

The $\delta^{13}\text{C}$ anomaly in the northeastern Atlantic

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Abstract. The $\delta^{13}\text{C}$ of dissolved inorganic carbon was measured on samples collected at 49°N in the northeast Atlantic in January 1994. Deeper than 2000 m, $\delta^{13}\text{C}$ exhibits the same negative correlation versus dissolved phosphate that is observed elsewhere in the deep Atlantic. Upward from 2000 m to about 600 m, $\delta^{13}\text{C}$ shifts to values more negative than expected from the correlation with nutrients at depth, which is likely due to penetration of anthropogenic CO_2 . From these data, the profile of the anthropogenic $\delta^{13}\text{C}$ decrease is calculated by using either dissolved phosphate or apparent oxygen utilization as a proxy for the preanthropogenic $\delta^{13}\text{C}$ distribution. The shape of the anthropogenic anomaly profile derived from phosphate is similar to that of the increase in dissolved inorganic carbon derived by others in the same area. The reconstruction from oxygen utilization results in a lower estimate of the anthropogenic $\delta^{13}\text{C}$ decrease in the upper water column, and the vertical anomaly profile is less similar to that of the dissolved inorganic carbon increase. A ^{13}C budget for the atmosphere, ocean, and terrestrial biosphere indicates that within the range of probable ocean CO_2 uptake the ratio of $\delta^{13}\text{C}$ to inorganic carbon change should be mostly influenced by the ^{13}C inventory change of the biosphere. However, the uncertainty in the ratio we derive prevents a strong constraint on the size of the exchangeable biosphere.

1. Introduction

The $^{13}\text{C}/^{12}\text{C}$ ratios of atmospheric CO_2 and dissolved inorganic carbon in the upper ocean have been decreasing because anthropogenic carbon dioxide produced by fossil fuel burning and deforestation is enriched in ^{12}C . The cumulative decrease observed in the atmospheric $\delta^{13}\text{C}$ (about -1.3% [Friedli *et al.*, 1986; Keeling *et al.*, 1989]) is considerably less than would have occurred if the 27% increase in atmospheric CO_2 over the last 200 years were caused solely by addition of this amount of anthropogenic CO_2 to a closed atmospheric gas volume (about -4%). The discrepancy is due to the rapid exchange of atmospheric CO_2 with the ocean and terrestrial biosphere, which dilutes the atmospheric $\delta^{13}\text{C}$ decrease. In regard to anthropogenic CO_2 uptake and $\delta^{13}\text{C}$ decrease in the sea, Heimann and Maier-Reimer [1996] reason that the spatial distribution of these anomalies in the ocean must be similar, since they have almost the same shape function in their atmospheric histories. This proposition is supported by experiments with their ocean carbon cycle model, which is forced by the histories of atmospheric CO_2 and $\delta^{13}\text{C}$. The temporal changes in the vertical inventory of dissolved inorganic carbon and of $\delta^{13}\text{C}$ vary widely over the surface of the ocean, but the ratio of these inventory changes at any particular location appears to be relatively constant [Heimann and Maier-Reimer, 1996]. This result suggests that the ratio of $\delta^{13}\text{C}$ decrease ($\Delta\delta^{13}\text{C}$) to dissolved inorganic

carbon increase (ΔC_T) in the global ocean might be obtained from a limited set of locations if it is possible to reconstruct the cumulative $\delta^{13}\text{C}$ and inorganic carbon concentration changes. As discussed in section 4, the ratio of these changes should provide an indication of the carbon mass of the terrestrial biosphere that exchanges readily with atmospheric CO_2 . The problem is to determine the relationship with sufficient precision. In the first part of this paper, we focus on the area of the northeastern Atlantic at 49°N near the European continental margin, and we begin by reconstructing the vertical distribution of the decrease in $\delta^{13}\text{C}$ that has occurred there. These results are then compared to the increase in dissolved inorganic carbon estimated by Körtzinger *et al.* [1998] in the same region.

Various ^{13}C flux balances have been used to estimate the contemporary rate of anthropogenic CO_2 uptake into the sea, either from observed temporal changes in the oceanic $\delta^{13}\text{C}$ [Quay *et al.*, 1992; Heimann and Maier-Reimer, 1996; Bacastow *et al.*, 1996] or from the isotopic disequilibrium between the air and sea surface [Tans *et al.*, 1993]. In their evaluation of the first of these methods, Broecker and Peng [1993] employed an overall budget of ^{13}C inventory changes in the atmosphere, terrestrial biosphere, and ocean to investigate two effects on the average $\delta^{13}\text{C}$ change in the system: (1) incremental addition of anthropogenic CO_2 to the ocean and (2) the masses of exchangeable carbon in the ocean and biosphere. We use a similar procedure to examine the effect of these two factors on the $\Delta\delta^{13}\text{C}/\Delta C_T$ ratio in the ocean. One might expect that the decrease in the $\delta^{13}\text{C}$ of dissolved inorganic carbon in the ocean should be greater than would be produced by the net uptake of anthropogenic CO_2 directly into a closed seawater volume, since the air-sea

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CO_2 exchange that dilutes the change in atmospheric $\delta^{13}\text{C}$ should enhance the ocean $\delta^{13}\text{C}$ decrease. However, this depends upon how much of the atmospheric dilution can be accounted for by exchange with the terrestrial biosphere. As discussed in section 4.2, it appears that if the exchangeable terrestrial carbon mass were large enough (about 2000 Gt C), the ratio of $\Delta\delta^{13}\text{C}$ to ΔC_T in the ocean would approach the closed system value and would not depend on the amount of anthropogenic CO_2 that has been taken up. This is likely not the case, since this would imply that virtually all of the terrestrial biosphere is exchanging with the atmosphere. Thus one would expect that the ratio of $\Delta\delta^{13}\text{C}$ to ΔC_T should be greater than that for uptake of anthropogenic CO_2 in a closed ocean system.

2. Methods

As part of the Ocean Margin Exchange Experiment (OMEX), samples for carbon isotope analysis were collected during January 1994 from a series of hydrocast stations across the European continental margin at about 49°N during

Meteor cruise M27/1 (Figure 1). This area is marked by a westward morphological protrusion of the margin known as the Goban Spur. The samples were poisoned with HgCl_2 , and analysis of the $\delta^{13}\text{C}$ of the total dissolved CO_2 was carried out within the following year at the Leibniz Laboratory of the University of Kiel. From these data (Table 1), we reconstruct the vertical distribution of the $\delta^{13}\text{C}$ decrease using either dissolved phosphate or apparent oxygen utilization (AOU) as proxies for the preanthropogenic $\delta^{13}\text{C}$ distribution. The dissolved phosphate reported here and used for this purpose was analyzed on board cruise M27/1 by the University of Hamburg. For AOU, we have made use of the data collected on Transient Tracers in the Ocean (TTO) stations 116 and 117 [Scripps Institution of Oceanography, 1986] that are very close to our OMEX stations. Dissolved oxygen measurements made on M27/1 generally have about the same average value as the TTO measurements for any given depth, but the former exhibit considerable scatter and therefore cannot be used for the reconstruction. Later in the same year, Körtzinger *et al.* [1998] measured dissolved inorganic carbon on an east-west section (*Meteor* M30/2) that passed close to

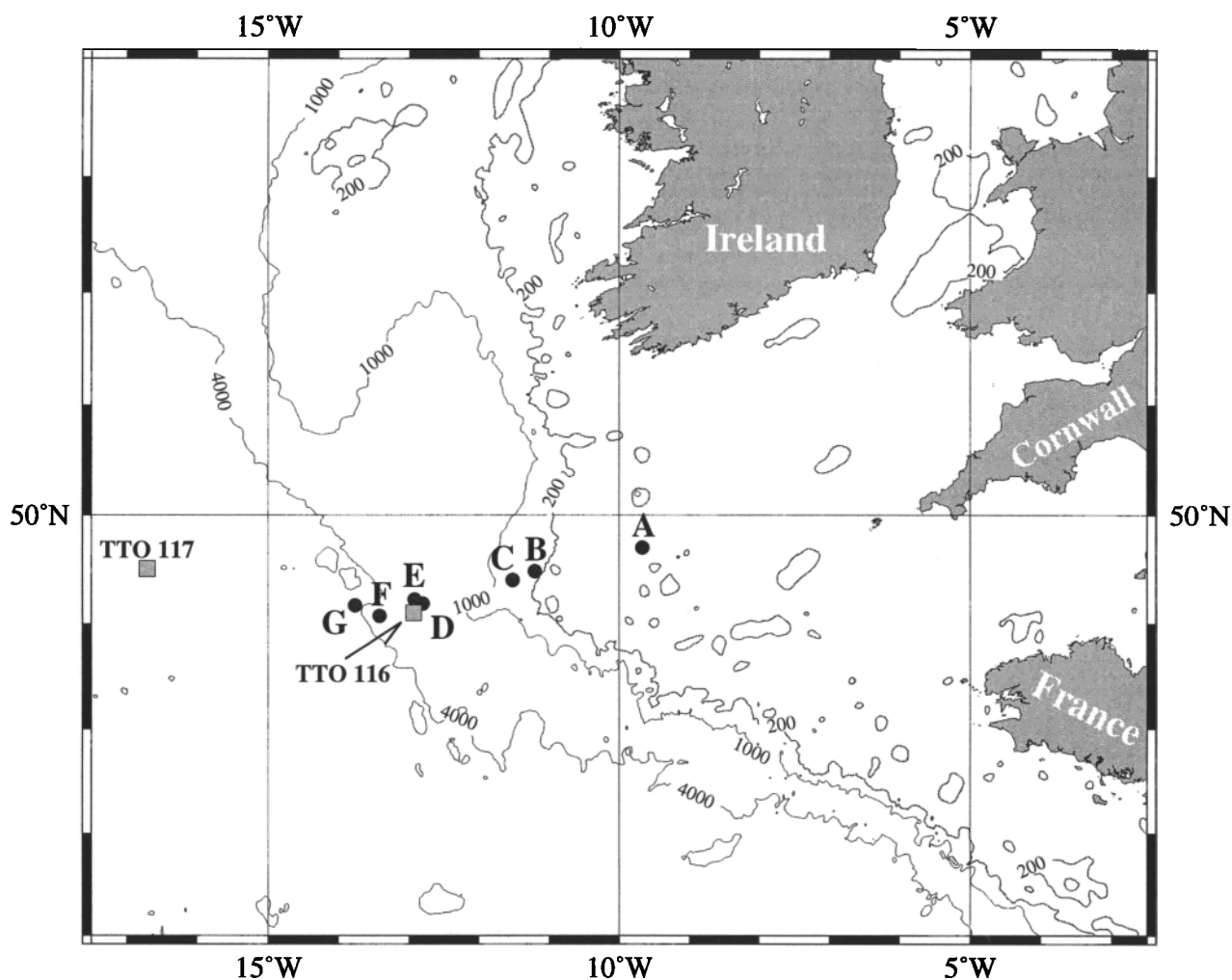


Figure 1. Location of Ocean Margin Exchange Experiment (OMEX I) hydrocast stations, taken during F/S *Meteor* cruise 27/1, January 1994, and Transient Tracers in the Ocean (TTO) stations 116 and 117, taken in June 1981.

Table 1. *Meteor 27/1* Phosphate and $\delta^{13}\text{C}$

Depth, m	PO_4 , $\mu\text{mol kg}^{-1}$	$\delta^{13}\text{C}$, ‰
<i>Station B, Jan. 3, 1994, 49°42.0'N, 9°40.0'W</i>		
9	0.48	0.96
19	0.47	0.98
28	0.47	1.07
43	0.47	0.95
74	0.47	1.06
117	0.48	1.00
159	0.48	1.02
180	0.48	1.02
207	0.47	(0.69)
<i>Station C, Jan. 4, 1994, 49°28.4'N, 11°12.2'W</i>		
10	0.51	0.91
52	(0.66)	1.13
101	0.49	1.15
152	0.49	1.14
202	0.49	0.92
301	0.49	0.95
400	0.72	0.83
451	0.76	0.94
501	0.81	0.88
553	0.83	0.81
630	0.86	0.88
<i>Station D, Jan. 5, 1994, 49°11.0'N, 12°48.2'W</i>		
9	0.44	1.07
103	0.43	1.02
200	0.45	1.01
499	0.72	0.76
705	0.87	0.84
903	0.95	0.83
990	0.97	0.85
1206	1.04	0.83
1308	1.05	0.88
1433	1.07	0.88
<i>Station F, Jan. 7, 1994, 49°03'N, 13°25'W</i>		
10	0.53	0.99
50	0.49	1.07
100	0.51	1.06
198	0.49	1.05
298	0.70	0.88
500	0.81	0.81
600	0.91	0.69

Table 1. (continued)

Depth, m	PO_4 , $\mu\text{mol kg}^{-1}$	$\delta^{13}\text{C}$, ‰
698	0.98	0.67
801	1.12	0.70
901	1.14	0.67
1001	1.17	0.84
1106	(0.88)	0.73
1200	1.18	0.76
1375	1.19	0.84
1500	1.17	0.84
1600	1.16	0.90
1690	1.15	0.83
1800	1.13	1.08
2105	1.16	1.00
2404	1.26	0.98
2704	1.35	0.97
3000	1.41	0.93
<i>Station G, Jan. 14, 1994, 49°01'N, 13°46'W</i>		
13	0.53	1.04
53	0.53	1.00
103	0.54	1.08
155	0.54	1.16
306	0.74	0.97
459	0.81	0.91
609	0.94	0.88
755	1.08	0.77
908	1.06	0.75
1108	1.12	0.68
1310	1.15	0.80
1509	1.12	0.73
1916	1.13	0.87
2117	1.16	1.00
2317	1.26	0.90
2520	1.26	1.04
2725	1.31	0.95
3029	1.38	1.04
3336	1.40	0.98
3641	1.45	1.01
3946	1.45	0.91
4240	1.47	0.98
4516	1.47	0.86

the OMEX area, and from these data, ΔC_T was estimated by back calculation to the pre-formed concentration of dissolved inorganic carbon, based on the methods of *Brewer* [1978] and *Chen and Millero* [1979].

3. Reconstruction of the Preanthropogenic $\delta^{13}\text{C}$ Distribution

The basis for estimating the preanthropogenic $\delta^{13}\text{C}$ distribution according to either dissolved phosphate or AOU will be discussed, in turn, separately. Although $\delta^{13}\text{C}$ tends to be correlated with both of these properties, differing reconstructions result. This can be foreseen from the vertical distributions of these three properties, which are shown in Figure 2 according to the scaling used in the reconstructions. The profile of $\delta^{13}\text{C}$ appears more uniform than that of the other two properties, and the average value of about 1.0‰ in the upper 300 m is low compared to previously reported $\delta^{13}\text{C}$ for surface waters [*Kroopnick*, 1985]. In the water column

below 1700 m, the profiles of phosphate and AOU appear to be similar, but a pronounced maximum in AOU at 900 m has no correspondence in the phosphate distribution, which is approximately constant from 900 m to 1800 m. This appears to be due to a transition in the preformed phosphate concentration from a value of $0.5 \mu\text{mol kg}^{-1}$ in the upper 900 m to a value of $0.8 \mu\text{mol kg}^{-1}$ at 1700 m (Figure 3).

3.1. Phosphate-Based Reconstruction

From Geochemical Ocean Sections Study (GEOSECS) measurements in 1972 [*Kroopnick*, 1985], it appears that $\delta^{13}\text{C}$ and dissolved phosphate may have exhibited a single linear correlation in a large volume of the Atlantic Ocean which includes all deep waters and those intermediate-depth waters north of about 35°S . Figure 4 shows Atlantic GEOSECS data in (1) waters north of 35°S with densities corresponding to $26.8 < \sigma_\theta < 27.7$ and (2) all waters with $\sigma_\theta > 27.7$. The data (listed by *Östlund et al.* [1987]) were not corrected as recommended by *Kroopnick* [1985] because the

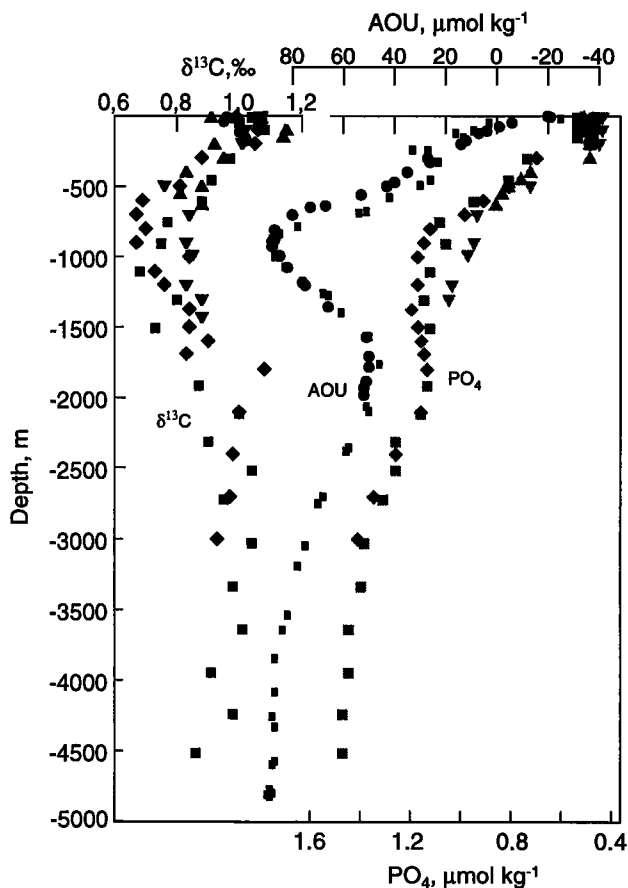


Figure 2. Vertical profiles of $\delta^{13}\text{C}$ and dissolved phosphate at the OMEX stations and apparent oxygen utilization (AOU) from the TTO stations. Different symbols distinguish the individual stations.

correction factors (which are based on the deviation from a global regression against oxygen utilization) for the northern Atlantic stations are systematically positive, and this may be due to real anthropogenic effects. The density layer, $26.8 < \sigma_\theta < 27.7$, lies at an intermediate-depth range of about 800 - 1800 m in most of the Atlantic, except where it outcrops in high latitudes [Zahn and Keir, 1994]. In the North Atlantic in winter, it appears that this density range surfaces over an annular area stretching from the Labrador Sea eastward over the European Basin [McCartney and Talley, 1982]. At phosphate concentrations greater than about $0.7 \mu\text{mol kg}^{-1}$, the trend of $\delta^{13}\text{C}$ versus PO_4 in both density ranges coincides, and the covariation appears to be linear (Figure 4). Surface phosphate concentrations in winter vary between 0.9 and $0.65 \mu\text{mol kg}^{-1}$ from 63°N to 47°N along 20°W [Takahashi et al., 1993], and the concentration of $0.7 \mu\text{mol kg}^{-1}$ is approximately that of the average preformed phosphate of North Atlantic Deep Water components [Broecker and Peng, 1982]. Thus the GEOSECS data in Figure 4 imply that north of 35°S in the Atlantic the natural pattern of $\delta^{13}\text{C}$ versus PO_4 in intermediate and deep waters is mostly influenced by mixing between end-member characteristics found in the northern winter surface and at depth in southern waters of the Atlantic Ocean.

If dissolved inorganic carbon and nutrients are biologically fixed into biomass and then removed from a closed volume of water, the $\delta^{13}\text{C}$ of the remaining dissolved carbon should increase by about 1.1‰ per $\mu\text{mol kg}^{-1}$ decrease in PO_4 [Broecker and Maier-Reimer, 1992]. As shown in Figure 4, the slope of $\delta^{13}\text{C}$ versus PO_4 of the intermediate and deep waters ($\text{PO}_4 > 0.7 \mu\text{mol kg}^{-1}$) is less negative than expected from biological fractionation alone, apparently because a light $^{13}\text{C}/^{12}\text{C}$ signal has entered the northern surface sources of these waters. Part of this signal may originate from anthropogenic CO_2 that has already penetrated these waters but has not yet appreciably affected older Circumpolar Deep Water in the south. In addition, there also appears to be a natural transfer of ^{13}C -deficient CO_2 into northern Atlantic surface waters by two processes: (1) one-way transfer of CO_2 through the atmosphere [Keir, 1993] and (2) poleward transport of surface water with low $\delta^{13}\text{C}$ [Lynch-Stieglitz et al., 1995].

The one-way transfer of CO_2 from sea to air carries a lower $\delta^{13}\text{C}$ than in the total inorganic carbon of the surface water, but the isotopic fractionation of the return flux of CO_2 to the sea is small [Siegenthaler and Münnich, 1981]. As a result, the atmospheric $\delta^{13}\text{C}$ is about 9‰ lower than the average $\delta^{13}\text{C}$ of surface waters. A region where the sea surface $p\text{CO}_2$ is undersaturated and represents a natural sink for atmospheric CO_2 , such as the northern Atlantic appears to be [Takahashi et al., 1993], should receive a one-way CO_2 influx with a $\delta^{13}\text{C}$ significantly less than that of sea surface dissolved inorganic carbon.

The nature of the upper ocean circulation in the Atlantic may also contribute to the lowering of preformed $\delta^{13}\text{C}$. Thermodynamically, the carbon isotopic fractionation between the sea and air increases as surface temperature decreases. For this reason, balanced air-sea exchanges of CO_2 tend to reduce the $\delta^{13}\text{C}$ of warm surface waters, and subtropical

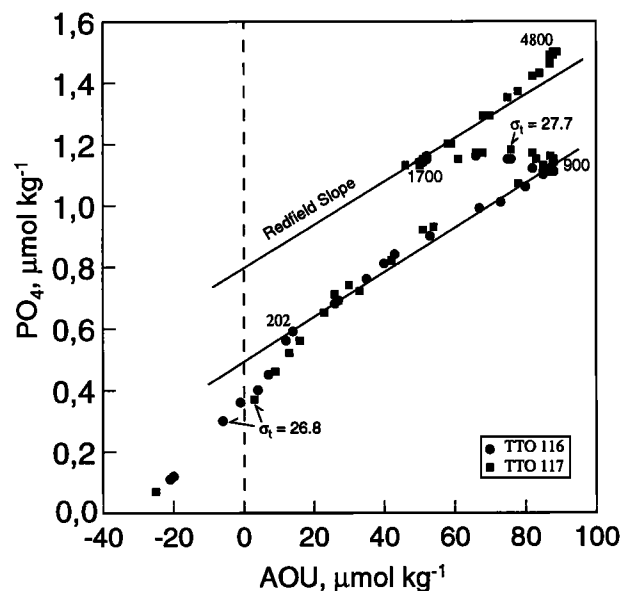


Figure 3. Phosphate versus apparent oxygen utilization at TTO stations 116 and 117. Here the phosphate concentrations are those analyzed on the TTO expedition.

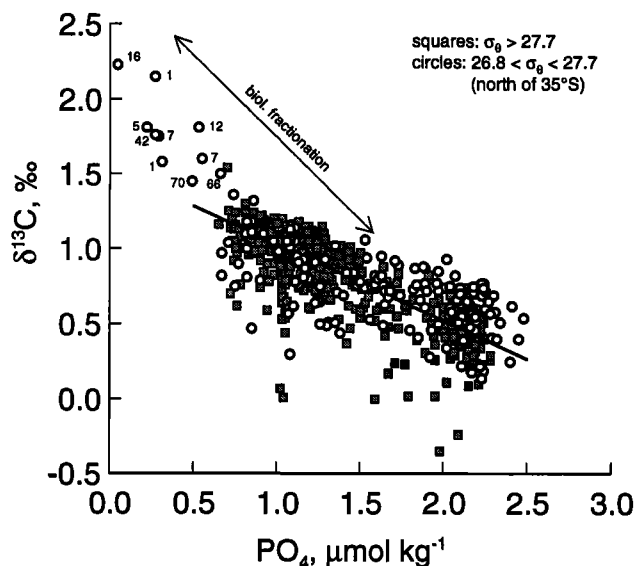


Figure 4. Atlantic 1972 Geochemical Ocean Sections Study (GEOSECS) $\delta^{13}\text{C}$ versus PO_4 within the density range of $26.8 < \sigma_\theta < 27.7$ north of 35°S (circles) and all waters with $\sigma_\theta > 27.7$ (squares). Numbers adjacent to the samples with low PO_4 concentration indicate depth in meters below surface. Lines indicate the linear regression of the deep water $\delta^{13}\text{C}$ versus PO_4 (squares) and the slope expected from biological fractionation in a closed system.

gyre waters have lower $\delta^{13}\text{C}$ than expected from their low nutrient values [Lynch-Stieglitz *et al.*, 1995]. Transport of warm waters northward followed by cooling feeds the formation of subsurface waters in the North Atlantic, and if the warm to cold water conversion rate is more rapid than the isotopic reequilibration of surface waters (timescale ~ 10 years) due to the cooling, this transport may also contribute to a natural reduction in the preformed $\delta^{13}\text{C}$ of subpolar mode and deep waters.

We note parenthetically that in Figure 4 the phosphate concentrations lower than $0.7 \mu\text{mol kg}^{-1}$ were found during summer within the surface mixed layer in the high northern latitudes, and the greater negative slope of $\delta^{13}\text{C}$ against these lower PO_4 values is similar to that expected from biological fractionation alone. This could occur because of rapid removal of carbon and phosphate during the spring bloom, starting from prebloom phosphate concentrations of about $0.8 \mu\text{mol kg}^{-1}$.

Although the entire water column near the Goban Spur is denser than $\sigma_\theta = 26.8$ in winter, the $\delta^{13}\text{C}$ values we measured do not show a linear relation to phosphate (Figure 5). The $\delta^{13}\text{C}$ - PO_4 trend in the deeper part of the water column follows the mixing line between North Atlantic and Circumpolar Deep Water observed elsewhere in the Atlantic [Lynch-Stieglitz *et al.*, 1995], but $\delta^{13}\text{C}$ appears to shift to noticeably lower values at phosphate concentrations less than about $1.2 \mu\text{mol kg}^{-1}$. In order to estimate the decrease in $\delta^{13}\text{C}$ over time, we assume here that the preanthropogenic $\delta^{13}\text{C}$ was linearly correlated with phosphate throughout the water column in winter in the northeastern Atlantic. This is implied by the GEOSECS observations in the western North Atlantic. As

shown in Figure 5, we define the preanthropogenic trend by assuming (1) that anthropogenic CO_2 has negligibly affected the $\delta^{13}\text{C}$ of the Circumpolar Deep Water that enters the Atlantic through the Vema Passage and (2) that the $\delta^{13}\text{C}$ of the winter mixed layer at the Goban Spur had decreased by 0.8‰ at the time of the measurements in 1994. The first assumption would seem reasonable since Circumpolar Deep Water contains a large component of old deep water returning from the Pacific, a small component of not-so-recently-formed North Atlantic Deep Water (NADW), and a small quantity of more recently formed Weddell Sea Bottom Water (WSBW) [Lynch-Stieglitz *et al.*, 1995]. The low values of radiocarbon found in WSBW indicate that even this component is poorly ventilated relative to carbon isotopes during its formation [Weiss *et al.*, 1979].

In regard to the second assumption, 0.8‰ is the average $\delta^{13}\text{C}$ decrease recorded in demosponges collected from the Caribbean and Coral seas (0.9 and 0.7‰ , respectively [Böhm *et al.*, 1996]). These records span the last two centuries up to the end of 1992, and we assume that $\delta^{13}\text{C}$ decreased by this amount in surface waters over the Goban Spur as well. Although the temporal decrease of surface ocean $\delta^{13}\text{C}$ due to anthropogenic CO_2 is not expected to be uniform spatially, the decrease simulated by the Hamburg model at the Goban Spur is similar to the $\delta^{13}\text{C}$ decreases at the locations where the sponges were collected [Bacastow *et al.*, 1996]. We refer specifically to their Figure 9a, which shows contours of the rate of change in $\delta^{13}\text{C}$ during the period 1983-1995. The Caribbean and the northeast European margin both exhibit rates of -0.018‰ year^{-1} , while the Coral Sea has about -

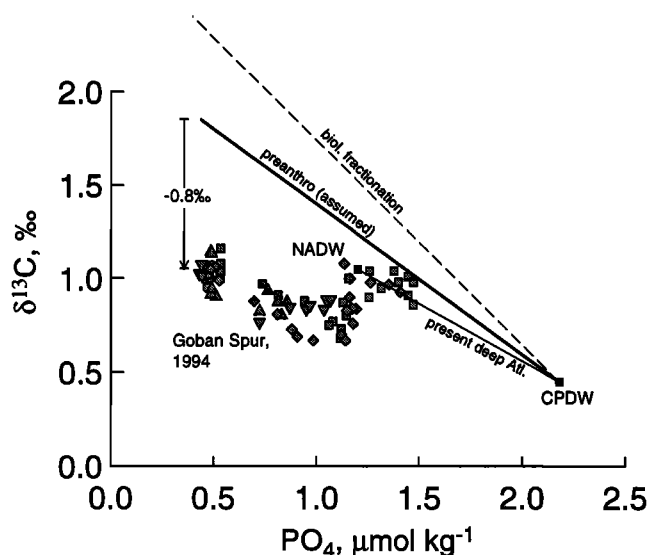


Figure 5. $\delta^{13}\text{C}$ versus PO_4 measured from OMEX hydrocast stations shown in Figure 1. Starting from the composition of Circumpolar Deep Water (CPDW), lines show mixing trend with North Atlantic Deep Water (NADW) [Lynch-Stieglitz *et al.*, 1995], effect of closed system biological fixation (dashed), and our assumed preanthropogenic trend in the study area. The preanthropogenic trend has a lower negative slope than produced by biological fixation, indicating that the preformed NADW is a natural sink for atmospheric CO_2 (see text). Equation for this line is $\delta^{13}\text{C}(\text{pre}) = 2.20 - 0.803 [\text{PO}_4]$.

0.020‰ year⁻¹. Other areas have quite different rates, as low as -0.004‰ year⁻¹ near Antarctica, for example.

The $\delta^{13}\text{C}$ of newly formed NADW is expected to be slightly greater in the preindustrial era than in 1972 (at the time of GEOSECS) but not as high as would be predicted from biological uptake from the composition of Circumpolar Deep Water. Our estimated preanthropogenic $\delta^{13}\text{C}$ - PO_4 trend falls inbetween these two limiting extremes (Figure 5). The predicted preanthropogenic $\delta^{13}\text{C}$ shown in Figure 5 is on average 0.09‰ greater than the five measured $\delta^{13}\text{C}$ values below 3300 m depth ($\text{PO}_4 \sim 1.45 \mu\text{mol kg}^{-1}$). Since these samples should not have been influenced by anthropogenic CO_2 , the assumed linear pre-anthropogenic correlation between $\delta^{13}\text{C}$ and PO_4 appears to slightly overestimate the temporal change in the deepest part of the water column.

3.2. $\delta^{13}\text{C}$ Anomaly (PO_4 -Based) versus Depth

The difference between our measured $\delta^{13}\text{C}$ and that predicted from the phosphate concentration ($\Delta\delta^{13}\text{C}$) of corresponding samples is plotted versus depth in Figure 6. The distribution indicates that the carbon isotope anomaly has penetrated rather deep in the water column at 49°N in the eastern Atlantic. This is to be expected from the active formation of subsurface waters in the North Atlantic in general. The 1800 m depth at the Goban Spur corresponds to

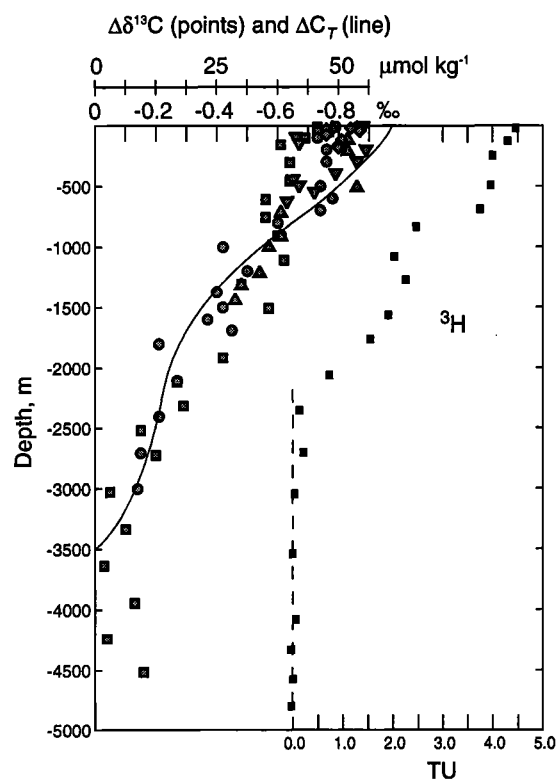


Figure 6. Phosphate-based $\Delta\delta^{13}\text{C}$ versus depth in the OMEX area (symbols left side). The solid line indicates the average ΔC_T in the eastern Atlantic (47° - 49°N) according to Körtzinger et al. [in press]. The axes are scaled to the ratio of their water column inventories (-0.016‰ per $\mu\text{mol C kg}^{-1}$). Square symbols at right show the vertical profile of tritium at TTO Station 117 [Östlund and Grall, 1987].

the core of the cyclonic circulation of Labrador Sea Water eastward across the Atlantic [Talley and McCartney, 1982]. Tritium measurements during TTO show that these transient tracers have begun to appear at the 2000 m level adjacent to the European margin [Östlund and Grall, 1987]. As shown in Figure 6, the shape of the profile of $\Delta\delta^{13}\text{C}$ is fairly similar to that of tritium, but the isotope signal appears to penetrate deeper than the bomb-produced tracer. This is to be expected because anthropogenic CO_2 has been added to the ocean over a longer time period than tritium.

The shape of the vertical profile of the phosphate-calculated $\Delta\delta^{13}\text{C}$ anomaly pattern is similar to the profile of excess CO_2 (Figure 6) calculated from total dissolved CO_2 measurements during *Meteor* cruise 30/2 in the same general area during October 1994 [Körtzinger et al., 1998]. To obtain the water column inventory, we averaged the $\Delta\delta^{13}\text{C}$ values in the upper 300 m (the depth of the mixed layer at the time of collection) and in 200 m intervals below the mixed layer. The $\Delta\delta^{13}\text{C}/\Delta C_T$ ratio obtained from the depth-integrated inventories of both quantities is -0.016‰ ($\mu\text{mol C kg}^{-1}$)⁻¹. This result is not purely observational, as it rests on the assumption that the $\delta^{13}\text{C}$ of Goban Spur surface waters decreased by 0.8‰. The uncertainty in this ratio appears to be ± 0.005 ‰ ($\mu\text{mol C kg}^{-1}$)⁻¹. This is based on a ± 0.1 ‰ uncertainty both in the measurements within the upper 300 m and in the proxy records, and a $\pm 10 \mu\text{mol kg}^{-1}$ uncertainty in the ΔC_T reconstruction.

The $\Delta\delta^{13}\text{C}/\Delta C_T$ ratio we obtain can be compared to the plot of vertically integrated rates of change in $^{13}\text{C}/^{12}\text{C}$ versus dissolved inorganic carbon simulated by the Hamburg ocean general circulation model [Heimann and Maier-Reimer, 1996]. The model uses prescribed histories of the atmospheric CO_2 and its $\delta^{13}\text{C}$ together with one of two alternate formulations of the gas exchange over the ocean surface. In both cases, the plot shows generally a good correlation between the two inventory changes, the slope being equivalent to $\Delta\delta^{13}\text{C}/\Delta C_T$. A close inspection of Heimann and Maier-Reimer's Figure 6 indicates that the relationship between these two inventory changes tends to be split into two trends with slopes of about -0.019‰ ($\mu\text{mol C kg}^{-1}$)⁻¹ and -0.016‰ ($\mu\text{mol C kg}^{-1}$)⁻¹, the latter corresponding to the value we derive from the phosphate reconstruction. In the model, all of the points that come from areas of greater accumulation of anthropogenic CO_2 , which should include the northeastern Atlantic, fall on the line with the lower negative slope.

3.3. AOU-Based Calculation of $\Delta\delta^{13}\text{C}$

As an alternative to the method above, we apply a procedure for estimating $\Delta\delta^{13}\text{C}$ from AOU that is essentially equivalent to that of Kroopnick [1985]. Our calculation does not include corrections for changes in alkalinity and preformed inorganic carbon concentration, but these corrections are minor. The global correlation of $\delta^{13}\text{C}$ versus AOU has a slope (-0.0074‰ per $\mu\text{mol O}_2 \text{ kg}^{-1}$) close to that expected from Redfield-ratio biological recycling in a closed ocean system. One assumes that the $\delta^{13}\text{C}$ of a water parcel at depth has changed from the preformed $\delta^{13}\text{C}$ in this proportion to the apparent oxygen utilization. Changes in the spatial distribution of the calculated preformed $\delta^{13}\text{C}$ are then ascribed

to the effects of anthropogenic CO_2 . Thus the spatial distribution of preanthropogenic, preformed $\delta^{13}\text{C}$ is assumed to be constant for the water volume under consideration. Kroopnick applied this procedure to individual water masses that are formed in the same region. Here this assumption applies to different water masses found in the water column.

Using the global $\delta^{13}\text{C}$ versus AOU slope, the $\delta^{13}\text{C}$ values observed in our deepest samples are predicted closely by a $\delta^{13}\text{C}$ intercept of 1.6‰ at oxygen saturation. This value is slightly greater than the value of 1.47‰ found in the regression of all deep water data [Kroopnick, 1985]. We assume here that the $\delta^{13}\text{C}$ anomaly in the water column is given by the deviation of the measured value from that predicted by $1.6 - 0.0074 \times \text{AOU}$. Here we have used the AOU from TTO stations 116 and 117 below 300 m (Figure 3) and an assumed AOU = 0 in the upper 300 m corresponding to the winter mixed layer.

The profiles of $\Delta\delta^{13}\text{C}$ obtained by the AOU method are compared to the average profile obtained from the phosphate method in Figure 7. Below 1700 m, the two methods yield coherent profiles, but there is a noticeable divergence in the profiles above this level. The AOU-predicted $\Delta\delta^{13}\text{C}$ at the surface is -0.6‰ as compared to the -0.8‰ indicated by the sponge proxy records [Böhm *et al.*, 1996]. The largest discrepancy occurs at 900 m depth, where the AOU-based $\Delta\delta^{13}\text{C}$ goes through a minimum of about -0.2‰. The phosphate-based $\Delta\delta^{13}\text{C}$, in contrast, indicates no minimum in the vertical distribution and gives a value of about -0.55‰ at this depth.

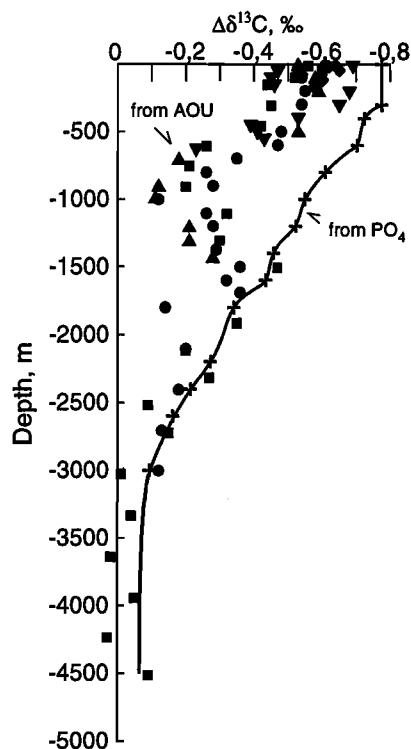


Figure 7. Solid points show $\Delta\delta^{13}\text{C}$ versus depth as calculated according to the AOU method. The curve shows the trend of $\Delta\delta^{13}\text{C}$ from the phosphate method, drawn through the depth-averaged values (crosses).

The core of outflow water from the Mediterranean Sea is found at 900 m depth at the Goban Spur, and one could ask whether the AOU maximum at this level is partly due to slow ventilation. However, from the tritium distribution at TTO 117, this would not seem to be the case, as its concentration at 900 m is greater than that found at the 1700 m level (Figure 6), where the AOU-based $\Delta\delta^{13}\text{C}$ goes through a relative maximum. Since the isotope anomaly is being introduced to the ocean over a longer time scale than tritium, it would not seem possible to simultaneously produce the tritium and AOU-based $\Delta\delta^{13}\text{C}$ profiles. The PO_4 -based $\Delta\delta^{13}\text{C}$ appears more similar to both the tritium and ΔC_T profiles, and we believe that this estimate of the penetration of the isotope anomaly is more realistic. In the case of the AOU-derived $\Delta\delta^{13}\text{C}$, its vertical inventory relative to that of ΔC_T is about -0.010‰ ($\mu\text{mol C kg}^{-1}$)⁻¹, about 60% of the PO_4 -derived estimate. As discussed in section 4.2, lower values of this ratio imply greater exchange capacity of the terrestrial biosphere. The AOU-derived $\Delta\delta^{13}\text{C}/\Delta C_T$ would imply an exchangeable carbon mass in the terrestrial biosphere of about 3000 Gt C, which is about 50% greater than the entire mass of the biosphere.

The two methodologies carry different implications concerning the surface distribution of preformed $\delta^{13}\text{C}$ and the impact of the natural biogeochemical fractionation in the upper water column. The phosphate method assumes that end-member mixing dominates all the way up to the winter surface sources for the water column. It also implicitly assumes that the spatial distribution of preformed $\delta^{13}\text{C}$ was correlated with that of preformed phosphate. Thus, corresponding to the preformed phosphate difference indicated by Figure 3, preformed $\delta^{13}\text{C}$ is implicitly assumed to have been on average 0.24‰ greater in surface sources for the upper 900 m than those for 1700 m. In contrast, it is assumed in the AOU method that the preformed $\delta^{13}\text{C}$ was constant for the water column.

The phosphate assumption implies that the full effect of local reoxidation of organic matter on the $\delta^{13}\text{C}$ distribution is reduced by the combination of isopycnal mixing and gas-exchange effects in the regions of water mass formation. This affects the calculation of $\Delta\delta^{13}\text{C}$ in the upper water column. For example, at 900 m, the natural decrease in $\delta^{13}\text{C}$ according to an AOU of $88 \mu\text{mol O}_2 \text{ kg}^{-1}$ is 0.65‰, equivalent to the observed increase of $0.6 \mu\text{mol P kg}^{-1}$ over its preformed value. However, in the phosphate method, this is accorded only an 0.48‰ decrease in $\delta^{13}\text{C}$ as the natural effect, since the slope of the $\delta^{13}\text{C}$ vs. PO_4 ($-0.8\text{‰ per } \mu\text{mol P kg}^{-1}$) is lower than that due to biological fractionation. Thus, at 900 m, the discrepancy between the two methods results from about a 0.2‰ difference in the implied preformed $\delta^{13}\text{C}$ and a 0.15‰ difference in the natural decrease due to the biogeochemical cycle. The discrepancy between the phosphate- and AOU-based $\Delta\delta^{13}\text{C}$ illustrates that carbon isotope oceanography needs to be better understood.

4. ^{13}C Mass Balance

In order to illustrate how the ratio of $\Delta\delta^{13}\text{C}$ to ΔC_T in the ocean depends on the amount of anthropogenic CO_2 added to the ocean and the mass of the exchangeable biosphere, we use a mass balance approach modified from Broecker and Peng

[1993]. This approach considers that certain pre-anthropogenic masses of carbon in the atmosphere (M_a^0), sea (M_s^0), and biosphere (M_b^0) have undergone "characteristic" $\delta^{13}\text{C}$ decreases up to the present time. Because the atmosphere is rapidly mixed, its $\delta^{13}\text{C}$ change is fairly uniform spatially. In the terrestrial biosphere and ocean, the decrease in $\delta^{13}\text{C}$ is not homogenous, as the atmospheric signal penetrates differently into these reservoirs. For the ocean, the characteristic $\delta^{13}\text{C}$ decrease is taken to be that of the surface water. Here M_s^0 corresponds to the "penetration depth" for the fossil fuel ^{13}C anomaly, that is, M_s^0 is the carbon mass which, multiplied by the surface ocean $\Delta\delta^{13}\text{C}$, yields the ^{13}C inventory change in the water column [Broecker and Peng, 1993].

For the terrestrial biosphere, it is difficult to estimate an average $\Delta\delta^{13}\text{C}$ relative to that of the atmosphere, in part because the size of the large amount of soil carbon and its turnover rate are both uncertain. Conceptually, we think of the "characteristic" $\delta^{13}\text{C}$ change of the biosphere ($\Delta\delta_b$) as the average change in $\delta^{13}\text{C}$ that occurs in the biospheric systems actively exchanging with the atmosphere, i.e. vegetation, wood, and detritus. According to the ecosystem model of Emmanuel *et al.* [1984], these systems contain about 700 Gt C with an overall average turnover time of about 12 years. When such a box model is forced by an exponential change with time constant $1/\mu$, the $\Delta\delta^{13}\text{C}$ of the various boxes tend to respond exponentially. In time, the $\Delta\delta^{13}\text{C}$ in a box with residence time $1/k$ tends to approach a ratio of $k/(k+\mu)$ relative to the $\Delta\delta^{13}\text{C}$ of the influx. Since the overall e-folding time for the accelerating rate of $\delta^{13}\text{C}$ decrease in the atmosphere has been about 30 years, $\Delta\delta_b$ is roughly estimated to be 70% (i.e., $30/(30+12)$) of the atmospheric $\delta^{13}\text{C}$ change ($\Delta\delta_a$). For this discussion, M_b^0 , which we loosely refer to as the exchangeable biospheric carbon, includes the active components above and the amount of the soil carbon delivering the equivalent of their average $\delta^{13}\text{C}$ change. For example, in the model of Emmanuel *et al.* [1984], carbon transferred from detritus and wood into soil carbon has about a 100 year residence time and therefore would exhibit a $\delta^{13}\text{C}$ change about 25% (i.e. $30/(30+100)$) of the anomaly $\delta^{13}\text{C}$ supplied from the "active" systems. Assuming a soil carbon mass of 1500 Gt C, M_b^0 in this case would be about $700 + 1500 \times 0.25 \approx 1100$ Gt C.

Given the preanthropogenic exchangeable carbon masses, the budget for ^{13}C can be described in terms of the product of the contemporary mass and $\delta^{13}\text{C}$ in each reservoir, $M_i \delta_i$ [Tans *et al.*, 1993]. Thus,

$$\sum_i M_i \delta_i = \delta^* \Delta M + \sum_i M_i^0 \delta_i^0 \quad (1)$$

where ΔM is the total amount of anthropogenic CO_2 added, δ^* is its average $\delta^{13}\text{C}$, and δ_i^0 is the pre-anthropogenic $\delta^{13}\text{C}$ characteristic of each reservoir. Isotopic fractionations by air-sea exchange and photosynthetic uptake into the biosphere result in natural differences in these $\delta^{13}\text{C}$ values. As a result, the $\delta^{13}\text{C}$ of anthropogenic CO_2 is about 20‰ lower than that of atmospheric CO_2 , is 30‰ lower than in surface water inorganic carbon, but is not very different than the bulk of the biosphere derived from the C3 photosynthesis pathway. Since $\Delta M = \sum \Delta M_i$, a relationship for the $\delta^{13}\text{C}$

changes can be obtained by subtracting $\sum (M_i^0 + \Delta M_i) \delta_i^0$ from both sides of (1), thus

$$\sum_i (M_i^0 + \Delta M_i) \Delta \delta_i = \sum_i \Delta M_i (\delta^* - \delta_i^0) \quad (2)$$

The right side of this relationship implies that the magnitude of the overall $\delta^{13}\text{C}$ decrease depends on the amount of anthropogenic CO_2 added, the partitioning of this CO_2 between the reservoirs, and the exchangeable carbon masses they contain. In the sections 4.1 and 4.2, we impose one of the following two conditions on equation (2): (1) the changes in atmospheric and biospheric $\delta^{13}\text{C}$ occur in proportion to the ocean's isotopic change, or (2) the change in atmospheric $\delta^{13}\text{C}$ is fixed at its proxy-observed value. In the first case, we are interested in the expected behavior of the $\delta^{13}\text{C}$ decrease in the ocean with variable amounts of anthropogenic CO_2 uptake. In the second case, we are interested in what could be deduced from the observed ratio of these two changes. Values common to both calculations are listed in Table 2.

4.1. $\Delta\delta_s$ versus ΔC_T

From ice core and air measurements it appears that atmospheric CO_2 has increased by 75 ppm over the last 200 years, equivalent to an accumulation of 159 Gt C (as of 1992 [Keeling and Whorf, 1994]). First, we calculate the changes in surface water $\delta^{13}\text{C}$ ($\Delta\delta_s$) that occur when various additional amounts of anthropogenic CO_2 have accumulated in the ocean and in the biosphere. For this purpose, we assume that the $\delta^{13}\text{C}$ changes in each reservoir occur in proportion to each other. In the case of the change in seawater $\delta^{13}\text{C}$, the exact proportions do not significantly affect the result because the upper ocean contains the largest exchangeable carbon mass, roughly 3 times that of the combined atmosphere and biosphere. We use $\Delta\delta_a/\Delta\delta_s = 1.6$ and $\Delta\delta_b/\Delta\delta_s = 1.1$, the former coming from the observed $\delta^{13}\text{C}$ changes in the ice core-atmosphere and the demosponge proxy records and the latter being based on the estimate of 0.7 for $\Delta\delta_b/\Delta\delta_a$ described in section 4. Substituting into (2), one obtains:

$$\Delta\delta_s = \frac{\sum_i \Delta M_i (\delta^* - \delta_i^0)}{(1.6M_a + 1.1M_b + M_s)} \quad (3)$$

where $M_a = (M_a^0 + \Delta M_a)$, etc. From the amount of anthropogenic CO_2 added to the ocean, ΔM_s , the change in inorganic carbon concentration is given by

Table 2. Values Employed in all Mass Balance Calculations

Parameter	Value
Atmospheric carbon masses:	
Pre-Anthropogenic	594 Gt
Cumulative Increase	159 Gt
$\delta^{13}\text{C}$ values	
Anthropogenic Source	-26.5‰
Preanthropogenic	
Atmosphere	-6.5‰
Surface Ocean	+2.5‰
Biosphere	-24.5‰

$$\Delta C_T = \frac{\Delta M_s}{M_s^0} C_T^0 \quad (4)$$

where M_s^0/C_T^0 corresponds to the ocean volume contained in the depth range of penetration. Broecker and Peng [1993] have estimated this depth to be about 570 m, containing about 5000 Gt C. In equation (3), ΔM_a is fixed at 159 Gt C, and ΔM_b is assumed to be zero in most cases or 100 Gt C for comparison. (100 Gt C would seem to be an upper limit for the "missing sink" [Siegenthaler and Sarmiento, 1993].) The $\delta^{13}\text{C}$ decrease of the ocean ($\Delta\delta_s$) and ΔC_T are then calculated according to variable amounts of carbon dioxide uptake in the ocean using (3) and (4). Thus the total amount of anthropogenic CO_2 produced is variable in this calculation and equals 159 Gt C + ΔM_b + ΔM_s . The covariations of $\Delta\delta_s$ versus ΔC_T that result are shown in Figure 8.

If only 159 Gt of anthropogenic carbon were produced and all of it somehow remained in the atmosphere (e.g., if ocean uptake were blocked by a rise in surface temperature), the $\delta^{13}\text{C}$ of all three reservoirs would still decrease because of the exchanges of atmospheric CO_2 . In this hypothetical case, the surface ocean $\delta^{13}\text{C}$ would decrease by about 0.4 to 0.5‰, assuming a 570 m penetration depth and an exchangeable biosphere of 700 - 2000 Gt C (solid curves in Figure 8). The total amount of anthropogenic CO_2 released must be larger than 159 Gt C, since generation by fossil fuel burning alone

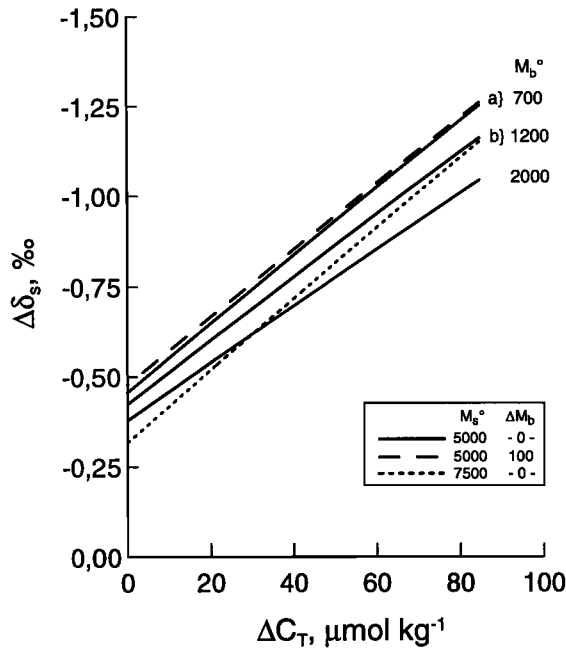


Figure 8. Calculated relationship between $\Delta\delta_s$ and ΔC_T resulting from variable amounts of anthropogenic CO_2 being taken up in the upper ocean. The $\delta^{13}\text{C}$ changes of the atmosphere, ocean, and biosphere are assumed to occur in fixed proportions. Numbers indicate constant carbon masses in gigatons. Solid curves show the effect of different exchangeable biospheric carbon masses. (a) For $M_b^0 = 700$ Gt C, dashed curve shows the effect of 100 Gt C biospheric uptake. (b) For $M_b^0 = 1200$ Gt C, dotted curve shows the effect of a 50% greater ocean penetration depth on the covariation.

has produced about 235 Gt C. The additional amount of release that has accumulated in the ocean augments the $\delta^{13}\text{C}$ decrease of all three reservoirs, but the ratio of $\Delta\delta_s$ to ΔC_T decreases as the amount taken up in the ocean becomes greater. In contrast, for a fixed amount of anthropogenic CO_2 taken up by the atmosphere and ocean, supplemental anthropogenic production that has accumulated in the biosphere has a negligible effect on the $\delta^{13}\text{C}$ changes. This is seen in comparison (a) in Figure 8, where the biospheric uptakes are 0 and 100 Gt C. The reason for this is that the additional anthropogenic carbon which is taken up in the biosphere has a $^{13}\text{C}/^{12}\text{C}$ ratio close to that of the anthropogenic source. Thus only the subtotal of the anthropogenic CO_2 that accumulates in the atmosphere and ocean produces an appreciable change in the $\delta^{13}\text{C}$ of the entire system.

For any given amount of this subtotal, dilution by larger exchangeable carbon masses in the biosphere and ocean produce smaller overall $\Delta\delta^{13}\text{C}$. However, the variation of $\Delta\delta_s$ with the change in ocean carbon concentration, ΔC_T , is not strongly affected by a $\pm 30\%$ variation in the size of the ocean's penetration depth. This is illustrated in comparison (b) in Figure 8, where M_s^0 is increased by 50%. In this case, at any given value of ΔC_T , 50% greater anthropogenic CO_2 is added to the ocean. The greater amount of exchangeable carbon in the ocean dilutes both $\Delta\delta_s$ and ΔC_T , although not in the same proportion. At low ΔC_T , the isotope signal coming from exchange with the atmosphere is more diluted by the larger ocean carbon mass, and $\Delta\delta_s$ is lower. However, the slope of the $\Delta\delta_s$ versus ΔC_T is somewhat greater for the larger M_s^0 , and the difference in the $\Delta\delta_s$ values calculated from the two penetration depths diminishes as ΔC_T increases.

4.2. Influence of Ocean Uptake and Biosphere Exchange on $\Delta\delta_s/\Delta C_T$

Presupposing that $\Delta\delta^{13}\text{C}$ and ΔC_T in the ocean will be precisely measurable, what could be deduced in regard to the perturbation of the carbon system by production of anthropogenic CO_2 ? Equation (2) can be written in terms of the $\Delta\delta_s/\Delta C_T$ ratio by substituting for the exchangeable carbon mass in the ocean,

$$(M_s^0 + \Delta M_s) = \Delta M_s / (\Delta C_T / C_T)$$

where C_T is the contemporary average concentration of dissolved inorganic carbon within the penetration depth. As shown above, the effect of net uptake of CO_2 in the biosphere changes $\delta^{13}\text{C}$ negligibly throughout the system, and the two terms involving ΔM_b in (2) can be dropped. After rearranging, we obtain

$$\frac{\Delta\delta_s}{\Delta C_T} = \frac{\delta^* - \delta_s^0}{C_T} + \frac{1}{\Delta M_s C_T} \times [\Delta M_a (\delta^* - \delta_a^0) - (M_a^0 + \Delta M_a) \Delta\delta_a - M_b^0 \Delta\delta_b] \quad (5)$$

Since $\Delta C_T/C_T = \Delta\delta_s/(\delta^* - \delta_s^0)$ for a closed addition of anthropogenic CO_2 to the ocean, the first term on the right in (5) is the closed-system $\Delta\delta_s/\Delta C_T$ ratio one would observe if anthropogenic CO_2 were added directly to an ocean having no

gas exchange with the atmosphere. The second term on the right is related to the augmentation of $\Delta\delta_s$ by gas exchange with the atmosphere, and this quantity varies inversely with the amount of ocean CO_2 uptake. From the atmospheric CO_2 increase of 159 Gt C and its $\delta^{13}\text{C}$ change of -1.3‰ , the first two terms in the brackets are constrained to about $159 \times (-20\text{‰}) - 753 \times (-1.3\text{‰}) = -2200\text{‰}$ Gt C. If the exchangeable carbon mass in the biosphere (M_b^0) were large enough to match this perturbation, $\Delta\delta_s/\Delta C_T$ would be independent of the amount of anthropogenic CO_2 added to the ocean. This is rather unlikely, since rapid exchange of the entire terrestrial biosphere (about 2000 Gt C \times -1‰ in $\Delta\delta_b$) with the atmosphere would be required. Although the biospheric ^{13}C inventory change is not very well known, it probably lies between -500 and -1500‰ Gt C [Siegenthaler and Oeschger, 1987; Keeling et al., 1989; Quay et al., 1992]. Therefore it appears that the ratio of $\Delta\delta_s$ to ΔC_T should be somewhat more negative than the ratio for the closed system (Figure 9).

In most tracer-calibrated box-diffusion models and in ocean general circulation models, the "deconvolved" airborne fraction, that is, the ratio of observed cumulative atmospheric increase to the sum of this amount plus model-predicted ocean uptake, is between 0.51 and 0.58 [Sarmiento et al., 1992; Siegenthaler and Joos, 1992]. For an atmospheric increase of 159 Gt C, the corresponding ocean uptake therefore lies between 115 and 156 Gt C. It appears that over this range of CO_2 uptake, the $\Delta\delta_s/\Delta C_T$ ratio does not vary very strongly for any particular value of the biospheric ^{13}C inventory change (Figure 9). For the probable ^{13}C inventory change between -500 and -1500‰ Gt C, the ratio of $\Delta\delta_s/\Delta C_T$ is expected to vary from about -0.020 to -0.016‰ ($\mu\text{mol C kg}^{-1}$). Unfortunately, the uncertainties in our estimate of this ratio are presently too large to constrain the exchangeable biocarbon mass more closely.

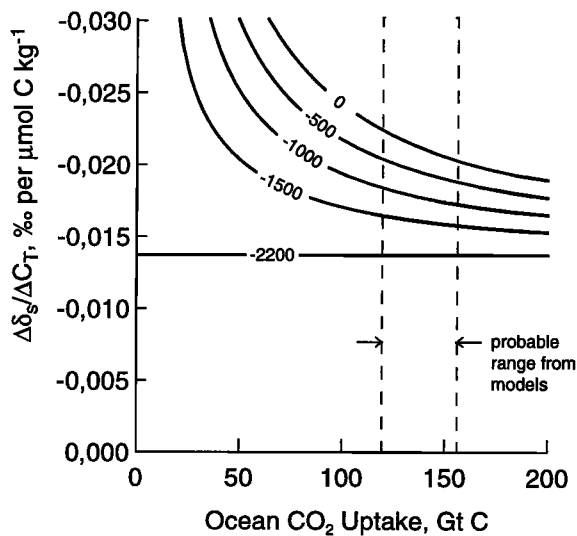


Figure 9. $\Delta\delta_s/\Delta C_T$ as functions of anthropogenic CO_2 uptake in the ocean as calculated from equation (5) for constant values of the ^{13}C biospheric inventory change, $M_b^0 \Delta\delta_b$ (indicated on each curve in ‰ Gt C). Since $\Delta\delta_b \approx -1\text{‰}$, the absolute value of the ^{13}C inventory change is a measure of the exchangeable biospheric carbon mass.

5. Concluding Remarks

At about 50°N in the eastern Atlantic, it appears that the phosphate method gives a better estimate of the $\Delta\delta^{13}\text{C}$ distribution than the calculation from AOU. This conclusion is based on the similarity of the phosphate-based $\Delta\delta^{13}\text{C}$ profile to that of ΔC_T and the correspondence of their ratio to that expected from the ^{13}C budget. In contrast, the $\Delta\delta^{13}\text{C}/\Delta C_T$ ratio derived from AOU appears to be low and would imply an impossibly large exchangeable biospheric carbon mass. The $\Delta\delta^{13}\text{C}/\Delta C_T$ ratio derived from the phosphate method agrees well with the ratio simulated by the Hamburg ocean geochemical model, but the uncertainty in the ratio we derive is rather large, and so this agreement could be fortuitous. Since the magnitude of the anthropogenic signals in the upper ocean should increase, a more precise determination of them may be possible in the future. If this can be accomplished in certain representative areas of the ocean, the ^{13}C inventory change of the biosphere might be obtained. A detailed global survey of the ocean would not be required.

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References

- Bacastow, R.B., C.D. Keeling, T.J. Lueker, M. Wahlen, and W.G. Mook, The ^{13}C Suess effect in the world surface oceans and its implications for oceanic uptake of CO_2 : analysis of observations at Bermuda, *Global Biogeochem. Cycles*, **10**, 335-346, 1996.
- Böhm, F., M.M. Joachimski, H. Lehnert, G. Morgenroth, W. Kretschmer, J. Vacelet, W.-C. Dullo, Carbon isotope records from extant Caribbean and South Pacific sponges: Evolution of $\delta^{13}\text{C}$ in surface water DIC, *Earth Planet. Sci. Lett.*, **139**, 291-303, 1996.
- Brewer, P.G., Direct observation of the oceanic CO_2 increase, *Geophys. Res. Lett.*, **5**, 997-1000, 1978.
- Broecker, W.S., and E. Maier-Reimer, The influence of air and sea exchange on the carbon isotope distribution in the sea, *Global Biogeochem. Cycles*, **6**, 315-320, 1992.
- Broecker, W.S., and T.-H. Peng, *Tracers in the Sea*, 690 pp., Lamont-Doherty Geological Observatory, Palisades, N.Y., 1982.
- Broecker, W.S., and T.-H. Peng, Evaluation of the ^{13}C constraint on the uptake of fossil fuel CO_2 by the ocean, *Global Biogeochem. Cycles*, **7**, 619-626, 1993.
- Chen, C.-T.A., and F.J. Millero, Gradual increase of oceanic CO_2 , *Nature*, **277**, 205-206, 1979.
- Emmanuel, W.R., G.G. Killough, W.M. Post, and H.H. Shugart, Modeling terrestrial ecosystems in the global carbon cycle with shifts in carbon storage capacity by land-use change, *Ecology*, **65**, 970-983, 1984.
- Friedli, H., H. Löttscher, H. Oeschger, U. Siegenthaler, and B. Stauffer, Ice core record of the $^{13}\text{C}/^{12}\text{C}$ ratio of atmospheric CO_2 in the past two centuries, *Nature*, **324**, 237-238, 1986.
- Heimann, M., and E. Maier-Reimer, On the relations between the ocean uptake of CO_2 and its carbon isotopes, *Global Biogeochem. Cycles*, **10**, 89-110, 1996.
- Keeling, C.D., and T.P. Whorf, Atmospheric CO_2 records from sites in the SIO air sampling network, in *Trends '93: A Compendium of Data on Global Change*, edited by T.A. Boden et al., Rep. ORNL/CDIAC-65, pp. 16-26, Carbon Dioxide Inf. Anal. Cent., Oak Ridge Nat. Lab., Oak Ridge, Tenn.

- Keeling, C.D., R.B. Bascastow, A.F. Carter, S.C. Piper, T.P. Whorf, M. Heimann, W.G. Mook, and H. Roeloffzen, A three-dimensional model of atmospheric CO_2 transport based on observed winds, 1, Analysis of observational data, in *Aspects of Climate Variability in the Pacific and Western Americas*, *Geophys. Monogr. Ser.*, vol. 55, edited by D.H. Peterson, pp. 165-236, AGU, Washington, D. C., 1989.
- Keir, R.S., Are atmospheric CO_2 content and Pleistocene climate connected by wind speed over a polar mediterranean sea?, *Global Planet. Change*, 8, 59-68, 1993.
- Körtzinger, A., L. Mintrop, and J.C. Duinker, On the penetration depth and the inventory of anthropogenic CO_2 in the North Atlantic Ocean, *J. Geophys. Res.*, in press, 1998.
- Kroopnik, P.M., The distribution of ^{13}C of ΣCO_2 in the world oceans, *Deep Sea Res., Part A*, 32, 57-84, 1985.
- Lynch-Stieglitz, J., T.F. Stocker, W.S. Broecker, and R.G. Fairbanks, The influence of air-sea exchange on the isotopic composition of oceanic carbon: Observations and modeling, *Global Biogeochem. Cycles*, 9, 653-655, 1995.
- McCartney, M.S., and L.D. Talley, The Subpolar Mode Water of the North Atlantic Ocean, *J. Phys. Oceanogr.*, 12, 1169-1188, 1982.
- Östlund, H.G., and C. Grall, Transient tracers in the ocean, North and Tropical Atlantic tritium and radiocarbon, *Data Rep. 16*, Tritium Lab., Rosenstiel Sch. of Mar. and Atmos. Sci., Univ. of Miami, Miami, Fla., 1987.
- Östlund, H.G., H. Craig, W.S. Broecker, and D. Spencer (Eds.), *GEOSECS Atlantic, Pacific, and Indian Ocean expeditions, Shorebased data and graphics, GEOSECS Atlas Ser.*, vol. 7, 200 pp., U.S. Gov. Print. Off., Washington, D. C., 1987.
- Quay, P.D., B. Tilbrook, and C.S. Wong, Oceanic uptake of fossil fuel CO_2 : Carbon-13 evidence, *Science*, 256, 74-79, 1992.
- Sarmiento, J.L., J.C. Orr, and U. Siegenthaler, A perturbation simulation of CO_2 uptake in an ocean general circulation model, *J. Geophys. Res.*, 97, 3621-3645, 1992.
- Scripps Institution of Oceanography, Transient tracers in the ocean, North Atlantic Study, *SIO Ref. 86-15*, La Jolla, Calif., 1986.
- Siegenthaler, U., and F. Joos, Use of a simple model for studying oceanic tracer distributions and the global carbon cycle, *Tellus, Ser. B*, 44, 186-207, 1992.
- Siegenthaler, U., and K.O. Münnich, $^{13}\text{C}/^{12}\text{C}$ fractionation during CO_2 transfer from air to sea, in *Carbon Cycle Modelling*, edited by B. Bolin, pp. 249-257, John Wiley, New York, 1981.
- Siegenthaler, U., and H. Oeschger, Biospheric CO_2 emissions during the past 200 years reconstructed by deconvolution of ice core data, *Tellus, Ser. B*, 39, 140-154, 1987.
- Siegenthaler, U., and J.L. Sarmiento, Atmospheric carbon dioxide and the ocean, *Nature*, 365, 119-125, 1993.
- Takahashi, T., J. Olafsson, J.G. Goddard, D.W. Chipman, and S.C. Sutherland, Seasonal variation of CO_2 and nutrients in the high-latitude surface oceans: A comparative study, *Global Biogeochem. Cycles*, 7, 843-878, 1993.
- Talley, L.D., and M.S. McCartney, Distribution and circulation of Labrador Sea Water, *J. Phys. Oceanogr.*, 12, 1189-1205, 1982.
- Tans, P.P., J.A. Berry, and R.F. Keeling, Oceanic $^{13}\text{C}/^{12}\text{C}$ observations: A new window on ocean CO_2 uptake, *Global Biogeochem. Cycles*, 7, 353-368, 1993.
- Weiss, R.F., H.G. Östlund, and H. Craig, Geochemical studies of the Weddell Sea, *Deep Sea Res., Part A*, 26, 1093-1120, 1979.
- Zahn, R., and R. Keir, Tracer-nutrient correlations in the upper ocean: Observational and box model constraints on the use of benthic foraminiferal $\delta^{13}\text{C}$ as paleo-proxies for the intermediate-depth ocean, in *Carbon Cycling in the Glacial Ocean: Constraints on the Ocean's Role in Global Change*, edited by R. Zahn et al., pp. 195-221, Springer-Verlag, New York, 1994.

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