



Sedimentological and geochemical investigations to understand source of sediments and processes of recent past in Schirmacher Oasis, East Antarctica



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ABSTRACT

Three sediment cores collected from GL-1, V-1 (Vetehiya) and L-6 lakes of Schirmacher Oasis, East Antarctica were studied for sediment components (sand, silt, clay, total organic carbon, total nitrogen, TOC/TN ratio and biogenic silica), major elements (Aluminium, Iron and Manganese) and trace metals (Chromium, Zinc, Lead, Cobalt, Cadmium and Nickel). High sand content in all the three cores revealed the release of coarser sediments through mechanical weathering in fluvio-glacial environment. Relatively, high biogenic silica along with high total organic carbon associated with high clay in some sections indicated high primary productivity due to the warming and exposure of the lakes to the ice-melt water influx. TOC/TN ratio for all the cores was found to be < 10 which indicated that the major source of organic matter was autochthonous. Metals were found to be strongly associated with clay and organic carbon in core V-1, with sand and clay in core L-6 while, with silt and organic matter in core GL-1 indicating their role in regulating the distribution of metals. Cadmium in lake GL-1 was found to be associated with total organic carbon and showed largely biogenic origin, while, Cd and Pb in lakes L-6 and V-1 were found to be of anthropogenic origin. All the other metals showed signatures of lithogenic origin.

1. Introduction

Lakes are local response systems which act as high-resolution archives of local and regional change that help in understanding source of sediment and depositional environment. The lakes integrate the processes of their surrounding catchments and therefore they are highly sensitive to changes in landscape. High latitude lakes have many similar characteristics with those of temperate latitude and are subject to similar landscape controls. They are modern day analogs of paraglacial and periglacial lakes that were common during glacial periods in temperate latitudes (Phartiyal et al., 2011). The changes in the lakes and their catchments during the past are well archived in the form of sedimentary record. Sediment column of a modern lake indicates that the sediment deposited at its bottom consists of relatively older sediments than the surface and therefore, a sediment column represents the deposition of sediments in a span of time.

Antarctic lakes and their catchments experience persistent low temperature, intense seasonality and severe freeze-thaw cycles and these characteristics are likely to increase their sensitiveness to

landscape and environmental change. When these lakes were compared with fresh water lakes of other areas it was found that these lakes are subject to different physical, chemical, and biological processes because of longer duration of polar days and nights, and these lakes are ice free for only 3–4 months in a year. During this period lakes are exposed to the atmosphere which influences the biogeochemistry of the lake ecosystem. Therefore, the extent and thickness of ice cover in the catchment area greatly influence the biogeochemistry of Antarctic lakes (Wharton et al., 1993; Fritsen and Priscu, 1999). Conversely, in lower latitudes, terrestrial inputs through river discharge, saline water influence, plenty of vegetation and considerable anthropogenic impacts play an important role in regulating the ecosystem of the lakes (Padma and Periakali, 1999; Jeelani and Shah, 2006; Chakraborty et al., 2015; Nazneen and Raju, 2017).

The sediment characteristics like grain size, total organic carbon (TOC) and Biogenic silica (BSi) were used earlier as proxies in order to understand the biogeochemistry, productivity and environmental behavior of the Antarctic lakes and surrounding ocean (Mortlock and Froelich, 1989; Muller and Schneider, 1993; Colman et al., 1995;

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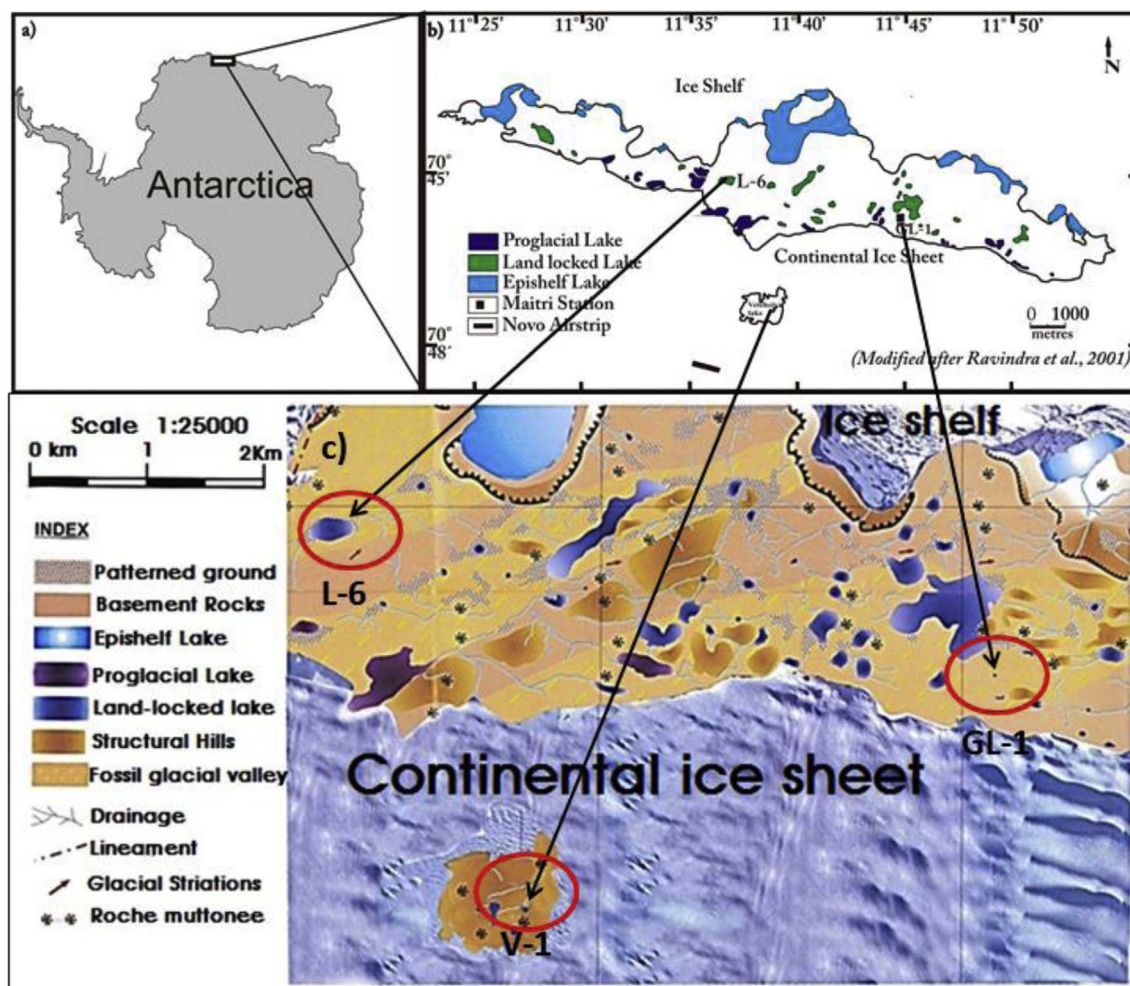


Fig. 1. a) Map of Antarctica showing the location of Schirmacher Oasis. b) Map of Schirmacher Oasis (modified after Ravindra et al., 2001) showing the sampling locations in the study area. c) Geomorphological map (modified after Geological survey of India (2006)).

Kamatani and Oku, 2000; Kaplan et al., 2002; Smith et al., 2006; Yoon et al., 2006; Govil et al., 2011). Smith et al. (2006) revealed that the lakes were nutrient limited and deficient in phytoplankton resulting in low productivity which decreases with depth and the organic matter found was marine derived. BSi, sand and TOC content of the sediments were estimated by Govil et al. (2011) and they reported that high sand (%) infers the glacio-fluvial deposition. The increased TOC in the upper part of the core possibly indicated presence of algal mat due to exposure of the lake to the ice-free conditions and siliceous microfossils were absent in the core resulting in low values of BSi. Significant correlation of BSi with other geochemical proxies (C and N) was reported by Shan et al. (2011) which confirmed that organic matter was predominantly derived from natural products of the lake. Mahesh et al. (2015) stated that the major source of organic matter is autochthonous derived from the microbial mat present at the core top.

The palaeoclimate record from Schirmacher Oasis is presented by many researchers. However, from the point of view of geochemical aspects, studies on provenance and sedimentary processes in Antarctic lakes are rare. Srivastava and Khare (2009) revealed that the source of sediments of various glacial and geological units exhibit almost similar characteristics as there is an intermixing of the sediments of various units due to ice, melt-water and wind activities. Therefore, it is essential to identify the source of sediments and depositional processes of these lakes. The objective of the present study, therefore, is to understand the source and depositional processes along the sediment column. In the present study an attempt is made to fill the gap of knowledge on sedimentary processes and identification of provenance through

geochemical proxies along the sediment column. Weathering of rocks present in the catchment area of Schirmacher Oasis is considered to be the major source of sediments. To achieve the objective, three sediment cores collected from GL-1, V-1 and L-6 lakes of Schirmacher Oasis, East Antarctica are used to understand the distribution and source of sediment components, organic matter, BSi and selected elements along with the processes involved during and after sediment deposition in the lakes of Schirmacher Oasis.

2. Study area

The Schirmacher Oasis situated in Queen Maud Land, East Antarctica, is a 35 km² ice-free area, located about 100 m above mean sea level (MSL), situated between the margins of continental ice sheet and ice-shelf (Fig. 1). The oasis consists of several hills of low elevation of ~200 m (Srivastava and Khare, 2009) and interspersed with around 120 freshwater glacial lakes. These glacial lakes originated during the late Pleistocene retreat of glaciers and their morphological and genetic behavior enabled their classification as epishelf, proglacial and land locked lakes (Ravindra and Laluraj, 2012) depending upon their geomorphic evolution. The region is marked with debris cover and valley systems having lakes which are either in glacially eroded bedrock or dammed by moraines or ice (Bormann and Fritzsche, 1995). In general, Schirmacher Oasis experiences milder climate as compared to other areas of Antarctica.

For the present study, sediment cores were collected from GL-1 lake (70° 46' 07.2" S; 11° 44' 04" E), V-1 lake (70° 47' 27" S; 11° 37' 46.6" E)

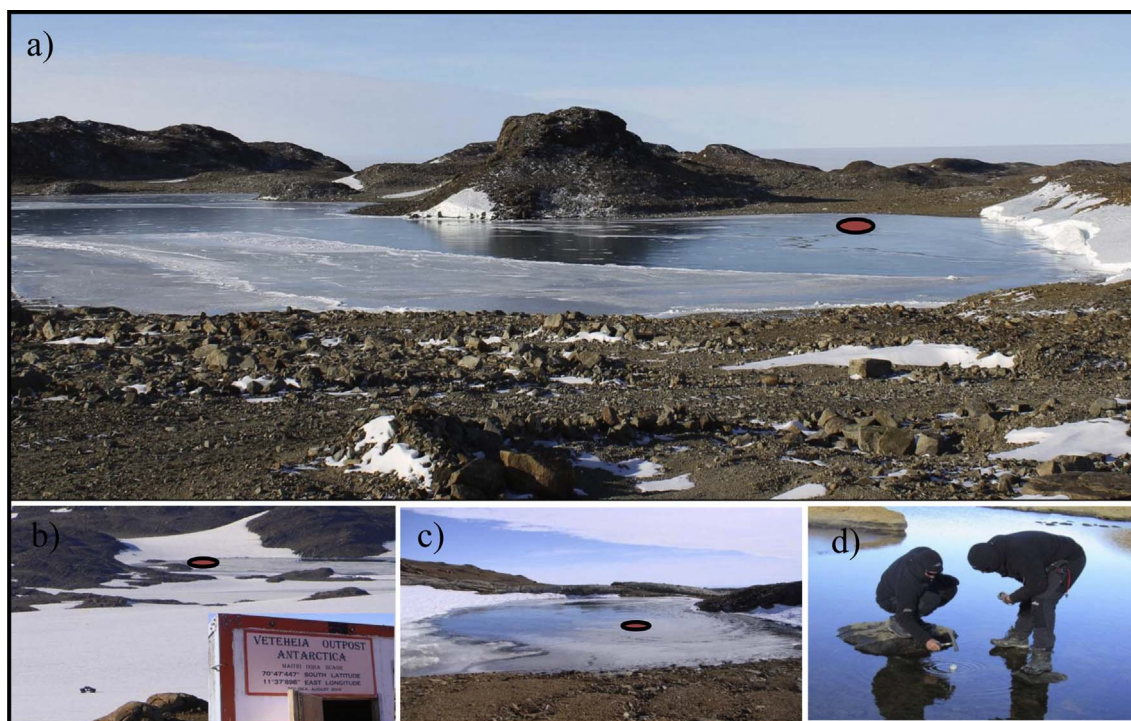


Fig. 2. Field photographs showing the core locations of core a) GL-1 b) V-1 c) L-6 d) sediment core collection.

and L-6 lake ($70^{\circ} 45' 16.6''$ S; $11^{\circ} 36' 03''$ E) situated ~ 0.25 km, 4 km and 6 km, respectively from Indian research station Maitri. These are land locked lakes and are dependent on seasonal snow.

The lake GL-1 is situated at an altitude of 115 m above MSL. The maximum water depth is about 4 m, the surface area is 0.005 km² and the catchment area is 0.023 km². This lake is surrounded by the adjacent smaller lakes and also by Priyadarshani or Zub Lake. The important geomorphic features noted in the catchment area are structural hills, glacial valleys and roche moutonees which are left open by the receding continental ice (Geological Survey of India, 2006). Growth of lichens and mosses were observed adjacent to the lake water body. Additionally, algal mats were noted on the surface of the lake. The pH of the lake water ranges from 6.1–7.4 suggesting acidic to neutral pH conditions of the lake during the sampling period.

The Vetehiya (V-1) Lake lies at an elevation of about 400 m above MSL. The water depth of the lake is about 2.5 m. This lake is comparatively small in size with an area of about 0.003 km². The catchment area of Vetehiya Lake is 0.017 km². As the lake is situated at a higher elevation, the morphological features associated are structural hill and typical development of roche moutonees having steep cut walls in the catchment area (Geological Survey of India, 2006). During sample collection in the field presence of algal mats were observed on the surface of the lake water. The pH of the water in the lake ranges from 6.78–7.0 indicating it to be slightly acidic to neutral in nature.

L-6 Lake has an oval shaped basin, covering an area of 0.007 km² situated at an elevation of 70 m above MSL, and has a water depth of about 4–4.5 m. Catchment area of the lake is almost 0.128 km² having geomorphic features such as glacial striations, roche moutonees, elementary development of surface channels and patterned ground formed mostly through subsurface flow regime (Geological Survey of India, 2006). According to Govil et al. (2016), earlier the lake basin was partially closed therefore it did not receive much clastic as well as biogenic sediments from the barren catchment area. Lower sand deposition in the lake supports a low-energy depositional environment of the basin. Further, the surface channels flowing through the large catchment area have low flow velocity due to low elevation gradient, facilitating deposition of relatively finer particles to the lake. The pH of

the lake water ranges from 6.71 – 7.75 suggesting acidic to neutral pH conditions of the lake during the sampling period.

Salinity of the lakes present in Schirmacher Oasis was low ranging between 0.09 and 2.05‰ (Ingole and Parulekar, 1993; Khare et al., 2008) as Schirmacher Oasis is 80–100 km away from the sea (Parry and Wadham, 2014). These lakes are typically covered by ice for 6–8 months and remain ice-free for the month of December and January. July and August records the lowest temperature (annual average temperature -10.4 °C, minimum temperature -22 °C) whereas December and January experience the warmest temperatures (maximum temperature $+0.9$ °C) resulting in numerous melt water streams. The annual average wind speed is 17.5 knots and winds blow mainly from southeast (Lal, 2006; Warriar et al., 2014) in this area. The terrain is predominantly gneissic with the felsic variety belonging to Precambrian age (Sengupta, 1986). The rock type consists of charnockites, enderbites, garnet-sillimanite gneisses with some foliated lamprophyres, amphibolites, dolerite, pegmatites and ophiolite rock types (Sengupta, 1986, 1988; Bose and Sengupta, 2003).

3. Materials and methodology

During the 31st Indian scientific expedition to Antarctica, January 2012, three sediment cores of varying length 40 cm (GL-1), 32 cm (V1) and 58 cm (L-6) were retrieved manually from near the periphery of the lake when lakes were ice-free. A PVC handheld corer was inserted by hammering manually into the lake sediment bed and then retrieved. Further, the cores were labeled, packed and stored in a deep freeze at < 4 °C. Field photographs taken at all the three lakes with coring location are presented in Fig. 2a, b, c. The cores were transported to the laboratory and core GL-1 and V-1 was sub sampled at 4 cm interval while L-6 was subsampled at 2 cm interval and later on dried at 60 °C. Sediment components (sand: silt: clay) were analyzed by the pipette method (Folk, 1968). A portion of each subsample was powdered and homogenized in an agate pestle and mortar, and used for the determination of TOC using the Walkley Black method (1947), adopted and modified by Jackson (1958). The total nitrogen (TN) concentration was measured in the Marine Stable Isotope Lab (MASTIL) at National Centre

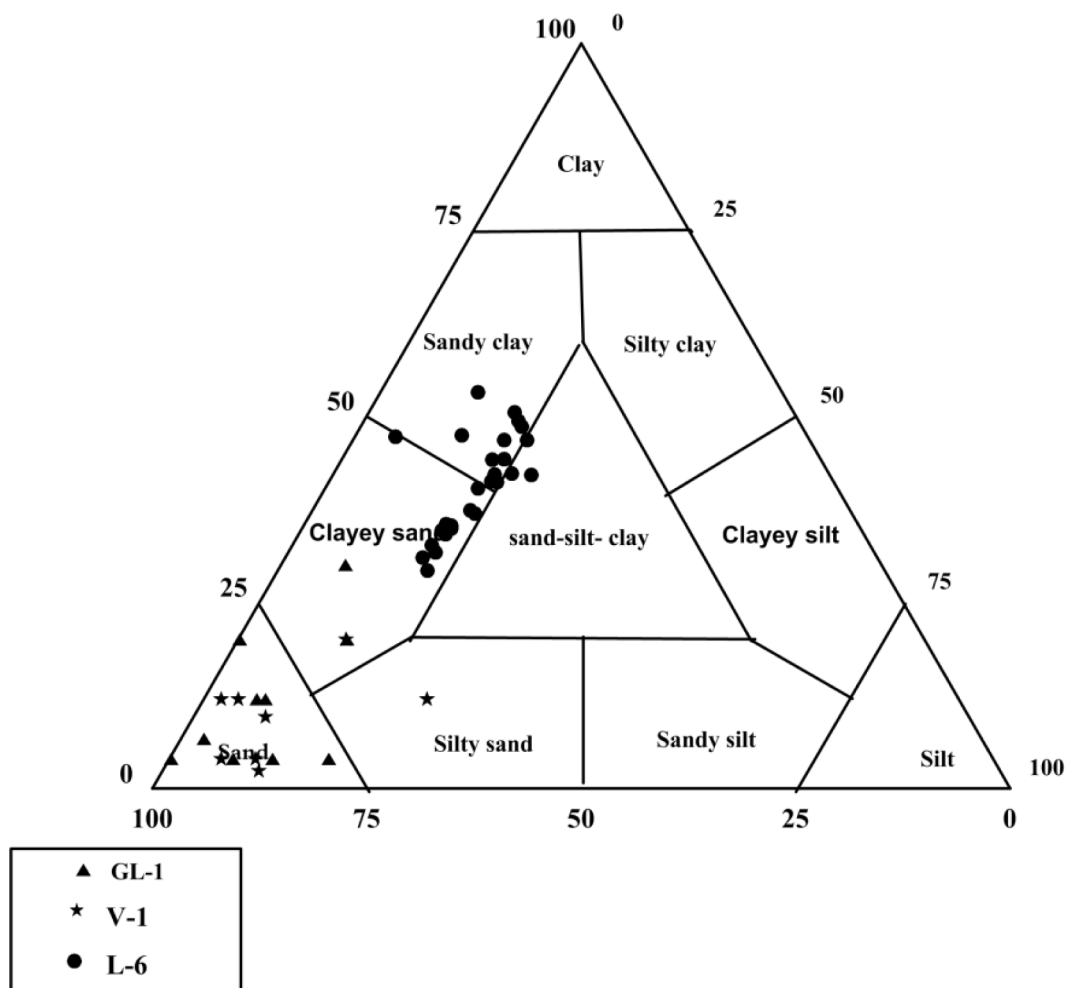


Fig. 3. Ternary diagram of sand-silt-clay percentages of sediments for core a) GL-1 b) V-1 and c) L-6.

for Antarctic & Ocean Research, Goa, India using an EA (Isoprime, Vario Isotope Cube). The precisions for N% are $\pm 0.63\%$ (1σ standard deviation) obtained by repeatedly running Sulfanilamide as the standard. BSi was measured by the wet alkaline extraction method, modified by Mortlock and Froelich (1989) and Muller and Schneider (1993). Duplicate measurements were conducted on each sample and relative error was noted to be less than 3%. Further, sediment samples were digested using HF, HNO₃ and HClO₄ acid mixture with a ratio of 7:3:1 for total metal analyses. The metals Iron (Fe), Manganese (Mn), Aluminium (Al), Nickel (Ni), Cadmium (Cd), Lead (Pb), Chromium (Cr), Cobalt (Co), Zinc (Zn) were analyzed using Atomic Absorption Spectrophotometer (Varian AAS 240 FS model). Together with the samples, certified reference standards from National Institute of Standards and Technology, USA were digested and run, to test the analytical accuracy of the method. The average recoveries were 90–97%. Internal chemical standards obtained from Merck were used to calibrate the instrument and recalibration checks were performed at regular intervals. Pearson's correlation was obtained between the different parameters by using the computer software STATISTICA (Statsoft, 1999). Further, to maintain the uniformity in data, average of two subsamples was taken in core L-6.

4. Results

4.1. Distribution of sediment components

The range and average values of sediment components of Core GL-1, V-1 and L-6 are presented in Table 1. The sand was predominant in core

GL-1 (avg. 80.87%) and in core V-1 (avg. 80.48%) as compared to core L-6 (avg. 42.02%). Silt was high in core L-6 (avg. 17.21%) and low in core GL-1 (avg. 7.46%) and clay was high in core L-6 (avg. 40.76%) and low in core V-1 (9.50%). Depth-wise distribution of sediments components are provided in Fig. 4a, b, c.

4.2. Distribution of organic components (TOC, TN, BSi) and C/N ratio

TOC was highest in core V-1 (avg. 1.05%) and lowest in L-6 (avg. 0.25%); TN was high in both the cores V-1 and L-6 (avg. 0.15% and 0.13%) and low in core GL-1 (0.08%) and Carbon/Nitrogen (TOC/TN) ratio was high in core GL-1 (8.52%) and V-1 (6%) and low in core L-6 (2.72%). BSi was high in cores GL-1 (1.56%) and V-1 (1.48%) and low in core L-6 (0.1%). Vertical distribution of TOC, TN, TOC/TN ratio and BSi in the three cores namely GL-1, V-1 and L-6 are presented in Fig. 4a, b, c respectively.

4.3. Distribution of major and trace metals

The range and average values for major and trace elements are shown in Table 1. Among the metals Al, Fe was slightly higher in core V-1 and Mn was higher in core L-6. Relatively, Pb and Co were higher in core GL-1 with considerable concentration of Cr, while, Cr, Ni and Zn were higher in core L-6 with considerable concentration of Co. Cd concentration was highest in core V-1 and its concentration ranges from 0.58 ppm to 1.23 ppm in the three cores and is slightly less than the value reported earlier (2 ppm) by Shrivastava et al. (2012). Vertical distribution of metals is presented in Fig. 5a, b, c respectively.

Table 1
Range and average values for sediment components of core a) GL-1 b) core V-1 c) core L-6.

	Core GL-1			Core V-1			Core L-6		
	Min	Max	Average	Min	Max	Average	Min	Max	Average
Sand (%)	62.50	95.80	80.87	62.00	90.00	80.48	32.51	53.32	42.02
Silt (%)	0.20	18.60	7.46	2.00	26.00	10.03	4.72	23.16	17.21
Clay (%)	4.00	30.00	11.67	2.40	20.00	9.50	29.27	53.20	40.76
TOC(%)	0.06	1.80	0.60	0.06	3.06	1.05	0.09	0.38	0.25
TN (%)	0.05	0.12	0.08	0.04	0.32	0.15	0.05	1.07	0.13
C/N	0.97	35.94	8.52	0.65	10.66	6.00	0.19	6.25	2.72
BSi (%)	0.50	2.09	1.56	0.28	2.74	1.48	0.03	0.37	0.10
Al (%)	5.77	10.67	7.64	8.49	14.89	10.81	6.68	12.49	8.89
Al/SiO ₂	1.43	6.83	2.65	1.73	18.48	5.45	17.48	164.48	83.08
Fe (%)	3.33	5.48	4.34	4.75	8.86	6.73	2.94	8.88	4.76
Mn(ppm)	464.00	682.25	553	616.50	1308.25	898	1518.00	2119.50	1845
Cr (ppm)	90.00	141.75	110	49.00	174.50	91.22	82.00	155.50	116
Co(ppm)	35.25	85.25	57.38	13.75	36.00	23.44	41.38	64.25	53.78
Ni (ppm)	2.25	69.50	33.05	31.75	87.25	49.44	68.88	126.63	100
Zn (ppm)	81.90	134.58	101	96.25	191.25	135	114.13	163.00	142
Cd (ppm)	0.01	3.04	0.58	0.24	1.97	1.23	0.40	1.30	0.92
Pb (ppm)	18.05	35.40	24.65	5.98	17.65	12.37	4.25	13.01	8.58

5. Discussion

5.1. Factors controlling grain size

The sediments of all the three cores displayed a dominance of sand with less percentage of silt and clay, which indicated that the intensity of mechanical weathering dominated the area releasing coarse grained material from the rocks in the catchment area (Reynolds and King, 1995; Santos et al., 2007). The high average percentage of sand in bottom and top sections of core GL-1, major portion of core V-1 and middle section of core L-6 (Fig. 4a, b, c) indicated deposition of sediments associated with fluvio-glacial input (Govil et al., 2011) suggesting warmer conditions in the region due to which coarse grained particles are transported from the catchment area into the lake-basin by glacial melt water as reported by Tatur et al. (2004) and Yoon et al. (2006). In addition to this, Doran et al. (2002) suggested that Katabatic winds which can move sediments up to sand size also contributed to the deposition of coarse-grained particles to lake. Therefore, sediment supply to the Antarctic lakes is mainly by glacio-fluvial melt water and intense wind (Katabatic winds) that helps in transporting coarse particles, which gets deposited on lake-ice and percolates through cracks in the lake-ice and get deposited on the lake-floor (Spaulding et al., 1997). While, higher clay from 20 cm to 12 cm and upper 4 cm in core GL-1, from 8 cm to the surface in core V-1 and the bottom section of core L-6 from 56 cm to 36 cm indicated the influx of finer material to the lakes by ice melt water suggesting lower melting in the region. In core L-6, relatively lower sand compensated by higher clay suggested difference in terrain morphology compared to other lakes as observed from the larger catchment area and low elevation gradient. In core GL-1 and V-1, larger input of coarser material was probably due to short transportation processes and smaller surface area.

5.2. Processes controlling preservation of organic elements (TOC, TN, BSi)

High TOC along with high clay in the upper section of core GL-1 and V-1 indicated the development of algal mat during ice free conditions in these lakes. During sampling algal mat was observed on the lake sediment surface and recorded in lithologs (Fig. 4a, b, c). The presence of microbial mats, formed as thick, cohesive and highly pigmented mats is well documented in Schirmacher Oasis lakes (Vincent, 1988). The association of organic matter in sediment and its accumulation seem to be strongly influenced by temperature and availability of oxygen (Manahan, 1974; Ingole and Dhargalkar, 1998). Low TOC in the lower

section of core GL-1 and V-1 indicated that the algal mat might have been decayed with time and buried in the sediments. However, Yoon et al. (2006) in King Georges Island, West Antarctica, attributed low TOC values to the existence of grounded glaciers at the sampling site before the formation of post-glacial lake environment. In cores V-1 and L-6, all along the length of the core, TOC showed similar distribution as that of clay. It is well established that the organic carbon is largely associated with finer sediments due to surface area/volume ratio of sediment grains (Muzuka and Shaghude, 2000). In core GL-1, TN showed similar distribution with that of sand in its lower section up to a depth of 16 cm and similar to clay in upper section from 16 cm to the surface (Fig. 4a, b, c) indicating nitrogen addition through weathering of rocks (Holloway and Dahlgren, 1999). In core V-1, higher TN from 4 cm to the surface must be due to the ability of cyanobacteria to fix nitrogen from the atmosphere during the ice-free conditions of the lake. Further, TOC and TN showed good correlation ($r^2 = 0.88$) in core V-1 indicating their similar source and poor correlation between them in core GL-1 ($r^2 = 0.064$) and L-6 ($r^2 = 0.0048$) indicated their different source. In core L-6, TN showed positive correlation ($r = 0.59$) with Fe which suggested that the nitrogen in sediments (Devol, 2008) might have been produced by the oxidation of NH_4^+ by Fe oxides under oxic conditions (Yang et al., 2012) in this lake.

BSi documents direct measure of biological production from the siliceous algae and diatoms (Conley, 1998; Kaplan et al., 2002). Biological productivity in lake sediment is largely characterized by the diatom production (Birnie, 1990; Roberts et al., 2001). Average values of BSi in the three cores varied between 0.1 and 1.56%, which indicated presence of very low silicate microfossils in these lakes. From the vertical distribution it was noted that relatively higher BSi along with high TOC associated with high clay from 12 cm to the surface in core GL-1 and V-1 indicated relatively high primary productivity due to the exposure of the lakes to the ice-melt water influx. In core L-6, BSi was very less but found to be relatively high from 36 cm to 24 cm showing a similar pattern as that of sand. Similar distribution of BSi, sand and Al in the middle section of this core may be either due to the incorporation of Al in diatom frustules (Van Bennekom et al., 1988) or low silica solubility in an extremely cold environment. This may have caused precipitation of dissolved BSi with Al in sediment (Rickert et al., 2002). Low values of Al/SiO₂ ratio in the middle section of the core supported precipitation of BSi with detrital Al, while higher values of Al/SiO₂ in the lower section of all the three cores indicated replacement of Si by Al in diatom frustules. BSi showed positive correlation with TOC (Table 3a and 3b) in core GL-1 and V-1 indicating that the content of BSi in these

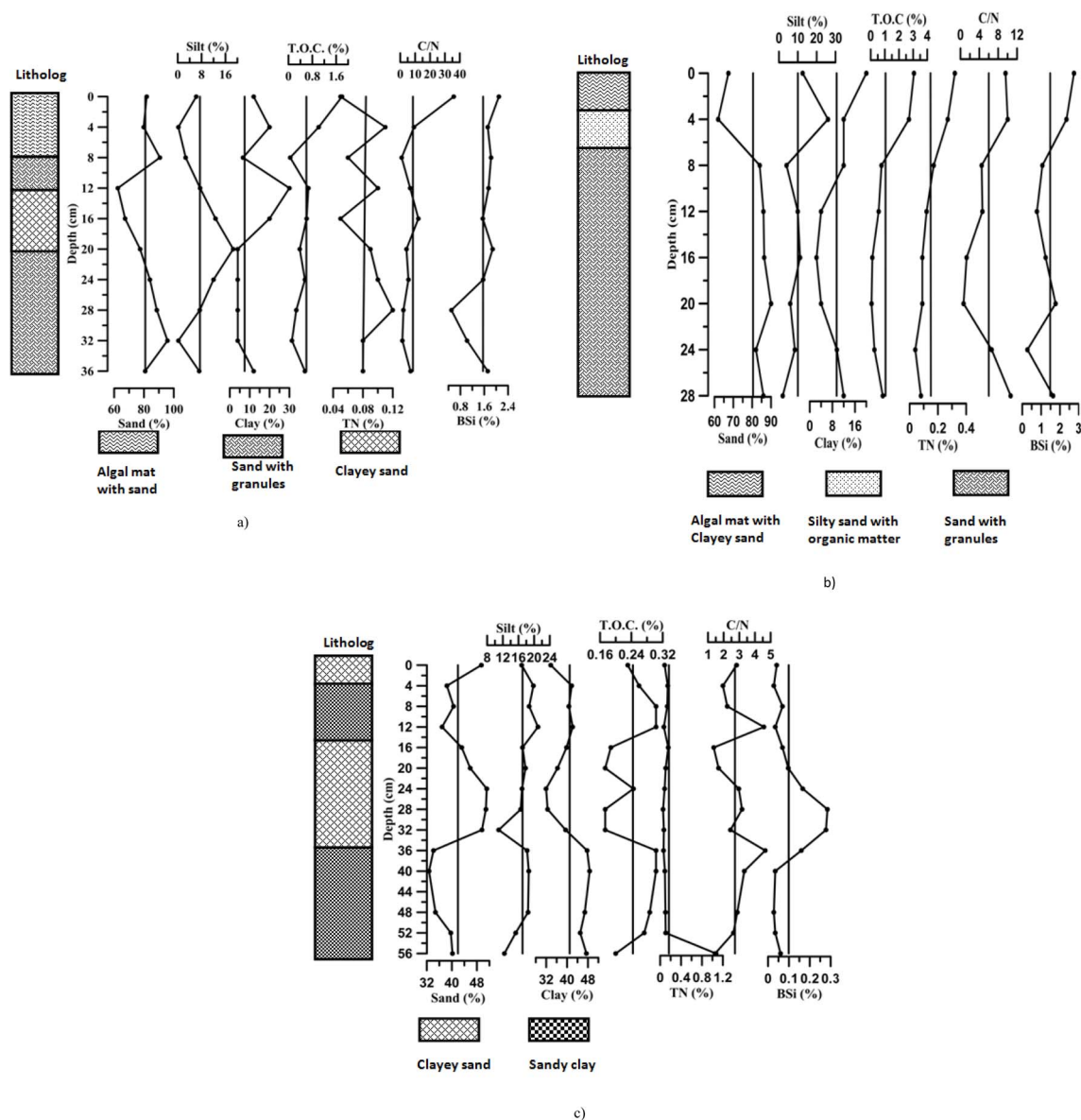


Fig. 4. Profile of sediment components, organic carbon and biogenic silica with depth in core (a) GL-1(b)V-1 and (c) L-6.

lakes was mainly controlled by the amount of algae in the lakes. In these lakes BSi is well associated with TOC suggesting that it has originated from biogenic source.

5.3. C/N ratio in identifying source of organic matter

The C/N ratios have been widely used to identify the source of organic matter into the lacustrine sediments (Talbot and Johannessen, 1992). High latitude lakes vary largely from that of the terrestrial lakes of the low latitudes mainly in terms of their source of organic matter. Terrestrial vegetation forms a significant component of the organic matter along with in-situ production by aquatic-organisms. However, in Antarctica terrestrial vegetation is less and there is an absence of vascular plants. Benthic cyanobacteria and diatoms dominate lake biomass and aquatic mosses form the highest forms of plants (Hodgson et al., 2003). Therefore, majority of organic matter is contributed through the production of aquatic organisms such as algae and cyanobacteria (Yoon et al., 2006; Hodgson et al., 2009a, 2009b). As per the classification of Meyers (1994) algae typically have atomic C/N ratios between 4 and 10, whereas vascular land plants have C/N ratios of 20 and greater. According to Talbot and Johannessen (1992)

autochthonous lacustrine organic matter is characterized by relatively low C/N ratios, typically < 10 as it is N-rich due to their high protein and lipid content. Lignin and cellulose, which are dominant components of terrestrial higher plants, are nitrogen poor and thus allochthonous organic matter has C/N ratios which are normally higher than 20 and may be > 200. Analysis of sediments of core GL-1, V-1 and L-6 gave average C/N values between 2.72 and 8.52 indicating the source of organic matter from aquatic source (in-situ) (Table 1). The results obtained are in good agreement with those obtained from sediment of Long Lake located in Schirmacher Oasis (Mahesh et al., 2015). The results obtained from C/N ratio have helped in distinguishing between organic matters of aquatic from terrestrial origin. The C/N ratio for all the three cores was less than 10 for the entire core length which indicated that the major source of organic matter was autochthonous. However, the high C/N ratio in core GL-1 at a depth of 16 cm and also on the surface indicated prolonged ice-free conditions and increased melt water which must have delivered terrestrial organic matter to the lake possibly from lichens and mosses. Also, the loss of N from the sediments during diagenesis or nitrogen limitation in the surface water due to high primary production must have resulted in the relatively large range of C/N ratio. The low C/N ratio (2.72) in core L-6

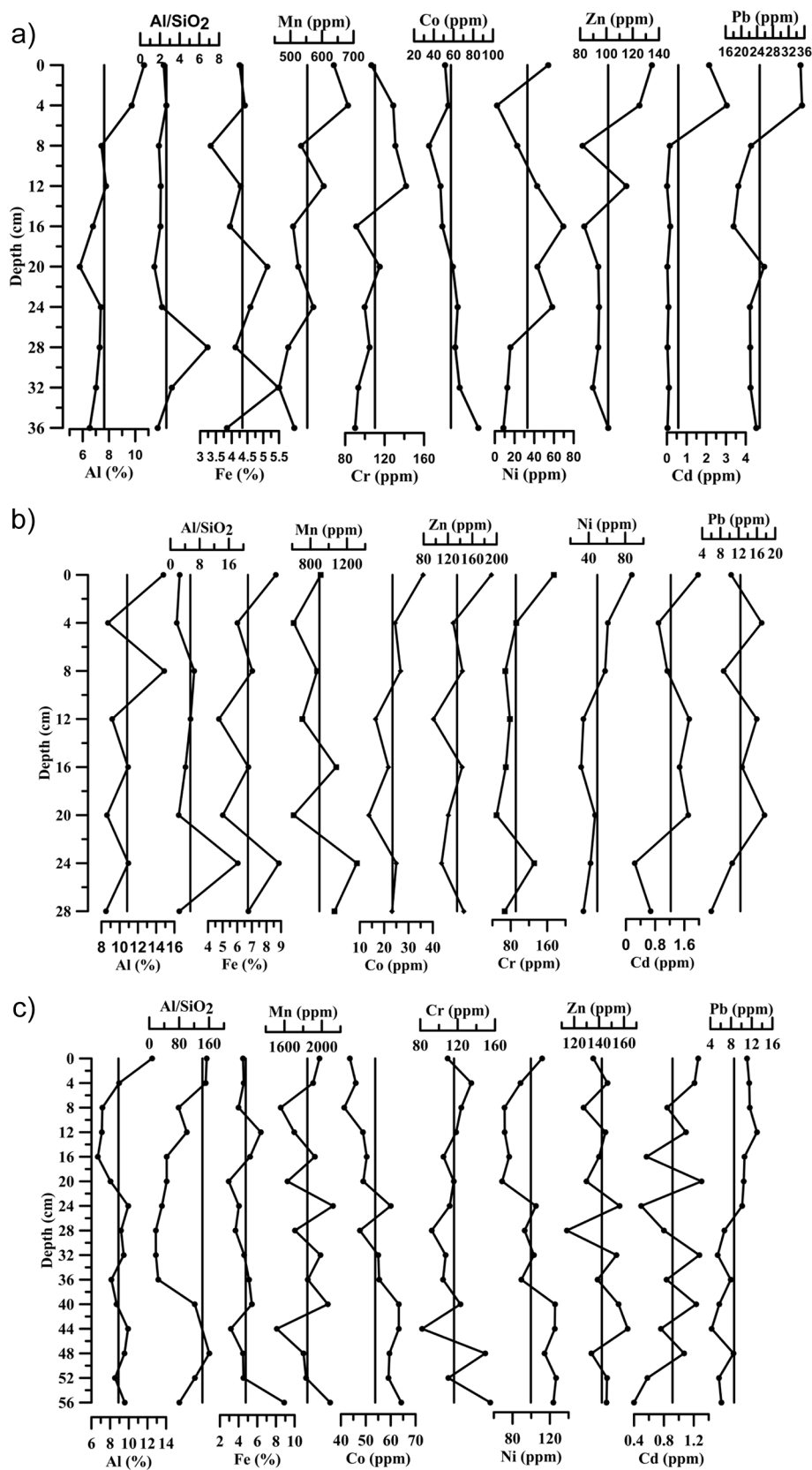


Fig. 5. (a) Profile of metals Al, Al/SiO₂, Fe, Mn, Fe/Mn, Cr, Zn, Pb, Co, Cd, Ni in sediment with depth of core GL-1. (b) Profile of metals Al, Al/SiO₂, Fe, Mn, Fe/Mn, Zn, Cr, Pb, Ni, Co, Cd in sediment with depth of core V-1. (c) Profile of metals Al, Al/SiO₂, Fe, Mn, Fe/Mn, Cd, Pb, Cr, Co, Zn, Ni in sediment with depth of core L-6.

Table 2

Average values of metals in three different cores (a) GL-1 (b) V-1 and (c) L-6, continental crust values (Wedepohl, 1995) and background values of orthogneiss rock from Schirmacher Oasis (Prasad et al., 2006).

Cores	Al %	Fe %	Mn (ppm)	Cr (ppm)	Co (ppm)	Ni (ppm)	Zn (ppm)	Cd (ppm)	Pb (ppm)
GL-1	7.64	4.34	553.43	110.20	57.38	33.05	101.32	0.58	24.65
V-1	10.81	6.73	898.03	91.22	23.44	49.44	135	1.23	12.37
L-6	8.89	4.76	1845.27	116.11	53.78	100	142.20	0.92	8.58
Continental crustal values	7.7440	3.0890	527.00	35.00	11.6	18.6	52.00	0.102	17.00
Orthogneiss (rock type of the area)	–	–	–	1349.00	–	98.00	123.00	1.00	18.00

may be due to the absorption of ammonia by clay particles derived from decomposition of organic matter accompanied by the remineralization and release of carbon.

5.4. Source and processes governing distribution of metals

In core GL-1 (Fig. 5a), the distribution pattern of all the trace elements, except Co, largely agreed with the trend of Al and Mn. Further, Cr and Zn showed a peak similar to that of Fe and Mn at 12 cm and from 8 cm to the surface, Zn, Cd and Pb showed similar distribution to that of Al, Fe and Mn indicating their similar source. Co distribution largely agreed with that of Fe throughout the length of the core. Increase in Al, Fe, Mn, Co, Zn, Cd and Pb concentration from 8 cm to surface coinciding with higher clay and TOC indicated association of metals with finer sediments and organic matter.

In core V-1 (Fig. 5b), trace metals Co, Cr, Ni and Zn showed a similar trend in their distribution with slight fluctuation around average line up to a depth of 12 cm and further increased towards the surface coinciding with clay and TOC. These metals therefore seem to be associated with finer sediments along with organic matter. The distribution of Co and Zn largely agreed with that of Fe from bottom to the surface and distribution of Cr and Ni agreed with Fe especially in upper section from 12 cm to surface indicating the role of Fe oxide in regulating the distribution of these metals. Increase in fresh water influx in recent years must have facilitated in higher concentration of metals within the lake along with clay and TOC. The clay acts as adsorbent and plays an important role in ion exchange reactions (Matini et al., 2011) and therefore involves in regulating distribution of metals. Cd and Pb showed different distribution trend compared to other trace metals indicating that they were from a different source.

In core L-6 (Fig. 5c), the trend of Co and Ni largely fluctuated but with a steadily decreasing trend from the bottom to the surface which largely agreed to that of Fe, Mn as Mn decreased from 56 to 54 cm, 40 to 20 cm and 12 to 8 cm with value at the bottom (2089.75 ppm) and at the top (1974.75 ppm), and in the lower section to that of clay suggesting their association with Fe, Mn oxide and clay. In the middle section of the core, metals Mn, Co, Ni, Zn showed a peak at 24 cm similar to Al which coincided with higher values of sand. These metals therefore seemed to have been derived from weathering of rocks namely gneisses and charnockites present in the catchment area. In the upper section from 12 cm to the surface, metals like Al, Mn, Cr, Ni, Cd showed a similar increasing trend. Fe, Co and Pb displayed decreasing trend towards surface. The metals Al, Fe, Mn, Cr, Ni, Zn and Co therefore seem to have a common lithogenic origin. In the upper section Co and Pb distribution was regulated by Fe-oxide. From the figure (Fig. 5c) it is noted that Cr decreased from 56 to 54 cm and 40 to 28 cm, Ni showed a decrease from 40 to 20 cm and increased from 8 cm to surface and Cd increased from 8 cm to the surface similar to that of Mn indicating the role of Mn-oxide in the diagenetic remobilization of metals. In addition, sediment components namely sand and clay played a significant role in the distribution of metals in this core.

It is clear from the distribution of trace metals in the three studied cores, that the finer sediments, organic carbon, rock type present in the catchment area and Fe-Mn oxides regulate the abundance and

distribution of metals. However, in addition to these factors, type of weathering, hydraulic sorting during transport to the lake basin, topographic setting and climatic conditions may play a role in regulating distribution of trace elements (Wronkiewicz and Condie, 1989; McLennan et al., 1990, 1993).

5.5. Understanding source and depositional processes – Statistical approach

When the sediment components namely sand, silt and clay were plotted on a ternary diagram (Fig. 3) three cores showed different classes of sediment indicating different conditions of deposition of sediments. In order to understand the difference in depositional processes between three lakes, an attempt was made to plot the data on isocon diagram (Fig. 6) (Grant, 1986). When all the parameters of the cores from lake GL-1 and V-1 were compared, it was seen that Al, Fe, BSi, TN, TOC, Cr and sand fell on the isocon line indicating minor variation between the cores with respect to these parameters. However, GL-1 core showed high concentration of Co, Pb and clay indicating the role of clay in the distribution of these elements, whereas, silt, Mn, Zn, Ni, Cd were more enriched in core V-1 indicating role of finer sediments and Mn-oxide facilitating the distribution of Zn, Cd and Ni. When core V-1 was compared with L-6, it was observed that Zn, Cd and TN fell close to the isocon line indicating minor variation between the cores. Silt, clay, Mn, Co, Cr and Ni are more pronounced in core L-6 indicating the role of finer sediments and Mn-oxide in the distribution of Co, Cr and Ni, while, Fe, TOC and BSi are enriched in core V-1. When data of cores L-6 and GL-1 were compared it was observed that Al, Fe, Cr, Co and TN fell close to the isocon line indicating not much variation between the cores in these parameters. Silt, clay, Mn, Zn, Ni and Cd were found high in core L-6 indicating the role of finer sediments and Mn-oxides in distribution of these trace elements. TOC, BSi, sand and Pb are more pronounced in GL-1 core. From the isocon diagram, it was noted that among all the three cores, L-6 constitutes higher concentration of metals. High concentration of metals associated with finer sediment components in L-6 Lake may be of geogenic origin.

Further, elemental associations signify that each paired element has an identical element source or common sink in sediments (Singh et al., 2002; Nyangababo et al., 2005). Pearson's correlation coefficient was computed for all the three cores to determine the inter-relationship between metals and sediment components and identify possible sources or sinks. In core GL-1 (Table 3a), silt displayed a significant positive correlation with Ni. Organic matter exhibited a significant positive correlation with metals Al, Mn, Cd, Pb and Zn. It is well established that organic matter is an important factor in the distribution and concentration of trace metals (Rubio et al., 2000). Positive correlation of organic matter with metals infer that organic matter present in sediments provides active sites for sorption of these metals as it has high complexation ability with trace metals (Mantoura et al., 1978; Boszke et al., 2004). Pearson's correlation coefficients for most of the metals namely Mn, Zn, Cd and Pb showed strong correlation with Al indicating that these metals were associated with aluminosilicate minerals (Rubio et al., 2000; Algarasamy and Zhang, 2008) suggesting their lithogenic nature. The strong association of these metals with Al rich phases demonstrated the role of sediment transport and mineral sorting in

Table 3

Pearson's correlation between sand, silt, clay, organic carbon, biogenic silica and elements in sediment core a) GL-1 b) core V-1 c) core L-6.

	Sand	Silt	Clay	TOC	TN	C/N	BSi	Al	Fe	Mn	Ni	Cd	Pb	Cr	Co	Zn
a)																
Sand	1.00															
Silt	-0.46	1.00														
Clay	-0.82	-0.12	1.00													
TOC	-0.33	-0.04	0.39	1.00												
TN	0.05	-0.03	-0.04	-0.25	1.00											
C/N	-0.23	0.01	0.25	0.94	-0.51	1.00										
BSi	-0.42	0.18	0.35	0.52	-0.50	0.49	1.00									
Al	0.01	-0.51	0.32	0.82	-0.10	0.73	0.30	1.00								
Fe	0.17	0.13	-0.27	-0.06	0.29	-0.11	-0.20	-0.14	1.00							
Mn	-0.35	-0.21	0.53	0.76	0.12	0.54	0.57	0.81	-0.13	1.00						
Ni	-0.52	0.67	0.16	0.30	-0.45	0.43	0.34	-0.03	-0.01	0.06	1.00					
Cd	0.00	-0.44	0.28	0.75	-0.01	0.59	0.35	0.87	-0.01	0.81	-0.19	1.00				
Pb	0.19	-0.31	-0.01	0.72	0.01	0.60	0.39	0.77	0.11	0.71	-0.26	0.91	1.00			
Cr	-0.29	-0.20	0.46	0.05	0.27	-0.10	0.34	0.30	-0.20	0.57	-0.14	0.25	0.18	1.00		
Co	0.22	0.10	-0.31	-0.08	0.31	-0.14	-0.28	-0.31	0.34	-0.32	-0.34	-0.17	0.01	-0.66	1.00	
Zn	-0.26	-0.26	0.46	0.87	0.10	0.71	0.41	0.83	0.06	0.84	-0.06	0.78	0.77	0.33	-0.01	1.00
Bold values represent correlation significant at P = < 0.05, N = 10.																
b)																
Sand	1.00															
Silt	-0.82	1.00														
Clay	-0.69	0.15	1.00													
TOC	-0.94	0.64	0.81	1.00												
TN	-0.86	0.61	0.71	0.94	1.00											
C/N	-0.68	0.30	0.79	0.73	0.48	1.00										
BSi	-0.65	0.45	0.56	0.79	0.80	0.41	1.00									
Al	-0.22	-0.15	0.56	0.30	0.45	0.03	0.10	1.00								
Fe	-0.33	-0.07	0.64	0.29	0.16	0.41	0.00	0.63	1.00							
Mn	0.22	-0.39	0.11	-0.29	-0.45	0.13	-0.48	0.25	0.76	1.00						
Ni	-0.74	0.36	0.82	0.83	0.88	0.41	0.70	0.64	0.43	-0.25	1.00					
Cd	0.01	0.05	-0.08	0.19	0.42	-0.38	0.45	0.23	-0.37	-0.56	0.33	1.00				
Pb	-0.13	0.57	-0.50	0.00	0.12	-0.43	0.13	-0.45	-0.65	-0.71	-0.03	0.40	1.00			
Cr	-0.63	0.30	0.72	0.64	0.53	0.52	0.28	0.53	0.77	0.34	0.68	0.03	-0.22	1.00		
Co	-0.65	0.19	0.89	0.71	0.66	0.62	0.42	0.75	0.82	0.36	0.75	-0.05	-0.56	0.80	1.00	
Zn	-0.43	0.01	0.72	0.61	0.63	0.37	0.70	0.63	0.54	0.13	0.69	0.31	-0.48	0.49	0.80	1.00
Bold values represent correlation significant at P = < 0.05, N = 8.																
c)																
Sand	1.00															
Silt	-0.31	1.00														
Clay	-0.88	-0.19	1.00													
TOC	-0.53	0.06	0.52	1.00												
TN	-0.10	-0.26	0.24	-0.07	1.00											
C/N	-0.25	0.12	0.19	0.67	-0.46	1.00										
BSi	0.53	-0.24	-0.43	-0.39	-0.17	0.04	1.00									
Al	0.43	-0.19	-0.35	-0.23	0.05	-0.16	0.09	1.00								
Fe	-0.34	-0.11	0.40	0.28	0.59	0.11	-0.23	-0.02	1.00							
Mn	0.26	0.01	-0.28	-0.37	0.13	-0.26	0.11	0.56	0.33	1.00						
Ni	0.02	-0.18	0.07	-0.26	0.16	-0.24	-0.06	0.64	0.18	0.70	1.00					
Cd	-0.15	-0.10	0.21	0.09	-0.24	0.12	-0.15	0.15	-0.24	-0.24	-0.01	1.00				
Pb	-0.09	0.29	-0.06	0.26	-0.15	0.24	-0.34	-0.35	0.00	-0.42	-0.57	0.09	1.00			
Cr	-0.34	0.20	0.25	0.08	0.37	-0.26	-0.35	0.22	0.43	0.36	0.34	-0.02	0.00	1.00		
Co	-0.20	-0.08	0.25	0.00	0.25	-0.03	0.05	0.22	0.39	0.61	0.64	-0.25	-0.56	0.41	1.00	
Zn	-0.15	-0.19	0.25	0.03	0.08	-0.08	-0.08	0.25	0.39	0.60	0.43	0.01	-0.25	0.42	0.55	1.00
Bold values represent correlation significant at P = < 0.05, N = 27.																

influencing the distribution of metal abundances (Dalai et al., 2004). Mn with Zn, Pb and Cd also exhibited strong positive correlation values which may indicate the role of Mn-oxide in the distribution and concentration of Zn, Pb and Cd. In core V-1 (Table 3b), clay showed good correlation with TOC as well as with metals Zn, Cr, Ni, and Co. Sand showed negative correlation with TOC and also with Ni. Ni and Co displayed a significant positive correlation with TOC indicating the role of TOC in governing distribution of elements in sediments. Al significantly correlated with Co indicating its lithogenic source. Ni showed significant positive correlation with Co indicating its co-precipitation with Co. Fe and Mn showed significant correlation with each other indicating that they are derived from similar source or with similar post

depositional behavior. Fe showed significant positive correlation with Cr and Co. Cr exhibited significant correlation with Zn while Co showed significant correlation with Zn. Majority of the trace metals except Cd and Pb were associated with clay and TOC indicating the role of finer sediments and TOC in regulating the distribution of metals in addition to Fe-Mn oxides. In core L-6 (Table 3c), TOC and clay showed a good association. Further, clay and TN displayed good correlation with Fe. The clay minerals are the main carriers of trace metals during mobilization and diffusion (Horowitz, 1991). Mn and Ni showed significant positive correlation with Al suggesting that they are from the same lithogenous source. Fe showed positive correlation with Co, Cr, Zn and Mn with Co, Ni and Zn, indicating the role of Fe and Mn oxides in the

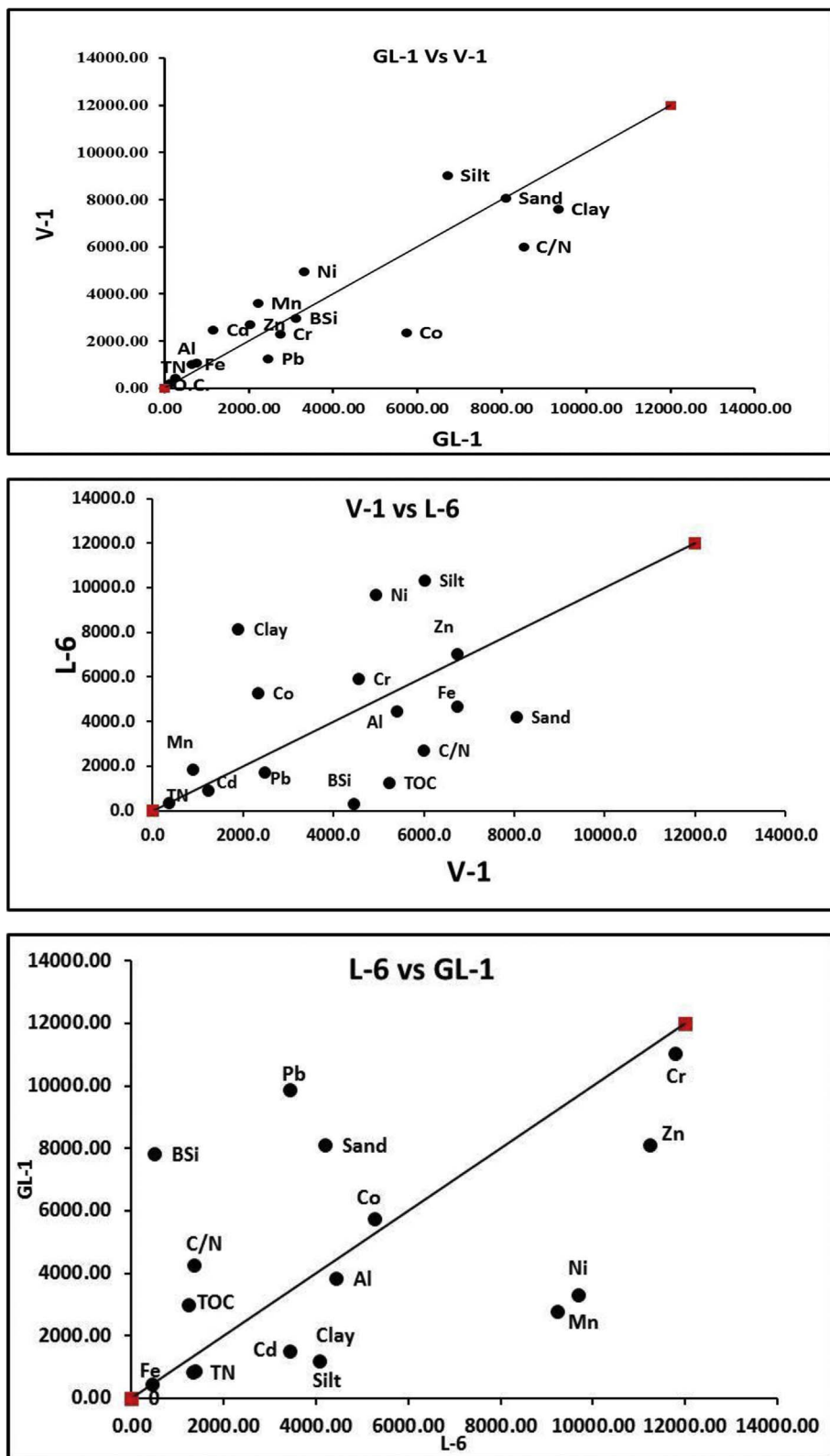


Fig. 6. Isocon diagram (Grant, 1986). Individual points represent average value of sediment components and elements in each core.

distribution of the trace elements. Ni with Co and Zn, Cr with Co and Zn, and Co with Zn exhibited significant positive correlations implying that a common mechanism regulated their concentration. Cd and Pb, however, did not show any significant correlation with the lithogenous elements in core V-1 and L-6 indicating an alternative source for these elements. The input of Cd and Pb in the sediments may be through

anthropogenic activities like use of leaded gasoline in vehicles used for logistic operations.

When the three cores studied were compared with respect to the correlation, it was observed that Lake L-6, has higher concentration of metals possibly due to the surface channels flowing through the catchment area of this lake, having low flow velocity due to low

elevation gradient facilitating transportation of relatively finer particles to the lake leaving behind coarser particles in the channel. In the lake GL-1 and V-1, presence of high concentration of coarse grained particles must have diluted the concentration of metals.

5.6. Comparison with the average crustal value

Further, when elemental concentrations in sediments were compared with average values of continental crust (Table 2) and also with the available background values of orthogneiss from the Schirmacher Oasis (Prasad et al., 2006), it was observed that almost all the trace metals and Al were largely in the comparable range. However, high concentration of Fe and Mn in sediments when compared with the crustal values must be due to the presence of gneisses, granulitic and charnockitic rocks as stated earlier. When these rocks undergo weathering in the catchment area, they release small oxide particles or as oxide coating on other particles (Sinha and Chatterjee, 2000). This must have contributed to higher concentration of Fe and Mn. Further, Fe and Mn are mobilized in the aqueous environment during post depositional processes. Co enrichment in sediments was assumed to be derived from mafic rocks. Higher Pb concentration in the region could be due to the input from wind transported aeolian materials by high glacial (Katabatic wind) and also from volcanic activity (Metcalf and Derwent, 2005) in addition to release from weathering of rocks from the catchment area and through human induced activities.

6. Conclusion

The study carried out on the sediment cores of Antarctic lakes GL-1, V-1 and L-6 revealed the dominance of sand indicating high intensity of mechanical weathering which released coarse grained material from the rocks in the catchment area through fluvio-glacial process. The grain size variation in the lake system was governed by a combination of factors i.e. melt water, aeolian action, surface area of the lake, catchment area geology and local hydrodynamic conditions. The TOC and BSi showed consistent change and positive correlation in some sections which indicated that the content of BSi, TOC and TN were responsible for primary productivity during ice-free conditions of the lake. The source of organic matter was predominantly autochthonous as it is controlled mainly by lake algae. Major elements Al, Fe and Mn showed a similar distribution pattern suggesting that they were from the same source and underwent similar processes of deposition. When elemental concentrations of sediment were compared with the crustal values, concentration of Fe and Mn was noted to be high in sediment, which was attributed to release of elements from granulitic and charnockitic rocks in the catchment area. Among the three cores, sediments in L-6 consist of higher metal concentration. Trace elements Cr, Co, Ni, Zn were associated with lithogenic elements Al, Fe and Mn indicating that these elements were derived naturally from weathering of rocks from the catchment area. However, Cd and Pb did not show such association in cores V-1 and L-6 suggesting a different source possibly anthropogenic may be due to the logistic activities taking place in the area. This makes it important to monitor the recent changes in metal concentration in lake sediments in order to protect this pristine environment. In lake GL-1, Cd was found to be of biogenic origin. Silt along with TOC in core GL-1, clay and TOC in core V-1 and sand and clay along with Mn-oxide (indicating diagenetic remobilization of metals) in core L-6 played a significant role in distribution of trace elements. In addition, factors like, type of weathering, hydraulic sorting during transport to the lake basin, topographic setting and climatic conditions may play a role in regulating trace elements abundance and distribution.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.polar.2018.01.003>.

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