Carbon isotope ratios of organic matter in Bering Sea settling particles: Extremely high remineralization of organic carbon derived from diatoms

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The carbon isotope ratios of organic carbon in settling particles collected in the highly diatom-productive Bering Sea were determined. Wet decomposition was employed to oxidize relatively fresh organic matter. The amount of unoxidised organic carbon in the residue following wet decomposition was negligible. The $\delta^{13}C$ of organic carbon in the settling particles showed a clear relationship against SiO$_2$/CaCO$_3$ ratio of settling particles: approximately –26‰ and –19‰ at lower and higher SiO$_2$/CaCO$_3$ ratios, respectively. The $\delta^{13}C$ values were largely interpreted in terms of mixing of two major plankton sources. Both $\delta^{13}C$ and compositional data can be explained consistently only by assuming that more than 98% of diatomaceous organic matter decays and that organic matter derived from carbonate-shelled plankton may remain much less remineralized. A greater amount of diatom-derived organic matter is discovered to be trapped with the increase of SiO$_2$/CaCO$_3$ ratio of the settling particles. The ratio of organic carbon to inorganic carbon, known as the rain ratio, therefore, tends to increase proportionally with the SiO$_2$/CaCO$_3$ ratio under an extremely diatom-productive condition.

Keywords: diatoms, coccolithophores, carbon isotope, organic carbon, remineralization, rain ratio

INTRODUCTION

Dissolved CO$_2$ in the surface layer of oceans is fixed as organic matter by phytoplankton such as diatoms and coccolithophores. The organic carbon then settles down through the water column, where it is remineralized to inorganic carbon mainly by bacteria or deposited on the seafloor (de la Rocha, 2003). Knowledge of the origin of the organic matter transported downwards in a water column aids understanding of the oceanic carbon circulation, but this remains unclear due to the complicated processes involved: degradation of organic matter, high biodiversity as well as trophic transfer. Carbon isotope ratios of organic carbon are useful in identifying sources of particulate carbon in seawater (Mayers, 1994; Harmelin-Vivien et al., 2008; Faganeli et al., 2009; Lara et al., 2010; Sanchez-Vidal et al., 2009). However, the above complexity has limited application only to large grouping of sources such as algae or marine phytoplankton or soil organic matter, etc. We expected that the system of the Bering Sea might be simpler due to the much higher production of diatoms than that in other seas. To discuss the fate of diatom-derived organic matter in settling particles and to understand the diatomaceous biological pump, settling particles collected in extremely diatom-productive areas should be the best material. In this study the samples of settling particles mainly from the most extreme diatom-productive Bering Sea were used and the degradation of diatom-derived organic carbon was discussed in terms of mixing using the organic matter content and carbon isotope ratio.

MATERIAL AND METHODS

The samples of settling particles were collected from two distinctly different subarctic environments using sediment traps, which were deployed from 2008/6/20 to 2009/6/7 (Takahashi et al., 2002): Station SA, centrally located at a pelagic subarctic Pacific station (49°N, 174°W; water depth 5406 m) and Station AB, located at a marginal sea station (53.5°N, 177°W; water depth 3788 m) in the Bering Sea (Fig. 1). Station AB is characterized by a highly siliceous water column and sediments. The highest marine dissolved silica concentration in the world (228 μmol/kg) was measured in Bering Sea bottom water (Edmond et al., 1979; Tsunogai et al., 1979), and the Bering Sea is one of the most biologically productive areas in the world (Sambrotto et al., 1984). The sediment traps at both Stations AB and SA were deployed approximately 600 m above the seafloor (deployment depth: 3188
m at Station AB, 4806 m at Station SA). The sample bottles were filled with 5% formaldehyde solution, which was buffered to pH 7.6 with sodium borate. Apparent swimmers were removed by hand-picking under a microscope when the original samples were split immediately following sample retrieval on land. The swimmers were further removed by sieving through a 1000-μm mesh net. Subsets of the samples were subjected to routine analysis for opal, calcium carbonate, and organic carbon contents after washing the filtered samples with water to remove salts and formaldehyde (Takahashi et al., 2002). A subset was further washed with acetic acid and water to prepare a carbonate-free sample. Bulk and carbonate-free samples were subjected to CHN analysis. The latter was converted to organic matter content using the Redfield ratio (Redfield et al., 1963); the difference in carbon amounts between of the two was converted to inorganic carbon or CaCO₃ content. Opal was determined by extraction with a 0.5 M Na₂CO₃ solution for 5 h and molybdate blue spectrophotometry.

It is known that wet-oxidation does not oxidize all of particulate organic carbon (POC) in seawater (Sharp, 1973; MacKinnon, 1981) unlike dissolved organic carbon (DOC) (Peltzer et al., 1996), and that it tends to result in a smaller concentration of POC than the dry-combustion method. We categorized organic carbon in labile carbon and refractory carbon according to the vulnerability to the wet-oxidation. The reason for the classification is to separately consider hydrocarbon fixed by phytoplankton and long-lived organic compounds including far-transported terrigenous organic matter in a water column. The former is restricted to labile carbon, whereas the latter is more likely to be classified to refractory carbon.

**Labile carbon**

The samples were centrifuged three times with the addition and removal of Milli-Q water to remove formaldehyde and sea salt. The particulate samples were dried for 1 day at 60°C. The wet-oxidation was employed to analyze labile organic carbon in the trapped samples. First, 0.2 g of potassium peroxodisulfate peroxoacid, 2 ml of 8 v/v% phosphoric acid, and 5 ml of water was added to 2 mg of sample in a glass ampule. Atmospheric CO₂ and inorganic carbon was removed by bubbling of oxygen gas for 10 min. The ampule was heated at 123°C for 1 h in an autoclave to achieve rather moderate oxidation. The produced CO₂ was recovered in an appropriate vacuum line and cryogenically purified. The quantity of the recovered CO₂ gas was determined by a capacitance monometer. The recovery procedure was checked by adding sucrose powder to a glass ampule and was in the range of 90 to 100%. The CO₂ was analyzed for δ¹³C by a dual-inlet mass spectrometer (SIRA10 VG ISOTECH). The precision of the measurement was typically less than 0.05‰. The international standards used to calibrate the laboratory standard are USGS24 (graphite) and NBS No. 19 IAÉA (TS limestone Vienna).
Refractory carbon

To measure the amount of the refractory carbon that had not been decomposed by wet oxidation, the residue of wet oxidation was recovered on a glass plate and dried in a drying oven at 60°C. 200 µg of recovered sample was encapsulated in an Ag cup. The amount of carbon was determined by an elemental analyzer (Fisons 1500NA).

Characterization of sediment trap samples

Infrared absorption spectroscopy (Perkin-Elmer, Spectrum One) and pyrolysis gas chromatography-mass spectrometry, a GC-MS (Agilent 6890GC-5972A MSD) with a pyrolyzer (Japan Analytical Industry JCI-22), were applied using standard protocols for subsidiary purpose, in hope for detecting some difference in chemical properties of carbon among the samples and for information of refractory carbon.

RESULTS AND DISCUSSION

Labile and refractory carbon

The amounts of labile and refractory carbon are shown in Table 1. The amount of refractory carbon was close to blank except AB-20#5, AB-20#11 and AB-20#17. The IR spectra of bulk samples shows some peaks corresponding to the functional groups of OH, CO$_3^-$, CH$_2$, and SiOH, possibly due to inorganic matter and sugar. Differences in organic matter cannot be identified among the samples from the spectra. The thermal decomposition GC-MS spectrum of refractory matter showed only anthropogenic organic compounds such as polyethylene and siloxane, and no natural organic carbon was detected. It is considered that the samples contain only labile carbon and that the carbon recovered as refractory carbon is not indigenous.

Carbon isotope ratio of labile carbon

The δ$^{13}$C values of labile carbon ranged from –19.7‰ (AB-20#2) to –24.9‰ (AB-20#20) (Table 1). They are roughly in the range of the values reported for particulate organic carbon (POC) in seawater (Harmelin-Vivien et al., 2008; Faganeli et al., 2009; Lara et al., 2010; Sanchez-Vidal et al., 2009), where values around –20‰ and less than –25‰ were often interpreted collectively as that of marine algae and terrestrial organic matter, respectively. In the case of our study, because we analyzed labile carbon, the lower value might not be due to stable organic matter (e.g., lignin) supplied from land, since lignin is likely to be resistant to wet oxidation (Saiz-Jimenez and DeLeeuw, 1987).

In the δ$^{13}$C values of labile carbon, seasonal variation can be seen with highest values in June and July and lowest ones in winter and spring (Table 1). A possible inter-

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Sampling date</th>
<th>Total mass</th>
<th>Opal</th>
<th>Organic matter</th>
<th>CaCO$_3$</th>
<th>Inorganic carbon</th>
<th>Others</th>
<th>Opal/CaCO$_3$</th>
<th>Labile C amount</th>
<th>Refractory C amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>SA-20#1</td>
<td>20-27Jun.</td>
<td>143.1</td>
<td>12.6</td>
<td>38.2</td>
<td>13.5</td>
<td>4.6</td>
<td>22.7</td>
<td>1.9</td>
<td>–21.21</td>
<td>–19.69</td>
</tr>
<tr>
<td>SA-20#2</td>
<td>27Jun.-7Jul.</td>
<td>593.9</td>
<td>69.6</td>
<td>34.1</td>
<td>8.0</td>
<td>1.6</td>
<td>42.5</td>
<td>1.6</td>
<td>–22.58</td>
<td>–21.96</td>
</tr>
<tr>
<td>SA-20#3</td>
<td>7-17Jul.</td>
<td>183.8</td>
<td>38.0</td>
<td>34.8</td>
<td>11.7</td>
<td>5.0</td>
<td>34.8</td>
<td>1.3</td>
<td>–20.61</td>
<td>–19.69</td>
</tr>
<tr>
<td>SA-20#5</td>
<td>27Jul.-3Aug.</td>
<td>170.0</td>
<td>44.3</td>
<td>23.4</td>
<td>1.6</td>
<td>1.8</td>
<td>11.7</td>
<td>0.3</td>
<td>–21.13</td>
<td>–20.61</td>
</tr>
<tr>
<td>SA-20#7</td>
<td>23Aug.-2Sep.</td>
<td>41.6</td>
<td>10.4</td>
<td>8.0</td>
<td>6.8</td>
<td>3.5</td>
<td>36.8</td>
<td>1.7</td>
<td>–21.96</td>
<td>–20.61</td>
</tr>
<tr>
<td>SA-20#9</td>
<td>12-22Sep.</td>
<td>112.0</td>
<td>27.8</td>
<td>7.0</td>
<td>1.0</td>
<td>1.8</td>
<td>42.2</td>
<td>1.7</td>
<td>–21.13</td>
<td>–20.61</td>
</tr>
<tr>
<td>SA-20#11</td>
<td>22Oct.-2Nov.</td>
<td>20.0</td>
<td>4.7</td>
<td>2.8</td>
<td>0.3</td>
<td>0.2</td>
<td>29.5</td>
<td>0.4</td>
<td>–22.98</td>
<td>–21.96</td>
</tr>
<tr>
<td>SA-20#13</td>
<td>9-27Nov.</td>
<td>124.0</td>
<td>32.6</td>
<td>9.5</td>
<td>1.9</td>
<td>1.8</td>
<td>33.8</td>
<td>2.7</td>
<td>–21.96</td>
<td>–20.61</td>
</tr>
<tr>
<td>SA-20#15</td>
<td>9-27Dec.</td>
<td>47.4</td>
<td>12.1</td>
<td>3.8</td>
<td>0.3</td>
<td>0.2</td>
<td>29.5</td>
<td>2.7</td>
<td>–21.96</td>
<td>–20.61</td>
</tr>
<tr>
<td>SA-20#17</td>
<td>22Jan.-2Mar.</td>
<td>46.6</td>
<td>13.2</td>
<td>3.8</td>
<td>0.3</td>
<td>0.2</td>
<td>29.5</td>
<td>2.7</td>
<td>–21.96</td>
<td>–20.61</td>
</tr>
<tr>
<td>SA-20#20</td>
<td>15Mar.-8Apr.</td>
<td>101.7</td>
<td>38.5</td>
<td>3.6</td>
<td>0.3</td>
<td>0.2</td>
<td>29.5</td>
<td>2.7</td>
<td>–21.96</td>
<td>–20.61</td>
</tr>
</tbody>
</table>

Table 1. The flux of total mass, opal, organic matter, CaCO$_3$, inorganic carbon and others of sediment trap samples, the percentage of labile and refractory carbon in total mass, and isotope ratio of labile carbon a, b: amounts relative to total mass.—: not measured.
pertation is the $\delta^{13}C$ varies with the productivity of major planktonic species. However, no significant correlation of $\delta^{13}C$ values with the flux ofopal ($r^2 = 0.15$, $p > 0.2$), organic carbon ($r^2 = 0.18$, $p > 0.2$) or CaCO$_3$ ($r^2 = 0.06$, $p > 0.4$) was observed; only opal/CaCO$_3$ ratio ($W_{\text{opal}}/W_{\text{CaCO}_3}$ in g/g) correlates with the $\delta^{13}C$ values ($r^2 = 0.66$, $p < 0.003$) (Fig. 2 upper). The observed variation is likely not to reflect variation of $\delta^{13}C$ value of a single component, but to primarily reflect mixing of two or more end members. Opal is mainly represented by diatoms, and CaCO$_3$ is represented by plankton with CaCO$_3$ shells (mostly coccolithophores and foraminifera). Using the isotope fractionation of diatom organic carbon (Burkhardt et al., 1999) and coccolithophore organic carbon (Rost et al., 2002) against CO$_2$ dissolved in the North Pacific Ocean ($\delta^{13}C = -10.4$, Ortiz et al., 2000), we have estimated the $\delta^{13}C$ value of organic carbon in diatoms and coccolithophore for the Bering Sea. We obtained $\delta^{13}C$ values of $-20.7 \pm 3.9\%e$ and $-25.5 \pm 2.6\%e$ to represent organic carbon of diatoms and coccolithophores, respectively. These values are dependent on various factors, mainly photon intensity, species, CO$_2$ and nutrient concentrations (Burkhardt et al., 1999; Rost et al., 2002; Laws et al., 1995) and should not be considered fixed. Higher growth rate would reduce isotope fractionation and could result in higher $\delta^{13}C$ in the assimilated carbon (Laws et al., 1995). Degradation could decrease $\delta^{13}C$ by $\sim 2\%$ following experiments using lake organic matter (Lehmann et al., 2002). In the case of terrigenous organic matter refractory ligneous components have lower $\delta^{13}C$ values than labile cellulose (Benner et al., 1987). In the case of marine phytoplankton void of ligneous components, the effect of degradation to $\delta^{13}C$ values would be smaller. Unfortunately, no systematic studies have been reported on the isotopic discrimination during degradation of planktonic organic matter.

To summarize, the insignificant correlation between $\delta^{13}C$ values and opal flux suggests that the growth rate may not be the primary factor to govern the isotopic ratio of organic matter. The fairly good matching of the values to those of the end-members indicates that the degradation processes cause minor discrimination in $\delta^{13}C$ composition, especially of diatomaceous organic matter. In the Bering Sea we neglect this effect.

The relationship between $\delta^{13}C$ of organic matter and $W_{\text{opal}}/W_{\text{CaCO}_3}$ (Fig. 2 upper) indicates that the carbon isotope ratio of the organic matter in the settling particles is largely consistent with a mixing of the two end members of diatom-derived organic matter and CaCO$_3$-shelled plankton-derived organic matter. In the following section, mixing calculations were made, taking account that the $\delta^{13}C$ values of both end members are subject to secondary variation.

Remineralization of organic matter

Since the contribution of refractory matter is negligibly small (Table 1), the data on the labile carbon was used exclusively to discuss the remineralization of planktonic organic carbon. The percentage of organic matter that was remineralized during the vertical settlement of diatoms and CaCO$_3$-shelled plankton was estimated by fitting mixing curves to the data, assuming that isotope discrimination during remineralization is negligibly small for the reason mentioned in the previous section. The CaCO$_3$-shelled plankton consisted mainly of coccolithophores and foraminifera, and approximately similar amounts of the both are observed in settling particles (Takahashi et al., 2002). The compositional and isotopic difference between coccolithophores and foraminifera were neglected for the convenience. This handling could potentially be a source of error in the model calculation in a sample with a small opal content. $\delta^{13}C$ value and concentration of organic carbon are expressed as

$$\delta^{13}C_{\text{org}} = \frac{f_{\text{opal}}D_{\text{opal}}W_{\text{opal}}\delta^{13}C_{\text{opal}} + f_{\text{CaCO}_3}\delta^{13}C_{\text{CaCO}_3}W_{\text{CaCO}_3}W_{\text{CaCO}_3}}{f_{\text{opal}}D_{\text{opal}}W_{\text{opal}} + f_{\text{CaCO}_3}D_{\text{CaCO}_3}W_{\text{CaCO}_3}}$$

(1)

and

$$C_{\text{org}} = \frac{f_{\text{opal}}D_{\text{opal}}W_{\text{opal}} + f_{\text{CaCO}_3}\delta^{13}C_{\text{CaCO}_3}W_{\text{CaCO}_3}}{W_{\text{opal}} + f_{\text{opal}}D_{\text{opal}}W_{\text{opal}} + f_{\text{CaCO}_3}\delta^{13}C_{\text{CaCO}_3}W_{\text{CaCO}_3}}$$

(2)

respectively. In the equations $W_{\text{opal}}$ and $W_{\text{CaCO}_3}$ represent the observed weight (g) of opal and CaCO$_3$ shell; $f_{\text{opal}}$ and $f_{\text{CaCO}_3}$ (g/g) are the weight (g) of organic matter in the fresh diatoms and CaCO$_3$-shelled plankton per unit weight (g) of opal and CaCO$_3$; $\delta^{13}C_{\text{opal}}$ and $\delta^{13}C_{\text{CaCO}_3}$ are first set to 4.5 and 0.3 (Pasche, 1998; Brzezinski, 1985); $D_{\text{opal}}$ and $D_{\text{CaCO}_3}$ are the remineralization indexes (dimensionless) to express the portion of unmineralized organic matter in the original organic matter in diatoms and CaCO$_3$-shelled plankton, respectively. When 0 and 100% of organic carbon is remineralized, $D = 1$ and 0, respectively. The $f$ values may be variable. For example, supply of iron can increase $f_{\text{opal}}$ values more than 50% (Hutchins and Bruland, 1998). $D$ values may also be variable. Therefore, the product of $D$ and $f$ is a practical parameter to describe the amount of carbon in sediment trap samples and $Df$ values are also shown. We have first ex-
Carbon isotope ratios of organic matter in Bering Sea settling particles

Fig. 2. Fitting of the observed $\delta^{13}$C values and organic matter content against the weight ratio of opal frustules and carbonate tests. Closed circles: Station AB, Open circles: Station SA. Remineralization index of organic matter in fresh carbonate-shelled plankton is fixed at 1 ($D_{\text{CaCO}_3-org} = 1$). (left) Mixing model fitting using a fixed $D_f$ ratio of organic matter in diatoms and CaCO$_3$ shelled plankton ($D_{\text{op-org}} = 0.005$ or 0.016; $D_{\text{CaCO}_3-org} = 1$; $f_{\text{op-org}} = 4.5$; $f_{\text{CaCO}_3-org} = 0.5$). Note that the product of $D$ and $f$ actually govern the fitting calculation. (center) Mixing model fitting with variable $D_{\text{op-org}}$ values ($D_{\text{op-org}} = 0.005$ or 0.016; $D_{\text{CaCO}_3-org} = 1$; $f_{\text{op-org}} = 4.5$; $f_{\text{CaCO}_3-org} = 0.5$). Only $D_{\text{op-org}}$ is varied as a representative of $D_{\text{op-org}}f_{\text{op-org}}$. The grey lines indicate the typical loci of data, when remineralization index of diatomaceous organic matter ($D_{\text{op-org}}$) is dependent on $W_{\text{op}}/W_{\text{CaCO}_3}$ ratio. (right) Mixing model fitting using variable $\delta^{13}$C values ($\delta^{13}$C$_{\text{op-org}} = -19$ or $-21$‰; $\delta^{13}$C$_{\text{CaCO}_3-org} = -27$‰; $D_{\text{op-org}} = 0.016$; $D_{\text{CaCO}_3-org} = 1$; $f_{\text{op-org}} = 4.5$; $f_{\text{CaCO}_3-org} = 0.5$). The grey line indicates the typical loci of data, when $\delta^{13}$C values of diatomaceous organic matter are dependent on $W_{\text{op}}/W_{\text{CaCO}_3}$ ratio. Note that the fitting to OM% data is not affected by $\delta^{13}$C value. All available compositional data ($n = 36$) (Takahashi et al., 2002) are used for the fitting. When 0 and 100% of organic carbon is remineralized, $D = 1$ and 0, respectively.
0.005 to 0.02 (D_{op-org} = 0.016). Only D_{op-org} is varied as a representative of D_{op-org}/f_{op-org}. All available compositional data (n = 36) (Takahashi et al., 2002) are used for the fitting.

**Case 1. δ¹³C, D and f values fixed**

We first adapted δ¹³C_{op-org} = −20‰ and δ¹³CCaCO₃-org = −25‰. They are near the central values of the estimated carbon isotope ratios. Adapting various D_{op-org} and D_{CaCO₃-org} values, we fitted the observed carbon isotope values (Fig. 2 left). A fairy good fit was obtained when D_{op-org} = 0.0051 (D_{op-org}/f_{op-org} = D_{CaCO₃-org}/f_{CaCO₃-org} = 0.0225:0.3), except for one data of Station SA. However, this set of parameters failed to explain the carbon component data (dotted lines in Fig. 2 left). When different set of D_{op-org} values was adopted for better fitting to carbon component data, then this set failed to fit to isotopic data (solid lines in Fig. 2 left). The model can quite well reproduce the observed data when D_{op-org} = D_{CaCO₃-org} = 0.016:1 (D_{op-org}/f_{op-org} = D_{CaCO₃-org}/f_{CaCO₃-org} = 0.072:0.3) and δ¹³C_{op-org} = −20‰ and δ¹³CCaCO₃-org = −28‰ (crosses in Fig. 2 left). But this δ¹³C_{CaCO₃-org} value is out of the range of the estimated value of coccolithophore-derived organic carbon.

**Case 2. δ¹³C fixed, D and f values varied**

At a condition of higher growth rate of diatoms, D_{op-org} can increase (Iversen and Ploug, 2010). If diatom growth is supported by a greater supply of silicic acid, f_{op-org} may decrease, but when it is supported by iron supply, f_{op-org} may increase (Hutchins and Bruland, 1998). They provide reasons for Case 2. The good fit to both the equations, which is indicated in gray lines in Fig. 2 center, was achieved by varying D_{op-org} or f_{op-org} values depending on W_{CaCO₃} ratios, although fitting to the component data in the low W_{CaCO₃} region is obscure due to the scattered data in this region. In the fitting D_{op-org} increased from 0.005 to 0.02 (D_{op-org}/f_{op-org} from 0.0225 to 0.09) with increasing W_{CaCO₃}/W_{CaCO₃} ratio. δ¹³C_{op-org} and δ¹³CCaCO₃-org are set to −20‰ and −25.5‰, respectively. The new set of δ¹³C values is slightly different from the first set. The scattered component data in the lower W_{CaCO₃}/W_{CaCO₃} region is probably due to the neglect of compositional and isotopic difference of foraminifera, and other reasons including contribution from fecal pellets, other plankton (e.g., radiolarians, microflagellates and ciliates), variable δ¹³C of coccolithophores. In this region, D_{CaCO₃-org} is more influential than D_{op-org}; the scattering data makes it rather difficult to confine the D_{CaCO₃-org} value, but it is considered to be higher than 0.1 (Fig. 3), even in the case of a high D_{op-org} value (D_{op-org} = 0.016).

**Case 3. δ¹³C varied, D and f values fixed**

In a condition for higher diatom growth, δ¹³C of assimilated carbon may increase (Laws et al., 1995). A good fit to both the OM(%) and δ¹³C data is achieved by changing the δ¹³C values of diatom-derived carbon from −21‰ to −19‰ depending on W_{CaCO₃}/W_{CaCO₃} ratios, when D_{op-org}/f_{op-org} = 0.072:0.3 (Fig. 2 right). However, this case fails to capture the vague dent seen in OM(%) in W_{CaCO₃}/W_{CaCO₃} range of 5 and 25.

The reality should lie somewhere between Cases 2 and 3. The key to discern Cases 2 and 3 is the presence or absence of the dent in OM(%) (see Fig. 2 center). The OM data may have been disturbed by many factors and the dent is quite obscure. The later discussion on "rain ratio" seems to support smaller D_{op-org} (or D_{op-org}/f_{op-org}) val-

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**Fig. 3.** Fitting of the observed organic matter content adopting varying D_{CaCO₃-org} values with a constant D_{op-org} value of 0.016 (f_{op-org} = 4.5; f_{CaCO₃-org} = 0.5). Only D_{op-org} is varied as a representative of D_{op-org}/f_{op-org}. All available compositional data (n = 36) (Takahashi et al., 2002) are used for the fitting.

**Fig. 4.** Organic carbon and inorganic carbon ratio (rain ratio) against the weight ratio of opal frustules and carbonate tests (f_{op-org} = 4.5; f_{CaCO₃-org} = 0.5). Only D_{op-org} is varied as a representative of D_{op-org}/f_{op-org} All available compositional data (n = 36) (Takahashi et al., 2002) are used for the fitting.
ues when \( W_{op}/W_{CaCO3} \) is small (see Subsection [“Rain ratio” dependence on \( W_{op}/W_{CaCO3} \) ratios]).

Whatever cases are, a remark can be addressed: \( D_{op-org} \) may be less than 0.02 and \( D_{CaCO3-org} \) may be greater than 0.1. Although most of diatom derived carbon is remineralized, it should be noted that, at the condition of \( W_{op}/W_{CaCO3} > 10 \), more than half of the organic carbon in settling particles is compatible to the origin of diatomaceous origin in the Bering Sea based on \( \delta^{13}C \) values.

“Rain ratio” dependence on \( W_{op}/W_{CaCO3} \) ratios

The \( D_{op-org} \) value as high as 0.02 in the higher \( W_{op}/W_{CaCO3} \) region is supported by the observed \( C_{org}/C_{CaCO3} \) ratio (“rain ratio”) relationship with the \( W_{op}/W_{CaCO3} \) ratios (Fig. 4). The slope of the rain-ratio increment approaches, from a smaller slope between \( D_{op-org} = 0.005 \) and 0.02 (or \( D_{op-org} = 0.0225 \) and 0.09) in the region of \( W_{op}/W_{CaCO3} < 10 \), to a value as high as that for \( D_{op-org} = 0.02 \) at a higher \( W_{op}/W_{CaCO3} \) ratio. The smaller \( D_{op-org} \) in this region seems to support Case 2 of mixing with variable \( D \) and \( f \) values. The proportional relationship between \( W_{op}/W_{CaCO3} \) and \( C_{org}/C_{CaCO3} \) ratio in the higher \( W_{op}/W_{CaCO3} \) region is compatible with the observed significant correlation between opal flux and organic carbon flux in a dia-
tom-productive sea (Otosaka and Noriki, 2005; Honda and Watanabe, 2010).

Recent experiments reported that the decay of organic matter in settling particles was affected by the diatom : coccolithophore ratio (Iversen and Ploug, 2010). Diatoms are likely to act as the glue for aggregate particles. The increase of the remineralized fraction (the decrease of \( D_{op-org} \) value) at the lower \( W_{op}/W_{CaCO3} \) region implies that the aggregate particles may not be large enough to avoid remineralization being short of glue.

CONCLUSION

It is concluded that more than 98% of diatom-derived organic matter is remineralized at the depth of 3000 m in the Bering Sea. As for carbonate-shelled plankton, less than 90% of its organic carbon is likely to be degraded at the depth. Despite the higher remineralization rate of organic matter of diatom origin, because diatoms carry much greater amounts of carbon than carbonate-shelled plankton, most of organic matter settling to the seafloor may originate from diatoms. The organic matter from diatoms accounts for the increasing rain ratio with increasing \( W_{op}/W_{CaCO3} \) values.

In a more average sea, where diatom production and, hence, opal to CaCO3 ratio are much smaller than the studied seas, the analysis should be extremely difficult due to the scattering of data in this region.

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