



Geochemical fractionation of Ni, Cu and Pb in the deep sea sediments from the Central Indian Ocean Basin: An insight into the mechanism of metal enrichment in sediment



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ABSTRACT

Metal speciation study in combination with major element chemistry of deep sea sediments provided possible metal enrichment pathways in sediments collected from environmentally different locations of Central Indian Ocean Basin (CIB). Metal speciation study suggests that Fe–Mn oxyhydroxide phase was the major binding phase for Ni, Cu and Pb in the sediments. The second highest concentrations of all these metals were present within the structure of the sediments. Easily reducible oxide phase (within the Fe–Mn oxyhydroxide binding phases) was the major host for all the three metals in the studied sediments. Major element chemistry of these sediments revealed that there was an increased tendency of Cu and Ni to get incorporated into the deep sea sediment via the non-terrigenous Mn-oxyhydroxide fraction, whereas, Pb gets incorporated mostly via amorphous Fe-hydroxides into the sediment from the CIB. This is the first attempt to provide an insight into the mechanism of metal enrichment in sediment that host vast manganese nodule.

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1. Introduction

Metal-sediment interactions play an important role in controlling metal distribution and speciation in different marine environments. Geochemical behaviors of trace/heavy elements, in marine sediments, vary with varying sediment types and their depositional environment. By far, no study has been done to understand the possible pathways of metal incorporation into deep sea sediments in the Central Indian Ocean Basin (CIB).

CIB is bounded by ridge systems on its three sides (western, eastern and southern) and receives a heavy continental input from the north due to the presence of Ganga–Brahmaputra delta system (Borole 1993; Pattan et al., 2005; Valsangkar, 2011 etc.). The sediments of CIB can be broadly classified into three major types: (i) terrigenous, (ii) siliceous and (iii) pelagic/red clay. Only on the ridge crests and seamount tops, some amount of calcareous sediment can be obtained. Terrigenous sediments are those which are formed due to the weathering of continental rocks. This includes river run off, atmospheric dusts and glacial deposits, which do not undergo

any major changes during its residence in seawater (Chester and Jickells, 2003). So, although a wide variety of continental minerals can be found from oceanic sediments, mostly quartz and clay minerals reach the open oceans. Siliceous sediments are formed in the regions of higher biological productivity and are mainly composed of opal-secreting planktons like diatoms and radiolaria. Some amount of biogenic silica is also contributed by silicoflagellates and sponges. The hard parts of these microorganisms forms the bulk of the coarse fraction (>63 μ) of the siliceous sediment. Pelagic clay, on the other hand, is mainly composed of the finest clay particles which reach the open oceans from the continents, or are produced in situ due to diagenesis and secondary alterations. They are usually formed in the areas where sedimentation rate is very low (a few mm per 1000 years) with minimum current activity. As a result, any suspended organic carbon gets enough time to oxidize before settling in the sediment. Moreover, the presence of ferric-oxide in this sediment imparts a red color to the sediment, for which it is also known as red clay.

Study of clay minerals from CIB area by Rao and Nath (1988) has revealed that kaolinite, illite and chlorite, found in the CIB sediments are mostly land derived (from Ganga–Brahmaputra delta system), whereas smectite is formed mainly as a weathered product of ridge rocks. Another type of Fe-rich smectite is found in the

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finer size fraction of these sediments, especially in the siliceous and red clay area, which is mostly produced by the early diagenetic effect on the sediments. [Nath et al. \(1989\)](#) has showed by R-mode factor analysis that, five major sources of major and trace elements can be identified in these sediments: (1) terrigenous (loaded with Fe, Ti, Al, Mg, Mn, P and K), (2) combined hydrogenetic-diagenetic (Mn, Ni, Cu, Co and Fe), (3) biogenic (Si), (4) sea-salts (Na and Mg) and (5) dissolution residue (Ba). According to [Banerjee \(1998\)](#), the metal enrichment procedure is hydrogenetic in terrigenous and red clay areas, diagenetic in siliceous sediment and a combination of hydrogenetic and early diagenetic in terrigenous–siliceous transition sediment. He has further reported that bulk of Ni resided in the hydrogenous fraction of red clay while, Cu got enriched due to the combined effect of hydrogenetic and early diagenetic processes in siliceous sediments. Thus, from the major element chemistry, an idea about the part of the element (e.g., Fe, Mn, Si etc.) associated with the terrigenous and non-terrigenous sources could be obtained which may further provide valuable information on the trace metal enrichment processes going on within the sediment.

This region also experiences the influence of cold, oxygen rich Antarctic Bottom Water (AABW) which enters into the basin through the northern saddles of Ninety East Ridge. The absence of an index radiolarian species from Neogene and extremely low rate of ^{230}Th accumulation in the sediment, compared to the sediment accumulation rate (2 mm/ka), suggest intense erosion of bottom sediment by AABW ([Banakar et al., 1991](#)). Apart from this, the presence of a number of fracture zones and seamounts within the basin, make the depositional environment of CIB sediments very diverse.

Systematic investigations on major and trace element geochemistry in CIB sediment have not been done. The processes of trace metals incorporation into deep sea sediment of CIB is lacking. Sequential extraction (SE) is an effective tool in such case to understand the metal association pattern within the different binding phases of the sediments ([Chakraborty et al., 2012, 2014a,b, 2015b](#)). However, it should be kept in mind that SE protocols are operationally defined fractionation procedures ([Templeton et al., 2000](#)) which does not necessarily represent the highly variable natural environment. The SE techniques suffer by several drawbacks. There are chances of back extraction and over estimation of the elements depending on the Eh, pH, temperature and duration of reaction time. Moreover, SE procedures are strongly matrix dependent and so the mineralogy of the different sediment types may also affect the procedures (river/lake sediments vs. deep-sea sediments). There are very few alternatives of SE protocols available in literature ([Chakraborty et al., 2011, 2014a,c; Petit et al., 2009](#)). Acidimetric titration method (a novel approach to study particulate trace metal speciation and mobility in sediment by [Petit et al. \(2009\)](#)) is one of them. However, operationally defined SE procedures are also increasingly considered now for environmental studies, related to the mobility of trace and heavy metals. Several SE protocols have been widely used in different sediment types after modifying as per requirement and have been found to provide useful information about the possible physico-chemical processes that might have taken place during the precipitation and final incorporation of the metals into the sediment. Two of them are European Community Bureau of References (BCR) protocol and the protocol proposed by [Poulton and Canfield \(2005\)](#), which have been widely used for metal speciation study in different types of sediments ([Maher, 1984; Koschinsky et al., 2001; Chakraborty et al., 2012; Ohta et al., 2014; Chakraborty et al., 2014a](#)). Thus, these protocols were used in the present study to understand metal speciation in different types of marine sediments of CIB.

One of the most significant features of this basin is the presence of vast polymetallic nodule field which are mainly concretionary bodies of manganese (Mn) and iron (Fe) oxides ([Nath et al., 1989; Banakar, 1991](#)). In Indian Ocean, CIB hosts the richest deposits of

these nodules which either sits on the sediment tops or remain fully or partly buried within the sediments ([Banerjee et al., 1991; Banerjee and Iyer, 1991](#)). Ni and Cu are the most important trace metals present in these nodules, reaching upto 0.7–0.8% at times. Concentration and nature of association of Pb in Fe–Mn nodules, is poorly understood in CIB sediments. Thus, an attempt was made to understand the possible pathways of Ni, Cu and Pb incorporation in four different sediment substrates from CIB by using major element chemistry of these sediments followed by different SE studies. This was the first attempt to provide an insight into the mechanism of metal enrichment in sediment that host vast manganese nodule.

2. Materials and methods

2.1. Study area and sampling

Sediment samples were collected from 24 stations during various cruises of *ORV Sagar Kanya* (6th, 7th and 8th) and *AA Sidorenko* (38th) between 4.98° and 17.05°S latitude and 73.73°E and 78.02°E longitude. Among them 19 were surface sediments, collected by sediment collection tube attached to the free-fall grabs and five were gravity cores, collected from five environmentally different locations of CIB. These samples were collected as a part of the “project surveys for polymetallic nodules” in CIB, covering three major sediment types, viz. terrigenous, siliceous and red clay. All the sediment samples were dried and packed in air tight zip lock bags and stored in screw cap plastic containers at room temperature. The topmost sections (0–5 cm) of the gravity cores were used only for metal speciation study. [Table 1](#) and SM-1 summarize the sampling locations and sediment types. The sampling locations of the 5 cores are also shown in [Fig. 1](#) with the following abbreviations of sediment types in parenthesis: T: terrigenous sediment, T-S: terrigenous–siliceous transition sediment, S1 & S2: siliceous sediment and RC: red clay.

2.2. Textural analysis

One gram of each samples (5 core tops) were wet sieved first to remove the >63 μ fraction. The finer size class was then made carbonate and organic carbon free for further grain size analysis in a ‘Laser Particle Analyzer’ (Malvern Mastersizer 2000 microns). The procedure has been vividly described by [Ramaswamy and Rao \(2006\)](#).

2.3. Total carbon (TC), inorganic carbon (TIC) and organic carbon (TOC) analysis

The total carbon (TC) content of the studied sediment samples were analyzed in a carbon and nitrogen elemental analyzer (Thermo Scientific Flash-EA 1112). Precision of the analysis was within $\pm 5\%$. Total inorganic carbon (TIC) content of the sediments was determined by Coulometer (UIC, Inc-CM5130 acidification module). Analytical grade calcium carbonate was used as the standard reference material. The accuracy and precision were well within $\pm 2\%$ ([Chakraborty et al., 2015a](#)). Total organic carbon (TOC) concentrations of the sediment samples were computed from the difference of TC and TIC contents.

2.4. Major and trace element analysis

The number of analyzed samples for the major and trace element chemistry were 24 (1 from terrigenous, 6 from terrigenous–siliceous transition, 10 from siliceous and 7 from red clay sediments). Prior to all major and trace element analyses, the sediment samples were hand ground by agate mortar pestle into fine powders. Each samples (0.55 g) were then fused into borate

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