



# Diagenetic aluminum uptake into diatom frustules and the preservation of diatom-bound organic nitrogen

Haojia Ren <sup>a,\*</sup>, Brigitte G. Brunelle <sup>a</sup>, Daniel M. Sigman <sup>a</sup>, Rebecca S. Robinson <sup>b</sup>

<sup>a</sup> Department of Geosciences, Guyot Hall, Princeton University, Princeton, NJ 08544, United States

<sup>b</sup> Graduate School of Oceanography, University of Rhode Island, Narragansett, RI 02882, United States

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## ABSTRACT

The chemistry and isotopic composition of siliceous diatom frustules and the organic matter bound within them have been used to reconstruct past changes in the environment. However, the alteration of biogenic silica in the sediments and its influence on the chemical properties of the diatom opal and diatom-bound organic matter has not been broadly studied. We use inductively coupled plasma atomic emission spectrometry and energy dispersive X-ray analysis to investigate the concentrations of various cations, especially aluminum, in cleaned diatom frustules extracted from sediments at three sites from the Bering Sea, where the opal content in the sediments and preservation conditions vary both spatially and over the last glacial cycle. Relative to cultured diatoms, cleaned diatom frustules from the sediments are found to have a high Al/Si ratio, most likely by homogenous Al incorporation but possibly also by formation of an aluminosilicate coating of significant thickness relative to the diatom walls. Variations in the Al/Si ratio of the cleaned diatoms among samples are strongly correlated with the aluminosilicate to opal ratio of the bulk sediment, suggesting that sedimentary clays are the primary source of the aluminum taken up by the diatoms. The aluminum and nitrogen contents of the diatom frustules are negatively correlated, which is best explained by the loss of intrinsic N during the chemical changes associated with Al incorporation. The lack of a consistent relationship between nitrogen isotopic composition and the aluminum content of the cleaned opal suggests that the diagenetic organic N loss does not fractionate N isotopes, which is as expected given that this loss process relates to the geochemistry of the opal, not the organic matter. Our findings help to explain the previous observations that opal from clay-rich sediments (1) requires harsher chemical cleaning to remove diagenetic N and (2) has diatom-native N that is better protected from alteration by excessively harsh chemical cleaning. The diagenetic alteration of the opal may have led to partial protection of the external N from the surrounding sediments. At the same time, the diatom frustules have been chemically 'hardened' by the diagenesis associated with Al uptake, reducing the chemical accessibility of the diatom-native N that remains.

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## 1. Introduction

Diatoms are one of the most important groups of primary producers in the ocean (Nelson et al., 1995; Tréguer et al., 1995). The siliceous frustules of diatoms dominate marine sediments in the high latitudes, especially in the Antarctic and North Pacific. Organic matter associated with biomineralization is trapped within the diatom frustules, and upon burial, it acts as an important recorder for past climate and biogeochemical changes. The elemental and isotopic ratios of bulk organic carbon and nitrogen in diatom frustules have been used to reconstruct past productivity and nutrient utilization (Shemesh et al., 1993; Sigman et al., 1999; Rosenthal et al., 2000;

Crosta and Shemesh, 2002; Robinson et al., 2004, 2005; Brunelle et al., 2007; Robinson and Sigman, 2008), as well as to date marine sediments using radiocarbon in regions where calcium carbonate is scarce (Zheng et al., 2002; Ingalls et al., 2004; Hatte et al., 2008). The richness of its information is being actively explored (Ingalls et al., 2010), and this research is at the frontier of paleoceanographic studies.

It is generally believed that the organic matter within diatom frustules is native to the diatoms and protected from early bacterial diagenesis (King, 1977; Swift and Wheeler, 1992; Kröger et al., 2000; Ingalls et al., 2003, 2004; Poulsen et al., 2003). Much evidence supports the protected nature of the diatom-bound organic material. For example, sequential acid digestions of diatoms yield stable carbon isotopic composition of the organic material (Singer and Shemesh, 1995), and the amino acid composition of the bulk diatom-bound organic matter is similar between Last Glacial Maximum and Holocene (Shemesh et al., 1993).

\* Corresponding author at: Research Center for Environmental Changes, Academia Sinica, 128 Sec. 2, Academia Rd., Nankang, Taipei 115, Taiwan, ROC. Tel.: +886 2 2653 9885x278; fax: +886 2 2783 3584.

E-mail address: [abbyren@gate.sinica.edu.tw](mailto:abbyren@gate.sinica.edu.tw) (H. Ren).

However, the preservation and dissolution mechanisms for biogenic silica in the sediments are not completely understood, and changes in the preservation conditions could potentially affect the preservation of the intrinsic organic matter. On average, 50–60% of diatomaceous opal produced in the euphotic zone redissolves within the upper 100 m of the water column (Nelson et al., 1995; Tréguer et al., 1995; Nelson and Brzezinski, 1997), and dissolution continues as the opal sinks through the deep sea and is incorporated into the sediments (Hurd, 1973; Jahnke et al., 1982; McManus et al., 1995), ultimately resulting in a very small fraction of marine biogenic silica being buried, about 3% in the modern ocean (Nelson et al., 1995; Tréguer et al., 1995). The dissolution rate for biogenic silica in the sediments is at least an order of magnitude lower than in the surface ocean. This difference does not appear to be fully explicable in terms of the elevated silicate concentration in sediment, which often still leaves the pore waters undersaturated with respect to opal solubility (Dixit et al., 2001). The unexpectedly low dissolution rate in the sediments is attributed to changes in environmental conditions (e.g., temperature and pH) (Dove and Rimstidt, 1994; van Cappellen and Qiu, 1997a,b; Dixit et al., 2001), the reduction of reactive surface area associated with aging (Dixit et al., 2001; Dixit and van Cappellen, 2002; van Cappellen et al., 2002a,b), and most importantly, diagenetic reactions with detrital materials in the sediments (van Bennekom et al., 1988, 1991; Dixit et al., 2001; van Cappellen et al., 2002a,b). It has been suggested by both laboratory and field studies that structural incorporation of Al(III) released from detrital minerals reduces the solubility of biogenic silica (van Bennekom et al., 1988, 1991; Dixit et al., 2001; van Cappellen et al., 2002b). The solubility of diatom frustules is lowered by as much as 25% when one out of every 70 Si atoms is substituted by an Al(III) ion (Dixit et al., 2001). Precipitation of authigenic aluminosilicate minerals also gives a low apparent solubility and contributes to the observed low asymptotic silicic acid concentration (Dixit et al., 2001; van Cappellen et al., 2002a,b). These diagenetic processes enhance the preservation of biogenic silica in marine sediments but also alter the physical and chemical structure of the material. Thus, the roles of these processes in the preservation of the diatom-bound organic matter are not straightforward and deserve consideration.

Several recent studies on the nitrogen isotopic composition of diatom-bound organic matter suggest that the effectiveness and the efficiency of a given cleaning protocol depends on whether the opal derives from sediment rich or poor in aluminosilicates (Robinson et al., 2004; Brunelle et al., 2007). While weak chemical oxidation appears insufficient to remove all external organic matter from diatom frustules concentrated from clay-rich samples, strong chemical oxidation results in occasional isotopic fliers in opal-rich samples and are probably associated with breakdown of the biogenic silica during the treatment (Robinson et al., 2004; Brunelle et al., 2007). These problems associated with changes in the opal content in the sediments appear related to the diagenetic alteration of biogenic opal and also challenge the notion of unaltered diatom-bound organic matter. Other aspects of the cleaning techniques were also questioned. For example, Brewer et al. (2008) found that the chemical leaching and physical methods (e.g., sieving, density separation) used to treat sediments for silica oxygen isotope studies could not completely separate biogenic silica from the sediments. This would undermine the use of diatom-bound organic matter if the residual mineral phases contained significant amounts of organics (or clay-bound ammonium in the case of N studies).

In this study, we undertook simple analyses of the bulk chemistry of the biogenic opal fractions that we had extracted from sediments for diatom-bound N isotope analysis. Even from extremely low-opal, high-clay samples, we find that our standard physical separation protocol for sedimentary opal leaves only trivial amounts of aluminosilicate (i.e. clay) in the opal sample, so far as studies of organic matter are concerned. Nearly all of the aluminum in our opal samples derives

from the incorporation of diagenetic aluminum into the opal, which occurs in rough proportion to the aluminosilicate content of the sediments. Aluminum content appears to be inversely correlated with the diatom-bound nitrogen content, but without clear correlations with nitrogen isotopic composition. The loss of opal-bound organic nitrogen appears to result from diagenesis of the mineral material and associated exposure of once-protected diatom-native organic matter, such that this loss process does not cause significant isotopic change in the remaining diatom-protected N. The observations can also explain the different behaviors of oxidative cleaning protocols in opal extracted from clay-rich and -poor sediments. Finally, the evidence for diagenetic aluminum incorporation into biogenic opal, even in opal-rich samples, raises concerns for any chemical or isotopic analysis of the biogenic opal itself that is intended to reconstruct surface ocean conditions.

## 2. Materials and methods

### 2.1. Materials

One piston core, JPC17 (53.93°N, 178.70°E), and two multicores, MC50B (54.50°N, 172.40°W) and MC16 (53.93°N, 178.70°E), from the Bering Sea, were sampled for trace metal analysis (Fig. 1). JPC17 appears to extend back to the previous interglacial. Over the length of the record, opal content varies dramatically, from below 10% in the last glacial maximum to above 95% in the current interglacial (Brunelle et al., 2007). We selected 28 separated and cleaned diatom samples over the full length of the record in JPC17 to analyze the concentrations of a number of cations (aluminum, calcium, iron, magnesium, and manganese), and to compare with variations of opal content in the bulk sediments, as well as diatom-bound N content and isotopic composition (Brunelle et al., 2007). In addition, 5 samples from the top 16 cm at site MC50B, and 4 samples from the top 22 cm at site MC16 were selected to compare changes in trace metal contents prior to and after reductive cleaning, in order to examine its efficiency in removing metal oxide coatings and other mineral phases from the samples. The opal content is generally below 50% in MC50B, and above 50% in MC16.

### 2.2. Diatom cleaning

We performed a series of cleaning steps to isolate diatom frustules from the sediments and to remove external organic matter: 1) addition of acid to remove  $\text{CaCO}_3$  (Sigman et al., 1999), 2) physical separation of the diatom fractions from the bulk sediment by sieving and density separation with heavy liquid (Sigman et al., 1999), 3) reductive cleaning with dithionite–citric acid to remove metal oxide coatings (Robinson et al., 2005), and 4) oxidative cleaning with ~55% perchloric acid at 100 °C for 2 h (Brunelle et al., 2007). This last step, designed for removing external organic contaminants, is generally considered harsher than peroxide oxidation, but is milder than boiling perchloric acid oxidation (Robinson et al., 2004). As suggested by Brunelle et al. (2007), this treatment is able to remove all the labile contaminants, yielding reproducible results for the nitrogen isotopic composition, and yet it does not seem to attack the diatom frustule-internal organic matter.

### 2.3. Trace metal chemistry

Aluminum content was determined by the FEI XL30 FEG-SEM equipped with a PGT-IMIX PTS EDX system at the Imaging and Analysis Center at Princeton University. About 0.2 mg of each sample was mounted on the plates and coated with gold. Samples were first examined under a scanning electron microscope (SEM) for presence of clay minerals or other mineral phases, as well as signs of dissolution (Fig. 2). This high-resolution field-emission SEM has an optimum image resolution of 2 nm. Multiple spots on diatom frustules as well as smaller

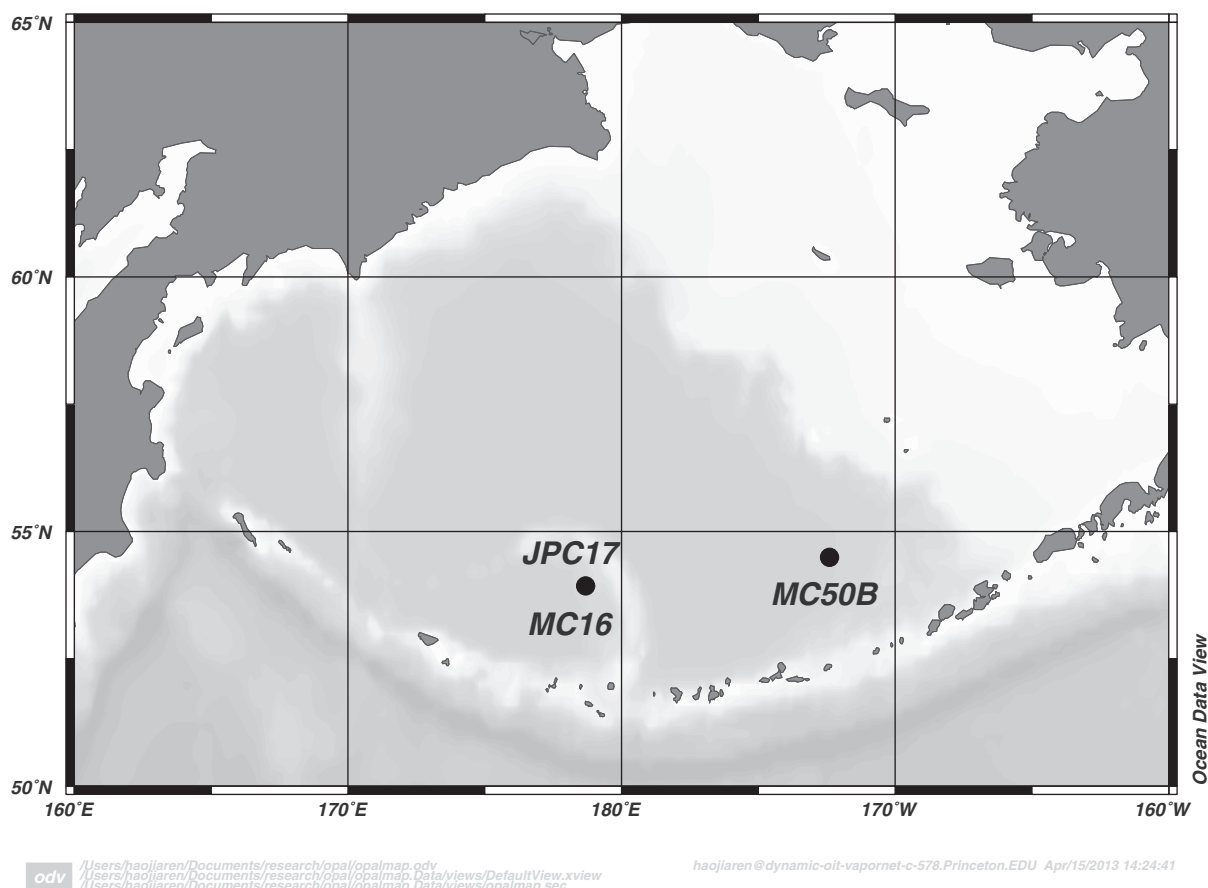


Fig. 1. Map showing locations of JPC17, MC16 and MC50B in the Bering Basin.

unidentified particles were analyzed for aluminum using energy-dispersive X-ray (EDX). The EDX system can provide X-ray acquisition to obtain a high-resolution two-dimensional elemental distribution map throughout the sample surface. 20 or more spots on different diatom specimens were randomly selected within each sample for analysis. A range of voltages and counting time were initially tested, and yielded no significant differences. Therefore, the subsequent measurements were made with a low voltage of 10 KeV, and for a counting time of 100 s. The relative standard deviations for EDX replicates were less than 5%, much smaller than the variation among the sampling sites within each sample. Measurements were made on cleaned samples from JPC17, as well as on samples from MC50B and MC16 prior to and after reductive cleaning.

Bulk elemental analyses were conducted on cleaned opal using inductively coupled plasma optical emission spectroscopy (ICP-OES),

and the results were compared with the averaged values from EDX. The ICP analyses were performed with an ICP 4300 optima DV in the Department of Geoscience at Princeton University. Opal was dissolved and evaporated with concentrated HF three times in a sandbath. The remaining solids were dissolved first in concentrated  $\text{H}_2\text{SO}_4$ , a good solvent for Al and Fe, then again in 1:1 HCl. The final products were brought into solution with ICP grade 2%  $\text{HNO}_3$ . Al, Ca, Mg, Fe and Mn were present in measurable quantities, but Mn concentration was generally one to two orders of magnitude lower than the other trace metals; thus, it is not reported here. For the reported data, precision is typically better than 1%. We report all elemental ratios in this paper as atomic ratios with a unit of mol/mol. While EDX directly gave atomic ratios, atomic ratios were calculated from the ICP results, assuming water content of 10% by weight in diatom opal so that silicon is 42% by weight of the opal sample.

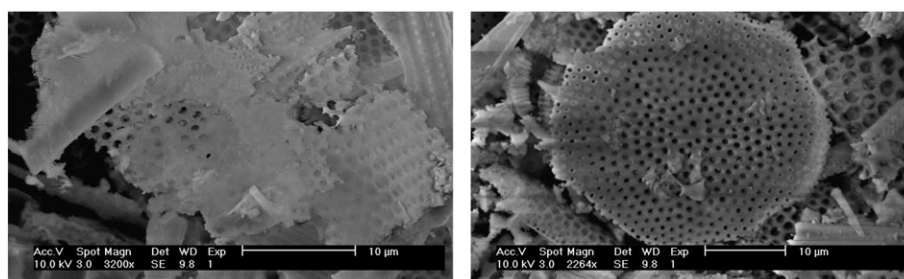


Fig. 2. Scanning electron microscopy images of cleaned diatom samples from JPC17. Both specimens are from core depth of 473 cm. The left panel appears to show precipitation of new mineral material on the surface as well as inside the pores of the diatom frustules. The image on the right shows frustule thinning, especially around the edge.

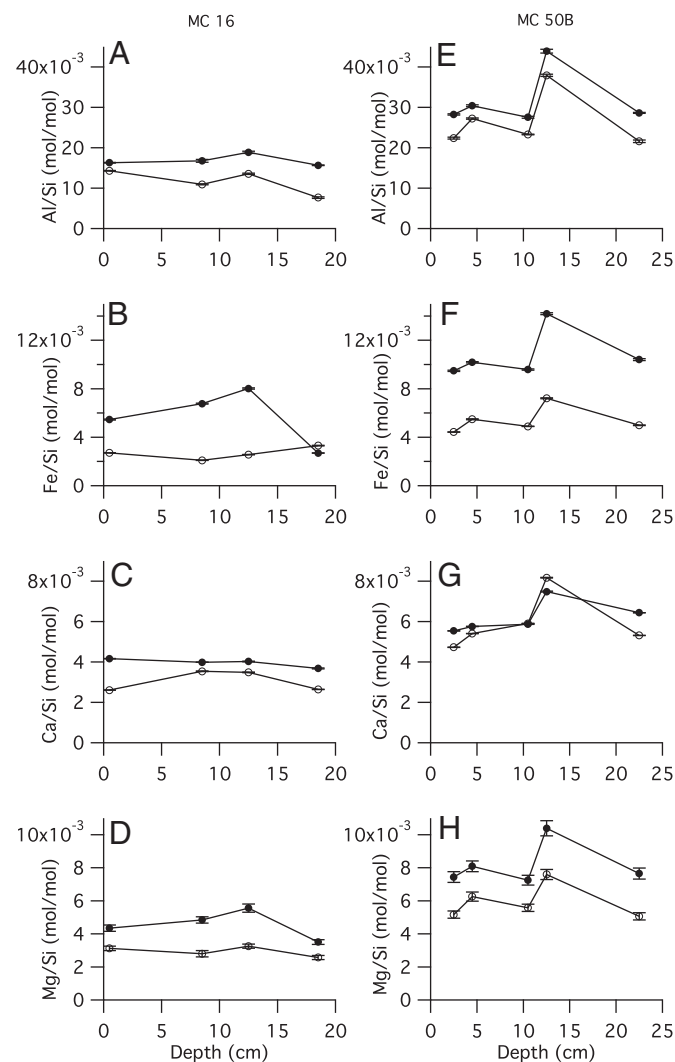
## 2.4. Opal content

Biogenic opal concentrations were determined using the method described by DeMaster (1981), adapted for use with an Astoria Analyzer colorimeter in the laboratory of Lars Hedin at Princeton University. Samples were leached with a 0.5 M NaOH solution at 85 °C, and aliquots taken every hour for 5 h. The leached silicate was reacted with molybdate in an acidic medium (hydrochloric acid) to form  $\beta$ -molybdosilicic acid, which was then reduced by tin(II) to form molybdenum blue. Precision was generally better than 4 wt.%.

## 3. Results and discussion

### 3.1. Association of trace metals with biogenic silica

Clay contaminants are not observed or detected with EDX, suggesting that the physical and chemical methods we applied to separate biogenic silica from the bulk sediments are efficient. The reductive cleaning removes cations from the samples at sites MC50B and MC16, but the remaining concentration of these cations is often a substantial fraction of their concentrations in the untreated samples (Fig. 3). In proportion to their initial concentrations, Fe decreases the most. This is expected, as the reductive cleaning was developed to



**Fig. 3.** Metal contents in diatom samples from MC16 (A–D) and MC50B (E–H), prior to (filled symbols) and after (open symbols) reductive cleaning. Error bars are estimated standard deviations from the replicates.

reduce oxidized metals such as Fe and Mn (Mehra and Jackson, 1958). However, the results suggest that a third of the Fe in the untreated samples and larger proportions of the Mg, Al, and Ca are associated with the diatom frustules in a more intrinsic way.

The analyses of metal contents in cleaned diatom samples from JPC17 show high aluminum to silica ratio, which are on average one order of magnitude greater than Ca, Mg and Fe. All of the measured trace metals exhibit the same patterns of variations as observed for Al among samples (Fig. 4A, B; including Mn, not shown). The Al/Si ratio measured with ICP range between 0.0034 and 0.0870, with an average value of 0.0289. Both the absolute values and the variations among samples were confirmed with EDX measurements (Fig. 4C, D). Because EDX measures the Al content of diatom frustules exclusively without the ambiguity of detrital clays, the similarity between the two again strongly suggests that the Al measured by ICP is incorporated into the biogenic silica.

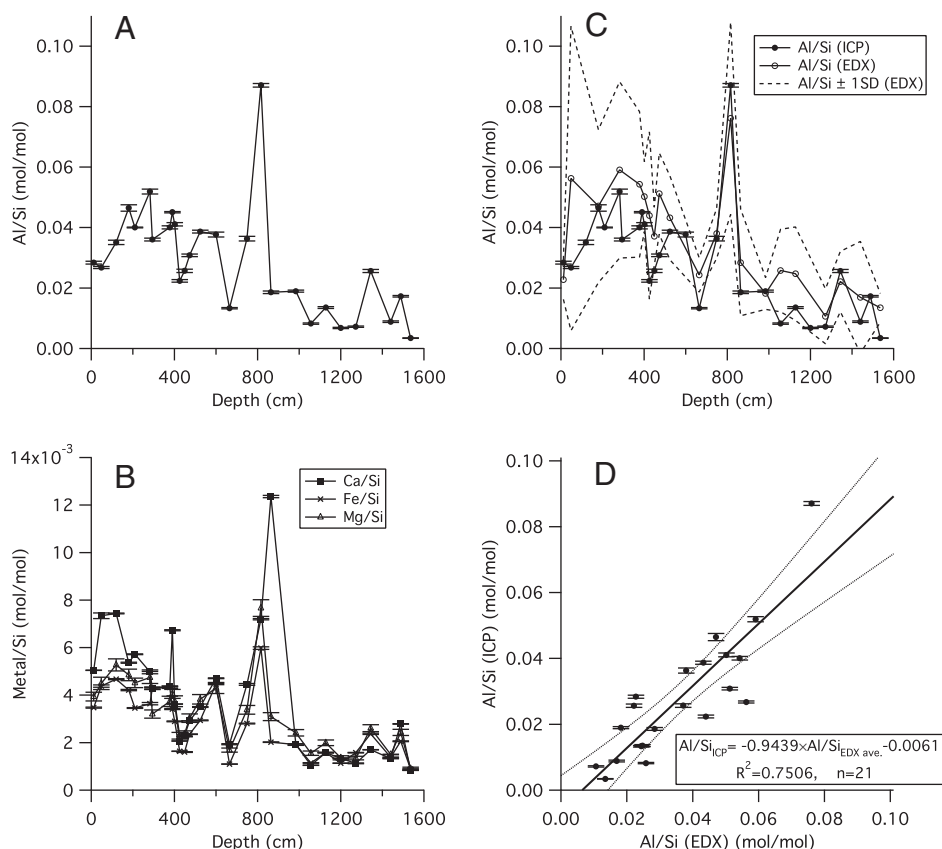
High aluminum content in diatom frustules has been reported previously in both the water column and deep sea sediments (Table 1). Diatom can take up aluminum during frustule biosynthesis, but this primary uptake yields an Al/Si ratio of up to  $10^{-4}$ – $10^{-3}$  for open ocean plankton assemblages (van Bennekom et al., 1991), at least one order of magnitude lower than that observed in deep sea sediments (Table 1). This may be explained by the low dissolved aluminum concentration in the open surface ocean relative to the sedimentary pore waters (van Beusekom et al., 1997) as well as the existence of an organic membrane that shields the siliceous frustules from the outer environment during growth and early diagenesis (Gehlen et al., 2002; Koning et al., 2007). Given the above, the high Al/Si ratio in diatom frustules extracted from deep sea sediments requires post mortem incorporation of Al. Field and laboratory studies have demonstrated that secondary uptake of aluminum occurs rapidly at the sediment–water interface and is quickly incorporated by either forming a new surface phase on the sample (aluminosilicate coating) or altering the existing mineral structure (structural incorporation) (van Cappellen and Qiu, 1997a; Dixit et al., 2001; Koning et al., 2007).

Our measured Al/Si ratio of the cleaned diatom frustules is similar to reported values for biogenic silica in the deep sea sediments (Table 1). Survival of the high aluminum content through our series of acidic, reductive, and oxidative treatments suggests that the diagenetically acquired aluminum is tightly bound into the diatom frustules. The combined ICP and EDX measurements do not provide a strong test for the type of association, that is, to differentiate aluminosilicate coating from structural incorporation. However, the similarity of the ICP and the average EDX-based measurements of Al/Si tend to argue for either pervasive Al incorporation or a coating of significant thickness relative to the diatom walls themselves.

### 3.2. Sources of aluminum

The Al/Si of the cleaned opal at all three sites is negatively correlated with the opal content in the bulk sediments, indicating positive correlation with the concentration of aluminosilicates, the dominant non-opal constituent (Fig. 5) (the carbonate content at JPC17 is generally below 5%, with slightly higher values during the last deglaciation (Brunelle et al., 2007)). Previous studies in the Southern Ocean have demonstrated that the dissolved aluminum to silicic acid ratio in the pore waters increases as the ratio between the aluminosilicates and biogenic opal in the sediments increases, and the aluminum is subsequently drawn down by either precipitation of authigenic clay minerals or incorporation within siliceous fossils (van Cappellen and Qiu, 1997a). Batch experiments also show that the pore-water aluminum concentration and the Al/Si ratio of diatom frustules in surface sediments are proportional to the amount of detrital material in the sediments (Dixit et al., 2001). Our finding of a negative correlation between the opal content in the sediments and the aluminum





**Fig. 4.** Downcore measurements of metal contents in cleaned diatom samples from JPC17 using inductively coupled plasma optical emission spectroscopy (A, B, and filled symbols in C, error bars are estimated standard deviations from the replicates) and using energy-dispersive X-ray spectroscopy (C: average value in open symbols; dashed lines indicate average value  $\pm$  standard deviation of the variation among the sampling spots within each sample), as well as the comparison between the two measurements (C, D). For panel D, the plotted linear regression (solid line) and 95% confidence interval (dashed lines) include the sample with high Al/Si value (sample at 816 cm). If this sample is excluded, the linear regression of the 20 samples is  $\text{Al/Si}_{\text{ICP}} = 0.748 \times \text{Al/Si}_{\text{EDX ave.}}$ , with a lower squared correlation coefficient of 0.682.

content associated with clean diatom frustules are consistent with these studies. We thus argue that the aluminum incorporated into diatom frustules is primarily released from the dissolution of lithogenic minerals in the sediment, such that a higher concentration of aluminosilicates in the bulk sediment results in greater secondary uptake of aluminum by the diatom frustules.

A linear regression describes relatively well the general relationship between Al/Si ratio of diatom frustules and the opal content in the sediments (Fig. 5B). One sample from JPC17 at the depth of 816 cm clearly falls out of this trend. Although the consistency of the ICP and EDX analyses on this sample excludes the presence of high aluminum contaminants associated with detrital materials, the factors that could contribute to the significantly higher concentration of aluminum (and other cations, Fig. 4B) in this sample are unclear. We exclude this data point in the subsequent discussion.

While our data are qualitatively consistent with previous evidence for pore water Al incorporation into diatom opal, our observed, roughly linear relationship between opal Al/Si and sediment opal content does not agree with laboratory experiments. Koning et al. (2007) have demonstrated in both batch and flow-through experiments that the aluminum content associated with diatom frustules reaches a stable value after several weeks, and the samples exposed to water with a higher concentration of dissolved aluminum do not appear to incorporate a significantly higher amount of Al than the samples exposed to water with lower aluminum concentration (Koning et al., 2007; Table 1). Therefore, the authors argued that the number of suitable reactive surface sites on the frustules perhaps controls the uptake of Al and that the saturation of these sites

prevents further Al incorporation (Koning et al., 2007). Although the concentrations of dissolved Al and Si in those experiments were representative of pore water concentrations, the reactions in the deep-sea sediments may well be more complicated and involve elements or compounds as the catalysts that were not considered in these experiments. The discrepancy may also arise from a distinction between the nature of the Al incorporation observed over several weeks to months in the laboratory and the Al incorporation mechanisms in marine sediments that apply over decades to millennia.

Our linear regression between diatom Al/Si and bulk sediment opal content predicts that the lowest Al/Si ratio is about  $4.5 \times 10^{-3}$  (with a 95% confidence interval of  $-5.1 \times 10^{-3}$  to  $1.4 \times 10^{-2}$ ) in sediments completely comprised of biogenic silica, which is comparable to some of the observed biogenic Al/Si in fresh diatoms from the surface ocean or sediment traps (e.g., van Bennekom et al., 1989; Gehlen et al., 2002), and diatom cultures (e.g., Gehlen et al., 2002), but is one or two orders of magnitude higher than the sediment trap data from the Southern Ocean (e.g., Dixit et al., 2001; Hendry and Rickaby, 2008; Hendry et al., 2010) (Table 1). The variation in the reported Al/Si ratio for the fresh diatoms may result from the different cleaning techniques, but it may also reflect the difference in their growing environment, e.g., the dissolved aluminum concentration in the water. We argue that the predicted minimum Al/Si value from our downcore observations may represent the biogenic uptake and/or early diagenetic uptake of aluminum in the water column or surface sediment. The regression also suggests a maximum Al/Si ratio of  $5.3 \times 10^{-2}$  (with a 95% confidence interval of  $7.1 \times 10^{-2}$  to  $3.6 \times 10^{-2}$ ) on diatom frustules when the opal content in the sediments approaches zero. The fact

**Table 1**

Reported Al/Si ratio in diatom frustules from the surface ocean, sediment traps, deep sea sediments, and in laboratory studies.

Sample origin	Species	Al/Si (mol/mol)	Reference
Surface water net tows	<i>Biddulphis</i>	0.0036	van Bennekom et al. (1989)
	<i>Biddulphis</i>	0.0108	
	<i>Rhizosolenia</i>	0.0035	
Zaire deep-sea fan sediment	Multiple species	0.13 ~ 0.165	van Beusekom et al. (1997)
Enderby Basin sediment	Multiple species	0.0027 ± 0.001	
Crozet Basin sediment	Multiple species	0.011 ± 0.005	
Sediment traps at 3444 m water depth at 63°S, 70°E	Multiple species	0.00023	Dixit et al. (2001)
Diatom cultures	<i>Porosira glacialis</i>	0.00007	Gehlen et al. (2002)
	<i>Thalassiosira nordenskiöldii I</i>	0.0013	
	<i>Thalassiosira nordenskiöldii II</i>	0.0038	
	<i>Lauderia annulata</i>	0.007	
North Sea surface water	<i>Biddulphia sinensis</i>	0.0083	
Wadden Sea tidal flat	Benthic assemblage	0.008	
Scotia Sea surface sediment	Multiple species	0.021	Rickert et al. (2002)
Southern Ocean downcore sediment	Multiple species	0.0007 ~ 0.0299	Lal et al. (2006)
Batch incubation and flow-through experiments	<i>Thalassiosira punctigera</i>	0.0012 ~ 0.0031	Koning et al. (2007)
Coastal Antarctic surface sediment (Marguerite Bay)	Multiple species	0.0021 ~ 0.028	Hendry and Rickaby (2008), Hendry et al. (2010)
Coastal Antarctic Sediment trap (Marguerite Bay)	Multiple species	0.000021 ~ 0.0003	
Coastal Antarctic downcore (Marguerite Bay)	Multiple species	0.007 ~ 0.029	
Southern Ocean surface sediment	Multiple species	0.00014 ~ 0.0198	Andersen et al. (2011)
Bering Sea sediment	Multiple species	0.0034 ~ 0.0870 (mean:0.029)	This study

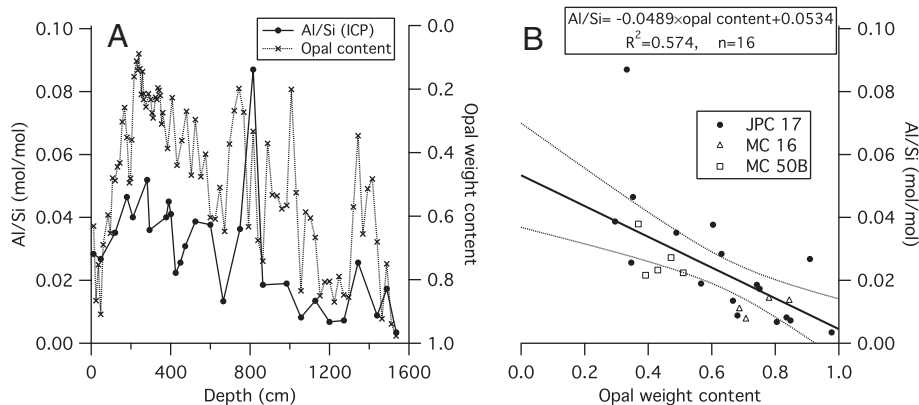
that it is much lower than common aluminosilicate minerals again confirms the absence of detrital contamination in our cleaned diatom samples.

### 3.3. Implications for the preservation of diatom-bound organic matter

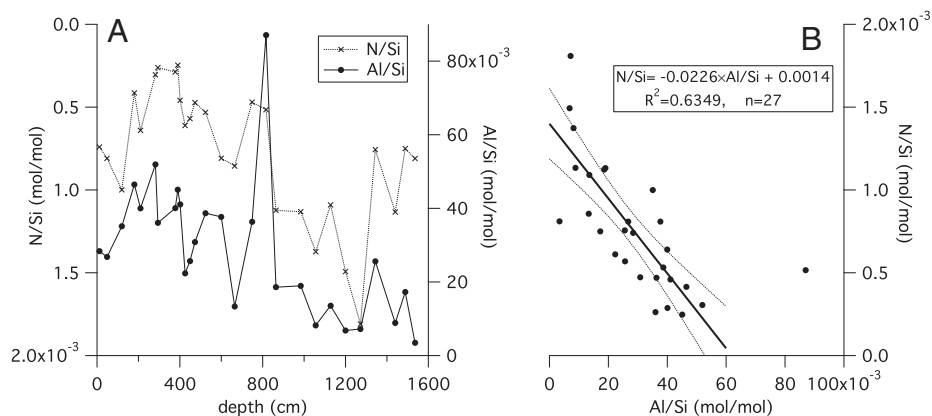
Under the SEM, all of the cleaned diatom frustules we examined show signs of dissolution (Fig. 2). Given the chemical and visual evidence for the diagenetic alteration of microfossils, we must consider whether the organic matter is affected.

The N and Al contents of the cleaned opal at JPC17 appear to fall on a roughly linear trend with negative slope, such that the N to Si atomic ratio decreases as the Al to Si ratio increases (Fig. 6). Another opal-poor sediment record from the open Subarctic Pacific also exhibits strong correlation between the opal content of the sediment and the N content of the cleaned opal (Fig. 8C) (Brunelle et al., 2010). We cannot assume that the N content of organic matter within the freshly produced diatom frustules remains constant over time. Thus, it is possible that the down-core changes derive from incorporation of less organic N into diatoms growing at times when the sediments accumulating in the Bering Sea and Subarctic Pacific had low opal content, due to changes

in the upper ocean nutrient conditions and/or diatom species abundance. While more species-specific studies are needed, the N content of the diatoms appears to be similar among a few different species in cleaned cultures, with the N/Si ratio of most of the studied species falling between  $1.3 \times 10^{-3}$  and  $1.7 \times 10^{-3}$  (Horn et al., 2011). Iron input to the surface ocean can impact the N/Si uptake and bulk biomass ratio by growing diatoms (Franck et al., 2000), but this may not translate to a change in the frustule elemental ratios, especially considering that a large number of the N-bearing compounds within the frustules are required for frustule construction (e.g., Kröger et al., 1999). Furthermore, in the opal-rich sediment records from the Southern Ocean, diatom-bound N content is shown to be quite similar, and only weakly or not correlated with changes in the opal content between the last ice age and Holocene (Fig. 8G, I) (Robinson et al., 2004), during which both iron input to the surface ocean (Kumar et al., 1995; Mahowald et al., 1999) and diatom species assemblages (Shemesh et al., 1989) probably varied significantly. In fact, there seems to be hardly any correlation between the opal content and diatom-bound N content when the opal content in the sediment is above 40%. This apparent difference between the opal-poor sites from the Subarctic Pacific and the opal-rich sites in the Southern Ocean suggests that the downcore changes in



**Fig. 5.** A) Downcore measurements of Al/Si atomic ratio in cleaned diatom samples (filled circles) and opal content (crosses) in the sediments (Brunelle et al., 2007) from JPC17, as well as B) direct comparison between the two measurements from the analyzed samples in JPC17 (filled circles). The plotted linear regression (solid line) and 95% confidence interval (dashed lines) do not take into account the one sample with exceptionally high Al/Si ratio. If considering this sample, the linear regression of the 17 samples is  $\text{Al/Si} = -0.0697 \times \text{opal content} + 0.0696$ , with a lower squared correlation coefficient of 0.530. The samples from MC50B (open squares) and MC16 (open triangles) also appear consistent with relationship observed in the downcore samples from JPC17.



**Fig. 6.** A) Downcore measurements of N/Si atomic ratio (crosses) and Al/Si atomic ratio (circles) of the cleaned diatom samples at JPC17, and B) direct comparison between the two measurements. The plotted linear regression (solid line) and 95% confidence interval (dashed lines) do not take into account the one sample with exceptionally high Al/Si ratio. If considering this sample, the linear regression of the 28 samples is  $N/Si = -0.0151 \times Al/Si + 0.0014$ , with a lower squared correlation coefficient of 0.473.

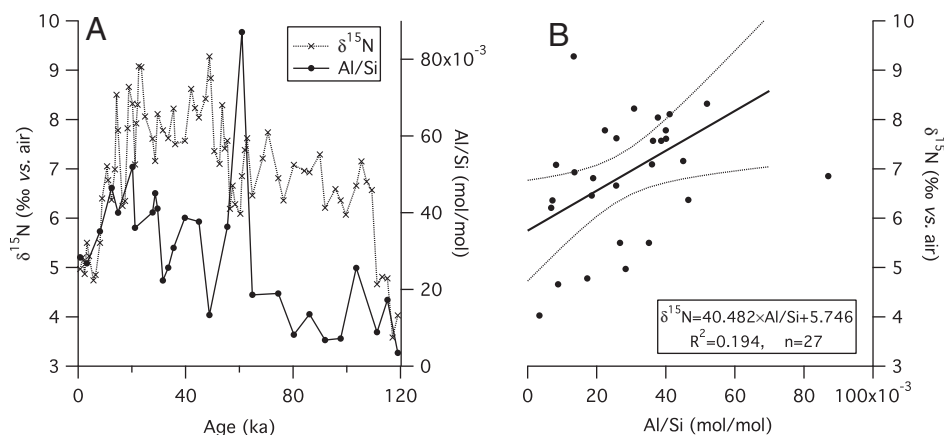
the diatom-bound N content in the former may result primarily from sedimentary processes. In this view, the large downcore changes in cleaned opal N/Si in JPC17 arise from its very large range in opal (and thus aluminosilicate) content.

It is at first tempting to explain the decrease in N/Si with increasing Al/Si as the result of dilution by the addition of N-free aluminosilicate coatings to the surface of diatom frustules. However, this mechanism would require a significant increase in diatom thickness and mass in the sediments relative to the surface ocean and sinking fluxes. For example, a decrease of N content by a factor of 2 would suggest doubling of the diatom weight. This significant change in diatom mass has not been observed in this or previous studies. Dilution is thus inadequate to explain the observation.

As aluminum uptake has been shown to significantly lower the solubility of biogenic silica in the sediments (van Cappellen and Qiu, 1997a; van Beusekom et al., 1997; Dixit et al., 2001), higher aluminum uptake enhances preservation of the biogenic silica, and lower aluminum content could be associated with greater dissolution of the diatom frustules. An inverse relationship between aluminum and nitrogen contents may thus also arise without significant nitrogen loss. In this case, changes in the N/Si ratio are due to preservation or dissolution of the biogenic silica, while the amount of N remains relatively constant within the frustules. However, if this explanation is right, the linear regression predicts a 25% greater loss of the biogenic silica as 1 out of 70 atoms of silica is not replaced by aluminum, i.e.

the Al/Si ratio decreases by 0.014. This significant loss of material would result in thinner frustules, and other clear signs of dissolution in the opal rich, low aluminum samples, which is not consistent with (and is more likely opposite to) what we have observed under the SEM. It is also hard to imagine such a significant loss of silicate frustules without any effect on the intrinsic organic matter. Moreover, the frustule N content of the opal-rich samples is consistent with the frustule N content in cultures (Horn et al., 2011). We thus conclude that preferential loss of biogenic silica alone in high-opal samples cannot explain the relationship between aluminum and nitrogen content.

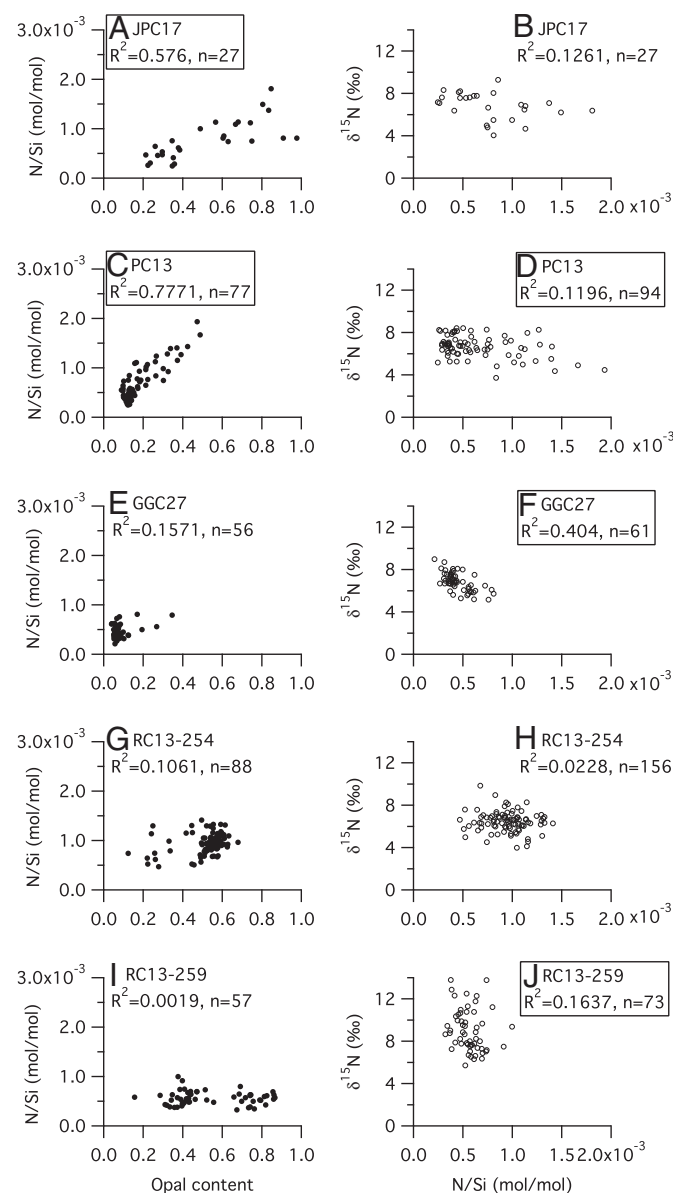
Finally, if aluminum is predominantly incorporated into the silica lattice, alteration of the existing structure of the frustules could potentially result in exposure and eventual loss of once-protected organic matter, which would yield the negative correlation between the aluminum and the nitrogen content. Excluding the sample at 816 cm, the linear regression between N/Si and Al/Si ratio in JPC17 predicts a N/Si ratio of  $1.4 \times 10^{-3}$  (with a 95% confidence interval of  $1.2 \times 10^{-3}$  to  $1.6 \times 10^{-3}$ ), or a N content of  $21 \times 10^{-6}$  mol/g of cleaned opal, when the Al content is near zero. This predicted N content in pristine diatoms is comparable to the average N content of fresh diatoms (Horn et al., 2011), as well as the upper range in diatom-bound N content previously reported in relatively opal rich marine sediments (Figs. 8, 9). N content approaches zero ( $6 \times 10^{-7}$  mol/gram of cleaned opal, or N/Si ratio around  $4 \times 10^{-5}$ ) when the Al/Si ratio is



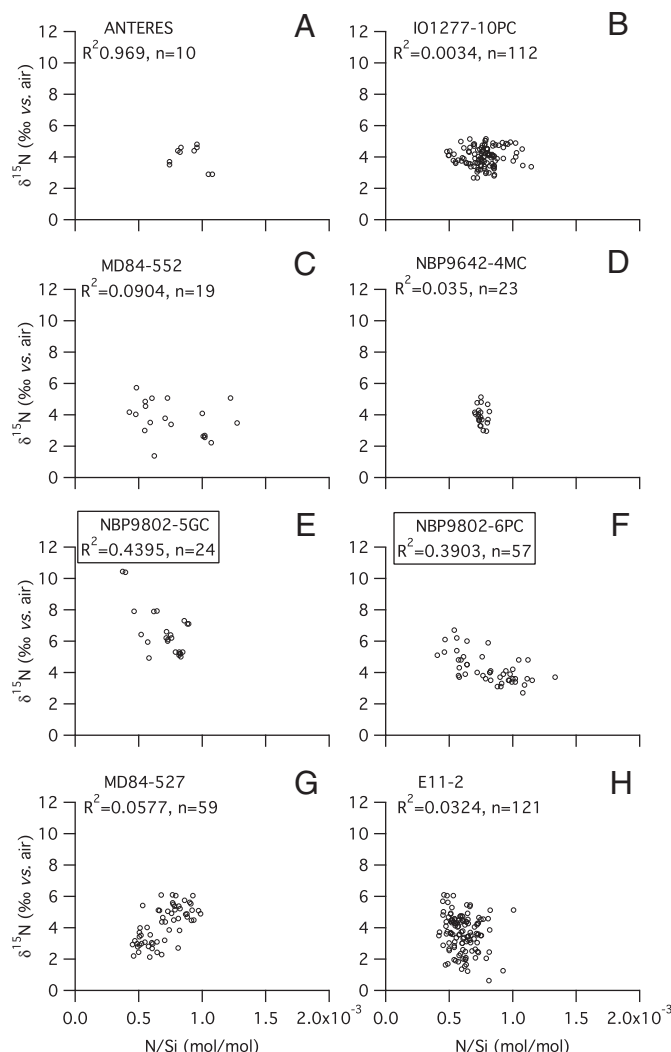
**Fig. 7.** Downcore measurements of the nitrogen isotopic composition of diatom frustule-bound organic nitrogen (crosses), and the Al/Si ratio (circles) of the cleaned diatom samples in JPC17 (A), and direct comparison between the two (B). The plotted linear regression (solid line) and 95% confidence interval (dashed lines) do not take into account the one sample with exceptionally high Al/Si ratio. The correlation is not significant at the 1% level. If considering this sample, the linear regression of the 28 samples is  $\delta^{15}N = 24.03 \times Al/Si + 6.137$ , with an even lower squared correlation coefficient of 0.116. The age model of JPC17 is from Brunelle et al. (2007) and Cook et al. (2005), which is based on foraminiferal  $\delta^{18}O$  stratigraphies of the planktonic species *Neogloboquadrina pachyderma* (sinistral) and of the benthic genus *Uvigerina*, as well as by seven radiocarbon dates (measured on *N. pachyderma* (s.) >150  $\mu m$ ).

$6 \times 10^{-2}$ , similar to the estimated value for the maximal Al/Si ratio of sedimentary opal from extrapolation of the relationship between Al/Si and opal content (Section 3.2, Fig. 5).

Taking the explanation of organic N loss as the correct one for the time being, we find no clear evidence for isotopic fractionation associated with this N loss. The correlation between aluminum content and the nitrogen isotopic composition at JPC17 is rather weak (Fig. 7; the correlation is not significant at the 1% level). Among the previously studied sites in the Southern Ocean and North Pacific, a few records show a slightly better negative correlation between the isotopic composition and the N content of the cleaned diatoms (Fig. 8, 9). However, such an inverse correlation could as easily arise from changes in the upper ocean conditions. For example, many studies have shown that during the glacial periods, these high latitude regions are characterized with higher diatom-bound  $\delta^{15}\text{N}$  and



**Fig. 8.** Comparison of the diatom-bound N content with the opal content of the sediment (filled symbols), and with the diatom-bound N isotopic composition (open symbols) in downcore sediments from previous studies in the North Pacific (JPC17 (Brunelle et al., 2007), GGC27, and PC13 (Brunelle et al., 2010)) and the Southern Ocean (RC13-254, and RC13-259 (Robinson and Sigman, 2008)). The records marked with boxes have correlations above the 1% significance level.



**Fig. 9.** Additional comparisons between the nitrogen isotopic composition and N content of the cleaned opal in downcore and surface sediments from previous studies in the Southern Ocean (ANTARES surface sediments, IO1277-10PC, MD84-552, NBP 96-4-2 MC4 (Robinson et al., 2004); E11-2, MD84-527 (Robinson et al., 2005); NBP9802-5GC, NBP9802-6PC (Robinson and Sigman, 2008)). The records marked with boxes have correlations above the 1% significance level.

low opal accumulation rate, suggesting more complete surface nutrient consumptions but perhaps less diatom productivity (Brunelle et al., 2007, 2010; Galbraith et al., 2008; Sigman et al., 1999; Robinson et al., 2004, 2005; Robinson and Sigman, 2008). If this is true, the high aluminum content of diatom frustules during the glacial periods would arise from the low opal content in the sediment, due to low opal flux to the seabed, but the high diatom-bound  $\delta^{15}\text{N}$  would be the result of surface ocean conditions. That is, the correlation would not speak of a direct causal connection. One of the best arguments for this interpretation is the wide range of  $\delta^{15}\text{N}$  to N content relationships observed from different sediment cores (Figs. 8, 9). For example, variations in the opal content in the open Subarctic Pacific core PC13 and in the Okhotsk Sea core GGC27 are similar over the last glacial/interglacial period, with high opal content ( $\sim 30\%$ ) during the warm intervals and low opal content ( $\sim 10\%$ ) during the cold intervals (Brunelle et al., 2010). However, the  $\delta^{15}\text{N}$  to N content relationship appears to be much stronger at GGC27, where the N content and opal content are shown to be only weakly correlated (Fig. 8).

Although more information about the mechanisms of aluminum uptake in the sediments is needed, our results point to loss of the



intrinsic organic matter during aluminum incorporation of the biogenic silica in the sediments. This is probably due to the exposure of once-protected, diatom-native organic N, as a result of the diagenetic process associated with Al incorporation. The lack of an overarching relationship between isotopic composition and nitrogen content in the records available to date suggests that (1) the N loss process does not involve N isotope fractionation, and (2) there is no major, coherent isotopic heterogeneity in diatom-bound organic N, such that no clear isotopic change occurs during the loss of part of the diatom-bound N pool. Future studies of the compound composition and compound-specific isotopic signature on cultures and sediment samples will help us to understand whether the lack of clear isotopic heterogeneity results from the lack of significant isotopic differences among different compounds or the lack of significant relative compositional changes associated with organic N loss.

### 3.4. Implications for cleaning methods

It is observed that, in clay-rich sediments, a stronger oxidative treatment is required to completely remove external organic matter associated with diatom frustules, while the diatom-bound N in these sediments also appears to be less vulnerable to isotopic alteration by harsh chemical treatment than is diatom-bound N from opal-rich sediments (Robinson et al., 2004; Brunelle et al., 2007). We argue that this is explained by diagenetic alteration of the diatom frustules in the sediments. On the one hand, the structural alteration due to aluminum uptake during diagenesis has probably worked to “harden” the diatom frustules, resulting in more complete protection of the remaining intrinsic organic matter in the sediments against harsh chemical treatments. On the other hand, the new mineral phases may interfere with complete removal of labile and external organic matter and/or mineral-associated ammonium during the cleaning. This external N is perhaps associated with and protected by the secondary high-Al opal phase, requiring harsher chemical treatment for complete removal.

## 4. Conclusions

In Bering Sea sediments extending back through the last 120 kyrs, we find the aluminum content of the separated and cleaned diatom frustules to be correlated with the aluminosilicate content of the bulk sediment. The aluminum is either incorporated homogeneously into the frustules or as an aluminosilicate coating on the surface of the diatom frustules; the consistency between analyses of frustule surfaces and bulk frustule material calls for at least some of the former and/or that the Al-rich coating has substantial thickness. Detrital aluminosilicates are probably the primary source of aluminum, with a greater concentration of aluminosilicates leading to higher Al incorporation into the diatom frustules. The structural alteration of the diatom frustules during aluminum uptake in the sediments has likely resulted in the loss of a fraction of the frustule's intrinsic organic matter by exposing it to the diagenetic environment. However, our study did not show any significant isotopic fractionation associated with this process, suggesting that diagenesis of the inorganic frustule controls the N loss. The formation of the new aluminosilicate phases also appears to ‘harden’ the diatom frustules during diagenesis, resulting in improved preservation of the remaining intrinsic organic matter and making the diatom frustules more resistant to chemical alteration during cleaning. However, the aluminum incorporation may also work to partially protect the once-external organic N, explaining the previously recognized need for harsher chemical cleaning when isolating the diatom-bound N from the clay-rich sediments.

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