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# Fate of copper complexes in hydrothermally altered deep-sea sediments from the Central Indian Ocean Basin

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# 1. Introduction

# ABSTRACT

The current study aims to understand the speciation and fate of Cu complexes in hydrothermally altered sediments from the Central Indian Ocean Basin and assess the probable impacts of deep-sea mining on speciation of Cu complexes and assess the Cu flux from this sediment to the water column in this area. This study suggests that most of the Cu was strongly associated with different binding sites in Fe-oxide phases of the hydrothermally altered sediments with stabilities higher than that of Cu-EDTA complexes. The speciation of Cu indicates that hydrothermally influenced deep-sea sediments from Central Indian Ocean Basin may not significantly contribute to the global Cu flux. However, increasing lability of Cu-sediment complexes with increasing depth of sediment may increase bioavailability and Cu flux to the global ocean during deep-sea mining.

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systems such as hydrothermal fluids, dissolved organic carbon (DOC) and sulphide (HS<sup>-</sup> or S<sup>2-</sup>) are important ligands for metal complexation. Evidence of an extensive spread of hydrothermal dissolved iron (Fe) in the Indian Ocean has been reported by Nishioka et al. (2013). The Japanese-GEOTRACES study in the Indian Ocean shows that Fe from hydrothermal fluid can be distributed over 3000 km distance around a depth of ~3000 m, and that a large fraction of the Fe in truly dissolved form. Dissolved Cu and Fe fluxes from hydrothermal fluid to the global ocean have been modelled recently by Sander and Koschinsky (2011). Their model and environmental observations also confirm that the majority of Cu present in high temperature hydrothermal fluid ends up in the near-field metalliferous sediments, massive seafloor sulphide deposits and sub seafloor mineralization and alteration (Hannington, 2013).

The discovery of increasing number of hydrothermally active sites globally make hydrothermal input one of the main potential, but poorly quantified sources of economically important metals in the ocean basins. There is also a high potential of using hydrothermally altered deep-sea sediments as a source of economically important metals in the near future (Keays and Scott, 1976). However, the consequences of deep-sea mining on metal speciation, bioavailability (in water column and sediments) and their impacts on living organisms are unknown. The high discharge of Cu from

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been accelerated by emerging economies. Hydrothermal vents have led to the formation of exploitable mineral resources via deposition of massive sulphide deposits on the seafloor. Mining companies are exploring underwater volcanic vents, hoping to extract metals such as gold (Au), copper (Cu), zinc (Zn), rare earth element etc (Birney et al., 2006). The initial stages of exploration are still underway and extraction could start in near future (Van Dover, 2014). However, the range and extent of potential impacts of deepsea mining on the environment are uncertain. An understanding of the metal fluxes from hydrothermal fluid to the global ocean, the fate of deposited metal complexes in hydrothermally altered deepsea sediment and their bioavailability is crucial to estimate the possible consequences of deep-sea mining. A recent study by Sander and Koschinsky (2011) suggests that dissolved organic ligands bind and stabilize metals from hydrothermal fluids and increase trace metal flux significantly to the global ocean. In anoxic

The growing demand for metals is a global concern which has

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hydrothermal vents into the deep ocean (Sander and Koschinsky, 2011; Klevenz et al., 2012; Rouxel et al., 2004; Thompson et al., 2013) encouraged us to study Cu speciation and the fate of Cu complexes in hydrothermally influenced deep-sea sediments and the sediment/water column interface in the Central Indian Ocean Basin (CIB). Cu has been reported to be distributed in different geochemical binding phases of sediment. Amorphous hydrous Fe–Mn oxides are one of the most important geochemical phases in hydrothermally altered sediment impacting the mobility and behaviour of trace metals (Petersen et al., 1993; Swallow et al., 1980; Turner, 2000). Total organic carbon (TOC) in sediment and dissolved organic carbon (DOC) in overlying water column also play a key role in the mobilization and sorption of metals. Sander et al. (2007) have reported that strong organic complexation plays an important role in chemical speciation of Cu in hydrothermal vent systems. In addition, Cu can also reside within the structure of the sediment (residual fraction) and as Cu-sulphide. The residual fraction of the metal in sediment is considered as inert and not available to biological system. The aim of this research was to understand speciation and fate of Cu complexes in hydrothermally altered sediments from CIB and assess the Cu flux from this sediment to the water column in this area. Three different independent extraction procedures were applied to understand Cu speciation and the fate of Cu complexes in these sediments from CIB.

### 2. Materials and method

#### 2.1. Study area and sampling

A sediment core (AAS61/BC#8) collected from the flank of a seamount (near Triple Junction Trace) at 16°S and 75°30′E in the CIB during the 61st cruise of RVAA Sidorenko in the year 2003 has yielded hydrothermally influenced sediment. This site is located at the southern end of 76 °30′E fracture zone (Fig. 1). The sediments were collected from an area that is dominated by pelagic clay (Nath, 2001; Nath et al., 1989). The core was collected from a water depth of 5010 m, using a box corer (Kastengreifer type) of dimension 50 cm  $\times$  50 cm  $\times$  50 cm. The core did not

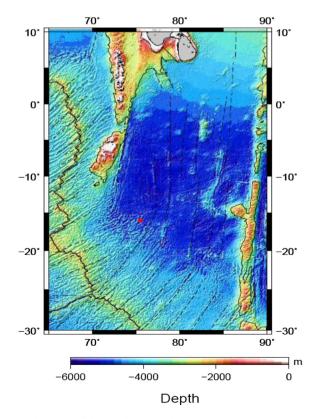


Fig. 1. Map of the sampling site in the Central Indian Ocean Basin.

show any apparent layering. It has been reported (Mascarenhas-Pereira et al., 2006) to contain volcanic glass, palagonite, pumice, micronodules and other lithic grains in the sand-sized fraction. The core also contained aluminium (Al)-rich spherules, Al<sup>0</sup> particles and microscopic concretions of hydrothermal origin (Iyer et al., 2007) The sediment also has shown features such as intense silicate dissolution, depleted organic carbon and significant Fe-enrichment which are indicative of hydrothermal alteration (Nath et al., 2008). Further, these sediments were found to have nontronite, ferruginous smectite of hydrothermal origin (Mascarenhas-Pereira and Nath, 2010). A negative Ce anomaly and positive Eu anomaly has been reported in these sediments (Mascarenhas-Pereira and Nath, 2010), both being indicative of presence of metalliferous component. The sediment core was collected, immediately sub sectioned, dried and packed in air tight zip lock bag and stored in screw cap plastic containers at room temperature. The initial colour of the sediments (at the three different depths) has been reported (Mascarenhas-Pereira et al., 2006: Iver et al., 2007: Nath et al., 2008: Mascarenhas-Pereira and Nath, 2010) to be dark brown and no change in the colour was observed during this study.

#### 2.2. Reagents

Ultrapure water of resistivity 18.2  $M\Omega$  cm<sup>-1</sup> was obtained direct from a Milli-Q-Plus water purification system (Millipore Corporation, USA), fitted with an organic purification column to remove organic matter. All the reagents used in this study were of suprapur grade.

Suprapur glacial acetic acid (100%) from Merck Millipore, Germany was used to prepare acetic acid solution of 0.11 M. Hydroxylamine hydrochloride (NH<sub>2</sub>OH.HCl) (99.99%) from Merck Millipore, Germany was used to prepare a solution of hydroxylamine hydrochloride (NH<sub>2</sub>OH.HCl) of 0.5 M. Pro analysis Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) 30% GR and ammonium acetate (CH<sub>3</sub>COONH<sub>4</sub>)(99.99%) was used to prepare 1M solution. Ethylenediaminetetraacetic acid disodium salt (EDTA) solution of 0.05 M concentration was prepared from 99.995% pure EDTA purchased from Sigma–Aldrich, USA. Hydrofluoric acid (suprapur, Merck Millipore, Germany) and nitric acid (HNO<sub>3</sub>) (ultrapur, Merck millipore, Germany) were used throughout the experiments. Perchloric acid (HClO<sub>4</sub>) (ExcelaR) and solution of sodium nitrate (NaNO<sub>3</sub>) solution was prepared from Experiment Salution of sodium nitrate (NaNO<sub>3</sub>) solution was prepared from extra pure grade NaNO<sub>3</sub> from Sigma–Aldrich, USA.

#### 2.3. Sequential extraction methods

Modified forms of the sequential extraction protocols by BCR (Quevauviller et al., 1993) and Poulton and Canfield, (2005) were used to study Cu speciation and its distribution in different binding phases of the sediments, latter method adopted for chemically separating iron-bearing mineral phases. It has been reported in literature (Canfield et al., 2007; Peltier et al., 2005; Poulton et al., 2010; Tan et al., 2013; Vink, 2002) that both the methods have been extensively used and verified. Briefly, in both protocols the chemistry of the solvents is increasingly aggressive and mobilise the most labile and weakest bound Cu species (first) followed by increasingly strongly bound Cu-complexes with different solid sediment phases. A detailed description of the two modified sequential extraction protocols are presented in the supplementary material Tables SM1 and SM2.

All extractions were carried out under oxic condition. After each extraction, the solution was centrifuged for 15 min. The supernatant solution was collected as the corresponding leach. The residue after each extraction was washed with ultrapure water and further used for the next extraction step.

A volume of 5.0 mL of the extracted liquid samples from each fraction were acid digested with a mixture of 1.5 mL  $H_2O_2$ , 1.5 mL  $HNO_3$  and 1.5 mL  $HClO_4$  and reduced to dryness in Teflon vessels on a hot plate. The residues were redissolved in 2% ultrapure HNO<sub>3</sub> and analysed by differential pulse anodic stripping voltammetry (DP-ASV) to obtain the concentrations of Cu in different phases of the sediments. Three replicates of each sample were analysed. The residual fractions of the sediments were digested with 10 mL of acid mixture (containing HF, HNO<sub>3</sub> and HClO<sub>4</sub> (in the ratio of 7:3:1) in Teflon vessels) on a hot plate. The procedure was repeated (several times) for complete digestion of the sediments. The residues were redissolved in 2% ultrapure HNO<sub>3</sub> for analysis by DP-ASV.

#### 2.4. Determination of total Cu concentrations

Total dissolved Cu concentrations in all digests were analysed by DP-ASV. Three replicates of each sample were analysed.

Voltammetric measurements were made with a computer controlled Autolab PGSTAT30 potentiostat/galvanostat (Eco Chemie BV, Utrecht, The Netherlands), equipped with a Metrohm 663 VA stand (Metrohm, Herisau, Switzerland). The working electrode was a hanging mercury drop electrode (Metrohm). The reference electrode was a Ag|AgCl|3M KCl electrode in a glass tube and fitted with a porous Vycor tip (Bioanalytical Systems, Inc., West Lafayette, IN, USA). The counter electrode was made from platinum (Metrohm).

#### 2.5. Kinetic extraction experiment

For kinetic extraction experiments, 3 g of sediment were added to 300 mL of 0.05 M EDTA solution (at pH 6.0) in a 500 mL Teflon bottle, and the mixture was continually stirred with a Teflon-coated magnetic stirring bar throughout the

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