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Carbon-13 in Tree Rings Indicates No Record of Sea-Surface Temperature

Abstract. *When the correct values for the temperature coefficient of carbon dioxide solubility in seawater are used, theoretical calculations show that no measurable carbon-isotope redistribution occurs between sea and air for any plausible change in the sea-surface temperature. Although this fact invalidates one possible paleothermometer, it somewhat simplifies the interpretation of carbon-13 data in terrestrial biological samples.*

The possible consequences of the "CO_2 greenhouse" are of increasing concern. Unfortunately, the historical data on atmospheric CO_2 concentrations are of such uncertain accuracy that they put few constraints upon mathematical models of the CO_2 system. The range of future projections is accordingly large, and it is rash to make predictions more precise than that the CO_2 concentration will double by about A.D. 2030. This uncertainty makes alternative data sources imperative, and ${}^{13}C/{}^{12}C$ ratios provide an important addition. One of the stated goals of the *Comprehensive Plan for CO_2-Effects Research and Assessment* is increased "use of the isotopes of carbon as clues to the contribution of the biosphere to recent changes in atmospheric CO_2" (*1*, p. v).

Because the surface ocean contains so much more total CO_2 than the atmosphere, air-sea exchange is an important determinant of the ${}^{13}C/{}^{12}C$ isotope ratio in the atmosphere and thus in nonmarine biological materials. Because this exchange is temperature-dependent, there has been speculation about a measurable influence on tree-ring isotopes arising from changes in the ocean temperature. (*2*).

The object of this report is to demonstrate that the sea-surface temperature does not appreciably affect isotope ratios that depend upon the atmospheric ratio. Conversely, sea-surface temperature changes cannot be inferred from terrestrial records.

Earlier speculations appear to have been influenced by an erroneous estimate of the temperature coefficient of the solubility of CO_2 in seawater. Although Hamberg (*3*) found correct values last century, I have shown (*4*) that the value of 4 percent per degree Celsius in common use today (*5-7*) is $(\partial P/\partial T)_{A,C}$, that is, it is the change in the partial pressure of CO_2 (P) with respect to temperature (T) at constant alkalinity (A) and constant total CO_2 ($C = CO_{2aq} + H_2CO_3 + HCO_3^- + CO_2^{2-}$) in solution. This coefficient is appropriate only to the theory (*6*) and experiment (*7*) for which it was derived and not to air-sea exchange. The condition of constant total CO_2 in solution is clearly violated if CO_2 moves between sea and air. The correct coefficient is $(\partial P/\partial T)_{A,\Sigma}$, where Σ indicates that the sum of CO_2 in sea and air must remain constant. Obviously, the magnitude of the temperature coefficient is a function of the depth (z) of the surface ocean assumed to be in active exchange with the atmosphere. For an ocean 100 m deep, this coefficient is almost exactly ten times smaller than the commonly quoted constant-C value, and reduces tenfold the apparent T sensitivity of P and of isotopic redistribution accompanying a change in T.

The calculation that I present below does not allow the usual approximations that make working with isotopic δ values convenient, and we must resort to the full equations. These are as follows:

$$R_x = {}^{13}C_x/{}^{12}C_x \qquad (1)$$

where x designates a particular sample,

$$R_0 = {}^{13}C_{PDB}/{}^{12}C_{PDB} \qquad (2)$$

where PDB designates the Pee Dee belemnite reference standard and $R_0 = 0.00112372$ (*8*),

$$\delta_x = (R_x/R_0 - 1)1000 \qquad (3)$$

$$K_s = R_{HCO_3^-}/R_{CO_2} = R_{sea}/R_{air} = (\delta_s + 1000)/(\delta_a + 1000) \qquad (4)$$

and

$$\delta_s = (\delta_a + 1000)K_s - 1000 = \delta_a + (K_s - 1)(1000 + \delta_a) \qquad (5)$$

If we ignore interaction with the marine biota, the computation follows the symbolic outline of Table 1. There are 18 equations relating 24 quantities, so that, if six independent parameters are known, the system is determinate.

Of the several evaluations (*9-11*) of K_s, I adopt that of Mook *et al.* (*10*), because it lies in the middle of the range of the other values and is the most internally consistent. Defining ϵ, they write

$$\epsilon = (K_s - 1)1000 = (9483/T) - 23.89 \qquad (6)$$

where T is in degrees Kelvin.

For simplicity, I ignore the oceanic maximum in C at a depth of 1 km, which is supported by the respiration of vertically migrating predators and by detrital oxidation, and assume that C is constant with depth. It is then possible to compute C (*4*) from A and P, for the wind-stirred layer is never far from equilibrium.

The only remaining troublesome quantity is P', the partial pressure after a change in T. This must be calculated (*4*) from the temperature-sensitive reaction functions for H_2CO_3. The exact value will depend upon which set of functions

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Table 1. Symbolic and numerical values of the parameters entering into the calculation of carbon isotope fractionation after an 0.2°C cooling throughout a surface ocean 75 m deep. Boldface data are input values, with P' calculated as described in the text; 0.2° is intended to represent the maximum cooling to be expected in the historical period, and the values of P and δ_a are representative of the early 1940's. The common unit for P, C, and Σ is the "ppm," equivalent to the mass of a micromole fraction of CO_2 in the International Civil Aviation Organization standard sea-level atmosphere, or 7.77×10^{12} kg of CO_2. The subscripts on the δ values are nonsignificant figures.

$T = 15$°C and $\epsilon = 9.020$				$T' =$ **14.8°C** and $\epsilon' = 9.043$				
^{12}P 303.6070	+	^{12}C 312.6755	=	$^{12}P'$ 303.3346	+	$^{12}C'$ 312.9479	=	$^{12}\Sigma$ 616.2825
^{13}P 3.3930	+	^{13}C 3.5259	=	$^{13}P'$ 3.3899	+	$^{13}C'$ 3.5290	=	$^{13}\Sigma$ 6.9189
P **307.0000**	+	C 316.2014	=	P' **306.7245**	+	C' 316.4769	=	Σ **623.2014**
δ_a $\mathbf{-5.48}_{00}$		δ_s 3.49_{07}		δ_a' -5.49_{87}		δ_s' 3.50_{09}		δ -0.92_{87}

is used. Here I have used Weiss' (*12*) solubility and Lyman's (*13*) reaction functions, at a total alkalinity of 2.3 equivalents per ton of seawater. I have included the effects of borate on the CO_2 system because the inclusion of this effect appreciably increases the temperature sensitivity of δ_a.

Since P and δ_a are observable, the atmospheric isotopic partial pressures ^{12}P and ^{13}P can be computed directly, as can δ_s. This makes ^{12}C and ^{13}C available, and thence $^{12}\Sigma$ and $^{13}\Sigma$.

The primed isotopic values can be expressed in terms of C', Σ, and, say, $^{12}\Sigma$, together with one unknown, x, which, to minimize loss of significant figures, we take to be $^{12}C'$, the largest of the primed unknowns. Thus

$$^{12}P' = (^{12}\Sigma - x) \tag{7}$$

$$^{13}P' = x + \Sigma - (C' + {}^{12}\Sigma) \tag{8}$$

$$^{12}C' = x \tag{9}$$

$$^{13}C' = (C' - x) \tag{10}$$

which can be substituted into

$$K_s' = R_s'/R_a' = (^{13}C')(^{12}P')/(^{12}C')(^{13}P') \tag{11}$$

to give

$$x^2(K_s' - 1) + x[K_s\Sigma - (K_s - 1)(C' + {}^{12}\Sigma)] - {}^{12}\Sigma C' = 0 \tag{12}$$

With the primed values known, δ_a' and δ_s' are obtained directly. Table 1 gives a numerical example which shows the effect of a 0.2°C cooling of the surface ocean at approximately the concentrations of atmospheric CO_2 that prevailed in 1940, on the assumption that the wind-stirred 75-m ocean layer exchanges with the atmosphere (an assumption which reproduces the observed prebomb ^{14}C Suess effect).

Table 2 gives a more extensive set of values for different exchange depths. Here the initial state is equilibrium with a 25°C ocean at a salinity of 35 per mil and an alkalinity of 2.3 equivalents per ton of seawater, and an atmosphere at 330 parts per million (ppm). This corresponds, roughly, to 1978 conditions in tropical waters.

The four-decimal-place accuracy of Tables 1 and 2 is for calculational purposes only, since one decimal place is hard to come by in practice and one cannot reverse the calculations to regain the exact starting figures because of loss of precision in the subtractions. The real information in Table 2 is the miniscule change in δ_a with T. The conclusion appears to be that, for any plausible T change over any acceptable depth, the change in δ_a vanishes into the current noise levels of biological records.

Table 2. Equilibrium limiting values. For each temperature (T) and depth (z) the three entries are, from the top down, P, δ_a, and δ_s. For the warmer waters (centered at 25°C), Σ is computed for an ocean at 25°C and an atmosphere at 330 ppm, with $\epsilon = 7.916$ and $\delta_a = -6.81$. For the colder water (centered at 5°C), the initial state is 5°C with $\epsilon = 10.203$.

z (m)	Σ (ppm)	$T = 20$°C and $\epsilon = 8.459$	$T = 30$°C and $\epsilon = 7.392$	$\Delta/\Delta T$
75	633.37	323.09	336.79	1.370
		−7.16	−6.48	0.068
		1.24	0.86	−0.38
100	734.46	321.08	338.77	1.769
		−7.20	−6.44	0.076
		1.19	0.91	−0.028
150	936.69	317.68	342.36	2.469
		−7.27	−6.38	0.089
		1.13	0.97	−0.016
575	2882.50	323.52*	336.51†	6.499
		−6.94*	−6.68†	0.130
		3.31*	3.33†	0.010

*$T = 4$°C and $\epsilon = 10.326$. †$T = 6$°C and $\epsilon = 10.081$.

At the bottom of Table 2 is a single entry at 5°C and 575 m. These parameters characterize the world ocean which best reproduces the historical atmospheric P data, if we assume mean annual global equilibrium between air and sea. Carbon transport within the surface ocean is a complex process, and P and δ_s do not approach equilibrium at the same rate or by the same mechanism. The values presented here represent limiting values which might be approached asymptotically after a perturbation. In any event, equilibrium calculations should precede, and delimit, attempts to unravel kinetics. For comparison with Tables 1 and 2, measured values of the biologically modified δ_s in the surface waters of the South Pacific (*14*) range from +2 at the surface to +1.5 at 500 m.

Column 5 of Table 2 estimates the temperature coefficients of P, δ_a, and δ_s. For comparison, $(\Delta P/\Delta T)_{A,C}$, which estimates the erroneously large temperature coefficient mentioned above, is 15.42 ppm per degree Celsius, larger by a factor of 2.4 than the maximum value of $(\Delta P/\Delta T)_{A,\Sigma}$ for equilibrium with 575 m of cold water. The temperature coefficient of δ_a is in good agreement with the value of 0.08 per mil per degree Celsius which Bottinga and Craig (*15*) deduced from the work of Deuser and Degens (*9*), but it is much smaller than the value of 0.3 per mil per degree Celsius suggested by Freyer and Weisberg (*16*).

The 10°C temperature range used in Table 2 is comparable to the maximum changes in the North Atlantic over the last 600,000 years (*17*), an indication that throughout the ice ages of the Quaternary there should be few terrestrial carbon-isotope records that are visibly influenced by sea-surface temperature. In particular, the 0.1° to 0.2°C cooling of the ocean after 1940 (*18*) is not likely to be observed in tree rings until such time as changes in δ of 0.01 per mil become significant.

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Giant Larvacean Houses: Observations from Deep Submersibles

Abstract. *The abundance of large, previously unknown larvacean feeding structures in the deep ocean is a striking contrast to the rarity of such forms taken in net hauls. In some areas, abandoned houses and their disintegrated parts provide a substrate for other organisms and contribute to organic aggregates.*

Our concepts of oceanic mesopelagic life are mainly based on samples taken with trawls, nets, and pumps. However, new insights have been gained by underwater scuba divers in shallow oceanic waters; these observers report that several planktonic forms secrete mucoid feeding structures that are generally destroyed by our usual collecting methods (*1*).

The most elaborate of these structures are produced by larvaceans, urochordates that retain the larval tunicate "tadpole" anatomy. Minute (3 to 6 mm), shallow-dwelling species secrete cocoonlike mucous "houses" that are an order of magnitude larger than the animals and are equipped with intake screens and complex internal filters. Protectively situated in its house, the animal filter-feeds by creating a flow of water through the apparatus with its undulating tail. When the sieves clog, the larvacean evacuates the house and rapidly secretes another, a process that can be repeated at 2- to 4-hour intervals (*2*). Larvacean houses were studied by an earlier generation of biologists who carefully ladled these fragile structures from surface waters (*3*), but the abundance and importance of the abandoned houses as a substrate for microcrustaceans and bacteria and as a source of organic aggregates have only recently been revealed by modern diving techniques (*2, 4*).

Some 70 years ago, rare catches from deep net tows of *Bathochordaeus charon*, a larvacean more than ten times larger than shallow-dwelling forms, were reported (*5*). Recent examination of midwater-trawl catches off the southern California coast has increased the known number of specimens of this giant form to 13 and extended their range to the eastern Pacific (*6*). Because the houses of *B. charon* have never been described [Chun (*3*) theorized that they must be the size of pumpkins], I report here on observations made more than 10 years ago from deep submersibles (*7*).

My observations indicated that there are several types of large larvacean houses, ranging in size from 30 to 100 cm, that are widely distributed in pelagic waters adjacent to the continental shelves of the western middle American coast (Fig. 1). Their abundance varies from an occasional individual to one per cubic meter, a density observed above thermoclines at depths of 25 to 50 m. Some of my observations suggest that abandoned giant larvacean houses provide a substrate for microcrustaceans and contribute to organic particulate material in deep waters as do smaller forms at surface levels (*2, 4*).

During early dives, certain large mucous structures seen from submersibles were an engima to me. The evidence which eventually led me to conclude that these were extremely large larvacean houses follows. With the exception of their size, the structures were roughly similar to textbook descriptions of minute larvacean houses, and intact structures contained a double-lobed nucleus which resembled the internal filter of smaller forms. In some cases, a slow rhythmic beating by an organism adjacent to the nucleus appeared identical in position and motion to that described for minute larvacean forms. Once, a pollywog-shaped organism, about 6 to 8 cm in length, was seen leaving and swimming rapidly away from a disintegrating mucous structure that had been hit by the submersible. Finally, after several futile attempts, a structure containing an occupant was captured in a suction device attached to the front of the submersible (*7*). The collecting process reduced the structure to mucus-like scum; the organism, however, was recovered intact and examined in its fresh state by Donald P. Abbott (Stanford University) who identified it as a larvacean. (Unfortunately, this specimen was subsequently lost.)

While I recall seeing at least five types of large larvacean houses, by recourse to photographs and motion-picture films I can give general descriptions of three types. Type 1 house (Fig. 2A) is approximately 70 to 100 cm in its greatest dimension. The form of the house differs, but it is essentially a flimsy sac that appears to be at least partially open at the bottom. One or two mucous strings usually trail

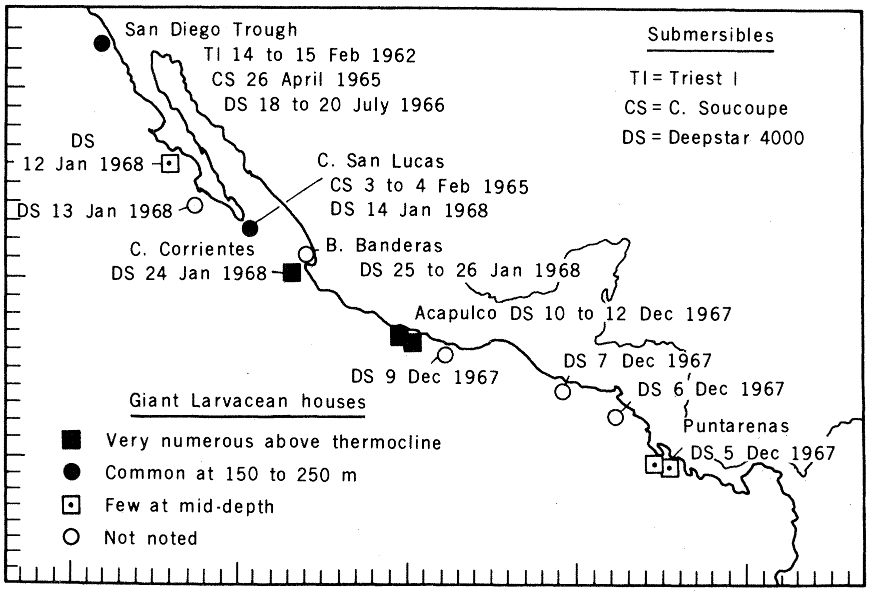

Fig. 1. Locations and dates of submersible dives and the observed relative abundance of large larvacean houses.