

Geochemical variability of copper and iron in Oman Margin sediments

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Abstract

An analysis of the geochemical distribution of selected trace metals among various geochemical phases of the sediments in the Oman Margin was carried out using a sequential extraction technique. The present study showed that most Cu in abyssal sediment is associated with only oxidisable mainly organic and sulphide bound metals with insignificant bound to exchangeable, carbonates, easily/moderately reducible fraction. The preservation of Cu in the sediments indicates the importance of primary production and upwelling in the overlying waters and an organic flux in the sedimentary deposition of open-ocean environments. The early diagenetically formed oxidisable mainly organic and sulphide fraction are not degraded and results in a pronounced association of Cu with organic fraction in the sediments of the Oman continental margin. The strong correlation between Cu, TOC and Fe oxides associated with the oxidisable fraction in one of the core indicates that it is likely to be the presence of sulphides.

Key words: trace metals; speciation; organic carbon; Oman Margin; Oxygen Minimum Zone.

1. Introduction

The strong summer (southwest) monsoon controls the climatic and oceanographic conditions of the northern Indian Ocean. The respiration of sinking particulate matter and the incursion of intermediate saline waters from nearby marginal seas contribute to the formation of an intense oxygen minimum zone (OMZ) at water depths of between ~50 m and 1000 m. The exceptionally high organic matter content observed in the sediments beneath the OMZ on the Oman Margin [1] make the Arabian Sea an ideal site to understand the degree of preservation of organic matter and bottom water oxygen conditions on sedimentary cycling of trace metals.

Organic carriers from the surface waters transport Cu, but it is also scavenged in deep waters and by sinking Mn oxyhydroxides; however, it is regarded as a 'nutrient-type' element due to its depletion in surface waters [2-5]. Under oxidizing conditions at the sediment-water interface most of the organic carrier phase of Cu is mobilized, releasing Cu into the dissolved phase. Some of this Cu migrates downward and is incorporated into the sediment, but most of it is recycled back into the water-column [6]. However, under oxygen-depleted conditions at the sediment-water interface, relatively large amounts of organic carriers can be incorporated in the sediment, thus retaining some of their associated Cu. During diagenesis, sediment phases formed or altered are amorphous iron and manganese hydroxides, organic matter, iron sulphide FeS, iron pyrites FeS₂, and iron carbonates FeCO₃. These phases "bind" trace metals through the processes of adsorption and co-precipitation.

Manganese associated with inorganic carrier phases is scavenged from the water column before it reaches the sediment surface [7-9]. Much of this Mn is transformed to oxides at the sediment surface [10-11,5] before being buried as the sediment accumulates. However, under reducing conditions, Mn can be utilized as secondary oxidants for the respiration of any organic carbon, which has escaped initial decomposition at the sediment surface. As this happens, the reduced Mn is released into solution as Mn²⁺, and migrates up the sediment column via an interstitial water concentration gradient, to be re-precipitated in the upper oxic layer of the sediments [12-13].

The distribution of elements in different mineral phases may be used for the palaeo-environmental interpretation of the sedimentary record. This distribution can be measured by

means of sequential extraction, in which sediment samples are suspended in solutions of successively increasing leaching strength [14-15,5].

The aim of this work was to study and determine the concentration of Cu, Fe and Mn in the sediments as well as the chemical form in which they occur. This study will provide independent monitoring data on the mineralogical forms/fractions: exchangeable, carbonate bound, reducible and oxidisable in oxic and sub-oxic depositional environments and its association with organic carbon is discussed here for the cores collected at the base of continental slope in the OMZ.

2. Materials and Methods

Undisturbed Cores were collected using a multi-corer from separate multiple-corer deployments [16] below the oxygen minimum zone (OMZ) during RRS Discovery cruise 211/94 (Fig.1; Table 1). Sediment samples were immediately frozen (-20°C) on board prior to transport to the laboratory where they were freeze-dried and stored at -20°C prior to analysis. Sediment cores collected below the OMZ area (12687#8 and 12687#10) at a depth of ~3400 m were sliced at 10 mm intervals down to 70 mm and at 20 mm intervals down to 290 and 330 mm respectively and immediately processed for analysis in the laboratory.

2.1. Analytical Methods

Sediment grain size distribution in each section of cores collected below the OMZ was determined with a Coulter Counter (Model LS 130). Water content in each section of cores collected below the OMZ was determined by weight loss after freeze drying.

Multi-stage sequential leaching techniques have been employed [17] and extensively reviewed by [18,11]. The scheme applied in this study is the ‘best working compromise’, linking operationally-defined host separations with geochemically meaningful fractions. The scheme was initially proposed by [14] and modified later by [18,11].

The extraction scheme consists of five steps, designed to selectively extract metals from geochemically significant fractions. Together, these five fractions comprise the “non-detrital” metal in the sediments.

Step 1: Surface adsorbed/exchangeable metals

Step 2: Carbonates

Step 3: Easily reducible solid phases

Step 4: Moderately-reducible mineral phases

Step 5: Oxidisable (Organic and/or sulphide) phases

Metals released in this fraction are expected to include metals strongly bound to organic matter. Metals occurring as insoluble sulphides (if such are present) under reducing conditions would also be released in this fraction.

Modifications from the earlier published schemes were as follows:

1) The magnesium chloride reagent (step 1) was replaced by ammonium acetate, because the former attacks carbonates [14,18]. The use of ammonium acetate also alleviates the more serious matrix problems encountered with magnesium chloride in GF-AAS; e.g. interference in lead determinations as a result of the formation of lead chlorides in the graphite furnace [19].

2) An additional step (step 3) was incorporated into the scheme to differentiate between the easily reducible fraction (mainly manganese oxy-hydroxides with small amounts of amorphous iron oxides) and the moderately reducible fractions (step 4; mainly crystalline iron oxides, together with some resistant manganese oxides). The reagent used for step 3 was sodium acetate (1 M) plus hydroxylamine hydrochloride (0.25 M).

In the discussion below the metal fractions are designated as M_x (M- Cu, Fe or Mn; x - step number). Cu was analysed by graphite furnace AAS (Perkin Elmer-AAS Model 1100 B; DL referred from Perkin Elmer Manual as recommended). Fe and Mn were determined by flame atomic absorption spectrophotometer (AAS, Perkin-Elmer Model, 2380).

3. Results and discussion

3.1. Bulk sediment parameters and distributions

Particle size and water content in the two abyssal cores, below OMZ were fairly comparable (Fig. 2a-c). The abyssal cores (12687#8 and 12687#10) reveal that sedimentation at this location may be influenced by turbidites, as shown by the particle-size distributions. The particle size distribution (Fig. 2a-b) shows a silt-rich sediment layer between 100 and 200 mm, with a much lower water content (Fig. 2c). Total organic carbon increases between 0-100 mm layer with a decrease in the 100-200 mm layer and again there is a slight increase below 200 mm

layer (Fig. 2d). A study reported a mean mixed-layer depth of 4.6 ± 0.2 cm and a mean D_b of 0.003 ± 0.0017 cm² d⁻¹ for Arabian Sea slope sediments located within the OMZ [20]. The sedimentation-rate estimates suggested that some bioturbation occurring below the mixed-layer depths. Mean Peclet numbers (i.e., [mixed layer depth]x[sedimentation rate]/[D_b]) for the mixed layer were ≤ 0.4 at five of six stations in the Oman Margin; at 1000 m, a sedimentation rate could not be estimated [20]. The high resolution records from Arabian Sea sediment cores showed that sedimentation rates during the Late Holocene remained constant [21]. The calibrated ¹⁴C ages for “clean” (i.e. un-coated) foraminifers indicate normal sedimentation for the last 13,000 yr. The results from piston core taken at the same location, showed that sedimentation rates decreased [22] sharply from the last glacial (ca. 30–50 cm kyr⁻¹), into the Holocene (5.6 cm kyr⁻¹).

3.2. Trace element (Cu, Fe and Mn) distributions

Fig. 3 (a-f) shows the downcore variation of oxidisable fraction of Cu (Step 5), Fe and Mn associated with easily reducible solid phases (Step 3), moderately-reducible mineral phases (Step 4), oxidisable phases (Step 5) and Mn associated with surface adsorbed/ exchangeable (Step 1) and carbonates (Step 2) phases.

There was no detectable surface adsorbed/exchangeable (Step 1) and carbonates fractions (Step 2) observed for Cu and Fe in the sediment. Iron and Manganese associated with easily reducible solid phases (Step 3) and moderately-reducible mineral phases (Step 4) has been discussed earlier [23]. In the Oman margin sediments, below the OMZ, the freshly formed oxide of easily reducible Fe spike co-occurs with the easily reducible Mn fresh oxide spike. Maximum concentrations of easily reducible Fe and Mn occur in the form of a 'spike' below the sediment surface. The maximum fresh oxide concentrations of easily reducible Mn ($\sim 9.5 \times 10^3$ $\mu\text{g g}^{-1}$ Mn) are upto three orders of magnitude higher than those of Fe (~ 500 $\mu\text{g g}^{-1}$ Fe). At the spike, easily reducible Mn makes up $\sim 40\%$ of the total non-detrital Mn, compared to the easily reducible Fe, which at the spike makes up only $\sim 25\%$ of the total non-detrital Fe in both the cores. The spike contains considerably more of the total non-detrital Mn than the total non-detrital Fe, and in fact dominates the distribution of total Mn in the top unit [23].

Fig. 3a,b,c shows the downcore distributions for the oxidisable (step 5) fraction of Cu, Mn and Fe (Cu₅, Mn₅, Fe₅). Partitioning data indicate that the non-detrital Cu was present only in

the Cu₅ (oxidisable) fraction for the cores below OMZ (Fig. 3a). The Cu₅ concentration in the two abyssal cores increased with depth in the upper 100 mm, then decreased sharply to a minimum at ~ 100-200 mm. The latter appears to be a turbidite layer, as discussed above. Below 200 mm, the Cu₅ concentration was approximately that observed in the upper 100 mm. The Mn₅ distribution in core 12687#8 (Fig. 3d) showed a similar distribution to that observed for copper. As determined by sequential leaching, however, there was no detectable non-detrital Mn observed in core 12687#10 (only Mn₅ fraction). In contrast, the Fe₅ fraction in the abyssal cores increased gradually with depth, with the exception of a sharp maximum at 80-100 mm.

3.3. Role of Cu in the diagenetic cycle of organic matter in the sediments

Copper is a micronutrient, essential for most physiological growth for marine and terrestrial organisms. Copper is frequently used as a tracer for biologic input; Cu behaves partly like a micronutrient in the water column [24] and appears to be released from organic carrier phases in sediments [25-26]. Chester et al. [5] reported that Σ Cu probably reaches the sediment surface in a variety of forms, i.e. detrital (refractory) phases, mildly and moderately reducible oxides (Cu_{3,4}) and in association with organic (Cu₅) phases, with the latter often being the most important. For example, in particulate material from the North Atlantic Ocean, more than 50% of Σ Cu was held in the Cu₅ fraction [5]. While this association with organic matter is an important factor in controlling copper fractionation in sediments, post-depositional diagenetic reworking of deposited copper may also result in an accumulation of copper as an insoluble sulphide mineral or in association with iron sulphide phases [27-28].

During the present study, the non-detrital partitioning data for Cu concentrations revealed that Cu mobilized by Steps 1 to 4 was not detectable in the abyssal sediments of the Arabian Sea, the copper being held exclusively in Cu₅ fraction (Fig. 3a). The correlation of Cu₅ vs Al (bulk concentration) was poor ($R^2 = 0.05$ for core 12687#8, $n = 18$; $R^2 = 0.36$ for core 12687#10, $n = 20$), clearly demonstrating the absence of a strong detrital input for copper in these sediments.

The Cu in the oxidisable fraction is thus thought to be mainly associated with biogenic carriers, which have settled through the water column [3,5,7]. Once the particulate material is deposited at the sediment surface, the organic-phase Cu (Cu₅) generally undergoes phase transformations as the organic carriers decompose. However, some of the organic-phase Cu may remain preserved in sediments, its amount depending on the diagenetic environment of

deposition. In rapidly accumulating sediments, the amount of Cu₅ retained can be significant. For example, the concentrations of Cu₅ in diagenetically active hemipelagic sediments of the Atlantic Ocean deposited in the marginal regions were relatively high (>10%; Thomas, 1987). In contrast, these concentrations decrease substantially below 10% towards the open ocean in less diagenetically active sediments, such as from the Mid-Atlantic Ridge. Fe and Mn seem to remain as oxide species [28].

The preservation of Cu₅ in bottom sediments is directly related to the amount of primary productivity in the overlying waters [5]. This relationship is confirmed for the copper in the abyssal cores (Fig. 4a) by a relatively strong correlation between Cu₅ and TOC ($R^2 = 0.80, 0.57$, $n = 18$ for core 12687#8 and $n = 20$ for core 12687#10 respectively, $p < 0.05$) in the Oman Margin sediments. Organic carbon (TOC) and major element values are referred from earlier studies [17]. There is thus a strong indication that the organic-phase Cu in the Oman Margin sediments displays a relict profile that has not been strongly altered by *in situ* diagenetic reactions. The association of Cu with the organic fraction has also been observed for Indian river sediments [29], the eastern Mediterranean [15] and Tees estuary [30]. Metals bound to organic matter and sulphides is clearly the most significant sink for Cu in the sediment [31]. This fact confirms the theory [32], which predicts that Cu is strongly related to organic matter and sulphides. Moreover, if the redox potential is low (reducing environment), Cu tends to form an insoluble complex (Cu₂S) in the presence of sulphur [33]. Copper is a chalcophilic element, it is mainly bound to sulphides in nature. It can be found in the reductive zone with smectite and clay minerals. Cu compounds concentrated mostly in the acid-soluble residue, and bound to organic matter/sulphide fractions [34].

3.4. Role of Fe in the diagenetic cycle of organic matter in the sediments

The behaviour of Fe in the organic fraction and its relationship with Cu, Mn and organic matter is discussed below.

Pyrite is known to be an important carrier phase for trace elements, and it is abundant in OMZ sediments [1,35]. Pyrite is formed by the sulphidation of iron oxides and that poorly reactive iron fraction is sulphidised only slowly [36]. Pyrite is formed in anoxic marine sediments by the reaction of dissolved sulphide, produced by microbial sulphate reduction, with detrital iron-bearing minerals [37-38]. Iron sulphide minerals is often, the initial products which

are probably transformed to pyrite by reaction with dissolved sulphide [39-40] and/or polysulphides [41-44]. There seem to be presence of Fe sulphides, of which pyrite is dominant in the oxygen-depleted marine sediment [e.g. 45-47]. Though, Fe (II) forms various iron sulphides during sulphate reduction, pyrite seems to be more stable in marine sediments and can be an indicator of bottom water conditions [36]. The bottom water oxygen concentration ($\sim 2.99 \text{ mL L}^{-1}$; Smith et al., 2000), does not reflect any changes in the level of Fe (associated with organic fraction) concentrations in the cores below OMZ. The similarity of Cu_5 and Fe_5 in the cores 12687#8 (Fig. 3a, e) and the significant relationship of Cu_5 vs. Fe_5 and TOC vs. Fe_5 (Fig. 4a-e) suggests that copper sulphide formation is a significant process at this site as there is a similar Fe_5 sulphide data for comparison because of pyrite measurements reported by Passier et al. [46].

In view of the absence of easily reducible Mn oxide (Mn_3) and moderately-reducible (Mn_4) oxides within OMZ sediments and the apparent recalcitrance of the moderately-reducible (Fe_4) oxides, sulphate is the most likely available electron acceptor for diagenetic reactions to proceed. The sulphate reduction and pyrite formation both within and below the organic-rich zones have occurred close to the sediment-water interface of the Arabian Sea [48]. Pyrite formation in the sediments of the Arabian Sea OMZ was limited by the availability of reactive iron oxides due to the low oxygen concentration of the OMZ, which resulted in the reduction of Fe oxides in the water column or at the sediment-water interface [48]. The significant downcore variation of Fe_4 oxides and strong correlation ($R^2 = 0.36$, $n=18$) with Fe_5 fraction suggests that the latter are probable associated with the sedimentary precipitation of sulphides (pyrite framboids being abundant in two of the OMZ sediment cores; [1]), this may further imply some diagenetic modification of Fe_4 . The significant correlation ($R^2 = 0.36$, $n=18$) between Cu_5 and Fe_5 fraction was observed in the core 12687#8 (Fig. 4d).

3.5. Role of Mn in the diagenetic cycle of organic matter in the sediments

A relatively high concentration of exchangeable Mn was observed when compared to the other metals (Cu and Fe). The relatively high concentration of exchangeable Mn suggests that the metal exists in the reduced form [14]. This can be explained by the fact that Mn(II) oxidation is a much slower process than Fe(II) oxidation in most natural waters [14]. The fraction containing the most Mn (Fig. 3b) was the easily reducible fraction (Mn_3) in most of the

sediments, where compounds of Mn in soil and sediments are released by a solution of hydroxylamine–hydrochloride [49-50].

Johnson et al. [51-52] showed that the highest Mn fluxes from sediments occurred at shallow shelf sediments, whereas OMZ site sediments exhibited the lowest Mn fluxes. Transport of Mn from continental margin sediments was observed by Johnson et al. [51] on the California continental margin. The transport of Mn from shallow to deeper waters can be expected when Mn oxides are reduced near the sediment-water interface of the shallow sediments. Reduced Mn effuses to the water column and is subsequently transported to deeper waters where it can re-precipitate in the water column or in more oxidizing sediment. The transport of dissolved Mn from upper slope sediments to oxidizing lower slope sediments is an important phenomenon observed by [53] in the eastern Arabian Sea margin. It is clearly evident that there is an absence of respiration of OM using Mn in the sediments at the depth of the OMZ. Mn oxides are apparently not making it to the sediment, i.e. they are reduced in the water column as they fall through the OMZ. In the sediments at the base of the Oman Margin, organic-phase (Mn_5) made up as much as 1% of the non-detrital Mn in core 12687#8, although it was not detectable in core 12687#10. A significant correlation ($p < 0.005$, ANOVA) between organic carbon and Mn in the organic fraction (Mn_5) exists in core 12687#8 ($R^2 = 0.62$, $n = 18$; Fig. 4c). Mn in the organic fraction (Mn_5) in this core is evidently associated with fine-grained particles and organic carbon [54].

Conclusions

The geochemical distribution of selected trace metals among various geochemical phases of the sediments in the Oman Margin was carried out using a sequential extraction technique. The present study showed that most Cu in abyssal sediment is associated with only oxidisable mainly organic and sulphide bound metals with insignificant bound to exchangeable, carbonates, easily/moderately reducible fraction. The relative importance of the oxidisable fraction for Cu, Fe and Mn in the sediments from the abyssal site on the Oman Margin and its relationship with organic carbon revealed that Cu, the organic matter and organic/sulphide fraction was the most important by far. This supports several previous scientific observations that Cu is often associated with organic matter and sulphides, the latter being perhaps in the form of cuprous

sulfide when found in anoxic conditions and in presence of sulphur compounds. This fact also explains the dependence of Cu solubilization towards the redox potential.

The preservation of Cu_s in bottom sediments is directly related to the amount of primary productivity in the overlying waters and organic-phase Cu found in the abyssal site revealed the presence of higher organic carbon content of these sediments. The early diagenetically formed organic fraction withstands subsequent degradation and results in a pronounced association of Cu with organic matter in the sediments of the Oman continental margin. The strong correlation between Cu, TOC and Fe oxides associated with the oxidisable fraction in one of the core indicates that it is likely to be the presence of sulphides.

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Fig. 1. Sample locations during RRS Discovery Cruise 211/94 on the Oman Margin

Fig. 2. Downcore variation of particle size (a, b), water content (c) and TOC (d) in a sediment core (12687#8 and 12687#10) below the oxygen minimum zone (OMZ) in the Arabian Sea

Fig. 3. (a-f). Downcore variation of Cu₅, Fe₃₋₅ and Mn₁₋₅ vs. depth below the OMZ.

Fig. 4. (a-e). Plot of Cu₅, Fe₅ and Mn₅ vs. TOC; Cu₅ vs. Fe₅ and Mn₅ below the OMZ

Table 1

Sample details and locations

| Sample number | Location | Water depth (m) | Core length (mm) |
|---------------|--------------|-----------------|------------------|
| 12687 # 8 | 18° 59.33' N | 3372 | 290 |
| | 58° 59.09' E | | |
| 12687 # 10 | 18° 59.42' N | 3385 | 330 |
| | 59° 00.92' E | | |

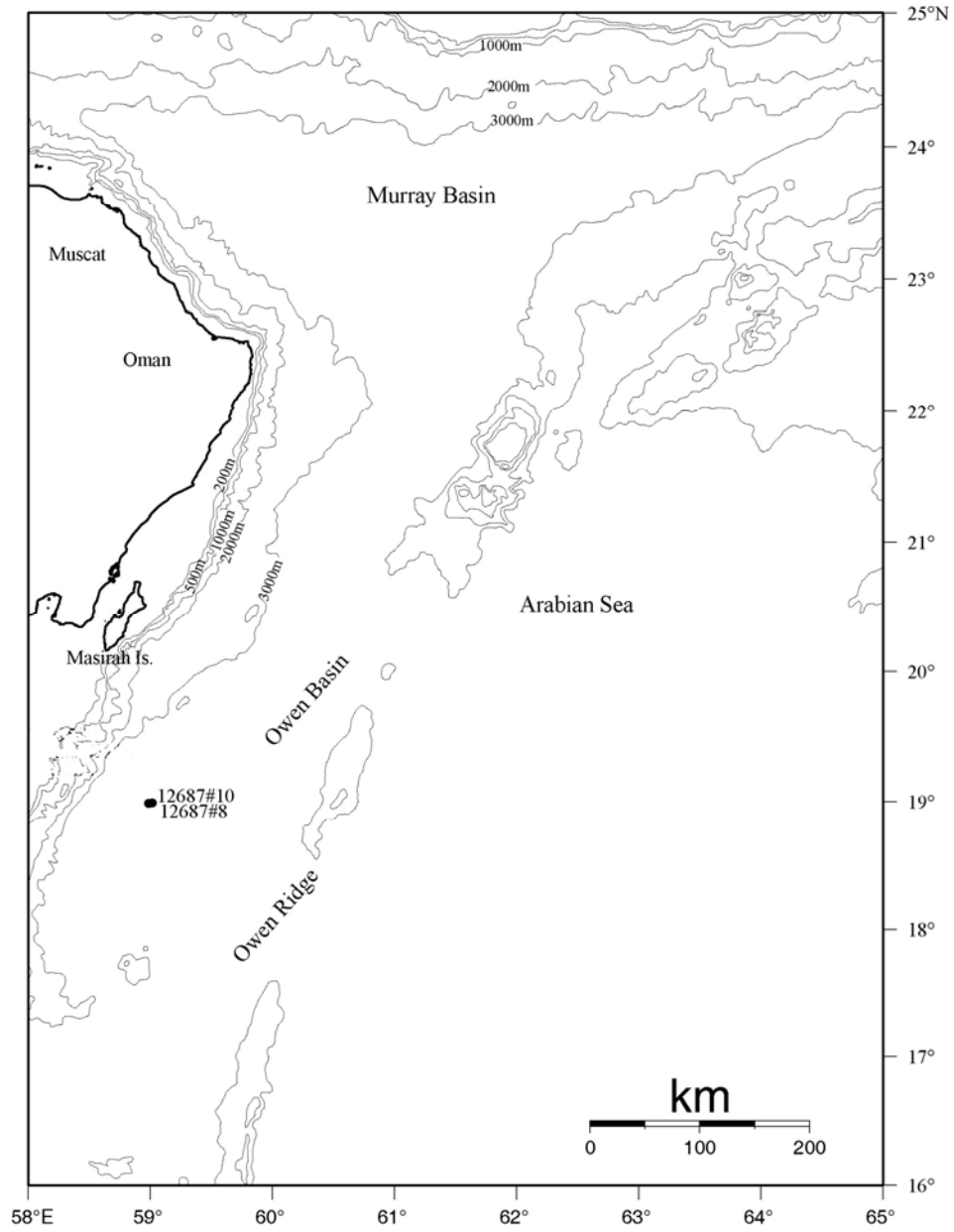


Fig. 1. Sample locations during RRS Discovery Cruise 211/94 on the Oman Margin.

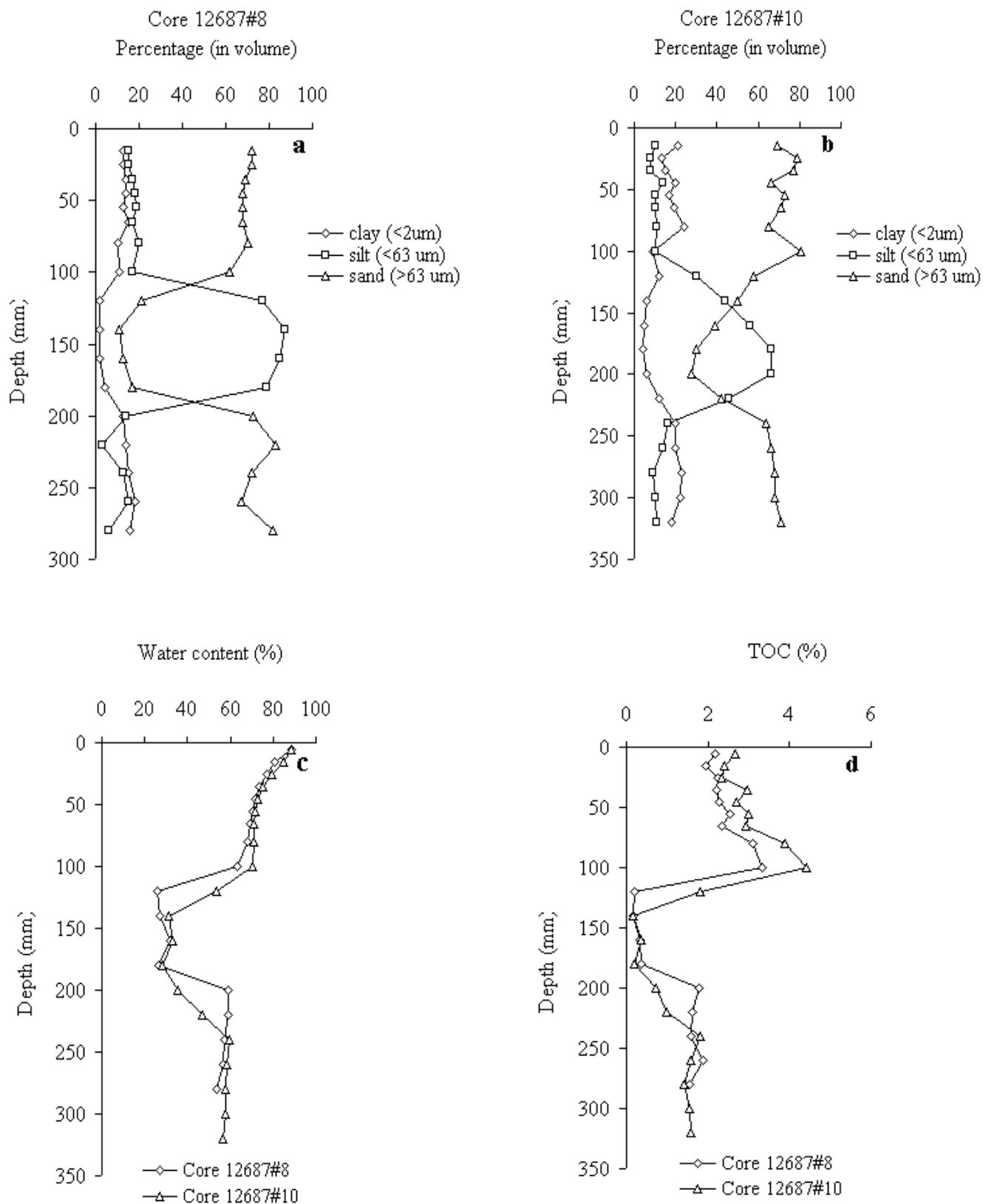
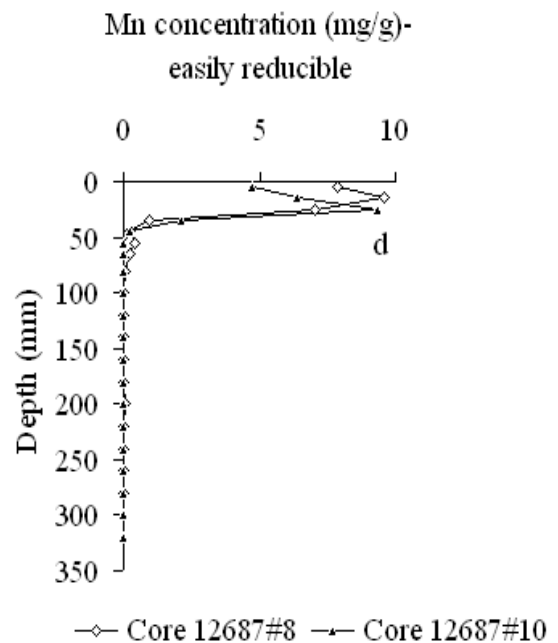
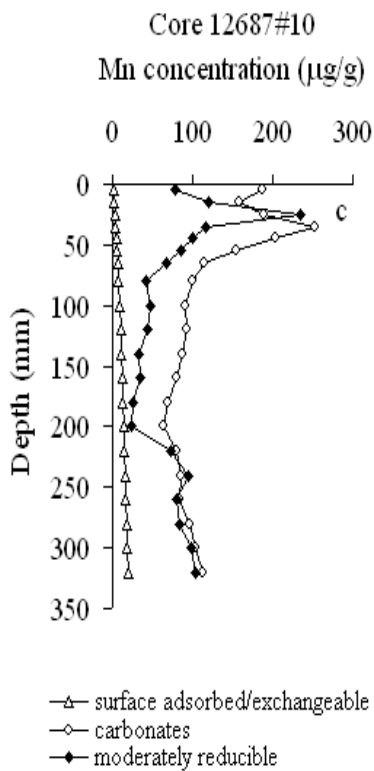
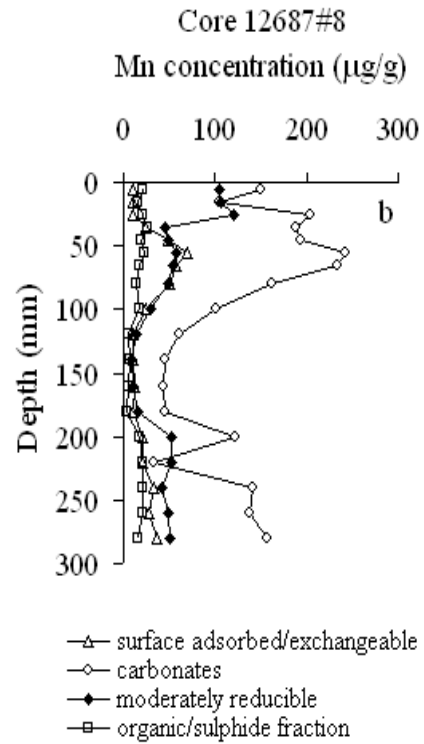
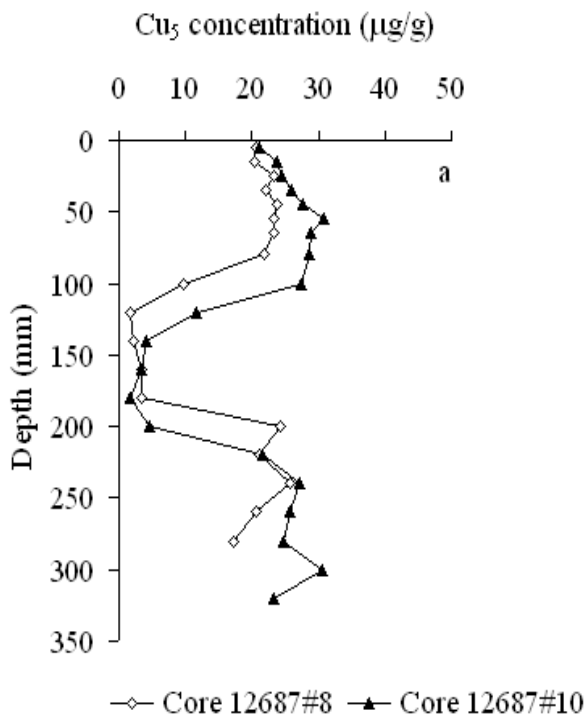


Fig. 2. Downcore variation of particle size (a, b), water content (c) and TOC (d) in a sediment core (12687#8 and 12687#10) below the oxygen minimum zone (OMZ) in the Arabian Sea.



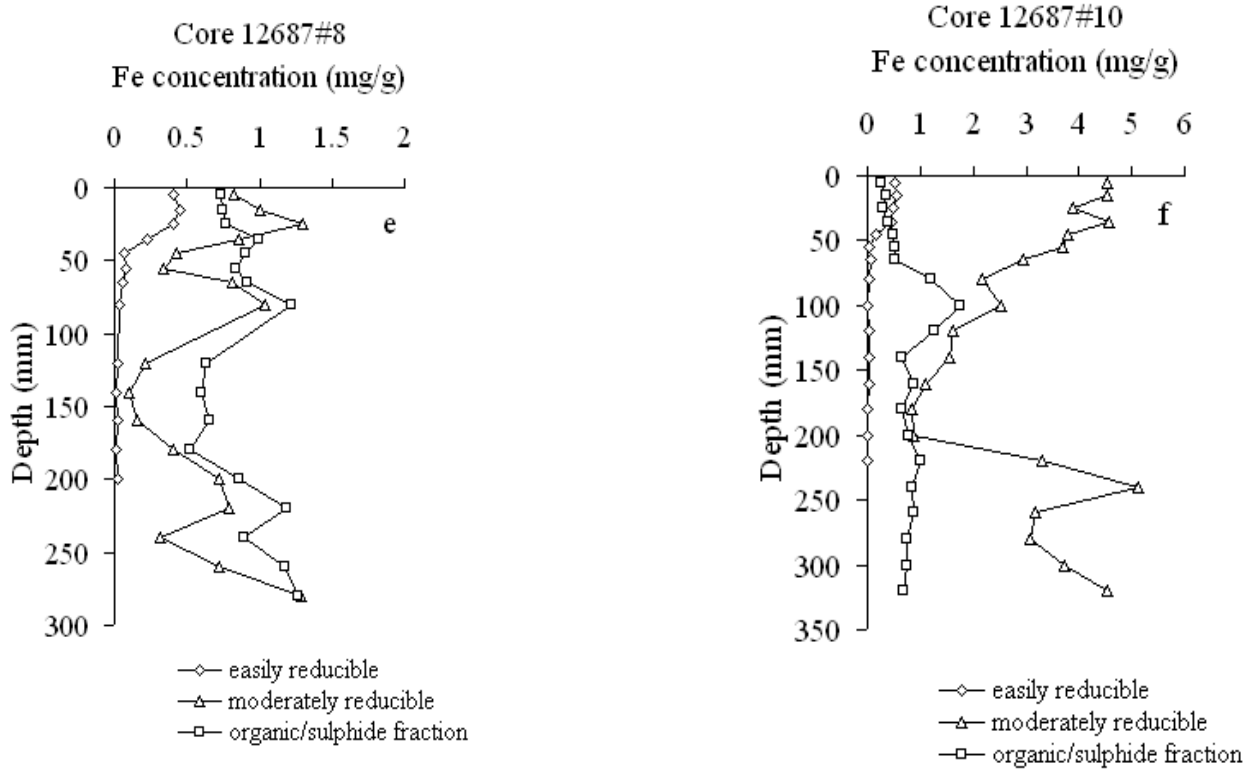


Fig. 3. (a-f). Downcore variation of Cu₅, Fe₃₋₅ and Mn₁₋₅ vs. depth below the OMZ.

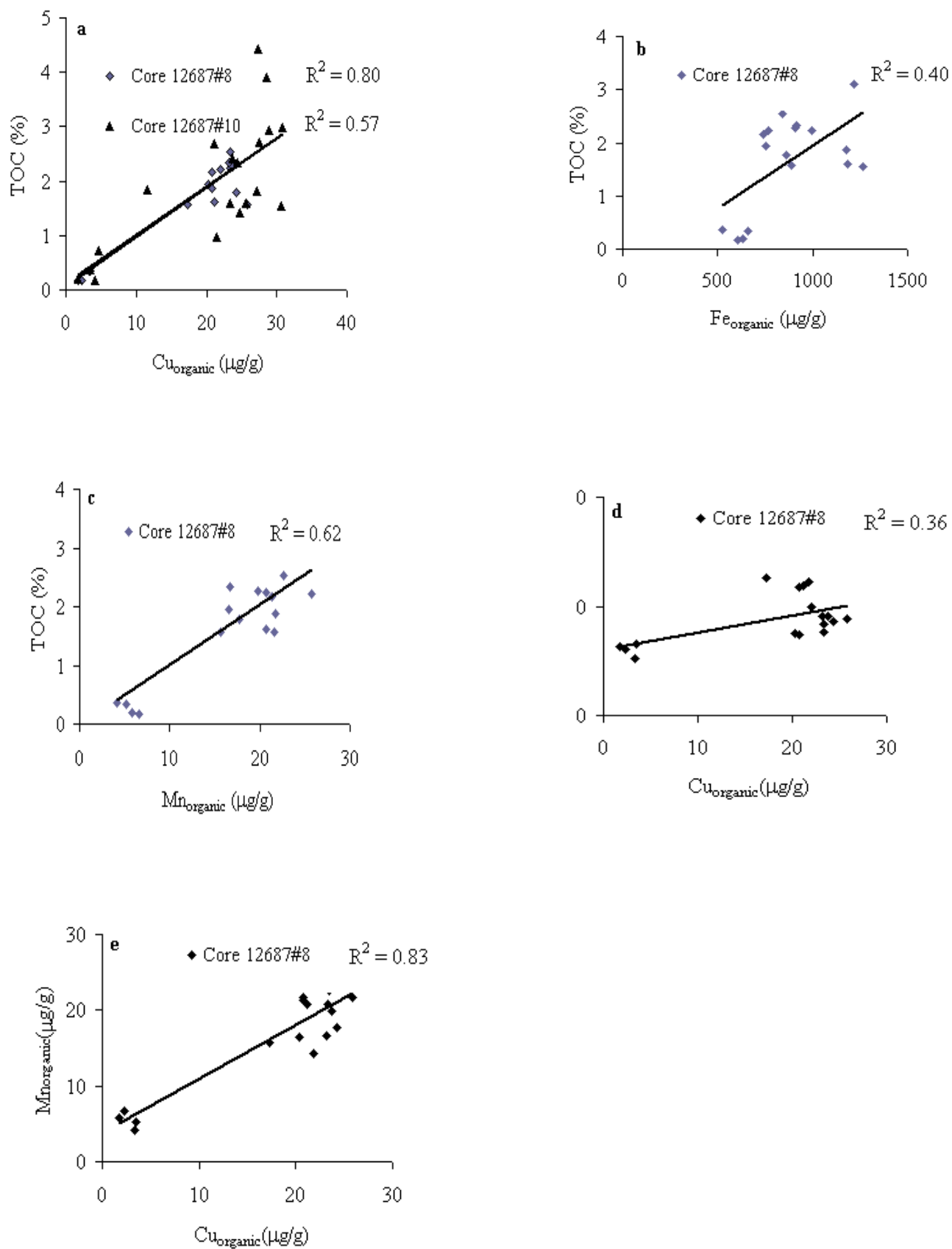


Fig. 4. (a-e). Plot of Cu_5 , Fe_5 and Mn_5 vs. TOC; Cu_5 vs. Fe_5 and Mn_5 below the OMZ.