the $^{18}O/^{16}O$ ratio of the accreted aragonite[20-25] (that is, sea surface temperature (SST), salinity or seawater composition). Variations in $\delta^{18}O$ caused by seasonal SST changes are insignificant, as each sample represents a 2.5-yr growth interval. Surface salinity measurements were made along a transect extending from the shore to the collection site, which was $\sim$600 m offshore. These results reveal that salinity values at the collection site (36.055–36.059‰) were within the range of values present in the western Caribbean Sea. The slight salinity gradient away from shore (on the order of $+0.03‰$) may represent a small input of fresh water from the island. A variation of this magnitude, however, would not significantly affect the $\delta^{18}O$ values ($\pm0.015‰$).

A cubic spline function was fitted to the $\delta^{13}C$ data set, with 4-point smoothing (solid line in Fig. 2*b*). $\delta^{13}C$ values from sclerosponge layers accreted during the nineteenth century average $+4.78\pm0.09‰$ (1 s.d.). Superimposed on this average value is an inter-annual oscillation of $0.2‰$ with a timescale of approximately two decades. A trend toward values that are 0.40–0.50‰ lower is evident in the upper 15 mm of the sclerosponge skeleton. This result is similar to that of Nozaki *et al.*[13], who revealed a decline in $\delta^{13}C$ of 0.50‰ in a Bermuda coral. Although there is little correlation between the short-term variations of $\delta^{13}C$ as recorded in the surface ocean by the sclerosponge and the Bermuda coral (Fig. 3), partially because of the uncertainty in the chronology of the sclerosponge bands, the overall trend toward lower values by 1972 is the same.

There is no apparent correlation between the $\delta^{13}C$ and $\delta^{18}O$ values in samples from the sclerosponge, in contrast to the direct relationship found in ahermatypic corals[17]. Thus, the two quantities are independent, which is essential if we are to conclude that the isotopic ratios in the skeletal material represent accretion in equilibrium with the seawater/carbonate system.

The $\delta^{18}O$ and $\delta^{13}C$ values expected for equilibrium inorganic precipitation of calcite in surface waters of the northwestern Atlantic Ocean are $-1.4$ to $-2.3‰$ (at SST of $28\pm1$ °C) and 2.4 to 2.6‰, respectively[17,26-28]. To compare these ranges with our data, we had to take into account the additional fractionation that occurs during the accretion of aragonite as opposed to calcite, which is $+0.6‰$ for $\delta^{18}O$ (ref. 29) and 1.8‰ for $\delta^{13}C$ (ref. 28). Thus, values for aragonite precipitated recently in equilibrium with surrounding sea water in the northern Jamaican region are $-0.8$ to $-1.7‰$ for $\delta^{18}O$ and 4.2 to 4.4‰ for $\delta^{13}C$. Our results fall within these ranges (average $\delta^{18}O$ of $-0.87‰$, $\delta^{13}C$ range of 4.2–4.5‰). This evidence, in addition to the fact that there is no apparent correlation between $\delta^{13}C$ and $\delta^{18}O$, suggests that the vital effect is insignificant and that the sclerosponge precipitates aragonite in equilibrium with the DIC/water
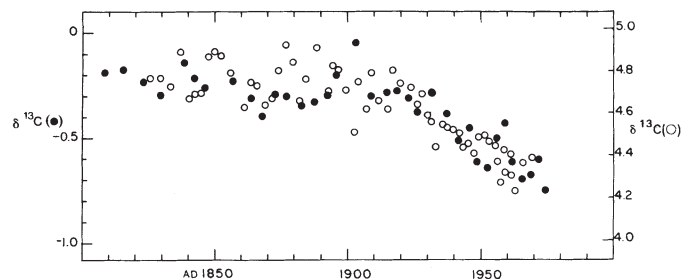


**Fig. 3** $\delta^{13}C$ trend in surface ocean water in the north-west Atlantic as revealed by a Bermuda coral[13] ($\bullet$, 5-yr averages) and by a Jamaican sclerosponge (present study) ($\bigcirc$, 2.5-yr averages). A decrease of $0.50\pm0.10‰$ is apparent from the mid-1800s to 1972.
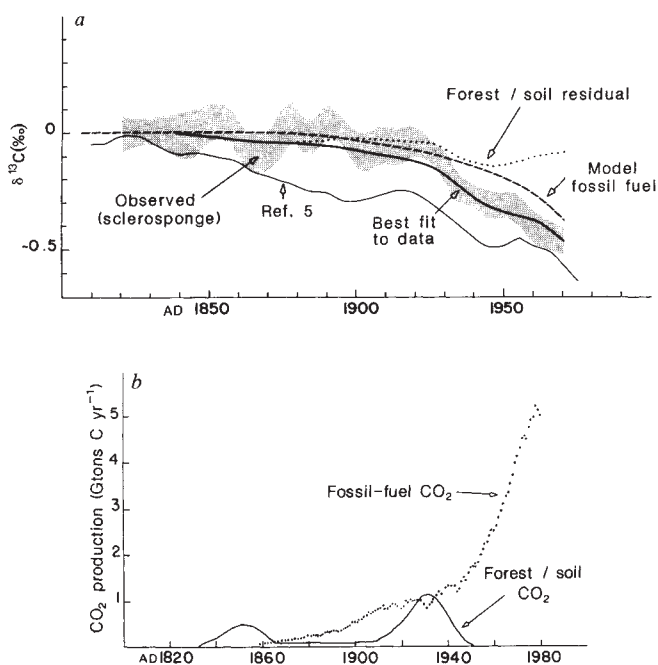
Fig. 4 *a*, Model calculations of the $\delta^{13}C$ trend in surface ocean waters. The stippled area represents the observed values from the sclerosponge. The decrease due to fossil-fuel $CO_2$ alone (– – –) was calculated from historical records[1,33]. The forest/soil component (. . . . .) was calculated by eliminating the fossil-fuel curve from the model-derived best fit of the observed sclerosponge measurements (heavy solid line). The surface-ocean curve calculated from the tree-ring data of Stuiver *et al.*[5] is shown for comparison (light solid line). *b*, Annual $CO_2$ production from fossil-fuel burning[1] and from forest/soil sources (present work) during the past two centuries. Integration of the two curves reveals that ~28% of the total excess $CO_2$ released into the atmosphere during 1820–1972 was derived from the terrestrial biota.

system in which it lives. In contrast to corals, sclerosponges pump large amounts of water through their channels[18]; this may provide a mechanism for the removal of metabolic $CO_2$ from the animal tissue, thus eliminating significant retention of respired $CO_2$ in the calcioblastic layer, and hence in the accreted aragonite.

Assuming that sclerosponges accrete aragonite in equilibrium with the surrounding sea water, their skeletons contain valuable information regarding the input of excess $CO_2$ to the oceans. Knowledge of both the timing and magnitude of the $\delta^{13}C$ change obtained from the stable isotope records in banded sclerosponge layers enables us to estimate the relative contributions to the atmosphere and oceans of the two major sources of $CO_2$: fossil fuels and forest/soil carbon.

A one-dimensional mixing model of the world carbon cycle, similar to that of Emanuel *et al.*[30], was used to estimate the timing and magnitude of excess $CO_2$ input to the atmosphere from the two major sources mentioned above. In this model, the ocean is constructed of 19 layers that are mixed diffusively, in a manner similar to the box-diffusion model of Oeschger *et al.*[31]. The biota is represented by the five major terrestrial carbon reservoirs. Values of the atmospheric $P_{CO_2}$ (partial pressure of $CO_2$) calculated using the model agreed (to within ±2 p.p.m.v.) with measurements obtained by Keeling *et al.*[32] from 1958 to 1982 at Mauna Loa.

The stippled region in Fig. 4*a* shows the range of $\delta^{13}C$ values in the surface ocean as recorded in the sclerosponge bands. Using the model, we calculate that the reduction in $\delta^{13}C$ expected in average surface ocean waters due to the input of fossil $CO_2$ alone[1,33] is 0.37‰ by 1972 (broken line); this is two-thirds of the value observed in the sclerosponge record. If

we assume that the north-west Atlantic is representative of average global surface ocean water, then it seems that there is an additional source of excess $CO_2$, presumably from deforestation and soil manipulation on land. In the model, we have added $CO_2$ derived from the reduction of the forest/soil reservoir ($\delta^{13}C = -26‰$) in order to obtain the best fit of the observed ocean $\delta^{13}C$ curve (heavy solid line in Fig. 4*a*). The change in $\delta^{13}C$ in the surface ocean calculated from the composite tree-ring curve of Stuiver *et al.*[5] is slightly greater than our observed trend (Fig. 4*a*). Figure 4*b* shows the annual $CO_2$ production (in gigatons C yr$^{-1}$) from the two sources of excess $CO_2$. The forest/soil contribution is approximately 38% the size of the fossil fuel contribution, representing a net input to the atmosphere of 53 G tons C from the terrestrial biosphere between 1820 and 1972. Using the combined observed ocean trend (Fig. 3) from the Bermuda coral and Jamaican sclerosponge, the estimate of the forest/soil $CO_2$ contribution remains the same.

Although the shape of the forest/soil curve is difficult to determine with any certainty because of the large signal-to-noise ratio in the ocean $\delta^{13}C$ records, these data do suggest that the change in $\delta^{13}C$ due to forest/soil $CO_2$ input was minimal between 1950 and 1972; this is in agreement with the results of studies of tree rings[5,9] and atmospheric $CO_2$ (ref. 34). Also, there was a significant decrease in $\delta^{13}C$ from 1845 to 1865, suggesting that the forest/soil component was an important net source of $CO_2$ to the atmosphere during the nineteenth century. However, it appears from the sclerosponge data that most of the excess terrestrial $CO_2$ was expelled into the atmosphere during the period 1920–1950 (Fig. 4*b*).

The bimodal nature of the forest/soil $CO_2$ input, as revealed here, has also been demonstrated by deconvolution of ice-core $CO_2$ data[35] and of tree-ring $\delta^{13}C$ records[5,36]. The similarity of recent results derived from independent geochemical data sets indicates that our understanding of the excess $CO_2$ problem is approaching a consensus—(1) the net input of $CO_2$ to the atmosphere from the biosphere between 1800 and 1975 was approximately half of that from fossil fuels, and (2) the net production of biospheric $CO_2$ has undergone two periods of peak production in the past two centuries, at 1820–1850 and 1880–1930.

An estimate of the partial pressure of $CO_2$ in the atmosphere during the early 1800s can be made using these data. Using historical records of the industrial production of $CO_2$ from fossil fuels[1,33] and the $P_{CO_2}$ record in the atmosphere[32], the preindustrial $P_{CO_2}$ is estimated at 292 p.p.m.v., if the biosphere was neither a sink nor a source of $CO_2$. Considering the biotic source of excess $CO_2$, which is estimated here to have been ~38% the size of the fossil-fuel source, the preindustrial $P_{CO_2}$ is decreased to 280 p.p.m.v.; this value is in agreement with measurements made by Neftel *et al.*[10] of air trapped in ice cores from Siple Station, Antarctica.

1. Keeling, C. D. *Tellus* **25**, 174–198 (1973).
2. Houghton, R. A. *et al. Ecol. Monogr.* **53**, 235–262 (1983).
3. Rebello, A. & Wagener, K. *Environmental Biogeochemistry* (ed. Nriagu, J. O.) 13–23 (Ann Arbor Science, Ann Arbor, 1976).
4. Pearman, G. J., Francey, R. J. & Fraser, P. J. B. *Nature* **260**, 771–773 (1976).
5. Stuiver, M., Burk, R. L. & Quay, P. D. *J. Geophys. Res.* **89**, (D7), 11731–11748 (1984).
6. Harkness, D. D. & Miller, B. F. *Radiocarbon* **22**, 291–298 (1980).
7. Francey, R. J. *Nature* **290**, 232–235 (1981).
8. Freyer, H. D. *Proc. 6th ORNL Life-Sci. Symp.*, Oak Ridge (eds Trabalka, J. R. & Reichle, D. E.) (Springer, New York, in the press).
9. Peng, T. -H. *Geophys. Monogr.* **32**, 123–131 (1985).
10. Neftel, A., Moore, E., Oeschger, H. & Stauffer, B. *Nature* **315**, 45–47 (1985).

11. Farquhar, G. D., O'Leary, M. H. & Berry, J. A. *Aust. J. Pl. Physiol.* **9**, 121-137 (1982).
12. Francey, R. J. & Farquhar, G. D. *Nature* **297**, 28-31 (1982).
13. Nozaki, Y., Rye, D. M., Turekian, K. K. & Dodge, R. E. *Geophys. Res. Lett.* **5**, 825-828 (1978).
14. Chivas, A. R., Aharon, P., Chappell, J., Vlastuin, C. & Kiss, E. *Proc. Inaugural Great Barrier Reef Conf.*, Townsville, 77-81 (J.C.U. Press, Townsville, 1983).
15. Weber, J. N. *Deep Sea Res.* **20**, 901-910 (1973).
16. Emiliani, C., Hudson, J. H., Shinn, E. A. & George, R. Y. *Science* **202**, 627-629 (1978).
17. Land, L. S., Lang, J. C. & Barnes, D. J. *Geochim. cosmochim. Acta* **41**, 169-172 (1977).
18. Hartman, W. D. & Goreau, T. F. *Symp. zool. Soc. Lond.* **25**, 205-243 (1970).
19. Benavides, L. & Druffel, E. R. M. *Coral Reefs* (in the press).
20. Swart, P. K. *Earth Sci. Rev.* **19**, 51-80 (1983).
21. Weber, J. N. & Woodhead, P. M. J. *J. geophys. Res.* **77**, 463-473 (1972).
22. Fairbanks, R. G. & Dodge, R. E. *Geochim. cosmochim. Acta* **43**, 1009-1020 (1979).
23. Weil, S. M., Buddemeier, R. W., Smith, S. V. & Kroopnick, P. M. *Geochim. cosmochim. Acta* **45**, 1147-1153 (1981).
24. Dunbar, R. B. & Wellington, G. M. *Nature* **293**, 453-455 (1981).
25. Druffel, E. R. M. *Geophys. Monogr.* **32**, 111-122 (1985).
26. Kroopnick, P. *Deep Sea Res.* **32**, 57-84 (1985).
27. Epstein, S., Buchsbaum, R., Lowenstam, H. A. & Urey, H. C. *Bull. geol. Soc. Am.* **64**, 1315-1326 (1953).
28. Rubinson, M. & Clayton, R. N. *Geochim. cosmochim. Acta* **33**, 997-1002 (1969).
29. Tarutani, T., Clayton, R. N. & Mayeda, T. K. *Geochim. cosmochim. Acta* **33**, 987-996 (1969).
30. Emanuel, W. R., Killough, G. G., Post, W. M., Shugart, H. H. & Stevenson, M. P. *Dep. Envir. Docum.* No. DOE/NBB-0062, UC-11, 79 (1984).
31. Oeschger, H., Siegenthaler, U., Schotterer, U. & Gugelmann, A. *Tellus* **27**, 168-192 (1975).
32. Keeling, C. D., Bacastow, R. B. & Whorf, T. P. *Carbon Dioxide Review: 1982* (ed. Clark, W. C.) 377-385 (Oxford University Press, 1982).
33. Rotty, R. M. *Carbon Cycle Modelling, SCOPE 16* (ed. Bolin, B.) 121-123 (Wiley, New York, 1981).
34. Keeling, C. D., Mook, W. G. & Tans, P. P. *Nature* **277**, 121-123 (1979).
35. Siegenthaler, U. & Oeschger, H. *Tellus* (in the press).
36. Peng, T.-H. & Freyer, H. D. *Proc. 6th ORNL Life Sci. Symp.* Oak Ridge (eds Trabalka, J. R. & Reichle, D. E.) (Springer, New York, in the press).
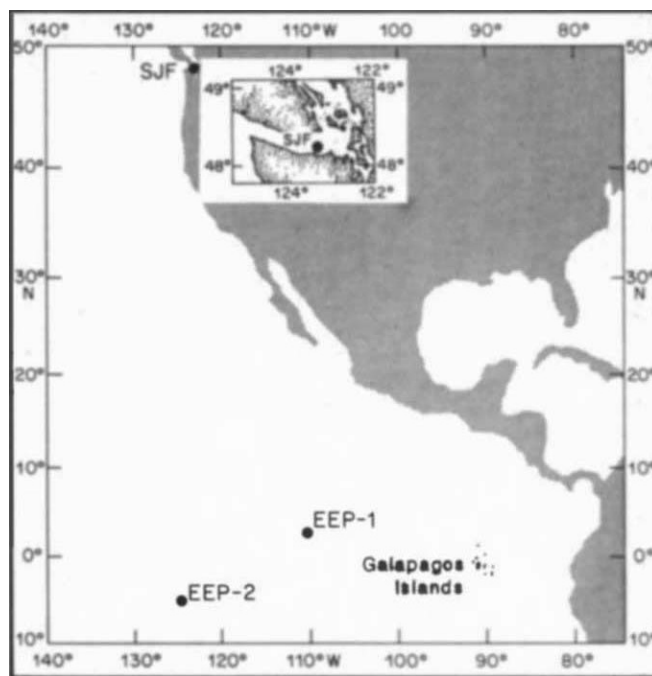
# Molecular evidence for a terrestrial component of organic matter dissolved in ocean water

Kathleen J. Meyers-Schulte & John I. Hedges

School of Oceanography, WB-10, University of Washington, Seattle, Washington 98195, USA

Fig. 1 Seawater sampling sites.

**Dissolved organic matter (DOM) in seawater represents one of the largest active carbon reservoirs on Earth[1]. Although mass-balance calculations suggest a substantial riverine input to the marine DOM pool[2], a terrestrial organic component has not been positively identified in open-ocean water. By using lignin-derived phenols as molecular-level probes of DOM (analogous to previous studies in sediments[3-5]), we report here the first unambiguous evidence for the presence of terrestrially derived DOM in open ocean water. Dissolved humic substances, isolated by resin adsorption from near-surface water of the eastern equatorial Pacific, yield lignin-derived phenols in compositional patterns which resemble those obtained from Amazon River water[6,7]. Total phenol yields from these open-ocean humic isolates are, on average, ~10% of those from Amazon humic substances, indicating that ~10% of dissolved marine humic material (and at least 0.5% of the bulk marine DOM) is terrestrially derived.**

The concentration of terrestrially derived organic matter in the marine DOM pool is one of the most ill-defined factors in the global carbon cycle[1]. The potential for a significant terrestrial contribution is evident from the calculation that the global DOM input by rivers[2] is sufficient to support ~70% of the oceanic DOM pool at its measured ($^{14}C$) average age of 3,400 yr[8]. Evidence that riverine DOM mixes conservatively in selected estuaries[9] suggests that most riverine DOM passes through estuaries to coastal waters[10], where its subsequent fate is unknown.

Direct biochemical analyses of marine DOM have yielded limited source-related information because the overall abundance of recognizable biochemicals is low (10-20%)[11-13] and their geographic origins are usually ambiguous. A portion of the DOM is comprised of a complex mixture of acidic polymers called humic substances which are produced by microbial degradation and condensation of biochemicals and can be isolated by adsorption onto resin[14]. Bulk isotopic and chemical analyses of humic isolates from seawater indicate a predominant marine

origin[15-18], but these measurements are not well suited for detection of minor constituents, and cannot preclude a terrestrial component. Degradative analyses of humic substances allow the greater sensitivity inherent in molecular level analyses, but to date have either yielded products of unclear geographic origin[18], have been applied to landlocked marine water[10] which may not be representative of the open ocean, or have not detected a terrestrial component of marine humus[19].

Using the lignin-biomarker technique[5], we report here the first direct evidence for the presence of terrestrially derived organic matter in open-ocean DOM. Lignin is a phenolic polymer which is produced solely by vascular land plants as structural units of their cell walls[20]. Its exclusive terrestrial source, high natural abundance on land, inherent chemical stability[21] and unmistakable suite of cupric oxide oxidation products render lignin an attractive molecular tracer for terrestrial organic matter in aquatic environments[6,7,22]. On oxidation by cupric oxide, lignin of all vascular plant tissues produces vanillyl phenols, which can be used as unambiguous general tracers of terrestrially derived material. In addition, syringyl phenols (produced only from angiosperm lignin) and cinnamyl phenols (produced only from non-woody tissues) denote specific vascular tissue sources[4,22]. Finally, the weight ratio of vanillic acid to vanillin, symbolized as $(Ad/Al)_v$ of fresh (undegraded) vascular plant tissues ranges from 0.1 to 0.2 (ref. 23), whereas higher values are characteristic of biodegraded lignin[5].

Previous applications of the lignin-biomarker technique to dissolved humic substances from lakes and rivers have demonstrated the ubiquitous presence of lignin structural units[6,7,22]. In particular, humic substances from the Amazon River system produce high yields of lignin oxidation products characterized by low syringyl/vanillyl (S/V) and cinnamyl/vanillyl (C/V) weight ratios and relatively high $(Ad/Al)_v$ values[6,7]. Because the Amazon is by far the world's largest river system and contributes approximately 20% of the total freshwater input to the ocean[2], it serves as a good model for the expected terrestrial component within the marine DOM pool.

We chose to study water from the Pacific Ocean which is at the most extreme end of the global ocean circulation pattern and least affected by direct river input. Both surface (depth 5 m) and sub-thermoclinic (150 m) water samples (400 l) were collected from two stations in the eastern equatorial Pacific Ocean