

THE INFLUENCE OF AIR AND SEA EXCHANGE ON  
THE CARBON ISOTOPE DISTRIBUTION IN THE SEA

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*Abstract.* We explore here the influence of the temperature dependence of isotope fractionation between atmospheric CO<sub>2</sub> and ocean ΣCO<sub>2</sub> on the distribution of carbon isotopes in the ocean. This is accomplished by an analysis of departures from the expected Redfield tie between PO<sub>4</sub> and δ<sup>13</sup>C. We find that for the surface ocean, the temperature influence largely compensates for the biologic influence. In the deep ocean, the temperature influence imprinted at the sites of deepwater formation reduces somewhat the biologically induced difference between the carbon isotope ratios for deep waters produced in the northern Atlantic and in the Antarctic. These same features are reproduced in the Hamburg ocean model. In order to assess the impact of changes in the ratio of ocean mixing rate to wind speed, we have made a model run in which CO<sub>2</sub> exchange rates between air and sea were everywhere doubled. As expected, the influence of the thermodynamic effect on the oceanic carbon isotope distribution is magnified.

INTRODUCTION

Our knowledge of the paleocirculation patterns in the deep ocean comes largely from measurements of stable isotope ratios (carbon and oxygen) and of trace metal concentrations (cadmium and barium) in the shells of planktonic and benthic foraminifera found in deep-sea sediments. The distributions in the ocean of <sup>13</sup>C/<sup>12</sup>C and Cd/Ca are generally viewed to be highly correlated one to the other and to those of PO<sub>4</sub> and NO<sub>3</sub>.

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However, for carbon isotope ratios, this tie is not perfect [Keir, 1991]. The reason is that while trace metals and nutrients circulate only through the sea, carbon circulates through the atmosphere as well. The temperature dependence of the carbon isotope fractionation between atmospheric CO<sub>2</sub> and surface ocean ΣCO<sub>2</sub> tends to disrupt the correlation between <sup>13</sup>C/<sup>12</sup>C ratios and the concentration of the nutrients and trace metals. The extent of this disruption depends on the relative strength of mixing within the sea and CO<sub>2</sub> exchange between the ocean and atmosphere. Because of the complex nature of mixing within the sea, it proves difficult to estimate the magnitude of the disruption. Ocean general circulation models (GCMs) offer a means to assess the sensitivity of this disruption to altered climatic conditions.

OPPOSING TENDENCIES: BIOLOGIC VERSUS  
THERMODYNAMIC

The carbon isotope-nutrient constituent separation about which we are concerned has its origin in the isotope fractionation between atmospheric CO<sub>2</sub> and surface ocean ΣCO<sub>2</sub>. Were there no air-sea fractionation, then the distribution of δ<sup>13</sup>C values within the sea should be tightly correlated with phosphate concentration. The relationship would be as follows:

$$\delta^{13}\text{C} - \delta^{13}\text{C}^{\text{M.O.}} \cong \frac{\Delta\text{photo}}{\Sigma\text{CO}_2^{\text{M.O.}}} \left( \frac{\text{C}}{\text{P}} \right)_{\text{org}} (\text{PO}_4 - \text{PO}_4^{\text{M.O.}}) \quad (1)$$

where M.O. stands for mean ocean, Δphoto is the carbon isotope separation during marine photosynthesis and C/P<sub>org</sub> is the carbon to phosphorus ratio in marine organic matter. Taking Δphoto to be -19‰, C/P<sub>org</sub> to be 128 and ΣCO<sub>2</sub><sup>M.O.</sup> to be 2200 μmol/kg, the equation becomes

$$\delta^{13}\text{C} - \delta^{13}\text{C}^{\text{M.O.}} \cong 1.1 (\text{PO}_4^{\text{M.O.}} - \text{PO}_4) \quad (2)$$

The  $\delta^{13}\text{C}$  for mean ocean carbon is about 0.5‰ and the mean ocean PO<sub>4</sub> concentration is about 2.2 μmol/kg. Hence

$$\delta^{13}\text{C} = 0.5 + 1.1 (2.2 - \text{PO}_4) = 2.9 - 1.1 \text{PO}_4 \quad (3)$$

This equation is of course an approximation for  $\Delta\text{photo}$  changes with the CO<sub>2</sub> content of surface water;  $\Sigma\text{CO}_2$  increases with increasing alkalinity and phosphate concentration, and C/P<sub>org</sub> likely varies somewhat from place to place in the sea. However, the deviations produced in this way are small compared to those stemming from air-sea isotope fractionation. Since the highest phosphate content surface waters are found in the polar oceans, one would expect them to have the lowest surface water  $\delta^{13}\text{C}$  values. For example, as the ambient PO<sub>4</sub> value in Antarctic surface waters is about 1.6 μmol/kg and that in tropical and temperate surface waters averages 0.2 μmol/kg, the  $\delta^{13}\text{C}$  for Antarctic surface waters should be about 1.5‰ lower than in Antarctic surface waters.

Working in the opposite direction is the thermodynamic effect related to air-sea CO<sub>2</sub> exchange which tends to make the  $\delta^{13}\text{C}$  values for cold surface waters higher than those for warm surface waters. At equilibrium the carbon isotope separation between atmospheric CO<sub>2</sub> and surface ocean  $\Sigma\text{CO}_2$  increases by about 1‰ per for each 10°C decrease in water temperature. Because of this dependence, were thermodynamic equilibrium achieved, it would produce a strong carbon isotope difference in the opposite sense; Antarctic surface waters would have 2 to 3‰ higher  $\delta^{13}\text{C}$  values than tropical and temperate surface waters.

Where between the two extremes the actual situation lies depends on the relative strength of air-sea CO<sub>2</sub> exchange on one hand and mixing between the sea's water masses on the other. The former works to establish thermodynamic equilibrium and the latter to establish a perfect correlation with phosphate. It will also depend on the distribution of phosphorus in high-latitude surface waters.

## OBSERVATIONS

Shown in Figure 1 is a plot of carbon isotope ratio against temperature for surface water samples obtained during the GEOSECS expeditions to the Atlantic and Indian oceans [Bacastow and Maier-Reimer, 1990]. As can be seen, no trend with temperature is discernable. In this figure, the same carbon isotope results are also plotted against phosphate content. Although a small decrease in  $\delta^{13}\text{C}$  with phosphate concentration is seen, it is not nearly as large as would be expected if the distribution were exactly biologic. Roughly speaking, in today's surface ocean the the biologic tendency is nearly balanced by the thermodynamic tendency. A similar situation exists in the Pacific Ocean [Kroopnick et al., 1977]. As reproduced in Figure 2, a traverse of surface waters collected along 150°W during the Hudson 1970 expedition does show a decrease for polar samples in the sense expected from fractionation during photosynthesis, but it is only about 0.7‰ (instead of 1.5‰). Unfortunately, no PO<sub>4</sub> determinations were made on these samples.

The carbon isotope-phosphate trend in Pacific and Indian Ocean deep waters follows expectation (see Figure 3). The  $\delta^{13}\text{C}$  value drops by about 1.1‰ per additional μmol/kg of PO<sub>4</sub>. However, the  $\delta^{13}\text{C}$ -PO<sub>4</sub> coordinate of new North Atlantic

Deep Water (NADW) lies below this trend and that for new Antarctic Bottom Water (AABW) lies above this trend (see Figure 4). These waters mix in the proportion one part NADW to two parts AABW to form the water entering the deep Indian and Pacific oceans.

The  $\delta^{13}\text{C}$ -PO<sub>4</sub> coordinates for waters from the warm regions of the surface ocean fall below the value expected if the  $\delta^{13}\text{C}$ -phosphate relationship were exactly biologic. This departure is not entirely thermodynamic; the values for surface water have been influenced by the drop in atmospheric <sup>13</sup>C/<sup>12</sup>C ratio caused by fossil fuel burning. Between 1800 and the time of the GEOSECS surveys (1972 - 1978), the  $\delta^{13}\text{C}$  for atmospheric CO<sub>2</sub> dropped by about 1.2‰ [Friedli et al., 1986]. Model results suggest that this change caused surface ocean

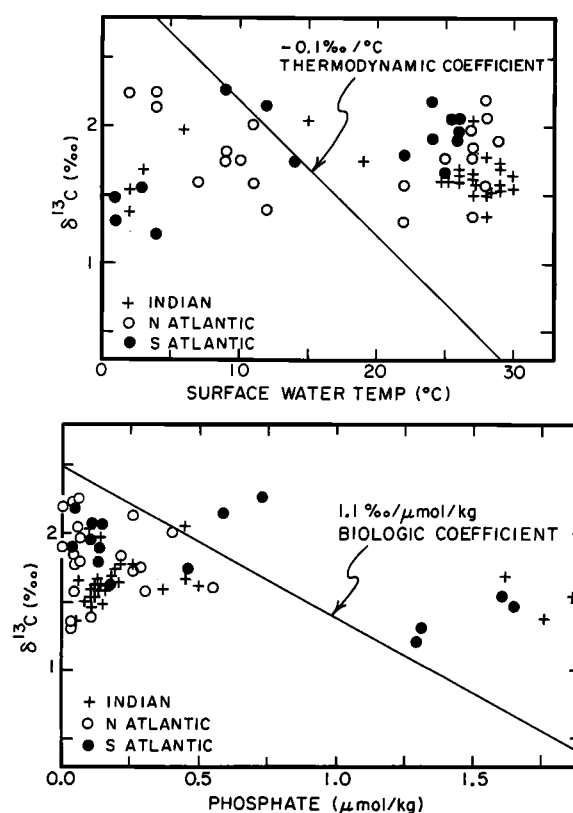


Fig. 1. (Upper panel) The relationship between the  $\delta^{13}\text{C}$  value for dissolved  $\Sigma\text{CO}_2$  and the temperature of surface mixed layer samples collected in the Atlantic and Indian Oceans as part of the GEOSECS program. The line shows the trend expected if thermodynamic equilibrium were achieved with atmospheric CO<sub>2</sub>. (Lower panel) The relationship between the  $\delta^{13}\text{C}$  value for dissolved  $\Sigma\text{CO}_2$  and the phosphate content of surface mixed layer samples from the Atlantic and Indian oceans collected as part of the GEOSECS program. The line is the trend expected were no exchange with atmospheric CO<sub>2</sub> to occur. The carbon isotope measurements were made in the University of Hawaii laboratory of Peter Kroopnick and in the Scripps Institution for Oceanography laboratory of Harmon Craig [Kroopnick, 1980, 1985; Ostlund et al., 1987].

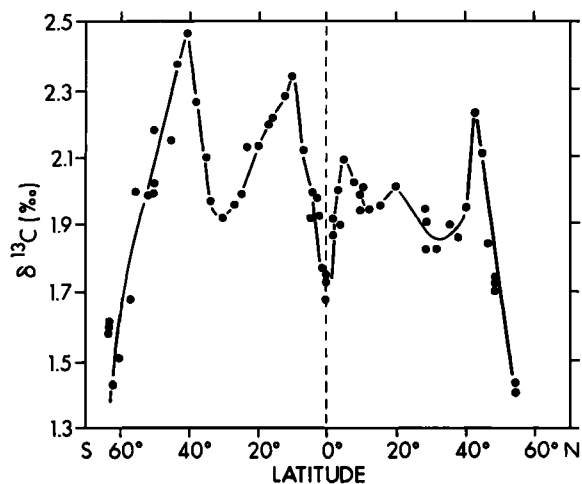


Fig. 2. Carbon isotope measurements on the ΣCO<sub>2</sub> from surface water samples collected during the Hudson 1970 expedition along 150°W in the Pacific Ocean [Kroopnick et al., 1977].

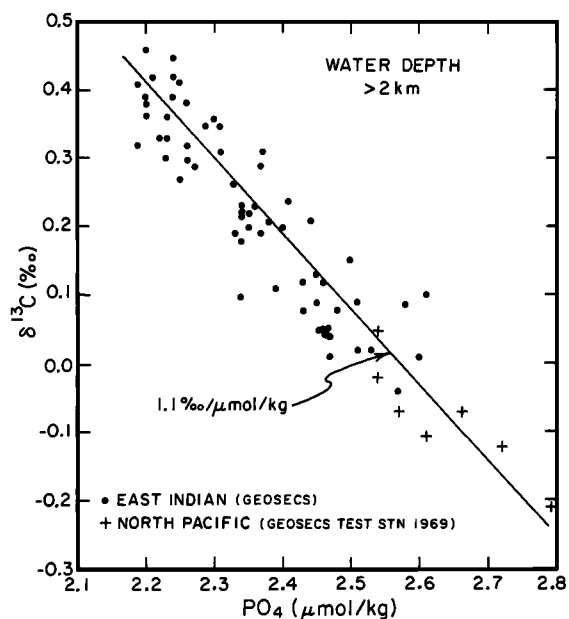


Fig. 3. Carbon isotope ratio versus phosphate content for deep waters in the eastern Indian Ocean (as measured by Peter Kroopnick in his University of Hawaii laboratory) [Ostlund et al., 1987] and for deep waters at the GEOSECS test station in the northeastern Pacific (as measured by Peter Kroopnick and Harmon Craig in the Scripps Institution of Oceanography laboratory) [Kroopnick et al., 1972; Kroopnick, 1985].

δ<sup>13</sup>C values to be lowered by an average of about 0.7‰. After a correction for the influence of fossil fuel CO<sub>2</sub> has been made, the warm surface ocean values move closer to the trend line defined by deep Indian and Pacific Ocean values (see Figure 3).

If the Redfield slope of 1.1‰ per μmol/kg is assumed to be uniform throughout the sea, then a measure of the influence of thermodynamic equilibration on the δ<sup>13</sup>C value for any given water sample is given by the relationship

$$\Delta\delta^{13}\text{C} = \delta^{13}\text{C} + 1.1 \text{ PO}_4 - 2.7 \tag{4}$$

where 2.7‰ is an arbitrary constant introduced to bring the Δδ<sup>13</sup>C values for waters lying on the trend for deep Pacific and Indian Ocean waters close to zero. New NADW has a Δδ<sup>13</sup>C value of about -0.5‰ and new AABW a Δδ<sup>13</sup>C value of about +0.2‰. Phosphate deficient surface waters in the warm parts of the ocean have values of about -1.0‰ before correction for the fossil fuel CO<sub>2</sub> induced change and -0.3‰ after this correction has been made (see Figure 4).

A map showing the Δδ<sup>13</sup>C values for surface water samples obtained as part of the GEOSECS program is shown in Figure 5. Note that the Δδ<sup>13</sup>C values for surface waters in the Antarctic are positive while those for the rest of surface ocean are negative.

The difference in carbon isotope ratio between deep Atlantic and deep Pacific water has importance in paleoceanography. This difference (as recorded in benthic foraminifera) is used as a measure of the strength of the Atlantic's conveyor circulation during the Quaternary [Oppo and Fairbanks, 1990; Raymo et al., 1990]. As can be seen from Figure 4, were the coordinates for NADW to lie on the trend for deep Pacific and Indian waters instead of below it, the present-day Atlantic-Pacific difference would be even larger. Thus the thermodynamic effect influences the magnitude of interocean difference in carbon isotope ratio for deep water. Hence glacial to

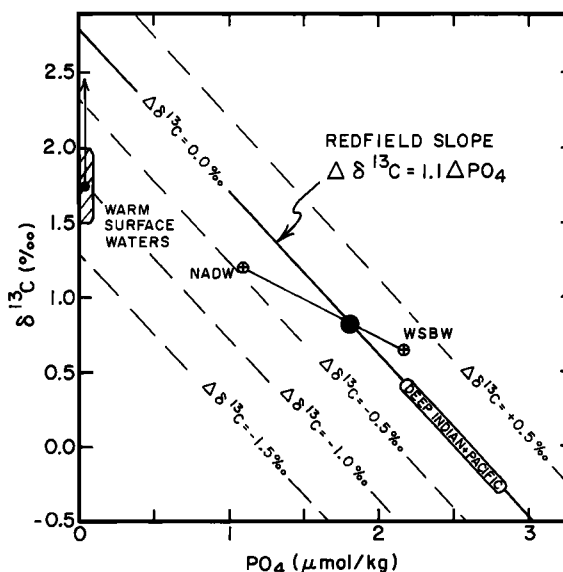


Fig. 4. Relationship between δ<sup>13</sup>C and PO<sub>4</sub> for major water types in the world ocean. The contours denote departures from the Redfield slope defined by deep waters in the Pacific and Indian oceans. The arrow associated with the warm surface ocean results is the approximate correction for the impact of fossil fuel CO<sub>2</sub>.

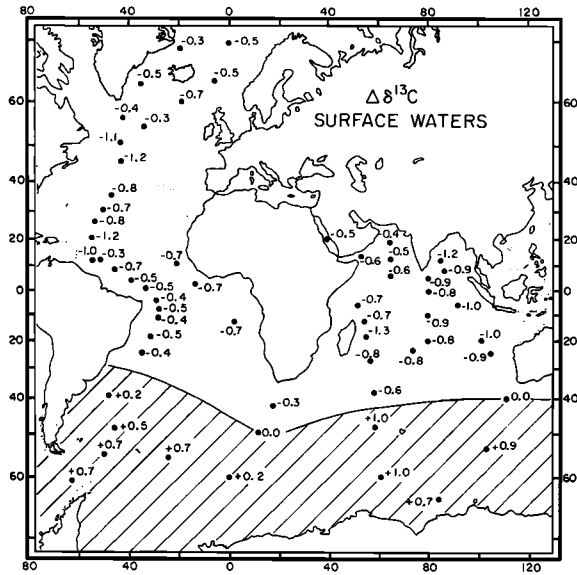


Fig. 5.  $\Delta\delta^{13}\text{C}$  values for surface waters in the Atlantic and Indian oceans based on measurements made as part of the GEOSECS program [Kroopnick, 1980, 1985; Ostlund et al., 1987]. Note that no correction has been made for the imprint of <sup>13</sup>C deficient fossil fuel CO<sub>2</sub>. In the shaded region, the values are positive. In the remainder of the ocean, they are negative.

interglacial changes either in CO<sub>2</sub> exchange rates or in ocean mixing rates would generate changes in the Atlantic-Pacific deepwater carbon isotope difference in addition to those created by changes in the deepwater nutrient distribution. However, as the above mentioned authors use end-member waters to calibrate the interocean <sup>13</sup>C difference, such changes would not alter the conclusions they draw about changes in the strength of NADW penetration into the deep Atlantic.

#### IMPLICATIONS FROM AN OCEAN GCM

Results for tracer runs made in Hamburg ocean GCM provide two pieces of additional information regarding the imprint of the thermodynamic effect on the distribution of carbon isotope ratios within the sea. First, the thermodynamic imprint on the carbon isotope distribution in the model can be isolated without concern about varying Redfield ratios. Second, the model allows an estimate to be made of the sensitivity of the thermodynamic imprint to changes in the ratio between the air-sea CO<sub>2</sub> exchange rate and the aggregate mixing rate within the sea.

The model is an extension of that created by Bacastow and Maier-Reimer [1990]. The main difference from that model is a more realistic current field, especially with regard to the formation and flow of NADW. The basic mechanism for the formation of soft tissue is the transformation of upwelled phosphate into particulate organic material. A prescribed optimum productivity is assumed to be reduced by lack of light and by convective turbulence. The optimum value was tuned to yield a realistic distribution of surface phosphate. During the formation of particulate organic material (POM), a

constant fractionation of -20‰ is used for  $\delta^{13}\text{C}$ . For the fractionation during air-sea CO<sub>2</sub> exchange, the functional relationship  $F(13) = [1.024 - 9.384/(T+273)]F(12)$  proposed by Mook [1974] was adopted. The newly formed POM is distributed with depth according to  $z^{-0.8}$  where  $z$  is the depth in kilometers. Once at depth, POM is assumed to move with the water. At locations with sufficient oxygen, the POM is remineralized with a time constant of 4 years. The prescribed Redfield ratios for POM in the model are everywhere

$$\text{P:N:C:-O}_2 = 1:17:122:175 \quad (5)$$

Phosphate is taken to be the limiting nutrient; nitrate enters only in the model's alkalinity formulation.

As the Hamburg model employs constant Redfield ratios, the biologic and thermodynamic influences on the distribution of <sup>13</sup>C/<sup>12</sup>C ratios within the model ocean can be accurately separated from one another. To do this, we use the formalism presented above.

$$\Delta\delta^{13}\text{C} = \delta^{13}\text{C} + 1.1 \text{ PO}_4 - 2.7 \quad (6)$$

where  $\Delta\delta^{13}\text{C}$  is the thermodynamic induced departure from biologic trend.

We show in Figure 6 the results of this exercise in a scatterplot for all the models' sea surface boxes. Phosphate-free surface waters have  $\delta^{13}\text{C}$  values ranging up to about 0.7‰ surface waters in the sub-Antarctic region have  $\delta^{13}\text{C}$  values ranging to about 1.3‰ higher than the Redfield trend. As in the real ocean, the overall trend in surface water of  $\delta^{13}\text{C}$  with phosphate content is quite small. On the average, the

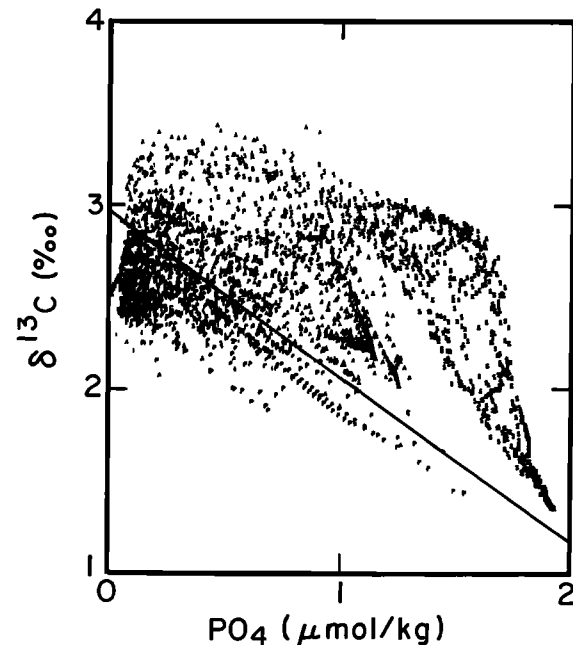


Fig. 6. Scatterplot for the  $\delta^{13}\text{C}$ -PO<sub>4</sub> relationship in surface waters as simulated in the Hamburg model. The model's Redfield trend is shown by the straight line. As can be seen, the thermodynamic influence creates departures ranging from 1.3‰ above to 0.5‰ below the model's Redfield line.

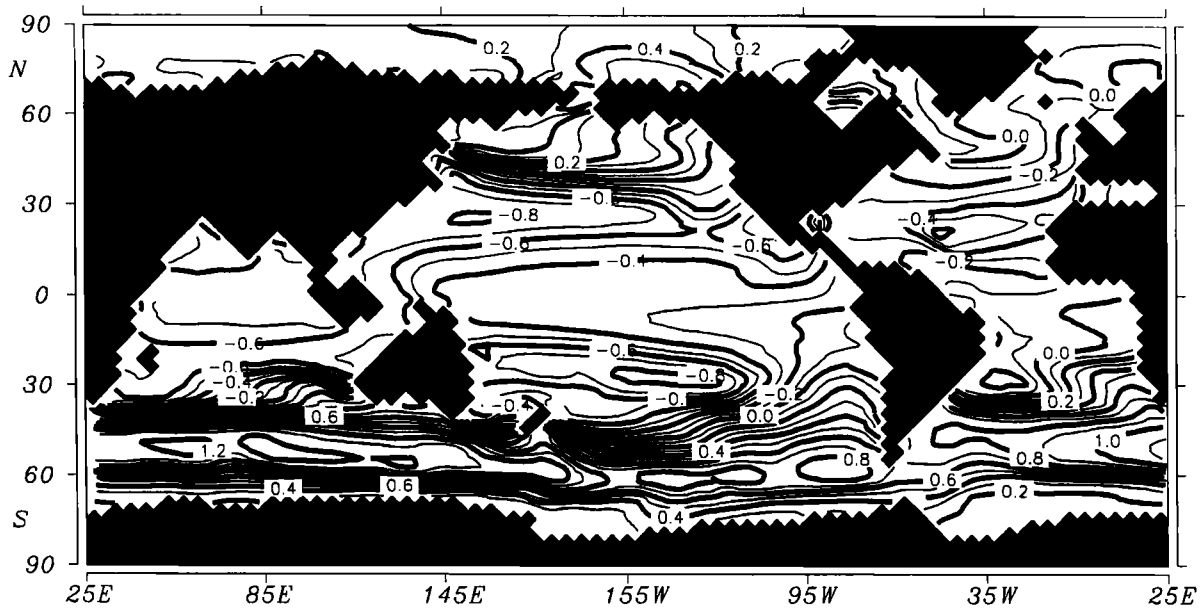


Fig. 7. Map showing the geographic distribution of departures in  $\delta^{13}\text{C}$  values for the Hamburg model surface waters from those expected were there no thermodynamic imprint on the carbon isotope distribution.

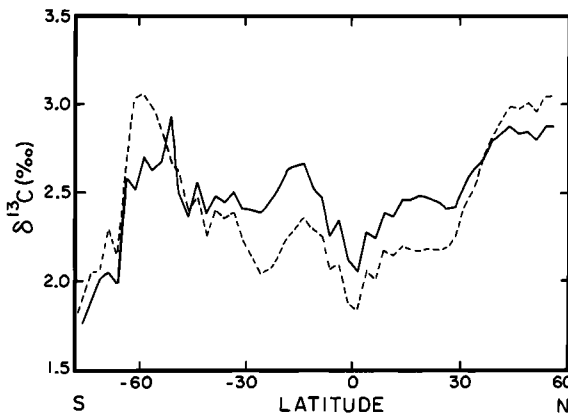


Fig. 8. The solid line shows the trend of  $\delta^{13}\text{C}$  with latitude (along 150°W) for Pacific Ocean surface waters as obtained in the Hamburg model for pre-industrial time. The dashed line shows how this distribution changes when the model's CO<sub>2</sub> exchange rate is doubled.

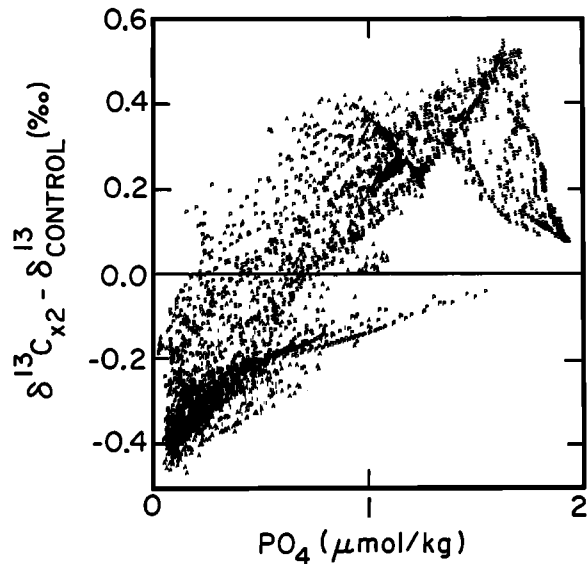


Fig. 9. Scatterplot showing the difference in carbon isotope ratio for surface waters between the model run with the doubled air-sea CO<sub>2</sub> exchange rate and the control run.

biological influence is balanced by the thermodynamic influence.

Shown in Figure 7, is the distribution of  $\Delta\delta^{13}\text{C}$  values for the model's surface ocean (prior to the addition of fossil fuel CO<sub>2</sub>). As for the real ocean, the highest values are seen in the Antarctic region. A feature appears in the model results (see Figure 8) which stands out in the Hudson 1970 traverse (see Figure 2), namely, the maximum in the  $\Delta\delta^{13}\text{C}$  values for the sub-Antarctic surface lying beneath the region of high wind speeds (45° to 55°S). This feature is of particular interest for through comparison of model results with ocean data, it offers a constraint on the gas exchange rate in regions of the ocean experiencing much larger than average wind speeds.

In order to determine the sensitivity of the oceanic distribution of the thermodynamic effect on the distribution of <sup>13</sup>C in the ocean, we have carried out a second model run where the air-sea CO<sub>2</sub> exchange rate was everywhere doubled. This is lower than expected from the Redfield trend and phosphate-rich equivalent to halving the rate of ocean mixing. In Figure 9 is shown the change in  $\delta^{13}\text{C}$  value in the model's surface boxes. Positive departures correspond to higher <sup>13</sup>C/<sup>12</sup>C ratios in the doubled wind velocity run. As would be expected, the  $\delta^{13}\text{C}$

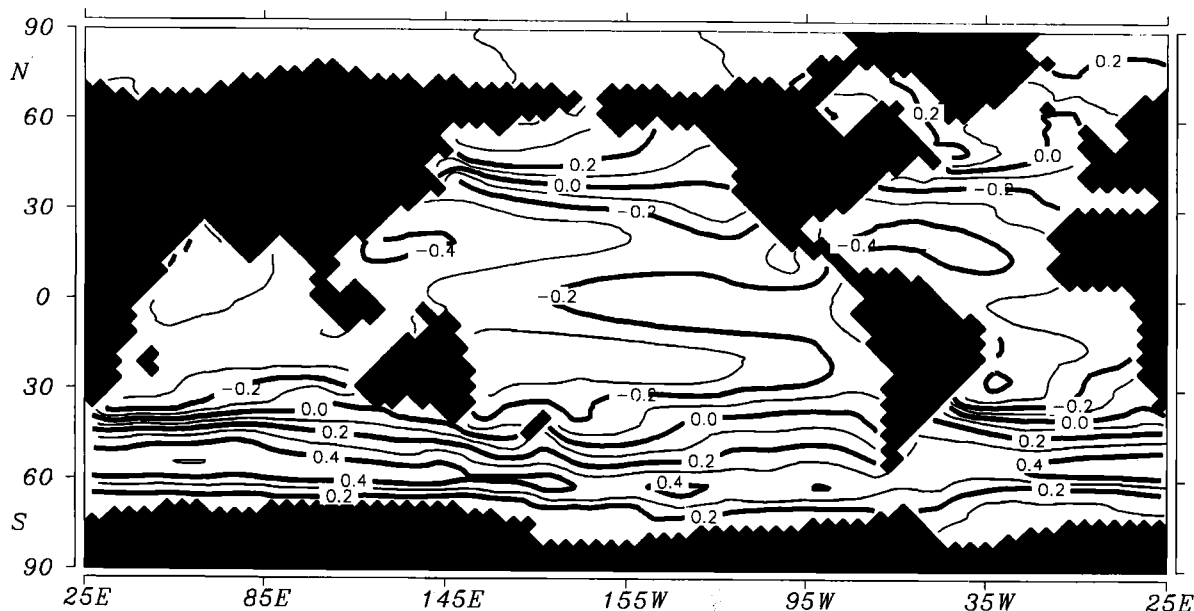


Fig. 10. Change in  $\delta^{13}\text{C}$  value (i.e.,  $\delta^{13}\text{C}_{\text{X}_2} - \delta^{13}\text{C}_{\text{control}}$ ) in surface waters caused by doubling the air-sea  $\text{CO}_2$  exchange rate in the Hamburg ocean model.

values for warm surface waters (i.e., waters with low  $\text{PO}_4$  content) decrease, while those for cold surface waters (i.e., waters with high  $\text{PO}_4$  content) increase. As can be seen in Figures 8 and 10, this change alters the trend with latitude in surface ocean  $\delta^{13}\text{C}$  values.

## CONCLUSIONS

The impact of the temperature dependence of isotope fractionation between atmospheric  $\text{CO}_2$  and surface ocean  $\Sigma\text{CO}_2$  makes itself felt in the ocean. While not producing major complications in the use of the  $^{13}\text{C}$  distribution in the deep sea as a paleocean-circulation indicator, its possible impact must be kept in mind. The strongest impacts are currently seen beneath the belt of strong wind speeds in the southern ocean.

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