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THERMODYNAMIC INFLUENCES ON THE MARINE CARBON ISOTOPE RECORD

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Abstract. Air-sea exchange represents an important controlling factor for the distribution of carbon isotopes in the modern ocean, even below the surface mixed layer. Here we show that this thermodynamic influence varies between water masses with a magnitude which is large relative to the amplitude of typical deep sea sediment $\delta^{13}\text{C}$ records. Thus, changes in air-sea exchange processes must be regarded as a significant source of variability for any marine $\delta^{13}\text{C}$ signal.

INTRODUCTION

Paleoceanographers commonly take the $\delta^{13}\text{C}$ of fossil foraminifera as a direct proxy for nutrient concentrations, an approach which has provided considerable insight to the past oceanic chemistry and circulation. For example, the mapping of glacial-age $\delta^{13}\text{C}$ values led to the realization that the production of North Atlantic Deep Water (NADW) was substantially different during the last glacial period [e.g. Boyle and Keigwin, 1985; Mix and Fairbanks, 1985; Duplessy et al., 1988; Oppo and Fairbanks, 1987]. However, with the increasing demand for precise testing of carbon cycle models, it has become necessary to recognize the nonbiological influences on the oceanic $\delta^{13}\text{C}$ signal. In particular, the capacity of the ocean's inorganic carbon pool to exchange

isotopically with the atmosphere creates the potential for significant $\delta^{13}\text{C}$ variability which deviates from the basic trend established through biological fractionation. In some areas of the surface ocean today, air-sea exchange completely masks the relationship between $\delta^{13}\text{C}$ and nutrients [Broecker and Peng, 1982; Broecker and Maier-Reimer, 1992; Charles and Fairbanks, 1990]. Surface waters having experienced varying degrees of isotopic equilibration with the atmosphere are subsequently incorporated in deep and intermediate water, and thus different thermodynamic influences are mixed throughout the ocean.

The need for a fuller understanding of these equilibration processes is underscored by the development of other nutrient tracers such as Cd [Boyle, 1988a] and Ba [Lea and Boyle, 1990] in foraminifera and Ge in diatoms [Froelich et al., 1989]. In many cases, these tracers differ dramatically from $\delta^{13}\text{C}$ in the deep sea sediment record, and air-sea exchange represents one principle mechanism for decoupling the tracers. Furthermore, interpretation of the recently established atmospheric $\delta^{13}\text{C}$ record spanning the last 20 kyr [Marino et al., 1992; Leuenberger et al., 1992] depends critically on the extent and conditions of air-sea isotopic exchange.

The purpose of this paper is to delineate the geographic influence of air-sea exchange on $\delta^{13}\text{C}$ in the modern ocean, while discussing the possible ramifications for paleoceanographic interpretations based on $\delta^{13}\text{C}$ in foraminifera. For Quaternary $\delta^{13}\text{C}$ records, gas exchange effects should be most prominent in upper layer water masses. However, over longer (Cenozoic) times, different water mass formation processes could result in different thermodynamic signatures in the deep ocean as well.

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GAS EXCHANGE EFFECT

Given sufficient time for isotopic equilibration to occur, air-sea exchange of CO_2 leaves surface waters enriched in ^{13}C relative to mean ocean water, and conversely, atmospheric CO_2 is left relatively depleted. In addition, isotopic fractionation upon gas exchange increases with decreasing temperatures. Seawater completely equilibrated with the atmosphere at 0°C should have a $\delta^{13}\text{C}$ value which is about 3‰ higher than the same seawater at 25°C [Mook et al, 1974]. However, as $\Delta^{14}\text{C}$ measurements clearly show, the vertical mixing of subsurface waters is everywhere fast enough that full carbon isotopic equilibrium is never achieved, even though chemical (CO_2) equilibrium may be approached [Broecker and Peng, 1982]. Thus, while never reaching its complete expression, the magnitude of the thermodynamic isotopic effect varies not only

with temperature, but also with CO_2 exchange rate and surface water residence times.

One means of establishing the relative importance of gas exchange for $\delta^{13}\text{C}$ (of ΣCO_2) in the present ocean is to normalize measured GEOSECS $\delta^{13}\text{C}$ values [from Kroopnick, 1985] to constant phosphate, a procedure which in principle eliminates all nutrient-related variability. The slope of the $\delta^{13}\text{C}$ - PO_4 relationship is not globally uniform, but in general, for every $1\mu\text{M}/\text{kg}$ increase of PO_4 , $\delta^{13}\text{C}$ decreases by about 1‰, a dependency close to that predicted from average C/P and $\delta^{13}\text{C}$ values in marine organic material [Broecker and Peng, 1982]. If nutrient cycling were the only control on $\delta^{13}\text{C}$, removing this slope should produce relatively constant $\delta^{13}\text{C}$ values: large spatially coherent deviations should reflect the influence of gas exchange. We used this approach previously to demonstrate that surface waters near the Antarctic Polar Front are

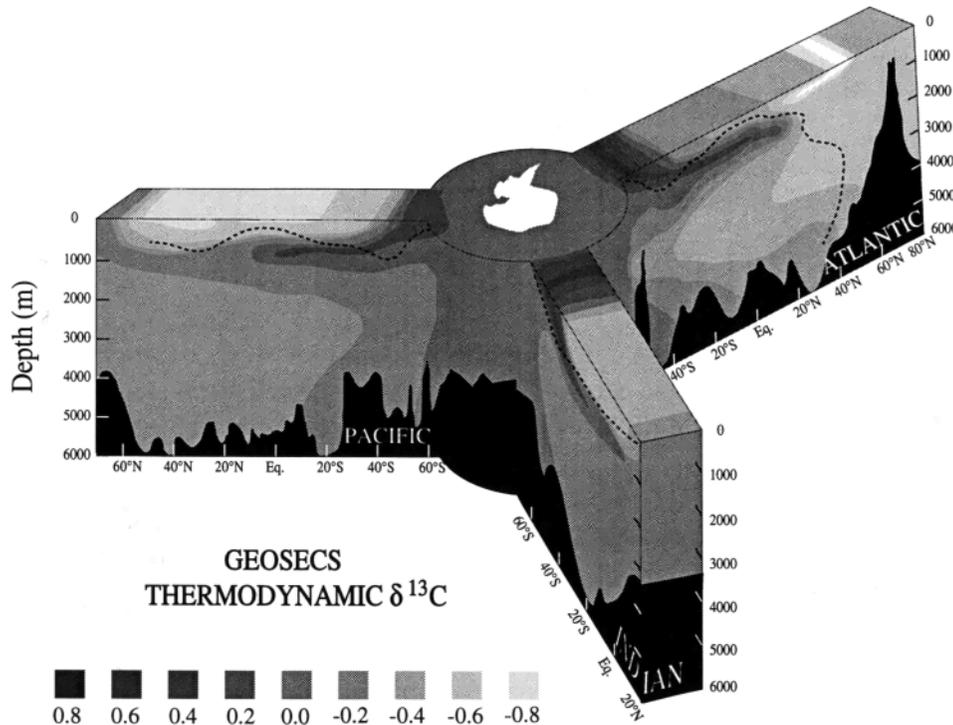


Fig. 1. GEOSECS $\delta^{13}\text{C}$, normalized to constant phosphate, with the following transformation: $\text{Normalized } \delta^{13}\text{C} = \delta^{13}\text{C} + (0.93 \times [\text{PO}_4]) - 2.4$. The rationale for this normalization is given in Charles and Fairbanks [1990] and Broecker and Maier-Reimer [1992]. The latter authors use a slightly different $\delta^{13}\text{C}$ - PO_4 relationship (based on a more selective analysis of the data) to make this normalization, but the results are not significantly different. This approach isolates the air-sea exchange influence. Antarctic water masses are characterized by thermodynamic enrichment (particularly in Antarctic Surface Waters and Antarctic Intermediate Water), while North Atlantic water masses show significant thermodynamic depletion. There is little variation in the deep waters of the Pacific and Indian Oceans. The contours were smoothed subjectively in the North Atlantic and North Pacific oceans, because the degree of scatter in these stations is fairly high. The dashed line shows the penetration of bomb ^{14}C at the time of the GEOSECS survey. All $\delta^{13}\text{C}$ values above the line are affected to some extent by anthropogenic disturbance because fossil fuel combustion lowers the ocean-atmosphere $\delta^{13}\text{C}$ [Broecker and Peng, 1982].

enriched in ^{13}C by as much as 1‰ through air-sea exchange [Charles and Fairbanks, 1990]. Apparently, high gas exchange rates in the subantarctic zone allow partial equilibration with the atmosphere at relatively cold temperatures, in effect labelling the surface waters with relatively high $\delta^{13}\text{C}$. Broecker and Maier-Reimer [1992] pointed out the same phenomenon with a similar procedure, while also comparing the effect in ocean model experiments run with different gas exchange rates.

Extending the phosphate normalization approach to GEOSECS profiles in all the ocean basins reveals some striking patterns (Figure 1). The most obvious is the tongue of thermodynamic enrichment which descends from the Antarctic Polar Front, coinciding almost perfectly with the salinity minimum which characterizes Antarctic Intermediate Water (AAIW). This distribution is what one would predict on the basis of the high Antarctic Surface Water and subantarctic values, since AAIW is derived almost entirely from these waters. The presence of this clear $\delta^{13}\text{C}$ trend in all the the ocean basins demonstrates that significant thermodynamic $\delta^{13}\text{C}$ effects are not limited to surface waters and must be considered at all depths, especially in water masses for which the contribution of surface waters is large. NADW is a case where the thermodynamic effect creates a relative depletion (by about 0.5‰ in comparison to Pacific Deep Water), presumably because the air-sea exchange in surface source waters occurs at warmer temperatures, before the cooling and sinking processes. This difference between AAIW and NADW gives rise to the especially detailed structure in normalized $\delta^{13}\text{C}$ at mid-depths in the Atlantic. Even at 20°N in the Atlantic, the AAIW $\delta^{13}\text{C}$ maximum is still well defined. As noted by Broecker and Maier-Reimer. [1992], Antarctic Bottom Water shows higher normalized values than Pacific Deep Water and NADW because it contains a small amount of partially equilibrated surface waters. Since no new deep water is formed in the Pacific, thermodynamic effects cannot be readily distinguished. The same applies to the deep Indian Ocean. The deep waters of these basins fall most nearly on the nutrient- $\delta^{13}\text{C}$ trend line expected from biological fractionation [Broecker and Maier-Reimer, 1992].

It is important to emphasize that phosphate-normalized $\delta^{13}\text{C}$ values are not the same as "preformed" $\delta^{13}\text{C}$ values. Preformed $\delta^{13}\text{C}$ values are perhaps best estimated by normalization to AOU (Apparent Oxygen Utilization) [G.P. Lohmann et al., Reassessment of the influence of temperature on the distribution of ^{13}C in the upper ocean, submitted to *Paleoceanography*, 1993], since oxygen deficit is in principle a better index of in situ respiration than is phosphate [Broecker and Peng, 1982]. However, preformed $\delta^{13}\text{C}$ values do not reflect a full separation of gas exchange and photosynthesis/respiration processes because in many regions (the Southern Ocean is a good example) preformed nutrients are

high and therefore affect the $\delta^{13}\text{C}$ values. In normalizing to constant phosphate to isolate the gas exchange component, the major assumptions we make are that nutrient properties follow constant "Redfield" proportions and that the $\delta^{13}\text{C}$ of organic matter is constant. These assumptions are almost certainly violated to some extent in the global ocean, but even considering the possible variability would not change the most important features of Figure 1. For example, the tongue of enriched $\delta^{13}\text{C}$ AAIW cannot be an artifact of the normalization, since C/P ratios in Antarctic surface and subsurface waters are close to the expected Redfield value [Chipman and Takahashi, 1989] and the use of more locally appropriate values for $\delta^{13}\text{C}$ of organic matter [Rau, et al., 1989] would actually increase phosphate-normalized $\delta^{13}\text{C}$ slightly.

PALEOCEANOGRAPHIC IMPLICATIONS

Deep Water

Foraminiferal $\delta^{13}\text{C}$ changes are often used to deduce past circulation patterns and intensities. This strategy relies on the assumption that the $\delta^{13}\text{C}$ (nutrient) differences between "end member" water masses remain relatively constant, or at least definable, and that mixing between end members can account entirely for $\delta^{13}\text{C}$ variability at a particular site through time. The thermodynamic effect could obviously interfere with this strategy if it caused end member $\delta^{13}\text{C}$ variability that was not monitored. For example, if the air-sea exchange processes in the North Atlantic were to become more like those in the Southern Ocean (with partial isotopic equilibrium at colder temperatures), this change could create the illusion of lower deep water nutrients and thus stronger NADW flow. As Broecker and Maier-Reimer (1992) suggest, it is not likely that changes in the thermodynamic effect in deep waters would be significant enough to overprint seriously the glacial-interglacial $\delta^{13}\text{C}$ signal resulting from circulation changes. After all, a change of 0.5‰ in $\delta^{13}\text{C}$ would require a 5°C change in average equilibration temperature, implying a fairly radical change in deep water formation processes. Nevertheless, realization that thermodynamic "tags" on various water masses might be sensitive to climate change emphasizes the importance of capturing end member variability.

This requirement applies especially to longer time scales, since the mechanisms for deep water formation and average ocean nutrient concentrations (the relative expression of air-sea exchange obviously depends on the total range of nutrients) could have been much different. Two pertinent examples occur during the late Pliocene, when the Atlantic-Pacific $\delta^{13}\text{C}$ differences were apparently higher than the modern difference by 0.2 per mil [Curry and Miller, 1989; Raymo et al., 1990], and during the Miocene, when deep-water $\delta^{13}\text{C}$ differences show the opposite

pattern, averaging one-half of the present difference [Miller and Fairbanks, 1985; Wright et al., 1991, 1992]. Relating $\delta^{13}\text{C}$ strictly to nutrients, these observations imply higher average ocean nutrients and more vigorous NADW flow during the Pliocene and, conversely, lower average nutrients and weaker NADW during the Miocene. Yet one could conceive of dramatically different scenarios by allowing regionally different thermodynamic influences and their mixture throughout the ocean to change [e.g. Wright et al., 1992]. The point is not that air-sea exchange completely explains these $\delta^{13}\text{C}$ anomalies, nor will it ever measurably affect mean ocean $\delta^{13}\text{C}$ values; on the other hand, it represents another variable to consider which, unlike $\delta^{13}\text{C}$ reservoir changes, can affect the $\delta^{13}\text{C}$ gradients in the ocean.

Upper Layer Water

The immediacy of the tie between $\delta^{13}\text{C}$ and nutrients from surface to intermediate depths affects

several prominent paleoceanographic themes. These include (1) estimating the strength of the biological "pump" of carbon by surface-to-deep $\delta^{13}\text{C}$ differences [Broecker and Peng, 1982; Shackleton et al., 1983], (2) testing hypothesized links between nutrient deepening, whole ocean alkalinity, and atmospheric CO_2 using intermediate depth $\delta^{13}\text{C}$ records [Boyle, 1988b], and (3) assessing the partitioning of carbon between terrestrial and oceanic reservoirs with the $\delta^{13}\text{C}$ of nutrient-free surface water [Curry and Crowley, 1987; Oppo and Fairbanks, 1989].

The fact that air-sea exchange effects are so spatially heterogeneous presents a fairly serious difficulty for carbon cycle models which interpret upper layer $\delta^{13}\text{C}$ signals. The reason is that, though conditions in the warm nutrient-free surface waters were probably always relatively constant, a variety of evidence suggests that the subpolar regions (where thermocline and intermediate waters communicate directly with the atmosphere) were strongly

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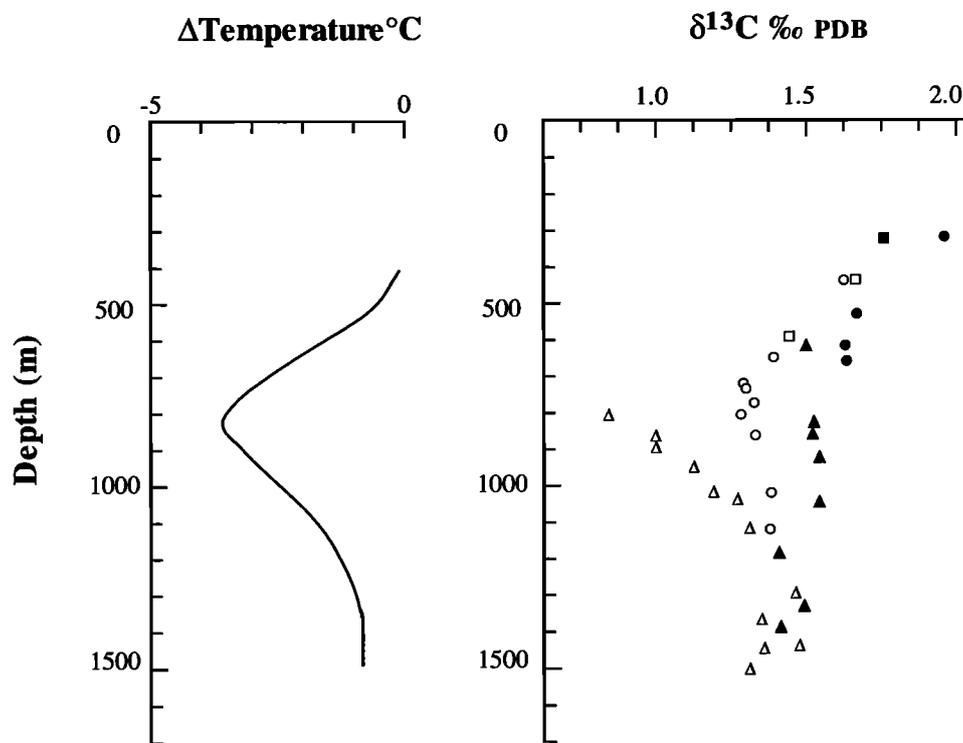


Fig. 2. Depth transect of carbon isotope values for the Holocene (open symbols) and last glacial maximum (solid symbols), taken from Slowey and Curry [1992]. The different symbol types refer to different species of benthic foraminifera. The ΔT (glacial-age change in temperature is calculated here by differencing the glacial-age and Holocene $\delta^{18}\text{O}$ profiles, subtracting a whole ocean change of 1.3‰ and multiplying the residual by -0.22). The lack of a glacial zone of carbon isotope depletion could be related either to the removal of nutrients, or colder air-sea equilibration temperatures, or both.

affected by Pleistocene climate change. Figure 1 shows that, at thermocline and mid-depths, there is almost a 1‰ difference between the thermodynamic influence on northern and southern source waters which eventually mix into the equatorial Atlantic. Thus, even subtle changes in the exchange processes occurring in these high-latitude "source" regions, or changes in the mixing of water masses with different thermodynamic tags, could account for a significant portion of the observed variability in the tropics, where the glacial-interglacial amplitude of $\delta^{13}\text{C}$ records is typically a few tenths of a per mil.

Evidence for actual changes in the thermodynamic influence on these timescales is not easily determined. If temperature reconstructions for the last

glacial maximum are reasonably accurate, the subpolar regions in both hemispheres cooled by 5°-10°C [CLIMAP, 1981]. All else constant, an equivalent change in equilibration temperature (not the same as the actual temperature of the water mass) would create an intermediate-to-thermocline ^{13}C enrichment ranging from 0.5-1.0‰. It is unlikely that the ocean would experience such an extreme, because mixing rates, gas exchange rates, residence times and the location of water mass formation probably varied in conjunction with temperature. However, the thermodynamic change resulting from ocean cooling would be in the same direction as nutrient depletion (which has been suggested on the basis of Cd/Ca ratios to be the prevailing condition

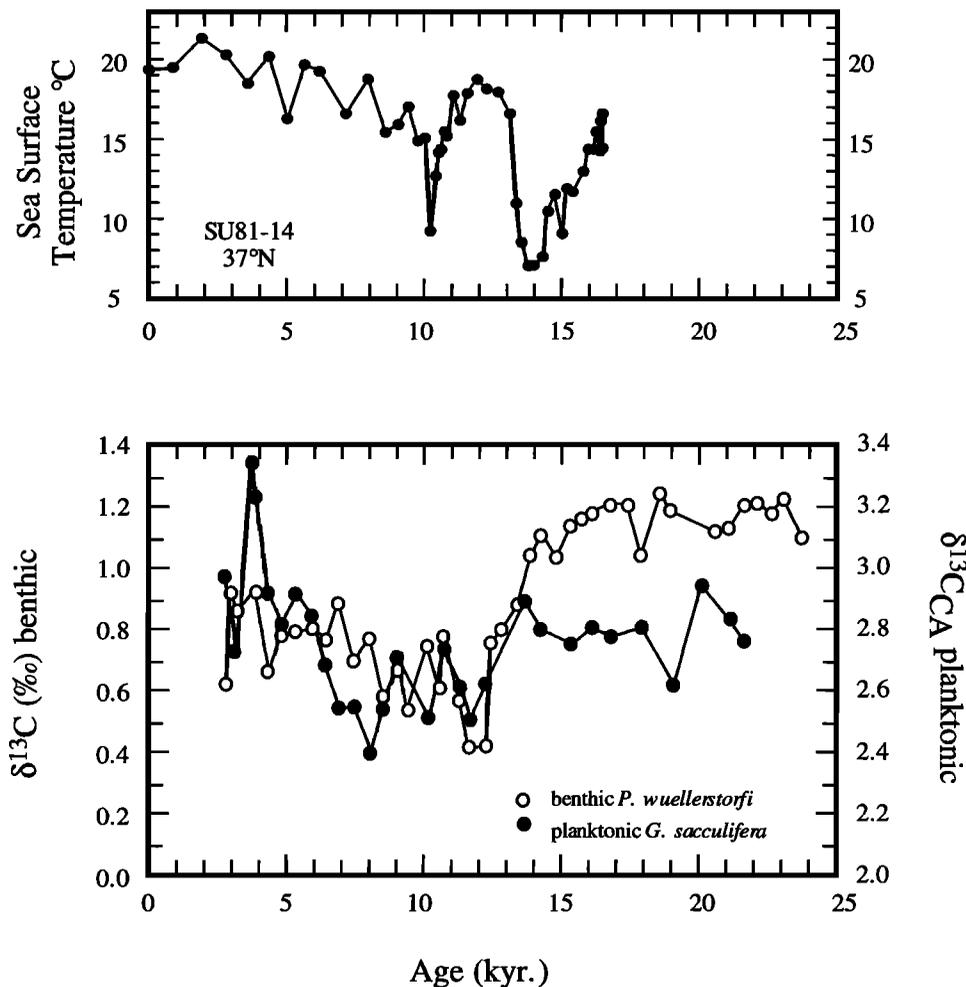


Fig. 3. Mid-depth Atlantic (1800 m) carbon isotope record from the Caribbean, taken from Oppo and Fairbanks [1987], plotted along with a typical North Atlantic sea surface temperature curve for the last 25,000 years [Bard et al., 1987]. If air-sea exchange affected these carbon isotope values, one would expect anticorrelation with temperature. In general, this inverse relationship is observed, so it remains difficult to separate nutrient-related changes from thermodynamic changes without additional information.

during glacial periods [Boyle, 1988a, 1988b]). Thus, without other supporting evidence, it is difficult to separate the nutrient and gas exchange components of upper layer $\delta^{13}\text{C}$ signals, even qualitatively. A recent example of this uncertainty comes from Slowey and Curry [1992], who determined isotopic ratios for the Last Glacial Maximum in a transect of cores spanning the North Atlantic thermocline. With the $\delta^{18}\text{O}$ data suggesting cooler water, the glacial $\delta^{13}\text{C}$ profile throughout the upper layer is consistent with nutrient depletion, thermodynamic enrichment, or both (Figure 2). Similarly, the record of mid-depth Atlantic $\delta^{13}\text{C}$ from Caribbean deep sea cores [Oppo and Fairbanks, 1987] conceivably could be interpreted as reflecting the North Atlantic Ocean temperature history (Figure 3), but Cd/Ca records [Boyle and Keigwin, 1987] suggest that nutrients may have changed as well.

There are, however, two clues that the air-sea exchange $\delta^{13}\text{C}$ component of the upper layer source water masses has in fact varied. The first is the planktonic $\delta^{13}\text{C}$ record of the tropical Atlantic over the last 30,000 years [Curry and Crowley, 1987; Oppo and Fairbanks, 1989]. The major changes in the nutrient-free surface water record, characterized by an unexpectedly small glacial-interglacial contrast and a significant deglacial minimum, coincide almost exactly with shifts in intermediate water chemistry. No such correlation would be expected if $\delta^{13}\text{C}$ was driven by nutrient variability alone and surface waters always remained nutrient free [Oppo and Fairbanks, 1989]. The second is the $\delta^{13}\text{C}$ record of atmospheric CO_2 , which is characterized by a glacial-age decrease of 0.4-0.7‰ [Marino et al., 1992; Leuenberger et al., 1992]. Barring major reductions in global ocean productivity, this large atmospheric decrease suggests increased thermodynamic fractionation, with air-sea exchange occurring at colder temperatures [Marino et al., 1992; Leuenberger et al., 1992]. This effect would be manifested preferentially in the intermediate and thermocline water masses, where the gas exchange imprint is most intense today.

The question then becomes how these apparently real thermodynamic effects may be quantified. For now, the best means for accomplishing this objective is by continuing to determine precisely the isotopic history of intermediate and thermocline source waters in conjunction with paired analyses of other nutrient tracers such as Cd/Ca. In this way, $\delta^{13}\text{C}$ variations could at least be normalized to constant trace element concentrations. The North Atlantic depth transect established by Slowey and Curry [1992] and its southern hemisphere counterpart (still in the development process [J. Lynch-Stieglitz et al., unpublished manuscript, 1993] provide the ideal materials for such an analysis. One problem with this approach, however, is that trace elements are themselves often not exact proxies for other nutrients, particularly at shallow (<400 m) depths [Boyle,

1988a; Frew and Hunter, 1992]. Alternatively, coupled ocean-atmosphere model experiments such as those presented by Broecker and Maier-Reimer [1992] will help target the water masses most sensitive to gas exchange effects. Ultimately, the task is made easier by the fact that any hypothesized shifts in air-sea exchange effects must satisfy the constraints imposed by the atmospheric CO_2 record.

CONCLUSIONS

Discriminating between the gas exchange and nutrient components of the marine $\delta^{13}\text{C}$ record is of obvious importance for models of both the carbon cycle and the past oceanic circulation. The analysis of the modern ocean presented here suggests that there are major, consistent differences in the air-sea exchange effect between various water masses. These thermodynamic tags on different water masses have likely varied in the past, and therefore this source of variability, while difficult to differentiate, cannot be overlooked. Once resolved, however, the air-sea exchange component will not merely pose a complication but will add to the growing number of constraints on past ocean-climate interactions.

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