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Selective depressions of surface silicic acid within cyclonic mesoscale eddies in the oligotrophic western North Pacific

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ABSTRACT

To reveal spatial dynamics of silicic acid [$Si(OH)_4$] in the poorly sampled oligotrophic western North Pacific, we investigated the surface distribution of $Si(OH)_4$ and associated biogeochemical parameters by using an underway survey system with a highly sensitive nutrient analyzer along the 138°E transect (between 30 and 34°N) and the 155°E transect (between 10 and 35°N) during the summers of 2007 and 2008. Surface $Si(OH)_4$ concentrations ranged from the detection limit (11 nmol L^{-1}) to 2462 nmol L^{-1}. High $Si(OH)_4$ concentrations (> 1000 nmol L^{-1}) and dynamic fluctuations were generally observed north of 23°N, while consistently stable low concentrations of 415–751 nmol L^{-1} were observed south of 23°N. Surface nitrate + nitrite (N+N) and phosphate (PO_4^{3-}) were typically depleted to < 20 nmol L^{-1}, except for PO_4^{3-} in the area south of 16°N. The majority of the study area was characterized by high-$Si(OH)_4$ and low-N+N and PO_4^{3-}. However, submesoscale/mesoscale depressions of $Si(OH)_4$ were locally observed in the cyclonic eddy fields north of 23°N. Among a total of six $Si(OH)_4$ depressions within the eddies, a complete $Si(OH)_4$ depletion (< 11 nmol L^{-1}) was observed on the cyclonic side near the Kuroshio axis (33.1°N, 138°E). This depletion was closely coupled with a diatom bloom, suggesting that $Si(OH)_4$ was exhausted by diatoms. All of the $Si(OH)_4$ depressions were selective and not accompanied by local depressions of N+N and PO_4^{3-}. This unique phenomenon might be driven by biogeochemical processes such as selective Si export (Si pump), anomalous Si uptake associated with diatom physiology, and/or Si uptake supported by N_2 fixation.

1. Introduction

Diatoms are currently responsible for 40% of primary production in the world's oceans (Nelson et al., 1995; Falkowski et al., 1998) and have a potential impact on new and export production (Legendre and Fèvre, 1989; Goldman, 1993; Scharek et al., 1999a, 1999b). Silicic acid [$Si(OH)_4$] is an essential nutrient for the growth of diatoms and is therefore an important factor that ultimately controls diatom production. The concentration of nutrients in the surface waters of the subtropical oceans is generally lower than that in equatorial, subarctic, and polar oceans owing to strong stratification and a low upward supply of nutrients. However, even in highly oligotrophic subtropical surface waters, $Si(OH)_4$ remains at conventionally detectable levels (> 0.1 μmol L^{-1}) while nitrate (NO_3^-), nitrite (NO_2^-), and phosphate (PO_4^{3-}) are near or at undetectable levels (Brzezinski and Nelson, 1995; Brzezinski et al., 1998). The surface water concentrations of $Si(OH)_4$ have been reported to be 0.6–3.0 μmol L^{-1} in the central and eastern parts of the subtropical North and South Pacific, including the Hawaii Ocean Time-series (HOT) program deep water station "ALOHA" (Brzezinski et al., 1998, 2011; Raimbault et al., 2008; Villareal et al., 2012; Krause et al., 2013). Furthermore, the concentrations of 0.4–0.9 μmol L^{-1} have been reported in the western subtropical North Atlantic, including the Bermuda Atlantic Time-series Study (BATS) site (Brzezinski and Nelson, 1995; Krause et al., 2009, 2010).

$Si(OH)_4$ concentrations in the surface waters of subtropical oceans are similar to the threshold concentrations (0.2–1.8 μmol L^{-1}) of net Si uptake by Si-limited cultured diatoms, *Chaetoceros debilis*, *Skeletonema costatum*, *Thalassiosira* spp., *Ditylum brightwellii*, and *Licmophora* sp. (Paasche, 1973; Conway and Harrison, 1977), and tend to be less than the half-saturation constants (0.2–97.4 μmol L^{-1}) for Si uptake by 15 species of cultured diatoms (Martin-Jézéquel et al., 2000). This information suggests that ambient $Si(OH)_4$ concentrations restrict Si uptake; in fact, a large number of field studies have confirmed the presence of Si uptake limitations in the subtropical North Atlantic and North Pacific (Brzezinski and Nelson, 1996; Brzezinski et al., 1998, 2011; Krause et al., 2010). However, several studies have demonstrated that

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diatom blooms in the central and eastern subtropical North Pacific during summer have highly efficient Si uptake kinetics, even at low $Si(OH)_4$ concentrations of ~1 μmol L^{-1} (Brzezinski et al., 1998, 2011; Krause et al., 2012, 2013). This observation implies that subtropical diatom blooms have the potential for drawing down $Si(OH)_4$ concentrations less than those observed in culture.

The mechanisms of the development of subtropical diatom blooms and parallel $Si(OH)_4$ removal are complex and worthy of investigation to improve our understanding of the biogeochemistry of subtropical oceans. Wilson et al. (2013) suggested that vertical nutrient supply, which stimulates the development of diatom blooms, is driven by physical mechanisms such as mixing at the subtropical front, breaking of internal waves, shoaling of the mixed layer depth, mesoscale eddy interactions, and winter mixing. Among them, mesoscale eddies sometimes enhance diatom blooms and anomalous $Si(OH)_4$ removal (Benitez-Nelson et al., 2007; Krause et al., 2010). Benitez-Nelson et al. (2007) suggested that the occurrence of a diatom bloom within a cyclonic eddy near the HOT station ALOHA would enhance the selective removal of $Si(OH)_4$ relative to $NO_3^- + NO_2^-$ (N+N). This hypothesis assumes the presence of "Si pumps," resulting in the selective export of Si relative to N or selective remineralization of N relative to Si, as observed in high-NO_3^- and low chlorophyll (HNLC) systems (Dugdale et al., 1995; Dugdale and Wilkerson, 1998).

$Si(OH)_4$ removal by subtropical diatoms also appears to be controlled by unique biological mechanisms. The energy for diatom cell wall silicification is generally linked to aerobic respiration rather than photosynthesis (Martin-Jézéquel et al., 2000). The extent of cell wall silicification is inversely correlated to the growth rate of diatoms under Si-replete condition; therefore, the assimilation of Si is highly different from that of other nutrient elements such as N, P, and Fe, which are closely linked to photosynthetic processes (Martin-Jézéquel et al., 2000). Numerical studies have demonstrated that N- or Fe-limited diatoms have a high cellular/uptake Si:N ratio of >1 (Harrison et al., 1976, 1977; Hutchins and Bruland, 1998; Takeda, 1998), whereas nutrient-replete diatoms have an Si:N ratio of approximately 1 (Brzezinski, 1985). Thus, a highly oligotrophic subtropical system, where nutrient limitations vary in space and time (Moore et al., 2013), may influence the selective $Si(OH)_4$ removal by diatoms. Furthermore, biological N_2 fixation potentially contributes to the development of diatom blooms in NO_3^--depleted subtropical surface waters. In the central and eastern subtropical North Pacific during summer, N_2-fixing diazotrophs, *Trichodesmium* spp. and *Richelia intracellularis*, were found to frequently occur together with the blooms of diatoms such as *Hemiaulus hauckii*, *Rhizosolenia* spp., and *Mastogloia woodiana* (Scharek et al., 1999a, 1999b; Dore et al., 2008; Villareal et al., 2011, 2012; Karl et al., 2012). Among the diatom species, *H. hauckii* and *Rhizosolenia* spp. were also found to often harbor *R. intracellularis* [i.e., diatom–diazotroph associations (DDAs)]. These DDAs were reported to aggregate and rapidly export to deeper water layers (Scharek et al., 1999a, 1999b; Villareal et al., 2011; Karl et al., 2012). Thus, N_2 fixation by these diazotrophs may play an important role in $Si(OH)_4$ removal by diatoms in the sense of non-limited growth.

The western part of the subtropical North Pacific is one of the ultra-oligotrophic domains of the world's oceans (Hashihama et al., 2009). The surface concentrations of N+N and PO_4^{3-} in this domain are extremely low and frequently subnanomolar. Furthermore, this domain is characterized by active N_2 fixation and the occurrence of *Trichodesmium* spp. and DDAs (Kitajima et al., 2009; Shiozaki et al., 2010). Despite recent progress in N and P studies within the western subtropical North Pacific, knowledge about Si dynamics, even regarding the surface distributions of $Si(OH)_4$, remains limited. Therefore, the present study aimed to investigate the distribution of $Si(OH)_4$ and other nutrients in the surface waters of the oligotrophic western North Pacific using a highly sensitive technique. The study also aimed to examine the relationship between $Si(OH)_4$ concentrations and associated parameters including hydrography, abundance of diatoms and diazotrophs, and pigment signatures.

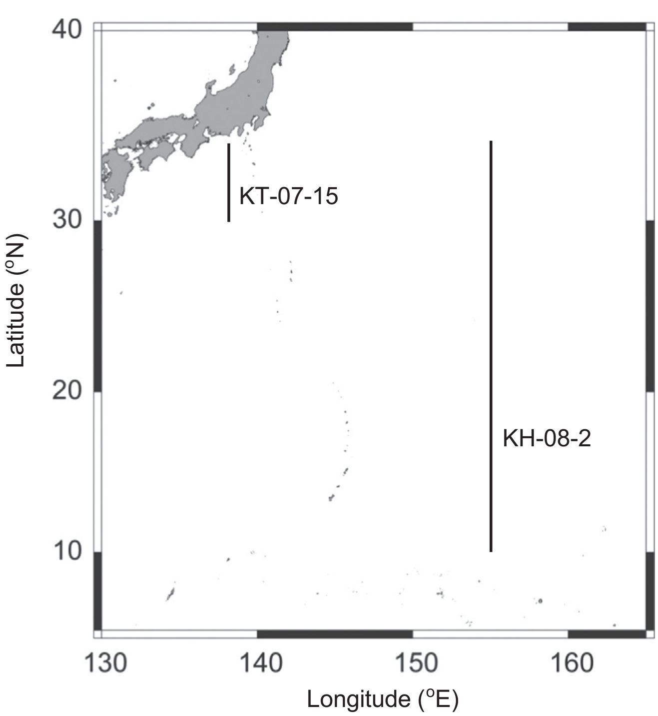

Fig. 1. KT-07-15 and KH-08-2 cruise tracks along the 138°E meridian and the 155°E meridian, respectively.

2. Materials and methods

Observations were conducted in the western subtropical North Pacific during KT-07-15 cruise on the research vessel (R/V) *Tansei-maru* from June 30 to July 1, 2007 and during KH-08-2 cruise on the R/V *Hakuho-maru* from September 1 to 10, 2008. Underway surveys were performed on a transect line between 30 and 34°N along 138°E during the KT-07-15 cruise and on a transect line between 10 and 34°N along 155°E during the KH-08-2 cruise (Fig. 1). Using the ship's intake water that was pumped from a depth of ca. 5 m (hereafter referred to as "the surface"), the water temperature, salinity, and in vivo chlorophyll fluorescence were measured continuously with a thermosalinometer (Ocean Seven 301, Idronaut, Brugherio, Italy) and a fluorometer [Minitrack, Chelsea Technologies Group, Surrey, United Kingdom (U.K.)]. Based on the method of Hashihama et al. (2010), chlorophyll fluorescence was converted to the concentration of total chlorophyll *a* [=chlorophyll *a* (Chl *a*)+divinyl chlorophyll *a* (DV chl *a*)] using pigment data that was determined through high-performance liquid chromatography (HPLC) as described below.

Nutrient concentrations in the intake water were measured using highly sensitive colorimetry that consisted of an AutoAnalyzer II (Technicon, now SEAL Analytical, Hampshire, U.K.) and Liquid Waveguide Capillary Cells [World Precision Instruments, Sarasota, Florida, United States of America (U.S.A.)] as described in Hashihama et al. (2009, 2010, 2013) for N+N, NO_2^-, and PO_4^{3-}, and in Hashihama and Kanda (2010) for $Si(OH)_4$. Nutrient analysis was conducted as a series of segmented continuous measurements as the flow lines of the analytical system were routinely washed. The detection limits that were estimated as being three times the