Isotopic studies on the roles of diatoms in the oceanic material circulation

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Doctoral Dissertation

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Abstract

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Diatoms are important producer, which are responsible for about half the primary production in the ocean. They fixed inorganic carbon as organic carbon by photosynthesis in frustules. Therefore, diatoms exert great influence on the circulation of carbon in the ocean. Diatoms incorporate silicon (Si) to their frustules and play an important role in the oceanic Si circulation. Diatoms settle down through water columns and organic matter and frustule in diatoms are mineralized/dissolved by bacteria and other consumers, by which they transport C and Si to the deep sea. Diatoms play a role of vertical transport of the two elements. In this dissertation the diatomaceous contribution to the oceanic circulation of organic C and some terrigenous elements by using C, Nd and Fe isotope ratio is investigated.

In Chapter 1, background of vertical transport of carbon and terrigenous elements by diatoms is introduced.

In Chapter 2, the fate of organic carbon derived from diatoms is discussed using carbon isotope of organic matter.

The δ^{13} C values of organic carbon in the settling particles correlates with opal/CaCO₃ ratio (W_{op}/W_{CaCO3}). It is shown that the carbon isotope ratio of the organic matter in the settling particles is largely explained by a mixing of the two end members of diatom-derived organic matter (-19‰, Rost et al., 2002) and CaCO₃-shelled plankton-derived organic matter (-25‰, Burkhardt et

al., 1999). Fitting the observed δ^{13} C values and organic carbon compositions to the mixing equations indicates that the decomposition rate depends the weight ratio of opal and CaCO₃ and that decomposition rate decreases when the ratio increases.

It is concluded that diatom frustules play a role of ballast in highly diatom-productive ocean, and that nearly 100% of diatom-derived organic matter is dissolved/decomposed during settling through water columns in normal oceans.

In Chapter 3 and 4, diatom involvement of some terrigenous elements are discussed.

(Neodymium) The ε_{Nd} value of the HA fraction is likely to be representative of that of dissolved Nd in seawater, since labile Nd in particles readily exchanges dissolved Nd in seawater (Tachikawa et al., 1997) and the ε_{Nd} value of seawater is considered to be -2.2, averaging all HA data of Station AB. The HF fraction for opal flux higher than 200 mg/m²/day is likely to be representative of diatom opal employing the "asymptotic method" and is estimated to have ε_{Nd} = +0.7. When calculated using the leftover theory (Akagi 2013), half the Nd in the diatom frustules was supplied from the deep water and the other half from terrigenous particles in the surface water of the Bering Sea. The terrigenous particles is required to have ε_{Nd} = +3.7 to produce the ε_{Nd} of diatom frustules. According to mixing calculation, the ε_{Nd} value of the new input is prescribed approximately by 3:1 mix of Nd from the Aleutian andesite +basalt (Kelemen et al., 2003) and Nd from Chinese loess (Ding et al., 2001; Jahn et al., 2001). This blend reproduces a surprisingly similar REE composition to that scavenged in the water column. The whole discussion provides a good support for the "asymptotic method". Diatoms should have converted relatively insoluble silicate minerals to relatively soluble carbonate, in the course of which silicate minerals have to be decomposed to liberate REEs in the minerals.

(Iron) The HF fraction for opal flux higher than 200 mg/m²/day is likely to be representative of diatom opal employing the "asymptotic method". The δ^{56} Fe values of diatom frustules estimated

0‰. The δ^{56} Fe values of dissolved Fe in seawater is estimated to be lower than -0.7‰ based on the δ^{56} Fe values of HA and the discussion by Fantle and Depaolo (2004). Additionally, the δ^{56} Fe of Fe reductive dissolution from sediment was assumed to be -2‰ (Conway and John, 2014). Therefore, to achieve δ^{56} Fe= 1‰ of seawater, diatom frustules and sediments are mixed at a ratio of 1:1. The Fe/Si in diatom frustules is 400 times of that of seawater and diatom frustules contain Fe 400 times as much as the maximum amount that can be absorbed from the seawater in diatom frustules. This corresponds to the estimation that less than 1/400 of Fe in diatom frustules is from seawater and that the majority is from silicate minerals and that most of Fe in diatom frustules was considered to deposit without dissolution.

Since Nd and Fe are only two representatives of terrigenous elements, it is considered that diatoms involve with the circulation of many other elements in the ocean.

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Chapter 1. General introduction

1.1 Diatoms

Diatoms are unicellular phytoplankton which bears silicate cell walls called frustules. They inhabit in a photic zone, and fix CO_2 dissolved in seawater or atmospheric CO_2 and absorb silicic acid. They are the most important plankton with respect to the influence on the carbon cycle, since diatoms are responsible for about half the primary production of the oceans (Falkowski *et al.*, 1998)

The well- known vertical profiles of dissolved silica in the oceans are classified to a "nutrient" type. This type of profiles clearly implies that diatom frustules formed in the surface, sink to the deep water and then most of them dissolved there. This vertical transport of diatom may have a potential to vertically transport some elements other than silicon.

1.2 Biological pump

The biological pump refers to biologically driven sequestration of carbon from the atmosphere to the deep sea.

This pump consists of the photosynthetic fixation of dissolved inorganic carbon in the euphotic zone followed by the gravitational settling flux of organic carbon. Approximately, 5-15 GT yr⁻¹ of carbon is transported from the surface layer to the oceans interior (Henson *et al.*, 2011). The C: Si ratio of marine diatom approximately 10 (Brzezinski, 1985). This value is contrasts with that of bearing plankton (Ca: C ratios near 1, Fagerbakke *et al.*, 1994). Therefore, diatoms may be an important careers of carbon.

Although the vertical transport carbon requests the presence of "ballast", it has not been clear what acts as a "ballast" in the case of the carbon in diatoms.

1.3 Terrigenous matter

Terrigenous elements have been frequently reported in diatom rich sediment and settling particles. Terrigenous elements are considered not to be in diatom frustules, but to be in concomitant clay.

It is important to separate terrigenous elements of diatom frustules from those of clay by physical and chemical separation. However, this would face great difficulty. Shemesh *et al.*, 1998 applied meticulous procedures including physical separation, cleanings and chemical separation to isolate diatom frustules from clay. They evaluated the results of the separation by monitoring Ge/Si ratios of the separates and concluded that they could not remove Ge even after the meticulous separation.

Akagi *et al.*, 2011 considered the chemical abundances of diatom frustules from an entirely different approach and reached the conclusion that diatom frustules contain silicates other than opal at concentrations as high as 10%. The sediment trap samples are from two stations (AB and SA) in the north and south of Aleutian Islands (Takahashi *et al.*, 2000). The concentrations of REEs and Al are plotted against opal flux, which is roughly a measure of diatom productivity. The concentrations of all REEs and Al exhibit hyperbolic relationships with opal flux, and become constant when the opal flux is greater than 200 mg /m²/day. (Fig. 1a, Akagi *et al.*, 2011).

This relationship seems to pose an enigmatic question. If the terrigenous elements are contamination from clay, the contaminant needs to be supplied proportionally to the diatom productivity. When diatom productivity is infinite, the contamination needs to be infinite. From the relationship, the dissolution kinetics of the diatom aggregated frustules has been worked out by Akagi et al. (2011).

 When sizes of the diatomaceous aggregates are greater, the surface areas of the aggregates per unit mass of diatom frustules (in contact with water) are smaller, and also the settling velocities of the aggregates to travel through a water column are greater according to Stokes' law,

2. Due to the lower solubility of tetravalent Ce than that of other trivalent REEs, only Ce tends to remain undissolved in the aggregates. This explains the development of positive Ce anomalies in samples of lower diatom productivities (Fig. 1b).

Akagi *et al.* (2011) suggested the "asymptotic method", where the asymptotic values may correspond to the composition of diatom frustules, which have merely been exposed to dissolution. In Akagi *et al.* (2011) the "tentative" REE composition of diatom frustules estimated based on the "asymptotic method" is compared to that of terrigenous matter. The tentative REE composition of diatom frustules cannot be explained simply by the contamination by terrigenous materials. In addition, if the REEs of diatom frustules with the "tentative" REE composition are dissolved in deep sea and are scavenged by carbonate, the amount of scavenged REEs was shown to have a constant distribution pattern over those dissolved in sea water at any sampling depths, which is similar to the partitioning pattern of acetic acid-soluble phase against those dissolved in seawater. It was concluded that the carbonate phase of particles scavenges dissolved REEs in water columns to produce differences in the vertical profile of REEs.

The whole discussion seems to strongly support the "asymptotic method"

If dissolved REEs in the deep water are the ultimate source of REEs of diatom frustules and if they are incorporated to the frustules together with Si, it is immediately clear that the amount of REEs dissolved is insufficient relatively to that of Si. For example, the ratio of Nd/Si in diatom frustules are greater than that dissolved in the deep water by a factor of 2.

As one of evidences for diatoms' intake of REEs, Akagi (2013) developed the "leftover theory". This theory was built-up assuming that the only REEs in the form of silicic acid complexes are incorporated by diatoms, and that REEs in other forms are left unincorporated in surface water. By this theory, one can calculate how much of REEs dissolved in deep water are incorporated by diatoms when they are diffused/advected to. Focusing on Nd in REEs, if the REE composition of diatom frustules obtained by "asymptotic method" is correct, amount of Nd taken in by diatoms in the surface layer is not enough to explain the REE composition of diatom frustules. The existence of unknown sources (terrigenous particles) has been indicated.

Here I performed

- Verification of the "asymptotic method"
- Analysis of the sources of terrigenous matter in Bering Sea and discussed
- Elemental circulation in ocean

by measuring Nd and Fe isotope ratios of sediment trap samples collected near the Aleutian Islands.

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Fig. 1.1 An example of the hyperbolic relationship observed for Al concentration (a) and REE pattern (Ce anomaly) (b) of siliceous fraction of settling particles with opal flux. Open circles show the data from the Bering Sea (Station AB) and closed circles from the Northern Pacific (Station SA).

<u>Chapter 2. The fate of organic carbon derived from diatoms and carbonate shelled plankton</u> 2.1 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 decomposed to inorganic carbon mainly by bacteria or deposited on the seafloor [de la Rocha, 2003]. So far CaCO₃ is believed to act as a ballast to weight down organic matter in the water column. However, the origin of the organic matter transported downwards in a water column with CaCO₃ acting as a ballast is not clear. It has been shown that diatom frustules in highly-diatom-productive areas tend to aggregate to form greater-sized particles and consequently suppress both the decomposition of organic carbon [Iversen and Ploug, 2010] and dissolution of biogenic opal [Akagi *et al.*, 2011]. To discuss the fate of diatom-derived organic matter in settling particles, settling particles collected in extremely diatom-productive areas is considered the best material. In this study the samples of settling particles were collected from extremely diatom-productive Bering Sea and less, but still very productive North Pacific Ocean.

2.2 Material and Methods

The samples of settling particles were collected from two distinctly different subarctic environments using sediment traps, which was 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. 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: 3188m 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 in port immediately after the trip. The swimmers were further removed by sieving through a 1000 - μ m mesh net. A subset of the samples were subjected to routine analysis for opal, calcium carbonate, and organic carbon contents [Takahashi *et al.*, 2000]. The conversion from organic carbon contents to organic matter contents was performed following Takahashi *et al.* (2000).

I defined organic carbon in labile carbon and refractory carbon according to the vulnerability to rather mild oxidation. The reason for the classification is to separately consider hydrocarbon fixed by phytoplankton and long-lived organic compounds 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 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 realize 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 CO₂ was analyzed for δ^{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 μ g of recovered sample was encapsulated in an Ag cup. The amount of carbon was determined by an elemental analyzer.

2.3 Results and Discussion

2.3.1 Labile and refractory carbon

The amounts of labile and refractory carbon are shown in Table 2.1. The amount of refractory carbon was close to that contained in the Ag cups used to hold sample 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.

2.3.2 Carbon isotope ration of labile carbon

The δ^{13} C values of labile carbon ranged from -24.9 ‰ (AB-20#20) to -19.7 ‰ (AB-20#2) (Table 2.1). No significant correlation of δ^{13} C values with the flux of opal (r=0.39, p>0.2), organic carbon (r=0.42, p>0.2) or CaCO₃ (r=-0.25, p>0.4) was observed; only opal/CaCO₃ ratio (W_{op}/W_{CaCO3}) correlates with the δ^{13} C values (r=0.81, p<0.003) (Fig. 2.1). Opal is mainly represented by diatoms, and CaCO₃ is represented by plankton with CaCO₃ shells (mostly

coccolithophores and foraminifera). Using the equations to describe the isotope fractionation of diatom organic carbon [Burkhardt *et al.*, 1999] and coccolithophore organic carbon [Rost *et al.*, 2002] against dissolved inorganic carbon (DIC) in seawater, and adapting δ^{13} C of DIC in the North Pacific Ocean [Ortiz *et al.*, 2000] to the equations, I have estimated the δ^{13} C value of organic carbon in diatoms and coccolithophores for the Bering Sea. I obtained δ^{13} C values of -19.0 ± 3.5 ‰ and -25.5 ± 2.6 ‰ to represent organic carbon of diatoms and coccolithophores, respectively. Fig. 2.1 indicates that the carbon isotope ratio of the organic matter in the settling particles is consistent with a mixing of the two end members of diatom-derived organic matter and CaCO₃-shelled plankton-derived organic matter.

2.3.3 Decomposition ratio of organic matter

Since the contribution of refractory matter is negligibly small (Table 2.1), the data on the labile carbon was used exclusively to discuss the mineralization of planktonic organic carbon. The percentage of organic matter that was decomposed/detached during vertical settlement of diatoms and CaCO₃ shelled plankton was estimated by fitting. The CaCO₃-shelled plankton consisted mainly of coccolithophores and foraminifera, and approximately similar amounts of the both are observed in settling particles [Takahashi *et al.*, 2002]. Neglecting the compositional difference between coccolithophores and foraminifera, ¹³C value and concentration of organic carbon are expressed as

$$\delta^{13}C = \frac{f_{op-org}D_{op-org}W_{op}\delta^{13}C_{op-org}+f_{caCO3-org}D_{caCO3-org}W_{caCO3}\delta^{13}C_{caCO3-org}}{f_{op-org}D_{op-org}W_{op}+f_{caCO3-org}D_{caCO3-org}W_{caCO3}}$$
(1)

and

$$C_{org} = \frac{f_{op-org} D_{op-org} W_{op} + f_{caCO3-org} D_{caCO3-org} W_{caCO3}}{W_{op+W_{caCO3}} + f_{op-org} D_{op-org} W_{op} + f_{caCO3-org} D_{caCO3-org} W_{caCO3}}$$
(2)

respectively. In the equations W_{opal} and W_{CaCO3} represent the observed weight of opal and CaCO₃ shell; f_{op-org} and $f_{CaCO3-org}$ are the weight of organic matter in the fresh diatoms and CaCO₃-shelled plankton per unit weights of opal and CaCO₃; f_{op-org} and $f_{CaCO3-org}$ are set to 4.5 and 0.3 [Paasche, 1998; Brzezinski, 1985]; D_{op-org} and $D_{CaCO3-org}$ are the decomposition/detached ratios of organic matter in diatoms and CaCO₃-shelled plankton, respectively. The *f* values may be variable. Even ±30% variation would not affect following discussion and they are treated as fixed values. I first adapted $\delta^{13}C_{op-org} = -19$ ‰ and $\delta^{13}C_{CaCO3-org} = -25$ ‰. Adapting various D_{op-org} and $D_{CaCO3-org}$ values, I fitted the observed carbon isotope ratio (Fig. 2.1). A fairy good fit was obtained when D_{op-org} : $D_{CaCO3-org} = 0.005$: 1 (see Fig. 2.1a), except for one data of Station SA. However, this set of parameters failed to explain the carbon component data (Fig. 2.1b). The good fit to both the equations, which is indicated in gray lines in Fig. 2.2a and b, was achieved only with varying D_{op-org} depending on W_{op}/W_{CaCO3} ratios, although fitting to the component data in the low W/W_{CaCO3} ratio and $\delta^{13}C_{op-org}$ and $\delta^{13}C_{CaCO3-org}$ are set to -20 ‰ and -25.5 ‰, respectively. The new set of $\delta^{13}C$ values is slightly different from the first set.

The δ^{13} C values of the end members were tuned to fit the observed data better in the higher W_{op}/W_{CaCO3} region at increased D_{op-org} values for a variable D_{op-org} condition.

The poorer fitting to the component data in the lower W_{op}/W_{CaCO3} region may be due to contribution from other plankton. 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. 2.2c), even in the case of a high D_{op-org} value ($D_{op-org} = 0.016$). With a low D_{op-org} value ($D_{op-org} = 0.005$), a $D_{CaCO3-org}$ value greater than 1 would give the best fitting (Fig. 2.2b). Most of the organic carbon from carbonate-shelled plankton is concluded to remain undecomposed. 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. 2.2d). The slope of the rain-ratio increment approaches a value as high as 0.02 with a higher W_{op}/W_{CaCO3} ratio (Fig. 2.2d). In other words more than 98% of organic carbon from diatoms must have been decomposed/detached. 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 decomposed fraction (the decrease of D_{op-org} value) at the lower W_{op}/W_{CaCO3} region implies that the aggregation may take a longer time before forming large-enough particles being short of glue.

2.3.4 Implications for biological pump

The contrasting fate of the organic matter originating from two different planktonic phases renders the analysis of the carbon transport through a water column with a normal productivity much simpler, as it can be concluded that organic carbon in particles is from any plankton other than diatoms. The present discoveries provide some new insights into the biological pump.

1. $CaCO_3$ has been identified to act as a ballast to weight down settling particles [Klaas and Archer, 2002; Armstrong *et al.*, 2002]. This study indicates the organic matter transported downwards with CaCO₃ acting as ballasts is more or less the carbon produced by CaCO₃-shelled plankton.

2. The rain ratio is reported to range between 0.5 and 1 in the most oceans [Klaas and Archer, 2002;

Armstrong *et al.*, 2002]. A rain ratio higher than 1 is achieved only when the diatom contribution is great. This may be limited to extremely diatom-productive areas such as Bering Sea, Southern Ocean and North Pacific Ocean.

3) In average oceans with normal diatom productivity ($W_{op}/W_{CaCO3} < 10$), the role of diatoms in the biological pump is to sequester CO₂ from the surface water to the deep water.

A carbon content as low as 0.5% in opal-rich sediment has been observed in the Southern Ocean [Demaster *et al.*, 1991]. The present study indicates that the typical carbon content is 3% (organic matter content is 7%) for opal-rich settling particles. 98% of organic matter produced by diatoms has been decomposed/detached during settlement and 2% of the organic carbon that survived ante-depositional decomposition are further decomposed by post-depositional diagenesis.

When opal is low, the contribution of fecal pellets and plankton other than coccolithophores and foraminifera (e.g. radiolarians, microflagellates and ciliates) to organic matter contents of settling particles may not be negligible. This may cause the rather scattered data in the region of lower W_{op}/W_{CaCO3} ratio. In a more average sea, where diatom production and opal to CaCO₃ ratio are much smaller than the studied seas, the analysis should be impossible due to the scattering of data in this region. The fate of the organic matter in plankton would not have been understood unless extremely opal-rich areas were not studied.

2.4 References

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Table 2.1 The flux of total mass, opal, organic matter, $CaCO_3$, inorganic carbon, others of sedimnt trap samples (Takahashi *et al.*, 2000), and the amount of non-refractory and refractory carbon and the carbon isotope ratio of non-refractory carbon.

Sample No.	Total mass	Opal	Organic Matter	CaCO ₃	Inorganic carbon	Others	Opal/Inorganic carbon	Labile Camount [*]	Refractory C amount ^b	Labile 8 ¹³ C
	mg m ⁻² d ⁻¹	cinton	%	%	‰					
SA-20 #1	131.6	82.1	9.6	21.3	2.6	18.7	31.6	3.1	- °	-21.25
AB-20 #2	591.9	438.9	34.1	8.0	1.0	110.9	438.9	1.7	- °	-19.69
AB-20 #3	383.8	284.0	23.4	5.0	0.6	71.4	473.3	1.9	e	-20.61
AB-20 #5	943.9	703.0	44.3	58.7	7.0	34.3	100.4	1.8	0.2	-22.58
AB-20 #7	145.3	108.8	9.8	4.5	0.5	137.9	217.6	2.1	< 0.03	-21.87
AB-20 #9	416.0	291.6	30.9	29.7	3.6	37.0	81.0	2.9	< 0.03	-22.41
AB-20 #11	200.8	126.1	15.1	30.1	3.6	22.2	35.0	2.9	0.4	-22.98
AB-20 #13	471.4	294.3	27.8	65.4	7.8	32.8	37.7	2.7	< 0.03	-24.02
AB-20 #15	48.6	25.2	3.8	4.3	0.5	63.8	50.4	2.6	< 0.03	-23.37
AB-20 #17	101.7	45.1	7.0	14.0	1.7	82.5	26.5	2.7	0.2	-23.85
AB-20 #20	18.4	10.5	1.6	2.8	0.3	29.5	35.0	2.8	< 0.03	-24.85

a, b: amounts relative to total mass

c: not measured



Fig. 2.1 Fitting of the observed δ^{13} C values (a) and organic matter content (b) against the weight ratio of opal frustules and carbonate tests. Fitting curves are drawn using a fixed decomposition ratio of organic matter in fresh diatoms ($D_{op-org} = 0.005$). Note that fitting is poor for the organic matter content. Closed circles: Station AB, Open circles: Station SA.



Fig. 2.2 Fitting of the observed $\delta^{13}C$ values (a) and organic matter content (b) against the weight

ratio of opal frustules and carbonate tests using several decomposition ratios. Decomposition ratio of organic matter in fresh carbonate-shelled plankton is fixed at 1 ($D_{CaCO3-org} = 1$). Fitting of the observed organic matter content (c) adopting varying $D_{CaCO3-org}$ values with a constant D_{op-org} value of 0.016. Organic carbon and inorganic carbon ratio ("rain ratio") against the weight ratio of opal frustules and carbonate tests (d). The grey lines in (a) and (b) indicate the typical loci of data, when decomposition ratio of diatomaceous organic matter is dependent on W_{op}/W_{CaCO3} ratio. Closed circles: Station AB, Open circles: Station SA.

Chapter 3. Diatoms spread a high ENd-signature in the North Pacific Ocean

3.1 Introduction

The dissolved neodymium in the North Pacific Ocean has ε_{Nd} values as high as 0, whereas those in the North Atlantic Ocean are as low as -14 (Lacan *et al.*, 2012). The strong influence of island arc matter in the Pacific Ocean and that of old continent matter in the Atlantic Ocean have been suggested (Goldstein and Hemming, 2003; Jones *et al.*, 2008; Lacan *et al.*, 2012). The good correlation of ε_{Nd} values of dissolved Nd against dissolved silica concentration in deep seawater was reported without substantial reasoning (Goldstein and Hemming, 2003). The flux of Nd from rivers and aerosols is too low to account for the distribution of Nd isotope values in the ocean and a 'missing source' of Nd along the continental margins has been inferred (Tachikawa *et al.*, 2003; Jones *et al.*, 2008). The dissolution of neodymium from the seafloor around the continents has been focused on as a candidate of missing sources seriously in recent model studies (Arsouze *et al.*, 2009; Rempfer *et al.*, 2011).

Recently diatom opal has been identified as a major carrier of rare earth elements (REEs) in seawater columns in the North Pacific Ocean (Akagi *et al.*, 2011).

The surface concentrations of dissolved REEs, expressed as "leftover", in any oceans have been well explained by the diatom-incorporation theory (Akagi, 2013). Briefly, in this theory, a surface-to-deep concentration ratio is smaller in the Pacific Ocean than in the Atlantic Ocean, because the portion of REEs complexed with silicic acids is greater in the silica-rich Pacific Ocean, and thus more effectively incorporated in diatom frustules together with dissolved silica. This theory also derives the equation of distribution coefficients of REEs in diatom opal to predict the REEs concentration in diatom opal in any ocean. The surface-to-deep concentration ratio explained by the theory implies that diatom frustules should be the dominant vertical carrier of REEs in all oceans except the Arctic Ocean, where no/small vertical gradient in the REE profiles is seen, resulting from the absence of dissolved silica throughout the water columns. The study also implied the presence of unknown input of REEs to diatom frustules to satisfy the steady state condition, indicating the presence of unknown sources of REEs in surface water (Akagi, 2013). The conclusion of model studies (Arsouze *et al.*, 2009; Rempfer *et al.*, 2011) is challenged by the idea of input in surface water by Akagi (2013) and Nd isotope dynamics of diatom silica frustules needs to be assessed.

The elemental composition of diatom frustules is poorly known. In the marine science community, the role of diatom silica frustules in trace element transport has been neglected, with diatom opal regarded as pure hydrated silica. The recent study (Akagi, 2013) has discovered that the diatoms take in not only dissolved silicate but also silicate REE complexes and that diatom silica frustules contains REEs at a concentration high enough to explain the concentration increase along water columns of any oceans. Substantially high concentrations of dissolved silicate in any oceans render the silicate complex one of the most dominant dissolved species in seawater (Akagi, 2013). This automatically implies that many other silicate-complex-forming metals such as aluminum and other high field strength elements can also be incorporated to diatom frustules. Akagi, (2013) concluded that as much as 0.1% Al can be contained in diatom frustules.

This implicitly leads to the view that the conventional chemical treatment for diatom opal separation using sodium carbonate solution may fail to reveal the true chemistry of diatom frustules, since most of the high field elements and their silica complexes may not be soluble in a weak alkaline sodium carbonate solution. (The complex formation constant is not pH dependent, because it is a water eliminating reaction.) One has to apply HF solution for the elemental analysis of diatom frustules at the expense of analytical error since clay is analyzed as well. Opal has also been shown to be very easily altered by silica dissolution and adsorbing cations (Akagi *et al.*, 2011; Dixit *et al.*, 2001), even during settlement (Akagi *et al.*, 2011). To explain the true nature of diatom

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opal, an extremely opal-rich condition is essential, the rationale for which is: extremely high opal production induces the mega-aggregation of diatom frustules, which reduces the transport time across a seawater column and surface area of aggregated frustule particles to contact with water and thus protects the particles from dissolution and/or adsorption (Akagi *et al.*, 2011). A threshold value for the extremely productive condition is between 150 and 200 mg /m²/day based on kinetic considerations (Akagi *et al.*, 2011). In the Bering Sea, the concentration of dissolved silica is more than 200 µmol/kg and opal production rates as high as 1000 mg /m²/day have been reported (Takahashi *et al.*, 2000). Such high values have seldom been reported in the other oceans including the Southern Ocean and the North Pacific Ocean.

The condition of the extremely high opal productivity also reduces the risk of terrigenous contamination (Akagi *et al.*, 2011). In this study, the neodymium and strontium isotope ratios of extremely opal-rich settling particles collected from the Bering Sea have been studied, with the objective that the unknown sources and entrances of the high ε_{Nd} signatures of the North Pacific Ocean seawater can be identified.

3.2 Summary of research background

The composition of typical diatom frustules was determined based on the dissolution kinetics of diatom frustules (Akagi *et al.*, 2011). Briefly, the dissolution of opal is greatly governed by the aggregation of diatom frustules and its rate is roughly proportional to the reciprocal of the 2nd power of productivity. When the productivity is infinite, the dissolution rate of aggregates is zero. The concentration of elements of the aggregated frustules should possess an original (or unaltered) value when diatom productivity is infinite.

The measured elemental composition of the siliceous fractions always gives asymptotic values when plotted against opal flux. The original REE and Al composition was determined from

the asymptotic values (referred to "asymptotic composition"), which correspond to values at infinite diatom productivity (Akagi, 2013). The asymptotic composition shows an Al concentration as high as 0.1% and REE concentration much lower than the crustal values with an heavy rare earth element (HREE) enrichment relative to shale (1/30 at light rare earth element (LREE) to 1/12 at HREE). The asymptotic composition is concluded to be the initial composition of diatom frustules for several reasons as listed below (Akagi, 2013; Akagi *et al*, 2013).

1. If the asymptotic composition represents terrigenous attachment to relatively pure opal, the amount of attached terrigenous matter should be in proportion to that of opal up to infinite diatom productivity. The asymptotic composition is, however, very distinct from that of terrigenous matter. Some sediment in the Pacific Ocean is known to show a slight HREE enrichment against shale (e.g. Nakai *et al.*, 1993; Asahara *et al.*, 2012). As mentioned later I interpret this not as a terrigenous signature, but as an influence of HREE-enriched diatom silicate frustules, with further concentration through opal dissolution (Akagi *et al.*, 2011), on sediment.

2. The field emission scanning electron microprobe (FE-SEM) images of several diatom frustules exhibited a rather dispersed distribution of Al (Akagi *et al.*, 2013).

3. When diatom frustules with the asymptotic composition dissolve in deep water, they release REEs as well as silica. The vertical profile of dissolved silica is almost exclusively a reflection of the dissolution of diatom frustules. Dissolution of diatom frustules with the asymptotic composition would release sufficient REEs to explain the observed concentration increase in deep water. The oversupplied REEs defined by leftover theory (Akagi., 2013) maintain an almost identical partitioning pattern against the observed concentration of seawater, which is similar to that ubiquitously seen between the acetic acid-soluble fraction of particles and seawater.

Oversupplied REEs = (REEs/Si) of the asymptotic composition x "Si – "REEs, (1)

where " Si and "REEs indicates the difference in the concentration of dissolved Si and

REEs, respectively, between deep water and surface water.

4. A box model adopting the asymptotic composition as diatom frustule composition gives a reasonable residence time of each REE in the water column, which is close to that obtained by independent methods (Akagi *et al.*, 2013).

5. The asymptotic composition corrected for Al, assuming Al is from terrigenous matter, seriously spoils the discussion of reasons 3 and 4.

There is no chemical procedure to separate the biogenic Al from terrigenous Al. One spectroscopic study using X-ray absorption spectroscopy reports that biogenic Al in diatom frustules has a coordination number of 4 and 6, whereas aluminosilicate has 6 only (Becks *et al.*, 2002). The Al/Si in the diatom frustules in their study (0.00007-0.008) is similar to that of our study (0.0042 \pm 0.0014).

Dissolution of diatom frustules with the asymptotic composition over-supplies all REEs, compared with that observed in deep water (see reason #3 above). The over-supplied REEs are removed from deep water by being scavenged by the carbonate/oxide phase of particles. The scavenged REEs have a specific abundance pattern, which shows enrichment in MREEs and depletion in LREEs and HREEs, relative to shale (the lower REE abundance pattern in Fig. 3.4; Akagi, 2013). The steady-state consideration anticipates that the amount of the scavenged REEs is supplied from a new source. In the case of Nd, the amount of the over-supply corresponds approximately to half the Nd in diatom frustules; half the Nd in diatom frustules should be supplied in the surface water to keep the steady-state. This discussion requests the presence of unknown input of REEs in the surface seawater.

3.3 Sample and methods

3.3.1 Settling-particle sampling

Sediment traps were deployed in two distinctly different subarctic environments: Station SA, centrally located at a subarctic pelagic 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) (Fig. 3.1). A PARFLUX-type sediment trap with 21 sample cups was tethered 600 m above the seafloor from Jun 2008 to Jun 2009 at Station SA (deployment depth: 4806 m) and from Jun 2008 to Jun 2009 at Station AB (deployment depth: 4806 m) and from Jun 2008 to Jun 2009 at Station AB (deployment depth: 3188 m) (Takahashi *et al.*, 2000). Station AB is characterized by a highly siliceous water column and sediments. In contrast, the water of Station SA is less productive. The trap samples were fixed in situ with 5% formaldehyde buffered to pH 7.6–8.0 with sodium borate. Apparent swimmers were removed by hand-picking under a microscope when the original samples were split in port immediately after the trip. The swimmers were further removed by sieving through a 1000 -µm mesh net.

3.3.2 Leaching procedure for HA, HC and HF fractions

Settling particles were chemically separated into three fractions: acetic-acid soluble (HA), acetic-acid insoluble but hydrochloric acid soluble (HC), and hydrochloric acid insoluble but hydrofluoric acid soluble (HF). The leaching procedures are basically the same as those employed in the earlier study (Akagi *et al.* 2011). The reason why the HC fraction was taken between the two treatments in this study is to remove anything but siliceous matter in HF fraction. A 16th aliquot of the sieved sediment trap suspension was centrifuged at 103 Gs for 10 min. The supernatant was removed and the residue was again centrifuged with 15 ml of ethanol for 10 min. The supernatant was recovered with centrifugation to collect HA fraction. The procedure was repeated twice with 2 ml of distilled water to remove HA and the water was combined to the HA fraction. The residue is further treated with 10 ml of 0.1 M HCl at 60 °C for 20 min in a water bath to collect the HC

fraction. Again the residue was washed with water twice similarly to the HA fraction and the water was combined to the HC fraction. The residue was transferred to a PTFE beaker, decomposed with a mixture of 6 M HNO₃ (1 ml), 40% HF (1 ml), and 60% HClO₄ (0.5 ml) to collect HF fraction. All fractions were evaporated to dryness, dissolved with 6 M HNO₃, and diluted with Milli-Q water to 10 ml of 0.1 M HNO₃ solution for further procedure of column separation for isotope measurement after the REE measurement with ICP-MS (Refer to Akagi *et al.*, 2011 for the detailed information).

3.3.3 Sr and Nd isotope ratio measurement

Detailed descriptions of the isotopic analysis are provided in Asahara *et al.* (2012). Briefly, strontium and Nd were extracted from the three fractions using ion exchange methods as follows. Each fraction was evaporated to dryness and was dissolved in 2.4 M HCl. Strontium and REEs were first extracted from the sample in the 2.4 M HCl using a cation exchange column (BioRad AG50W-X8, 200–400 mesh) with hydrochloric acid (2.4 M and 6M HCl) as eluent. Neodymium was then isolated from the extracted REE fraction using another cation exchange column (BioRad AG50W-X8, 200–400 mesh) with α -hydroxy isobutyric acid (α -HIBA) eluent (Asahara *et al.*, 2012).

Additionally, barium was eliminated from the isolated Nd fraction using a cation exchange column with 2 M HNO₃ and 6 M HCl as eluent. This procedure is important to intensify Nd ion beams especially when the amount of Nd in samples is small. The Sr and Nd fractions were dried, redissolved in a drop of concentrated HNO₃ to be converted to a nitrate form, and dried again.

The Sr and Nd isotope ratios (⁸⁷Sr/⁸⁶Sr and 143Nd/144Nd) were measured using magnetic sector-type thermal ionization mass spectrometers, VG Sector 54-30 and GVI IsoProbe-T at Nagoya University, respectively. One microlitter of 2 M H₃PO₄ was loaded on a Ta single filament

prior to the Sr loading. The Sr fraction was dissolved with pure H₂O, and approximately 100 ng of it was loaded on the filament. The ⁸⁸Sr ion beam intensity was adjusted to 1 V (=1×10–11 A). ⁸⁷Sr/⁸⁶Sr ratios were normalized to ⁸⁶Sr/⁸⁸Sr= 0.1194. Half microliter of 2 M H₃PO₄ was loaded on a side filament in a Re triple-filament assembly prior to the Nd loading. The Nd fraction was dissolved with pure H₂O, and approximately 10 to 50 ng of it was loaded on the filament. The ¹⁴⁴Nd ion beam intensity was adjusted to 0.05–0.5 V (=0.5–5×10–12 A). ¹⁴³Nd/¹⁴⁴Nd ratios were normalized to ¹⁴⁶Nd/¹⁴⁴Nd=0.7219. The value of repeated analysis of NBS987 standard during this study was 0.710241±0.000021 (2 σ , n=8) [reference value: 0.71025 (Faure, 2001)] and that of JNdi-1 were 0.512115±0.000012 (2 σ , n=9, ¹⁴⁴Nd=0.5 V), 0.512117±0.000025 (2 σ , n=6, ¹⁴⁴Nd=0.25 V), 0.512098±0.000043 (2 σ , n=9, ¹⁴⁴Nd =0.1 V) and 0.512123±0.000053 (2 σ , n=4, ¹⁴⁴Nd=0.05 V) [reference value: 0.512115±0.00007 (Tanaka *et al.*, 2000)]. The data were not corrected to the values of the standards. Procedural blanks of Sr and Nd were 0.2–2 ng and 0.01– 0.1 ng, respectively. They are considered to be negligible amounts for blank correction.

3.4 Results and Discussion

3.4.1 Neodymium and strontium isotopic ratios of the HA, HC, and HF fractions

The results reveal differences in ε_{Nd} values between the HA and HF fractions: the highest ε_{Nd} values occur in the HF fractions and lowest values in the HA fractions (Table 3.1, Fig. 3.2). The ε_{Nd} values of the HF fractions are higher than any reported values of seawater and those of the HA fractions are similar to or higher than those reported for dissolved neodymium in the North Pacific Ocean (-10< ε_{Nd} <0; average $\varepsilon_{Nd} = -3.9$) (Lacan *et al.*, 2012). The HC fractions show ε_{Nd} values slightly lower than those of the HF fractions. It is likely that the HC fraction contains a portion of Nd from clay and that of the residual HA fraction. The values of the HF fractions converge to about one in ε_{Nd} unit when opal flux (Takahashi *et al.*, 2012) increases (Fig. 3.2).

The Sr isotope of the HF fraction is also different from that of the HC and HA fractions which show the typical seawater value [0.70918±0.00001 (Faure and Mensing, 2005)] (Table 3.1, Fig. 3.3). This shows the necessity of the treatment for HC fraction to avoid the cross-over of the HA fraction onto the HF fraction. In the case of the two SA samples the differences in ε_{Nd} values among the three fractions are small. It is due to the greater contribution of a low ε_{Nd} source in their HF fractions, which would be loess as discussed later.

3.4.2 ε_{Nd} values of seawater and diatom opal

The ε_{Nd} value of the HA fraction is likely to be representative of that of dissolved Nd in seawater, since labile Nd in particles readily exchanges dissolved Nd in seawater (Tachikawa *et al.*, 1997) and the ε_{Nd} value of seawater is considered to be -2.2, averaging all HA data of Station AB. The HF fraction for opal flux higher than 200 mg/m²/day is likely to be representative of diatom opal (see "Chapter 3.2"). The rare earth composition of the five HF fractions for opal flux > 200 mg/m²/day (data not shown) was identical to that reported for unaltered diatom frustules, and close to that predicted by the diatom-incorporation theory (Akagi, 2013). I present ε_{Nd} values ranging from 0 to 2 as the values of fresh diatom opal in the Bering Sea and from the convergence the most typical value is considered to be 0.7, averaging the three data with opal flux > 400 mg/m²/day. In the Nd-Sr isotope diagram the typical diatom opal value can be explained by mixing of island arc (Kelemen *et al.*, 2003), Chinese loess (Jahn *et al.*, 2001), and seawater sources (Fig. 3.3), whereas the data for low opal flux tended to scatter (Fig. 3.2), reflecting the contamination of opal with island arc (for AB20 #14) and loess matter (for SA20 #3 and #5).

3.4.3 Budget of Nd in diatom opal and a water column

As mentioned in Chapter 3.2, simple dissolution of diatom opal and the steady-state consideration confine the inputs of Nd in the diatom frustules: half Nd from the deep water and half from an unknown supply in surface water. Also the scavenged REE component with a

specific REE composition with MREE enrichment relatively to shale (see Fig. 3.4) should somehow be supplied.

Assuming $\varepsilon_{Nd} = -2.2$ of the HA fractions as seawater value and typical opal value $\varepsilon_{Nd} = 0.7$, this requires newly input Nd to have $\varepsilon_{Nd} = 3.6 [2x (\varepsilon_{Nd} \text{ of opal}) - (\varepsilon_{Nd} \text{ of seawater})]$. The ε_{Nd} value of the new input is prescribed by approximately 3:1 mix of Nd from the Aleutian andesite+ basalt (Kelemen *et al.*, 2003) and Nd from Chinese loess (Ding *et al.*, 2001; Jahn *et al.*, 2001). This blend reproduces a surprisingly similar REE composition to that scavenged in the water column with difference being less than 20% except for Ce with anomalous tetra-valence in an aqueous system (Table 3.2, Fig. 3.4). This line of discussion implies that the diatoms may rather unselectively incorporate REEs from the blend and changes them from a refractory silicate form to an easily dissolvable carbonate or oxide form in the studied stations (Fig. 3.4).

As mentioned earlier, the ε_{Nd} of the siliceous matter can also be explained in terms of contamination of opal with admixed terrigenous matter of island arc matter and loess. The former could shift the ε_{Nd} to higher values, and the latter to lower values. As mentioned earlier, we have no chemical method to separate the contamination from diatom opal. The reasons why the admixing of terrestrial material is refuted have been discussed in Akagi (2013) and Akagi *et al.* (2013) (see "Chapter 3.2"). Here another reason can be added to the discussion. A dissolution rate of silicate minerals in seawater is elusive and dissolution of aeolian dusts as well as island arc rock is not consistent with observed distribution of ε_{Nd} values of dissolved seawater (Siddall *et al.*, 2008; Oka *et al.*, 2009). Many studies conclude that the dissolution rate of silicate minerals in seawater columns is very small (Siddall *et al.*, 2008; Jones *et al.*, 1994; Greaves *et al.*, 1994). The idea of contamination of opal with the source rock fails to explain the actual dissolution of REEs from the rock, which manifests as ε_{Nd} signature of dissolved REEs in seawater, to form easily-soluble scavenged REEs, as illustrated in Fig. 3.4.

3.4.4 Incorporation of terrigenous minerals by diatoms

This study indicates that Nd in the Bering Sea water is supplied from terrigenous minerals indirectly by the action of diatoms. The encounter of silicate particles with diatoms is identified as the gateway of REEs into the ocean geochemical cycle. This indicates a greater supply of Nd to the Pacific Ocean water than to the Atlantic Ocean water, due to a higher concentration of dissolved silica in the Pacific Ocean than in the Atlantic Ocean. It is considered that greater contact of silica-rich upwelling water with island arc matter is one of the most important reasons for the high ϵ_{Nd} signature in the Pacific Ocean. In fact, most of the upwelling zones in the east Pacific Ocean are located along the island arcs (NOAA, 2013). One of the authors witnessed that clay-like substances floating over the surface for more than a few weeks. The diatom-mediated dissolution of aluminosilicates may give the reason for the hitherto-unexplained missing relationship between the proximity to the island arcs and ϵ_{Nd} values and likely relationship of ϵ_{Nd} of dissolved Nd and advective water (Goldstein and Hemming, 2003) and also present a new source in the oceanic REEs.

The question is "How diatoms may incorporate rare earth elements from terrigenous matter as well as from those dissolved in seawater?" Recently the hypothesis of incorporation of metal-silicic acid complexes through silica channels successfully explained the observed vertical profiles of dissolved REEs in any oceans (Akagi, 2013). This manner of incorporation may endow diatoms with an evolutional advantage to absorb linearly-arrayed silicate polymers at an expense of impure silica frustules or with an additional advantage of reduced solubility of opal. The incorporation of Al in opal may make the silica frustules much less soluble by forming kaolinite (Dixit *et al.*, 2001). However, rather direct incorporation of rare earth elements from terrigenous matter to diatom frustules is beyond our knowledge, although one can see an advantage to diatoms: to adsorb silica. An analogous situation exist on land, where plants have been reported to enhance

weathering rate of silicate minerals to absorb nutrients like dissolved silica or potassium (Akter and Akagi, 2006; Akagi *et al.*, 2012; Griffiths *et al.*, 1994), and probably a similar reason can be postulated to happen in diatoms. In the case of land plants this is operated with the aid of mycorrhizal symbiosis (Griffiths *et al.*, 1994), but nothing similar/compatible is known about diatoms. One possibility is the symbiosis of diatoms with specific bacteria that can increase dissolution of silicate minerals (Vandevivere *et al.*, 1994) in seawater.

3.4.5 New interpretation on previous model studies and observations

Although our studied area is located in a rather unique sea, there are two reasons that this new knowledge can be applied to other oceans.

1. Since the diatom-incorporation theory, which has been developed based on the data from the North Pacific Ocean, explains the surface and deep REE concentration levels of any oceans, diatom opal is now considered as the most important agent of transport an distribution of REEs in all ocean columns (Akagi, 2013).

2. According to the dissolution/alteration kinetics (Akagi *et al.*, 2011), very few areas in the Pacific Ocean may be productive enough to avoid the alteration of opal, implying that one can expect no further information on the fresh diatom opal from other areas.

Employing this reasoning, I compare the conclusions of this study with those by the model studies (Siddall *et al.*, 2008; Jones *et al.*, 2008; Oka *et al.*, 2009; Arsouze *et al.*, 2009; Rempfer *et al.*, 2011). The present study presents the diatom-mediated dissolution of silicate minerals as one of the most important sources of REEs in the oceans, which apparently conflicts with the conclusions from the model studies. Here it will be shown that these conclusions are actually quite compatible with the findings of our study.

First of all, the presence of extra-input itself, one of the model requirements, is consistent with this study. Earlier model studies with only classical REE sources such as river water and

airborne matter request the extra-input of Nd (Tachikawa *et al.*, 2003) especially in a ε_{Nd} high source (Jones *et al.*, 2008). The present study also leads to the diatom-mediated dissolution of silicate minerals in the surface water as an extra-input, which must be more important in the silica-rich Pacific Ocean with ε_{Nd} high values. "Reversible scavenging" and "recycling" are two of the most important keys in the model studies (Siddall *et al.*, 2008; Oka *et al.*, 2009).

"Reversible scavenging" was introduced for dissolved Nd to mirror the particulate ε_{Nd} signature as well as to attain the concentration increase in deeper seawater (Siddall *et al.*, 2008; Oka *et al.*, 2009). In reversible scavenging, the dissolved Nd is scavenged by particles in the surface and subsequently returns to a dissolved phase in the deep water according to the partitioning constant between seawater and particles, and is transported to the surface to be recycled. Our interpretation is: the dissolved Nd is incorporated by diatoms in the surface and a portion of Nd returns to a dissolved phase and the rest is scavenged by a carbonate/oxide phase (almost identical to "reversible scavenging"); the dissolved Nd is transported to the surface and is incorporated by diatoms together with dissolved silica (identical to "recycling").

Another key factor in the model studies is "boundary exchange" (Lacan and Jeandel, 2005), where dissolved Nd in seawater is exchanged with Nd of continental margin seafloor so as to acquire the ε_{Nd} signature of each ocean (Arsouse *et al.*, 2009; Rempfer *et al.*, 2011). I interpret this as follows. The upwelling zone is located in the continental margin (NOAA, 2013) and diatoms may grow most actively by being fuelled with an intensive supply of dissolved silica in the upwelling water deep. Diatoms also digest silicate particles in the continental margin, imprinting the ε_{Nd} signature of each ocean to their opal frustules. The consequent dissolution of opal resolution modifies the ε_{Nd} signature of the deep ocean water, while part of the dissolved Nd is scavenged by carbonate/oxide phases at the same time (Akagi, 2013) dampening the concentration increase. The model studies seem to have successfully identified three key mechanisms to reproduce the ε_{Nd}

values in the oceans, whatever true carrier of Nd is.

The model studies tried to explain the concentration mainly by flow of the water from the seafloor in the continental margin (Arsouse *et al.*, 2007, 2009; Rempfer *et al.*, 2011), while the new interpretation explains it by the dissolution of diatom opal. It should be noticed that any of the model studies requires introduction of a priori conditions explicitly or implicitly. Some models introduced boundary conditions such as Nd concentrations and ε_{Nd} values in surface water (Jones *et al.*, 2008; Siddall *et al.*, 2008) or ε_{Nd} values of water above the seafloor (Arsouse *et al.*, 2009; Rempfer *et al.*, 2011). One should be cautious about the introduction of an "a priori condition" to model studies. For example, Rempfer *et al.*, (2011) introduced an a priori condition of the Nd concentration of seawater above seafloor at varying depths in the continental margin. It is quite possible that the introduction of the "a priori" condition reproduces the concentration distribution even though the boundary exchange does not play an important role.

A piece of evidence against the diatom-mediated REE supply is that the ε Nd imprinted matter on the seafloor is not opal, but rather refractory aluminosilicate (Nakai *et al.*, 1993; Asahara *et al.*, 2012). Opal was recently discovered to alter to a more refractory phase by dissolution of silica and absorption of aluminum during settlement (Akagi *et al.*, 2011) as well as after deposit (Dixit *et al.*, 2001) and it is considered that the evidence is not against, but supportive to the diatom-mediated REE supply.

The diatom-mediated dissolution of silicate minerals naturally explains the observed relationship between ε_{Nd} of deep seawater and dissolved silica concentration (Goldstein and Hemming, 2003), since circum-Pacific matter with higher ε_{Nd} signature on the west and lower on the east is dissolved by silica-requiring diatoms. Strictly speaking, however, when only the data for the Pacific Ocean is considered, the relationship is unclear. In the Pacific Ocean the presence of two typical terrigenous sources with higher or lower ε_{Nd} values can be dissolved through the action

of diatoms, whereas in Atlantic Ocean only similar terrigenous sources with lower ε_{Nd} values are present.

Some recent observational studies promote Papua New Guinea as a typical area of boundary exchange of the high ε_{Nd} sources to the Central Pacific Ocean (Amakawa *et al.*, 2013; Grenier *et al.*, 2013). This may be correct, but the involvement of diatoms cannot be ruled out, considering the higher ε_{Nd} values near the surface and the depth of anomalous silica concentration. I am inclined to interpret this as follows: the surface flow in areas of complicated seafloor geography effectively activates vertical mixing as well as the supply of high ε_{Nd} local terrigenous matter, effectively augmenting the encounter of diatoms with the high ε_{Nd} matter. The high ε_{Nd} feature may appear most distinctively the low Nd concentration near surface and at opal dissolution depths.

3.5 Conclusion

 ε_{Nd} values higher than any values reported for the North Pacific seawater were discovered in the silicious fraction of settling particles. Based on its asymptotic values against the opal flux, a fresh opal values was determined to be $\varepsilon_{Nd} = 0.7$, which is higher than seawater values and indicates that diatoms are an important transporters of ε_{Nd} values of terrigenous silicate minerals, which contain island arc matter with high ε_{Nd} values in the Pacific Ocean. A steady-state consideration leads to the idea that diatoms incorporate silicate minerals in island arc rock and loess directly.

The conclusions by the two previous studies (Akagi *et al.*, 2013; Akagi 2013) (i.e., presence of extra input to account for half the Nd in diatom frustules in the Bering Sea) are compatible with those of this study, which provides a good isotopic agreement with the previous investigations. This study strongly supports the idea of diatom involvement in the oceanic REE

cycle and seems to request some reconsideration of the model studies (Siddall *et al.*, 2008; Jones *et al.*, 2008; Arsouze *et al.*, 2009; Rempfer *et al.*, 2011).

3.6 References

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	¹⁴³ Nd/ ¹⁴⁹ Nd ε _{Nd}	⁸⁷ Sr/ ⁸⁶ Sr	Opal flux
AB20 #1 HA	0.512511(58) -2.5(1.1)	0.709158(17)	858.7
HC	0.512647(21) 0.2(0.4)	0.709147(17)	
HF	0.512676(12) 0.7(0.2)	0.708044(13)	
AB20 #2 HA	0.512522(38) -2.3(0.7)	0.709164(14)	438.9
HC	0.512650(15) 0.2(0.3)	0.709145(16)	
HF	0.512682(8) 0.9(0.2)	0.707865(16)	
AB20 #5 HA	0.512551(40) -1.7(0.8)	0.709165(14)	703.0
HC	0.512631(26) -0.1(0.5)	0.709128(14)	
HF	0.512665(9) 0.5(0.2)	0.708239(16)	
AB20 #10 HA	0.512499(23) -2.7(0.4)	0.709139(16)	362.4
HC	0.512588(15) -1.0(0.3)	0.709172(16)	
HF	0.512622(7) -0.3(0.1)	0.708777(16)	
AB20 #13 HA	0.512528(15) -2.2(0.3)	0.709139(14)	294.3
HC	0.512671(21) 0.6(0.4)	0.709138(14)	
HF	0.512727(8) 1.7(0.2)	0.707841(16)	
AB20 #14 HA	0.512560(13) -1.5(0.3)	0.709157(17)	29.2
HC	0.512720(12) 1.6(0.24)	0.709119(14)	
HF	0.512796(8) 3.1(0.2)	0.707280(16)	
SA20 #3 HA	0.512528(30) -2.2(0.6)	0.709169(16)	28.8
HC	0.512557(16) -1.6(0.3)	0.709129(18)	
HF	0.512534(7) -2.0(0.1)	0.708582(17)	
SA20 #5 HA	0.512481(30) -3.1(0.6)	0.709160(14)	13.1
HC	0.512445(130)-3.8(2.5)	0.709143(16)	
	0 = 1 2 = 1 = (1 2) 2 = 1 (0 2)	0 200522/1/2	

Table 3.1 Neodymium and strontium isotope data of settling particles, along with opal flux data.

In parentheses precision is shown as 2 σ . # Unit: mg m $^{\text{-2}}$ day $^{\text{-1}}$

Table 3.2 Concentration of rare earth elements (μ g/g) and Nd isotope ratio for three possible sources, along with those for an input composite and the observed scavenged concentration.

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Но	Er	Tm	Yb	Lu	¹⁴³ Nd/ ¹⁴⁴ Nd	ϵ_{Nd}
Sources																
Basalt ^a	5.98	14.4	2.21	8.8	2.33	0.8	2.28	0.43	2.81	0.52	1.36	-	1.4	0.21	0.51303	7.6
Andesite ^b	16.0	37.3	-	20.2	3.95	1.12	3.61	0.43	3.06	-	1.77	1.00	1.32	0.19	0.51308	8.6
Loess ^c	35.7	71.4	8.21	31.0	6.39	1.32	5.9	0.87	5.17	1.06	3.06	0.45	3.0	0.44	0.51211	-10.3
Input ^d	0.88	1.95	-	1	0.203	0.055	0.188	-	0.168	- 3	0.096	5 -	0.081	0.012	0.51282	3.6
Scavenged ^e	0.748	2.94	-	1	0.24	0.054	0.201	-	0.186	<u>5</u> -	0.096	5 -	0.074	0.010		

a Aleutian basalt from Kelemen et al. (2003)

b Aleutian andesite from Kelemen et al. (2003)

c Chinese loess. Chinese Loess Plateau data (Ding et al., 2001) are cited for composition, because the loess from Chinese Loess Plateau were identified in the St. Elias Mountain (64°34'N), Canada, over the Bering Sea (Zdanowicz et al., 2006). Nd isotope data are cited from Jahn et al. (2001).

d A composite example to make ε_{Nd} =1 using the three sources (Nd concentration is normalized to 1). The example is prescribed by mixing them at the ratio of 0.1:0.9:0.36 in Nd basis.

e The difference of the amounts supplied by opal dissolution from that observed in deep water of the North Pacific Ocean (Akagi, 2013). Nd concentration is normalized to 1 for easy comparison with the input composition.

- Data are unavailable or values are not calculated due to missing data.



Fig. 3.1 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).



Fig. 3.2 ε_{Nd} values of HA, HC, HF fractions of settling particles collected from Bering Sea plotted against opal flux. Open marks are for Station AB. Closed marks for Station SA. Error bars represent $2\sigma_m$. Typical values for North Pacific seawater are average $\pm \sigma$ calculated from compiled data in Lacan *et al.* (2012).



Fig. 3.3 Nd isotope and Sr isotope diagram of HA, HC, HF fractions of settling particles collected from Bering Sea. Open marks are for Station AB. Closed marks for Station SA. The dotted curve represents the mixing between Aleutian rock (Kelemen *et al.*, 2003) and Chinese loess (Jahn *et al.*, 2001). The vertical line shows the seawater ⁸⁷Sr/⁸⁸Sr value [0.70918 (Faure and Mensing, 2005)]. Typical ε_{Nd} values for North Pacific seawater are average $\pm \sigma$ calculated from compiled data in Lacan *et al.* (2012). Note that errors of HF fractions are smaller than the size of marks.

Fig. 3.4 Schematic showing of Nd geochemical cycle to explain the ε_{Nd} of the typical diatom opal ($\varepsilon_{Nd} = 0.7$). Assuming the averaged ε_{Nd} value of the HA fractions ($\varepsilon_{Nd} = -2.2$) represent that of dissolved seawater, the ε_{Nd} value of extra input is estimated about 3.6. The REE composition of input was mixed from possible REE sources by adjusting the ε_{Nd} value of the mixture to 3.6 mixing (see Table 3.2). The output composition is the averaged difference data (REErecon-REEobs) from Akagi (2013). The shale-normalized pattern of input is almost identical to that of output, keeping the steady-state of the water column system. Normalizing values are from McLennan (1989). The vertical position of the input pattern was adjusted to compare with the output pattern.

<u>Chapter 4. Iron isotope ratio of diatom frustules estimated using aggregation-controlled</u> dissolution kinetics

4.1 Introduction

Iron isotope has been a promising tool to identify its source in the oceanic system (Conway and John, 2014; Fantle and DePaolo, 2004). Diatom frustules have been identified to be important carriers in seawater columns (Akagi, 2013 b; Akagi *et al.*, 2011). Neodymium isotopic study has revealed that diatoms incorporated REEs rather directly from silicate minerals (Akagi *et al.*, 2014). This novel path may explain the presence of Al of a 0.1% level in diatom frustules (Akagi *et al.*, 2013; Andersen *et al.*, 2011; Beck *et al.*, 2002) as well as enigmatic oceanic Nd isotope ratios, which is related silicic acid concentration (Goldstein and Hemming, 2003). The acquisition mechanism of metal elements by diatoms is unknown, but it is likely that the stability of silicic acid and metal complex may be one of the factors to control (Akagi, 2013a). Since Fe³⁺ has one of the highest stability constants of silicic acid complexation (Thakur *et al.*, 2007), iron is likely incorporated into the diatom frustules and diatoms are likely to exert an important influence on iron circulation within water columns.

However, the determination of foreign metals in diatom frustules is tricky business, as the possibility of contamination of terrigenous matter having a high iron concentration has always resulted in ambiguity. Recent study using rare earth elements (REEs) has created one method to determine the foreign elements in diatom frustule (Akagi *et al.*, 2013; Akagi *et al.*, 2011). Briefly, when diatom productivity is high, diatom frustules form mega-aggregates, which settle down through a water column with a minimum contact with seawater medium due to a greater settling rate as well as a smaller relative surface area per mass of the aggregates (Akagi, 2013; Akagi *et al.*, 2011). The compositions of aggregates tend to remain unaltered when diatom productivity is extremely higher. When the composition of siliceous fraction of setting particles is plotted against

the opal flux, it always forms a hyperbolic relationship with a non-zero asymptotic value. The asymptotic values are defined as the composition of diatom frustules. The REE composition thus obtained has led to the innovation of oceanic REE circulation (Akagi, 2013a; Akagi *et al.*, 2014). Nd isotopic composition of diatom frustules was determined by applying this method, where ε_{Nd} values of siliceous fractions are plotted against opal flux data (Akagi *et al.*, 2014).

Here I have used the same protocol to determine the iron isotopic values of diatom frustules using sediment trap samples collected in the Bering Sea, one of the most productive areas with respect to diatom production.

4.2 Method

4.2.1 Settling-particle sampling

Sediment traps were deployed in two distinctly different subarctic environments: Station SA, centrally located at a subarctic pelagic 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) (Fig. 4.1). A PARFLUX-type sediment trap with 13 sample cups was tethered 600 m above the seafloor from August 10, 2008 to July 17, 1996 at Station SA and from August 7, 2009 to June 27, 1996 at Station AB (Takahashi *et al.*, 2002). Station AB is characterized by a highly siliceous water column and sediments. In contrast, the water of Station SA is less productive. The trap samples were fixed in situ with 5% formaldehyde buffered to pH 7.6–8.0 with sodium borate. Apparent swimmers were removed by hand-picking under a microscope when the original samples were split in port immediately after the trip. The swimmers were further removed by sieving through a 1000-µm mesh net.

4.2.2 Leaching procedure for HA, HC and HF fractions

Settling particles were chemically separated into three fractions: acetic-acid soluble (HA),

acetic-acid insoluble but hydrochloric acid soluble (HC), and hydrochloric acid insoluble but hydrofluoric acid soluble (HF). The leaching procedures are basically the same as those employed in the earlier study (Akagi *et al.*, 2011; Akagi *et al.*, 2014). A 16th aliquot of the sieved sediment trap suspension was centrifuged at 10^3 Gs for 10 min. The supernatant was removed and the residue was again centrifuged with 15 ml of ethanol for 10 min. The supernatant was removed and the residue was treated with 40% acetic acid for 10 min and the solution was recovered with centrifugation to collect HA fraction. The procedure was repeated twice with 2 ml of water to remove HA and the water is combined to the HA fraction. The residue is further treated with 10 ml of 0.1 M HCl at 60°C for 20 min in a water bath to collect the HC fraction. Again the residue was washed with water twice similarly to the HA fraction and the water was combined to the HC fraction. The residue was transferred to a PTFE beaker, decomposed with a mixture of 6 M HNO₃ (1 ml), 40% HF (1 ml), and 60% HClO₄ (0.5 ml) to collect HF fraction.

All fractions were evaporated to dryness, dissolved with 6 M HNO₃, and diluted with Milli-Q water to 10 ml of 0.1 M HNO₃ solution for further procedure of column separation for isotope measurement.

4.2.3 Iron isotope ratio measurement

The three fractions were dried and then dissolved in 8 M HCl. Iron was extracted with an anion exchange method (BioRad AG1-X8 200-400mesh, 1ml). Prior to the sample loading, the resin was cleaned by 0.4M HCl, 1M HNO₃ and ultrapure water and conditioned with 2ml of 8M HCl. After sample loading with 1ml of 8M HCl, 5ml of 8M HCl and 5ml of 3M HCl were passed through the resin to elute the matrix elements. Iron was eluted with 4ml of 0.4M HCl. The Fe fraction was dried and dissolved in 1% HNO₃.

The Fe isotope ratio (⁵⁶Fe/⁵⁴Fe) was measured with a multi-collector inductively coupled plasma mass spectrometer (MC-ICPMS, Thermo Neptune Plus) at the Research Institute for

Humanity and Nature (Japan). The δ^{56} Fe values were calculated relative to the average of IRMM-14 measurements bracketing each sample. Samples were generally introduced into the plasma torch using a quartz spray chamber equipped with Teflon nebulizer (50 or 100 µl/min) and the sampling cone was 10 cone. Under these conditions, the sample solutions of 0.5 to 3 ppm in 1% HNO₃ were introduced to measure iron isotopes.

4.3 Results and discussion

4.3.1 Difference in δ^{56} Fe values among the three fractions

The δ^{56} Fe values of the three fractions separated from settling particles are summarized in Table 1. The δ^{56} Fe values are lower in the order of HA (from -0.7 to -0.5‰), HC (from -0.7 to -0.2‰) and HF fractions (from -0.2 to 0.1‰). Fe in the HC fraction may represent Fe in an oxide form, but should include Fe dissolved from the siliceous matter. I took the HC as the analytical crossover of the HA and HF fractions and did not discuss the data further. It is reported that the δ^{56} Fe values of scavenged Fe is higher than those of dissolved Fe (Fantle and DePaolo, 2004). This indicates that δ^{56} Fe values of dissolved Fe in seawater is lower than -0.7%. It is likely that the Fe supplied from reductive sediments contribute to the dissolved Fe(Conway and John, 2014; Fantle and DePaolo, 2004).

4.3.2 δ^{56} Fe values of diatom frustules

The δ^{56} Fe values of siliceous fractions (HF fractions) are plotted against opal flux in Fig. 4.2 Although only one data of the HF fraction is for a condition of an extremely higher opal flux (>200 mg /m²/day), similarly to the Nd values, the values tend to scatter at lower opal flux and to converge at higher opal flux. From this relationship, I concluded that the δ^{56} Fe values of diatom frustules are approximately 0%. This value is practically identical to those of terrigenous matter

(Fantle and DePaolo, 2004).

According to the budget of Nd in the diatom frustules, a half of Nd in diatom frustules is from seawater and the other half from that in silicate minerals (Akagi *et al.*, 2014). This statement corresponds to the estimation that less than 1/500 of Fe in diatom frustules is from seawater and that the majority is from silicate minerals, based on the Fe/Si ratio of seawater(Nozaki, 1997) and that of terrigenous matter. This explains the reason that Fe in diatom frustules is isotopically identical to that in silicate matter.

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		δ ⁵⁶ Fe			Opal flux mg /m²/ day
	Sampling time 2008-2009	HA	HC	HF	
AB20 #1	20-27 Jun	-0.54(0.02)	-0.43(0.02)	-0.04(0.05)	858.7
AB20 #4	17-27 Jul	-0.66(0.01)	-0.62(0.06)	-0.04(0.02)	133.9
AB20 #8	2-12 Sep	-0.74(0.01)	-0.34(0.08)	-0.08(0.01)	145.2
AB20 #12	22 Oct – 9 Nov	-0.71(0.04)	-0.69(0.05)	-0.16(0.13)	119.5
AB20 #18	8-28 Apr	-0.54 (0.01)	-0.48(0.01)	0.04(0.10)	16.6
SA20 #1	20-27 Jun	-0.48(0.02)	-0.39(0.03)	0.08(0.01)	82.1
SA20 #4	17-27 Jul	-0.47(0.02)	-0.40(0.02)	-0.05(0.03)	90.1
SA20 #18	8-28 Apr	-0.54(0.09)	-0.18(0.04)	0.05(0.03)	<16

Table 4.1 Iron isotope data of settling particles, along with opal flux.

In parentheses precision is shown as 2σ .



Fig. 4.1 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).



Fig. 4.2 δ^{56} Fe values of HF fractions of settling particles collected from Bering Sea plotted against opal flux. Closed marks are for Station AB. Open marks for Station SA. Error bars represent $2\sigma_m$.

Chapter 5. General Conclusion

• Carbon

In normal oceans nearly 100% of diatom-derived organic matter is dissolved/decomposed during settling through water columns. The inorganic carbon fixed by the diatoms is eventually segregated as carbonate ions in the deep sea.

• Nd

A half the amount of Nd in diatom frustules is estimated to be derived from that dissolved in the deep water (Akagi 2013) and, the rest from that terrigenous particles supplied to the surface water of the Bering Sea.

The terrigenous particles is considered to be a 3:1 mixture of loess particles and Aleutian Islands material on the basis of Nd based on the Nd isotope ratio studied in this study.

In addition, the REEs incorporated from the terrigenous particles to diatom frustules at surface ocean are scavenged by carbonate particles in deep water forming a steady state with respect to the budget of REEs. This further implies that less-soluble (or refractory) REEs in silicate minerals are transformed to soluble (or labile) REEs in carbonate by physiological action of diatoms.

• Fe

The amount of Fe in diatom frustules is 400 times as great as the ratio of Fe/Si dissolved in deep water. This can be explained consistently by the diatom incorporation of elements in terrigenous particles. Only by employing the "asymptotic method", consistent discussion can be made. This conclusion indicates that diatom frustules are not pure opal, but contain some terrigenous elements including REEs and validates the "asymptotic method"

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Terrigenous elements include many elements other than Nd and Fe studied here and this study implies that diatoms are involved in the oceanic cycles of many elements. It is thus anticipated that study of diatomaceous involvement in the oceanic element cycles will provide a breakthrough in the marine chemistry of elements.