

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

Parthasarathi Chakraborty*¹, Sylvia G. Sander², Saranya Jayachandran¹, B. Nagender Nath¹, G. Nagaraju¹, Kartheek Chennuri¹, Krushna Vudamala¹, N. Lathika¹, Maria Brenda L. Mascarenhas-Pereira¹

*¹National Institute of Oceanography (CSIR), India, Dona Paula, Goa, 403004, India. Phone-91-832-2450495; Fax: 91-832-2450609; E-mail: pchak@nio.org

² University of Otago, Department of Chemistry, NIWA/UO Research Centre for Oceanography, PO Box 56, Dunedin 9054, New Zealand,

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.

KEY WORDS: Metal-sediment interaction, deep-sea sediment, Cu, hydrothermal alteration, sequential extraction, kinetic extraction method.

CAPSULE: Hydrothermally influenced deep-sea sediments from Central Indian Ocean Basin may significantly contribute to the global Cu flux during deep-sea mining.

1. Introduction

The growing demand for metals is a global concern which has 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 (Dover, 2014). However, the range and extent of potential impacts of deep-sea 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 deep-sea 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 systems such as hydrothermal fluids, dissolved organic carbon (DOC) and sulphide (HS^- or S^{2-}) 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 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 plays 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 (Figure 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 ×50 cm ×50 cm. The core did not 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, Al⁰ 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; Iyer 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 $18.2 \text{ M}\Omega \text{ cm}^{-1}$ 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 ($\text{NH}_2\text{OH}\cdot\text{HCl}$) (99.999%) from Merck Millipore, Germany was used to prepare a solution of hydroxylamine hydrochloride ($\text{NH}_2\text{OH}\cdot\text{HCl}$) of 0.5 M. Pro analysis Hydrogen peroxide (H_2O_2) 30% GR and ammonium acetate ($\text{CH}_3\text{COONH}_4$)(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_3) (ultrapur, Merck millipore, Germany) were used throughout the experiments. Perchloric acid (HClO_4) (ExcelaR) and sodium acetate (CH_3COONa)(ExcelaR) were purchased from Fisher Scientific. A 0.1 M solution of sodium nitrate (NaNO_3) solution was prepared from extra pure grade NaNO_3 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 (2007) 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 Table SM1 and SM2.

All extractions were carried out under oxic condition. After each extraction, the solution was centrifuged for 15 minutes. 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 H₂O₂, 1.5 mL HNO₃ and 1.5 mL HClO₄ and reduced to dryness in Teflon vessels on a hot plate. The residues were redissolved in 2% ultrapure HNO₃ and analysed by 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, HNO₃ and HClO₄ (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 HNO₃ for analysis by differential pulse anodic stripping voltammetry (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 analyzed.

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, three grams 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 experiment. The ratio of the mass of sediment to the volume of EDTA solution (mass/volume) was set at 0.01, as this ratio provided sufficiently high metal concentrations in the extract to be accurately quantified, while requiring a minimum amount of sediment. A special effort was made to maintain a homogeneous suspension in order to avoid changing the mass/volume ratio during sampling. Larger mass/volume ratios would be undesirable, as they could cause problems with filtration. At set time intervals, 2 mL of the suspension were filtered through a 0.2 µm syringe filter (Millex syringe filter with mixed cellulose ester membrane). Sample aliquots were collected over a period of 72 hours. The initial time for the kinetic

measurement (i.e. $t = 0$) was taken as the time just before the sediment was added to the EDTA solution. 1.5 mL of the EDTA containing liquid samples taken at different time intervals were acid digested with 3 mL of a mixture of H_2O_2 : HNO_3 : $HClO_4$ (ratio of 1:1:1) in Teflon vessels on a hot plate (at $\sim 200^\circ C$). The residues were re-dissolved in 2% ultrapure HNO_3 and analysed by DP-ASV.

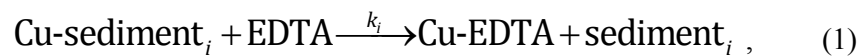
The kinetic experiments were performed in triplicate for all the samples to ensure repeatability of results. To account for instrument drift, the sensitivity of the instrument was monitored throughout each experiment by analysing a standard solution followed by a reagent blank between every 5 samples.

3. Theory:

3.1 The Kinetic Model

The kinetic model proposed by Olson and Shuman (Olson and Shuman, 1985) was adapted (Chakraborty and Chakrabarti, 2006; Chakraborty et al., 2006; Chakraborty et al., 2009; Chakraborty et al., 2011; Chakraborty et al., 2012) to investigate the kinetically labile forms of Cu. It is based on the assumption that each sediment sample consists of n different components, in which each component, Cu-sediment _{i} , exists in equilibrium with its dissociation products: the Cu^{2+} or extractable Cu complexes, a naturally occurring heterogeneous complexant, sediment _{i} . The subscript, i , represents different binding sites of the naturally-occurring heterogeneous complexant.

The extraction of metals from the sediment using EDTA is represented by the following reactions (charges are omitted for simplicity):



where Cu-sediment _{i} and Cu-EDTA represent the metal ion Cu, bound to a sediment binding site, sediment _{i} , and EDTA, respectively. If EDTA is added in large excess, the Cu is extracted from the original sediment binding site with a rate constant k_i . The change in concentration of Cu-sediment _{i} with time is given by the following pseudo first-order rate law.

$$-\frac{dc_{Cu\text{-sediment}_i}}{dt} = k_i c_{Cu\text{-sediment}_i} \quad (2)$$

The integrated rate law derived from equation 2, expressed in terms of the concentration of Cu-EDTA, shows that the concentration of metal extracted, $c_{Cu\text{-EDTA}}$, rises exponentially over time to a

limiting value, as shown in Eq. 3. Unfortunately, it is impossible to study the individual binding sites separately, or to *a priori* know the number of discrete binding sites, and there may be a nearly continuous distribution of sediment binding sites. Hence, Eq. 3 is written as a summation of exponentials.

$$c_{\text{Cu-EDTA}}(t) = \sum_{i=1}^n c_{\text{Cu-sediment}_i} (1 - e^{-k_i \cdot t}) \quad (3)$$

This system described by equation 3 can be approximated by a two or three-component first-order reaction model.

$$c_{\text{Cu-EDTA}}(t) = c_1(1 - e^{-k_1 \cdot t}) + c_2(1 - e^{-k_2 \cdot t}) \quad (4)$$

Where, $c_{\text{Cu-EDTA}}(t)$ is the concentration of Cu extracted by EDTA at time t , c_1, c_2 are the concentrations of EDTA-extractable Cu initially bound to labile (quickly extracted), or inert (with respect to the time scale of measurement) sediment binding sites, respectively, and k_1, k_2 are the corresponding dissociation rate constants. The use of two kinetic components (labile and slowly-labile and inert) to describe similar systems is well reported in the literature (Gutzman and Langford, 1993; Jardine and Sparks, 1984; Sparks, 1987; Sparks, et al., 1998)

4. Results and Discussion

4.1 Mineralogy and major elemental composition of sediment core

Mineralogy determined by X-ray Diffractometry (XRD) is nearly similar in all the three sediment samples and they typically contained quartz, plagioclase, biotite, authigenic minerals phillipsite, analcime and birnessite (dehydration product of Mn-oxide minerals) (Supporting Material Fig SM1). Major element composition of the three sediment samples from the core is presented in Table SM3 and the values of major rock-forming elements have varied within a narrow range. They were characterized by low SiO_2 (40-42%), Al_2O_3 (13.4 to 13.7%), TiO_2 (0.7 to 0.93%), MgO (2.8 to 2.9%) and CaO (2 to 2.2%) compared to Mid-Ocean Ridge Basalt (MORB), but were enriched in Fe_2O_3 (11.8 to 13%), K_2O (2.7-2.8%) and P_2O_5 (1 to 1.1%) compared to MORB. The iron-bearing minerals may either be amorphous or below the detection limit of XRD. Both mineralogy and major element chemistry data, however, suggest a near uniform lithology within these sediments.

The total Cu concentrations at different depth of the core were determined by differential pulse anodic stripping voltammeter (DP-ASV), see Table 1. They were in good agreement with the Cu

concentrations reported by Mascarenhas-Pereira and Nath (2010), determined by ICPMS (see Supplementary Material Table SM4). The total concentration of Cu was $\sim 354 \text{ mg.kg}^{-1}$ or 356 mg.kg^{-1} in the surface sediment and gradually decreased with the increasing depth to ~ 253 or 283 mg.kg^{-1} at 10-15 cm and ~ 227 or 261 mg.kg^{-1} at 15-18 cm measured by DP-ASV or ICP-MS, respectively.

4.2 Cu speciation in the hydrothermally influenced deep-sea sediment core

Speciation and distribution of Cu in the hydrothermally influenced sediment at three different depths was studied by using two different equilibrium based sequential extraction protocols (as shown in the Supplementary Material Table SM1 and SM2). The distribution of Cu associated with different binding phases in the sediments is presented in Table 1 and Figure 2.

The BCR sequential extraction protocol was applied to understand the distribution of Cu in the different phases in the hydrothermally altered sediments. The concentrations of the Fraction 1 (Cu_{exch}), consisting of water soluble, exchangeable and carbonate and bicarbonate complexes of Cu were found to be in the range of 0.0 - 0.36 % of the total Cu in the sediments. As expected, the concentrations of these weak Cu complexes were low due to their exchangeable nature with the different ligand in the liquid phase and the availability of more binding sites on other stronger binding phases within the sediments. Sander and Koschinsky (2011) have reported that dissolved organic Cu-binding ligands found in hydrothermal fluid and the background deep ocean water form soluble complexes with Cu that probably decreased the concentration of Cu in the Fraction 1 of the studied sediments. This stabilization of Cu is also thought to be a mechanism to transport Cu from hydrothermal fluids into the deep ocean.

Concentrations of Cu associated with Fe/Mn oxides (Fraction 2, Cu_{Fe}) were high, between $\sim 18\%$ and 41% of the total Cu in the sediments. Association of Cu with Fe/Mn oxide phases was maximum in the sediment collected at a depth of 4-10 cm (40.72%) followed by 10-15 cm (20.72%) and 15-18cms (18.93%). The relative distribution of Cu in the studied sediments is shown in Fig. 2. The high concentration of Fe in the studied sediment probably indicates that different binding or adsorbing sites were available for Cu in the Fe/Mn oxide phases within the studied sediments.

It is well known that the geochemistry of Cu can be strongly controlled by sorption onto iron (hydr-) oxides and clay minerals. Adsorption of Cu to FeOOH phases controls the release of Cu during sulphide oxidation (Bonnissel-Gissing et al., 1998; Juang and Wu, 2002; Öhlander et al., 2003). In the deep oceans, the Cu-FeOOH association is less clear. In the lower water column, Cu is scavenged by the particulate fraction (Boyle et al., 1977) but released during early diagenesis at the ocean floor.

The resulting benthic source enriches bottom waters in Cu (Boyle et al., 1977). However, if Fe-Mn oxide hydroxide phases are forming at the sediment-water interface, the flux of Cu into bottom water is diminished (Callender and Bowser, 1980; Fernex et al., 1992). Adsorption of Cu(II) onto colloidal iron oxides produced at hydrothermal vents at mid ocean ridges does occur (Feely et al., 1992; Savenko, 2001) but is not a major control on the concentration of Cu in seawater (Elderfield and Schultz, 1996). The incorporation of Cu in metal-rich ridge-crest sediments is a minor component of the overall cycle of the element in the deep water column (Boyle et al., 1977).

The concentrations of Cu associated with organics (Fraction 3, $Cu_{C_{org}}$) present in the studied sediments were found to be negligible, i.e., within a range of 0-0.27%. It has been reported that the concentrations of total organic carbon (TOC) in the studied sediments were low and not detectable below the depth of 4-6cm (Mascarenhas-Pereira and Nath, 2010). This depletion in organic carbon content in the studied sediment accompanied with intense radiolarian dissolution gives a clear indication of the hydrothermal alteration of the sediment. Dissolution of amorphous silica and organic matter degradation were found to be wide spread in ridge-flank hydrothermal systems compared to non-hydrothermal settings suggesting an intense hydrothermal effect (Elderfield and Schultz, 1996). The low concentrations of TOC in the studied sediments reduced the concentrations of Cu associated with organic matter in all the studied sediments.

Cu present as residual fraction (Fraction 4, Cu_{res}) were within the range of (~ 58-82%) and possibly bound to sulphides. In anoxic systems such as hydrothermal fluids, sulphide (HS^- or S^{2-}) is one of the most important ligands for metal complexation. When hot hydrothermal fluids discharge at the sea floor, a large portion of the sulphide-forming metals-such as Cu and iron precipitate as sulphides in the direct vicinity of the vents. Chalcopyrite ($CuFeS_2$) has been found as the primary Cu containing ores in the vicinity of hydrothermal vents. Most of the Cu minerals occur either as primary or alteration products. It has been reported that sea floor hydrothermal fields on the mid-Atlantic ridge contain mainly chalcopyrite ($CuFeS_2$), and isocubanite ($CuFe_2S_3$), bornite (Cu_5FeS_4), covellite (CuS), and digenite (Cu_9S_5) with varying degrees. Chalcopyrite ($CuFeS_2$) has also been reported in the hydrothermal vent areas of East Pacific Rise and has been reported to be replaced by covellite (CuS) and rare digenite (Cu_9S_5). Covellite has also been reported (Wheat and McDuff, 1994) to occur as massive material and as networks of interlocking plates. The major fractions of Cu which were present as residual part in the studied sediments (Fraction 4) were probably different Cu-sulphides (Keays and Scott, 1976; Feely et al., 1994; McKay et al., 1974). The certified sediment reference material BCR-701 was also analysed following the same extraction protocols. A good recovery of Cu was found from the different phases of the reference sediment (see Table 1).

A major fraction of the extractable Cu was found (by following BCR extraction protocol) to associate with Fe-oxide phases (i.e. Cu-Fe_e) in these hydrothermally altered sediments. Thus, further sequential extraction study, as proposed by Poulton and Canfield (2005), was performed to understand the distribution of Cu within the Fe-mineral phases. The analysis of the extracts revealed that Cu was associated with three operationally derived Fe-oxide pools viz., 1) easily reducible oxides, including ferrihydrite and lepidocrocite ($\text{Cu-Fe}_{\text{ox}1}$); 2) other reducible oxides, including goethite, hematite and akaganerite ($\text{Cu-Fe}_{\text{ox}2}$); and 3) magnetite ($\text{Cu-Fe}_{\text{mag}}$).

Figure 2 and Table 1 show the distribution of Cu associated with these different Fe-mineral phases. The highest concentration of Cu was found to be associated with easily reducible Fe-oxide phases, (possibly lepidocrocite and ferrihydrite) ($\text{Cu-Fe}_{\text{ox}1}$) followed by the reducible Fe-oxides phases (indicative of goethite, hematite and akaganerite), ($\text{Cu-Fe}_{\text{ox}2}$) in the studied sediments. The lowest concentration of Cu was found to be associated with leach representing magnetite ($\text{Cu-Fe}_{\text{mag}}$).

It is interesting to note that the association of Cu with $\text{Fe}_{\text{ox}1}$, (ferrihydrite, lepidocrocite) in the studied sediments gradually decreased, whereas, the association of Cu with $\text{Fe}_{\text{ox}2}$ (goethite /akaganerite) gradually increased down the sediment core. . This finding indicates that a major fraction of Cu associated with different Fe minerals phases (ferrihydrite, lepidocrocite, goethite /akaganerite) were mainly originated from hydrothermal activity in the studied sediments.

However, equilibrium based sequential extraction protocols for Cu speciation may not represent a dynamic natural system, such as deep-sea sediment around hydrothermal systems, correctly (Templeton et al., 2000). The competing ligand exchange method (CLEM) was applied using EDTA as the competing ligand to understand kinetic speciation of Cu complexes in the sediment. Concentrations of dynamic Cu complexes and their dissociation rate coefficients were determined in suspensions of the sediments.

4.3 Kinetic speciation of Cu in the sediments

Kinetic speciation of Cu in the hydrothermally influenced sediments at three different depths was studied by using EDTA as a competing ligand. Figure 3 shows the changes in concentrations of extracted Cu in EDTA solution from the studied sediments as a function of time. Each curve displays an exponential increase in Cu concentration (in EDTA solution) relative to the total Cu concentration (in sediment) with time. Figure 3 shows that the rates of extraction of Cu from the Cu-sediment complexes (from the different depth) by EDTA were different. However, equilibrium was reached for all the sediments (three depths) only after 48 hrs.

The experimental data from the kinetic extraction curves were fitted to two-component first-order reaction model. Each curve in Fig. 3 show two different features, a fast rising section that represents the rapid dissociation rate (k_{d1}) of labile Cu-sediment complexes ($c_1\%$), and a slowly rising section which corresponds to relatively more strong Cu-sediment complexes ($c_2\%$) with slower dissociation rate constants (k_{d2}) (see Table 2).

The kinetic study showed that the top layer (4-10 cm) had the smallest percentage of labile Cu-complexes (only 6.1%) with the fastest dissociation rate constant ($k_{d1}= 9.0 \times 10^{-3} \text{ s}^{-1}$); the sediment below this (collected at 10-15 cm) had only marginally more labile Cu-complexes (8.4%) with dissociation rate constant of $2.7 \times 10^{-3} \text{ s}^{-1}$. About 1/3 of total Cu (29.5%) in the sediment collected at 15-18 cm depth were found to be labile with a k_{d1} value of $0.5 \times 10^{-3} \text{ s}^{-1}$.

The second part of all the curves, those recline almost parallel to X-axis, can be attributed to slow dissociation (k_{d2}) of strong, more inert Cu-sediment complexes ($c_2\%$). Slow dissociating Cu complexes ($c_2\%$) were found to be predominant in the upper layer of the sediment depth 4-10cm. The concentrations of Cu-sediment complexes with slow dissociation rates (k_{d2}) (within the time scale of measurements) were found to decrease with depths from 10-15cm to 15-18 cm (91.6% and 70.47% of total Cu present in the sediments). The Pearson correlation analysis suggests that the inert Cu-complexes (c_2) (obtained from kinetic speciation study) had positive correlation ($R^2= 0.63$) with the Cu associated with Fe-oxide phases (Fraction 2) (obtained by BCR sequential extraction protocol). A very strong positive correlation ($R^2= 0.93$) was found between the inert Cu-complexes (c_2) with easily reducible oxides ($\text{Fe}_{\text{ox}1}$). This indicates that Cu may associate very strongly with Fe-oxide phases in hydrothermally altered sediment and may not be bioavailable.

This is the first time we report that non-residual forms of Cu (associated with Fe-oxide phases) may form quite stable (unable to extract by EDTA solution) complexes in the deep-sea sediments altered by hydrothermal activity. This study suggests that Cu strongly associate with ferrihydrite and lepidocrocite goethite, hematite, akaganerite and magnetite type minerals in hydrothermally altered sediments. However, the nature of interactions between Cu and these minerals are not known. The sources of these Fe phases in the sediments are probably hydrothermal fluids. Inert Cu complexes are mainly present as sulphides in hydrothermally altered deep-sea sediments. The high stability of Cu-complexes in hydrothermally altered sediments from CIB may contribute little to the Cu flux to the overlying water column. Kinetic speciation study of Cu showed that lability of Cu complexes gradually increased with the increasing depth of the hydrothermally influenced deep-sea sediments from CIB. The sediment from the upper layer did not significantly contribute to the Cu flux to the

overlying water column. However, increasing lability of Cu-complexes with the increasing depth of sediment (as reflected from the increasing dissociation rate constant of Cu-complexes) suggests that any disturbances (such as mining) of hydrothermally altered deep-sea sediment may bring up labile Cu-complexes from the bottom of the sediments to the water column and may increase bioavailability and Cu flux to the ocean. A very strong positive correlation ($R^2 = 0.92$ and 0.99) was found between the dynamic Cu-complexes (c_1) with reducible oxides (Fe_{ox2}) and magnetite (Fe_{mag}) phases. The labile Cu complexes were probably associated with reducible Fe-oxide (Fe_{ox2}) and magnetite (Fe_{mag}) phases in the studied sediments. The data (presented as supporting material Table SM3) suggest that the relative percentage of easily reducible Fe-oxide (Fe_{ox1}) gradually decreased and reducible Fe-oxide (Fe_{ox2}), and magnetite (Fe_{mag}) phases gradually increased with increasing depth of the sediment core. It could therefore be expected that with the increasing depth, the lability of Cu complexes increases due to an increased association of Cu with reducible Fe-oxide (Fe_{ox2}), and magnetite (Fe_{mag}) phases in the sediment.

This study suggests that Cu can be strongly associated with different binding sites in Fe-oxide phases of hydrothermally altered sediments with stabilities higher than that of Cu-EDTA complexes. Cu, in the form of sulphides can also be one of the most important Cu fractions in hydrothermally influenced deep-sea sediments from Central Indian Ocean Basin. Increase in lability of Cu-complexes with increasing depth suggests that deep-sea mining of hydrothermally altered sediments may bring up labile Cu-complexes to the top and alter the delicate balance between the role of Cu as micronutrient and toxicant in maintaining life at the deep sea. However, further extensive study (using multiple sediment cores from different locations) is required to conclude that the lability of Cu-sediment complexes increase with increasing depth of sediment, and Cu flux to the overlying water column would increase during any disturbance of the sea-floor.

Acknowledgements

Authors are thankful to the Director, NIO, Goa for his encouragement and support. This work is a part of the Council of Scientific and Industrial Research (CSIR) supported Project GEOSINKS (PSC0106). K.C and K. V. and N.G acknowledge the financial support from University Grant Commission, India. M/s C. Moraes, G. Prabhu, A. Kazip are thanked for their help in XRD and XRF analyses. This article bears NIO contribution number XXXX.

References:

- Birney, K., Griffin, A., Gwiazda, J., Kefauver, J., Nagai, T., Varchol, D., 2006. Potential deep-sea mining of seafloor massive sulphides: A case study in Papua New Guinea. Available at <http://www.bren.ucsb.edu/research/documents/VentsThesis.pdf>
- Bonnissel-Gissing, P., Alnot, M., Ehrhardt, J.-J., Behra, P., 1998. Surface oxidation of pyrite as a function of pH. *Environmental Science and Technology*, 32(19), 2839–2845.
- Boyle, E. A., Sclater, F. R., Edmond, J. M., 1977. The distribution of dissolved copper in the Pacific. *Earth and Planetary Science Letters*, 37(1), 38–54.
- Callender, E., Bowser, C. J., 1980. Manganese and copper geochemistry of interstitial fluids from manganese nodule-rich pelagic sediments of the northeastern equatorial Pacific Ocean. *American Journal of Science*, 280(10), 1063–1096.
- Canfield, D. E., Poulton, S. W., Narbonne, G. M., 2007. Late-Neoproterozoic deep-ocean oxygenation and the rise of animal life. *Science (New York, N.Y.)*, 315, 92-95.
- Chakraborty, P., Babu, P. V. R., Sarma, V. V., 2011. A multi-method approach for the study of lanthanum speciation in coastal and estuarine sediments. *Journal of Geochemical Exploration*, 110(2), 225–231.
- Chakraborty, P., Babu, P. V. R., Sarma, V. V., 2012. A study of lead and cadmium speciation in some estuarine and coastal sediments. *Chemical Geology*, 294, 217–225.
- Chakraborty, P., Chakrabarti, C. L., 2006. Chemical speciation of Co, Ni, Cu, and Zn in mine effluents and effects of dilution of the effluent on release of the above metals from their metal–dissolved organic carbon (DOC) complexes. *Analytica Chimica Acta*, 571(2), 260–269.
- Chakraborty, P., Gopalapillai, Y., Murimboh, J., Fasfous, I. I., Chakrabarti, C. L., 2006. Kinetic speciation of nickel in mining and municipal effluents. *Analytical and Bioanalytical Chemistry*, 386(6), 1803–1813.
- Chakraborty, P., Zhao, J., Chakrabarti, C. L., 2009. Copper and nickel speciation in mine effluents by combination of two independent techniques. *Analytica Chimica Acta*, 636(1), 70–76.
- Dover C L V, 2014, Impacts of anthropogenic disturbances at deep-sea hydrothermal vent ecosystems: A review, *Marine Environmental Research* DOI: 10.1016/j.marenvres.2014.03.008
- Elderfield, H., Schultz, A., 1996. Mid-ocean ridge hydrothermal fluxes and the chemical composition of the ocean. *Annual Review of Earth and Planetary Science*, 24, 191–224.
- Feely, R. A., Massoth, G. J., Baker, E. T., Lebon, G. T., Geiselman, T. L., 1992. Tracking the dispersal of hydrothermal plumes from the Juan de Fuca Ridge using suspended matter compositions. *Journal of Geophysical Research: Solid Earth*, 97 (B3), 3457–3468.
- Feely, R. A., Massoth, G.J., Trefry, J.H., Baker, E.T., Paulson, A.J., Lebon, G.T., 1994. Composition and sedimentation of hydrothermal plume particles from North Cleft segment, Juan de Fuca Ridge. *Journal of Geophysical Research: Solid Earth*, 99 (B3), 4985–5006.

- Fernex, F., Février, G., Bénéaim, J., Arnoux, A., 1992. Copper, lead and zinc trapping in Mediterranean deep-sea sediments: probable coprecipitation with Mn and Fe. *Chemical Geology*, 98(3), 293–306.
- Gutzman, D. W., Langford, C. H., 1993. Kinetic study of the speciation of copper (II) bound to a hydrous ferric oxide. *Environmental Science and Technology*, 27(7), 1388–1393.
- Hannington, M., 2013. The role of black smokers in the Cu mass balance of the oceanic crust. *Earth and Planetary Science Letters*, 374, 215–226.
- Iyer, S. D., Mascarenhas-Pereira, M. B. L., Nath, B. N., 2007. Native aluminium (spherules and particles) in the Central Indian Ocean Basin sediments: Implications on the occurrence of hydrothermal events. *Marine Geology*, 240(1), 177–184.
- Jardine, P. M., Sparks, D. L., 1984. Potassium-calcium exchange in a multireactive soil system: I. Kinetics. *Soil Science Society of America Journal*, 48(1), 39–45.
- Juang, R.-S., Wu, W.-L., 2002. Adsorption of sulfate and copper (II) on goethite in relation to the changes of zeta potentials. *Journal of Colloid and Interface Science*, 249(1), 22–29.
- Keays, R. R., Scott, R. B., 1976. Precious metals in ocean-ridge basalts; implications for basalts as source rocks for gold mineralization. *Economic Geology*, 71, 705–720
- Klevenz, V., Sander, S. G., Perner, M., Koschinsky, A., 2012. Amelioration of free copper by hydrothermal vent microbes as a response to high copper concentrations. *Chemistry and Ecology*, 28(5), 405–420.
- Mascarenhas-Pereira, M. B. L., Nath, B. N., 2010. Selective leaching studies of sediments from a seamount flank in the Central Indian Ocean Basin: Resolving hydrothermal, volcanogenic and terrigenous sources using major, trace and rare-earth elements. *Marine Chemistry*, 121(1), 49–66.
- Mascarenhas-Pereira, M. B. L., Nath, B. N., Borole, D. V., Gupta, S. M., 2006. Nature, source and composition of volcanic ash in sediments from a fracture zone trace of Rodriguez Triple Junction in the Central Indian Ocean Basin. *Marine Geology*, 229(1), 79–90.
- McKay, D., Swinkels, G., Szarmes, K., 1974. Hydrometallurgical process for extraction of copper and sulphur from copper iron sulphides. US Patent (No. US3816105 A).
- Nath, B. N., 2001. Geochemistry of sediments. *Indian Ocean Perspect*, 2, 645–689.
- Nath, B. N., Borole, D.V., Aldahan, A., Patil, S.K., Mascarenhas-Pereira, M.B.L., Possnert, G., Ericsson, T., Ramaswamy, V., Gupta, S.M., 2008. 210Pb, 230Th, and 10Be in Central Indian Ocean Basin seamount sediments: Signatures of degassing and hydrothermal alteration of recent origin. *Geophysical Research Letters*, 35(9) doi:10.1029/2008GL033849.
- Nath, B. N., Rao, V. P., Becker, K. P., 1989. Geochemical evidence of terrigenous influence in deep-sea sediments up to 8 S in the Central Indian Ocean Basin. *Marine Geology*, 87(2), 301–313.
- Nishioka, J., Obata, H., Tsumune, D., 2013. Evidence of an extensive spread of hydrothermal dissolved iron in the Indian Ocean. *Earth and Planetary Science Letters*, 361, 26–33.

- Öhlander, B., Thunberg, J., Land, M., Höglund, L. O., Quishang, H., 2003. Redistribution of trace metals in a mineralized spodosol due to weathering, Liikavaara, northern Sweden. *Applied Geochemistry*, 18(6), 883–899.
- Olson, D. L., Shuman, M. S., 1985. Copper dissociation from estuarine humic materials. *Geochimica et Cosmochimica Acta*, 49(6), 1371–1375.
- Peltier, E., Dahl, A. L., Gaillard, J.-F., 2005. Metal speciation in anoxic sediments; when sulphides can be construed as oxides. *Environmental Science and Technology*, 39, 311–316.
- Petersen, W., Wallmann, K., Schröer, S., Schroeder, F., 1993. Studies on the adsorption of cadmium on hydrous iron (III) oxides in oxic sediments. *Analytica Chimica Acta*, 273(1), 323–327.
- Poulton, S. W., Canfield, D. E., 2005. Development of a sequential extraction procedure for iron: implications for iron partitioning in continentally derived particulates. *Chemical Geology*, 214(3–4), 209–221.
- Poulton, S. W., Fralick, P. W., Canfield, D. E., 2010. Spatial variability in oceanic redox structure 1.8 billion years ago. *Nature Geoscience*, 3, 486–490.
- Quevauviller, P., Ure, A., Muntau, H., Griepink, B., 1993. Improvement of analytical measurements within the BCR-programme: single and sequential extraction procedures applied to soil and sediment analysis. *International Journal of Environmental Analytical Chemistry*, 51(1–4), 129–134.
- Rouxel, O., Fouquet, Y., Ludden, J. N., 2004. Copper isotope systematics of the Lucky Strike, Rainbow, and Logatchev sea-floor hydrothermal fields on the Mid-Atlantic Ridge. *Economic Geology*, 99(3), 585–600.
- Sander, S. G., Koschinsky, A., 2011. Metal flux from hydrothermal vents increased by organic complexation. *Nature Geoscience*, 4(3) 145–150.
- Sander, S. G., Koschinsky, A., Massoth, G., Stott, M., Hunter, K. A., 2007. Organic complexation of copper in deep-sea hydrothermal vent systems. *Environmental Chemistry*, 81–89.
- Savenko, A. V., 2001. Coprecipitation of Manganese, Copper, Zinc, Lead, and Cadmium with Iron Hydroxide in Hydrothermal Plumes (By the Data of Laboratory Modeling). *Oceanology C/C of Okeanologiya*, 41(4), 502–507.
- Sparks, D. L., 1987. Kinetics of soil chemical processes: Past progress and future needs. *Future Developments in Soil Science Research*, 61–73, ISBN: 978-0-89118-872-8.
- Sparks, D. L., 1998. Kinetics of sorption/release reactions on natural particles. In *Structure and Surface Reactions of Soil Particles*, Huang, P. M., Senesi, N., Buffle, J., Eds.; J Wiley; New York, pp 413.
- Swallow, K. C., Hume, D. N., Morel, F. M., 1980. Sorption of copper and lead by hydrous ferric oxide. *Environmental Science and Technology*, 14(11), 1326–1331.
- Tan, Q.-G., Ke, C., Wang, W. X., 2013. Rapid assessment of Metal Bioavailability in marine sediments using coelomic fluid of Sipunculan worms. *Environmental Science and Technology*, 47, 7499–7505.

Templeton, D. M., Ariese, F., Rita C. U., Danielsson, M., Muntau, H., Van Leeuwen, H.P., Lobinski, R., 2000. Guidelines for terms related to chemical speciation and fractionation of elements. Definitions, structural aspects, and methodological approaches (IUPAC Recommendations 2000). *Pure and Applied Chemistry*, 72(8), 1453–1470.

Thompson, C. M., Ellwood, M. J., Wille, M. A., 2013. Solvent extraction technique for the isotopic measurement of dissolved copper in seawater. *Analytica Chimica Acta*, 775, 106–113.

Turner, A., 2000. Trace metal contamination in sediments from UK estuaries: an empirical evaluation of the role of hydrous iron and manganese oxides. *Estuarine, Coastal and Shelf Science*, 50(3), 355–371.

Vink, J. P. M., 2002. Measurement of heavy metal speciation over redox gradient in natural water. Sediment interfaces and implications for uptake by benthic organisms. *Environmental Science and Technology*, 36, 5130-5138.

Wheat, C. G., McDuff, R. E., 1994. Hydrothermal flow through the Mariana Mounds: Dissolution of amorphous silica and degradation of organic matter on a mid-ocean ridge flank. *Geochimica et Cosmochimica Acta*, 58(11), 2461–2475.

Table 1: Copper (Cu) speciation in hydrothermally influenced deep-sea sediment and the sediment standard reference material (BCR-701) by following the modified BCR protocol. The association of Cu with different phases of Fe-oxides in the studied sediments by following a sequential extraction protocols proposed by Poulton and Cranfield to know. . Details of both extraction protocols are given in the Supplementary Material Tables SM1 and SM2.

Sample ID	BCR extraction (in % of total Cu)					mod. Poulton and Cranfield extraction (in% of Cu _{Fe})		
	Total Cu (ppm)	Fraction 1 Cu _{exch}	Fraction 2 Cu _{Fe}	Fraction 3 Cu _{Corg}	Fraction 4 Cu _{res}	Cu-Fe _{ox1}	Cu-Fe _{ox2}	Cu-Fe _{mag}
AAS-61 BC 8								
4-10cm	354±6	0.3±1	40.7±3.1	0.3±0.1	58.5±3.2	69.3±4.6	29.7±1.2	1.0±0.2
10-15cm	253±7	0.1±0.1	20.7±2.5	0.0	79.2±5.8	63.0±3.2	33.9±2.2	3.1±0.3
15-18cm	227±5	0.0	18.9±3.1	0.2±0.1	80.9±6.9	51.4±2.3	38.8±3.8	9.9±0.9
BCR-701								
Reported by								
EU	275±13	49.3±1.7	124±3	55.2±4	38.5±12.0			
commission								
In this study	266±8	52.6±2.1	106±7	56.0±1.0	36.7±6.2			
Recovery	97.0%	103%	88.3%	100%	95.3%			

Table 2: Kinetically distinguishable relative Cu species and their corresponding dissociation rate constants at different depths of sediment core AAS-61 BC 8.

depth	C ₁ (%)	k _{d1} x 10 ⁻³ (s ⁻¹)	C ₂ (%)	k _{d2} (s ⁻¹)
4-10cm	6.1 ± 0.3	9.0±0.8	93.9±6.1	< 1x 10 ⁻⁶
10-15cm	8.4±0.5	2.7± 0.2	91.6±2.4	< 1x 10 ⁻⁶
15-18cm	29.5±2.5	0.5±0.1	70.5±1.8	< 1x 10 ⁻⁶

Figure captions

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

Figure 2. Relative fractions of Cu associated with different phases of sediment at three integrated depths. Left bars for each depth represent fractions 1-4 from BCR extractions and right bars are the relative distributions of Cu associated with iron oxides (Cu-Fe_e) separated into the reducible Fe-oxides ferrihydrite and lepidocrotite ($\text{Cu-Fe}_{\text{ox1}}$), goetite, akaganeite and hematite ($\text{Cu-Fe}_{\text{ox2}}$) and magnetite ($\text{Cu-Fe}_{\text{mag}}$).

Figure 3. Kinetically labile Cu in the sediment at three integrated depth after leaching with 0.05 M EDTA. Values are presented as percentage of the total Cu concentration (as given in Table 1).

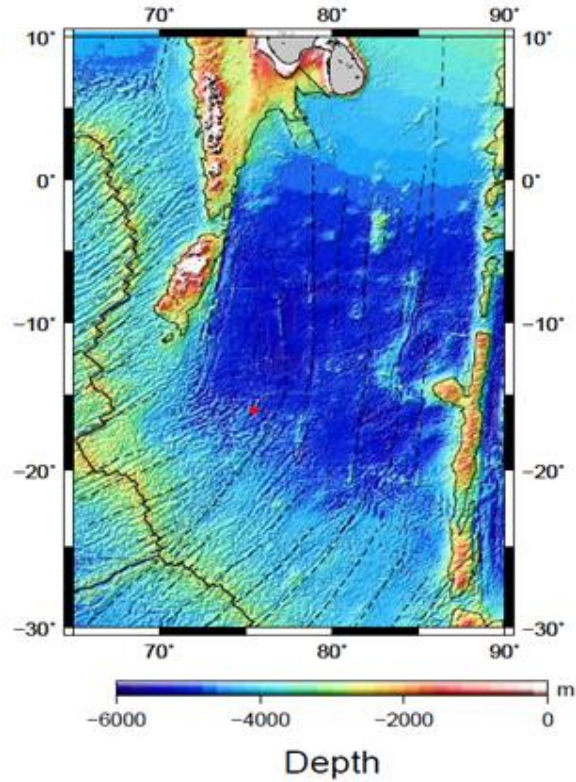


Figure 1. Map of the sampling site in the Central Indian Ocean Basin

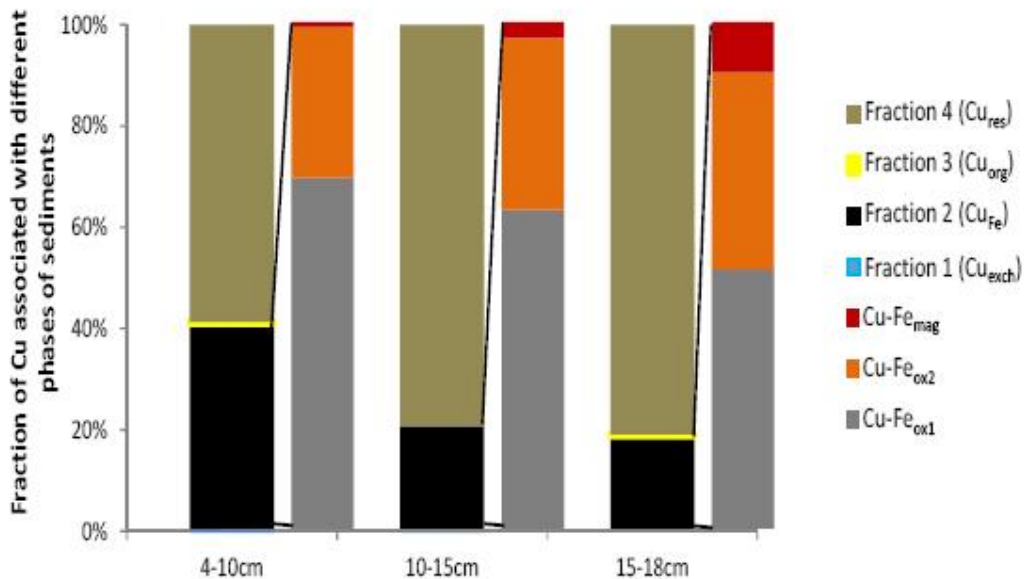


Figure 2. Relative fractions of Cu associated with different phases of sediment at three integrated depths. Left bars for each depth represent fractions 1-4 from BCR extractions and right bars are the relative distributions of Cu associated with iron oxides (Cu_{Fe}) separated into the reducible Fe-oxides ferrihydrite and lepidocrotite ($Cu-Fe_{ox1}$), goetite, akakganeite and hematite ($Cu-Fe_{ox2}$) and magnetite ($Cu-Fe_{mag}$).

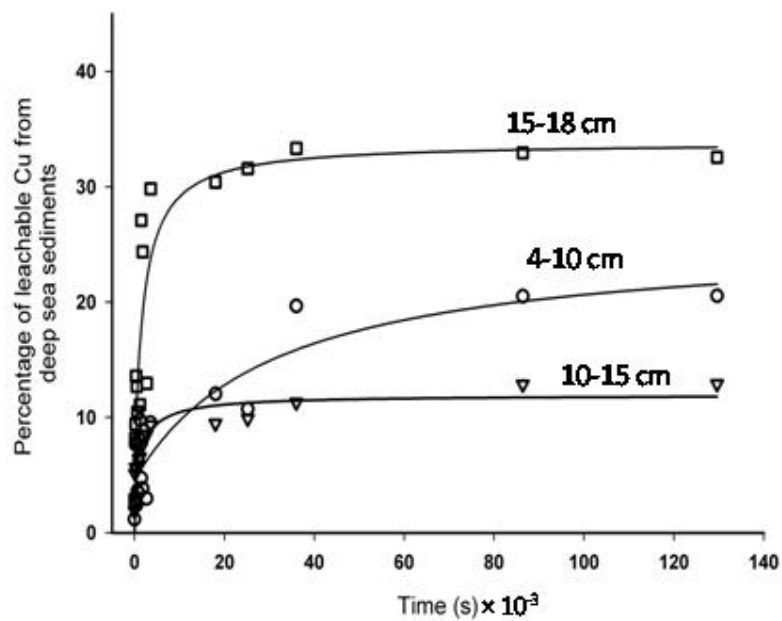


Figure 3. Kinetically labile Cu in the sediment at three integrated depth after leaching with 0.05 M EDTA. Values are presented as percentage of the total Cu concentration (as given in Table 1)

Supplementary Material

Details of the extraction schemes for Cu, from different phases of sediments and further from different target phases of Fe

	Page
Table SM1: Modified sequential extraction protocol by (BCR)	2
Table SM2: Sequential extraction protocol by Poulton and Canefield	3
Table SM3: Major element content of sediment core bulk and leach residues.	4
Table SM4: Total metal concentrations in sediment cores	4

Table SM1: Modified sequential extraction protocol as developed by the Community Bureau of Reference (BCR) (Quevauviller et al., 1993) to differentiate Cu-species associated with different sediment phases. Sample size used 1 g.

Extraction	Cu-target phases:	Terminology
0.11 M CH ₃ COOH, m/v = 40 16 h end-over-end shaker	Exchangeable, water soluble & carbonate	Fraction 1
0.5 M hydroxylamine-HCl, pH 1.5, (HNO ₃ 2 M, fixed volume), m/v = 40 16h end-over-end shaker	Cu associates with Fe/Mn oxide phases	Fraction 2
Digestion: H ₂ O ₂ 30%, (85 ⁰ C) Extracting agent: CH ₃ COONH ₄ , pH 2 (HNO ₃), m/v = 50, 16 h end-over-end shaker	Cu-associated with organic carbon	Fraction 3
Open digestion	Cu within the mineral structure of sediments	Fraction 4

Table SM2: Sequential extraction protocol adapted from by Poulton and Canefield (2005) to differentiate Cu-species associated with Fe/Mn oxide phases (Fraction 2 of BCR protocol) Sample size used 0.2g.

Extraction	Target phases: Cu associated with	Terminology
1 M CH ₃ COONa, pH4.5 10ml, 24 h	exchangeable & carbonate Fe	Cu-Fe _{exch&carb}
1 M hydroxylamine-HCl (in 25% v/v acetic acid) 10ml, 48h	reducible oxides of Fe (ferrihydrite, lepidocrocite)	Cu-Fe _{ox1}
Na dithionite (50 g/l), pH 4.8, 10ml, 2h	reducible oxides (goethite, akaganeite, hematite)	Cu-Fe _{ox2}
0.2 M ammonium-oxalate, pH 3.2, 10ml, 6h	magnetite	Cu-Fe _{mag}

Table SM3: Major element content of sediment core AAS61/8 at different depth and MAG-1 standard reference material in (wt %) bulk and leach residues.

Sample(sediment depth)	Residue ^a %	SiO ₂	Al ₂ O ₃	TiO ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	
AAS61/8												
4-10cm	84.1 Bulk	42.3	13.6	0.7	11.9	2.1	2.9	2.0	4.8	2.8	1.1	
10-15cm	85.1 Bulk	41.6	13.7	0.8	13.2	1.9	2.8	2.2	4.8	2.8	1.1	
15-18cm	84.3 Bulk	46.5	14.1	0.77	11.06	2.17	2.73	2.16	1.32	2.87	1.02	
MAG-1 ^c	Bulk	50.8	16.1	0.72	7.29	0.10	3.09	1.42	3.81	3.70	0.16	
	Certified value	50.4	16.4	0.75	6.80	0.10	3.00	1.37	3.83	3.55	0.16	

^a Residue left on leaching with hot 50% HCl.

^b The elemental concentrations are not weight corrected.

^c MAG-1 is a certified reference material. It is a fine grained gray-brown clayey mud with low carbonate content, from the Wilkinson Basin of the Gulf of Maine.

Table SM4: Total metal concentrations of reported elemental analysis by ICP-MS and total Cu analysed by DPASV

Data from DPASV ^a		Reported average value of elements - ICP-MS data								
Depth cm	Cu ppm	Cu ppm	Pb ppm	Fe (%)	Mn (%)	Al (%)	Cr ppm	Co ppm	Ni ppm	Zn ppm
4 - 10	354	356	19.2	7.34	1.39	6.77	27	145	538	19.2
10 - 15	253	283	18.2	8.24	1.39	6.63	25	143	353	18.2
15 - 18	227	261	17.7	8.15	1.31	6.65	25	138	297	17.7

^a this work

^b Mascarenhas-Pereira and Nath, 2010)

AAS-61/BC-08

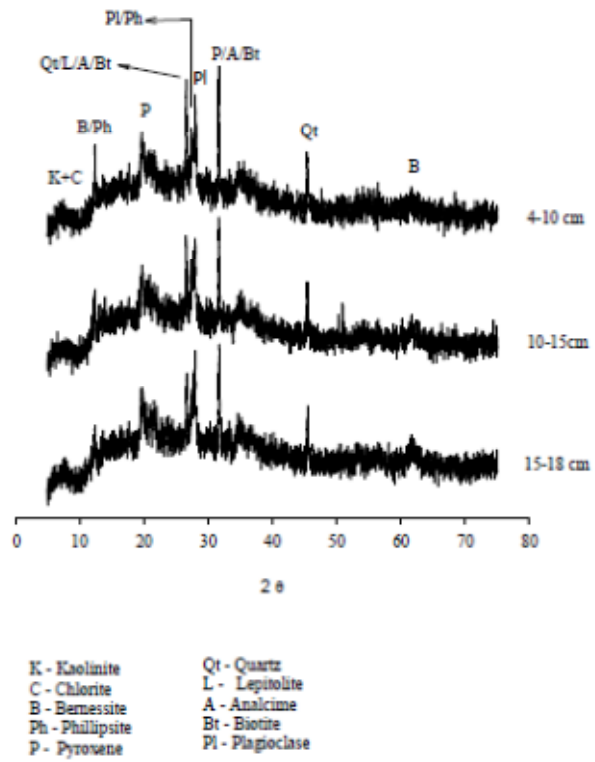


Figure SM1: X-Ray diffractogram of the studied sediment at three different depths