

The proportion of remineralized nitrate on the ice-covered eastern Bering Sea shelf evidenced from the oxygen isotope ratio of nitrate

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[1] We present measurements of nitrate and its natural abundance oxygen isotope composition ($^{18}\text{O}/^{16}\text{O}$) in the water column of the broad and shallow eastern Bering Sea shelf in the late winter and early spring of 2007 and 2008. In both years, nitrate concentrations showed a characteristic decrease, from $25\ \mu\text{M}$ at the slope to $\leq 5\ \mu\text{M}$ inshore. The $^{18}\text{O}/^{16}\text{O}$ ratio of nitrate ($\delta^{18}\text{O}_{\text{NO}_3}$ versus SMOW) also decreased from 3.2‰ at the slope to 1.5‰ inshore in 2007 and to as low as -1‰ inshore in 2008, indicating that nitrate inshore was nitrified at least once since having been entrained as nitrate from the slope. The shoreward decrease was less pronounced in 2007 due to ^{18}O enrichment of nitrate from incident phytoplankton assimilation in the ice-covered water column, whereas little to no algal growth in the water column was evident in 2008. By comparing the $\delta^{18}\text{O}$ of nitrate to that of ambient water in spring 2008, we estimate the fraction of nitrate that was remineralized in situ rather than recently advected from the slope. These estimates indicate that 20%–100% of the nitrate in winter water of the middle and inner shelves derives from regeneration directly on the shelf rather than from the seasonal entrainment of slope waters, with recycling being the dominant mode of seasonal nitrate recharge from the 70 m isobath shoreward. These observations indicate substantial nutrient recycling on the shallow shelf, which has direct implications for the extent of fixed N loss to benthic denitrification and the fertility of the eastern shelf.

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1. Introduction

[2] The exceptional productivity of the eastern Bering Sea shelf derives primarily from the shoaling of nutrient-rich waters from the Pacific onto the shallow continental shelf. Intermediate depth waters of the open Bering Sea contain a large reservoir of macronutrients from the remineralization of sinking organic material within the ocean interior. Deep winter mixing in the open Bering Sea brings these nutrients to the surface in proximity of the steep slope and the shallow shelf, where they remain largely unutilized [Aguilar-Islas

et al., 2007; Sambrotto *et al.*, 2008]. The entrainment of slope waters onto the shelf supplies the nutrients that fuel primary production, the concentration of which ultimately determines the carrying capacity of the shelf.

[3] The entrainment of nutrients onto and across the wide shelf has direct implications for shelf productivity, yet the relative contributions of cross-shelf fluxes and biogeochemical recycling on the shelf nutrient budget remain poorly constrained. During the growing season, nutrients are drawn down throughout the euphotic zone, which extends to the bottom on the shoreward portion of the shelf [Walsh and McRoy, 1986]. Over the winter, when solar insolation is low and much of the shelf is ice covered, nitrate concentrations have been shown to increase steadily in the water column [Whitledge *et al.*, 1986], until the inception of marginal ice spring blooms that consume surface nitrate [Niebauer and Alexander, 1985; Sambrotto *et al.*, 1986; Mordy *et al.*, 2012]. The wintertime increase, or “recharge,” of nitrate and other nutrients in “winter water” of the southeastern shelf is commonly stated to derive principally from the entrainment of nutrient-rich slope waters onto the shelf [Coachman and Walsh, 1981; Hansell *et al.*, 1993; Stabeno *et al.*, 2002b; Rho *et al.*, 2005; Stabeno *et al.*, 2007]. Cross-shelf Ekman transport is strongest in fall and winter, causing a net movement of surface waters from inshore to offshore, presumably

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matched by some compensating subsurface flows of slope waters [Danielson *et al.*, 2011]. The seasonal recharge of nutrients by the entrainment of slope waters is also reportedly evidenced by a consistent nitrate-salinity relationship observed at the end of winter on the southeastern Bering Sea shelf [Hansell *et al.*, 1993; Stabeno *et al.*, 2002b; Rho *et al.*, 2005], wherein the more or less conservative behavior of shelf nitrate in winter water appears to trace the seasonal mixing of nutrient-rich saline slope waters with nutrient-deplete fresher waters shoreward.

[4] Yet some of the nutrients in winter water are likely remobilized from the sediment. The eastern Bering Sea shelf is not only shallow but also particularly broad (~500 km), such that shelf waters, especially those on the middle shelf and shoreward, are unlikely to be flushed entirely in a single season [Coachman and Walsh, 1981; Coachman, 1986]. Moreover, seasonal nutrient recharge principally by onshore entrainment of slope waters—presumably displacing nutrient-deplete shelf waters—would then require that the nutrient flux from the slope be more or less matched by an equivalent export of biogenic particulate matter off-shelf, on an annual basis. Based on a model forced by local wind observations, Walsh and McRoy [1986] argued that 50% of the organic material produced on the southeastern portion of the outer shelf domain between 55°N and 58°N is exported directly to deeper waters off the slope, but that the particulate organic material produced on the less dynamic middle shelf at these latitudes is largely retained on the shelf, accounting for the abundant secondary production in the water column and benthos. A substantial role for nutrient recycling on the shelf is supported by the relatively elevated ammonium concentrations observed in winter water [Whitledge *et al.*, 1986; Rho *et al.*, 2005] as well as by observed nutrient efflux from the shelf sediments [Glover and Reeburgh, 1987; Lomstein *et al.*, 1989; Rowe and Phoel, 1992; Henriksen *et al.*, 1993; Devol *et al.*, 1997]. In this respect, some of the increase in nitrate concentrations in winter water likely originates from the nitrification of shelf ammonium [Whitledge *et al.*, 1986; Rowe and Phoel, 1992; Granger *et al.*, 2011]. Considering the different processes described in the literature, a better understanding is required of the extent to which shelf nutrients are replenished seasonally from the slope versus recycled in situ.

[5] In a recent study, we have observed that the $^{15}\text{N}/^{14}\text{N}$ ratio of nitrate ($\delta^{15}\text{N}_{\text{NO}_3}$ versus air) in winter water decreases inshore and northward, in association with increasing ammonium concentrations [Granger *et al.*, 2011]. This suggests that some nitrate in shelf waters derives from the partial nitrification of ammonium, yielding ^{15}N -deplete nitrate; isotope fractionation in the biological oxidation of ammonium to nitrate is significant, with an isotope effect ϵ ranging from 14‰ to 38‰ in nitrifier cultures [Casciotti *et al.*, 2003; Santoro *et al.*, 2011] (ϵ (‰) = $(^{14}k/^{15}k - 1) \times 1000$, where k is the reaction rate constant of the respective isotopologues). While indicative that some fraction of the nitrate in winter water is remineralized in situ, $\delta^{15}\text{N}_{\text{NO}_3}$ by itself does not provide quantitative constraints on the extent of N recycling, as this would require specific knowledge of the amplitude of N isotope discrimination by nitrification in situ, a parameter that has varied among cultured strains [Casciotti *et al.*, 2003; Santoro *et al.*, 2011], and concurrent measurements of the $\delta^{15}\text{N}$ of ammonium.

[6] Here we exploit the sensitivity of the natural abundance $\delta^{18}\text{O}_{\text{NO}_3}$ to nitrification, to provide an estimate of the contribution of newly nitrified nitrate to the shelf nitrate pool. The newly nitrified nitrate in shelf waters has a lower $\delta^{18}\text{O}$ than the nitrate originating from the slope. Nitrate $\delta^{18}\text{O}$ thus reflects the proportion of seasonal nutrient replenishment from remineralization relative to physical entrainment. We show that a substantial portion of the nitrate on the middle and inner shelf originates from remineralization in situ, up to 100% inshore and northward, indicating the central importance of N cycling to shelf fertility.

2. Sampling Locations and Methods

[7] We sailed aboard the icebreaker *USGS Healy* from 10 April to 11 May 2007 and 31 March to 6 May 2008 as part of the Bering Sea Ecosystem Study (BEST: cruises *HLV-07-01* and *HLV-08-02*). Discrete hydrographic lines from inshore to off-shelf and spanning a latitude range from 56°N to 62°N were visited in both years, along with additional stations that were visited in only one of the two sampling campaigns (Figure 1).

[8] Hydrographic measurements were made using a conductivity-temperature-depth profiler, which was equipped with a transmissometer and a fluorometer. Seawater was collected from an attached rosette of 24 Niskin bottles. Salinity calibration samples were collected at all stations and analyzed on board with a salinometer. Nutrients (NO_3^- , NO_2^- , PO_4^{3-} , $\text{Si}(\text{OH})_4$, and NH_4^+) were analyzed directly on board with a custom nutrient autoanalyzer using standard methods [Mantoura and Woodward, 1983; Gordon *et al.*, 1994]. Dissolved oxygen was determined on board by Winkler titrations [Carpenter, 1965]. In situ fluorescence was converted to chlorophyll *a* concentrations with an empirical calibration using a subset of discrete measurements of water column chlorophyll *a* concentrations [Napp, 2007; Lomas/BIOS, 2008].

[9] Seawater samples for nitrate isotope analyses were collected at 6–10 m depths throughout the water column. These were prefiltered through a 0.2 mm polyethersulfone membrane into 60 mL high-density polyethylene bottles and were stored frozen until analysis. Nitrite was removed with sulfamic acid prior to isotope analysis [Granger and Sigman, 2009] in the few samples where nitrite comprised $\geq 5\%$ of the sum of nitrate plus nitrite. The $^{15}\text{N}/^{14}\text{N}$ and the $^{18}\text{O}/^{16}\text{O}$ of nitrate were analyzed by the “denitrifier method” [Sigman *et al.*, 2001; Casciotti *et al.*, 2002], which is described in more detail for the current samples in Granger *et al.* [2011]. Isotope ratios of water and nitrate are reported in delta notation (δ) in units of per mil (‰) as follows:

$$\delta^{15}\text{N} = \left(\left[\frac{\left(\frac{^{15}\text{N}}{^{14}\text{N}} \right)_{\text{sample}}}{\left(\frac{^{15}\text{N}}{^{14}\text{N}} \right)_{\text{standard}}} \right] - 1 \right) \times 1000 \quad (1a)$$

and

$$\delta^{18}\text{O} = \left(\left[\frac{\left(\frac{^{18}\text{O}}{^{16}\text{O}} \right)_{\text{sample}}}{\left(\frac{^{18}\text{O}}{^{16}\text{O}} \right)_{\text{standard}}} \right] - 1 \right) \times 1000 \quad (1b)$$

[10] Measurement error among replicates averaged 0.2‰ for N and 0.3‰ for O isotope ratios of nitrate [Granger, 2007; Sigman and Granger, 2008]. All of the hydrographic and isotope measurements presented here and pertinent

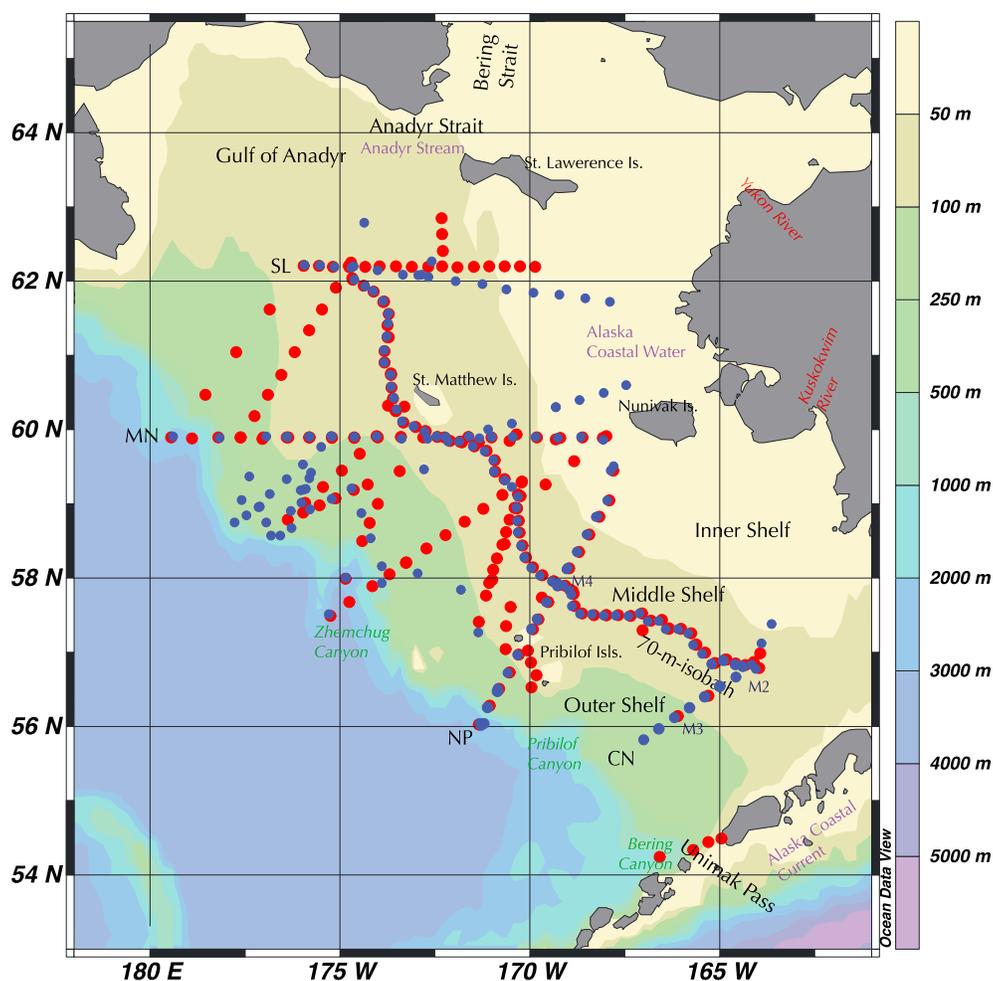


Figure 1. Cruise tracks during *HLY-07-01* (blue) and *HLY-08-02* (red) in spring 2007 and 2008, respectively. Note the location of hydrographic lines and mooring locations: CN (Canyon-Nunivak), 70 m isobath, NP (Nunivak-Pribilof), MN (St. Matthew-Nunivak), SL (St. Lawrence), and the location of the M2, M3, and M4 moorings. Map generated with Ocean Data View (R. Schlitzer, Ocean Data View, 2013, <http://odv.awi.de/en/home/>).

metadata files are available from the BEST data archive (<http://www.eol.ucar.edu/projects/best/>).

[11] Seawater samples were collected in sealed tubes in April 2008 for water $^{18}\text{O}/^{16}\text{O}$ isotope analyses, which were conducted at the Stable Isotope Laboratory at Oregon State University, Corvallis, following a standard protocol detailed in *Epstein and Mayeda* [1953]. The reported measurement error among replicate $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ analyses is 0.05‰.

3. Results and Discussion

3.1. Water Column Properties of the Shelf

[12] Full or partial sea ice covered many of the shelf stations, extending over the middle shelf down to $\sim 58^\circ\text{N}$ in 2007, and to the shelf edge and south of the Pribilof Islands to 56°N in 2008 (Figure S1 in the supporting information). Salinity decreased shoreward in both years, from ~ 34 practical salinity unit (psu) at the slope to as low as 30.5 at the inner shelf (Figure S2). In both years, bottom water temperatures were uniformly low at stations under ice cover on the middle and inner shelf, between -1.5°C and -1.9°C , and were slightly warmer ($\sim -0.5^\circ\text{C}$) at stations close to the 100 m

isobath front and at ice-free stations on the southern middle shelf (Figure S2). The water column at ice-covered stations of the inner and middle shelves was homogeneous, whereas sea ice retreat contributed to the inception of shallow mixed layers and consequent marginal ice blooms at ice edge stations, particularly in 2007 (Figure S3). Bottom water temperatures at the outer shelf domain increased seaward, from -0.5°C at the 100 m isobath to $\sim 3^\circ\text{C}$ in 200 m deep slope waters. Oxygen concentrations in bottom waters were mostly undersaturated in both years, particularly so in 2008 when the median O_2 supersaturation was -15% , compared to -8% in 2007. While consistent with net heterotrophy of ice-covered waters in both years, corresponding chlorophyll *a* measurements bear evidence of incident algal growth, especially in 2007 (Figures S2 and S3). Bottom water chlorophyll *a* concentrations ranged from undetectable to upward of $5 \mu\text{g L}^{-1}$ at many ice-covered stations and marginal ice blooms (Figure S2). The presence of photosynthetic O_2 in the ice-covered water column in 2007 was further confirmed from measurements of the triple isotope composition of dissolved O_2 in ice-covered waters, which indicated that photosynthetic O_2 comprised a mean of $7\% \pm 4\%$ of ambient O_2

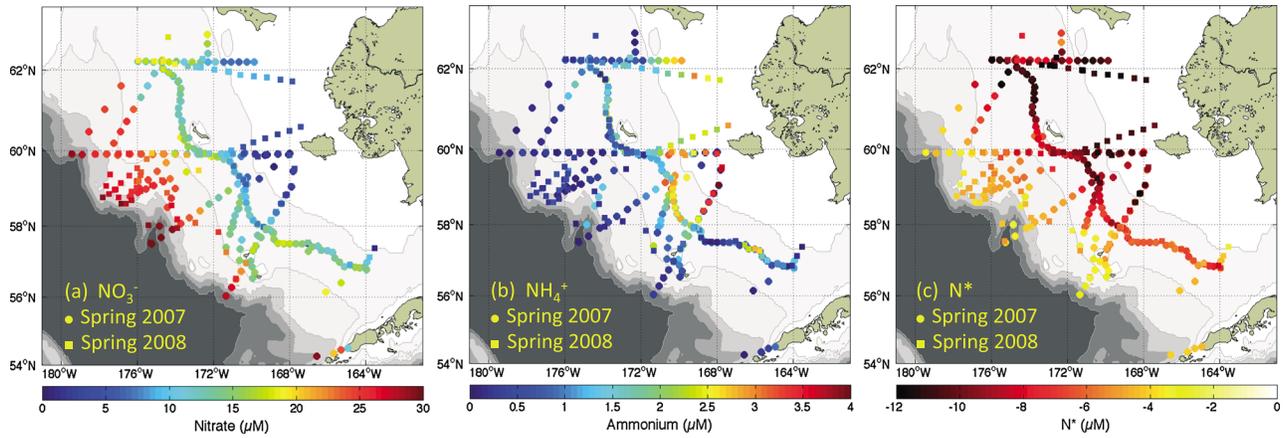


Figure 2. (a) Nitrate concentrations at bottom water depths to 200 m. (b) Ammonium concentrations at bottom water depths to 200 m. (c) N^* at bottom water depths to 200 m. N^* (μM) = $[\text{NO}_3^-] + [\text{NO}_2^-] + [\text{NH}_4^+] - 16^* [\text{PO}_4^{3-}] + 2.9$.

(M. G. Prokopenko et al., Mixed layer depth controls the instantaneous net to gross production ratios and potential export efficiency in spring blooms of the eastern Bering Sea shelf, submitted to *Deep-Sea Research Part II: Topical Studies in Oceanography*, 2013; hereafter, “Prokopenko et al., submitted”). In contrast, relatively little chlorophyll *a* was detected in shelf waters in 2008, except at a few stations visited in late spring on the southernmost shelf. The timing of the cruise in 2007 corresponded with the northward retreat of sea ice and the consequent inception of marginal ice blooms, whereas sea ice retreat was at a comparatively early stage by the end of the cruise in 2008.

3.2. Nutrient Distributions in Winter Water

[13] Nitrate concentrations in shelf winter waters in 2007 and 2008 showed a characteristic decrease inshore with decreasing salinity in both years, from $\sim 25 \mu M$ in slope to $\leq 5 \mu M$ near the coast (Figure 2a). Nitrate concentrations as well as phosphate and silicic acid covaried roughly linearly with salinity throughout most of the shelf south of $60^\circ N$, as observed by others (Figure 3) [Hansell et al., 1993; Rho et al., 2005]. Note that waters bearing clear evidence of recent phytoplankton growth (as per [chlorophyll *a*] $> 1.5 \mu g L^{-1}$) were omitted from this analysis, such that the data presented here describe winter water at the inner and middle shelves, largely confined to stations under ice cover, and subsurface waters from stations at the outer shelf. Two points of inflection are discernible in the nitrate-salinity plot, each coincident with the respective hydrographic fronts that separate the three distinct shelf domains (Figure 3a): the coastal, middle, and outer shelf. The nitrate-salinity trends can be interpreted as indicating mixing of nutrient-rich slope waters with fresher, nutrient-deplete Alaska Coastal Waters inshore. Waters inshore of the 50 m isobath front derive from the relatively fresher, nutrient-poor Alaska Coastal Current [Stabeno et al., 2002a] and are diluted by river discharge, particularly from the Kuskokwim and Yukon Rivers. These rivers are notably oligotrophic and do not contribute to N and P budget of the shelf [Guo et al., 2004]. The nitrate-salinity relationship in the middle shelf domain then delineates mixing between the outer and coastal domains, with intermediate salinities of ~ 31.6 psu and nitrate concentrations averaging $10\text{--}15 \mu M$.

The outer shelf domain extends seaward from the hydrographic front at the 100 m isobath (the middle front) to the abrupt shelf break at 200 m depth. On the more northern portion of the shelf north of $60^\circ N$, additional end-members contribute to the nutrient budget, including more saline, nutrient-rich Anadyr waters and nutrient-poor freshwaters from the Yukon River [Schumacher and Kinder, 1983; Danielson et al., 2006]. The nonconservative behavior of nutrients in this region may also reflect modifications by ice formation, at the St. Lawrence polynya and leeward of the Alaska coast [Schumacher and Kinder, 1983].

[14] The decrease in nitrate concentrations shoreward derives not only from interdomain mixing but is also a consequence of benthic denitrification [Tanaka et al., 2004; Granger et al., 2011]. The N deficit is quantified here by N^* , where $N^* = [\text{dissolved inorganic nitrogen}] - 16 \times [\text{PO}_4^{3-}] + 2.9$ [Gruber and Sarmiento, 1997]. We note that this definition of N^* is technically inaccurate, as this semiconservative tracer is generally defined in units of $\mu mol kg^{-1}$; however, this discrepancy is negligible with respect to the relationships and arguments presented herein. N^* on the eastern shelf is on the order of $-3 \mu M$ in slope waters as well as in Alaska Coastal Current waters entering Unimak Pass, decreasing to as low as $-12 \mu M$ inshore and northward in both years (Figure 2c). Input from oligotrophic rivers would act to increase (dilute) N^* inshore rather than decrease it. The more rapid mineralization of P over N from the benthos was suggested as a mechanism underlying the apparent N deficit on the shelf [Coachman and Walsh, 1981]; however, this implicitly argues for an unusually high rate of organic N burial in these shelf sediments, for which there is no evidence. In a similar vein, non-Redfield stoichiometry of export production could manifest as a water column N deficit as defined by N^* . Yet benthic mineralization (if not mediated by denitrification) would subsequently remobilize nutrients to the shallow winter water column, erasing transient disequilibria in water column nutrient stoichiometries originating from organic matter export. Thus, the N deficit incurred in shelf waters arises from a net loss of N relative to P due to organic matter decomposition fuelled by nitrate respiration in sediment. The decreasing N^* trend inshore is thus superposed onto end-member mixing of nitrate among shelf domains (Figure 3d).

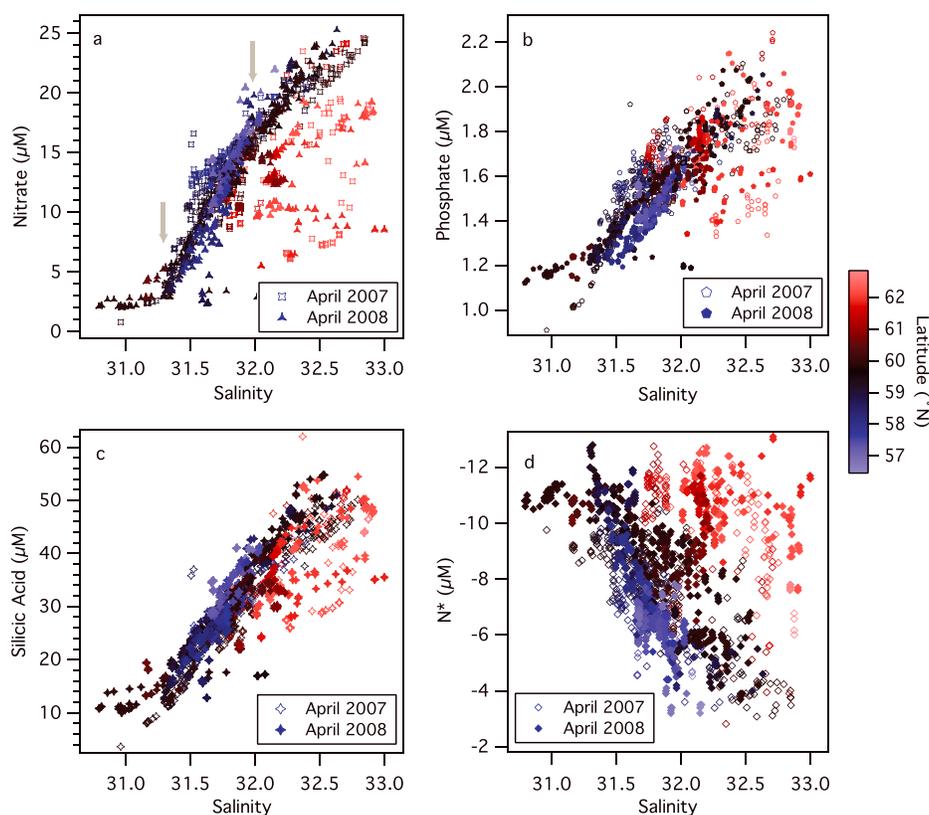


Figure 3. Nutrient concentration N^* plotted as a function of salinity in winter water of the eastern Bering Sea shelf in April 2007 and April 2008. Water column measurements are plotted for stations at which there was no apparent nutrient drawdown due to incident phytoplankton growth ($[\text{chlorophyll } a] \leq 1.5 \mu\text{g L}^{-1}$). Grey arrows mark the approximate salinity at the two hydrographic fronts, the 50 m isobath (~ 31.9 psu) and 100 m isobath (~ 31.4 psu) fronts, respectively. (a) Nitrate versus salinity. (b) Phosphate versus salinity. (c) Silicic acid versus salinity. (d) N^* versus salinity.

[15] The elevated ammonium in winter water indicates that some fixed N is recycled in situ rather than newly entrained from the slope. Ammonium was pervasive in winter water in April of 2007 and 2008, increasing shoreward from undetectable in slope waters to $4 \mu\text{M}$ inshore in both years (Figure 2b). Some nitrite was also present, though in trace amounts relative to ammonium and nitrate (data not shown). Ammonium concentrations are typically greatest immediately after the spring and fall blooms, upward of $10 \mu\text{M}$ on the middle shelf, arising largely from subsurface and/or benthic mineralization [Whitledge *et al.*, 1986; Rowe and Phoel, 1992; Rho *et al.*, 2005; Mordy *et al.*, 2008]. From late fall to late winter, ammonium concentrations decrease monotonically but persist [Whitledge *et al.*, 1986]. The lower ammonium concentrations in winter water compared to late fall could be construed as resulting from either (a) wintertime flushing of the ice-covered shelf waters with slope waters, replacing ambient dissolved inorganic N with “new” nitrate from the slope, or (b) the nitrification of ambient ammonium to nitrate during winter. In this regard, we concluded previously that some of the nitrate in winter water does originate from nitrification in situ, as evidenced by a decrease in nitrate $\delta^{15}\text{N}_{\text{NO}_3}$ inshore with increasing ammonium [Granger *et al.*, 2011]. Here we turn to the $\delta^{18}\text{O}_{\text{NO}_3}$ measurements to provide a quantitative estimate of the extent to which nitrate in winter water derives from remineralization directly on the shelf.

3.3. Contribution of Remineralization to Shelf Nitrate

[16] Nitrate $\delta^{18}\text{O}$ measured in waters of the ice-covered shelf in April of 2007 and 2008 decreased from the slope inshore and northward, particularly in 2008. Nitrate $\delta^{18}\text{O}$ in slope waters at 150 m depth was $\sim 3.2\text{‰}$, decreasing to 1.5‰ at some stations on the middle shelf in 2007, and as low as -1‰ at the inner shelf domain in 2008 (Figure 4). Qualitatively, this supports the conclusion reached from corresponding $\delta^{15}\text{N}_{\text{NO}_3}$ measurements [Granger *et al.*, 2011] that nitrate is increasingly remineralized inshore. Nitrate $\delta^{18}\text{O}$ is sensitive to the extent of nitrification, in that $\delta^{18}\text{O}_{\text{NO}_3}$ of newly nitrified nitrate is similar to and tracks the $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ of ambient seawater [Casciotti *et al.*, 2002; Buchwald and Casciotti, 2010; Buchwald *et al.*, 2012]. Buchwald *et al.* [2012] recently reported a range in $\delta^{18}\text{O}$ of newly nitrified nitrate ($\delta^{18}\text{O}_{\text{nit}}$) between -1.5‰ and 1.3‰ relative to ambient water observed in nitrifier cocultures (ammonia and nitrite oxidizers) as well as in field sample incubations. A specific $\delta^{18}\text{O}_{\text{nit}}$ value of 1.1‰ above ambient seawater was estimated from $\delta^{18}\text{O}_{\text{NO}_3}$ in the eastern Mediterranean basin, where subsurface nitrate originates exclusively from remineralization in situ [Sigman *et al.*, 2009b]. Furthermore, in that study, an admittedly sparse global nitrate isotope data compilation was best simulated in a multiple-box global ocean model if it was assumed that $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ of newly nitrified nitrate tracks the $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ of ambient water [Sigman *et al.*, 2009b].

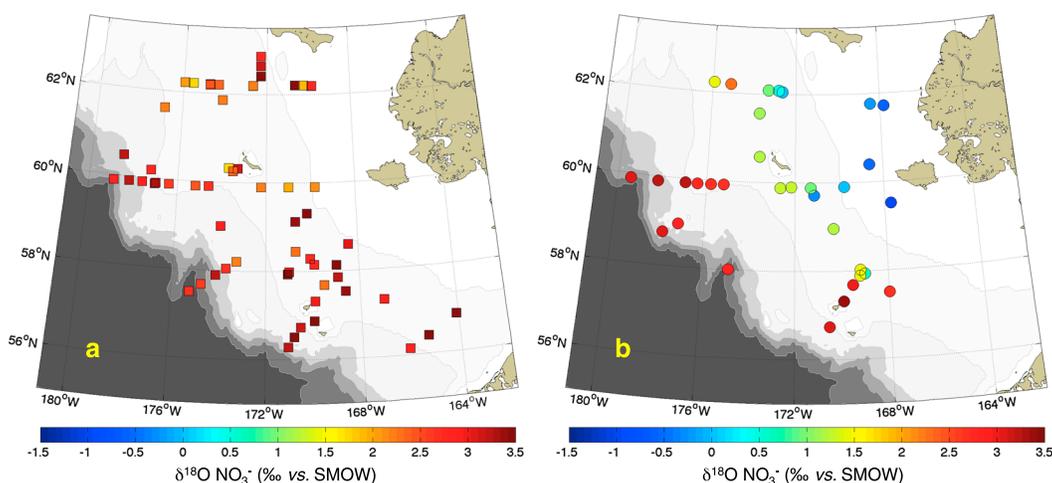


Figure 4. $\delta^{18}\text{O}_{\text{NO}_3^-}$ at bottom water depths of the eastern Bering Sea shelf to 200 m in (a) April 2007 and (b) April 2008.

[17] In our Bering shelf data set, the decrease in $\delta^{18}\text{O}_{\text{NO}_3^-}$ inshore is more pronounced in 2008 than that in 2007, which could be interpreted as indicative of a smaller proportion of remineralized nitrate on the shelf in spring 2007. However, water column oxygen and chlorophyll *a* concentrations as well as nitrate $\delta^{15}\text{N}$ suggest that the difference is due to ^{18}O enrichment of nitrate by algal assimilation in winter water in 2007, overprinting the $\delta^{18}\text{O}_{\text{NO}_3^-}$ imparted previously by nitrification (Figures S2 and S3). This difference aside, the observed decrease in $\delta^{18}\text{O}_{\text{NO}_3^-}$ in winter water from the slope inshore in both years is best explained as an increase in the proportion of newly nitrified nitrate. Indeed, nitrification is the only known mechanism for lowering ocean $\delta^{18}\text{O}_{\text{NO}_3^-}$. The $\delta^{18}\text{O}_{\text{NO}_3^-}$ of 3.2‰ in the slope end-member is elevated by $\sim 2.6\text{‰}$ relative to the expected $\delta^{18}\text{O}_{\text{nit}}$ of nitrification in this setting (i.e., relative to $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ of ambient water). This ^{18}O enrichment is partly due to nitrate assimilation in the open Bering Sea surface [Lehmann *et al.*, 2005; Granger *et al.*, 2011]. It is also partly due to a weak $\delta^{18}\text{O}$ elevation (above $\delta^{18}\text{O}_{\text{nit}}$) in the deep waters entrained into the Bering Sea surface, which largely represents the basin-scale impact of water column denitrification at the eastern Pacific margins [Lehmann *et al.*, 2005; Sigman *et al.*, 2005; Sigman *et al.*, 2009a].

[18] Benthic denitrification on the eastern shelf is not expected to confer ^{18}O enrichment to water column nitrate, because ^{18}O -enriched nitrate at the sediment depth of denitrification generally does not communicate with water column nitrate [Brandes and Devol, 1997; Lehmann *et al.*, 2004; Lehmann *et al.*, 2007; Granger *et al.*, 2011]. Rather, given active nitrification in surface sediment, which is partially coupled to underlying denitrification, nitrate released from the benthos assumes the $\delta^{18}\text{O}_{\text{nit}}$ value of newly nitrified nitrate [Granger *et al.*, 2011].

[19] In order to derive estimates of the proportion of shelf-remineralized nitrate relative to slope-derived nitrate, $\delta^{18}\text{O}_{\text{NO}_3^-}$ of shelf nitrate was compared to corresponding measurements of $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ of ambient water. Based on the evidence presented above, we assume that $\delta^{18}\text{O}_{\text{nit}} = 1.1\text{‰} + \delta^{18}\text{O}_{\text{H}_2\text{O}}$. The accuracy of this prescription is admittedly uncertain, as the $\delta^{18}\text{O}_{\text{nit}}$ produced by nitrification on the Bering shelf could differ from that inferred for the

Mediterranean and elsewhere. Nevertheless, as illustrated below, this assumption fits with the observed patterns in $\delta^{18}\text{O}_{\text{NO}_3^-}$ on the shelf. Shelf water $\delta^{18}\text{O}_{\text{H}_2\text{O}}$, measured in samples from the 2008 cruise, ranged widely, from -0.5‰ at the slope to -2.5‰ inshore (Figure S4). We restrict our analysis to the 2008 cruise samples, for which corresponding $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ were measured and for which $\delta^{18}\text{O}_{\text{NO}_3^-}$ was not evidently elevated by incident algal nitrate assimilation. A corresponding analysis of the 2007 samples is unfeasible, because the $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ of water was not measured directly and because the extent of nitrate assimilation and associated isotope effects cannot be assessed with sufficient certainty to tease out the impact of assimilation on the ambient $\delta^{18}\text{O}_{\text{NO}_3^-}$. It should also be noted that any unrecognized nitrate assimilation effect in the 2008 samples [e.g., Mordy *et al.*, 2012] would cause us to underestimate the relative importance of on-shelf nitrification as a nitrate source to springtime shelf water column.

[20] Our estimates for spring 2008 suggest that the proportion of newly nitrified nitrate on the shelf was spatially variable, from 0% near the slope to 100% inshore (Figure 5). At the inner shelf domain, nitrate stemmed entirely from remineralization in situ. This is expected, given the isolation of Alaska Coastal Waters from the potential entrainment of nitrate from slope waters in winter. On the middle shelf near the 100 m front, the proportion of newly nitrified nitrate ranged from 5% to 15%. Farther inshore along the 70 m isobath, remineralized nitrate comprised between 50% and 95% of the total water column inventory, except at the southernmost station ($\sim 57^\circ\text{N}$), at which remineralized nitrate was 25%. This latter estimate agrees with previous estimates that 20%–30% of the nitrate in winter water of the southeastern middle shelf—at the current location of the M2 mooring (Figure 1)—originates from the nitrification of ammonium released from sediment [Whitledge *et al.*, 1986]. Along the northernmost St. Lawrence line (SL), on the middle shelf, the proportion of remineralized nitrate was variable, from as low as 20% to 100% inshore. Finally, at the outer shelf domain, the proportion of newly nitrified nitrate ranged from 0% to no more than 20% of ambient nitrate. Notwithstanding some uncertainty in the defined $\delta^{18}\text{O}_{\text{nit}}$ ($1.1\text{‰} + \delta^{18}\text{O}_{\text{H}_2\text{O}}$) and the potential for variations in the ascribed slope

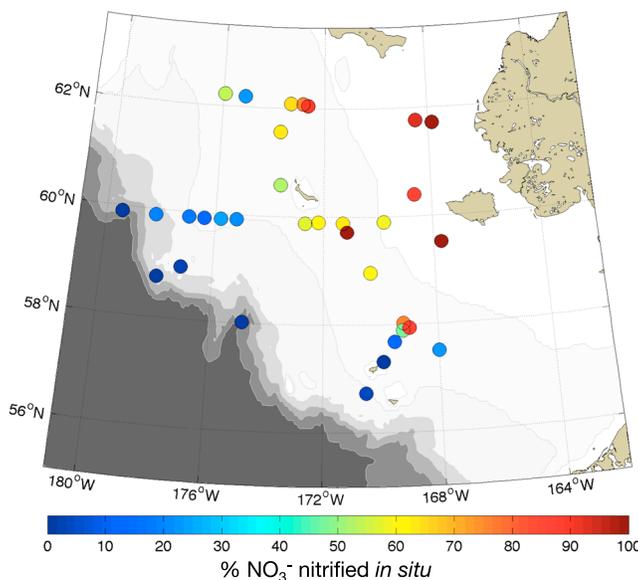


Figure 5. The proportion of ambient nitrate that was supplied to shelf waters by nitrification in situ in April 2008.

$\delta^{18}\text{O}_{\text{NO}_3}$ end-member ($\sim 3.2\text{‰}$), the respective measurement errors associated with $\delta^{18}\text{O}_{\text{NO}_3}$ (0.3‰) and $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ (0.05‰) propagate to standard deviations ranging between $\pm 10\%$ and $\pm 20\%$ among estimates of the fraction of remineralized nitrate. Overall, the inherent spatial patterns indicate that nitrate inshore is largely sourced from mineralization in situ rather than from advection of “new” nutrients from the slope.

[21] The proportion of remineralized nitrate also appeared to vary in time at given locations. In particular, $\delta^{18}\text{O}_{\text{NO}_3}$ measured in 2008 at a station located at the approximate location of the M4 mooring (57.9°N , 169.1°W ; Figure 6b), which was visited at three consecutive times during the cruise, yielded noticeably different estimates of remineralized nitrate each time, from 50% to 75% and 85%, respectively (Figure 5). The station at M4 corresponds to an area at the approximate junction of distinct water masses [Stabeno *et al.*, 2007]. The weakest remineralization signal at this station

associated with the highest concentrations of nitrate and silicic acid (14 and $31 \mu\text{M}$, respectively) and the highest salinity (31.8), all of which are characteristic of more off-shelf waters, whereas the largest fraction of nitrified nitrate was associated with the lowest water column nitrate and silicic acid concentrations (9 and $24 \mu\text{M}$) and salinity (31.6), characteristic of waters with more inshore character. Thus, the different $\delta^{18}\text{O}_{\text{NO}_3}$ likely reflect the relatively dynamic hydrography of this location.

[22] The values derived here likely constitute *conservative* estimates of the proportion of regenerated nitrate in shelf waters in April 2008, because any concurrent biological N transformation would conspire to *increase* $\delta^{18}\text{O}_{\text{NO}_3}$ in winter water from its nitrified value. As mentioned above, any nitrate assimilation would cause an enrichment in $\delta^{18}\text{O}_{\text{NO}_3}$ with an isotope effect of $\sim 5\text{‰}$ [e.g., DiFiore *et al.*, 2009], which would erase the imprint of nitrification in winter water. This effect also applies if nitrate assimilation in the fall and/or

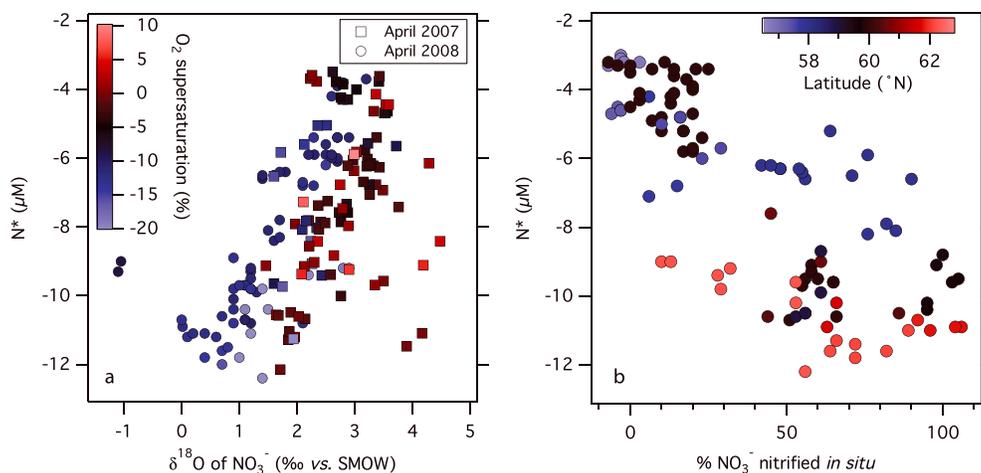


Figure 6. (a) N deficit (N^*) in water column samples versus corresponding $\delta^{18}\text{O}_{\text{NO}_3}$ in April 2007 and 2008. (b) N^* versus the proportion of nitrate nitrified in situ relative to imported slope nitrate in April 2008.

winter was active but did not fully consume the available nitrate, in which case the high $\delta^{18}\text{O}$ nitrate would be left in the winter water column [e.g., *Wankel et al.*, 2007]. Second, nitrate from the denitrification zone located deeper in the sediments could plausibly be released to the water column by bioturbation, which would raise the $\delta^{18}\text{O}$ (and $\delta^{15}\text{N}$) of bottom water nitrate. Finally, nitrate that was remineralized in waters bearing a more marine $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ end-member and is then mixed with more inshore, *nitrate-deplete* waters that have a lower $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ (Figure S4) will lead to a nitrate-to-water difference that underrepresents the concentration of regenerated nitrate. Thus, N transformations cooccurring with nitrification would act to raise the $\delta^{18}\text{O}_{\text{NO}_3}$ above its nitrification value, such that the estimated proportion of remineralized nitrate at many stations in 2008 is likely greater than that derived here.

[23] We speculate that much of the mineralization of organic material evidenced by the nitrate isotopes in winter water may occur in association with benthic mineralization. Shelf blooms result in a substantial export of algal biomass to the subsurface (Prokopenko et al., submitted), with most of it apparently reaching the shallow benthos, as evidenced by thorium-234 deficits throughout the water column following the spring blooms [*Moran et al.*, 2012]. In addition, the N deficit on the shelf (N^*) correlates with the fraction of nitrate nitrified in situ, which was derived from $\delta^{18}\text{O}_{\text{NO}_3}$, and such a correlation is most easily explained if the remineralization of shelf nitrate is driven by benthic mineralization as reflected in the extent of benthic denitrification (Figure 6) [*Granger et al.*, 2011]. The relationship also reveals that $\delta^{18}\text{O}_{\text{NO}_3}$ was comparatively more ^{18}O enriched for a given N^* value in 2007, further supporting the view that $\delta^{18}\text{O}_{\text{nit}}$ of the newly nitrified nitrate was overprinted by nitrate assimilation in the ice-covered water column in 2007.

[24] The spatial distribution of regenerated nitrate on the eastern shelf suggests that relatively little nitrate is newly entrained from slope waters inshore of the 70 m isobath, at least from M4 northward. This appears consistent with observations of shelf hydrography. Winter winds drive mean off-shelf Ekman transport along most of the eastern shelf [*Danielson et al.*, 2012a], with evidence of localized on-shelf transport. A tidally induced anticyclonic flow has been documented around the Pribilof Islands, which introduces nutrient-rich waters from the 100 m isobaths westward to the middle shelf [*Kowalik and Stabeno*, 1999; *Stabeno et al.*, 2008]. This feature appears corroborated by the elevated proportion of slope-derived nitrate to the northeast of the Pribilof Islands. *Mordy et al.* [2010] noted that, while many satellite-tracked drifters that have been deployed at the outer shelf follow bathymetry, some are entrained by the on-shelf flow that originates west of the Pribilof Islands and extends northward, stalling near the 70 m line south of St. Matthew Island; this also appears consistent with the patterns observed here.

[25] Overall, the results illustrate that much of the nitrate available for the spring bloom upon ice retreat originates from mineralization in situ. The inherent capacity of shallow continental shelves to retain nutrients and systematically remobilize these to the sunlit surface underlies the highly productive nature of these systems [*Nixon*, 1981]. In this respect, $\delta^{18}\text{O}_{\text{NO}_3}$ provides an explicit tracer of the Bering shelf's capacity to retain and resupply fixed N for primary production.

3.4. Seasonal Entrainment of Slope Waters and Shelf Climatology

[26] The proportion of slope-derived nitrate on the eastern shelf in April 2008 relative to that remineralized in situ is presumably representative of a so-called “cold year.” In such years, prevailing northwesterly winter winds are associated with a lower net discharge of eastern shelf waters to the Arctic at Bering Strait, in favor of compensating discharge of Anadyr waters [*Danielson et al.*, 2012b]. The summertime cold pool on the middle shelf, which restricts exchange with warmer surrounding waters [*Coachman and Charnell*, 1979; *Wyllie-Echeverria and Wooster*, 1998; *Stabeno et al.*, 2001; *Zhang et al.*, 2012], is also more persistent in cold years and typically extends to more southerly reaches beyond the Pribilof Islands [*Stabeno et al.*, 2007]. *Stabeno et al.* [2001] found that cold years with increased sea ice coincide with reduced on-shelf fluxes of salty nutrient-rich waters. Accordingly, *Danielson et al.* [2012a] observed that mean annual on-shelf transport along the eastern shelf break is significantly reduced compared to that in less frequent “warm” years. The differences of shelf circulation between cold and warm years may have implications for the N budget of the eastern shelf. Nitrate and its sister nutrients, phosphate and silicic acid, may be involved in proportionally more cycles of assimilation and remineralization during cold years, given less nutrient replenishment from slope waters. This could result in a larger proportional N loss from denitrification due to repeated cycles of production and remineralization and, thus, progressively less N available for primary production as shelf waters age. This potential dynamic merits consideration in the context of changing physical conditions on the shelf into the future, which could manifest as a shift in the mean prevailing wind directions associated with the position of the Aleutian Low [*Niebauer et al.*, 1999; *Stabeno et al.*, 2001]. Shelf N availability will depend on the physical changes that the future may bring to the Bering shelf, which are as yet difficult to forecast. Nevertheless, a predictive understanding of the biogeochemical sensitivities to the physical conditions of the Bering shelf appears within reach.

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