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Concentrations and distribution of biogenic barium in surface sediments of Prydz Bay, Antarctica

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Abstract Concentrations of biogenic barium were investigated in surface sediments of Prydz Bay, Antarctica, during the 21st and 27th CHINARE cruises. Factors controlling the observed distribution are explored. Biogenic barium concentrations obtained from a sequential extraction procedure are compared with total concentrations obtained from the normative calculation based on a total digestion, and differences in the results are examined. Concentrations of biogenic barium, calculated by the normative calculation, were much higher than the concentrations obtained through sequential extraction; this discrepancy is the result of the occurrence of barium associated with Mn/Fe oxides, which represents an important component of total barium in these sediments. Concentrations of biogenic barium obtained from the sequential extraction range from 104 to 445 $\mu g \cdot g^{-1}$, and the average concentration was 227 $\mu g \cdot g^{-1}$. The highest concentrations of biogenic barium occur in the central area of the bay, where the seawater is more stable, while lower values occur in the bank and the ice shelf. Biogenic barium is significantly linearly correlated with biogenic barium and organic carbon, and similar in distribution of Chl *a*, which may indicate that primary productivity of phytoplankton in the surface water column is the main environmental factor regulating barium concentration and distribution.

Keywords **biogenic barium, sequential extraction, sediment, Prydz Bay**

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1 Introduction

Many observations indicate a link between particulate biogenic barium (mainly barite) and oceanic productivity. High barite concentrations have been measured in sediments underlying highly productive waters, and in the water column, fluxes of particulate biogenic barium and organic carbon (OC) are strongly correlated[1-2]. From these observations, empirical relationships have been established that allow, based on biogenic barium fluxes, the quantitative determination of modern and past oceanic productivity. In particular, Dymond et al.[3] and Francois et al.[4] generated an algorithm that links modern export production with trapped biogenic barium flux. Recently, records of biogenic barium were measured in sediment cores in the Antarctic continental margin in the area of the Weddell, Lazarev, and Cosmonaut seas. Generally, good correlations between the barium and opal records of sediment cores indicate the usefulness of biogenic barium as a tracer of oceanic export production in the Southern Ocean[5]. Export production was also assessed quantitatively based on the biogenic barium record using the approaches of Dymond et al. in the Indian sector of the Southern Ocean, and the estimated value was consistent with the directed measurements of export production[6-7].

Various mechanisms responsible for the formation of biogenic barium in seawater have been postulated in the scientific literature and evidence for two possible mechanisms exists[4,8]. The first mechanism comprises the precipitation of barite, provided by organisms such as acantharians, which occurs upon the dissolution of celestite (skeletal material) as a source of barium and sulfate. The second includes a passive barite formation process. Supersaturation of barite occurs in microenvironments by sulfate enrichment from decaying labile organic sulfur and the

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concomitant diffusive uptake of dissolved barium from surrounding seawater.

Numerous studies have emphasized the importance of the Southern Ocean in regulating atmospheric carbon dioxide. Prydz Bay is the focus region of Chinese Antarctic research, and is one of the biggest bays around the continent of Antarctica along with Weddell Sea and Ross Sea. However, little research on the biogeochemistry of the area exists. In this study, we examine the spatial distribution of biogenic barium in surface sediments of Prydz Bay, which will help us to further understand the factors governing biogeochemistry in this special area.

2 Materials and methods

2.1 Study area

Prydz Bay (70°−80°E, 66°45′−69°30′S) is a semi-enclosed bay obstructed by the Four Ladies Bank and the Frame Bank located in the northeast and northwest of the bay, respectively. It contains the largest ice shelf in East Antarctica, and sea ice cover varies seasonally. The freezing and thawing stages last 7 months and 5 months, respectively, and the extent of sea ice cover is the greatest in September and the lowest in February[9]. During the melting period, bidirectional melting is observed; sea ice melts from north to south in the abyssal zone, and from south to north in the coastal region of Prydz Bay.

2.2 Materials

During the cruises of the 21st and 27th Chinese National Antarctic Research Expedition (CHINARE), nine surface sediments (0−1 cm) were taken from Prydz Bay at the sampling stations shown in Figure 1 and Table 1. Most of the surface sediment samples were collected as grab samples. Others were collected using a sediment collector with four tubes. The tubes were 10 cm in diameter and 60 cm in height, and the total core lengths ranged from 10 to 30 cm. Sediments in the upper 10 cm of each core were subsampled at 1 cm intervals. Sediment samples were frozen in centrifuge tubes and stored until analysis for Ba, Al, biogenic slicate (BSi), OC, and total nitrogen (TN).

2.3 Methods

The dried and powdered subsamples with the weight of 0.2 g (accuracy of 0.000 1 g) were weighed into Teflon bombs. The samples were then digested using concentrated acids (HNO_3, HCl, HF, and $HClO_4$) and the final digested solutions were brought up to a total volume of 25 mL with Milli-Q purified water.

The distribution of different barium phases was determined in the samples by a sequential extraction technique[10]. Approximately 100 mg of dried and powdered sediment was washed sequentially with several different solvents in four steps: (1) Barite was extracted by applying 25 mL of 2 mol·L^{-1} NH_4Cl (brought to pH 7 with ammonia).

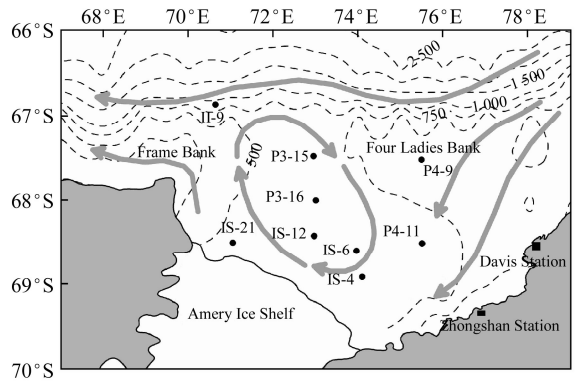

Figure 1 Map of the sampling stations in Prydz Bay, Antarctica. Arrows indicate the direction of surface circulation and black dots represent sediment sampling sites.

Table 1 Information on the sediment sampling stations

Cruise	Station	Time	Lon./°E	Lat./°S	Depth/m
21st CHINARE	IS-4	2005-02	74.08	68.90	678
21st CHINARE	II-9	2005-02	70.64	66.88	416
27th CHINARE	IS-6	2011-01	73.94	68.59	717
27th CHINARE	IS-12	2011-01	72.95	68.42	748
27th CHINARE	P4-9	2011-01	75.47	67.53	421
27th CHINARE	IS-21	2011-01	71.05	68.49	777
27th CHINARE	P3-15	2011-01	72.94	67.49	575
27th CHINARE	P3-16	2011-01	72.99	68.00	647
27th CHINARE	P4-11	2011-01	75.48	68.50	638

This step was repeated six times. (2) 25 mL each of 0.15 mol·L^{-1} Na-citrate and 0.5 mol·L^{-1} $NaHCO_3$ (pH=7.6), along with 1.125 g Na-dithionite, was applied to extract Ba associated with manganese and iron oxides. (3) 25 mL of 1 mol·L^{-1} Na-acetate (buffered at pH 4 with acetic acid) was applied to extract Ba associated with carbonates. (4) The residue of the sediments was dissolved with 5 mL of a 6.5∶2.5∶1 mixture of $HClO_4$ (60%), HON_3 (65%), and H_2O, and 5 mL HF (40%). Following each step, tubes containing the samples were centrifuged at 4 000 rpm, after which the solution was decanted, and the samples were washed with Milli-Q purified water, which was added to the decanted solution.

Ba and Al were analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES). The analysis of international standard reference rocks (GBW 07314 and GBW07315) was conducted as a quality control measure; the measured concentrations were within 5% of the standard certified value for each element. The relative standard deviation (RSD) was 5.0% for Ba and 2.5% for Al.

Other parameters, such as $BSiO_2$, were analyzed according to GB (17378−2007)[11]. All of the samples were analyzed for OC and TN using an Elementar Vario MICRO cube, and the relative standard deviation (RSD) was less

than 1%.

3 Results and discussion

3.1 Biogenic barium estimate

The normative calculation, with the assumption that the barium carrier phases of the surface sediments are mainly barite and aluminosilicates[12], is the most widely applied method for the estimation of biogenic barium concentration. Hydrothermal barite may be an important component of total barium, since it is restricted to areas with hydrothermal activities[13]. The biogenic barium (mainly barite) concentration was calculated using the following equation:

$$BBa=Ba_{total}-Al_{sed}\times(Ba/Al)_{terr} \quad (1)$$

where BBa is the concentration of biogenic barium, Ba_{total} and Al_{sed} are the concentrations of Ba and Al in the samples and $(Ba/Al)_{terr}$ is the terrigenous ratio of the two elements. The average $(Ba/Al)_{terr}$ is 0.003 7 in the Indian sector of the Southern Ocean[14], and 0.006 7 for pure terrigenous sediments in the southern Weddell Sea[15]. The results are shown in Table 2.

In many marine environments, some Ba may be present in Mn/Fe oxides, or associated with carbonates. Biogenic barium, calculated by the normative calculation, includes barite and Ba associated with other phases, which are unlikely to be related to carbon export. At present, the only method available to obtain quantitative information on biogenic barium in sediments is sequential extraction. This method involves the application of a sequence of solvents to determine the operationally defined solid speciation of an element, and barite is separated from all other major barium-containing mineral phases, such as barium associated with Mn/Fe oxides (Table 2). The amount of barium associated with carbonates was low, hence is not listed in Table 2.

Table 2 The concentration of total barium and estimated biogenic barium in Prydz Bay sediments

Station	Total barium/(μg·g^{-1})	Normative calculation BBa/(μg·g^{-1})		Sequential extraction/(μg·g^{-1})	
		$(Ba/Al)_{terr}$ =0.003 7	$(Ba/Al)_{terr}$ =0.006 7	BBa	Ba-Mn/Fe
IS-4	675	494	348	115	
II-9	561	412	291	104	
IS-12	630	473	345	189	
IS-6	513	415	335	255	148
P4-9	874	706	562	210	402
IS-21	837	602	411	116	445
P3-15	654	548	462	445	123
P3-16	592	484	397	351	178
P4-11	550	441	353	259	208

A comparison of the biogenic barium concentrations from the sequential extraction and the normative calculation clearly shows that the normative calculation may introduce significant errors to the results, as the contents of biogenic barium are much higher than that obtained from sequential extraction. Barium associated with Mn/Fe oxides make up a significant component of the total barium, ranging from 18.8% to 53.1% of total barium. Therefore, the concentration of biogenic barium obtained from the normative calculation includes barite and barium associated with Mn/Fe oxides, forms that are unlikely to be related to export production.

The comparison also shows that the terrigenous Ba/Al ratio is the critical factor in the normative approach, and that erroneous assumptions based on this ratio may introduce significant errors in the calculation of biogenic barium. The results of the sequential extraction indicate that the barium carrier phases of the analyzed Prydz Bay surface sediments are mainly barite, aluminosilicates, and barium associate with Mn/Fe oxides. When the terrigenous Ba/Al ratio is set to 0.003 7, the contents of biogenic barium, calculated by the normative calculation, are in accordance with the sum of the concentrations of biogenic barium and barium associated with Mn/Fe oxides, calculated by sequential extraction, and the analysis of the residue after the sequence extraction shows that the average Ba/Al ratio is nearly 0.003 7, which is similar to the result estimated by Reitz et al.[15].

3.2 Concentrations and distribution of biogenic barium in surface sediments

The total barium concentration in the surface sediments in Prydz Bay ranges from 513 to 874 μg·g^{-1}, with an average concentration of 654 μg·g^{-1}. The higher concentrations of total barium occur at the edge of the ice shelf and the Four Ladies Bank. The concentration of biogenic barium obtained from the sequential extraction ranges from 104 to 445 μg·g^{-1}, and the average concentration is 227 μg·g^{-1}. Biogenic barium in surface sediments shows a different trend than that observed for total barium. The higher concentrations of biogenic barium occur in the central area of the bay, where the seawater is more stable, and lower values

are found in the bank and the edge of the ice shelf (Figure 2). The highest biogenic barium concentration was found at station P3-15 (445 μg·g^{-1}), and the next at station P3-16 (351 μg·g^{-1}). The stations near the edge of ice shelf were lower in biogenic barium than the two stations in the central area of the bay, with concentrations of 115 and 116 μg·g^{-1}, and the lowest concentration was found at station II-9, near the Frame Bank (104 μg·g^{-1}).

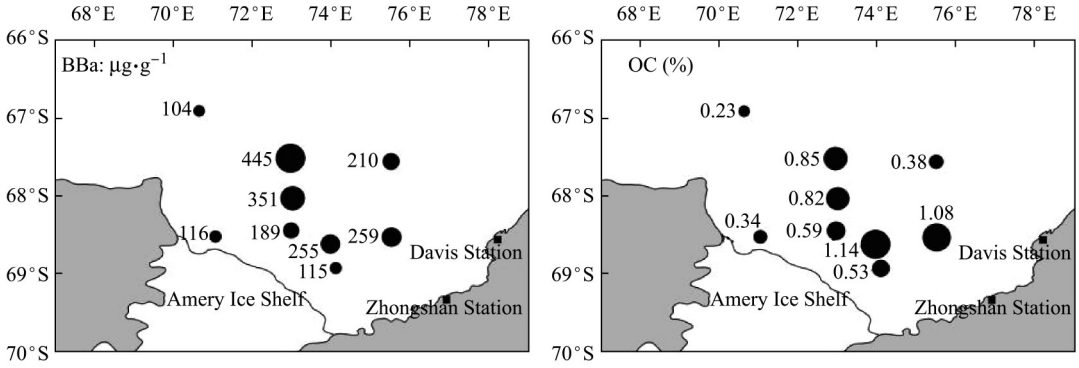

Figure 2 The spatial distribution of biogenic barium and OC in surface sediments of Prydz Bay.

3.3 Factors governing barite distribution

The modern sedimentation rates in Prydz Bay given by Yu et al.[16] are between 0.47 and 1.88 mm·a^{-1} and the average value is 1.06 mm·a^{-1}. The sediment record provides a qualitative and quantitative tool to estimate changes in export production over the last two decades. According to Liu et al.[17], Zhu et al.[18] and Qiu et al.[19], a higher abundance of phytoplankton and chl *a* occurred in Prydz Bay and the adjacent continental shelf, while a lower abundance occurred on the continental slope; the trend is the same as that observed for biogenic barium[17-19]. Some researchers believe that diatoms are the dominant phytoplankton responsible for export production from the surface ocean in Prydz Bay. BSi is produced in surface waters mostly by diatoms, and is one of the major biogenic components of oceanic sediments. BSi therefore provides a tool for the reconstruction of past variations in the efficiency of the biological pump[20]. The data obtained for this study indicate that biogenic barium shows a strong positive correlation with BSi in the surface sediments (r=0.96, n=9). This demonstrates that the distribution of biogenic barium is closely related to the efficiency of the biogenic pump in Prydz Bay. The distribution of OC in surface sediments, presented in Figure 2, was quite similar to that of biogenic barium; lower concentrations occur in the bank and the edge of the ice shelf, and show a strong positive correlation with biogenic barium (r=0.67, n=9); however, the correlation is not as strong as the correlation between biogenic barium and BSi, which may result from the differential recycling of BSi and OC during their transport to the deep sea; additionally, BSi and biogenic barium have higher preservation efficiency compared with OC. These observations indicate that the distribution of biogenic barium and primary productivity are strongly correlated in Prydz Bay.

The distribution of biogenic barium in surface sediments of the central Equatorial Pacifc was found to be influenced by biological production processes in the upper layer of the water column, as well as the redox activity of the sedimentary environment[12]. Generally, biogenic barium was better preserved in oxic environments than in anoxic environments because under anoxic conditions barite is lost as a result the reduction of sulfate by thiobacillus. The content of OC and TN in sediments can be used as indicators of the sedimentary redox environment both for sources of organic matter and for preservation conditions[21]. The organic matter rich sedimentary environment may turn suboxic or even anoxic because of organic matter degradation, which results in the transport of barite. Neither OC nor TN was anticorrelation with biogenic barium in the studied area. In one study, the element vanadium (V) was successfully implied in the reconstruction of the sedimentary redox environment, as the concentration of V was controlled by the redox status of the sediment. Additionally, the source of V was unique, and the element was not readily transported after it was settled and buried[22]. Oxic-suboxic environments were not enriched in V, but anoxic environments. Wang et al.[23] analyzed V in sediments of Prydz Bay.We compared its concentration deducted the detrital V from terrigenous matter with biogenic barium and found no distinct correlation. Different redox status indicators all showed no correlation between redox status and concentration of biogenic barium, which indicates that the influence of redox activity of the sedimentary environment on the distribution of biogenic barium is not obvious.

4 Conclusions

The concentration of biogenic barium in surface sediments of the Prydz Bay indicated by the normative calculation is much higher than the concentration obtained from sequential extraction. This discrepancy is the result of the occurrence of barium associated with Mn/Fe oxides, which make up a significant portion of the total barium in these samples.

The normative calculation may therefore introduce significant errors to results. The barium carrier phases of the analyzed Prydz Bay surface sediments are mainly barite, aluminosilicates (with an average Ba/Al ratio of 0.003 7), and barium associated with Mn/Fe oxides.

Sequential extraction data for total barium indicate a concentration of biogenic barium range between 104 and 445 $\mu g \cdot g^{-1}$, and an average concentration of 227 $\mu g \cdot g^{-1}$. Higher concentrations of biogenic barium occur in the central area of the bay, where the seawater is more stable, while lower concentrations occur in the bank and the ice shelf. Biogenic barium is significantly linearly correlated with BSi and OC, and similar in distribution of Chl *a*, which may indicate that primary productivity of phytoplankton in the surface water column is the main environmental factor controlling the concentration distribution of biogenic barium. Therefore, biogenic barium may provide a tool for the examination of historical variations in the efficiency of the biological pump in Prydz Bay.

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