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# Source, processes and productivity from distribution of surface sediments, Prydz Bay, East Antarctica

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### ABSTRACT

Source of sediments and depositional processes of surface sediments along the Prydz Bay were investigated through grain size, organic carbon, nitrogen, phosphorus, calcium carbonate and metal concentration. High content of sand and higher values of  $Al_2O_3$  and TiO<sub>2</sub> at shallow water depth indicate their terrigenous source and relatively higher hydrodynamic conditions near the coast.  $AI_2O_3/TiO_2$  ratio ranging from 3.77- 12.73 suggests a mafic source for the sediments. C/N ratio ranging from 5.76 to 9.13 indicates autochthonous (in-situ) source for organic matter, for which phytoplanktons and algae may be the major contributors. However, N/P ratio lower than the Redfield ratio indicated a limitation of either N or P in the study area. Calcium carbonate concentration is low possibly due to increased loads of clay which must have caused the dilution of carbonates. Metals like Fe, Mn and Mg exhibit strong correlation with lithogenic elements while, the trace metals such as Cd, Co, Cu, Ni and Zn show significant correlation with organic elements indicating that lithogenic and biogenic inputs are their main sources. Trace elements namely, Cd and Zn show nutrient like behavior suggest the role of trace metal in addition to nutrients in the regulation of productivity. Thus, the present study provides an understanding of recent sedimentary environments and processes, which are used as a tool to interpret palaeoenvironmental records.

## 1. Introduction

Terrigenous and biogenic inputs constitute a major part of the sediments accumulated in the Southern Ocean. Grain size, organic matter and metal composition are good indicators to interpret source and origin of the sediments in Antarctica and its surrounding oceans. Grain size is susceptible to environmental changes and has been widely used to study depositional environments ([Gao and Collins, 2001](#page-7-0)). A combination of different processes, such as, abrasion, selective transport and mixing of sediments are responsible for changes in grain size [\(Wang](#page-8-0) [et al., 2016](#page-8-0)). Organic and geochemical imprints in the sediments are a function of complex interactions between the source area and sedimentation, and their association helps in identification of the provenance. These proxies help in interpreting source and processes of sedimentation in high latitude regions where, chemical weathering is weak ([Wang et al., 2016](#page-8-0)).

Prydz Bay exhibits the largest shelf on the eastern margin of Antarctica [\(Harris et al., 1998\)](#page-7-1). It receives sediments supplied by the Lambert Glacier/Amery Ice Shelf, draining approximately 10% of the total Antarctic ice volume [\(Forsberg et al., 2008](#page-7-2)). The pristine marine environment preserves a detailed record of past climatic conditions prevailed in east Antarctica. Studies in this area are largely focused on the reconstruction of palaeo records, however, reports on sedimentary processes are rare. [Diekmann \(2007\)](#page-7-3) stated that detrital materials in the southern part of Southern Ocean have glaciogenic input from the Antarctic region. [Harris et al. \(1998\)](#page-7-1) suggested four main factors affecting sedimentation i.e. movement of the Amery ice shelf and adjacent ice sheets, ocean current circulation patterns, distribution of sea ice and water depth. [Diekmann and Kuhn \(1999\)](#page-7-4), [Diekmann \(2007\)](#page-7-3) pointed out that temperature was an important factor for ice formation and thus for transportation and deposition of ice-rafted debris (IRD). [Borchers](#page-7-5) [et al. \(2011\)](#page-7-5) provided a set of mineralogical data (clay minerals and heavy minerals) in Prydz Bay. Further, [Sun et al. \(2013\)](#page-7-6) reported that anthropogenic influence in the Prydz Bay is not significant, however, biogenic and lithogenic inputs are main sources of trace elements. [Wang et al. \(2016\)](#page-8-0) stated that grain size and heavy minerals are useful proxies for interpreting glacial dynamics and detailed study of sediment provenance. Therefore, with an aim to fill the gaps, a study on grain

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size, organic elements carbon, nitrogen, phosphorus, major (Al, Ti, Fe, Mn and Mg) and trace metals (Cu, Ni, Zn, Cd, Pb and Co) was undertaken to understand sedimentary characteristics, their source, depositional processes and productivity in the recent past of the Prydz Bay.

### 2. Regional setting

Prydz Bay is an embayment along the Antarctic margin between 66<sup>0</sup> E and  $79^{\circ}$  E [\(Sun et al., 2013](#page-7-6)). On the southern side, it is surrounded by Amery Ice Shelf (AIS) and spreads to the edge of the continental shelf northwards at about 67<sup>°</sup> S. The Amery Depression dominates the inner continental shelf, which is mostly 600–700 m deep. The depression is bordered by two shallow banks (< 200 m): Fram Bank to the northwest and Four Ladies Bank to the northeast, forming a spatial barrier to exchange water with the outer oceanic water ([Smith and Treguer,](#page-7-7) [1994\)](#page-7-7). Prydz Bay is characterized by a clockwise gyre in front of the Amery Ice Shelf ([Smith et al., 1984](#page-7-8); [Passchier et al., 2003\)](#page-7-9) covering almost the entire bay. It is covered by sea ice for almost whole year except few days in summers. Icebergs are also observed on the eastern side of the bay, which have originated from the West Ice Shelf and brought southward by the coastal current under the influence of cyclonic winds ([Smith et al., 1984\)](#page-7-8). In the bay, most of the icebergs and floating ice mass are found near the outlet glaciers. The glaciers entering the bay primarily come from the Ingrid Christensen Coast, including the Sorsdale Glacier which flows south of the Vestfold Hills and the glaciers that contribute to the Publication Ice Shelf. Four Antarctic research stations are located on the shore of Prydz Bay, the Indian station Bharati (69.4077<sup>0</sup> S, 76.1872<sup>0</sup> E), Chinese station Zhongshan (69.378 $^{\rm 0}$  S, 76.388 $^{\rm 0}$  E), the Russian station Progress (69.388 $^{\rm 0}$  S, 76.388 $^{\rm 0}$ E) and the Romanian station Law Racovita (69.398 $^{\circ}$  S, 76.388 $^{\circ}$  E).

Geologically, Prydz Bay is part of the Pan-African Prydz Belt, which is recognized as a result of tectonic processes initiating in the Archean ([Wilson et al., 1997](#page-8-1); [Boger et al., 2001;](#page-7-10) [Liu et al., 2006\)](#page-7-11) and comprises of three Archean cratonic blocks, a Grenvillian granulite terrane and a Pan-African high-grade belt ([Liu et al., 2006](#page-7-11)). The Archean blocks, exposed in the southern Prince Charles Mountains, Vestfold Hills and Rauer Islands, comprise primarily of orthogneiss; while the Grenvillian granulite is mainly exposed in the northern Prince Charles Mountains and consists of a metamorphic complex including felsic orthogneiss, gneiss, mafic granulite and charnockite ([Li, 2006\)](#page-7-12). The Pan-African high-grade belt mainly distributes along the Prydz Bay coastline and consists of mafic-felsic composite orthogneisses and migmatitic paragneisses ([Fitzsimons and Harley, 1991](#page-7-13); [Dirks and Wilson, 1995;](#page-7-14) [Liu](#page-7-11) [et al., 2006](#page-7-11)).

# 3. Materials and methodology

#### 3.1. Sampling and analytical procedures

A total of seven surface sediment samples between depth range of 31–140 m were collected during February 2015 from the continental shelf of Prydz Bay using Grab sampler ([Fig. 1](#page-2-0)). The samples were preserved in cold storage in pre-numbered plastic bags. In the laboratory, each sediment sample was later dried at 60 °C in the oven and used for further analysis. Grain size analysis was carried out by the pipette method of [Folk \(1968\)](#page-7-15) which is based on stoke's settling velocity principle. Freeze dried samples were analyzed for total carbon (TC) and total nitrogen (TN) concentration using an EA (Isoprime, Vario Isotope Cube). The analytical precisions for TC and TN are  $\pm$  0.31% and  $\pm$ 0.30% (1σ standard deviation) obtained by repeatedly running Sulfanilamide as the standard. Total inorganic carbon (TIC) was measured by using UIC carbon coulometer. Total organic carbon (TOC) was calculated by subtracting TIC from TC. Calcium carbonate  $(CaCO<sub>3</sub>)$  was computed using the values of TIC. Biogenic silica (BSi) was extracted from the freeze-dried sample using 25 ml of 1%  $Na<sub>2</sub>CO<sub>3</sub>$  in an 85 °C water bath for 5 h and measured by the wet alkaline extraction method,

modified by [Mortlock and Froelich \(1989\)](#page-7-16) and [Muller and Schneider](#page-7-17) [\(1993\)](#page-7-17) where intensity of blue silicon-molybdenum complex was measured at 810 nm using UV-1800 (Shimadzu) visible spectrophotometer. Duplicate measurements were conducted on each sample and relative error was noted to be less than 3%. The sediment for total phosphorus analysis was digested using HF:  $HNO<sub>3</sub>$ :  $HClO<sub>4</sub>$  mixture and brought to liquid phase as adopted by [Yu et al. \(2013\)](#page-8-2) and further determined following the procedure by [Murphy and Riley \(1962\)](#page-7-18) where the intensity of phospho-molybdenum blue complex was measured at 880 nm using UV-1800 (Shimadzu) visible spectrophotometer. The accuracy of phosphorus analysis was determined using a digested sample of certified standard GSJ JLK-1 and relative error was noted to be less than 3%. Further, ground sediment samples were digested in Teflon beakers using HF,  $HNO<sub>3</sub>$  and  $HClO<sub>4</sub>$  acid mixture with a ratio of 7:3:1 for total metal analyses ([Jarvis and Jarvis, 1985](#page-7-19)). The metals Fe, Mn, Al, Mg, Co, Zn, Cu and Ti were analyzed using Flame Atomic Absorption Spectrophotometer and Cd, Ni and Pb using Graphite Furnace Atomic Absorption Spectrophotometer (Thermo Scientific-SOLAAR M6 AAS model). Together with the samples, certified reference standards JLK-1 from the Geological Survey of Japan were digested and run to test the analytical accuracy of the method. The average recoveries were 94% for Ti; 95% for Mn and Co; 96% for Mg, Fe, Cu, Ni, Cd and Al and 99% for Zn and Pb. Internal chemical standards obtained from Merck were used to calibrate the instrument, recalibration checks were performed at regular intervals.

# 3.2. Statistical analysis

Based on the crustal composition ( $[M/A]$ <sub>crust</sub>), the proportion of the lithogenic input of trace metals (M lith) was estimated ([Tribovillard](#page-8-3) [et al., 2011](#page-8-3)) as follows:

 $M_{\text{lift}} = M-M_{\text{lift}}$ , where M is the metal

where Al <sub>sample</sub> and Al <sub>crust</sub> [\(Wedepohl, 1995](#page-8-4)) were the concentration of the element Al in the sample and in the continental crust respectively. Al was used as a normalizer, as it is a conservative element and has no significant anthropogenic source.

The biogenic trace metal (M  $_{bio}$ ) is computed by using the formula: M  $_{\text{bio}} = M \cdot M$  lith.

Pearson's correlation test ( $p < 0.05$ ) was employed to verify the possible correlation between the different parameters. Factor analysis was performed to understand the source of metal input in sediments. Data were processed by using the computer software STATISTICA-6 ([Statsoft, 1999\)](#page-7-20).

#### 4. Results and discussion

#### 4.1. Sediment components

Sand, silt and clay fraction of the studied samples range from 4.64 to 24.58%, 49.88–82.16% and 13.20–34.80% respectively, with the average of 15.27%, 63.71% and 21.01% respectively. Among sediment components silt is predominant. Sand is highest at station P1, silt show decreasing trend from station P3 to P7 and clay is highest at station P4. Further, the data on sediment components of surface sediments from Prydz Bay is presented in [Fig. 2.](#page-2-1) Grain size analysis of surface sediments (P1-P7) has indicated an overall decrease in sediment size with increasing water depth away from the coast. The sediment components shows the dominance of clayey silt (21.01% clay, 63.71% silt). Textural analysis has been used to infer the hydrodynamic conditions of the depositional environment. For this purpose, a ternary diagram [\(Fig. 3\)](#page-3-0) proposed by [Pejrup \(1988\)](#page-7-21) has been used. The hydrodynamics are distinguished in the diagram into four sections labeled as I to IV. Section I indicates the very calm hydrodynamic condition and section II to

<span id="page-2-0"></span>

Fig. 1. Geological map of the Larsemann Hills, Prydz Bay, East Antarctica, showing major lithological units and sample locations (modified after [Tong et al., 2017\)](#page-7-22). The inset shows the position of the Larsemann Hills in Prydz Bay.

<span id="page-2-1"></span>IV indicate increasingly violent hydrodynamic conditions. Further, sections A to D provides an environment with respect to the size of the sediments. When the data was plotted, surface sediments collected from Prydz Bay mostly fell in section III(C), with single point been part of IV (D) indicating less violent to violent conditions prevailed facilitating deposition of finer sediments.

Relatively higher sand content in the shallower areas of the bay corresponds to the glaciomarine input that may be due to the combined effect of coastal currents and iceberg scouring. The study area remains covered largely by sea ice and floating ice in winter, with scattered



Fig. 2. Histogram showing percentage of sediment components in the samples.

<span id="page-3-0"></span>

Fig. 3. Triangular diagram for classification of hydrodynamic conditions of Prydz Bay (after [Pejrup, 1988](#page-7-21)).

occurrences of icebergs in the Prydz Bay ([Passchier et al., 2003\)](#page-7-9). When these icebergs calve from the ice-shelves and outlet-glaciers, they gradually melt and release coarse material debris into the sea. At shallower depths, high energy environment must have facilitated deposition of coarse grain sediments and its winnowing effects transported the finer fraction of sediments away from the coast. The high energy environment, water depth and topography together play an important role in regulating the sedimentation processes of the area studied ([Wang et al.,](#page-8-0) [2016\)](#page-8-0). Sediment supply to the Prydz Bay is mainly by glacio-fluvial meltwater, however, supply due to intense wind (katabatic winds) that helps in transporting terrigenous material derived from erosion and weathering of the catchment rocks, which gets deposited on ice and percolates through cracks in the ice and get deposited in the Bay ([Spaulding et al., 1997](#page-7-23)) cannot be ruled out. Therefore, the removal of fine-grained material leaving behind the coarser and its subsequent transport into the shallow marine environment also corresponds to the aeolian deposition of sediment in the inshore environment ([Franklin,](#page-7-24) [1997\)](#page-7-24).

## 4.2. Organic elements (C, N, P and BSi)

TOC and TN concentration varies within a range of 1.49%–3.40% and 0.23% to 0.59% respectively ([Fig. 4](#page-4-0)). TOC (3.40%) and TN (0.59%) were highest at station P4 at 60 m water depth while least concentrations of TOC (1.49%) and TN (0.23%) were noted at station P1 at 31 m water depth. TOC and TN ([Fig. 5](#page-4-1)a) indicated a strong association with each other as with high organic carbon, the nitrogen concentration increased indicating that most of the TN was associated with TOC and therefore, it can be considered as a measure of organic nitrogen ([Kurian](#page-7-25) [et al., 2013](#page-7-25)). Total phosphorus (TP) in the Prydz Bay varied from 0.013 to 0.036% [\(Fig. 4](#page-4-0)). Its high concentration was noticed at station P4 at 60 m water depth while minimum at station P7 at 140 m. Scatter plots of TOC and TN with TP revealed a poor association with each other ([Fig. 5b](#page-4-1) and c) indicating a differential pathway for phosphorus or the possible influence of diagenesis on phosphorus.

C/N ratio is used extensively to identify the source of organic matter in sediments ([Sweeney et al., 1980;](#page-7-26) [Jasper and Gagosian, 1993;](#page-7-27) [Meyers,](#page-7-28) [1997\)](#page-7-28). Algae, typically have atomic C/N ratios between 4 and 10, whereas vascular land plants have C/N ratios of 20 and greater ([Meyers, 1994](#page-7-29)). Marine and freshwater phytoplanktons have a C/N ratio of 5–6 ([Prahl et al., 1994;](#page-7-30) [Meyers, 1997](#page-7-28)) whereas the terrestrial higher vascular plants which are poor in nitrogen have a C/N ratio of 12–14 [\(Hedges et al., 1986](#page-7-31); [Lamb et al., 2006\)](#page-7-32). In Prydz Bay, the C/N ratio ranging between 5.76 and 9.13 [\(Table 1](#page-5-0), [Fig. 4\)](#page-4-0) indicates its marine source (in situ). The values obtained can be classified following

[Meyers \(1994\)](#page-7-29) as exclusively derived from algae ( $C/N < 10$ ).  $C/N$ ratio was found to be low for the studied coastal area may be because either C or N is diagenetically affected or the bacterial action might have caused dissolution of organic matter, lowering the ratio. N/P (molar) ratios were low and varied between 3.93 and 11.53 indicating nitrogen deficiency either due to the strong removal of N in coastal waters by denitrification ([Howarth and Marino, 2006](#page-7-33)) or by incorporation of P more rapidly than N into the sediments. C/P (molar) ratios varied from 27.20 to 63.39, with the lowest ratio at station P2 at 40 m water depth and the highest ratio at station P7 at 140 m water depth.  $CaCO<sub>3</sub>$  content in Prydz Bay ranges from 0.83% to 3.50% ([Table 1](#page-5-0)) except for stations P-2 and P-6 show exceptionally high  $CaCO<sub>3</sub>$  content of 28.74% and 48.56% respectively possibly due to high inorganic carbon content. In general, high  $CaCO<sub>3</sub>$  in the nearshore sediments may be due to glacial meltwater and terrigenous sediments which bring nutrients along with them facilitating high productivity. However, higher values were obtained only for two stations.

The molar C: N: P ratios are used to decipher nutrient biogeochemical cycling in the oceans and productivity changes. [Red](#page-7-34)field, [1934,](#page-7-34) [1958](#page-7-35) suggested that when neither of the nutrients is in limiting conditions, the ratio is 106:16:1 and fluctuation from this standard condition suggested a limitation of C, N or P. C/N ratio was found close to Redfield ratio in all the samples except P2 and P6 wherein C/N ratios were higher. Nitrogen is generally remineralized in marine sediments ([Ramaswamy et al., 2008](#page-7-36)) and may have been diagenetically affected in the present case elevating the C/N ratios. [Meybeck \(1982\)](#page-7-37) suggested that autochthonous organic matter is characterized by relatively low C/ N ratios, typically < 10, whereas, [Hedges et al. \(1986\)](#page-7-31) stated that allochthonous organic matter has C/N ratios normally higher than 20 and may be > 200. In Prydz Bay, C/N ratio for all the samples is lower than 10 indicating the autochthonous origin of organic matter. [Forsberg](#page-7-38) [\(1980\)](#page-7-38) and [Hellstrom \(1996\)](#page-7-39) suggested that N: P ratio above 17 indicates P limitation; a ratio below 10 suggests N limitation and values between 10 and 17 indicate that either of the nutrients may be limiting. N: P ratio < 11.53 indicates either N or P may be the limiting nutrient in the study area. C/P molar ratio ranges from 27.20 to 63.39 [\(Table 1\)](#page-5-0) which is lower than the Redfield ratio (106:1) may be due to the degradation of organic matter before it gets buried in the sediments. Low C/P ratios are mostly observed in areas with low organic carbon preservation. Even though there is a possibility of the huge amount of terrestrial input of organic matter brought to the Prydz Bay by the glacier melt, the TOC content was found low. This may be due to the strong currents close to the shelf associated with the southern boundary of the ACC with velocities of up to 28 cm s−<sup>1</sup> [\(Read et al., 1995\)](#page-7-40), which may transport finer sediments and organic matter.

The biogenic opal or biogenic silica concentration in the Southern Ocean is ascribed to the siliceous diatom productivity [\(Chase et al.,](#page-7-41) [2003;](#page-7-41) [Bradtmiller et al., 2006\)](#page-7-42). BSi concentration ranges from 16.42% to 35.41% in the surface sediments of Prydz Bay. BSi shows significant correlation with TOC ( $r = 0.79$ ) and TN ( $r = 0.76$ ) indicating that its content was controlled by the amount of algae [\(Shan et al., 2011](#page-7-43)) along with other phytoplanktons. The close relationship between BSi and other geochemical parameters confirmed that sedimentary organic matter was predominantly derived from the natural products of the ocean. Increase in BSi concentration is accompanied by a decrease in carbonate content suggesting that when diatom dominates the surface waters, coccolithophore production declines and vice-versa. Such relationship observed by [Manoj and Thamban \(2015\)](#page-7-44) suggests the influence of nutrients on the survival and proliferation of the two major producers of the ocean, hence affecting overall productivity.

Calcium carbonate (CaCO<sub>3</sub>) content is generally controlled by surface water productivity, the rate of carbonate dissolution and dilution by the non-carbonate fraction. The low values of  $CaCO<sub>3</sub>$  can be attributed to the decreased carbonate productivity and/or increased dissolution. In the study area,  $CaCO<sub>3</sub>$  is associated with sand and clay shows negative correlation ( $r = -0.003$ ) with CaCO<sub>3</sub> suggesting that

<span id="page-4-0"></span>

Fig. 4. Distribution of total organic carbon (TOC), total nitrogen (TN), total phosphorus (TP) and C/N ratio in surface sediments along the Prydz Bay.

due to increase in clay concentration  $CaCO<sub>3</sub>$  concentration must have decreased. Further, the increase of TOC is accompanied with the decrease of CaCO<sub>3</sub>. It indicates that the  $CO<sub>2</sub>$  produced by the decomposition of organic carbon and production of organic acids reduces the pH of anoxic pore waters enough to dissolve CaCO<sub>3</sub> that reaches the sediment-water interface [\(Nioti et al., 2013](#page-7-45)).  $CaCO<sub>3</sub>$  and TOC are inversely related implying different origin for inorganic and organic carbon throughout the sedimentation process.

<span id="page-4-1"></span>

Fig. 5. Scatter plots between a) total organic carbon (TOC) and total nitrogen (TN), b) total organic carbon (TOC) and total phosphorus (TP) and c) total nitrogen (TN) and total phosphorus (TP).

<span id="page-5-0"></span>





 $M = molar ratio$ .

#### 4.3. Geochemical elements

The geochemical data were classified into terrigenous i.e. Al, Ti, Fe, Mn and Mg [\(Shimmield and Pedersen, 1990\)](#page-7-46), biogenic and organicassociated i.e. Cu, Ni, Zn, Cd, Pb and Co components ([Dymond et al.,](#page-7-47) [1992\)](#page-7-47).

## 4.3.1. Terrigenous elements (Al, Fe, Ti, Mn and Mg)

Metal concentration in the study area are in the order of Fe > Al > Mg > Ti > Mn [\(Fig. 6](#page-5-1), [Table 2](#page-6-0)). Bulk concentration of metals like Al, Ti, Fe, Mn and Mg in the marine sediments generally reflects the concentration of terrigenous aluminosilicate phases ([Shimmield and Mowbray, 1991](#page-7-48)). Variations in these elements are predominantly controlled by a varying supply of detrital material. In Prydz Bay, most of these elements reveal similar variability indicating their similar lithogenic source and common depositional processes. Metals like Al and Mg exhibited strong correlation ( $r = 0.87$ ) indicating their terrigenous source and common post-depositional behavior. The Al content in marine sediments is an indicator of lithogenous input as the average concentration of Al in different rocks varies by only 10% from an average crustal value ([Turekian and Wedepohl, 1961\)](#page-8-5). Ti show strong correlation with Fe ( $r = 0.97$ ) and Mn ( $r = 0.95$ ). These metals, thus, support their lithogenic nature, derived from the weathering of rocks such as gneisses present in the catchment area, hence, these metals are classified as terrigenous elements. The supply of terrigenous material to the Prydz Bay is mainly due to either by glaciomarine input (glaciogenic) or, by erosion and weathering of the catchment rocks, introduced to the sea via iceberg rafting, melt out and roll over in the periphery of the Prydz Bay; or, by strong katabatic winds (aeolian).

#### 4.3.2. Biogenic and organic-associated elements

Overall abundance of metal concentrations in the sediments follows the order:  $Cu > Ni > Zn > Co > Cd > Pb$  ([Fig. 6](#page-5-1), [Table 2](#page-6-0)). The enrichment of these elements along with carbonate, TOC and opal in marine sediments has been used as palaeo-productivity indicators ([Collier and Edmond, 1984](#page-7-49); [Shimmield and Pedersen, 1990\)](#page-7-46). Metals

like Co ( $r = 0.84$ ), Cu ( $r = 0.85$ ) and Zn ( $r = 0.93$ ) show strong correlation with TOC indicating the role of organic matter in their distribution. Ni exhibited significant correlation with TOC ( $r = 0.93$ ), TN  $(r = 0.91)$  along with BSi  $(r = 0.81)$  indicating their biogenic source. Cd showed a positive correlation with TOC ( $r = 0.65$ ) and strong correlation with phosphorus ( $r = 0.97$ ). Zn showed a positive correlation with BSi ( $r = 0.61$ ) and strong correlation with TOC ( $r = 0.93$ ) and TN  $(r = 0.83)$  indicating that all these elements are derived biogenically and are classified as biogenic and organic associated element. Elements absorbed and assimilated by marine organisms are released back into the water column as biological material, forming biogenically sourced material in the sediments. In the Prydz Bay, the average bulk content of Cd, Co, Cu, Ni and Zn were 6.82 ppm, 16.57 ppm, 166.56 ppm, 110.29 ppm and 22.91 ppm respectively and their respective biogenic proportion are 6.81 ppm, 15.45 ppm, 165.19 ppm, 108.50 ppm and 17.91 ppm respectively suggesting that ∼99.85%, 93.24%, 99.18%, 98.38% and 78.18% of these elements respectively are derived from biogenic input. While the remaining portion 0.15%, 6.76%, 0.82%, 1.62% and 21.82% of these elements were associated with silicates. However, Pb (avg. 1.56 ppm) was found to be of lithogenic origin as biogenic input is negligible. Lithogenic sources probably have made less contribution in this region, may be because most of the lithogenic fraction are used up by phytoplankton resulting in high values of the biogenic fraction. In the absence of fluvial input and lack of soil around the Prydz Bay trace elements in the sediments originated from lithogenic inputs and marine biogenic deposition as observed by [Gasparon](#page-7-50) [and Matschullat \(2006\)](#page-7-50). [Isla et al. \(2004\)](#page-7-51) stated that the biogenic deposition should be high on the continental shelf than that in the deep ocean. In the study area, high biogenic input on the continental shelf was evidenced by the high content of BSi and TOC suggesting extensive biological processes in the area. Anthropogenic activities at the research stations located along the coastline must have contributed negligible levels (lower than natural variability) of trace metals to the Prydz Bay.

<span id="page-5-1"></span>

Fig. 6. Box and Whisker plots of metal concentrations in surface sediments along the Prydz Bay (The horizontal bar in the box displays the mean value, the ends of the Whiskers to the maximum and minimum values. The top and bottom of the boxes include half the data points between the average and the extremes of the range).

<span id="page-6-0"></span>



#### <span id="page-6-1"></span>Table 3

Factor loadings of the surface sediments of Prydz Bay.

	Factor 1	Factor 2	Factor 3	Factor 4
% of total variance Cumulative % of total variance	54.59297 54.59297	20.91565 75.50862	8.95644 84.46506	7.65108 92.11614
Sand	$-0.06129$	0.729500	$-0.644542$	$-0.116021$
Silt	$-0.60056$	$-0.511604$	0.594266	$-0.009980$
Clay	0.90837	0.048844	$-0.244841$	0.121750
<b>TOC</b>	0.86131	$-0.462760$	$-0.064796$	$-0.1217255$
TN	0.71257	$-0.633398$	$-0.220968$	$-0.083818$
C/N	0.00739	0.715003	0.355253	0.043098
BSi	0.60841	$-0.684476$	0.346088	0.201080
P	089793	0.192201	0.263040	0.194881
A1	$-0.75627$	$-0.310019$	$-0.119662$	$-0.31215$
Тi	$-0.65222$	$-0.354236$	$-0.267456$	0.612015
Fe	$-0.67356$	$-0.503757$	$-0.161232$	0.487350
Mn	$-0.79865$	$-0.387047$	$-0.288872$	0.358350
Mg	$-0.92536$	$-0.157308$	0.183532	$-0.227946$
Cd	0.88642	0.145304	0.283678	0.294648
Co	0.65852	$-0.469783$	$-0.287372$	$-0.092849$
Сu	0.98543	0.046701	$-0.037447$	0.007453
Ni	0.82995	$-0.435136$	0.106586	$-0.107688$
Pb	$-0.52999$	$-0.578339$	$-0.019837$	$-0.556243$
7.n	0.80725	$-0.357679$	$-0.315916$	$-0.122366$
<b>Explored Variance</b>	10.37266	3.973973	1.701724	1.453705
<b>Proportion Total</b>	0.54593	0.209156	0.089564	0.076511

Extraction: Principal components (marked loadings are significant  $> 0.7$ ).

## 4.4. Factor analysis

R–mode factor analysis has been performed to support interpretation made on the source of metal input in sediments of the continental shelf, Prydz Bay. The factor loadings are presented in [Table 3.](#page-6-1) Four factors could be extracted contributing to about 54.59, 20.92, 8.96 and 7.65 percent of the variance respectively which account for a cumulative percentage of 92.12 with Eigen value  $> 1$ . For the first factor, clay, TOC, TN, TP, Cd, Cu, Ni and Zn are observed to be positively loaded, thus indicating their association with organic matter along with fine-grained sediments. Metals like Al, Mn and Mg are found to be negatively loaded indicating their common lithogenic nature. Factor 2, 3 and 4 are less significant and does not represent any major association.

#### 4.5. Relationship between nutrients and trace elements

TOC (1.49%), TN (0.23%) and TP (0.014%) are found low near the coast at station P1 at 30 m water depth indicating minimum nutrient concentrations in oligotrophic surface water and further, showed an increase with increasing water depth. Low concentrations of Cd (4.86 ppm) and Zn (13.25 ppm) at station P1 suggest their depletion caused by its use by marine phytoplanktons. Cd shows strong positive correlation with P and Zn, and exhibiting significant correlation with TOC and TN which indicate their similar behavior suggesting the role of trace metal along with the nutrients in the regulation of productivity. Cd, is generally detrimental to living organisms, however, along with

Zn it has a nutrient-like profile [\(Morel et al., 1994](#page-7-52)). Its concentration is well correlated to that of P that the accumulation of Cd in the fossilized tests of marine organisms is used as a measure of past nutrient concentrations in the sea [\(Sunda, 2012](#page-7-53)). Cd enhances the growth rate of some marine phytoplankton and can be used as a substitution for Zn when Zn is limited ([Morel et al., 1994\)](#page-7-52). High Zn concentration is usually found below the photic zone; however, thermohaline and winddriven upwelling can bring high-nutrient and high-zinc to the surface, especially in polar regions [\(Sunda, 2012](#page-7-53)). The near-surface processes such as algal uptake, settling and shallow water regeneration can influence the composition of nutrients and trace metals.

# 4.6.  $Al_2O_3/TiO_2$  ratio

The geochemical characteristics of clastic sediments have been used to find out the provenance signature ([Taylor and McLennan, 1985](#page-7-54)). The range of  $Al_2O_3/TiO_2$  ratio for the Prydz Bay is 3.77–12.73 suggesting mafic rocks must be the probable source rocks ([Hayashi et al., 1997\)](#page-7-55) for the sediments. The sediments must have derived from orthogneiss rocks present in the catchment area.  $Al_2O_3/TiO_2$  (12.73%) was high at station P1 at 31 m water depth while least at station P4 (3.77%) at 60 m water depth. Higher  $Al_2O_3$  and TiO<sub>2</sub> values near the coast may be due to higher detrital flux indicating a higher input of terrestrial material. [Shimmield and Pedersen \(1990\)](#page-7-46) earlier reported the concentration of heavy minerals due to strong current and winnowing action near the coast.

## 5. Conclusion

Surface sediments from Prydz Bay, East Antarctica were investigated to understand sedimentary characteristics, depositional processes, source and productivity in the recent past. Grain size distribution indicates that the direction of sediment transport was away from the coast and high energy conditions near the shore suggesting high detrital influx. TOC and TN show strong association with each other indicating their common source and their association with finegrained sediments. Nutrient concentrations i.e., C, N, P and BSi are found low on the surface due to the removal of nutrients by algal uptake. Similar behavior was exhibited by the trace elements such as Cd and Zn to that of nutrients indicating a close relationship between the trace elements and nutrients. Major metals like Al, Ti, Fe, Mn and Mg were found to be of lithogenic nature. Trace metals were derived from both biogenic and lithogenic sources, however, the biogenic input is dominant indicating extensive biological processes in the area. The present study carried out using multiproxy approach provided baseline dataset of characteristics of modern sedimentary processes along the Prydz Bay.

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## Appendix A. Supplementary data

Supplementary data related to this article can be found at  $\frac{http://dx.}{$  $\frac{http://dx.}{$  $\frac{http://dx.}{$ [doi.org/10.1016/j.polar.2018.06.002.](http://dx.doi.org/10.1016/j.polar.2018.06.002)

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