· Article ·

Advances in Polar Science

doi: 10.3724/SP.J.1085.2013.00113

June 2013 Vol. 24 No. 2: 113-118

The content and distribution of Ge in the sediments of Prydz Bay, Antarctica

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Received 8 March 2013；accepted 10 April 2013

Abstract The content and distribution of Ge is investigated in sediments from the Southern Ocean (Prydz Bay, Antarctica). The content of Ge_{total} in the sediments ranges from 1.14×10^{-6} to 2.35×10^{-6} (average of 1.71×10^{-6}) and the highest value occurs at station P3-9 where water depth is > 1 000 m. The lowest value occurs at station P4-13 which is near the edge of the Amery ice shelf. The surface sediments have 16%–68% Ge_{bio} within Ge_{total}. The distribution trends of Ge_{bio} and Ge_{total} are generally similar, and the values outside Prydz Bay are higher than within the bay, bounded at 67°S. The vertical distribution of Ge in sediment cores presents higher values at the surface than in underlying sediments. Values of Ge_{bio} appear to positively correlate with biogenic silica ($BSiO_2$) in surface sediments from non-polynyas sea. The vertical distribution of Ge_{bio} and $BSiO_2$ is similar in sediments of station P3-16.

Keywords **Ge, sediment, Prydz Bay, Southern Ocean**

Citation: Shen C, Hu C Y, Sun W P, et al. The content and distribution of Ge in the sediments of Prydz Bay, Antarctica. Adv Polar Sci, 2013, 24:113-118, doi: 10.3724/SP.J.1085.2013.00113

1 Introduction

Germanium (Ge) can be distinctly lithophile, siderophile, chalcophile or organophile in different environments[1]. The abundance of Ge in oceanic crust is 1.5×10^{-6}, and 1.6×10^{-6} in continental crust[2]. Ge and silicon (Si) have similar chemical behavior[3] and follow some of the same geochemical pathways[4], and indeed Ge is a pseudo-isotope of Si[5]. In the oceanic environment concentrations of Ge_i and Si are linearly related[4]. Ge^{4+} and Si^{4+} have similar ionic and covalent radii, allowing them to exist in an isomorphous substitution relationship in nature. Ge/Si ratios also show great promise as a tracer for the biogeochemical Si cycle, such as using Ge to trace the transformation of Si in the deep-sea environment[6-7].

Diatoms are the dominant phytoplankton and the primary constituent of deep-sea sediments around Antarctica[8]. Southern Ocean sediments account for 25%–50% of all biogenic silica ($BSiO_2$) burial worldwide, but only contribute 5% to global primary productivity[9]. Some studies indicate that diatoms can transfer Ge from sea water to sediments in proportions similar to Si. This study investigates the distribution of Ge and its geochemistry within sediments of Prydz Bay based on data collected during the CHINARE-21, 24, 25 and 27 cruises，which took place during December 2004−February 2005, February 2008−March 2008, February 2009, and February 2011, respectively. The aim is to better understand the biogeochemical processes of Ge and $BSiO_2$ in the Southern Ocean.

2 Materials and methods

2.1 Materials

The area investigated during the cruise of CHINARE-21, 24, 25, 27 and the sampling stations are shown in Figure 1 and Table 1. Six multiple undisturbed sediment cores were collected using a sediment collector with four tubes. The tube diameter was 10 cm, the height 60 cm, and the total core length ranged from 10 cm to 35 cm. The sediment in the upper 10 cm of each core was sliced into 1 cm intervals, and the lower part (below 10 cm) sliced into 2 cm intervals. A further 15 surface sediment samples were collected by grab sampling. Sediment samples were frozen in a centri-

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fuge tube and stored until analysis.

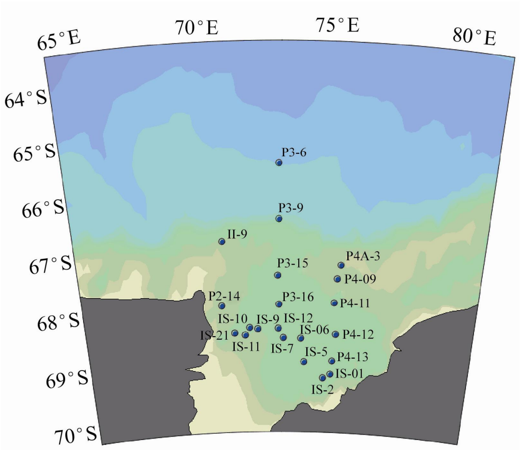

Figure 1 The sampling stations in Prydz Bay, Antarctica.

Table 1 Location and depths of sampling stations in Prydz Bay

Station	Cruise	Longitude/°E	Latitude/°S	Depth/m
IS-01	27	75.31	69.20	730
IS-2	24	74.98	69.27	870
IS-5	24	74.11	68.99	707
IS-06	27	73.94	68.59	717
IS-7	25	73.18	68.58	744
IS-9	24	72.06	68.43	505
IS-10	24	71.71	68.40	565
IS-11	25	71.51	68.53	500
IS-12	27	72.95	68.42	748
IS-21	27	71.05	68.49	777
II-9	21	70.64	66.88	363
P2-14	25	70.52	68.01	480
P3-6	25	72.99	65.51	3045
P3-9	25	72.99	66.50	1538
P3-15	27	72.94	67.49	575
P3-16	27	72.99	68.00	647
P4-09	27	75.47	67.53	421
P4-11	24	75.38	67.96	491
P4-12	27	75.48	68.50	638
P4-13	24	75.37	68.97	723
P4A-3	24	75.60	67.29	403

2.2 Analytical methods

Samples were weighed out into 0.2 g subsamples (accuracy of 0.000 1 g) and placed into a 100 mL PTFE digestion tank. The samples were digested in a solution of 7 mL HNO_3 and 3 mL HF (according to USEPA METHOD 3052). Microwave digestion (CEM Mars, U.S.) was carried out as follows: rapid heating to 180℃ in 5 min, continued digestion for 25 min at 180℃. The final digested solutions were fixed to a 25 mL volume by addition of Milli-Q purified water. All glassware and sampling bottles were dipped in nitric acid (1:3) for > 24 h and washed with MILLI-Q purified water repeatedly.

Concentrations of Ge and Al were determined by ICP-MS (ELAN DRC-e, Perkin Elmer) from the digestion solution according to USEPA METHOD 3052. Analysis conditions were as follows: nebulizer gas: 0.99 $L \cdot min^{-1}$; auxiliary gas: 1.2 $L \cdot min^{-1}$; plasma rate: 16 $L \cdot min^{-1}$; ion lens: 14 V; RF power: 1 100 W. Certified reference materials used in the analysis include: GBW07357 (China), MESS-3 (Canada). The relative standard deviation (RSD) is 2.03% for Ge and 1.46% for Al.

On some occasions it was necessary to calculate the enrichment factors of Ge_{bio}, as follows:

$$Ge_{bio} = Ge - Ge_{terr}$$

$$Ge_{terr} = Al_{sample} \times (Ge/Al)_{crustal}$$

where Ge and Al_{sample} represent the total weight % concentrations of elements Ge and Al, respectively and $(Ge/Al)_{crustal}$ represents Ge/Si (mol) in the lithosphere[10-11]. Other parameters, such as $BSiO_2$, were analyzed according to GB (17378-2007).

3 Results and discussion

3.1 Content and distribution of Ge in surface sediments

The content of Ge in surface sediments of Prydz Bay is shown in Figure 2 (Ge_{total}, Ge_{bio}, Ge_{terr}). The values of Ge_{total} range from 1.14×10^{-6} to 2.35×10^{-6} and the average content is 1.71×10^{-6}. This is higher than the average content of marine sediments (1.2×10^{-6})[12]. The Ge content outside of Prydz Bay is higher than inside (with the boundary demarcated by the 67°S latitude), which may result from hydrogeological conditions. The highest value was found at station P3-9 with a value of 2.35×10^{-6} where the water depth is > 1 000 m. South of 67°S, the stations near the edge of continental shelf and lacking polynya were higher than the two areas of polynya. The lowest values of 1.36×10^{-6} and 1.14×10^{-6} were found at stations P2-14 (Darnley polynya, 68°E–70.5°E)[13] and P4-13 (Prydz Bay polynya, 75°E–79°E), respectively.

The content of Ge_{bio} (calculated in section 2.2) in surface sediments was found to be in the range of 0.23×10^{-6}–1.53×10^{-6}, with an average content of 0.84×10^{-6}. The distribution trend is similar to Ge_{total}. The highest value also occurred at station P3-9, and the lowest value at II-9 (Frame Bank). The ratio Ge_{bio}/Ge_{total} was found to be between 16% and 68%, with the highest values at P3-9 (65%) and P4-11 (68%) and the lowest value at II-9 (16%).

The content of Ge_{terr} in surface sediments (as calculated in section 2.2) was found to be in the range of 0.53×10^{-6}–1.25×10^{-6}, with an average of 0.87×10^{-6}. This is close to the value of Ge_{bio}, and thus the Ge_{terr} content is negligible. However, the distribution of Ge_{terr} is different

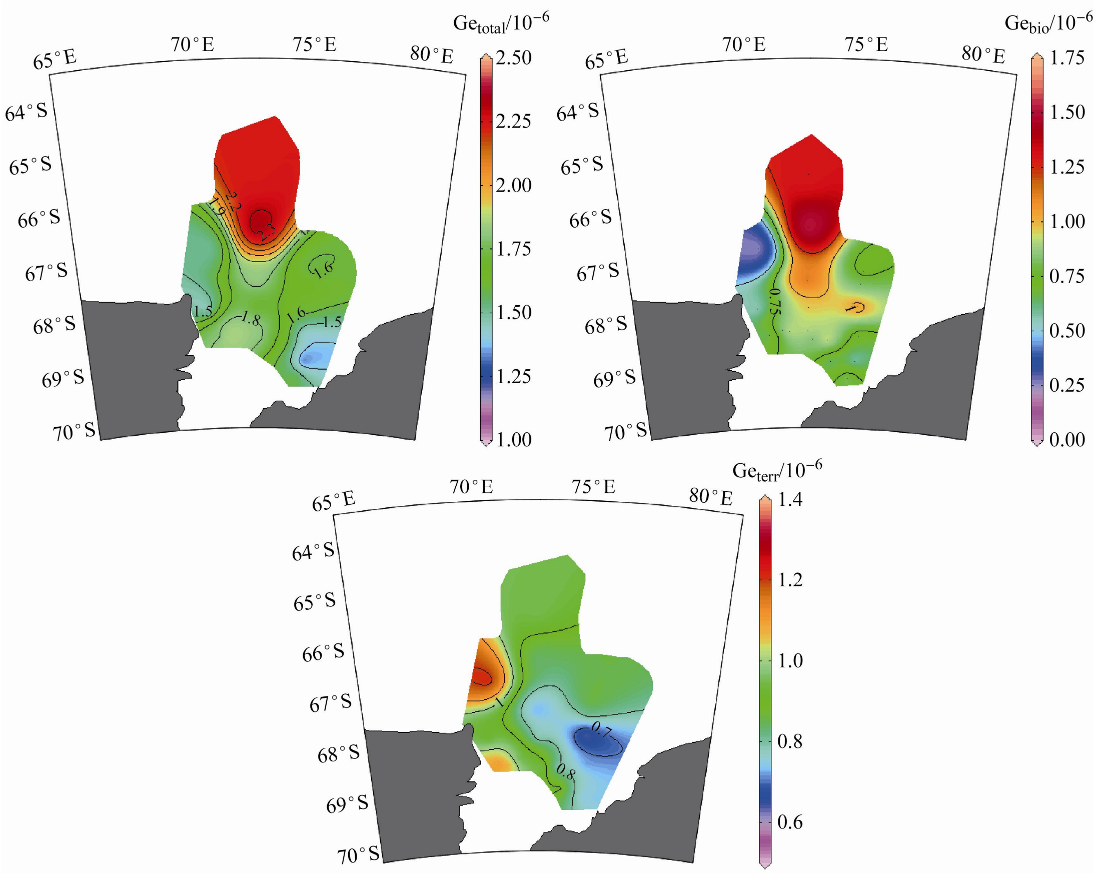

Figure 2 Distribution of Ge_{total}, Ge_{bio} and Ge_{terr} in surface sediments of Prydz Bay.

from Ge_{total} and Ge_{bio}. For example, the station with the highest value of Ge_{terr} has the lowest Ge_{bio}.

3.2 Vertical distribution of Ge in sediment cores

Stations P3-6, P3-16 and II-9 were selected to study the vertical distribution of Ge. The analytical results (Figure 3a) show that the concentration within subsurface sediments is higher than in surface sediments. Station P3-6, located in a deep-sea area, has a higher Ge content than the other two stations, and the average content is 2.39×10^{-6}. Below a depth of 8 cm in the core there is a sharp decrease in Ge with depth. The average Ge content of P3-16 is 1.54×10^{-6} and 1.25×10^{-6} at station II-9.

At station P3-16 the distribution trend of Ge_{bio} and Ge_{total} is similar (Figure 3b), with the concentration of Ge_{bio} in the range of 0.13×10^{-6}–1.18×10^{-6} (average of 0.85×10^{-6}). From 0–6 cm depth in the sediment core, the concentration changes slightly and Ge_{bio} varies significantly below 6 cm.

3.3 Relationship between Ge and Si

The $BSiO_2$ content of surface sediments from Prydz Bay is shown in Figure 4. It is accepted that $BSiO_2$ originates from siliceous phytoplankton such as diatoms, radiolarians, silicoflagellates, and sponge spicules[14]. Diatoms, in particular, build up their frustules by absorbing silicic acid from the surface layer. The highest abundance of phytoplankton in Prydz Bay is south of 67°S, although there was no sharp gradient of $BSiO_2$ in this area compared with previously reported trends[15]. Notably, the highest value of Ge_{bio} was found north of 67°S (out of bay) while the highest value of $BSiO_2$ was found south of 67°S (in the bay).

Because more stations are concentrated south of 67°S, two different study areas were partitioned (polynya and non-polynya)[13]. In the surface sediments of non-polynya (Figure 5), Ge_{bio} correlates positively with $BSiO_2$ (r=0.881, n=11), while Ge_{bio} and $BSiO_2$ appear to share no correlation (r=−0.598, n=7). Although some studies have shown that the oceanic cycles of Ge and Si share similarities[4,16], it is evident that they exhibit geochemical differences greater than an order of magnitude in the dissolved ratios for marine systems. It is possible that less Ge occurs in opal than expected[17], based on global inputs of Ge and Si, suggesting that other Ge sinks exist.

The data from station P3-16 shows Ge_{bio} and $BSiO_2$ share a similar vertical distribution in the sediment core (Figure 6), and further analysis showed that concentrations in the top of the core were highest. Although there is a little difference above 7 cm, the concentrations (both Ge_{bio} and $BSiO_2$) have a small fluctuation, and correlate positively (r=0.766, n=18), suggesting that there is a relationship between them in the burial process experienced by sediment interface recirculation.

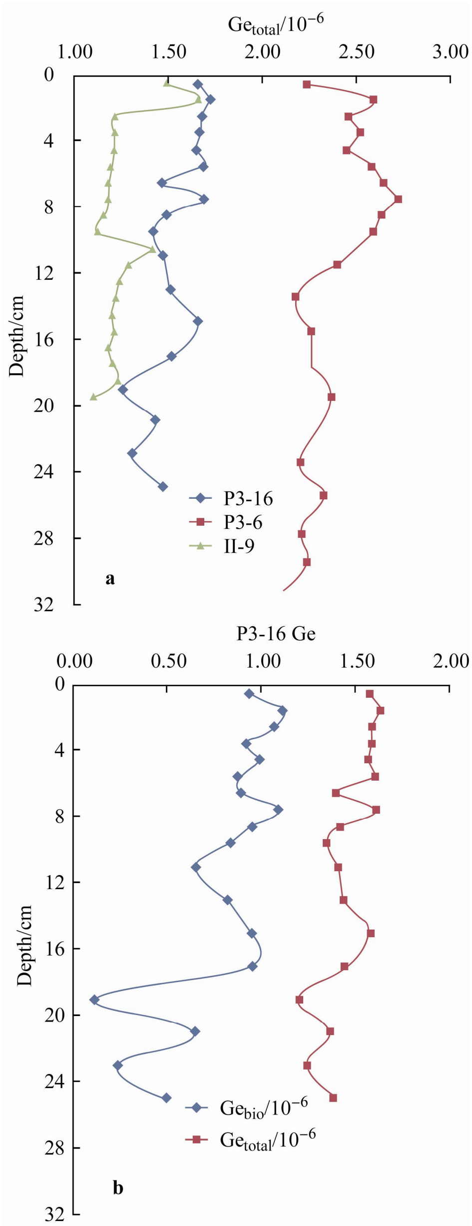

Figure 3 Vertical distribution of Ge in sediments; Ge_{total} at stations P3-16, P3-6 and II-9 (**a**); Ge_{total} and Ge_{bio} at station P3-16 (**b**).

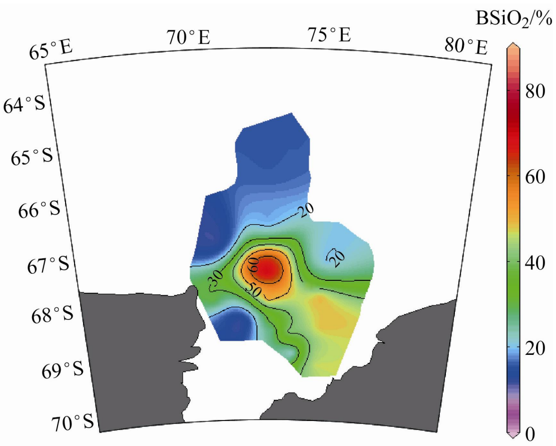

Figure 4 Distribution of $BSiO_2$ in surface sediments of Prydz Bay.

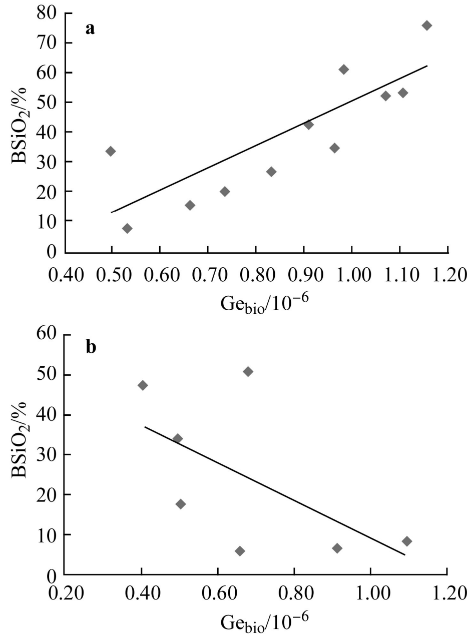

Figure 5 Correlation between Ge_{bio} and $BSiO_2$ in the area of polynya (**a**) and non-polynya (**b**).

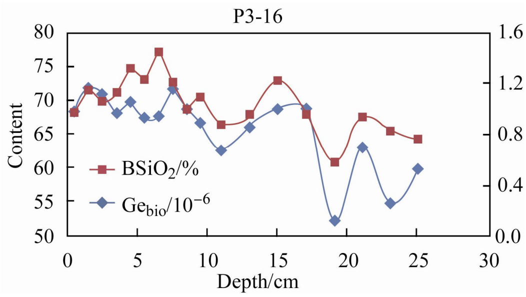

Figure 6 Vertical distribution (note X-axis is depth) of Ge_{bio} and $BSiO_2$ in sample P3-16.

3.4 Other controlling factors on distribution

Some models have shown that more Ge is supplied to the sea than can be removed by diatom shell accumulation in sediment[18]. A growing body of evidence now suggests that Ge is removed from the ocean, into marine sediments, independently of Si[18-19]. It is possible that Ge is scavenged by iron oxyhydroxide precipitation at an oxic/anoxic boundary. In the sediment samples of Prydz Bay we found that Ge correlates positively with Fe (r=0.846, n=21) (Figure 7), indicating that Fe plays an important role in the distribution of Ge in the surface sediments.

The elemental abundance is also strongly controlled by the sediment grain size. The relationships between Ge and clay content and sand content are shown in Figure 8 (stations in Prydz Bay). The Ge_{bio} content positively correlates with the clay fraction (r=0.856, n=11) and Ge_{terr} positively correlates with the sand fraction (r=0.825, n=11). This suggests that the clay fraction can absorb biogenic components.

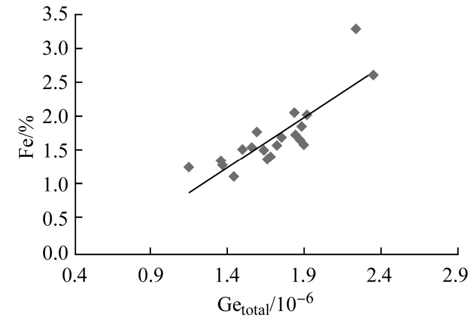

Figure 7 Correlation between Ge_{total} and Fe in surface sediments of Prydz Bay.

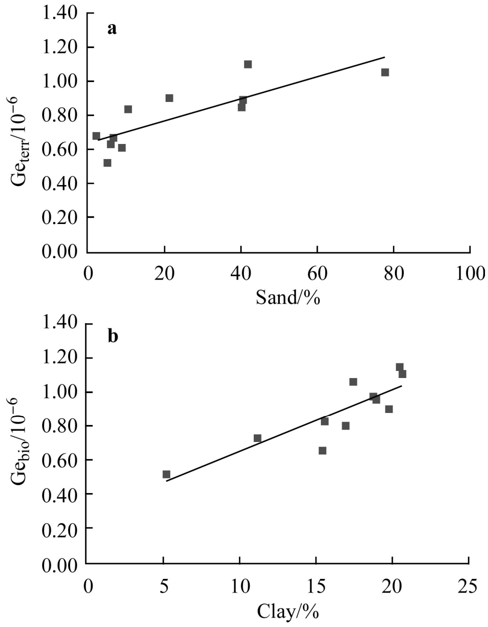

Figure 8 Correlation between Ge_{terr} and sand (**a**) and Ge_{bio} and clay (**b**) in surface sediments of Prydz Bay.

4 Conclusions

From the above results and discussion it is possible to draw the following conclusions:

(1) The content of Ge_{total} in sediments of Prydz Bay is in the range of 1.14×10^{-6}–2.35×10^{-6} and the average content is 1.71×10^{-6}. The highest value occurred at station P3-6 with a water depth > 1 000 m. The lowest value was found at station P4-13 near the edge of the Amery ice shelf. The percentage of Ge_{bio} in Ge_{total} is between 16% and 68% in surface sediments, while Ge_{terr} content was negligible. The concentration of Ge displayed a down-core decrease.

(2) South of 67°S (i.e., within Prydz Bay), the surface sediments of non-polynya ocean indicate that Ge_{bio} correlates positively with $BSiO_2$. However, Ge_{bio} and $BSiO_2$ appear not to correlate, as indicated by Ge and Si exhibited geochemical differences at the water-sediment interface. Iron-bearing phases may influence Ge cycling; and the elemental abundance is strongly controlled by the grain size of the sediment. The vertical distribution of Ge_{bio} and $BSiO_2$ at station P3-16 suggests there is an important relationship between these two constituents during the burial process.

Acknowledgements This research is supported by the National Natural Science Foundation of China (Grant nos. 41076134, 41206182), the Chinese Polar Environment Comprehensive Investigation & Assessment Programmes (Grant nos. CHINARE2013-04-01, CHINARE2013-01-04 and CHINARE2013-04 04).

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