Diatoms spread a high ε_{Nd}-signature in the North Pacific Ocean

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The Nd and Sr isotopes of the acetic-acid-soluble, hydrochloric-acid-soluble, hydrofluoric-acid-soluble (siliceous) fractions of settling particles collected in the highly diatom productive Bering Sea were measured. The siliceous fraction exhibits ε_{Nd} values higher than that of the acetic acid extractable fraction or that dissolved in North Pacific seawater. Recent studies concluded that the siliceous fraction of settling particles collected in an area of extremely high diatom production consists almost exclusively of diatom frustules, that diatom frustules are a major Nd transporter in the ocean water column, and that half the Nd in diatom frustules should be supplied from an unknown input other than that diffused/advected from the deep seawater. The Nd isotope system of the siliceous fraction provides the first evidence that diatoms transport the high ε_{Nd} signature to the oceanic system. The unknown input is the dissolution of silicate rocks which are somehow supplied to the sea surface. In the Bering Sea one of the sources of the high ε_{Nd} values was identified to be island arcs. This diatom-mediated dissolution of silicate particles may be a mechanism to explain the rather pervasive island arc Nd isotope signature in the Pacific Ocean where there are surrounding island arcs.

Keywords: diatom silica frustules, neodymium isotope, seawater, island arc, loess

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 frustules have 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 frustules 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) and Akagi *et al.* (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 hydrofluoric acid (HF) 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 silica frustules, 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 m^{-2}day^{-1} 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 m^{-2}day^{-1} 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.

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 HREE enrichment relative to shale (1/30 at 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 we 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 Eq. (1) maintain an almost identical partitioning pattern against the observed concentration of seawater, which is similar to that ubiq-

uitously seen between the acetic acid-soluble fraction of particles and seawater.

Oversupplied REEs
= (REEs/Si) of the *asymptotic composition* × ΔSi
 $- \Delta$REEs,   (1)

where ΔSi and ΔREEs 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 4 and 5 (Akagi *et al.*, 2013).

 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 (Beck *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 ± 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. 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.

SAMPLE AND METHODS

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. 1). A PARFLUX-type sediment trap with 13 sample cups was tethered 600 m above the seafloor from June 2008 to June 2009 at Station SA (deployment depth: 4806 m) and from
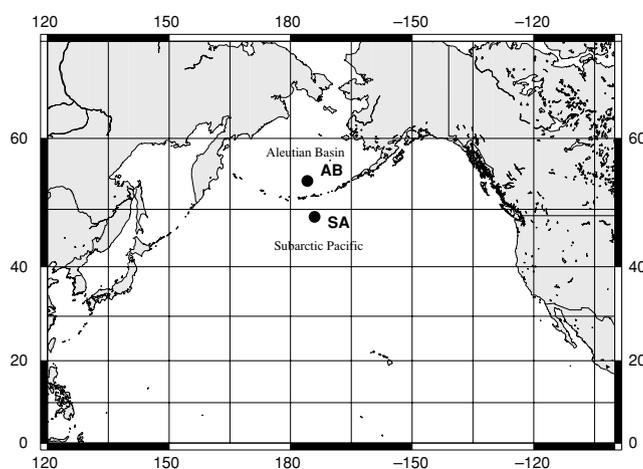

Fig. 1. Map showing the two sampling stations in the North Pacific Ocean: Station AB (53.5°N, 177°W) and Station SA (49°N, 174°W).

June 2008 to June 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.

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 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 was combined to the HA fraction. The residue is further treated with 10 ml of 0.1 M HCl for 20 min 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 trans-

Table 1. Neodymium and strontium isotope data of settling particles, along with opal flux data

		^{143}Nd/^{144}Nd	ε_{Nd}	^{87}Sr/^{88}Sr	Opal flux [mg m^{-2}day^{-1}]
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 ± 0.2	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 ± 0.2	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 ± 0.2	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	
	HF	0.512515 ± 12	–2.4 ± 0.2	0.708573 ± 16	

The errors in the final digits are $2\sigma_m$. The data are not corrected to the values of standards.

ferred to a PTFE beaker, decomposed with a mixture of 6 M HNO$_3$ (1 ml), 40% HF (1 ml), and 60% HClO$_4$ (0.5 ml) to collect HF fraction.

All fractions were evaporated to dryness, dissolved with 6 M HNO$_3$, and diluted with Milli-Q water to 10 ml of 0.1 M HNO$_3$ 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).

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 HNO$_3$ 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 HNO$_3$ to be converted to a nitrate form, and dried again.

The Sr and Nd isotope ratios (^{87}Sr/^{86}Sr and ^{143}Nd/^{144}Nd) 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 H$_3$PO$_4$ was loaded on a Ta single filament prior to the Sr loading. The Sr fraction was dissolved with H$_2$O, and approximately 100 ng of it was loaded on the filament. The ^{88}Sr ion beam intensity was adjusted to

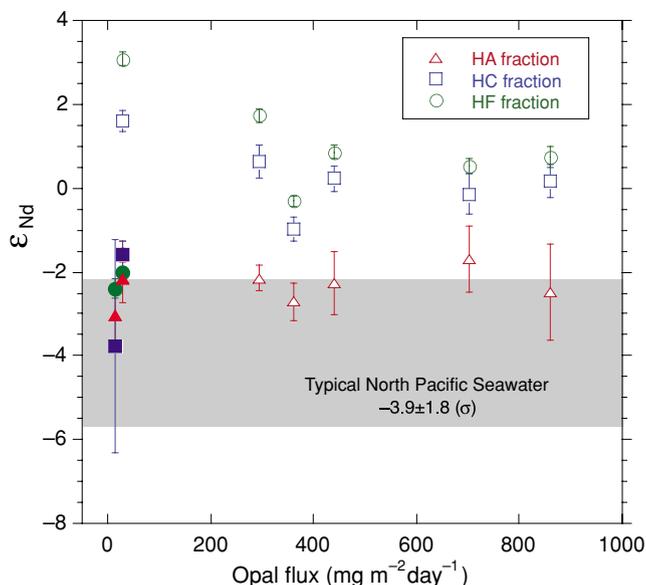Fig. 2. ε_{Nd} values of HA, HC, HF fractions of settling particles collected from Bering Sea plotted against opal flux. Open marks are for Station AB. Closed marks for Station SA. Error bars represent $2\sigma_m$. Typical values for North Pacific seawater are average $\pm \sigma$ calculated from compiled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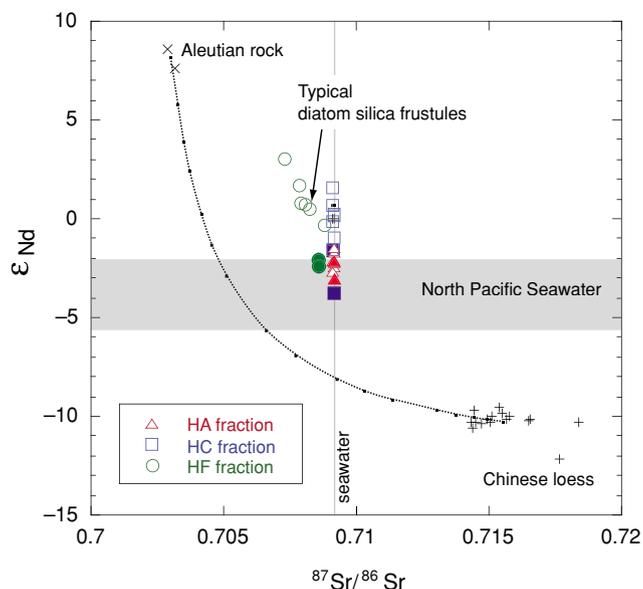

Fig. 3. Nd isotope and Sr isotope diagram of HA, HC, HF fractions of settling particles collected from Bering Sea. Open marks are for Station AB. Closed marks for Station SA. The dotted curve represents the mixing between Aleutian rock (Kelemen et al., 2003) and Chinese loess (Jahn et al., 2001). The vertical line shows the seawater $^{87}Sr/^{88}Sr$ 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.

1 V (=1 × 10⁻¹¹ A). $^{87}Sr/^{86}Sr$ ratios were normalized to $^{86}Sr/^{88}Sr = 0.1194$. Half microliter of 2 M H_3PO_4 was loaded on a side filament in a Re triple-filament assembly prior to the Nd loading. The Nd fraction was dissolved with H_2O, and approximately 10 to 50 ng of it was loaded on the filament. The ^{144}Nd ion beam intensity was adjusted to 0.05–0.5 V (=0.5–5 × 10⁻¹² A). $^{143}Nd/^{144}Nd$ ratios were normalized to $^{146}Nd/^{144}Nd = 0.7219$. The value of repeated analysis of NBS987 standard during this study was 0.710241 ± 0.000021 (2σ, n = 8) (reference value: 0.71025 (Faure, 2001)) and that of JNdi-1 were 0.512115 ± 0.000012 (2σ, n = 16, ^{144}Nd = 0.5 V), 0.512117 ± 0.000025 (2σ, n = 6, ^{144}Nd = 0.25 V), 0.512098 ± 0.000043 (2σ, n = 9, ^{144}Nd = 0.1 V) and 0.512123 ± 0.000053 (2σ, n = 4, ^{144}Nd = 0.05 V) (reference value: 0.512115 ± 0.000007 (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.

RESULTS AND DISCUSSION

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 1, Fig. 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 ($-10 < \varepsilon_{Nd} < 0$; 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 or 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. 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 1, Fig. 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.
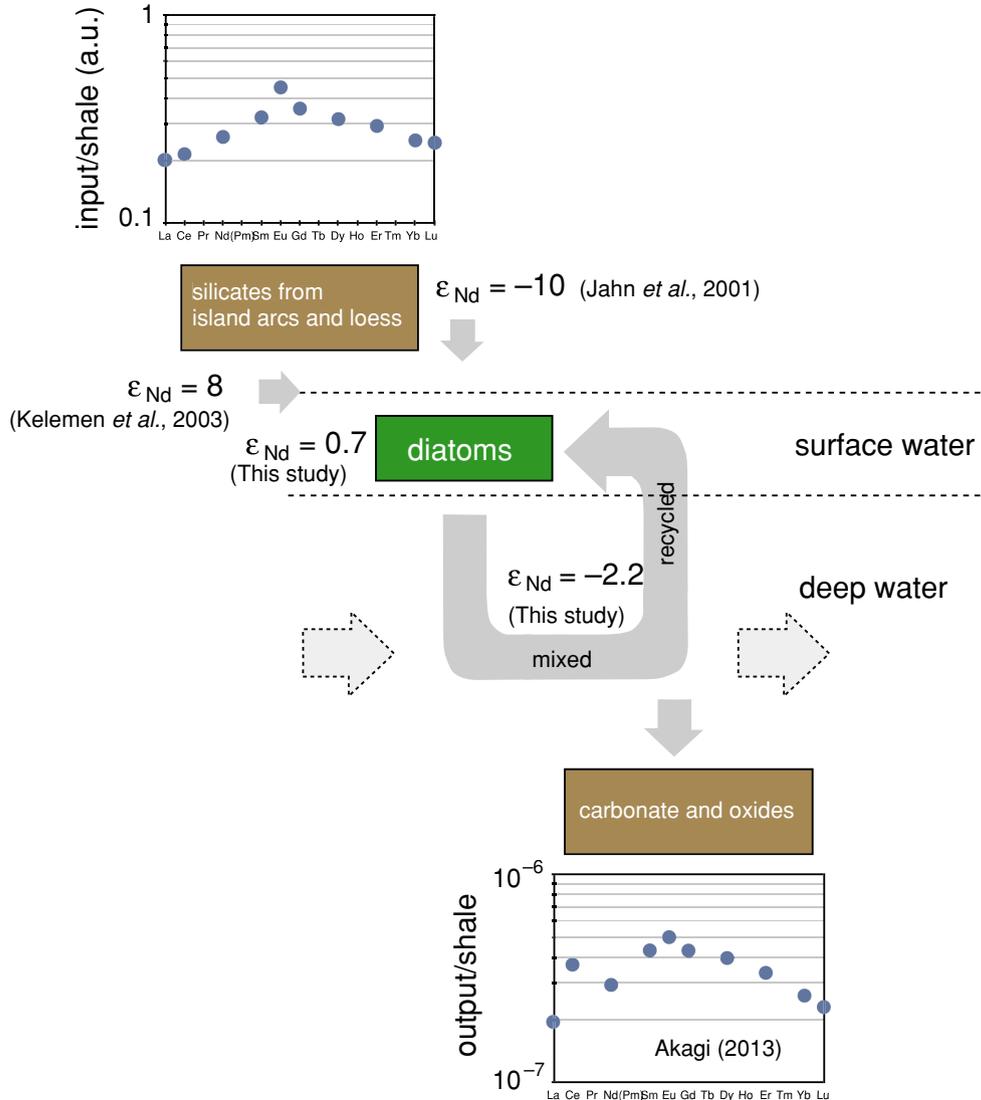
Fig. 4. Schematic showing of Nd geochemical cycle to explain the ε_{Nd} of the typical diatom frustules (ε_{Nd} = 0.7). Assuming the averaged ε_{Nd} value of the HA fractions (ε_{Nd} = –2.2) represent that of dissolved seawater, the ε_{Nd} value of extra input is estimated about 3.6. The REE composition of input was mixed from possible REE sources by adjusting the ε_{Nd} value of the mixture to 3.6 (see Table 2). The output composition is the averaged difference data (REE_{recon}–REE_{obs}) 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.

ε_{Nd} values of seawater and diatom silica frustules

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/m^2/day is likely to be representative of diatom frustules (see Section "Summary of Research Background"). The rare earth composition of the five HF fractions for opal flux >200 mg/m^2/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). We present ε_{Nd} values ranging from 0 to 2 as the values of fresh diatom frustules 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/m^2/day. In the Nd–Sr isotope diagram the typical diatom frustule value can be explained by mixing of island arc (Kelemen *et al.*, 2003), Chinese loess (Jahn *et al.*, 2001), and seawater sources (Fig. 3), whereas the data for low opal flux tended to scatter (Fig. 2), reflecting the

Table 2. Concentration of rare earth elements (μg/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	Ho	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	—	1.32	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	—	0.096	—	0.081	0.012	0.51282	3.6
Scavenged[e]	0.748	2.94	—	1	0.24	0.054	0.201	—	0.186	—	0.096	—	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} = 3.6 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 dissolution of diatom frustules 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.

contamination of frustules with island arc (for AB20 #14) and loess matter (for SA20 #3 and #5).

Budget of Nd in diatom frustules and a water column

As mentioned in Section "Summary of Research Background", 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. 4) should somehow be supplied.

Assuming ε_{Nd} = −2.2 of the HA fractions as seawater value and typical frustule value ε_{Nd} = 0.7, this requires newly input Nd to have ε_{Nd} = 3.6[2 × (ε_{Nd} of diatom frustules) − (ε_{Nd} 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 2, Fig. 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. 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 silica frustules. The reasons why the admixing of terrestrial material is refuted have been discussed in Akagi (2013) and Akagi *et al.* (2013) (see Section "Summary of Research Background"). 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. 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 (K.H.) 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 silica frustules. (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.

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 frustules is now considered as the most important agent of transport and 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 frustules from other areas.

Employing this reasoning, we 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). We 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 diatom frustules. The consequent dissolution of frustule 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 repro-

duce 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 frustules. 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 (Rempfer *et al.*, 2011). 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 terrigeous 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. We are 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.

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 diatom frustule 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, 2013; Akagi *et al.*, 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).

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