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Size-specific opal-bound nitrogen isotope measurements in North Pacific sediments

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Abstract

The nitrogen isotope composition of diatom opal ($\delta^{15}N_{db}$) is a valuable recorder of nitrate utilization in the polar surface oceans and a measure of the efficiency of the biological pump. Past down-core records of $\delta^{15}N_{db}$ involved the measurement of the biogenic opal fraction up to 150 μm in size, which should represent the bulk of the preserved diatoms but may also include non-diatom opal such as radiolaria and sponge spicules. In this study, the opal from subarctic Pacific and Bering Sea sediments from the Holocene back to the last glacial was separated into different size fractions to measure their individual $\delta^{15}N$. We found a general trend of decreasing $\delta^{15}N$ with increasing size at all sites and through time. Microscopic investigation of smear slides and image area analysis of microphotographs of the analyzed opal revealed that the larger size fractions contained greater proportions of sponge spicules and radiolaria. Manual isolation and measurement of the sponge spicules showed that they have a very low $\delta^{15}N$ ($\sim -11‰$). Ultrasonication during sample preparation caused greater spicule and radiolaria contamination due to fragmentation of these relatively large fossils, leading to a dramatic $\delta^{15}N_{db}$ decrease with increasing size and lower $\delta^{15}N_{db}$ across all size fractions in sonicated versus non-sonicated samples. Nevertheless, these contaminants were also present albeit less abundant in the various size fractions of samples separated without sonication, and these samples also showed a $\delta^{15}N_{db}$ decrease with increasing size. Simple isotope mass-balance calculations of Holocene Bering Sea sediments indicate that most of the $\delta^{15}N_{db}$ variations among the larger size fractions can be explained by the relative abundance of low-$\delta^{15}N$ sponge spicules in each fraction. However, some of the size fraction $\delta^{15}N$ differences in the downcore records require a different explanation. Both diatom inter- or intra-species effects are evident and indicate lower $\delta^{15}N_{db}$ among the larger (centric) versus smaller (pennate) diatom species and a $\delta^{15}N_{db}$ decrease with increasing size of centric diatom frustules.

Contamination of N by non-diatomaceous opal should not normally compromise total-diatom-bound $\delta^{15}N$ (0–150 μm) because the non-diatom opal typically contributes less than ~5% to the total opal. However, the early deglacial (Heinrich Stadial 1-correlative) period in the subarctic North Pacific is an important possible exception: a substantial fraction of its low concentration of opal appears to be sponge spicules and radiolaria, such that the reconstructed total-diatom $\delta^{15}N_{db}$ decrease at this time may be an artifact. While the glacial-age sediments are also vulnerable to non-diatom contamination, this should work to lower $\delta^{15}N_{db}$, such that the observed high glacial $\delta^{15}N_{db}$ in North Pacific sediments cannot be explained by contamination. Thus, the previous interpretation of enhanced nutrient consumption in the North Pacific regions during the last ice age remains valid.

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1. INTRODUCTION

In the modern high nutrient, polar and subpolar regions of the ocean such as the Antarctic and the subarctic North Pacific, phytoplankton productivity appears to be limited by a combination of iron and light (Martin and Fitzwater, 1988; Martin et al., 1990; Mitchell et al., 1991; Maldonado et al., 1999). The incomplete consumption of the major nutrients nitrate and phosphate represents a missed opportunity for the sequestration of carbon dioxide in the ocean interior (Ito and Follows, 2005; Marinov et al., 2006).

Sedimentary nitrogen (N) isotopes have been developed as a tool to study past changes in the oceanic N cycle. The $\delta^{15}N$ of the nitrate in the surface waters of the high latitude regions is elevated by partial nitrate assimilation, due to preferential uptake by phytoplankton of ^{14}N-bearing nitrate (with $\delta^{15}N = (^{15}N/^{14}N_{sample}/^{15}N/^{14}N_{ref} - 1) * 1000‰$, where N_{ref} is N_2 in air) (Sigman et al., 1999a). Therefore, the $\delta^{15}N$ of surface nitrate and thus also sinking organic matter reflects the degree of nitrate consumption in these nutrient-rich high latitude regions (Altabet and Francois, 1994). In order to reconstruct past nutrient consumption, the $\delta^{15}N$ of bulk sedimentary N has been studied. However, it can be biased by diagenetic alteration during sinking and burial and by allochthonous N input (Altabet and Francois, 1994; Schubert and Calvert, 2001; Meckler et al., 2011). Therefore, the organic N emplaced and subsequently trapped within microfossils has been targeted for $\delta^{15}N$ analysis, as it is physically protected from diagenetic alteration (Shemesh et al., 1993, 2002; Sigman et al., 1999b; Crosta and Shemesh, 2002; Robinson et al., 2004, 2005; Brunelle et al., 2007, 2010; Robinson and Sigman, 2008; Ren et al., 2009, 2012; Meckler et al., 2011). As diatoms are the most abundant phytoplankton in the high latitudes of the North Pacific and Southern Ocean, diatom-bound $\delta^{15}N$ ($\delta^{15}N_{db}$) has been developed as a proxy to reconstruct past surface nitrate utilization in those regions.

Few down-core $\delta^{15}N_{db}$ records exist to date from the North Pacific region, all indicating higher $\delta^{15}N_{db}$ values associated with glacial periods relative to interglacials (Brunelle et al., 2007, 2010). The elevated nitrate consumption likely resulted from restriction of the upward nutrient supply (Jaccard et al., 2005). Such a change would have worked to raise the efficiency of the biological pump, lowering atmospheric CO_2 during those times.

The existing North Pacific $\delta^{15}N_{db}$ records generated so far measured the total-diatom assemblage in a given sediment sample (total-$\delta^{15}N_{db}$ hereafter, comprising the 0–150 μm fraction), leaving unaddressed the potential isotopic differences among different diatom species and size fractions. For other stable isotope measurements making use of diatom microfossils, such species- and/or size-dependence has recently been reported. Henley et al. (2012) hypothesized that diatom species composition can influence $\delta^{13}C_{db}$, based on the comparison of modern ocean $\delta^{13}C_{POC}$ and diatom species assemblage. Jacot Des Combes et al. (2008) suggested that C isotope fractionation by diatoms is species specific, as other environmental variables (temperature, sea-ice, [CO_2 (aq)] and primary productivity) failed to explain the observed down-core $\delta^{13}C_{db}$ trends. While a number of culture, sediment trap and down-core studies did not identify a species effect on $\delta^{18}O_{db}$, other down-core studies report evidence for it (Swann and Leng, 2009, for a review and references). Finally, culture experiments indicate that Si isotope fractionation by diatoms is species-dependent (Sutton et al., 2013).

Regarding nitrogen, it is well known that different diatom species assimilate nitrate with different degrees of isotope fractionation (Waser et al., 1998; Needoba et al., 2003; Granger et al., 2004, 2010). There is also culture evidence for interspecies differences in the $\delta^{15}N$ offset between diatom biomass and the organic N emplaced within the frustule (Horn et al., 2011). Jacot Des Combes et al. (2008) found that Antarctic sediments that contained >10% of *Eucampia antarctica*, a diatom species associated with sea ice, typically had a higher measured $\delta^{15}N_{db}$, with highest abundances of *E. antarctica* and highest $\delta^{15}N_{db}$ occurring in samples from the Last Glacial Maximum (LGM). Thus, it is possible that the general $\delta^{15}N_{db}$ increase observed during the last glacial might not be indicative of enhanced nitrate consumption and thus a more efficient biological pump, but rather reflects a shift in the diatom species composition. This is obviously a major concern for the use of $\delta^{15}N_{db}$ as a proxy to reconstruct past surface ocean nutrient consumption.

The initial goal of this study was to determine the contribution of varying diatom species and sizes to the total-$\delta^{15}N_{db}$ and to address the impact of changing diatom species assemblage on glacial/interglacial (G/IG) down-core $\delta^{15}N_{db}$ records, in order to complement previous investigations of other diatom-bound stable isotope systems. This was pursued by sieving the diatom opal into different size fractions, with the aim to separate monospecific diatom fractions for $\delta^{15}N_{db}$ analysis. The progress of this work highlighted an additional dynamic – contamination of the $\delta^{15}N_{db}$ signal by the organic N bound within radiolaria and sponge spicules – that appears to be particularly important in the North Pacific, especially during times of lowest opal flux. In addition to revealing these effects, the data yield insights into how artifacts may be minimized in paleoceanographic $\delta^{15}N_{db}$ records.

2. MATERIALS AND METHODS

2.1. Core locations and age models

This study used sediments from the subarctic Pacific and the Bering Sea (Table 1). The subarctic Pacific sediments were collected during INOPEX cruise SO202 aboard the *R/V Sonne* in July–August 2009. Core SO202-07-6 is a box core retrieved from Detroit Seamount in the NW subarctic Pacific (51°16.287'N, 167°41.982'E, 2340 m water depth), while core SO202-27-6 is a box core from Patton Seamount from the NE subarctic Pacific (54°17.77'N, 149°36.01'W, 2919 m water depth) (Fig. 1). The data for cores 07-6 and 27-6 are reported against depth, with the time periods of the Holocene, Bølling-Allerød (BA), Heinrich Stadial 1 (HS1) and the Last Glacial Maximum (LGM) indicated qualitatively, based on tuning the $\delta^{15}N_{db}$ and $\delta^{15}N_{bulk}$ records of 07-6 and 27-6 to published