

Distribution of N* in the Sea of Okhotsk and its use as a biogeochemical tracer of the Okhotsk Sea Intermediate Water formation process

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Received 1 November 2005; received in revised form 16 May 2006; accepted 26 May 2006

Available online 7 July 2006

Abstract

Nutrient data collected from the Sea of Okhotsk in July 1998, September 1999, and June 2000 were used to calculate N*, the deviation from the stoichiometric relationship between nitrogenous nutrients and phosphate. Intermediate water from east of Sakhalin to the Bussol Strait had low N* values ($< -5 \mu\text{mol kg}^{-1}$), which led to very low N* values of approximately $-11 \mu\text{mol kg}^{-1}$ in the northwestern shelf bottom water. The low N* distribution is consistent with distributions of low temperature and low salinity at densities around $26.8\sigma_\theta$, which are characteristic of the Okhotsk Sea Intermediate Water (OSIW) and the Dense Shelf Water (DSW) that is a source water of the OSIW. To assess N* as a new tracer of OSIW formation and to determine whether the low N* signature is created by *in situ* biogeochemical processes or reflects a conservative property of the water mass, we analyzed the nitrogen isotopic ratio of nitrate, $\delta^{15}\text{NO}_3^-$. Although low N* usually suggests the occurrence of denitrification in a water column with large isotopic fractionation, neither the intermediate nor shelf bottom waters had high $\delta^{15}\text{NO}_3^-$ values, indicating that denitrification in the water column did not cause these low N* values. Sedimentary denitrification with little isotopic fractionation and phosphate dissolution from sediment likely caused the extremely low N* of the shelf bottom water. The low N* of the intermediate water must thus be unaffected by *in situ* biogeochemical processes and instead reflect the intrusion of shelf bottom water into the offshore intermediate layer. Our results show that N* acts as a conservative tracer of the OSIW formation process. Because the water masses characterized by low N* are created at the shelf bottom, N* is a valuable tracer of DSW which originates from continental shelf areas.

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Keywords: Sea of Okhotsk; Sedimentary denitrification; Nitrogen isotopes; Tracers; Ocean circulation

1. Introduction

The Okhotsk Sea Intermediate Water (OSIW) is characterized by low temperature ($\sim 0^\circ\text{C}$), low salinity (~ 33.45), and high oxygen content ($\sim 170 \mu\text{mol kg}^{-1}$) at densities of approximately $26.75\text{--}26.85\sigma_\theta$ (Talley, 1991; Wong et al., 1998; Itoh et al., 2003). The OSIW is

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believed to be a source water that ventilates the North Pacific Intermediate Water (NPIW) and is defined by a salinity minimum along an isopycnal surface of approximately $26.8\sigma_\theta$ (Talley, 1991; Wong et al., 1998; Itoh et al., 2003). Therefore, to clarify NPIW formation, it is important to understand the process of OSIW formation. Previous studies of OSIW have applied various tracers, including temperature, salinity, dissolved oxygen, oxygen isotopes, and chlorofluorocarbons (CFCs), to characterize this water mass (Kitani, 1973; Talley, 1991; Wong et al., 1998; Yamamoto et al., 2001; Itoh et al., 2003; Yamamoto-Kawai et al., 2004). These studies have suggested the following OSIW formation process. Dense Shelf Water (DSW), as dense as $27.0\sigma_\theta$, is formed at the northwestern shelf by surface cooling and brine injection during sea ice formation (Kitani, 1973). This DSW is ventilated to an equilibrium depth and subsequently moved southward by the East Sakhalin Current and mixed isopycnally with the Western Subarctic Water coming from the North Pacific (Talley, 1991; Yamamoto et al., 2001; Mizuta et al., 2003). In the Kuril Basin, this water is further modified by both isopycnal mixing with Soya Warm Current waters and diapycnal mixing around the Kuril Straits (Watanabe and Wakatsuchi, 1998; Wong et al., 1998; Itoh et al., 2003; Yamamoto-Kawai et al., 2004). Thus formed, the OSIW flows out from the Bussol Strait to join in the formation of the NPIW (Talley, 1991; Watanabe and Wakatsuchi, 1998; Yamamoto-Kawai et al., 2004). Here, we propose N^* as a new DSW tracer controlled by completely different mechanisms than previous tracers.

Gruber and Sarmiento (1997) introduced the tracer $N^* = ([NO_3^-] - 16[PO_4^{3-}] + 2.9) \times 0.87$ to investigate the nitrogen budget between a specific water mass and the atmosphere, assuming that an ordinary biological ocean process consumes or regenerates nitrogen and phosphorus at a constant N/P ratio (i.e., 16) and does not affect the N^* value unless nitrogen is exchanged between the ocean and the atmosphere. In this study, N^* is defined as $([NO_3^-] + [NO_2^-] + [NH_4^+] - 16[PO_4^{3-}] + 2.9) \times 0.87$ because water samples from the subsurface and benthic layers of the Sea of Okhotsk contain large amounts of ammonium and nitrite as a result of organic matter decomposition. Denitrification, consuming nitrate instead of oxygen for bacterial respiration in low-oxygen water masses or low-oxygen pore waters in sediments, decreases N^* ; nitrate is consumed regardless of phosphate levels (e.g., Lehmann et al., 2005). Terrestrial and atmospheric nitrogen inputs increase N^* ; river waters have N/P ratios much higher than the

seawater value of 16 (e.g., Tian et al., 1993), and atmospheric deposition supplies nitrate regardless of phosphate levels. Nitrogen fixation also increases N^* ; however, this process does not occur in the high-latitude Sea of Okhotsk, which is outside the habitat range of nitrogen fixers (Capone et al., 1997). As noted above, the N^* value should prove a useful tracer of water masses affected by denitrification and terrestrial and atmospheric nitrogen inputs. Because biological production is extremely high in the northwestern shelf region of the Sea of Okhotsk (Saitoh et al., 1996; Sorokin and Sorokin, 1999), denitrification may occur in or under the DSW, and therefore the low N^* signature may serve as a tracer of OSIW formation. Unlike other conservative tracers, the low N^* signature is not created at the sea surface, but this signature may be modified by denitrification within the water column and at the ocean floor. Therefore, to assess changes in the low N^* signature during the process of OSIW formation, we also measured the nitrogen isotopic ratio of nitrate ($\delta^{15}NO_3^-$), which is a tracer of water masses affected by denitrification and terrestrial and atmospheric nitrogen inputs.

Because $\delta^{15}NO_3^-$ is determined by nitrate uptake by phytoplankton (e.g., Altabet et al., 1991; Nakatsuka and Handa, 1997; Sigman et al., 1999; Yoshikawa et al., 2005), nitrogen fixation (Montoya et al., 2002), terrestrial and atmospheric nitrogen inputs (Fry, 1991; Paerl and Fogel, 1994; Hastings et al., 2004), and denitrification in a water column (Brandes et al., 1998; Voss et al., 2001; Sigman et al., 2003), $\delta^{15}NO_3^-$ is widely used as a tracer of the oceanic nitrogen cycle. Ordinarily, $\delta^{15}NO_3^-$ in the euphotic layer rises to the surface because of nitrate uptake by phytoplankton and has a constant value below the euphotic layer. When denitrification occurs in a water column, $\delta^{15}NO_3^-$ increases because of large isotopic fractionation (Brandes et al., 1998; Voss et al., 2001; Sigman et al., 2003). On the other hand, if sedimentary denitrification occurs, $\delta^{15}NO_3^-$ does not increase because of near zero isotopic fractionation (Brandes and Devol, 1997; Sigman et al., 2003; Lehmann et al., 2005). When terrestrial and atmospheric nitrogen inputs occur, $\delta^{15}NO_3^-$ decreases because the $\delta^{15}N$ values of terrestrial and atmospheric nitrogen are approximately 0‰ and much lower than that of marine nitrogen (Fry, 1991; Paerl and Fogel, 1994; Hastings et al., 2004). Thus, denitrification in a water column and terrestrial and atmospheric nitrogen inputs alter both $\delta^{15}NO_3^-$ and N^* , whereas sedimentary denitrification does not alter $\delta^{15}NO_3^-$, but does alter N^* . By comparing N^* with $\delta^{15}NO_3^-$, we discuss the processes that affect N^* in the Sea of

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