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

Saki Yasuda,[1] Tasuku Akagi,[1]* Hiroshi Naraoka,[1] Fumio Kitajima[1] and Kozo Takahashi[2]

[1]Department of Earth and Planetary Sciences, Faculty of Sciences, 33 Kyushu University,
6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan
[2]Hokusei Gakuen University, Oyachi 2-3-1, Atsubetsu-ku, Sapporo 004-8631, Japan

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 par-

ticles 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

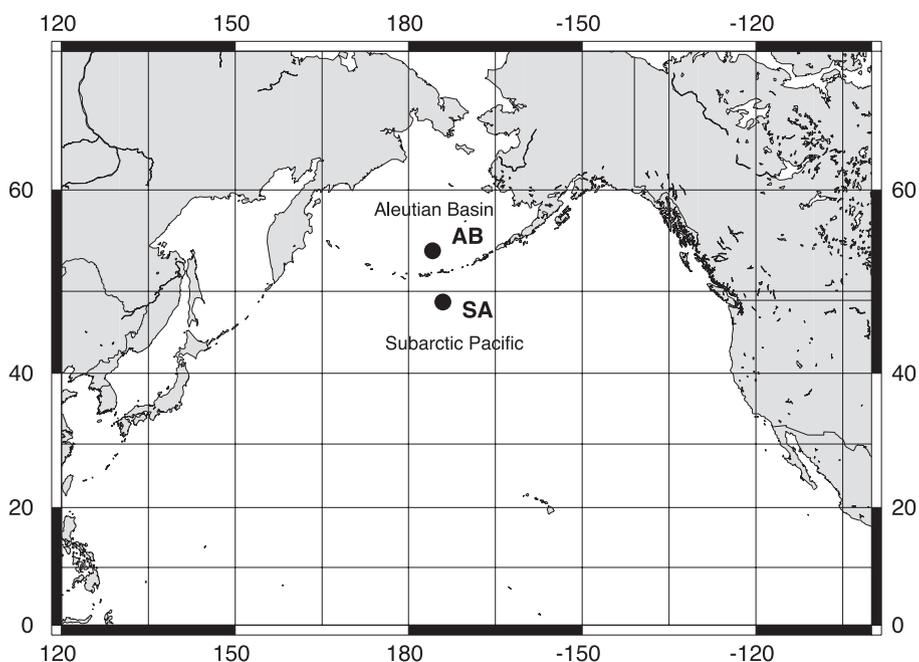*Corresponding author (e-mail: akagi@geo.kyushu-u.ac.jp)

Fig. 1. Map showing the two sampling stations in the North Pacific Ocean: Station AB (53.5°N, 177°W) and Station SA (49°N, 174°W).

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 $CaCO_3$ content. Opal was determined by extraction with a 0.5 M Na_2CO_3 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 CO_2 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 CO_2 was recovered in an appropriate vacuum line and cryogenically purified. The quantity of the recovered CO_2 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 CO_2 was analyzed for $\delta^{13}C$ 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 IAEA (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_2^-, 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 1. The flux of total mass, opal, organic matter, CaCO3, inorganic carbon and others of sediment trap samples, the percentage of labile and refractory carbon in total mass, and isotope ratio of labile carbon

Sample No.	Sampling date open–close	Total mass mg m^{-2} d^{-1}	Opal mg m^{-2} d^{-1}	Organic matter mg m^{-2} d^{-1}	CaCO$_3$ mg m^{-2} d^{-1}	Inorganic carbon mg m^{-2} d^{-1}	Others mg m^{-2} d^{-1}	Opal/CaCO$_3$ mg/mg	Labile C amount[a] %	Refractory C amount[b] %	Labile δ^{13}C ‰
SA-20 #1	20–27/Jun.	131.6	82.1	9.6	21.3	2.6	18.7	3.85	3.1	—	−21.25
SA-20 #2	27/Jun.–7/Jul.	591.9	438.9	34.1	8.0	1.0	110.9	54.9	1.7	—	−19.69
SA-20 #3	7–17/Jul.	383.8	284.0	23.4	5.0	0.6	71.4	56.8	1.9	—	−20.61
SA-20 #5	27/Jul.–3/Aug.	943.9	703.0	44.3	58.7	7.0	34.3	12.0	1.8	0.2	−22.58
SA-20 #7	23/Aug.–2/Sep.	145.3	108.8	9.8	4.5	0.5	137.9	24.2	2.1	<0.03	−21.87
SA-20 #9	12–22/Sep.	416.0	291.6	30.9	29.7	3.6	37.0	9.82	2.9	<0.03	−22.41
SA-20 #11	9–22/Oct.	200.8	126.1	15.1	30.1	3.6	22.2	4.19	2.9	0.4	−22.98
SA-20 #13	9–27/Nov.	471.4	294.3	27.8	65.4	7.8	32.8	4.50	2.7	<0.03	−24.02
SA-20 #15	22/Jan.–28/Feb.	48.6	25.2	3.8	4.3	0.5	63.8	5.86	2.6	<0.03	−23.37
SA-20 #17	19/Mar.–8/Apr.	101.7	45.1	7.0	14.0	1.7	82.5	3.22	2.7	0.2	−23.85
SA-20 #20	8–28/May	18.4	10.5	1.6	2.8	0.3	29.5	3.75	2.8	<0.03	−24.85

a, b: amounts relative to total mass.
—: not measured.

pretation is the δ^{13}C varies with the productivity of major planktonic species. However, no significant correlation of δ^{13}C values with the flux of opal ($r^2 = 0.15$, $p > 0.2$), 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_{op}/W_{CaCO3} in g/g) correlates with the δ^{13}C values ($r^2 = 0.66$, $p < 0.003$) (Fig. 2 upper). The observed variation is likely not to reflect variation of δ^{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 (δ^{13}C = –10.4, Ortiz *et al*., 2000), we have estimated the δ^{13}C value of organic carbon in diatoms and coccolithophores for the Bering Sea. We obtained δ^{13}C values of –20.7 ± 3.9‰ and –25.5 ± 2.6‰ 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 δ^{13}C in the assimilated carbon (Laws *et al*., 1995). Degradation could decrease δ^{13}C by –2% following experiments using lake organic matter (Lehmann *et al*., 2002). In the case of terrigenous organic matter refractory ligneous components have lower δ^{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 δ^{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 δ^{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 δ^{13}C composition, especially of diatomaceous organic matter. In the Bering Sea we neglect this effect.

The relationship between δ^{13}C of organic matter and W_{op}/W_{CaCO3} (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 δ^{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. δ^{13}C value and concentration of organic carbon are expressed as

$$\delta^{13}C_{org}$$
$$= \frac{f_{op\text{-}org}D_{op\text{-}org}W_{op}\delta^{13}C_{op\text{-}org} + f_{CaCO3\text{-}org}D_{CaCO3\text{-}org}W_{CaCO3}\delta^{13}C_{CaCO3\text{-}org}}{f_{op\text{-}org}D_{op\text{-}org}W_{op} + f_{CaCO3\text{-}org}D_{CaCO3\text{-}org}W_{CaCO3}}$$

(1)

and

$$C_{org}$$
$$= \frac{f_{op\text{-}org}D_{op\text{-}org}W_{op} + f_{CaCO3\text{-}org}D_{CaCO3\text{-}org}W_{CaCO3}}{W_{op} + W_{CaCO3} + f_{op\text{-}org}D_{op\text{-}org}W_{op} + f_{CaCO3\text{-}org}D_{CaCO3\text{-}org}W_{CaCO3}}$$

(2)

respectively. In the equations W_{opal} and W_{CaCO3} represent the observed weight (g) of opal and CaCO$_3$ shell; $f_{op\text{-}org}$ and $f_{CaCO3\text{-}org}$ (g/g) are the weight (g) of organic matter in the fresh diatoms and CaCO$_3$-shelled plankton per unit weights (g) of opal and CaCO$_3$; $f_{op\text{-}org}$ and $f_{CaCO3\text{-}org}$ are first set to 4.5 and 0.3 (Paasche, 1998; Brzezinski, 1985); $D_{op\text{-}org}$ and $D_{CaCO3\text{-}org}$ 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 $f_{op\text{-}org}$ 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-
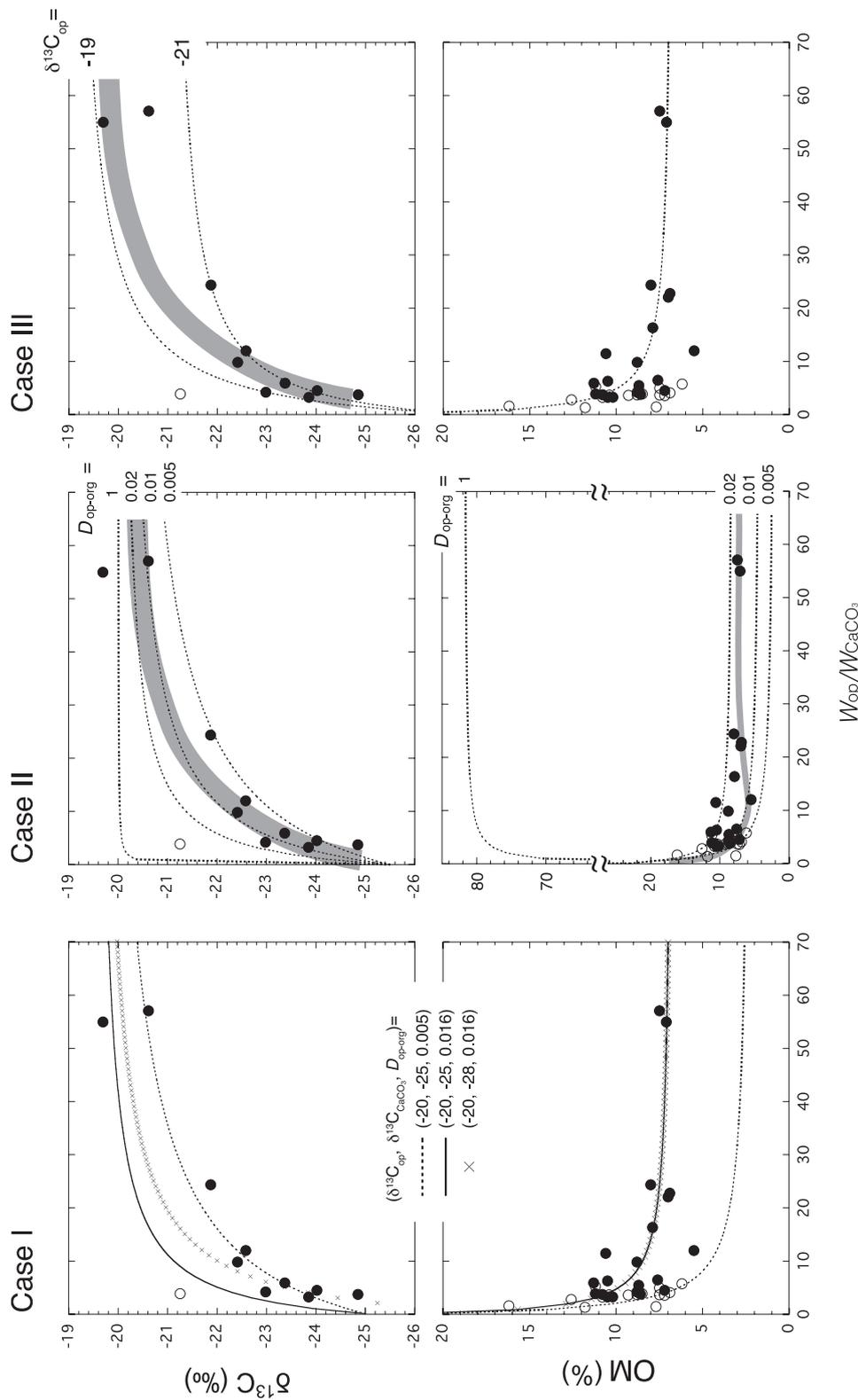
Fig. 2. Fitting of the observed $\delta^{13}C$ values and organic matter content against the weight ratio of opal frustules and carbonate tests. Closed circles: Station AB, Open circles: Station SA. Remineralization index of organic matter in fresh carbonate-shelled plankton is fixed at 1 ($D_{CaCO3\text{-}org} = 1$). (left) Mixing model fitting using a fixed Df ratio of organic matter in diatoms and $CaCO_3$ shelled plankton ($D_{op\text{-}org} = 0.005$ or 0.016; $D_{CaCO3\text{-}org} = 1$; $f_{op\text{-}org} = 4.5$; $f_{CaCO3\text{-}org} = 0.5$). Note that the product of D and f actually govern the fitting calculation. (center) Mixing model fitting with variable $D_{op\text{-}org}/f_{op\text{-}org}$ values ($\delta^{13}C_{op\text{-}org} = -20‰$; $\delta^{13}C_{CaCO3\text{-}org} = -25.5‰$; $D_{CaCO3\text{-}org} = 1$; $f_{op\text{-}org} = 4.5$; $f_{CaCO3\text{-}org} = 0.5$). Only $D_{op\text{-}org}$ is varied as a representative of $D_{op\text{-}org}/f_{op\text{-}org}$. The grey lines indicate the typical loci of data, when remineralization index of diatomaceous organic matter ($D_{op\text{-}org}$) is dependent on W_{op}/W_{CaCO3} ratio. (right) Mixing model fitting using variable $\delta^{13}C_{op\text{-}org}$ values ($\delta^{13}C_{op\text{-}org} = -19$ or $-21‰$; $\delta^{13}C_{CaCO3\text{-}org} = -27‰$; $D_{op\text{-}org} = 0.016$; $D_{CaCO3\text{-}org} = 1$; $f_{op\text{-}org} = 4.5$; $f_{CaCO3\text{-}org} = 0.5$). The grey line indicates the typical loci of data, when $\delta^{13}C$ values of diatomaceous organic matter are dependent on W_{op}/W_{CaCO3} 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.

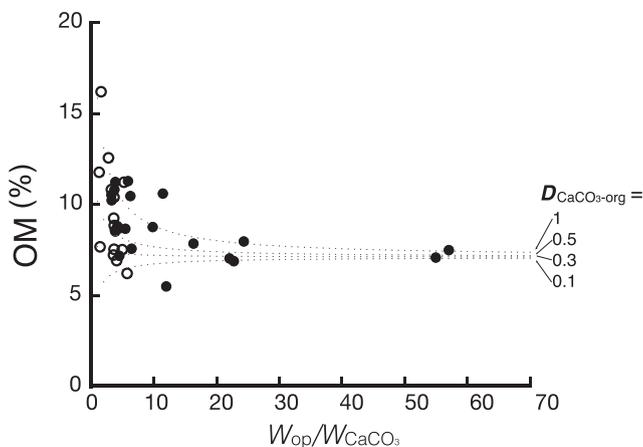Fig. 3. Fitting of the observed organic matter content adopting varying $D_{CaCO3\text{-}org}$ values with a constant $D_{op\text{-}org}$ value of 0.016 ($f_{op\text{-}org}$ = 4.5; $f_{CaCO3\text{-}org}$ = 0.5). Only $D_{op\text{-}org}$ is varied as a representative of $D_{op\text{-}org}f_{op\text{-}org}$.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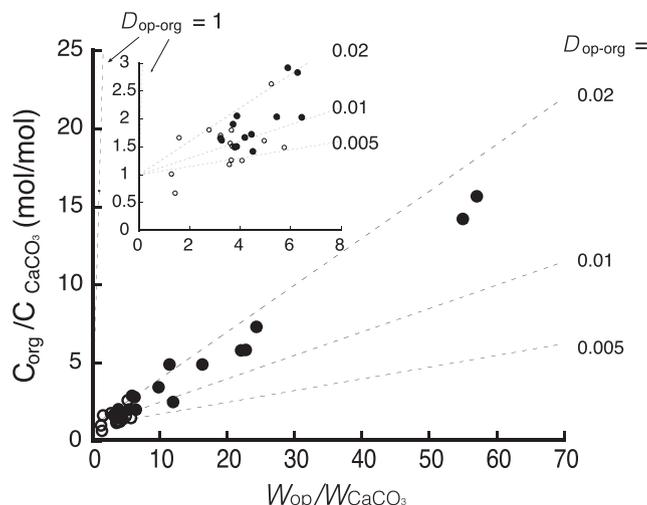

Fig. 4. Organic carbon and inorganic carbon ratio (rain ratio) against the weight ratio of opal frustules and carbonate tests ($f_{op\text{-}org}$ = 4.5; $f_{CaCO3\text{-}org}$ = 0.5). Only $D_{op\text{-}org}$ is varied as a representative of $D_{op\text{-}org}f_{op\text{-}org}$. All available compositional data (n = 36) (Takahashi et al., 2002) are used for the fitting.

amined the fixed parameters to start with to see how the model can reproduce the observational data. The more number of compositional data are available throughout the year (Takahashi *et al*., 2002), and in the model all available data (n = 36) were used.

Case 1. $\delta^{13}C$, D and f values fixed   We first adapted $\delta^{13}C_{op\text{-}org}$ = −20‰ and $\delta^{13}C_{CaCO3\text{-}org}$ = −25‰. They are near the central values of the estimated carbon isotope ratios. Adapting various $D_{op\text{-}org}$ and $D_{CaCO3\text{-}org}$ values, we fitted the observed carbon isotope values (Fig. 2 left). A fairy good fit was obtained when $D_{op\text{-}org}$: $D_{CaCO3\text{-}org}$ = 0.005:1 ($D_{op\text{-}org}f_{op\text{-}org}$: $D_{CaCO3\text{-}org}f_{CaCO3\text{-}org}$ = 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 $D_{op\text{-}org}$ 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 $D_{op\text{-}org}$: $D_{CaCO3\text{-}org}$ = 0.016:1 ($D_{op\text{-}org}f_{op\text{-}org}$: $D_{CaCO3\text{-}org}f_{CaCO3\text{-}org}$ = 0.072:0.3) and $\delta^{13}C_{op\text{-}org}$ = −20‰ and $\delta^{13}C_{CaCO3\text{-}org}$ = −28‰ (crosses in Fig. 2 left). But this $\delta^{13}C_{CaCO3\text{-}org}$ value is out of the range of the estimated value of coccolithophore-derived organic carbon.

Case 2. $\delta^{13}C$ fixed, D and f values varied   At a condition of higher growth rate of diatoms, $D_{op\text{-}org}$ can increase (Iversen and Ploug, 2010). If diatom growth is supported by a greater supply of silicic acid, $f_{op\text{-}org}$ may decrease, but when it is supported by iron supply, $f_{op\text{-}org}$ 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 with varying $D_{op\text{-}org}$ or $f_{op\text{-}org}$ values depending on W_{op}/

W_{CaCO3} ratios, although fitting to the component data in the low W_{op}/W_{CaCO3} region is obscure due to the scattered data in this region. In the fitting $D_{op\text{-}org}$ increased from 0.005 to 0.02 ($D_{op\text{-}org}f_{op\text{-}org}$ from 0.0225 to 0.09) with increasing W_{op}/W_{CaCO3} ratio. $\delta^{13}C_{op\text{-}org}$ and $\delta^{13}C_{CaCO3\text{-}org}$ are set to −20‰ and −25.5‰, respectively. The new set of $\delta^{13}C$ values is slightly different from the first set. The scattered component data in the lower W_{op}/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 $\delta^{13}C$ of coccolithophores. In this region, $D_{CaCO3\text{-}org}$ is more influential than $D_{op\text{-}org}$; the scattering data makes it rather difficult to confine the $D_{CaCO3\text{-}org}$ value, but it is considered to be higher than 0.1 (Fig. 3), even in the case of a high $D_{op\text{-}org}$ value ($D_{op\text{-}org}$ = 0.016).

Case 3. $\delta^{13}C$ varied, D and f values fixed   In a condition for higher diatom growth, $\delta^{13}C$ of assimilated carbon may increase (Laws *et al*., 1995). A good fit to both the OM(%) and $\delta^{13}C$ data is achieved by changing the $\delta^{13}C$ values of diatom-derived carbon from −21‰ to −19‰ depending on W_{op}/W_{CaCO3} ratios, when $D_{op\text{-}org}f_{op}$: Df_{CaCO3} = 0.072:0.3 (Fig. 2 right). However, this case fails to capture the vague dent seen in OM(%) in W_{op}/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 $D_{op\text{-}org}$ (or $D_{op\text{-}org}f_{op}$) val-

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: $D_{op\text{-}org}$ may be less than 0.02 and $D_{CaCO3\text{-}org}$ 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 considered to be of diatomaceous origin in the Bering Sea based on $\delta^{13}C$ values.

"Rain ratio" dependence on W_{op}/W_{CaCO3} ratios

The $D_{op\text{-}org}$ 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 $D_{op\text{-}org} = 0.005$ and 0.02 (or $D_{op\text{-}org}f_{op\text{-}org} = 0.0225$ and 0.09) in the region of $W_{op}/W_{CaCO3} < 10$, to a value as high as that for $D_{op\text{-}org} = 0.02$ at a higher W_{op}/W_{CaCO3} ratio. The smaller $D_{op\text{-}org}$ 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 diatom-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 $D_{op\text{-}org}$ 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 $CaCO_3$ 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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