doi: 10.3724/SP.J.1085.2012.00211

December 2012 Vol. 23 No. 4: 211-216

The distribution and concentration of particulate biogenic silica in surface waters of Prydz Bay, Antarctica, during the austral summer of 2011

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Received 26 August 2012; accepted 29 Sepember 2012

Abstract The concentrations and distributions of particulate biogenic silica (PBSi) in the upper surface waters of Prydz Bay, Antarctica, were investigated during the 27th Chinese National Antarctic Research Expedition cruises of January 2011. We aimed to characterize the correlations between PBSi and plankton, nutrients and particulate organic carbon. The results showed that the concentrations of biogenic silica ranged from 0.76—19.72 μmol·dm^{-3} and the average concentration of biogenic silica was 6.06 μmol·dm^{-3}. The distribution of surface PBSi had significant regional characteristics: The concentrations were higher south of 67°S than to the north. The distribution of PBSi, chlorophyll ***a*** and particulate organic carbon showed similar patterns, and PBSi distribution had a negative correlation with that of silicate. In the vertical direction, the mole ratio of PBSi and POC (Si_{bio}/C_{org}) decreased with increasing depth. This trend indicated a higher rate of PBSi dissolution, or a lower rate of organic matter remineralization rate, in the upper 200 m.

Keywords **biogenic silica, particle, phytoplankton, particulate organic carbon, Prydz Bay**

Citation: Hu C Y, Shen C, Zhang H S. The distribution and concentration of particulate biogenic silica in surface waters of Prydz Bay, Antarctica, during the austral summer of 2011. Adv Polar Sci, 2012, 23:211-216, doi: 10.3724/SP.J.1085.2012.00211

0 Introduction

There has been a major increase in the number of studies focusing on the silicon (Si) biogeochemical cycle over the last two decades. Some researchers believe that diatoms are one of the dominant phytoplankton responsible for export production from the surface ocean[1-5]. This is believed to contribute to the transport of particulate matter, including carbon, to the deep ocean via a process known as the biological pump. Consequently, silicate and silica may play an important role in the global carbon cycle, thereby affecting the world's climate[4-5]. Biogenic silica (BSi) is produced in surface waters of the world's oceans, mostly by diatoms, but also by radiolarians and silicoflagellates[6]. BSi is one of the major biogenic components of oceanic sediments, and provides a tool for the reconstruction of past variations in the efficiency of the biological pump[6-7]. Thus, given the reproducibility of the BSi signal and its considerable potential as a paleoceanographic tool, biogeochemists need a better understanding of the mechanisms controlling its production and fate in today's ocean.

Diatoms are a critical component of the biological pump in the Southern Ocean, and particulate biogenic silica (PBSi) can be used as a proxy for carbon production in surface waters[8]. The Southern Ocean represents a crucial study area for better comprehension of the global biogeochemical cycles of silicon and carbon. Recent studies have shown that the high BSi accumulation rates are related to a higher BSi rain rate in the Southern Ocean, which are directly related to unusually high BSi production in surface waters[9-10]. To understand the processes of BSi production in surface waters, PBSi distribution and the correlation among PBSi and phytoplankton, nutrients and particulate organic carbon (POC) in the upper surface waters of Prydz Bay were investigated during the twenty seventh Chinese

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National Antarctic Research Expedition (the 27th CHINARE) cruises. Differences between annual concentrations during the 24th—27th CHINARE cruises are also discussed.

1 Materials and methods

1.1 Study area and sampling

We collected samples on four cruises of the R/V *XUE LONG* icebreaker between February 2005 and January 2011. The sampling period of the 27th CHINARE cruise was conducted from 1—16 January 2011, in Prydz Bay, Antarctica. The sampling stations are presented in Figure 1, with the sampling transects crossing the edge of the ice shelf, the continental shelf, the continental slope and the deep ocean area. PBSi samples during the 24th—26th CHINARE were collected from 26 February until 5 March 2005, 7—18 February 2009 and 13—26 February 2010.

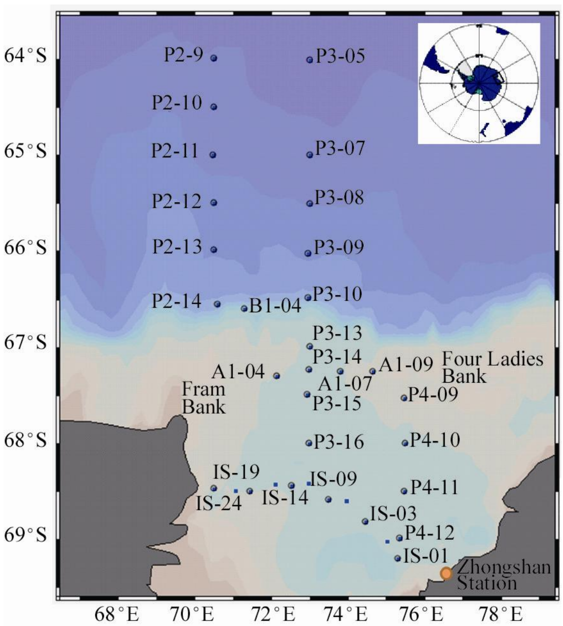

Figure 1 The 27th CHINARE cruise sampling stations in Prydz Bay.

For PBSi extractions, 2 L samples were vacuum filtered onto 0.4 μm polycarbonate membranes. For POC determinations, between 2 L and 3 L were vacuum filtered onto pre-combusted Whatman GF/F filters. For chlorophyll *a* (chl *a*) extraction, 0.5 L of seawater was filtered onto WhatmanGF/F filters using vacuum filtration. All filters were then frozen and stored for further analysis.

1.2 Sample analysis

PBSi filters were dried in an oven (60℃) for 24 h and processed using the hot NaOH digestion method of Tréguer et al. for PBSi samples in ocean water[11]. POC filters were dried at 60℃ for 24 h, then treated via fuming with HCl to remove carbonates. Finally, filters were later analyzed for carbon with a TOC–SSM5000 analyzer. Chl *a* concentrations were determined using Turner Designs fluorometer, Model 10. Silicate (SiO_3^{2-}-Si) samples were analyzed using the method in "Specifications for Oceanographic Survey" (GB/12763.4-2007).

2 Results and discussion

2.1 PBSi distribution in Prydz Bay

The concentrations of PBSi in the surface waters of Prydz Bay during the austral summer of 2010—2011 ranged from 0.76 to 19.72 μmol·dm^{-3}, with an average concentration of 6.06 μmol·dm^{-3}, which is similar to the concentrations of PBSi (0.1—18.9 μmol·dm^{-3}) found in the surface waters of the Weddell Sea during the austral summer of 2006[12]. The distribution of PBSi in surface water shows a south-north decrease in concentration (Figure 2a): PBSi concentration in the southern area of 67°S is higher than in the northern area of 67°S. According to hydrogeological conditions, four different study areas were partitioned, i.e., the edge of ice shelf, continental shelf, continental slope and deep ocean. The average concentrations at these four areas were 8.80, 2.66, 1.87, and 2.56 μmol·dm^{-3}, respectively (Figure 2b). The highest concentration of PBSi was found at station P3-16, and the lowest at station P3-10.

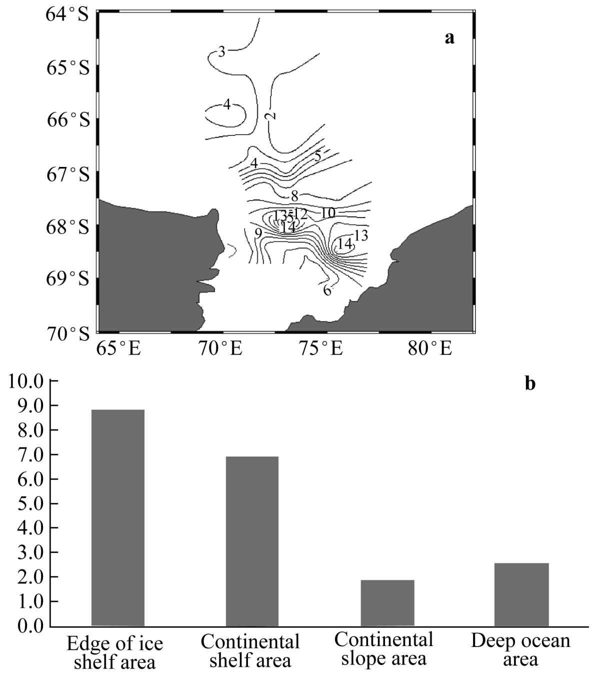

Figure 2 **a**, Distribution of PBSi in surface waters and **b**, in different areas of Prydz Bay in 2011 (unit is μmol·dm^{-3}).

Figure 3 shows the vertical distribution of PBSi in the water column. The concentration in the upper waters was higher than in deeper water. In transect P3 (73°E), the profile concentration changed dramatically in the area south of 67°S, and only slightly in the area north of 67°S. In the upper 100 m of the water column south of 67°S, the average concentration was 3.66 μmol·dm^{-3}, decreasing to 0.58

μmol·dm^{-3} below 100 m. However, north of 67°S the concentration fell to 1.81 μmol·dm^{-3} in the upper 100 m and decreased to 0.26 μmol·dm^{-3} below 100 m.

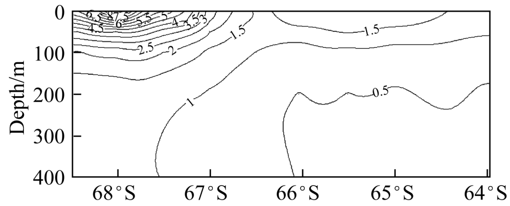

Figure 3 PBSi profile of transect P3 (73°E) in Prydz Bay (unit is μmol·dm^{-3}).

Figure 4 shows the average concentrations of PBSi in the surface waters of Prydz Bay during the austral summers of 2008—2011. The average concentration of PBSi (14.11 μmol·dm^{-3}) in the austral summer of 2008 was much higher than in other years. The lowest average concentration (5.15 μmol·dm^{-3}) was found in 2009. In 2010 and 2011, the average concentrations were 7.66 and 6.06 μmol·dm^{-3}, respectively. The surface distribution of PBSi in different years is shown in Figure 5. In 2009 and 2011, the concentrations in surface waters of the P3 transect show the same decreasing trend from the edge of the ice shelf area in the bay to the deep ocean area outside the bay.

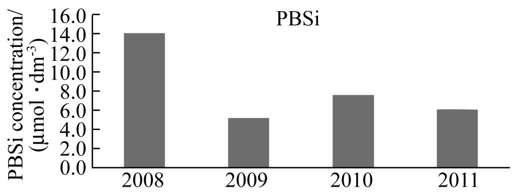

Figure 4 Annual variation of PBSi concentrations in surface waters of Prydz Bay during the austral summers of 2008—2011.

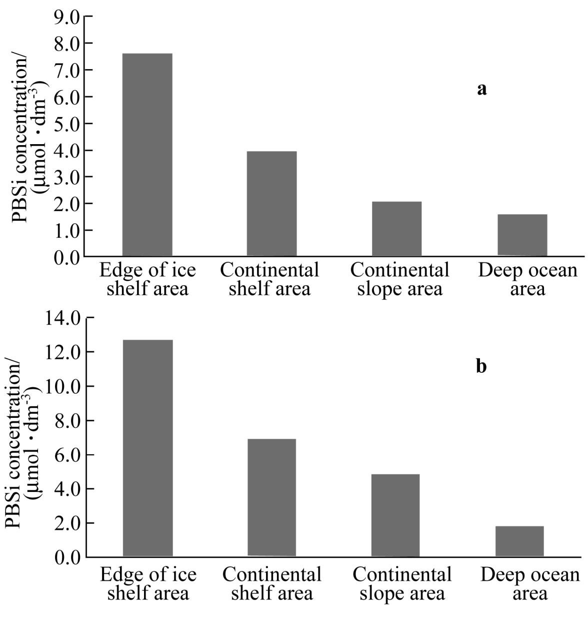

Figure 5 PBSi concentrations in surface water of different areas in the P3 transect of Prydz Bay (**a**, 2009; **b**, 2010).

2.2 Relationship between PBSi and silicate

Surface-layer silicate in Prydz Bay is shown as a function of latitude in Figure 6. It ranged from 27.61—61.51 μmol·dm^{-3}, decreased from north to south, and showed the opposite trend compared with PBSi. Diatoms are the main agents of new autotrophic production in most of the Southern Ocean[6]. Silicate availability is potentially limiting diatom growth and productivity; however, the average concentration of silicate in Prydz Bay was 50.13 μmol·dm^{-3}, which is much higher than the ~2 μmol·dm^{-3} of Si required to limit diatom growth[13]. Therefore, the availability of silicate is not a limiting factor controlling diatom production in Prydz Bay.

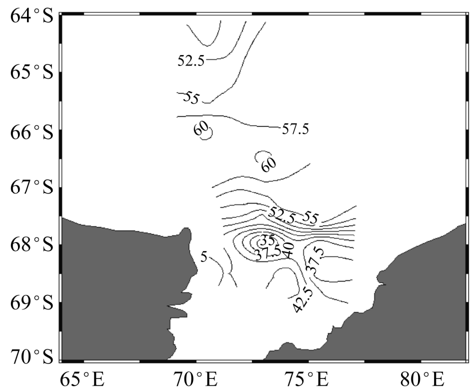

Figure 6 Distribution of silicate in the surface waters of Prydz Bay (unit is μmol·dm^{-3}).

Diatom blooms removed silicate from surface waters in austral summer to form amorphous silica skeletons; their post mortem dissolution is an important biogeochemical process that begins in the water column when the silica skeleton is exposed to the undersaturated seawater[6,14-18]. In the upper 200 m of the water column of Prydz Bay, PBSi and silicate show a negative correlation ($r = -0.67$, $n = 161$, Figure 7). Figure 8 shows the increase of silicate with depth, opposing the trend seen with PBSi. In the upper 100 m, the concentration of silicate increased dramatically, rising to about 80 μmol·dm^{-3} below 200 m, and remaining constant. This represents the loss of biogenic silica through dissolution in the upper surface waters.

2.3 The relationship between PBSi and phytoplankton

According to Zhu et al.[19] and Sun et al.[20], a higher abundance of phytoplankton and chl *a* occurred in Prydz Bay and the adjacent continental shelf, and a lower abundance occurred on the continental slope and the deeper open sea area. Diatoms were the dominant composition of the production, accounting for 99.75%. Distribution of chl *a* in surface waters, presented in Figure 9, showed similar distribution patterns to PBSi. Chl *a* concentrations ranged from 0.18—6.00 μg·dm^{-3}, and higher concentrations occurred south of 67°S. In the upper 200 m of the water column of Prydz Bay, the PBSi and chl *a* showed a significant positive correlation (r = 0.80, n = 161; Figure 10), indicating the dominant control of biological factors on the PBSi distribution in the austral summer of Prydz Bay.

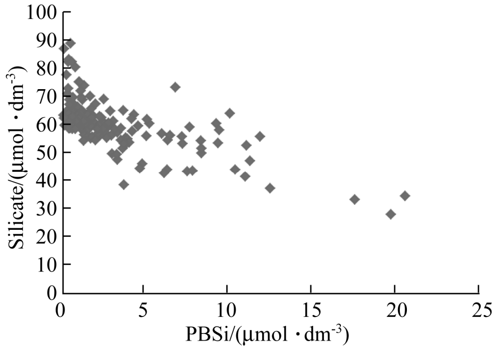

Figure 7 Relationship between PBSi and silicate in the upper 200 m of water in Prydz Bay.

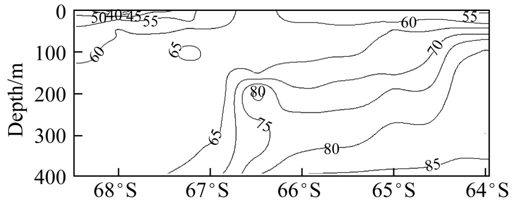

Figure 8 Silicate profile of section P3 in Prydz Bay (unit is μmol·dm-3).

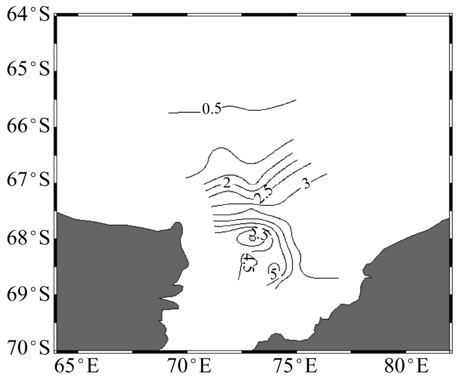

Figure 9 Distribution of chl *a* in surface waters of Prydz Bay (unit is μmol·dm-3).

Prydz Bay is a semi-enclosed one with obstruction of Four Ladies Bank and Frame Bank located in the northeast and northwest of the bay, respectively[21]. The water exchange is relatively weak, and the stability of the water is strong in the area south of 67°S, and the nutrients in the upper water were continuously supplemented[22-23]. The bay has conditions beneficial for the growth and propagation of phytoplankton photosynthesis in the area south of 67°S. However, the area of the bay north of 67°S was affected by the Antarctic divergence zone with strong upwelling of circumpolar deep water (CDW)[24], which was the transition region between the west and east drift. Such conditions decreased the vertical stability of the water column, and disturbed the growth of phytoplankton. Therefore, the cell abundance of phytoplankton, chl *a* and PBSi concentrations inside and outside the bay were quite different.

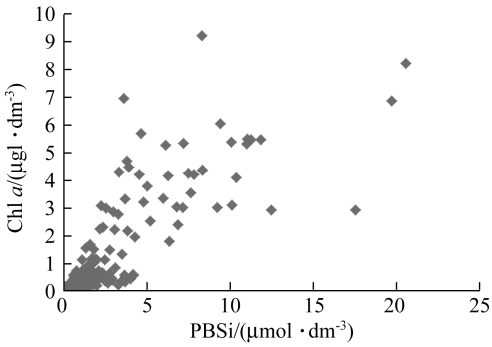

Figure 10 Relationship between PBSi and chl *a* in the upper 200 m of water in Prydz Bay.

2.4 Relationship between PBSi and POC

POC concentrations ranged from 79.02—649.02 μg·dm^{-3}, with an average concentration of 349.75 μg·dm^{-3} (Figure 11). The distribution was quite similar to that of PBSi, with maximum values found south of 67°S from the surface to 100 m, and showing a strong positive correlation with PBSi (r = 0.70, n = 157; Figure 12). In the study area, diatoms were the key components in the biological pump, by which biogenic silica and organic carbon are transported into the deep sea. Because of the dissolution of biogenic silica and remineralization of organic matter during transport, the change of Si_{bio}/C_{org} molar ratio can reflect the differential recycling of Si and C during the transport process to deep water. In our study, the molar ratio of Si_{bio}/C_{org} of the surface-layer was 0.21, greater than the typical Si/C molar ratio of 0.13 that is reported for diatoms growing under nutrient-replete conditions[25]. It decreased to 0.14 at 50 m, and 0.09 at 200 m (Figure 13). This could reflect higher rates of biogenic silica dissolution, or lower rates of organic matter remineralization in the upper 200 m. However, the high ratio of Si_{bio}/C_{org} (2.6) at 1 000 m[26], which is greater than the molar ratio of the upper 200 m, could mean better biogenic silica preservation, or higher rates of organic matter remineralization during the processes of exporting biogenic matter from the upper ocean to the deep ocean. Such variability of the Si_{bio}/C_{org} molar ratio contrast at different water depths indicates that the Prydz Bay is not different from other ocean systems in terms of the decoupling between the Si and C cycles[27].

3 Conclusions

The concentration and distribution of PBSi were investigated, together with the distribution of silicate, POC and chl *a*, on a series of transects across Prydz Bay. The results obtained during the 27th CHINARE cruise show the PBSi

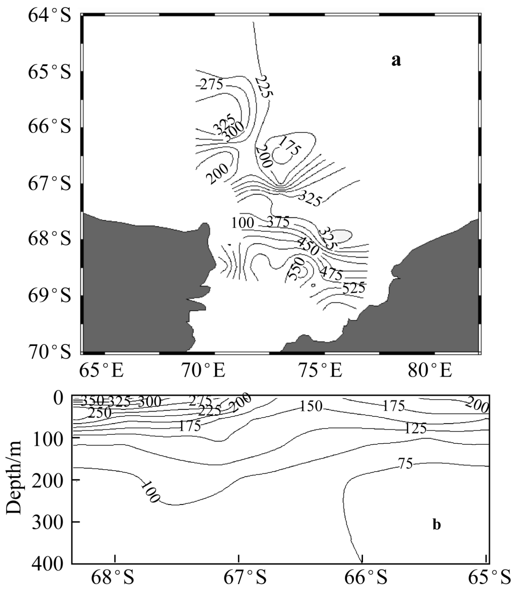

Figure 11 Distribution of POC in surface water (**a**), and a vertical profile of section P3 (**b**) in Prydz Bay (unit is μg.dm^{-3}).

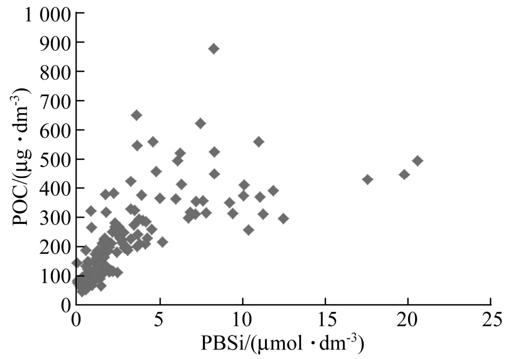

Figure 12 Relationship between PBSi and POC in depths of up to 200 m water of Prydz Bay.

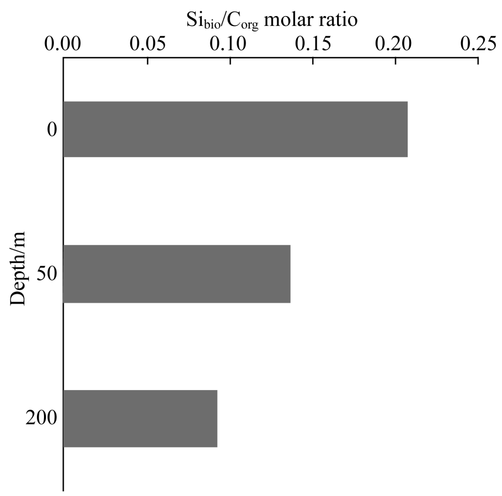

Figure 13 Si_{bio}/C_{org} molar ratio at depths of up to 200 m water of Prydz Bay.

concentrations ranged from 0.76 μmol·dm^{-3} to 19.72 μmol·dm^{-3} in the surface waters of Prydz Bay in the austral summer of 2010—2011, with an average concentration of 6.06 μmol·dm^{-3}. The annual difference in the average concentration of PBSi in surface water is obvious, with a distribution pattern similar to those for 2008—2011, with higher concentrations located in the southern area of 67°S, and decreasing with depth in the upper water columns.

Our results indicate that the average concentration of silicate was much higher than the limiting concentration for diatom growth and was not the limiting factor controlling diatom production. In the water column, the distribution of PBSi was strongly coupled with chl *a* and POC, which suggests that this was an area where phytoplankton were dominated by siliceous organisms. Compared with higher concentrations of PBSi in surface waters, low concentrations of PBSi extended from depths of 50—200 m, which could mean that there was significant dissolution of siliceous particles in the upper 200 m. Decreases in the Si_{bio}/C_{org} molar ratio of particulate matter in the upper 200 m are also an indicator of a strong preferential recycling of silica over organic matter in the upper 200 m, and the much higher Si_{bio}/C_{org} molar ratio at 1 000 m could reflect a more rapid recycling of POC compared with that of PBSi.

Acknowledgements This research is supported by the National Natural Science Foundation of China (Grant no. 41076134 and 41206182), the Scientific Research Fund of the Second Institute of Oceanography, SOA (Grant nos. JT1009, JT1208, JG1217 and JG1218), the Chinese Polar Environment Comprehensive Investigation & Assessment Programmes (Grant nos. CHINARE 2012-01-04 and CHINARE 2012-04-04) and the SOA Young Marine Science Foundation (Grant no. 2012536). Data were issued by the Data-sharing Platform of Polar Science(http://www.chinare.org.cn) maintained by PRIC and Chinese National Antarctic & Arctic Data Center.

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