RESEARCH/REVIEW ARTICLE

Sources and geographic heterogeneity of trace metals in the sediments of Prydz Bay, East Antarctica

Wei-Ping Sun,[1,2] Chuan-Yu Hu,[2] Huan-Xin Weng,[1] Zheng-Bing Han,[2] Chen Shen[2] & Jian-Ming Pan[2]

[1] Department of Earth Sciences, Zhejiang University, 310027 Hangzhou, China
[2] Second Institute of Oceanography, State Oceanic Administration, 310012 Hangzhou, China

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Correspondence
Wei-Ping Sun, Department of Earth Sciences, Zhejiang University, Hangzhou 310027, China.
E-mail: sunwp1998@hotmail.com

Abstract

In this study, we have determined the contents and distribution of zinc and cadmium in the surface sediments from Prydz Bay, East Antarctica. The main sources of the trace elements and their geographic heterogeneity, and the relation between Zn and Cd, are discussed based on the cluster analysis, principle component analysis and considerations of biogenic and lithogenic inputs. The results show that the contents of trace metals range from 34.6 to 96.6 mg kg^{-1} for Zn, and from 0.254 to 0.441 mg kg^{-1} for Cd. Calculations of the enrichment factor indicated no significant anthropogenic impact. Biogenic and lithogenic inputs are the main sources of trace metals. They are almost equal for Zn and Cd at the Amery Ice Shelf edge, while the continental shelf and deep ocean are dominated by biogenic inputs. The contribution of biogenic inputs is much higher for Zn than for Cd at the deep ocean. Calculations of biogenic trace metals revealed different relationships between biogenic Zn and biogenic Cd, which reflect the biological uptake by phytoplankton in the water column.

Zinc (Zn) and cadmium (Cd) belong to the Zn-family (ΠB) in the periodic table and have similar biochemical behaviours in the marine environment (Liao 1992). As trace nutrients, they are depleted in the upper layer of the water column because of biological uptake by marine phytoplankton and are strongly correlated with macronutrients (Bruland 1980; Morel et al. 1994; Frew et al. 2001; Hendry et al. 2008; Sun et al. 2011), for example, Cd with phosphate and Zn with silicate. Moreover, biological cycles of inorganic Zn and Cd are closely coupled through the substitution of Cd for Zn by marine phytoplankton in the Zn-limited seawaters (Morel et al. 1994; Lee & Morel 1995; Lane & Morel 2000). However, the relation between Zn and Cd and their difference in deposition and preservation in marine sediments are still unclear because of the complicated source composition, including natural and anthropogenic inputs. The former include lithogenic sources, that is, mineral particles directly derived from crust and rock weathering, terrigenous input from soils, and biogenic sources, including terrestrial vegetation and marine biological deposition. The latter include pollutants from industry, agriculture and domestic sewage. As marine sediment acts as both a source and a sink for many trace elements (Cave 2005) and plays a prominent role in the biogeochemical process trace elements, it is important to better understand the source composition and behaviour of these trace elements in the sediment.

Prydz Bay is the largest sea shelf on the east margin of Antarctica (Harris et al. 1998). The pristine marine environment benefits research on the source composition and behaviour of trace elements because the geological substrate constitutes the main source of inorganic chemical species to the local environment (Gasparon & Matschullat 2006). Once elements get into the marine environment, they can follow two different paths: some enter biological processes and are deposited as body remains or faecal pellets on the sea floor, representing a biogenic element source; another portion takes part only in physico-chemical processes and is deposited in sediments, constituting a lithogenic source. The aim of this work was to determine the content and

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distribution of Zn and Cd in sediments, to estimate the proportions of lithogenic and biogenic inputs and to reveal the main sources of them in the sediments from different geographic zones of Prydz Bay.

Organic matter, measured as total organic carbon (TOC), and grain size are the most important properties to be taken into account when investigating the behaviour of trace metals in sediments (Giordano et al. 1999; Cai et al. 2011). As diatoms form a major component of the plankton and sediment in the Southern Ocean (Taylor et al. 1997) and biogenic silica (BSi) comprises an average proportion of 30.9% (with respect to total sediment) in the sediments of Prydz Bay (Hu et al. 2007), BSi instead of TOC was selected to identify the biogenic source of trace elements. Crustal elements, such as Al, Fe and Mn, which are abundant in the Earth's crust, were chosen as indicators of lithogenic input.

Materials and methods

Study area and sampling

Prydz Bay is an embayment along the Antarctic margin between 66°E and 79°E. It is bounded on the southern side by Amery Ice Shelf (AIS) and extends northwards to the edge of the continental shelf at about 67°S (Fig. 1). The Amery Depression dominates the inner continental shelf, which is mostly 600–700 m deep. The depression is bordered by two shallow banks (<200 m): Fram Bank to the north–west and Four Ladies Bank to the north–east, forming a spatial barrier to water exchange with the outer oceanic water (Smith & Tréguer 1994). Four Antarctic research stations are located on the shore of Prydz Bay (Fig. 1). These are the Chinese station Zhongshan (69.37°S, 76.38°E), the Russian station Progress (69.38°S, 76.38°E), the Romanian station Law-Racovita (69.39°S, 76.38°E) and the Australian station Davis (38.58°S, 77.97°E).

Sixteen surface sediment samples and three sediment cores were collected using a stainless steel grab and multi-corers, respectively, during several expeditions from 2004 to 2011. The sampling stations (Fig. 1) represent a broad range of geographic zones, including the edge of the AIS (referred to here as IS stations), the continental shelf (P2, P4, P3–15 and P3–16 stations) and deep ocean (P3–6 and P3–9 stations). The total length of the sediment cores was 30 cm for IS-5, 33 cm for P3–6 and 26 cm for P3–16. Immediately after collection and section, samples were placed into plastic bags and stored at −20°C and then freeze–dried in the laboratory before chemical and physical analysis.

Analytical procedures

Metals were determined by inductively coupled plasma mass spectrometry using an Agilent 7000 (Agilent

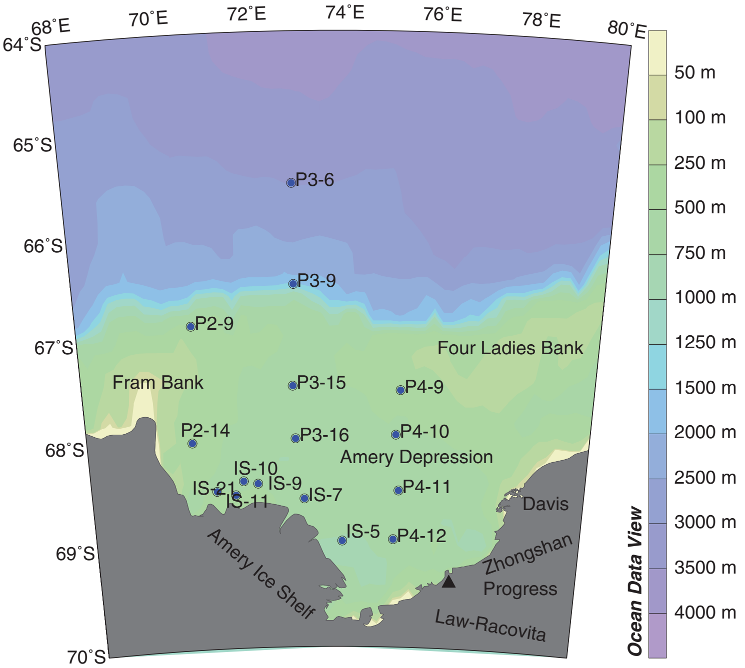

Fig. 1 Study area and sampling stations.

Technologies, Santa Clara, CA, USA) after microwave-assisted digestion using a Mars instrument (CEM, Matthews, NC, USA) with a HNO_3–HF mixture in accordance with US EPA Method 3052. Certified reference material (MESS-3 Marine Sediment Reference Material for Trace Metals and Other Constituents) from the National Research Council Canada was used to test the analytical accuracy and relative standard deviation (RSD) to indicate the repeatability of the data. The recovery ranged from 99 to 110% and the RSD were generally $<5.6\%$. All plastic and glass laboratory containers used for trace metal analysis were soaked with 30% (v/v) HNO_3 (analytical grade, 69% w/w) for 24 h and triple rinsed with MilliQ water. All reagents used for analysis were guaranteed grade. BSi content was determined using a Na_2CO_3 leaching analysis procedure (Mortlock & Frölich 1989). The grain size analysis was carried out using an H 2250 Laser Diffraction Helos System (Sympatec, Clausthal-Zellerfeld, Germany).

Enrichment factor and statistical analysis. Trace metal content was compared with reported natural abundance of the metal in the Earth's crust by normalizing against a conservative, lithogenic element with no significant anthropogenic source (Bowen 1979), such as Al, Ti or Li. This is a well-known method to determine the natural or anthropogenic input of trace metal and is expressed as enrichment factor (EF). In this study, Al is used as the normalizing element because it is most commonly used in the geochemical literature and it can be very accurately measured (Sutherland 2000). EF is calculated from the following formula:

$$\mathrm{EF} = (\mathrm{M/Al})_{\mathrm{sample}} / (\mathrm{M/Al})_{\mathrm{nature}}$$

where $(\mathrm{M/Al})_{\mathrm{sample}}$ is the ratio of trace metal to Al in the sample and $(\mathrm{M/Al})_{\mathrm{nature}}$ is the background value in the nature, which usually refers to the chemical composition of the Earth's crust. As marine sediment develops in diverse environments, it is more reasonable to normalize the $(\mathrm{M/A})_{\mathrm{sample}}$ ratio to the corresponding ratio in the parent material (Santos et al. 2005) than to the chemical composition of the Earth's crust, such as background values from local soils or sediments without anthropogenic influence. In the study, three samples, representing the three different geographic zones, from the bottom end 2–4 cm of the cores were chosen as references; these were most likely deposited under pre-industrial conditions, assuming an average sedimentation rate of 1.04 mm a^{-1} in Prydz Bay (Yu et al. 2009). An EF value >1 indicates the enrichment of an element (Blaser et al. 2000) with respect to the local background value. An EF value <2 may indicate enrichment by natural processes, like biogenic deposition, and if the EF value is >2, it may indicate contamination (Sutherland 2000).

Based on the crustal composition ($[\mathrm{M/Al}]_{\mathrm{crust}}$), the proportion of the lithogenic input of trace metal ($\mathrm{M}_{\mathrm{lith}}$) can be estimated (Tribovillard et al. 2011) as follows:

$$\mathrm{M}_{\mathrm{lith}} = \mathrm{Al}_{\mathrm{sample}} \times (\mathrm{M/Al})_{\mathrm{crust}}$$

The biogenic trace metal ($\mathrm{M}_{\mathrm{bio}}$) and the ratio of biogenic to lithogenic input (bio/lith) are then obtained as follows:

$$\mathrm{M}_{\mathrm{bio}} = \mathrm{M} - \mathrm{M}_{\mathrm{lith}}$$
$$\mathrm{M}_{\mathrm{bio/lith}} = \mathrm{M}_{\mathrm{bio}} / \mathrm{M}_{\mathrm{lith}}$$

The bio/lith input ratio was calculated on the basis of the average contents of Al, Zn (Sheraton et al. 1984; Stüwe et al. 1989) and Cd (Gasparon & Matschullat 2006) in the rocks from the Prydz Bay area, 75 mg kg^{-1} for Zn, 0.33 mg kg^{-1} for Cd and 71 500 mg kg^{-1} for Al, for example, $(\mathrm{Zn/Al})_{\mathrm{crust}} = 1.05 \times 10^{-3}$ and $(\mathrm{Cd/Al})_{\mathrm{crust}} = 5 \times 10^{-6}$.

Principle component analysis (PCA) was carried out to estimate the lithogenic and biogenic contributions of trace metals in the sediments. The rotation method used was Varimax with Kaiser normalization and the rotation was converged in three iterations. Cluster analysis (CA) was applied to identify the difference source compositions of Zn and Cd with respect to the geographic zones of the sampling stations. The average linkage between groups was used to obtain the dendrogram. Data were processed with SPSS version 18 software.

Results

Physico-chemical characteristics

The contents of trace metals in the surface sediments range from 34.6 to 96.6 mg kg^{-1} for Zn, and from 0.254 to 0.441 mg kg^{-1} for Cd. These values are comparable to those from the Weddell Sea (Niemistö & Perttiä 1995), Ross Sea (Ciaralli et al. 1998; Ianni et al. 2010) and the coast of East Antarctica (Gasparon et al. 2007). As shown in Table 1, the contents of Zn, Fe and Mn are highest at the deep ocean stations, where the content of Cd is lowest. The highest contents of Cd and BSi are observed at the continental shelf, where the contents of Al, Fe and Mn are lowest. The content of Al is highest at the edge of the AIS.

Figure 2 shows the results from the grain size analysis of the surface sediments. There is a significant difference in the degree of sorting, as shown by the sand (63 μm to 2 mm), silt (4 μm to 63 μm) and clay (<4 μm) fractions with a good relationship to the distance from the AIS.

Table 1 Chemical parameters (average values) in the surface sediments and M/Al ratios from the bottom end of sediment cores.

	Edge of Amery Ice Shelf	Continental shelf	Deep ocean
Zn (mg kg^{-1})	50.9	62.7	95.7
Cd (mg kg^{-1})	0.304	0.343	0.275
Al (mg kg^{-1})	28 800	17 000	21 900
Fe (%)	1.84	1.48	2.60
Mn (mg kg^{-1})	437	229	522
BSi (%)	6.51	18.59	6.96
Zn (mg kg^{-1})[a]	59.7	85.1	116.5
Cd (mg kg^{-1})[a]	0.253	0.232	0.203
Al (mg kg^{-1})[a]	34 700	21 900	30 300
Zn/Al	1.72×10^{-3}	3.88×10^{-3}	3.84×10^{-3}
Cd/Al	7.3×10^{-6}	10.6×10^{-6}	6.7×10^{-6}

[a] Average content of two samples from the bottom end of the core.

Samples from the edge of the AIS can be classified as sandy sediment, with the sand fraction ranging from 42.1 to 81.7%, with an average of 65.5%. With the exception of station P2–9, samples from the continental shelf and deep ocean are dominated by the silt fraction (from 43.9 to 77.1%, with an average of 67.8%) with a more abundant clay fraction. Station P2–9 is located at the edge of the continental shelf and is exposed to the Antarctic Divergence, leading to a good sorting of sediments under the high energetic hydrodynamic conditions coupled with shallow water depth. The coarse fraction is therefore relatively high at this station, just like those located at the edge of AIS.

PCA and CA

PCA and CA were performed on the data matrix composed of 16 objects (sampling stations) and nine variables (the contents of Zn, Cd, Al, Fe, Mn and BSi, and the proportions of clay, silt and sand fractions).

Figure 3 shows the associated component biplot and Table 2 shows the matrix generated from PCA. The first two components account for 82.6% of the total variance. In particular, the first component accounts for 57.2% and the second component 25.4%. The first component shows significantly positive loading on Zn, BSi, clay and silt fractions, and negative loading on Al, Mn and sand fraction. However, the loadings of Fe and Cd on the first component exhibit low positive values. The second component shows positive loading on Al, Fe Mn and Zn, and negative loading on Cd and BSi. Sand, silt and clay show insignificantly loading on the second component, suggesting that grain size is slightly weighing on the second component.

The result from CA (Fig. 4) shows that the classification of sampling stations with respect to the physicochemical characteristics of the sediments is generally consistent with the geographic zoning. However, the

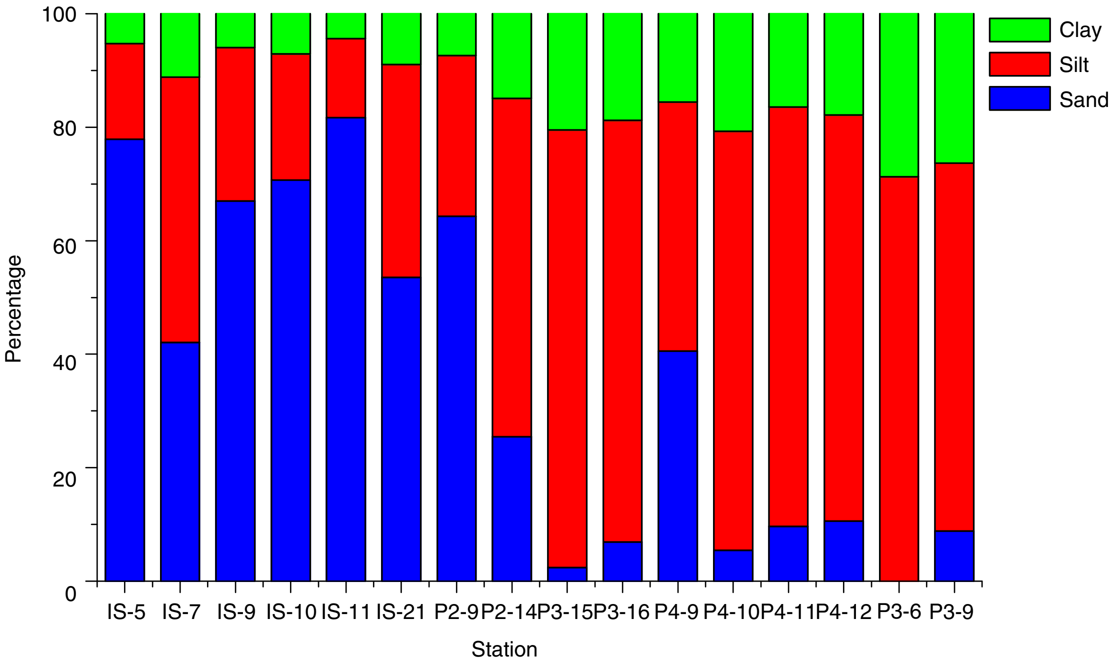

Fig. 2 Grain size characteristics from sediments taken from the different samplings stations. IS stations were those at the edge of the Amery Ice Shelf. Stations at the continental shelf were P2, P4, P3–15 and P3–16. The deep ocean stations were P3–6 and P3–9. The total length of the sediment cores was 30 cm for IS-5, 33 cm for P3–6 and 26 cm for P3–16. Grains 63 μm — 2 mm in size were sand; silt grains were 4 μm —63 μm, and clay was <4 μm.

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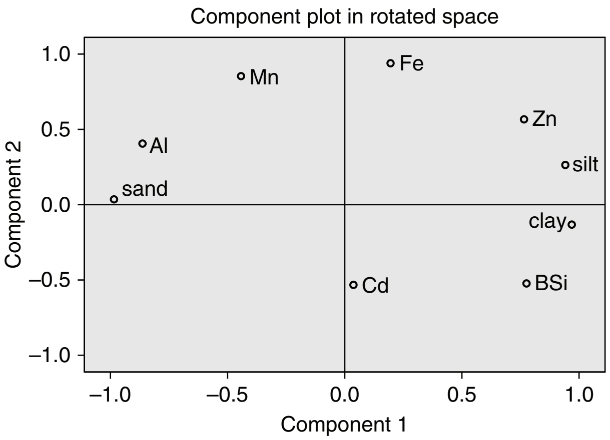

Fig. 3 Component biplot.

physico-chemical behaviour of the sediment from station P2–9, which geographically belongs to the continental shelf, is much more similar to those from the edge of the AIS.

Enrichment factors

Using the reference M/Al ratios in the end of cores from three different geographic zonings (Table 1), the EFs were calculated. These were generally <2 (Fig. 5), indicating no significant anthropogenic effect.

Table 3 shows the ranges, mean and median values of the ratios for the three different geographic zones. The two sources of Cd are almost equal at the AIS edge, while the ratio of bio/lith for Zn is less than 1. A higher biogenic contribution is observed both for Zn and Cd at the other two regions.

Discussion

Sources of trace elements

Despite human activities undertaken by research stations on the shore of Prydz Bay, no significant anthropogenic effect on Cd and Zn in the sediment is observed in terms of the calculated EFs, which are generally less than 2. The result is different from the reports for Deception and Penguin islands (Guerra et al. 2011) and Admiralty Bay (Santos et al. 2006; Santos et al. 2007; Ribeiro et al. 2011) in West Antarctica, where more research stations are established and the cumulative impacts from scientific activities are greater. Given the absence of fluvial input and the lack of true soils (Gasparon & Matschullat 2006) around the bay, Zn and Cd in the sediments definitively originate from lithogenic inputs and marine biogenic deposition. Mineral particles, which are derived from the erosion and weathering of the surrounding basement rocks and released from the melting ice sheet (especially at the edge of the AIS) and icebergs, are the main form of lithogenically sourced material (Niemistö & Perttiä 1995). Trace elements absorbed and assimilated by marine organisms from seawater and food are released back into the water column as biological material, including body remains and faecal pellets, and are ultimately deposited on the sea floor, forming the biogenically sourced trace elements in the sediments.

Table 2 Rotated component matrix.

	Component 1	Component 2
Zn	0.765	0.567
Cd	0.037	−0.532
Al	−0.863	0.406
Fe	0.196	0.939
Mn	−0.443	0.854
BSi	0.776	−0.523
Sand	−0.984	0.036
Silt	0.969	−0.132
Clay	0.941	0.264

A notable grain size effect on the first component is observed from PCA. Examining grain size is a good way to distinguish different sources of marine sediments. The coarse fraction is most likely from lithogenic input. The fine fraction in the sediments contains a great number of autochthonic organic substances derived from biological production in the seawater and plays an important role on the enrichment of trace metals. The first component can therefore be regarded as the "source-controlled factor." BSi and the fine fraction (silt and clay) are both indicators for biogenic input and have significantly positive loadings on the first component. Therefore, Zn, which is strongly correlated with BSi ($r = 0.452$), silt ($r = 0.781$) and clay ($r = 0.723$), is most likely also mainly from biogenic sources. In contrast, Al, Mn and sand, which are negatively loading on the first component, are generally derived from lithogenic input. The slightly positive weights of Cd and Fe on the first component suggest that they are almost equally determined by biogenic and lithogenic inputs.

Geographic heterogeneity

Phytoplankton bloom occurs both at the edge of the AIS and the continental shelf because of the forming of ice-free water, stratification of the water column, suitable weather conditions and enough sunlight during the austral summer. Biomass rapidly increases in a short time and is exported to the sea floor as biological pellets. However, the deep ocean area of Prydz Bay is considered

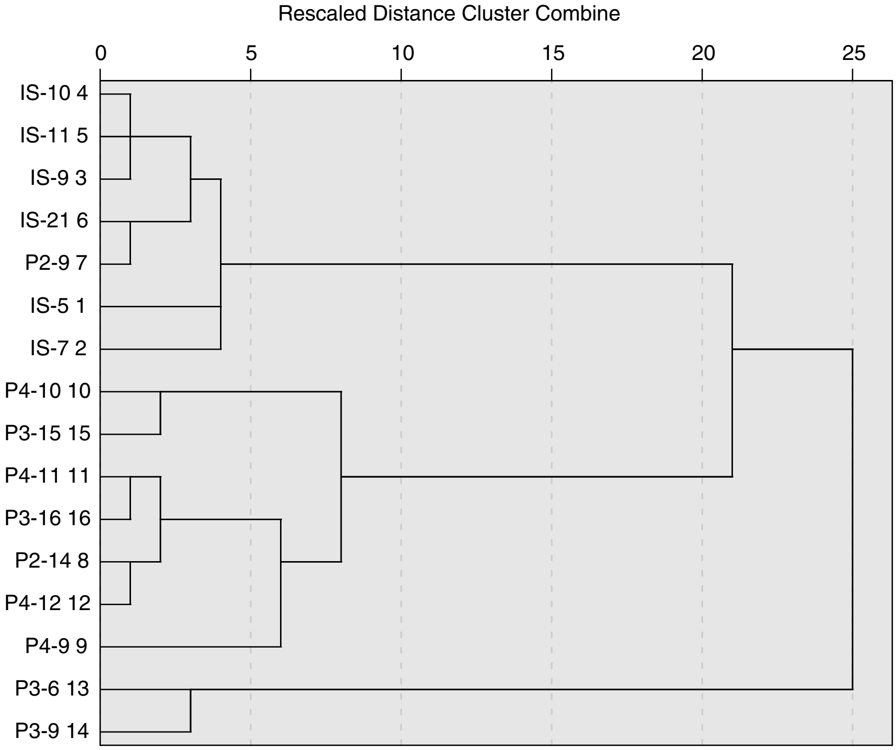

Fig. 4 Dendrogram obtained from cluster analysis, using average linkages between groups. IS stations were those at the edge of the Amery Ice Shelf. Stations at the continental shelf were P2, P4, P3–15 and P3–16. The deep ocean stations were P3–6 and P3–9.

to be a region with high nutrients and low chlorophyll (Sun et al. 2012). A low contribution from lithogenic sources probably takes place in this area, so it is possible that most of the lithogenic trace elements are used by phytoplankton, giving rise to the high values of bio/lith ratios observed. In theory, biogenic deposition should be higher at the edge of the AIS and continental shelf than that in the deep ocean (Isla et al. 2004). In fact, biological input is highest on the continental shelf, as evidenced by the highest content of BSi (Table 1), suggesting the presence of extensive biological processes in this area (high Chl a). However, low contents of BSi are observed at the edge of the AIS (Table 1) that are comparable to those from the deep ocean, suggesting a low proportion of biological input. Stations at the edge of AIS are dominated by the sand fraction, which is most probably released from the melting of the AIS and drift ice. Dilution effect of mineral particles leads to low proportion of BSi in the sediments. In short, trace metals in the sediments are mainly controlled by biogenic input at the continental shelf and the deep ocean, but lithogenic and biogenic inputs both play prominent roles at the edge of the AIS. This hypothesis is supported by the classification of sampling stations using CA (Fig. 4) and the ratios of bio/lith.

As shown in Fig. 4, there is a much closer relation between the continental shelf and deep ocean than either of them with the AIS edge, suggesting similar assemblages of trace metals at the continental shelf and deep ocean, and a different assemblage at the AIS edge. High ratios of bio/lith for Zn and Cd at the continental shelf and deep ocean (Table 3) indicate that the source

Table 3 Ratios of biogenic to lithogenic input in the sediments from the three geographic zones sampled.

	Zn			Cd		
	Range	Mean	Median	Range	Mean	Median
Amery Ice Shelf	0.26–1.07	0.68	0.76	0.68–1.62	1.14	1.04
Continental shelf[a]	1.30–4.19	2.63	2.21	2.04–3.70	3.05	3.21
Deep ocean	2.91–3.44	3.18	3.18	1.47–1.54	1.51	1.51

[a] P2–9 is not included.

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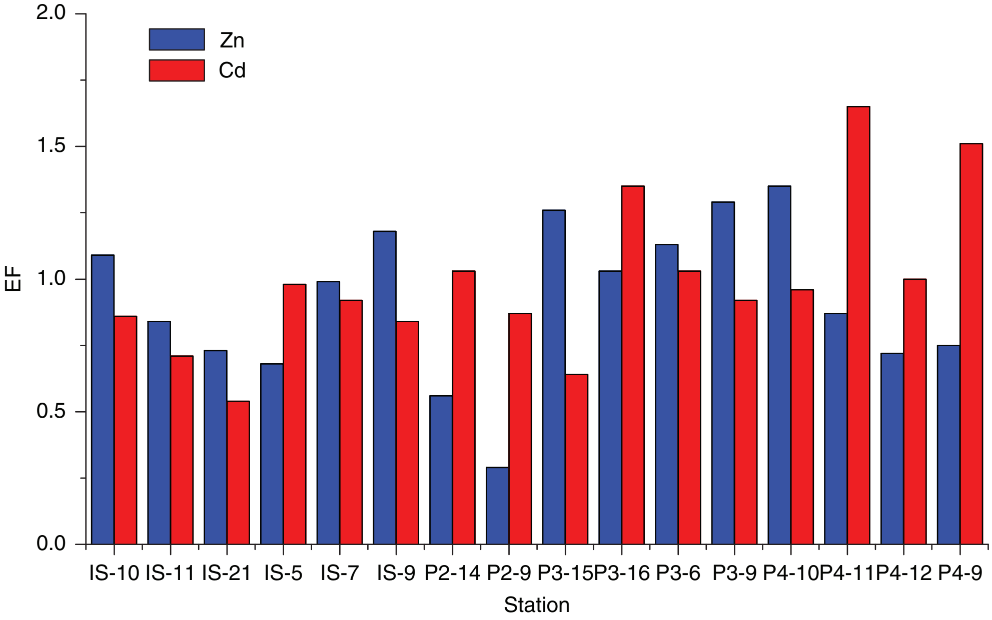

Fig. 5 Enrichment factor (EF) values for Zn and Cd. IS stations were those at the edge of the Amery Ice Shelf. Stations at the continental shelf were P2, P4, P3–15 and P3–16. The deep ocean stations were P3–6 and P3–9.

composition of the sediments from these two areas is similar and dominated by biogenic input. However, the bio/lith ratios of about one at the edge of AIS for Zn and Cd (Table 3) support the hypothesis that biogenic and lithogenic inputs are almost equal in the sediments at the AIS edge.

However, the highest ratio of bio/lith for Cd is observed at the continental shelf, most likely owing to the highest phytoplankton biomass and consequently the highest output of organic matters. In contrast, the ratio for Zn is highest at the deep ocean area, where the phytoplankton biomass is the lowest. The contrast between Zn and Cd is probably due to the controlling environmental factors for the deposition, resolution and preservation of Zn and Cd in the water column and sediment, that is to say, the second component (result from PCA). Cd and BSi both negatively weight the second component (Fig. 4), suggesting that Cd is controlled by organic matter. Higher input of organic matters leads to the higher proportion of biogenic Cd in the sediments, or high organic matter benefits the reserve of Cd in sediment (Nimistö & Perttiiä 1995; Ravanelli 1997). Zn, Fe and Mn positively weight on the second component (Fig. 4), suggesting that Zn may be dictated by Fe–Mn oxides in the water column and sediments. As the contents of Fe and Mn are highest at the deep ocean (Table 1), more biological pellets (including biogenic Zn) would be absorbed by Fe–Mn oxides during deposition through the longest depositional pathway in the water column (water depth is 1538 m for station P3–9, and 3054 m for station P3–6, respectively). At the same time, the anaerobic condition in the deep ocean creates an environment suitable for the formation of ferrous sulfide, which can adsorb insoluble zinc sulfide (Liao 1992) and further benefits the preservation of Zn in the sediments (Santos et al. 2005).

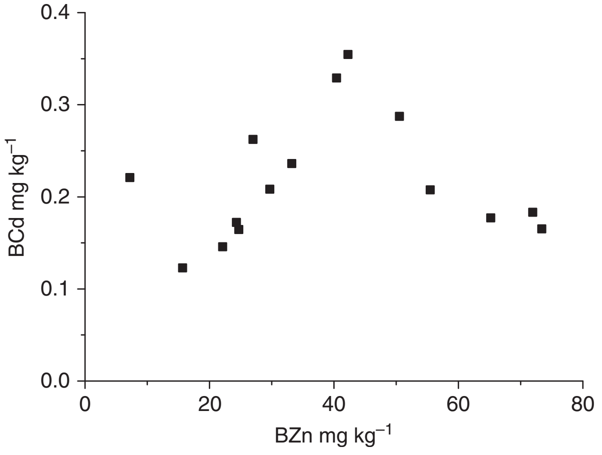

Fig. 6 Relation between biogenic Zn (BCd) and Cd (BZn) in the surface sediments.

Relation between Zn and Cd

Zn and Cd have similar chemical behaviours and are usually intergrown and associated in minerals. If Zn and Cd in the sediments are only directly derived from mineral particles, their composition in the sediments would be similar to the mineral assemblage of the host rocks, and a positive linear relationship between Zn and Cd in the sediments would be observed. However, Zn and Cd are from both lithogenic and biogenic sources, making the relation between them in the sediments and their behaviours during biogeochemical process not so simple to interpret from their contents in the sediments. Based on the estimated contents of trace metals from biogenic sources, different relationships between biogenic Zn and biogenic Cd are observed (Fig. 6): (1) Zn and Cd are positively correlated ($r = 0.972$, $n = 9$) when the content of biogenic Zn ranges from 10 to 50 mg kg^{-1}; (2) Zn and Cd are negatively correlated ($r = -0.916$, $n = 5$) when the content of biogenic Zn is >50 mg kg^{-1}; (3) the content of biogenic Cd is abnormally high when the content of biogenic Zn is <10 mg kg^{-1}. Because biogenic trace metals in the sediments mainly originate from the output of phytoplankton living in the upper water column, deposited on the seafloor as pellets, the relation between Zn and Cd in the sediments could reflect the uptake process of them by phytoplankton in the water column. The presence of three types of relationship indicates that the uptake of Cd is continuously increasing with that of Zn when the content of Zn in the seawater is "ideal." However, the uptake of Cd is depressed when the Zn content in the water becomes too high, whereas the uptake of Cd is stimulated when the Zn content is below a certain level. This is consistent with the idea that phytoplankton take up more Cd as a substitution for Zn in Zn-limited seawater (Morel et al. 1994; Lee & Morel 1995; Lane & Morel 2000).

Conclusions

Zn and Cd in the sediments of Prydz Bay are not significantly anthropogenically influenced. Biogenic and lithogenic inputs are the main sources of trace elements and they are almost equal for Zn and Cd at the AIS edge. At the continental shelf and deep ocean, biogenic input is dominant and its proportion is much higher for Zn than for Cd at the deep ocean area. Three types of relationship between biogenic Zn and biogenic Cd were discerned, reflecting the biological uptake of trace nutrients by phytoplankton.

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