The distribution of $\delta^{13}C$ in total dissolved inorganic carbon in the central North Pacific Ocean along 175°E and implications for anthropogenic CO$_2$ penetration

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Abstract

We measured the quantity of $\delta^{13}C$ in total dissolved inorganic carbon in seawater collected between 48°N and 15°S along 175°E in the central North Pacific during the Northwest Pacific Carbon Cycle Study program (NOPACCS) in 1993 and 1994, focusing on the distribution of $\delta^{13}C$ on isopycnal surfaces of 25.6, 26.0, 26.4, 26.8 and 27.2 $\sigma_T$ in the main pycnocline of the North Pacific. The distribution of $\delta^{13}C$ was controlled largely by biological cycling. Using apparent oxygen utilization as a measure of biological effects on $\delta^{13}C$ variation, we calculated preformed values of $\delta^{13}C$ at the time when the water left the surface. The preformed $\delta^{13}C$ showed a trend of increasing southward in the subtropical region on all the surfaces. Variations in preformed $\delta^{13}C$ on the surfaces between 25.6 and 26.4 $\sigma_T$ in the subtropical region most likely reflect the penetration of $^{13}C$-depleted anthropogenic CO$_2$, because there was no other effect acting on the preformed $\delta^{13}C$. We applied another approach, using dissolved phosphate, to correct for biological effects on $\delta^{13}C$ distribution. The results of both methods allowed us to determine the changes in $\delta^{13}C$ due to the penetration of anthropogenic CO$_2$. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Pacific Ocean; dissolved inorganic carbon; anthropogenic; isotope

1. Introduction

The distribution of $\delta^{13}C$ in total dissolved inorganic carbon (TCO$_2$) in seawater has been used to study biological carbon cycling in seawater (Kroopnick, 1974, 1980, 1985). As research progressed, the importance of air–sea exchange as an influence on $\delta^{13}C$ in seawater became apparent (Oppo and Fairbanks, 1989; Keir, 1991; Broecker and Maier-Reimer, 1992; Charles et al., 1993; Zahn and Keir, 1994; Lynch-Stieglitz et al., 1995). The $\delta^{13}C$ in both atmospheric CO$_2$ and TCO$_2$ in the upper ocean have been decreasing because of dilution with $^{13}C$-depleted anthropogenic CO$_2$ (Friedli et al., 1986; Keeling et al., 1989). The decrease in $\delta^{13}C$ in the carbon reservoir due to anthropogenic carbon is referred to...
North Pacific based on observations between latitude 48°N and 15°S along 175°E during the Northwest Pacific Carbon Cycle Study program (NOPACCS) in 1993 and 1994. Many researchers have conducted intensive research on oceanic uptake of anthropogenic CO₂ in the subtropical North Pacific (Tsunogai et al., 1993; Winn et al., 1994, 1998; Watanabe et al., 1996; Takahashi et al., 1999). We focus on isopycnal surfaces of 25.6, 26.0, 26.4, 26.8 and 27.2 σt. First, we investigated the observed distributions of δ¹³C and AOU on those surfaces. We then calculated the level of δ¹³Cpre and discuss its distribution on the isopycnal surfaces. We also calculated δ¹³Cane, the air–sea exchange signature of δ¹³C (Broecker and Maier-Reimer, 1992; Lynch-Stieglitz et al., 1995), using a PO₄-based correction for biological effects. We discuss the distribution on the isopycnal surfaces of δ¹³Cane, which will also reflect the effect of anthropogenic CO₂ penetration.

2. Area description and methods

2.1. Sampling and analytical methods

The data discussed here were collected aboard the R/V Hakurei-Maru during the NOPACCS cruises in August–September 1993 and May–June 1994 from latitude 48°N to 15°S along longitude 175°E. Sampling locations are shown in Fig. 1 and Table 1. The hydrographic data are available from the Japan Oceanographic Data Center. The distribution of potential temperature, salinity and potential density (σt) is shown in Fig. 2. The relationship between potential temperature and salinity (TS diagram) is shown in Fig. 3.

Surface samples were obtained using a polyethylene bucket under dead slow condition. Subsurface were obtained using twelve 12-l Niskin bottles, which were attached to CTD/RMS (CTD: Sea Bird electronics CTD system SBE-911, RMS: General Oceanics Rosette Multi-Bottle Array System1015-12). Dissolved oxygen was measured on shipboard by the electric potentiometric titration method using Ag/AgCl combined electrode (Radiometer Model VIT90 ABCU91). PO₄ was measured on shipboard by the molybdate–ascorbic acid method using a spectrophotometer (Hitachi Model U-1000). TCO₂ was
Fig. 1. Cruise track of NOPACCS cruises. Open squares indicate sampling locations of the NH93-2 cruise and open circles indicate sampling locations of the NH94-1 cruise.

Oceanography was conducted during a NOPACCS cruise in April–May 1995, using the same analytical method as in this study. According to the results, TCO₂ measured on shipboard by the phosphate–helium purging method using a gas chromatograph (Shimazu Model GC-14A) with thermal conductivity detector (Weiss and Craig, 1973; Gamo and Horibe, 1980). The precision of TCO₂ analysis was estimated to be approximately 4 µmol kg⁻¹. Measurement of TCO₂ in certified reference materials (CRMs) distributed by Dr. A.G. Dickson of Scripps Institute of Oceanography was conducted during a NOPACCS cruise in April–May 1995, using the same analytical method as in this study. According to the results, TCO₂ determined by our GC system was about 9 µmol kg⁻¹ lower than that certified for the reference materials. Although the TCO₂ data probably contain some bias, the bias would provide insignificant effect in the anthropogenic CO₂ signal calculated by the method that we use in following section. Seawater samples for ¹³C analysis were collected in 100-ml glass bottles, immediately poisoned with 0.2 ml of a saturated solution of HgCl₂ after sampling, and stored at room temperature. The extraction of TCO₂ for ¹³C analysis was carried out in the laboratory using a modification of the system of Kroopnick (1974) in January–February 1995. All ¹³C samples were analyzed by mass spectrometer (Finnigan MAT 251) in the laboratory of Nagoya University. The precision of the extraction procedure was estimated by replicated analysis (n = 10) to be 0.05‰ (standard deviation). The precision of the ¹³C analysis was estimated to be 0.02‰ (standard deviation). The data are given as the per mil deviation of the ¹³C to ¹²C isotopic ratio relative to PDB standard material:

\[
\delta^{13}C = \left[ \frac{R_{\text{sample}}}{R_{\text{PDB-standard}}} - 1 \right] \times 1000
\]

### Table 1

Sampling station locations, dates and depths. Asterisks in the sampling depth column indicate that sampling depth was close to the seabed.

<table>
<thead>
<tr>
<th>Cruise</th>
<th>Station number</th>
<th>Date</th>
<th>Latitude</th>
<th>Longitude</th>
<th>Sampling depth</th>
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<tr>
<td>NH93-2</td>
<td>1</td>
<td>15 Aug. 1993</td>
<td>48°07'N</td>
<td>175°02'E</td>
<td>0–5152 m*</td>
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<td>4</td>
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<td>44°00'N</td>
<td>175°00'E</td>
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<tr>
<td>NH93-2</td>
<td>5</td>
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<td>42°00'N</td>
<td>175°00'E</td>
<td>0–3048 m</td>
</tr>
<tr>
<td>NH93-2</td>
<td>6</td>
<td>21 Aug. 1993</td>
<td>39°59'N</td>
<td>175°00'E</td>
<td>0–4932 m*</td>
</tr>
<tr>
<td>NH93-2</td>
<td>9</td>
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<td>33°00'N</td>
<td>175°00'E</td>
<td>0–3044 m</td>
</tr>
<tr>
<td>NH93-2</td>
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<td>30°00'N</td>
<td>175°00'E</td>
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<tr>
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</tr>
<tr>
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<td>4°00'S</td>
<td>175°00'E</td>
<td>0–5264 m*</td>
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<tr>
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<td>21°00'N</td>
<td>175°00'E</td>
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</tr>
<tr>
<td>NH94-1</td>
<td>2</td>
<td>21 Apr. 1994</td>
<td>19°00'N</td>
<td>175°00'E</td>
<td>0–4049 m*</td>
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<tr>
<td>NH94-1</td>
<td>4</td>
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<td>13°00'N</td>
<td>175°00'E</td>
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<tr>
<td>NH94-1</td>
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<td>6°01'N</td>
<td>175°01'E</td>
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<td>0°01'N</td>
<td>175°01'E</td>
<td>0–4853 m*</td>
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<tr>
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<td>3 May 1994</td>
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<td>175°00'E</td>
<td>0–3038 m</td>
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<td>175°00'E</td>
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</tr>
<tr>
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<td>175°00'E</td>
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<tr>
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<td>26 May 1994</td>
<td>30°00'N</td>
<td>175°01'E</td>
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Fig. 2. Profiles of (a) potential temperature, (b) salinity and (c) potential density observed between latitude 48°N and 15°S along longitude 175°E.
where $R = ^{13}C/^12C$, $R_{\text{sample}}$ and $R_{\text{PDB-standard}}$ represent the $^{13}C/^12C$ for the sample and standard, respectively (Craig, 1957).

2.2. Factors controlling $\delta^{13}C$ in $\text{TCO}_2$

Both the remineralization of organic matter and the dissolution of calcium carbonate cause $\text{TCO}_2$ changes in subsurface waters. According to Chen (1982), the change in $\text{TCO}_2$ in the deep water is represented by the following equation:

$$\text{TCO}_2^{\text{meas}} = \text{TCO}_2^{\text{pre}} + \text{TCO}_2^{\text{org}} + \text{TCO}_2^{\text{carb}}$$

(2)

where $\text{TCO}_2^{\text{meas}}$, $\text{TCO}_2^{\text{pre}}$, $\text{TCO}_2^{\text{org}}$ and $\text{TCO}_2^{\text{carb}}$ are the measured values of $\text{TCO}_2$, the preformed value of $\text{TCO}_2$, $\text{TCO}_2$ derived from the remineralization of organic matter, and $\text{TCO}_2$ derived from the dissolution of calcium carbonate, respectively. The $\delta^{13}C$ of $\text{TCO}_2$ in deep water is controlled by the level of $\delta^{13}C$ and quantity of $\text{TCO}_2^{\text{pre}}$, $\text{TCO}_2^{\text{org}}$ and $\text{TCO}_2^{\text{carb}}$ as follows:

$$\delta^{13}C_{\text{meas}} \text{TCO}_2 = \delta^{13}C_{\text{pre}} \text{TCO}_2^{\text{pre}} + \delta^{13}C_{\text{org}} \text{TCO}_2^{\text{org}} + \delta^{13}C_{\text{carb}} \text{TCO}_2^{\text{carb}}$$

(3)

where $\delta^{13}C_{\text{meas}}$, $\delta^{13}C_{\text{pre}}$, $\delta^{13}C_{\text{org}}$ and $\delta^{13}C_{\text{carb}}$ are the measured $\delta^{13}C$ in $\text{TCO}_2$, the $\delta^{13}C$ in $\text{TCO}_2^{\text{pre}}$, the $\delta^{13}C$ in $\text{TCO}_2^{\text{org}}$, and the $\delta^{13}C$ in $\text{TCO}_2^{\text{carb}}$, respectively.

Since phytoplankton preferentially assimilate the lighter isotope of carbon during photosynthesis, the organic matter they produce has less $\delta^{13}C$ than has seawater. Simultaneously, the $\delta^{13}C$ of $\text{TCO}_2$ increases during their photosynthesis. When the organic matter is remineralized, $\delta^{13}C$ of $\text{TCO}_2$ decreases due to the addition of $\text{TCO}_2^{\text{org}}$ with a lower $\delta^{13}C$ level. Between latitude 40°S and 40°N, most values of $\delta^{13}C$ in organic matter fall between $-22\%e$ and $-18\%e$, while lower values are observed in Arctic and Antarctic waters (Rau et al., 1982; Rau et al., 1989; Goericke and Fry, 1994). The production of calcium carbonate shells by marine organisms at the sea surface and their dissolution in deeper layers will also affect the $\delta^{13}C$ of $\text{TCO}_2$. $\delta^{13}C$ of calcium carbonate is controlled by the isotopic composition of $\text{TCO}_2$, seawater and isotopic fractionation factors. Generally, the carbonate in shells has an isotopic composition similar to that of the seawater in which it was produced (Craig, 1954; Keith and Weber, 1964); hence, the effect of production and dissolution of carbonate shells on $\delta^{13}C$ in $\text{TCO}_2$ is thought to be insignificant.

2.3. Determination of preformed $\delta^{13}C$

With regard to $\delta^{13}C_{\text{pre}}$:

$$\delta^{13}C_{\text{pre}} = \frac{\delta^{13}C_{\text{meas}} \text{TCO}_2 - \delta^{13}C_{\text{org}} \text{TCO}_2^{\text{org}} - \delta^{13}C_{\text{carb}} \text{TCO}_2^{\text{carb}}}{\text{TCO}_2^{\text{meas}} - \text{TCO}_2^{\text{org}} - \text{TCO}_2^{\text{carb}}}$$

(4)

When the stoichiometric ratio in the remineralization of organic matter is constant, we can determine $\text{TCO}_2^{\text{org}}$ from the decrease in dissolved oxygen. To correct for the change in solubility of oxygen with temperature, the changes in dissolved oxygen were measured in terms of AOU, which is defined as the difference between the saturation value calculated for the potential temperature of the sample and the measured value. We can determine $\text{TCO}_2^{\text{org}}$ as follows:

$$\text{TCO}_2^{\text{org}} = R_{C/O} \text{AOU}$$

(5)
where $R_{C/O}$ is the carbon-to-oxygen stoichiometric ratio. In this study, we use stoichiometric ratios of $P/N/C/O = 1/16/117/170$ following Anderson and Sarmiento (1994). Because the dissolution of calcium carbonate is accompanied by a change in alkalinity, we can determine $\text{TCO}_2$ from the change in total alkalinity (TA) in seawater as follows:

$$\text{TCO}_2 = 0.5(\text{TA}_{\text{meas}} - \text{TA}_{\text{pre}})$$  \hspace{1cm} (6)

where $\text{TA}_{\text{meas}}$ and $\text{TA}_{\text{pre}}$ mean measured and preformed values of TA, respectively. In previous studies, $\text{TA}_{\text{pre}}$ has been determined as a temperature function formulated according to the observed relationship between the salinity normalized values of surface TA and temperature Chen and Pytkowicz, 1979; Chen, 1982.

Kroopnick (1985) calculated $\delta^{13}C_{\text{pre}}$ for the Antarctic Intermediate Water and the North Atlantic Deep Water by substituting $-25\%e$ for $\delta^{13}C_{\text{org}}$, and $+2\%e$ for $\delta^{13}C_{\text{carb}}$. This computational scheme requires $\text{TA}_{\text{pre}}$ to be determined as a function of potential temperature. Kroopnick (1985) used $\text{TA}_{\text{pre}}$ that had been determined based on data from the Geochemical Section Studies GEOSECS. However, because the temperature relationship of surface TA has large spatial variations, the complicated water mass structure makes it difficult to determine the appropriate $\text{TA}_{\text{pre}}$ as a function of temperature, especially in the North Pacific. Accordingly, we propose a simplified computational scheme to calculate $\delta^{13}C_{\text{pre}}$ as a substitute for Eq. (4). On the basis of the fact that the carbonate shells of marine organisms generally have $\delta^{13}C$ similar to that of the seawater in which they were produced, we assumed that $\delta^{13}C_{\text{carb}}$ is the same as $\delta^{13}C_{\text{pre}}$. Then we substituted $R_{\text{org}}$ for \((\text{TCO}_2 / \text{TCO}_2)$ and obtained the following equation with regard to $\delta^{13}C_{\text{meas}}$:

$$\delta^{13}C_{\text{meas}} = \delta^{13}C_{\text{pre}} + (\delta^{13}C_{\text{org}} - \delta^{13}C_{\text{pre}})R_{\text{org}}.$$  \hspace{1cm} (7)

In the region where both $\delta^{13}C_{\text{pre}}$ and $\delta^{13}C_{\text{org}}$ are spatially constant, we can derive $\delta^{13}C_{\text{org}}$ by the relationship between $\delta^{13}C_{\text{meas}}$ and $R_{\text{org}}$. Next, we obtained following equation with regard to $\delta^{13}C_{\text{pre}}$ by the rearrangement of Eq. (7):

$$\delta^{13}C_{\text{pre}} = \frac{\delta^{13}C_{\text{meas}} - \delta^{13}C_{\text{org}}R_{\text{org}}}{1 - R_{\text{org}}}.$$  \hspace{1cm} (8)

Both the potential temperature and salinity showed insignificant variations on isopycnal surfaces greater than 27.7 $\sigma_T$ in this region (Fig. 3). Therefore, we regard the properties of the water in this region as unaffected by the mixing of different types of waters. We predict that $\delta^{13}C$ of the water in this region has not been affected directly by anthropogenic $\text{CO}_2$ because the water lost contact with the atmosphere in pre-industrial time. Consequently, we consider that $\delta^{13}C_{\text{pre}}$ is almost constant in this region. As mentioned above, the $\delta^{13}C$ of particulate organic matter has a narrow range of variation (from $-18\%e$ to $-22\%e$) between latitude 40°S and 40°N (Goericke and Fry, 1994). Therefore, we consider that $\delta^{13}C_{\text{org}}$ is also almost constant in the region investigated here.

We determined $\delta^{13}C_{\text{org}}$ from the relationship between $\delta^{13}C_{\text{meas}}$ and the values of $R_{\text{org}}$ in the observed region (Fig. 4) on the assumption that both $\delta^{13}C_{\text{pre}}$ and $\delta^{13}C_{\text{org}}$ are spatially constant on isopycnal surfaces greater than 27.7 $\sigma_T$ in this region. We can represent the relationship between $\delta^{13}C_{\text{meas}}$ and $R_{\text{org}}$ in this region as follows:

$$\delta^{13}C_{\text{meas}} = 1.1 - 22.5R_{\text{org}}.$$  \hspace{1cm} (9)

Accordingly, we determined $\delta^{13}C_{\text{org}}$ as $-21.4 \pm 1.0\%e$ from Eqs. (7) and (9). This value agrees well with the value reported by Goericke and Fry (1994). In the following discussion, we used this value as
\[ \delta^{13} C_{\text{org}} \] and calculated \[ \delta^{13} C_{\text{pre}} \] from Eq. (8). As we describe later, the choice of the stoichiometric ratio would affect our estimate of \[ \delta^{13} C_{\text{org}} \] to a certain extent but would not affect the results of our computational scheme of \[ \delta^{13} C_{\text{pre}} \].

We shall now use Eq. (4) to calculate \[ \delta^{13} C_{\text{pre}} \] exactly according various assumed values of \[ \delta^{13} C_{\text{carb}} \] and compare the result to the approximate formula in Eq. (8). We assume that \[ \text{TCO}_{\text{org}}^{\text{meas}} = 2350 \mu \text{mol kg}^{-1} \], \[ \text{TCO}_{\text{carb}}^{\text{meas}} = 200 \mu \text{mol kg}^{-1} \], \[ \delta^{13} C_{\text{meas}} = -0.8 \% \] and \[ \delta^{13} C_{\text{org}}^{\text{meas}} = -21.4 \% \]. These values are close to those found in the deep layer of the North Pacific where the contribution to TCO$_2$ from the dissolution of calcium carbonate is significant. On this condition, Eq. (4) would give \[ \delta^{13} C_{\text{pre}} = -1.14 \% \] when \[ \delta^{13} C_{\text{carb}} = 0 \% \], and \[ \delta^{13} C_{\text{pre}} = -1.10 \% \] when \[ \delta^{13} C_{\text{carb}} = +2 \% \]. On the other hand, Eq. (8) would give \[ \delta^{13} C_{\text{pre}} = -1.12 \% \]. This suggests that a change in presumed value of \[ \delta^{13} C_{\text{carb}} \] within the probable range would insignificantly affect \[ \delta^{13} C_{\text{pre}} \] calculated by Eq. (4) and that our approximate formula in Eq. (8) would give reasonable values of \[ \delta^{13} C_{\text{pre}} \].

Before turning to a closer examination of the results of \[ \delta^{13} C_{\text{pre}} \], we must refer to the possible error that could be introduced by remineralization of organic matter with lower \[ \delta^{13} C \] than in organic matter produced in temperate latitudes. For the Antarctic Bottom Water (AABW) component, which is the main component of the deep waters in the Pacific, the remineralization of significantly 13-C-depleted organic matter produced in the surface waters of the Antarctic Ocean would happen near the start of its journey after being formed. Therefore, a contribution of the AABW component would cause underestimation of \[ \delta^{13} C_{\text{pre}} \]. Eq. (9) implies a \[ \delta^{13} C_{\text{pre}} \] of +1.1 \% for waters heavier than \[ \sigma_{\theta} = 27.7 \], which is a little lower than expected. For example, a global regression of \[ \delta^{13} C \] against AOU for the heavier waters gave \[ \delta^{13} C_{\text{pre}} = +1.5 \% \] at AOU = 0 (Kroopnick, 1985). The difference between the values of \[ \delta^{13} C_{\text{pre}} \] for the waters is mainly due to this effect.

Here, we must also consider the influence of the 13-C-Suess effect on temporal changes in \[ \delta^{13} C \] in organic matter and carbonate produced at the sea surface. The water below the 27.7 \[ \sigma_{\theta} \] isopycnic surface circulates in time scales of several hundreds of years in this region. Therefore, we predict that the \[ \delta^{13} C \] change in this region would result from the gradual accumulation of TCO$_2^{\text{org}}$ and TCO$_2^{\text{carb}}$ over the past several hundred years. Consequently, the mean values of \[ \delta^{13} C_{\text{org}} \] and \[ \delta^{13} C_{\text{carb}} \] below the 27.7 \[ \sigma_{\theta} \] surface in this region would reflect the mean \[ \delta^{13} C \] values of organic matter and the carbonate produced at the surface in the past several hundred years. Considering the change in \[ \delta^{13} C \] in atmospheric CO$_2$ during this period (Friedli et al., 1986), the 13-C-Suess effect on \[ \delta^{13} C_{\text{org}} \] and \[ \delta^{13} C_{\text{carb}} \] below the 27.7 \[ \sigma_{\theta} \] isopycnic surface is relatively small. Therefore, in this region, the 13-C-Suess effect does not affect the validity of our approximation that \[ \delta^{13} C_{\text{carb}} \] is the same as \[ \delta^{13} C_{\text{pre}} \]. The value of \[ \delta^{13} C_{\text{org}} \] that we determined here would be close to that of organic matter produced at the surface in this region in pre-industrial time.

Water on isopycnic surfaces less than 26.8 \[ \sigma_{\theta} \] in this region circulates in time scales of a few decades (Watanabe et al., 1994; Warner et al., 1996). The dissolution of calcium carbonate has a small effect on the TCO$_2$ change on those surfaces because the water is supersaturated with regard to calcium carbonates in most of the region. Accordingly, we consider that the changes in \[ \delta^{13} C \] of TCO$_2$ in this region result mainly from the remineralization of organic matter produced in the past few decades. Hence, the values of \[ \delta^{13} C_{\text{carb}} \] in this region would be close to those of \[ \delta^{13} C \] in organic matter produced at the present sea surface. Assuming that isotopic fractionation during photosynthesis is constant, we predict that \[ \delta^{13} C \] in organic matter produced at the sea surface has decreased at the same rate of the \[ \delta^{13} C \] decrease in surface waters from pre-industrial times to the period of our observation. This 13-C-Suess effect on \[ \delta^{13} C_{\text{org}} \] would cause underestimation of \[ \delta^{13} C_{\text{pre}} \] in the upper pycnocline. We take this effect into consideration later.

2.4. Determination of the air–sea exchange signature of \[ \delta^{13} C \]

According to Broecker and Maier-Reime (1992), if there were no air–sea exchange, the relationship between \[ \delta^{13} C \] and PO$_4$ in the ocean would be:

\[ \delta^{13} C = \Delta \text{photo} \cdot R_{\text{C}} \cdot (\text{PO}_4 - \text{PO}_4^{\text{M.O.}}) / \text{TCO}_2^{\text{M.O.}} \]

(10)
where M.O. represents the mean ocean value, $\Delta_{\text{photo}}$ is $\delta^{13}\text{C}$ fractionation during photosynthesis relative to seawater $\delta^{13}\text{C}$, and $R_{C/p}$ is the stoichiometric ratio of carbon to phosphate. Substituting reasonable values ($\delta^{13}\text{C}^{\text{M.O.}} = 0.3$, $\Delta_{\text{photo}} = -19\%_c$, $\text{TCO}^{\text{M.O.}} = 2200\mu\text{mol kg}^{-1}$, $R_{C/p} = 128$, $\text{PO}_4^{\text{M.O.}} = 2.2\mu\text{mol kg}^{-1}$), Broecker and Maier-Reimer (1992) obtained the following relationship.

$$\delta^{13}\text{C} = 2.7 - 1.1\text{PO}_4.$$ (11)

This relationship closely matches that for deep water in the Indian and Pacific Oceans because of the homogeneity of the source waters.

In the previous sections, we used the stoichiometric ratio of P/N/C/O = 1/16/117/170 of Anderson and Sarmiento (1994) and estimated that $\Delta_{\text{photo}}$ is close to $-22.5\%_c$ for the water on isopycnal surfaces greater than 27.7 $\sigma_t$ (Fig. 4). Hence, to achieve consistency in values used in this study, we substituted those values for $R_{C/p}$, $\Delta_{\text{photo}}$ and the mean values for water below the 27.7 $\sigma_t$ surface ($\delta^{13}\text{C}^{\text{M.O.}} = -0.22\%_c$, $\text{TCO}^{\text{M.O.}} = 2320\mu\text{mol kg}^{-1}$, $\text{PO}_4^{\text{M.O.}} = 2.58\mu\text{mol kg}^{-1}$). From these data, we obtained the same relationship as in Eq. (11).

By subtracting the $\delta^{13}\text{C}$ value calculated from Eq. (11) from the measured value of $\delta^{13}\text{C}$, we can determine the air–sea exchange signature in the ocean-surface $\delta^{13}\text{C}$. Broecker and Maier-Reimer (1992) defined the measure of how much the $\delta^{13}\text{C}$ is affected by air–sea exchange as $\Delta\delta^{13}\text{C}$, which was renamed $\delta^{13}\text{C}_{\text{ss}}$ by Lynch-Stieglitz et al. (1995). $\delta^{13}\text{C}_{\text{ss}}$ thus has a different meaning from $\delta^{13}\text{C}_{\text{pre}}$ (Lynch-Stieglitz et al., 1995). $\delta^{13}\text{C}_{\text{ss}}$ is determined by the following equation.

$$\delta^{13}\text{C}_{\text{ss}} = \delta^{13}\text{C} + 1.1\text{PO}_4 - 2.7.$$ (12)

Various factors can change the $\delta^{13}\text{C}$ of surface water during air–sea exchange. One is equilibrium fractionation during air–sea exchange. Because of the temperature dependence of the isotope fractionation factor, TCO$_2$ in surface water, when in isotopic equilibrium with the atmosphere, becomes more $^{13}\text{C}$ enriched relative to atmospheric CO$_2$ by about 0.1% per degree of cooling (Mook et al., 1974). Another factor is the effect of invasion and evasion of atmospheric CO$_2$. This effect is explained in detail by Lynch-Stieglitz et al. (1995). Isotopic equilibrium between seawater and the atmosphere takes about 10 times as long as TCO$_2$ equilibrium; hence, TCO$_2$ in surface water will be $^{13}\text{C}$ enriched in oceanic CO$_2$ source areas. In oceanic CO$_2$ sink areas, TCO$_2$ in the surface water will be $^{13}\text{C}$ depleted.

By definition, water with $\delta^{13}\text{C}_{\text{ss}}$ of 0%$_c$ has the same air–sea exchange signature as deep water in the Pacific and Indian oceans. Both air–sea CO$_2$ exchange at low temperature and the evasion of CO$_2$ from surface water can enrich the surface water $\delta^{13}\text{C}$ and make the $\delta^{13}\text{C}_{\text{ss}}$ value positive. Conversely, both air–sea CO$_2$ exchange at high temperature and the invasion of atmospheric CO$_2$ tend to decrease $\delta^{13}\text{C}$ of surface ocean (Lynch-Stieglitz et al., 1995).

3. Results and discussion

3.1. The distribution of $\delta^{13}\text{C}$

Of the isopycnal surfaces that we are investigating in the main pycnocline of the North Pacific, those of 25.6 and 26.0 $\sigma_t$ form outcrops in the North Pacific subtropical gyre in winter (Van Scoy et al., 1991). The 26.4 $\sigma_t$ surface outcrops only in the northwestern part of the subpolar gyre in the North Pacific. The 26.8 $\sigma_t$ surface, which does not outcrop in the North Pacific, corresponds to the core of a low-salinity tongue of the North Pacific Intermediate Water (NPIW) that spreads southward from the subpolar region to the tropical region of the North Pacific. The 27.2 $\sigma_t$ surface also does not outcrop in the North Pacific. This surface corresponds to the core of the Antarctic Intermediate Water (AAIW) that spreads northward from sub-Antarctic region. As mentioned, our focus is on the distribution of $\delta^{13}\text{C}$ in the subtropical region of the North Pacific; we defined the northern and southern boundaries of this region as the latitudes between 40°N and 33°N and between 6°N and 13°N, respectively.

We linearly interpolated values of $\delta^{13}\text{C}$ and AOU on the five isopycnal surfaces (Fig. 5). On the surfaces between 25.6 and 26.4 $\sigma_t$, $\delta^{13}\text{C}$ generally decreased from the subpolar region to southern end of the subtropical region. The horizontal variation in $\delta^{13}\text{C}$ was inversely correlated with that of AOU. On the 26.8 $\sigma_t$ surface, the horizontal variation of $\delta^{13}\text{C}$ showed a trend dissimilar to those of shallower surfaces. The $\delta^{13}\text{C}$ in the subpolar region on this
surface showed considerably lower values than in the shallower surfaces because the water contained considerably more TCO$_{\text{org}}$. Since this surface does not outcrop in the North Pacific, the water could not have exchanged gases with the atmosphere directly. Therefore, it remains oxygen depleted in the subpolar region unlike the shallower water. Although the AOU clearly increased southward in the subtropical region on the 26.8 $\sigma$$_\theta$ surface, the $\delta^{13}$C showed no general tendency.
On the 27.2 \( \sigma_t \) surface, \( \delta^{13}C \) increased southward in the subtropical region, although there was no clear variation in AOU. The regional mean values of \( \delta^{13}C \) in the subtropical region were consistently lower on the deeper density surfaces, which corresponds to the fact that the deeper water contains more TCO\(_{2,4}\) as predicted from AOU. Note that the variation in \( \delta^{13}C \) would not correspond quantitatively to that of AOU. For example, although there is large difference in AOU between the subpolar and equatorial regions on the 25.6 \( \sigma_t \) surface, the values of \( \delta^{13}C \) in those two regions were almost the same. This feature implies that the distribution of \( \delta^{13}C \) is controlled largely by the biological carbon cycle, but the air–sea exchange of CO\(_2\) and the \(^{13}\)C-Suess effect also affect the distribution of subsurface \( \delta^{13}C \).

3.2. Distribution of preformed \( \delta^{13}C \)

3.2.1. Distribution on the isopycnal surfaces

We linearly interpolated \( \delta^{13}C_{\text{pre}} \) for the five isopycnal surfaces (Fig. 6). The variation in \( \delta^{13}C_{\text{pre}} \) along these surfaces is caused mainly by two processes: (1) temporal change of surface \( \delta^{13}C \) in the source region due to the effect of anthropogenic CO\(_2\); and (2) mixing of waters from different origin, hence, with different \( \delta^{13}C_{\text{pre}} \). Although convective mixing has some contribution in subpolar and equatorial regions, isopycnal mixing is generally dominant in the change of water properties. Since the surface \( \delta^{13}C \) has large spatial variation, the mixing of waters from different source regions can cause change in \( \delta^{13}C_{\text{pre}} \) on the isopycnal surfaces. Such mixing also causes change in potential temperature and salinity on the isopycnal surfaces.

We plotted the potential temperature along the isopycnal surfaces to determine whether there was any effect of water mixing on the spatial variation of \( \delta^{13}C_{\text{pre}} \) (Fig. 7).

On all the five isopycnal surfaces, there was a common general trend of \( \delta^{13}C_{\text{pre}} \) increase southward from the subpolar to the equatorial region. The mean values of \( \delta^{13}C_{\text{pre}} \) in the subtropical region were generally higher on the deeper density surfaces. In the subtropical region, potential temperature on the 27.2 \( \sigma_t \) surface increased gradually from north to south. This feature implies that the properties of the water change gradually due to mixing in the subtropical region. The extremely low concentrations of chlorofluorocarbons (CFCs) on this isopycnal surface in the North Pacific (Watanabe et al., 1994; Warner et al., 1996) suggest that the effect of anthropogenic CO\(_2\) penetration is negligible on this sur-
Fig. 7. The horizontal distribution of potential temperature on isopycnal surfaces of 25.6, 26.0, 26.4, 26.8 and 27.2 \( \sigma_t \). Average values in the subtropical region on each surface are shown in parentheses.

The potential temperature on the 26.8 \( \sigma_t \) surface also gradually increased southward in the subtropical region. Although this surface does not outcrop in the North Pacific, a significant level of CFCs decreasing southward from the subpolar to the equatorial region has been found (Watanabe et al., 1994; Warner et al., 1996). This implies that anthropogenic CO\(_2\) possibly affects the distribution of \( \delta^{13}C_{pre} \) on this surface. However, it is difficult to distinguish the effect of anthropogenic CO\(_2\) penetration on the variation in \( \delta^{13}C_{pre} \) from isopycnal mixing effects.

We consider that water mixing does not affect the \( \delta^{13}C_{pre} \) variations along the isopycnal surfaces between 25.6 and 26.4 \( \sigma_t \) in the subtropical region because the potential temperature shows almost no variation. Since these isopycnal surfaces outcrop in the North Pacific, the water should have directly exchanged CO\(_2\) with the atmosphere in the source regions recently. Therefore, we conclude that the trend of a northward decrease in \( \delta^{13}C_{pre} \) in those regions reflects temporal changes in surface \( \delta^{13}C \) in the source region due to the effect of anthropogenic CO\(_2\). Our conclusion is consistent with the fact that the water contains significant concentrations of CFCs that decrease southward in this region (Watanabe et al., 1994; Warner et al., 1996). The difference in \( \delta^{13}C_{pre} \) on the surfaces between latitude 33\(^\circ\)N and 13\(^\circ\)N is 0.40 ± 0.07\(\%\) on 25.6 \( \sigma_t \), 0.41 ± 0.07\(\%\) on 26.0 \( \sigma_t \) and 0.28 ± 0.07\(\%\) on 26.4 \( \sigma_t \). The rate of decrease of surface water \( \delta^{13}C \) is predicted to be about 0.02\(\%\) \( yr^{-1} \) (Bacastow et al., 1996), this difference in \( \delta^{13}C_{pre} \) corresponds to change within a few decades, which is consistent with the time scale of upper ocean circulation in this region (Watanabe et al., 1994; Warner et al., 1996).

3.2.2. Influence of the \( ^{13}C \)-Suess effect of organic matter

As mentioned, we must consider the \( ^{13}C \)-Suess effect of \( \delta^{13}C_{org} \) on the estimates of \( \delta^{13}C_{pre} \). We noted above that the actual value of \( \delta^{13}C_{org} \) in the upper pycnocline should be lower than the \( \delta^{13}C_{org} \) value that we used because of the \( ^{13}C \)-Suess effect. \( \delta^{13}C \) of the atmospheric CO\(_2\) has decreased by 1.4\(\%\) from pre-industrial times to the period of our observation. Accordingly, we recalculated as a test the values of \( \delta^{13}C_{pre} \) on the 25.6, 26.0 and 26.4 \( \sigma_t \) isopycnal surfaces, using a value 1.4\(\%\) lower than that used above. The mean values of \( \delta^{13}C_{pre} \) in the
subtropical region on these isopycnal surfaces increased by 0.02‰e, 0.03‰e and 0.05‰e, respectively. The difference in $\delta^{13}\text{C}_{\text{pre}}$ between 33°N and 13°N on the surfaces increased by 0.03‰e, 0.04‰e and 0.03‰e, respectively. These changes are small compared with the spatial variation of $\delta^{13}\text{C}_{\text{pre}}$ in this region at present. In regard to the $^{13}\text{C}$-Suess effect, it is unlikely that the $\delta^{13}\text{C}$ decrease of surface waters has kept up with the $\delta^{13}\text{C}$ decrease of the atmospheric CO$_2$. This is because of the relatively long time it takes for the surface ocean mixed layer to equilibrate isotopically with the atmosphere. In models this does not happen (Broecker and Peng, 1993), and the surface ocean $^{13}\text{C}$ proxy records do not indicate this either (Böhm et al., 1996). Therefore, 1.4‰e is the upper limit of the effect of decreasing $\delta^{13}\text{C}$ in the particulate carbon. However, the $^{13}\text{C}$-Suess effect of $\delta^{13}\text{C}_{\text{org}}$ will make larger contributions to $\delta^{13}\text{C}$ in the future as the surface $\delta^{13}\text{C}$ decreases.

3.2.3. The influence of uncertainty in stoichiometric ratios

In the calculation of $\delta^{13}\text{C}_{\text{pre}}$, we used the C/O stoichiometric ratio to correct for biological effects on the distribution of $\delta^{13}\text{C}$. The stoichiometric ratio has been the subject of scientific debate. The “traditional” P/N/C/O stoichiometric ratio of Redfield et al. (1963) is 1/16/106/138, based on planktonic decomposition studies. However, several modifications have been proposed from recent studies based on correlated chemical changes in seawater (Broecker et al., 1985; Takahashi et al., 1985; Minster and Boualahid, 1987; Boualahid and Minster, 1989; Anderson and Sarmiento, 1994). In this study, we used the stoichiometric ratios of P/N/C/O = 1/16/117/170 proposed by Anderson and Sarmiento (1994), which generally support the results of Broecker et al. (1985) and Takahashi et al. (1985).

We tentatively determined $\delta^{13}\text{C}_{\text{org}}$ and recalculated $\delta^{13}\text{C}_{\text{pre}}$ based on the “traditional” stoichiometric ratios of Redfield et al. (1963) by the same computational scheme used in this study, and then compared the results with the values based on the stoichiometric ratios of Anderson and Sarmiento (1994). The stoichiometric ratios of Redfield et al. (1963) gave $\delta^{13}\text{C}_{\text{org}}$ as $-19.1$‰e from the relationship between $\delta^{13}\text{C}$ and $R_{\text{org}}$ below the 27.7 $\sigma_g$ surface. This value is also consistent with the range of the $\delta^{13}\text{C}$ in organic matter reported by Goerlitz and Fry (1994). The mean values of $\delta^{13}\text{C}_{\text{pre}}$ on the isopycnal surfaces in the subtropical region were 0.78‰e on 25.6 $\sigma_g$, 0.81‰e on 26.0 $\sigma_g$, 0.82‰e on 26.4 $\sigma_g$, 1.00‰e on 26.8 $\sigma_g$ and 1.17‰e on 27.2 $\sigma_g$. The differences in $\delta^{13}\text{C}_{\text{pre}}$ between latitude 33°N and 13°N on the upper three surfaces were 0.40 ± 0.07‰e on 25.6 $\sigma_g$, 0.42 ± 0.07‰e on 26.0 $\sigma_g$ and 0.28 ± 0.07‰e on 26.4 $\sigma_g$. These values are essentially identical to those determined by the stoichiometric ratios of Anderson and Sarmiento (1994). This agreement is probably because the effects of changes in $\delta^{13}\text{C}_{\text{org}}$ and TCO$_2$ on $\delta^{13}\text{C}_{\text{pre}}$ cancel each other out. This suggests that a change in stoichiometric ratios within the probable range would not affect the results of our computational scheme of $\delta^{13}\text{C}_{\text{pre}}$ when the assumption is sufficiently correct that the stoichiometric ratios and $\delta^{13}\text{C}_{\text{org}}$ are spatially constant in the region of our study.

There is a caveat regarding the assumption that the stoichiometric ratios are constant. In most of the studies on stoichiometric ratios based on chemical changes of seawater, the upper ocean layers (above 400 m) have not been analyzed due to inapplicability of the technique. A slight change in the estimated proportions of TCO$_2$ and TCO$_2$ would affect the results of the $\delta^{13}\text{C}_{\text{pre}}$ calculation because the difference between $\delta^{13}\text{C}_{\text{org}}$ and seawater $\delta^{13}\text{C}$ is significantly larger than the range of variation of seawater $\delta^{13}\text{C}$. Therefore, uncertainty in the stoichiometric ratio may affect the values of $\delta^{13}\text{C}_{\text{pre}}$ when the stoichiometric ratios are not constant throughout the region of study. Clearly, intensive investigation of stoichiometric ratios in the upper ocean is needed.

3.3. Distribution of $\delta^{13}\text{C}_{\text{as}}$

The horizontal variations in $\delta^{13}\text{C}_{\text{as}}$ in the five isopycnal surfaces between 25.6 and 27.2 $\sigma_g$ are shown in Fig. 8. There was a southward trend of increasing $\delta^{13}\text{C}_{\text{as}}$ as well as $\delta^{13}\text{C}_{\text{pre}}$ in the subtropical region on all surfaces. As mentioned above, the mixing of different types of water has no effect on the spatial variation of $\delta^{13}\text{C}$ on the 25.6, 26.0 and 26.4 $\sigma_g$ surfaces in this region; hence, this north to south trend reflects the effect of anthropogenic CO$_2$. We consider that the variation in $\delta^{13}\text{C}_{\text{as}}$ on the 26.8
Fig. 8. The horizontal distribution of $\delta^{13}$C as on isopycnal surfaces of 25.6, 26.0, 26.4, 26.8 and 27.2 $\sigma_g$. The average values in the subtropical region on each surface are shown in parentheses. The differences in $\delta^{13}$C on isopycnal surfaces were 0.45 $\pm$ 0.07‰ on 26.0 $\sigma_g$ and 0.24 $\pm$ 0.07‰ on 26.4 $\sigma_g$. These values are similar to those found in the variation in $\delta^{13}$C$^{pre}$ in the same region.

4. Summary

(1) The distribution of $\delta^{13}$C of TCO was delineated between latitude 48°N and 15°S along longitude 175°E during the Northwest Pacific Carbon Cycle Study (NOPACCS) program in 1993 and 1994.

(2) Biological cycling was concluded to be the main factor that controls $\delta^{13}$C. However, the spatial variation of $\delta^{13}$C cannot be explained by biological cycling only.

(3) On the basis of the data observed in deep layers, we determined the mean isotopic composition of organic matter in the observed region to be $-21.4 \pm 1.0$‰, using the variation of $\delta^{13}$C, dissolved oxygen and TCO$_2$. This value is consistent with those previously measured.

(4) We calculated the value of preformed $\delta^{13}$C at the sea surface. The southward trend of increasing preformed $\delta^{13}$C on isopycnal surfaces between 25.6 and 26.4 $\sigma_g$ was most likely due to the penetration of anthropogenic CO$_2$.

(5) The differences in preformed $\delta^{13}$C between latitude 33°N and 13°N on the surfaces were 0.40 $\pm$ 0.07‰ on 25.6 $\sigma_g$, 0.41 $\pm$ 0.07‰ on 26.0 $\sigma_g$ and 0.28 $\pm$ 0.07‰ on 26.4 $\sigma_g$.

(6) Although the $^{13}$C-Suess effect of organic matter produced recently at the sea surface might affect the calculated values of preformed $\delta^{13}$C in the upper layers, the effect was insignificant compared with the observed variation in preformed $\delta^{13}$C.

(7) If the assumption that the stoichiometric ratios are constant throughout the region of study was sufficiently correct, the results of our computational scheme of preformed $\delta^{13}$C would not be affected by which stoichiometric ratios we chose.

(8) On the basis of the close correlation between $\delta^{13}$C and dissolved phosphate, we calculated the effect of air–sea exchange on $\delta^{13}$C variation. We also found the effect of anthropogenic CO$_2$ penetration on $\delta^{13}$C distribution on isopycnal surfaces between 25.6 and 26.4 $\sigma_g$ using this approach. The magnitude of this anomaly was similar to that found in the distribution of preformed $\delta^{13}$C.
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References


Rau, G.H., Sweeney, R.E., Kaplan, I.R., 1982. Plankton $^{13}$C, $^{12}$C


Tsunogai, S., Ono, T., Watanabe, S., 1993. Increase in total carbonate in the western North Pacific water and a hypothesis on the missing sink of anthropogenic carbon. J. Oceanogr. 49, 305–315.


