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SCIENTIFIC COMMENT

Variability of the $\delta^{13}\text{C}$ of dissolved inorganic carbon at a site in the north Pacific Ocean

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Abstract—We present a depth profile of $\delta^{13}\text{C}$ -DIC (dissolved inorganic carbon) and a time-series of surface water $\delta^{13}\text{C}$ -DIC from seawater samples collected at a single site during the *Eve* cruise in the North Pacific in June of 1987. Our deep water results confirm those reported by KROOPNICK (1985) for GEOSECS Station 213 (10° west of *Eve* site). We observed a small but significant decrease in the $\delta^{13}\text{C}$ of DIC in the upper 500 m of the water column over 13 years since the GEOSECS survey. This is likely due, at least in part, to the input of additional fossil fuel-derived CO_2 to the upper ocean. We observed a significant change in surface water $\delta^{13}\text{C}$ over a short time period (2 days) that was the result of a change in the shallow surface water mass. This change emphasizes the need for caution when conducting seasonal studies.

INTRODUCTION

NUMEROUS PROCESSES CONTRIBUTE to the $\delta^{13}\text{C}$ signature of total DIC in seawater. The important processes are remineralization of organic matter to CO_2 , removal of CO_2 by plants during photosynthesis in the euphotic zone, input of CO_2 from atmosphere to surface ocean, and vertical or lateral advective transport of different water masses (KROOPNICK, 1974, 1985). Understanding the $\delta^{13}\text{C}$ of DIC will provide a further constraint on the carbon cycle in the oceans and help us understand the invasion of fossil fuel CO_2 into the main thermocline (0–1000 m). It will also allow a better understanding of paleorecords of $\delta^{13}\text{C}$ in forams by indicating how short-term changes in $\delta^{13}\text{C}$ in their living environments affect their isotopic signatures.

We examined the $\delta^{13}\text{C}$ of DIC in surface seawater at a single site in the north-central Pacific over a 28-day time period. The only temporal change we observed was not related to the warming of the surface waters from late June to early July, but to a change in the water mass that was sampled. We also examined the $\delta^{13}\text{C}$ of DIC in a depth profile to compare these data to those collected during GEOSECS.

COLLECTION SITE

All samples were collected from a single site, $31^\circ 0' \text{N}$, $159^\circ 0' \text{W}$, aboard the R/V *Melville* on the *Eve* cruise. The site lies in the north-eastern region of the subtropical Pacific gyre. We reoccupied the site, within 0.5 nautical mile, just prior to each cast between 6 June and 3 July 1987. This was part of two larger projects with Peter Williams and Ken Smith to observe the flux and cycling of carbon in an oligotrophic ocean region.

20-mL samples of unfiltered water were collected for isotopic analysis from Gerard and Niskin bottle casts. All samples from the Gerard casts were collected between June 6th and 15th and the Niskin samples on July 2nd. Surface waters, also unfiltered, were collected every other day for 28 days using a Jabsco pump and hose placed at a depth of about 2 m off the quarterdeck of the ship. Samples were also taken for TCO_2 , alkalinity, salinity, temperature, oxygen, and

chl-a. The water was poisoned with 100 μL of a saturated HgCl_2 solution immediately upon collection and stored without a headspace at 4°C in the dark until isotopic analysis. Between September and December of 1987, 2-mL aliquots were stripped using 1 mL of 100% H_3PO_4 according to standard techniques (MCNICHOL et al., 1991). Local surface seawater from Woods Hole Chemotaxis dock, handled in a manner identical to the samples, was used as a standard for the seawater analyses. In September 1987, a large water sample was collected and split into approximately thirty-five individual standards. These standards were analyzed routinely during the course of analyzing the samples over a period of 3.5 months.

The isotopic analyses were made at WHOI using a VG 602E Micromass isotope ratio mass spectrometer in the laboratory of Lloyd Keigwin. Prior to running any samples, the mass spectrometer was calibrated daily using gas generated on-line from the NBS-20 isotope standard; all results are reported relative to PDB. We used the results from the seawater standards to determine the precision of our analyses, $\pm 0.1\text{‰}$. In addition to measuring standards, we ran duplicate analyses, throughout the course of our study, on 17% of our samples and found an average difference of less than 0.06‰.

RESULTS

The depth profile of $\delta^{13}\text{C}$ DIC observed from 3 to 5765 m is shown in Fig. 1. There is a general trend toward decreasing $\delta^{13}\text{C}$ values with depth. The surface values decrease as the oxygen minimum zone (~ 900 m) is approached because of the addition of isotopically light CO_2 from the oxidation of organic matter. Below this zone, deep circulation patterns replenish the bottom waters and cause $\delta^{13}\text{C}$ to increase (KROOPNICK, 1985).

These data can be compared to the GEOSECS $\delta^{13}\text{C}$ data from Station 213 taken in September 1974, located 10°W of the *Eve* site. The data plotted in Fig. 1 are those reported in the GEOSECS shore-based data atlas (OSTLUND et al., 1987) with the correction of 0.1‰ discussed by KROOPNICK (1985). After a thorough examination of $\delta^{13}\text{C}$ data collected during GEOSECS from the Atlantic, Pacific, and Indian oceans, it became apparent to P. M. Kroopnik that there

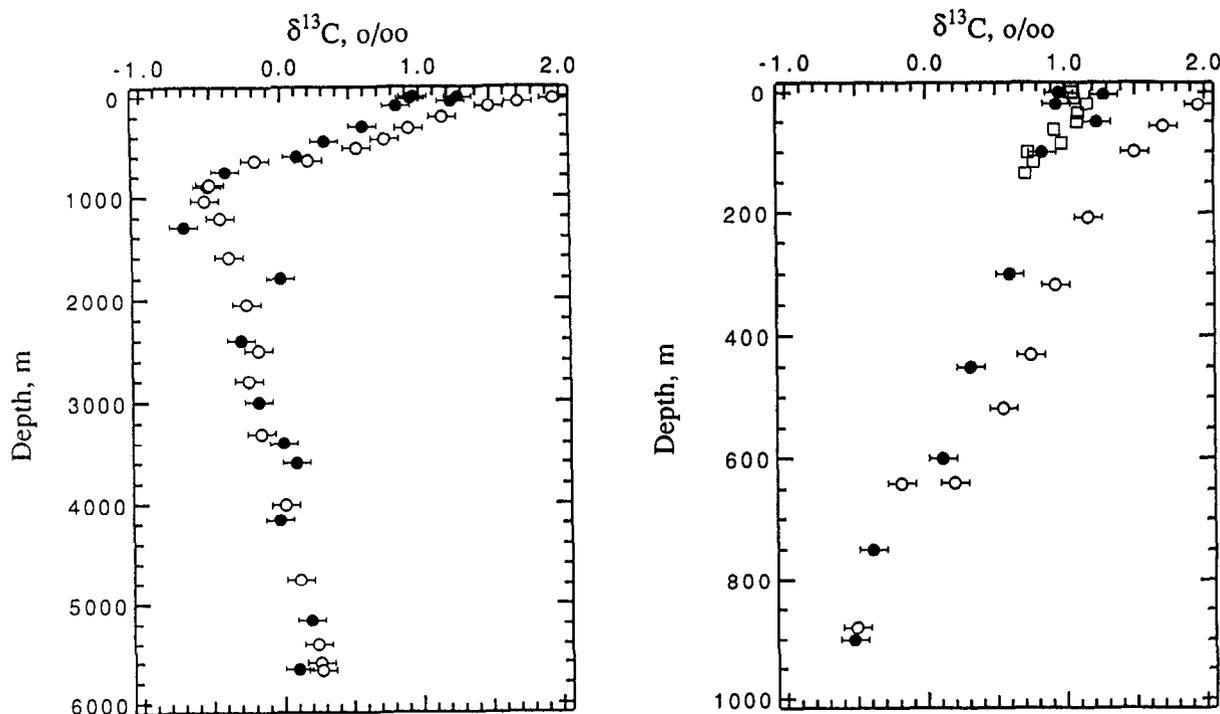


FIG. 1. Depth profiles of $\delta^{13}\text{C}$ -DIC from this study (\bullet , Gerard barrels; \square , Niskin bottles) and from GEOSECS Station 213 (\circ) from (a) 0–5760 m and (b) 0–900 m, with 1σ error bars shown. The data from GEOSECS have been corrected by adding 0.1‰ (KROOPNICK, 1985).

were inconsistencies in the isotopic data that were mostly due to errors in sample handling. He observed that plots of AOU vs. $\delta^{13}\text{C}$ were linear for each individual station and for all the stations together, and that when there were deviations from linearity, they were usually only observed in $\delta^{13}\text{C}$ and not in other measured properties. From this observation he used an AOU- $\delta^{13}\text{C}$ plot to derive offset factors to correct apparent inconsistencies in his data. Corrections of this sort necessarily decrease the level of confidence one has in a set of data. However, our results are in good agreement with P. M. Kroopnik's below 600 m, which indicates that the corrected data from this station are reliable.

Above 600 m depth, the $\delta^{13}\text{C}$ values we measured are consistently lower, i.e., more enriched in ^{12}C , than the GEOSECS data (Fig. 1b). The agreement below 600 m suggests that this is a real difference and not an analytical artifact. Another interesting feature is that our data show relatively constant values of $\delta^{13}\text{C}$ in the surface 100 m while P. M. Kroopnik's data indicate a strong gradient (Fig. 1b). The values obtained from a hydrocast on July 2 are also shown in Fig. 1b; they confirm the constancy of the data in the surface waters.

The $\delta^{13}\text{C}$ -DIC measurements for surface water samples collected over the 28-day occupation of our site are shown in Fig. 2. This record indicates that there is one significant change between days 5 and 7, from an average $\delta^{13}\text{C}$ of 0.9‰ to 1.2‰. The values are relatively constant before day 5 and after day 7. Figure 2 also shows the changes in the surface water temperature and salinity over the same 28-day period. At the same time that there is a change in the $\delta^{13}\text{C}$ values, there is a significant change in the salinity. The temperature is steadily increasing over the period of the cruise.

DISCUSSION

The observed differences in the $\delta^{13}\text{C}$ DIC in the upper 650 m of the water column between the *Eve* data and the GEOSECS Station 213 data (OSTLUND et al., 1987) are likely due to temporal and/or spatial changes. There have been thirteen years between the GEOSECS and *Eve* cruises. We know that isotopically light CO_2 has been and continues to be added to the atmosphere and the oceans (KEELING et al., 1979), and our observations are consistent with this hypothesis. If we assume a consumption rate of 0.4×10^{15} mol C/yr and an input rate of half that (0.2×10^{15} mol C/yr) to the upper 300 m of the water column from 1974 to 1987, and a DIC concentration of 2.1 mM, we calculate a decrease in $\delta^{13}\text{C}$ -DIC of 0.25‰ over the 13-year period. This is about half of the offset observed between the two data sets (Fig. 1b).

We suspect there was a seasonal cycle in the $\delta^{13}\text{C}$ of surface waters due to the production and oxidation of organic matter. The GEOSECS data were collected in September, while our data were collected in June/early July. The isotopic change is consistent with the photosynthetic removal of CO_2 between June and September, although this is unlikely here given the time elapsed (2 months) and the oligotrophic nature of the waters (INOUE and SUGIMURA, 1985; TILBROOK, 1982; DEUSER et al., 1968). At a similar site in the Pacific (20°N, 158°W), TILBROOK (1982) observed no change in surface water $\delta^{13}\text{C}$ over 10 months. In addition, the magnitude of the change we observe is about half that seen in just 2 days at the same site. The time-series data collected from the surface seawater indicate a significant isotopic shift (Fig. 2a)

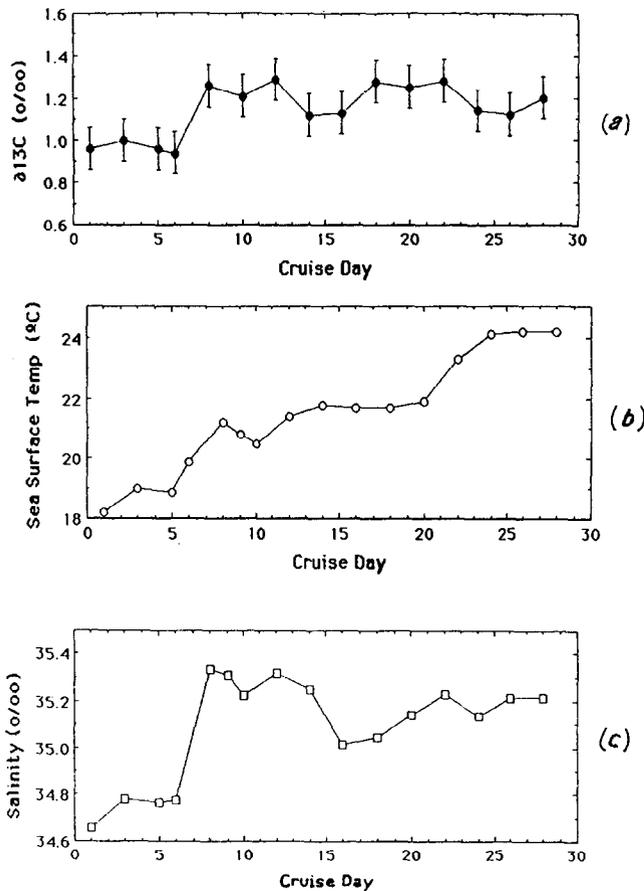


FIG. 2. Time-series data analysis of surface water: (a) $\delta^{13}\text{C}$ -DIC; (b) sea surface temperature; and (c) salinity. A shift in $\delta^{13}\text{C}$ and salinity is apparent between days 6 and 8, suggesting entry into a new water mass.

between day 6 and day 8. We use the temperature, salinity (Fig. 2b,c), oxygen, and $\Delta^{14}\text{C}$ of DIC data to help explain these isotopic data. The sea surface temperature increased from about 18° to 24°C over the 28-day period. The salinity values showed a large increase between days 6 and 8, and the oxygen measurements (E. Druffel and P. Williams, unpubl. data) decreased 25 $\mu\text{mol}/\text{kg}$ over 17 days. If the change in oxygen were due to the oxidation of organic matter and there were no exchange with atmospheric CO_2 , we would expect the $\delta^{13}\text{C}$ of DIC to decrease from 0.9 to 0.7‰, whereas we observe an increase of 0.3‰. Radiocarbon ($\Delta^{14}\text{C}$) in DIC was measured in the same samples from the Gerard barrels, and these results showed a significant change in the average $\Delta^{14}\text{C}$ and the standard deviation of the averages before ($\Delta^{14}\text{C} = 125.5 \pm 2.5$ ($N = 4$)) and after ($\Delta^{14}\text{C} = 134.1 \pm 5.5$ ($N = 12$)) day 7 of the cruise. The salinity jump that is coincident with the isotopic increases suggests that we have actually sampled two bodies of water, despite our rigorous reoccupation of the same site.

Further confirmation of a different water mass comes from examination of the T - S plot. Using the data collected from the 7 CTD casts between 0 and 200 m we observe that the data fall into two groups (Fig. 3). The data converge between

17 and 15°C, which corresponds to depths between 25 and 55 m. It appears that during the first part of the cruise, we were sampling a cooler, less saline body of water. This may not be evident in the time-series temperature plot because these data were from 3 m depth and had likely been affected by solar warming.

Thus, it appears that two bodies of water were sampled over the time period of this cruise and that each body of water had its own distinct isotopic signature. Within each body of water, there was no observable change in the $\delta^{13}\text{C}$ of DIC over time despite the fact that the temperature increased 6°C. A seasonal signal in $\delta^{13}\text{C}$ of DIC has been observed at other locations, but more sampling is necessary to define it at our site. The observed shift in surface seawater $\delta^{13}\text{C}$ over 2 days appears to weaken our conclusion that the observed difference between our data and P. M. Kroopnik's is partly due to the input of isotopically light CO_2 from the atmosphere. However, the differences in the bodies of water persist only to a depth of 25–50 m, while the observed differences in the isotopic profiles persist to almost 600 m. At the surface the observed difference is almost 1‰, much greater than the shift of 0.3‰ seen in our time-series study.

CONCLUSIONS

We have confirmed the deep water GEOSECS data from Station 213 in the Pacific. We suggest that there has been a significant decrease in the $\delta^{13}\text{C}$ of DIC in the surface waters over 13 years, likely due to the additional input of fossil fuel-derived CO_2 to the oceans. We wish to emphasize that spatial variability can be important over very short distances when studying surface waters. This phenomenon has been observed

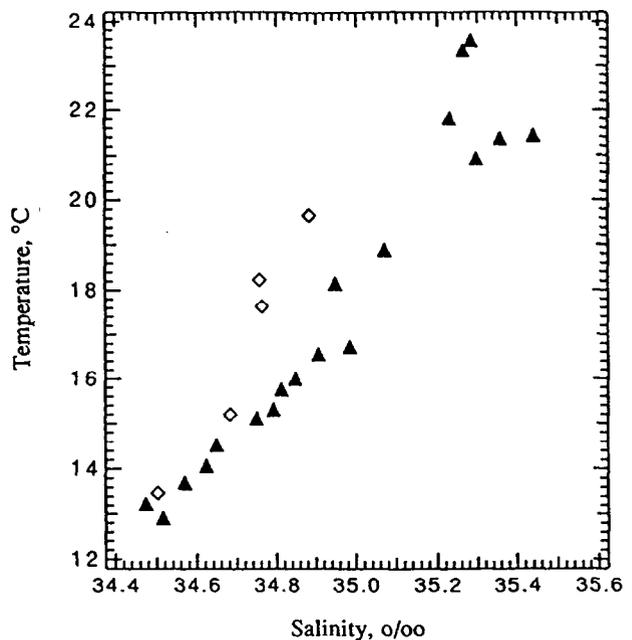


FIG. 3. T - S plots from CTD data made during days 1–6 (\diamond) and during days 8–22 (\blacktriangle) of the *Eve* cruise. There was an apparent shift to a new water mass between days 6 and 8 at the *Eve* site.

and reported previously, but we feel it is important enough to re-emphasize.

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