Association of trace elements with various geochemical phases in the Indian sector of Southern Ocean during past 22,000 years and its palaeoceanographic implications

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Adopting sequential extraction procedures, Ba, Cu, Mn, Ni, V and Zn concentrations were determined in the moderately reducible, organically bound, carbonate-associated and adsorbable fractions within a sediment core collected from the Indian sector of the Southern Ocean. The elemental abundances were studied with reference to the Last Glacial Maximum (LGM), deglaciation and Holocene periods. The study showed, with the exception of Ba, elemental abundances in the following order: moderately reducible > organically bound > carbonate-associated > adsorbable fractions. Ba showed high affinity to organically bound and carbonate-associated fractions. Ba concentration revealed large variability (200–1400 ppm) within the carbonate-associated fraction and is related to the reduced carbonate productivity during LGM and increased carbonate productivity during deglaciation as well as Holocene intervals. The relative increase in the concentration of V, Mn and Ni in the reducible fraction suggests enhanced suboxic conditions during LGM. The decreased concentrations of V, Mn and Ni during the deglaciation and late Holocene indicate oxygenated conditions. The suboxic conditions during LGM could be attributed to reduced ventilation resulting from reduced strength of the global thermohaline circulation at this time interval.

Keywords: Last Glacial Maximum, redox condition, sequential extraction, Southern Ocean, trace element.

Processes influencing the recycling and burial of elements in marine sediments affect the geochemical cycle of oceans on different timescales. Major processes controlling the concentration of elements in marine sediments are detrital influx, biological productivity, authigenic precipitation as well as the submarine hydrothermal activity. Sedimentary proxy records have been effectively used in the past towards the reconstruction of sea surface temperature, productivity and environmental changes on millennial to centennial timescales. The Southern Ocean is unique among the world’s oceans due to its circumpolar connectivity and close interactions with other oceans. The biogeochemical cycles in the Southern Ocean have a large impact on global climate change, as it is a region of intermediate and deep water mass formation, apart from being a High Nutrient Low Chlorophyll (HNLC) region. It plays an important role in controlling the atmospheric CO₂ concentration. Geochemical cycling of trace metals, particularly iron, also influences the bioavailability of nutrients as well as productivity in the Southern Ocean. Transportation and distribution of trace metals in the Southern Ocean is controlled by processes like atmospheric fallout, oceanic upwelling, advection through currents, melting of ice as well as export from the euphotic zone by settling and remineralization.

The Southern Ocean played a major role in the modulation of CO₂ concentration during the glacial–interglacial periods and its relation to natural climate variability. It has been reported that the concentration of CO₂ in the atmosphere during the last glacial period was approximately 80 ppm lower than in the pre-industrial times. The mechanisms attributed to such low CO₂ levels include: (i) an increase in the strength of biological pump of the Southern Ocean as a result of changes in the supply or utilization of nutrients or light; (ii) an increase in the alkalinity of the Southern Ocean and (iii) inhibiting gas exchange between the deep sea and the atmosphere in the Southern Ocean either by increase of Antarctic sea ice or midwater stratification. Enhanced CO₂ during the deglaciation and interglacial periods has been explained by the increased wind-driven upwelling and deep water ventilation during these periods.

The Southern Ocean palaeoceanography is mainly controlled by the past fluctuations in oceanic fronts and changes in important water masses such as advancement of Antarctic Bottom Water (AABW) and strong currents related to the Antarctic Circumpolar Current (ACC). These water masses play an important role in the global climate system as reservoirs of heat, freshwater and dissolved gases and act as a damping mechanism on variations in the global climate. The southern westerlies are the most dominant atmospheric circulation in the Southern Ocean and are considered to have significantly changed positions in the past, associated with shifting of frontal regimes. The westerlies are also the carriers of aeolian dust transported to the open ocean, which fertilizes the water column by trace nutrients like iron and is related to the changes in atmospheric CO₂ content in respect of relative positions of the westerlies and ACC.

A few studies were conducted in the Indian sector of the Southern Ocean sediments with a focus on the trace metal geochemistry. Several workers highlighted the role of trace metals in the Southern Ocean processes. The mechanisms by which these trace metals participate in marine biogeochemical cycles are still not well understood. In the Southern Ocean biogeochemical cycling, Fe is considered to be a limiting factor for the biological productivity that could directly influence the atmospheric
CO₂ concentration\(^4,15\). Distribution of Zn, Ni, Cu, Ba, Cd and U is found to correlate with major nutrients implying that common biogeochemical processes control their oceanic distribution\(^12\). Zn is known to be incorporated into diatom frustules and hence co-varies with Si\(^16\). Ni and Cu concentrations provide indirect evidence for controls on biological uptake and regeneration cycles\(^17\). The correlation of Cd and P concentrations in the ocean corresponds well with the marine biological productivity\(^13\). The variations in redox-sensitive elements such as Mn, Cd and U in marine sediments have been used to understand the past oceanic oxygen levels at the sediment–water interfaces\(^18,19\). The Southern Ocean sediments are ideally suited to decipher the regional and global changes in trace metal contribution and its palaeoceanographic significance. The present study using a sediment core from the Indian sector of the Southern Ocean investigates the changes in various leachable fractions of trace metals and the processes involved in their distribution during the last glacial to interglacial period. The Indian sector of the Southern Ocean is characterized by strong and complex physico-chemical and biological characteristics due to the confluence in latitudinally restricted zone of subtropical, subantarctic and polar frontal regimes (Figure 1). During the 200th expedition of ORV Sagar Kanya, a gravity core (SK200/22a) was collected from a water depth of 2,300 m within the sub-Antarctic zone of the Indian sector of the Southern Ocean at 43°42′S lat. and 45°04′E long. (Figure 1). The sedimentological and rock magnetic variations in the sediment core have been reported earlier\(^20,21\). The ages of the sediment at different depth intervals of the core were determined by \(^14\)C dating of handpicked planktic foraminiferal species, Globigerina bulloides and Neogloboquadrina pachyderma, using an accelerated mass spectrometer (AMS). The radiocarbon ages were corrected and converted to calendar years using the CALIB 5.0.2 program\(^22\). For calibration, \(A\)–\(R\) correction value of 800 years was used for the core location\(^23\). Accordingly, the top 185 cm of the core was used for the present study. This segment of the core represents the past 22,000 years (22 ka), including the LGM and the present interglacial period. The sedimentation rates of the core vary from 4 to 10 cm/ka and are highest during the glacial interval (Figure 2). Subsamples of the core at 4 cm interval were subjected to sequential leaching experiments following the protocol by Tessier et al.\(^24\). The various fractions (adsorbable, carbonate-associated, moderately reducible, organically bound) were sequentially extracted using 40 mg of sediment. The exchangeable/adsorbable fraction was obtained by treating the sample with ammonium acetate for 15 min at room temperature. The carbonate fraction was obtained by treating the residue with 1 M sodium acetate at room temperature. The moderately reducible fraction (bound to Fe–Mn oxides) was obtained by treating the above residue with 0.25 M hydroxyl ammonium hydrochloride for 6 h at 90°C. The organically bound fraction was obtained by extracting the residue with 0.01 M nitric acid and hydrogen peroxide at 85°C for 3 h. The leaching procedures were verified by repeating the extractions in duplicate splits of selected samples. The concentrations V, Mn, Ni, Cu, Zn, Ba from each fraction were determined using ICP-MS (Thermo Elemental X 7 Series) equipped with a collision cell. Continuous calibration with standard and blanks was performed during measurements. Blank levels for different elements were within 0.5 ppm. As no certified standard
Table 1. Average trace element concentration in different geochemical phases for different periods (in ppm)

<table>
<thead>
<tr>
<th></th>
<th>Time-period</th>
<th>Ba</th>
<th>Cu</th>
<th>Mn</th>
<th>Ni</th>
<th>V</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorbable/exchangeable</td>
<td>Interglacial</td>
<td>41.1</td>
<td>0.75</td>
<td>2.4</td>
<td>0.16</td>
<td>0.90</td>
<td>1.4</td>
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<td></td>
<td>Early deglacial</td>
<td>59.2</td>
<td>0.66</td>
<td>1.0</td>
<td>0.12</td>
<td>0.61</td>
<td>0.75</td>
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<tr>
<td></td>
<td>LGM</td>
<td>44.2</td>
<td>0.69</td>
<td>0.79</td>
<td>0.43</td>
<td>0.61</td>
<td>0.85</td>
</tr>
<tr>
<td></td>
<td>Average concentration</td>
<td>48.2</td>
<td>0.7</td>
<td>1.4</td>
<td>0.24</td>
<td>0.71</td>
<td>1</td>
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<tr>
<td>Carbonate-associated</td>
<td>Interglacial</td>
<td>925.3</td>
<td>2.9</td>
<td>4.3</td>
<td>0.88</td>
<td>0.40</td>
<td>4.5</td>
</tr>
<tr>
<td></td>
<td>Early deglacial</td>
<td>697.3</td>
<td>1.3</td>
<td>2.0</td>
<td>1.6</td>
<td>0.98</td>
<td>3.7</td>
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<tr>
<td></td>
<td>LGM</td>
<td>540.5</td>
<td>0.84</td>
<td>1.3</td>
<td>1.3</td>
<td>0.87</td>
<td>2.4</td>
</tr>
<tr>
<td></td>
<td>Average concentration</td>
<td>721.0</td>
<td>1.7</td>
<td>2.5</td>
<td>1.3</td>
<td>0.75</td>
<td>3.5</td>
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<tr>
<td>Moderately reducible</td>
<td>Interglacial</td>
<td>128.5</td>
<td>15.3</td>
<td>56.0</td>
<td>2.9</td>
<td>6.4</td>
<td>21.8</td>
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<tr>
<td></td>
<td>Early deglacial</td>
<td>95.4</td>
<td>13.2</td>
<td>19.1</td>
<td>2.5</td>
<td>6.3</td>
<td>13.9</td>
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<tr>
<td></td>
<td>LGM</td>
<td>166.4</td>
<td>23.6</td>
<td>5.7</td>
<td>9.8</td>
<td>17.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Average concentration</td>
<td>130.1</td>
<td>13.3</td>
<td>32.9</td>
<td>3.7</td>
<td>7.5</td>
<td>17.9</td>
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<tr>
<td>Organically bound</td>
<td>Interglacial</td>
<td>364.8</td>
<td>2.4</td>
<td>5.0</td>
<td>1.9</td>
<td>1.0</td>
<td>9.4</td>
</tr>
<tr>
<td></td>
<td>Early deglacial</td>
<td>279.2</td>
<td>1.3</td>
<td>3.3</td>
<td>1.4</td>
<td>2.3</td>
<td>3.3</td>
</tr>
<tr>
<td></td>
<td>LGM</td>
<td>260.9</td>
<td>0.79</td>
<td>2.0</td>
<td>0.94</td>
<td>2.1</td>
<td>2.7</td>
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<td></td>
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<td>1.5</td>
<td>3.4</td>
<td>1.4</td>
<td>1.8</td>
<td>5.1</td>
</tr>
</tbody>
</table>

Figure 3. Down core variation of Ba, Cu, Mn, Ni, V and Zn distribution in adsorbable fraction.

Reference materials are available for the analysis of sequentially extracted leaches, only the precision and reproducibility could be estimated. Rhodium was employed as an internal standard for better precision in ICP-MS measurements. The reproducibility of all trace element values determined by duplicate analyses was better than 6%.

Distribution of trace elements in four different geochemical fractions is shown in Table 1 and Figures 3–6. The order of elemental distribution in different fractions is as follows: moderately reducible fraction > organically bound fraction > carbonate-associated fraction > adsorbable/exchangeable fraction, except for Ba (Table 1). Ba shows significant association with carbonate and organically bound fraction. We discuss the down core geochemical variations with reference to three time-periods: glacial (22–18 ka), early deglacial (18–12 ka) and interglacial (1–12 ka; Figures 3–6). The redox-sensitive
Figure 4. Down core variation of Ba, Cu, Mn, Ni, Zn and V distribution in carbonate-associated fraction.

elements like V and Ni show higher concentrations during the glacial periods, while Mn shows a higher concentration during the interglacial period in all the four fractions (Table 1 and Figures 3–6). Ba shows a significantly higher concentration during the interglacial period in the carbonate-associated fraction. Within the organically bound fraction, Ba, Cu and Zn showed an increase in concentration during glacial period (Figures 4 and 6). In the organically bound fraction, Ba shows a positive correlation with Cu \( (r = 0.46, n = 49) \) and Zn \( (r = 0.59, n = 49) \).

Barium is the dominant element in the adsorbable fraction (Figure 3), possibly due to its greater ability to form surface complexes. Ba, Cu and Ni were higher during the interglacial period, whereas V was lowest during this period. The increased values of Ba, Cu and Ni are synchronous with the enhanced Mn concentration, pointing to the scavenging capability of the Fe–Mn oxides. Ba is also higher in the carbonate-associated fraction (Figure 4) which indicates its affinity towards the carbonate species. Gradual increase of Ba in the carbonate fraction from early deglaciation to Holocene indicates increase in productivity with increase in sea surface warming. There are studies showing increased export production occurring either at glacial/interglacial transitions or during interglacial intervals. The low concentrations of Ba, Cu and Zn (Table 1) in the carbonate fraction during the glacial period may also indicate the higher alkalinity of the Southern Ocean. It has been established that the apparent reductions in the North Atlantic Deep Water (NADW) during LGM lead to an increase in deep-water nutrients and dissolution of carbonate sediments in the Southern Ocean.

The redox-sensitive elements, in general, are higher in the moderately reducible fraction (Figure 5) due to the high adsorption capacity of the Fe–Mn oxides associated with this fraction. Dominant elements (V, Cu, Ba) in this fraction are adsorbed on the Fe–Mn oxides and are thermodynamically unstable under anoxic conditions. V, Cu and Ba concentrations in this fraction are higher during LGM compared to those in the subsequent deglaciation period, with V remaining uniformly low during the deglacial and Holocene intervals. Previous studies have indicated that V is highly redox-sensitive, with enhanced preservation under reduced environments. Relatively depleted V and enhanced Mn concentration in this fraction during Holocene support increase of oxygen in the bottom water of the Southern Ocean during the period. The variations of Cu and Zn imitate that of Ba, suggesting dominant control of biological productivity and related biogeochemical processes on their distribution.

The organically bound fraction (Figure 6) is dominated by Ba (125–450 ppm) followed by Cu (1–10 ppm) and Zn (10–30 ppm). Higher concentration of Ba in this fraction could be due to its association with marine phytoplankton, which incorporates Ba during metabolic uptake and is removed from the water column by adsorption on sinking organic particles and its release during decay. The biological uptake of Zn and Cu as well as their regeneration cycle is well established. Barium is moderately correlated with Cu \( (r = 0.46, n = 49) \) and Zn \( (r = 0.59, n = 49) \). Therefore, the temporal variations of Ba, Cu, Ni
and Zn support a significant increase in biological productivity during the early deglaciation and decreasing productivity towards late glacial to Holocene boundary. The concentration of Ba, Cu and Zn increases again during the Holocene (Figure 6). Several geochemical proxy records from the Southern Ocean indicate increased
productivity towards the end of LGM and the beginning of subsequent deglaciation.

Concentrations of redox-sensitive elements such as V and Ni are high during LGM (Table 1 and Figure 5), suggesting the suboxic bottom water conditions during LGM. Under reducing conditions, V (V) is reduced to V (IV) and forms vanadyl ions (VO$^2+$), related hydraloxy species and insoluble hydroxides. Such a condition is supported by the reported reduction in dissolved oxygen in the deep water during LGM, possibly associated with a reduced deep circulation through the North Atlantic. The Holocene is characterized by enhanced concentration of Mn, suggesting more oxidizing condition during late Holocene. Such a condition supports strengthened deep-water ventilation during the Holocene.

The present study of selected trace element species during the past 22 ka reveals that the Ba, Cu and Zn are largely associated with biological sources, whereas V, Mn and Ni are associated with oxic/suboxic conditions at the sediment–water interface. The concentration profile of Ba in the carbonate-associated fraction indicates reduced carbonate productivity during the glacial period and its increase during deglaciation to Holocene transition. The speciation studies show that the biologically controlled trace elements contribute more towards the organically bound and carbonate-associated fractions, whereas the redox-sensitive elements are higher in the moderately reducible and adsorbable fractions. The glacial–interglacial variations of the redox-sensitive elements support a reduced ventilation of the deep-water column due to a cessation of reduced strength of the global thermohaline circulation during LGM and its subsequent strengthening during the Holocene.

29. Howard, W. R. and Prell, W. L., Late Quaternary CaCO$_3$ produc- tion and preservation in the Southern Ocean: implications for
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Primary productivity and organic matter distribution during SW and NE monsoon from Alleppey mudbanks, Kerala, India

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Formation of mudbank during summer monsoon and its dissipation during winter is a characteristic feature of the southwest coast of Kerala, South India. Both southwest (SW) and northeast (NE) monsoons play an important role in the overall run-off-related changes and sedimentation pattern in this region that govern the primary productivity in the region. The present study is an attempt to assess primary productivity and precipitation-induced run-off-related changes using biotic proxies (diatoms and palynofacies) during NE and SW monsoons, from the surface sediments of the Alleppey mudbanks along Kerala coast. ANOVA test was performed on diatoms and palynofacies to assess their significance during both monsoonal periods. The study provides a significant insight into the monsoon-controlled palynofacies distribution behaviour pattern that attests to the concept of precipitation-induced high run-off during SW monsoon being the governing factor in the formation of mudbanks in this region.

Keywords: Diatoms, monsoons, mudbank, palynofacies, primary productivity.

The state of Kerala, situated on the southwest coast of the Indian subcontinent, is bestowed with 41 westerly-flowing rivers and estuarine complexes with a coastline extending for more than 560 km. The formation of mudbanks during the southwest (SW) monsoon period is a unique phenomenon that is exhibited at certain locations along the coastal region (Malabar coast) of Kerala$^{1,2}$ (Figure 1). The Alleppey region along the Malabar coast experiences formation of mudbanks during the SW monsoon period$^3$. Mudbanks are patches of calm, turbid water with heavy suspended load of clay-size particles less than 1 μm in size$^{1-4}$. The historical record of Alleppey mudbanks is known since 1885, the formation of which is an annual phenomenon during June to August$^5$. The geographical extent of the mudbanks and their nature and formation based on sediment characteristics have been discussed in detail, demonstrating fine deposition of silt and mud$^{6-9}$. The phenomenon of coastal upwelling for mudbank formation is regarded to be one of the major factors along the Malabar coast, Kerala$^{10}$. Mudbank formation by run-off-induced activity and coastal upwelling during monsoon...