

Bottom water oxygenation history in southeastern Arabian Sea during the past 140 ka: Results from redox-sensitive elements

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ABSTRACT

The concentrations of multiple redox-sensitive elements such as Re, U, Mo, Cd, V, Sb, and Tl were determined in sediments from the southeastern Arabian Sea (9°21' N; 71°59' E) to understand the bottom water oxygenation history throughout the past 140 ka. The enrichment of redox-sensitive elements (Re, U, Cd and Sb) above average crustal abundances suggests that the Last Glacial Maxima (17.48 ka), stadials of Marine Isotope Stage (MIS)-5 (5b and 5d) and Glacial Termination (GT)-II (133 ka) were associated with suboxic bottom water conditions. Sediments deposited during these suboxic conditions show the highest Re content (up to 54 ppb normalized to a carbonate free basis) which is highly enriched over average continental crust (0.4ppb) and these sediments appear to be the major sink for the global mass balance estimation. Marine Isotope Stages 1, 3, 4 and interstadials of MIS-5 (5a, 5c & 5e) were all associated with near oxic conditions. Overall, the lack of enrichment of Mo and V above crustal abundance, and a high Re/Mo (ppm/ppm) ratio (avg. 18.2×10^{-3}) suggest that sediments of the southeastern Arabian Sea never contained free H₂S during the last 140 ka. These changes in the bottom water oxygen content can be related to the oceanic circulation pattern during this time and in part are reflected in relationships between the timing of redox changes and paleoproductivity proxies.

Keywords: Redox-sensitive elements (Re, U, Mo, Cd, V, Sb and Tl), southeastern Arabian Sea, sediment core, suboxic, oxic, Bottom water oxygen, Last Glacial Maxima, Marine Isotope Stage, Oceanic circulation.

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1. Introduction

Elemental concentrations in marine sediments are mainly controlled by the detrital source (fluvial or aeolian), biological processes/associations, authigenic precipitation from the water column (hydrogenesis) and by submarine hydrothermal activity. In the marine system, the depositional environment can be either oxic (marked by the presence of O₂ and an absence of H₂S), suboxic (low dissolved oxygen levels of ~ 1-2ml/l and the absence of H₂S) or anoxic (absence of O₂ and presence of H₂S). Some of the redox-sensitive trace and minor elements may be either concentrated or depleted relative to average continental crust under these varying redox conditions at the time of deposition. The distribution of redox-sensitive elements in marine sediments thus has the potential to provide information on redox conditions of the bottom water (Calvert and Pedersen 1993; De La Rocha, 2004; Tribovillard et al., 2005). Instead of using a single redox-sensitive element to understand depositional conditions it is always better to use multiple redox-sensitive elements which respond differently to the redox state (Yarincik et al., 2000). Modern oceans are losing dissolved oxygen at high rates, and this is particularly significant in many coastal areas and in open oceans at intermediate water depths, where intense oxygen minimum zones are created (Naqvi et al., 2006). These changes may be driven by enhanced nutrient inputs leading to higher rates of export production and ocean ventilation (Nameroff et al., 2004). Bottom water oxygenation sometimes may just likely be attributed to migration of the OMZ during waxing and waning of upwelling (Challands et al., 2009). Recent study has shown that redox conditions can be highly variable over short times scales: consequently the effects on redox-sensitive trace metals can be rather complex (Algeo and Ingall, 2007) and as yet, such effects on trace metal uptake by sediments are incompletely understood.

Rhenium, U and Mo are the most commonly used redox-sensitive trace elements in ocean waters and have received considerable attention as promising paleo-tracers (Calvert and Pedersen, 1993; Rosenthal et al., 1995a; Crusius et al., 1996; Crusius and Thomson, 2000; Nameroff et al., 2004; Algeo and Lyons, 2006). In oxygenated water these elements are present as perrhenate (ReO₄⁻), a uranyl carbonate complex (UO₂(CO₃)₃⁴⁻) and molybdate (MoO₄²⁻) with oceanic residence times of ~750, ~ 500 and ~780 ka respectively (Bertine, 1972; Colodner et al., 1993; 1995; Crusius et al., 1996;

Crusius and Thomson, 2000; Chaillou et al., 2002). These species are conservative in the oxygenated oceans with a constant concentration in the entire ocean basin, but are highly enriched in anoxic sediments where bottom water oxygen concentrations are zero (Brumsack, 1986). However, local and global factors may change oceanic redox conditions and thus alter the distribution of redox-sensitive elements. Diagenetic reactions that obscure the relationship between sedimentary metal accumulation and reducing conditions may complicate the interpretation of redox-sensitive elements in sediment. Bottom water oxygen concentrations play an important role in shifting oxygen gradients in the sediment column, altering the biogeochemical environment and also affecting the macro- and megafauna. Changes in oceanic oxygenation occur during interglacial and glacial periods and these have been associated with anoxic and oxic bottom water conditions, for example in the southern Indian Ocean (Bareille et al., 1998) and in the Cariaco Basin (Yarincik et al., 2000). In the southeastern Arabian Sea, Sarkar et al. (1993) have suggested that near-anoxic bottom water conditions occurred during the last glacial cycle (Isotope Stage 2, 3 and 4) based on the U content of marine sediment. There are however no reports of the redox conditions beyond MIS-4 (> 75 ka) in the southeast Arabian Sea. In a earlier study of a sediment core from the southeastern Arabian Sea, Pattan et al. (2003) used a range of productivity proxies to understand productivity fluctuations. In the present study, multiple redox-sensitive elements (Re, U, Mo, V, Cd, Sb and Tl) are determined in sediments from the southeastern Arabian Sea to understand the bottom water oxygenation history during the last 140 ka; to determine the factors responsible for their variation; and compare the timing of redox conditions with productivity proxies.

2. Materials and Analytical Methods

A 5.52 m long gravity sediment core (SK-129/CR-05) was raised from a water depth of 2300 m at 9°21' N and 71° 59' E from the southeastern Arabian Sea during *ORV Sagar Kanya* cruise 129 (Fig.1). The sediment cores lies beyond the present day oxygen minimum depth. The sediment core was sampled at 2 cm intervals, dried and powdered. A total of 41 samples from the sediment core were analysed in the present study. The age model for the core is derived from foraminiferal oxygen isotope data

which has been published by Pattan et al. (2003). For trace elements analysis, approximately 0.2 g of oven dried sediment was accurately weighed into PTFE beakers. To this was added 5 ml of HCl, which was left to stand overnight before being evaporated to dryness. 15 ml of HF and 4 ml of HClO₄ was then added, again left cold overnight before evaporating to dryness at about 180°C. The HF/HClO₄ stage was repeated until all material had dissolved. Finally, 5 ml of HClO₄ was added and evaporated to dryness before the residue was taken into solution in 100 ml of 5 % HNO₃. All acids used were Analar grade or better. Blanks, duplicate samples and the USGS reference material QLO-1 (Quartz Latite) were also prepared by the same method.

Analyses were performed on a VG PlasmaQuad II + STE (ICP-MS) at Aberystwyth University. Samples were analysed initially in “scanning mode” where the entire mass range is scanned 100 times in 60 seconds to determine the concentrations of about 40 elements, including V, Cd, Sb, Tl, Th and U. Concentrations of selected redox-sensitive elements (Mo and Re) were determined using a “peak jumping” method, where the spectrometer spends a longer time interval acquiring a signal from each analyte peak, before jumping to the next element. Dwell times of 10.24 ms per channel were used for Se and Mo, and 40.94 ms for Re with 5 channels per peak to optimize detection limits and count rates over 50 s acquisition. Calibration for both scanning and peak jumping analyses was achieved using Ru as the internal standard against a single multi-element standard solution, and performed offline.

Lower limits of detection (LLD) are calculated for an element as

LLD = (3 x standard deviation of blank counts) x (concentration of analyte in standard/analyte counts from standard). -----[1]

In scanning mode, LLDs (calculated back to the solid) are typically equivalent to < 0.1 ppm, and in peak jumping mode they drop by an order of magnitude or more to the 0.001 -0.01 ppm range. Concentrations in the samples for most elements of interest typically are > 10 x LLD. Analytical accuracy was assessed by the analysis of the USGS Certified Reference Material QLO-1 (USGS-2006). This gave results typically within ± 5 % of recommended or certified values (see Table1), and in all cases, determined concentrations were within the quoted uncertainty of the accepted values. Analytical precision, given as the coefficient of variation (CV %) was determined by analyses of

several duplicate samples, and was typically better than $\pm 5\%$, although at low concentrations (below 1 ppm) this increases to around $\pm 10\%$. Even at the extremely low concentrations at which Re occurs in the samples, analytical precision in peak jumping mode of $\pm 10\%$ was obtained.

Redox-sensitive elemental concentrations have been calculated on carbonate-free basis using the following equation.

$$\{X\}_{CF} = \{X\} \text{ element in bulk sediment} * 100 / (100 - \text{wt \% calcium carbonate}) \text{ -----[2].}$$

where X is the element whose concentration needs to be calculated.

3. Results

The concentration of redox-sensitive elements (ppm) on a carbonate-free basis, along with total organic carbon, calcium carbonate and bulk Al content (%) from the sediment core (SK-129/CR-05) from the southeastern Arabian Sea are presented in Table 2 along with average crustal values for these trace elements (Taylor and McLennan, 1985, 1995). Throughout the text and in Table 2, the redox-sensitive element concentrations are given as their carbonate-free equivalent. Calculation to a carbonate-free basis helps in interpreting the analyses by allowing the direct comparison of concentration data with continental crustal values by removing the dilution effect of carbonate in the sediments. Concentrations of redox-sensitive elements, total organic carbon, calcium carbonate and Al in the analysed sediment core are presented in Figure 2a and Sb, Tl and Cd in Figure 2b. Ratios of Re/Mo, U/Th and Re/TOC are plotted against sediment age in Figure 3. Rhenium and U show large variations from 5.6 ppb to 54.5 ppb and 2.06 ppm to 16.4 ppm respectively. Similarly, Mo and V vary from 0.42 ppm to 14.9 ppm and 147 ppm to 283 ppm in the sediment core respectively. High ratios of Re/Mo (ppb / ppm), Re/TOC (ppb / %) and U/Th (ppm / ppm) were recorded during LGM, stadials of MIS-5 and GT-II (Fig.3).

4. Discussion

4.1 Rhenium

Rhenium is one of the most useful redox-sensitive elements and can be used to reveal the intensity of past reducing conditions in marine sediments. Rhenium is

conservative in nature and exhibits similar behaviour to U, Mo, V and Tl in oxygenated seawater. Rhenium occurs at a relatively high concentration in seawater as a result of the solubility of its oxyanion (Colodner et al., 1993). Rhenium is removed from solution in anoxic/suboxic conditions via diffusion into sediment pore waters to depths where it is adsorbed or precipitated from solution, leading to a strong enrichment in reducing marine sediments (Crusius et al., 1996). The highest Re concentration in the sediment core studied here (54.5 ppb) gives an enrichment of 135 times over the crustal abundance of 0.4 ppb (Taylor and McLennan, 1995). The calcium carbonate content of the core varies from 30 to 67 % (Pattan et al., 2003, see Table 2) and this calcareous ooze contains very little Re (<0.05 ppb), as Re is not incorporated into calcite shells (Colodner et al., 1993). The high Re content in these sediments suggests that authigenic Re is present in these sediments. Rhenium enrichment is greater than many other redox sensitive elements as a result of the high ratio of $(\text{metal})_{\text{sea water}}/(\text{metal})_{\text{crust}}$ (Crusius et al., 1996), which reflects both the solubility of ReO_4^- and the relatively small lithogenic flux (cf. Crusius et al., 1996). Sediments from Marine Isotope Stages (MIS) 1, 3 and 4 and interstadials of MIS-5 (5a, 5c and 5e) have comparatively low Re contents (~ 5 ppb), reflecting near-oxic bottom water conditions (Fig.2 a). This Re content (~5 ppb) is a little higher than in oxic pelagic sediments and ferromanganese nodules from Pacific Ocean formed in oxic environments (Boyko et al., 1986; Koide et al., 1986; Colodner et al., 1993). It thus appears that interglacials were associated with more oxic bottom water, retaining Re in solution. In contrast, sediments from the Last Glacial Maximum (MIS-2), stadials of MIS-5 (5b and 5d) and at GT-II (~133 ka) have high Re contents up to 54.5 ppb suggesting suboxic conditions (Table 2). There is one more moderate high Re peak of ~ 21 ppb at 46 ka. This Re content is lower than those reported for modern anoxic sediments with concentrations between 5-130 ppb (Koide et al., 1986); between 20 -184 ppb in sediments from the Black Sea (Ravizza et al., 1991); 330 ppb from eastern Mediterranean sapropels and 40 to 600 ppb in Cretaceous black shales in Atlantic (Warning and Brumsack, 2000). Metalliferous sediments from the East Pacific Rise and hydrothermal sulphide deposits also have elevated Re contents (Boyko et al., 1986). The enrichment of Re in the southeastern Arabian Sea is unlikely to be a result of the incorporation of hydrothermal sulphide because no such occurrence has been reported in

this region. Therefore, the high Re contents of 50-54.5 ppb in the studied core during the Last Glacial Maximum (17.48 ka) are likely to be the result of deposition under suboxic conditions. Similar Re enrichment is reported in sediment cores from the Japan Sea, (15-20 ppb at 9-10 cm depth) and in sediments from the Pakistan margin (up to 42 ppb at 30-35 cm depth) and these occurrences suggest suboxic conditions probably during the LGM (Crusius et al., 1996) and this could plausibly be the major sink of Re in the global mass balance calculations.

4.2 Uranium

In oxic seawater, U is present as soluble U(VI) in the form of uranyl tricarbonate species, $(\text{UO}_2(\text{CO}_3)_3^{4-})$ which is chemically unreactive (Calvert and Pedersen, 1993). Under reducing conditions U(VI) is reduced to U(IV) which is less soluble, particle reactive and may precipitate as UO_2 , U_3O_7 or U_3O_8 or may be adsorbed onto the sediment or clay mineral surfaces (Mangini, 1978; Barnes and Cochran, 1990; Klinkhammer and Palmer, 1991; Tribovillard et al., 2005). The U concentration in the studied core is low (~4 ppm) during MIS-1, 3 and interstadials of MIS-5 (5a, 5c and e) suggestive of oxic conditions. High U concentrations of between 10 to 16 ppm during the LGM, 46.5 ka, stadials of MIS-5 (5b and 5d) and GT-2 may indicate reducing conditions at these times (Table 2, Fig.2 a). Uranium and organic carbon show a positive correlation ($r = 0.545$, $n = 41$, see Table 3) suggesting removal of U by organic carbon (Mangini, 1978; Fig. 4). Authigenic U enrichment (5-8 ppm) in Atlantic sediments during the last glacial stage (12-24 ka) was attributed to a process caused by changes in sediment accumulation rate (Thomson et al., 1990). Similarly, Rosenthal et al. (1995a) and Chase et al. (2001) observed enrichment of authigenic U in the last glacial maxima sediments. In the present sediment core there is no major change in sediment accumulation rate (Pattan et al., 2003), hence the possibility of post depositional diagenesis causing U enrichment can be excluded. This is further supported by very low and uniform Mn contents in the studied core (0.01% to 0.02 %, Pattan Unpubl. Data) which are well below average crustal abundances (0.14 %; Taylor and McLennan, 1995), again indicating diagenesis is not responsible for U enrichment. Sarkar et al. (1993) reported enrichment of authigenic U during glacial periods in the deep eastern Arabian Sea.

Uranium behaves in a very similar manner to Re ($r = 0.831$, $n=41$, see Table 3; Fig.4) and this strong correlation suggests that changes in redox conditions during the deposition of these sediments may be responsible for similar enrichments of both of these elements at particular depths.

4.3 Molybdenum

Molybdenum is conservative in oxic seawater, behaves similarly to Re and has a residence time of ~ 780 ka (Collier, 1985; Emerson and Husted, 1991; Barling et al., 2001). It occurs in seawater as Mo(VI)O_4^{2-} (molybdate, Manheim and Landgren, 1978) and in reducing conditions it is reduced to Mo(IV)S_4^{2-} , tetrathiomolybdate (Calvert and Pedersen, 1993 ; Emerson and Husted, 1991). The main source of Mo into the oceans is by weathering and erosion of terrigenous material ($\sim 90\%$) with a lesser input ($\sim 10\%$) from low temperature hydrothermal sources (McManus et al., 2002). The marine geochemistry of Mo is characterized by its removal under sulphidic anoxic conditions by incorporation into pyrite and in more oxygenated waters Mo is associated with Mn oxide (Erickson et al., 2000; Zheng et al., 2000; Algeo and Maynard 2004; Algeo and Lyons 2006; Tribovillard et al., 2008). Further, Erickson et al., (2000) suggested that Mo precipitation occurs when a threshold of $\sim 11 \mu\text{M}$ of H_2S is attained. Enrichment of Mo in the anoxic sediments and depletion of Mo in the corresponding water column indicate removal of Mo (Emerson and Husted, 1991). Pore water Mo depletion has also been found in seasonally anoxic basins suggesting diffuse loss of Mo into sulphide containing anoxic sediments (Colodner et al., 1995). Therefore sedimentary Mo enrichment can be potentially used as a proxy of palaeo-anoxia.

Molybdenum content in the sediment core peaks at 14.9 ppm (Table 2) and is enriched around 15 times compared to continental crust. High Mo contents in sediments from the last 5 ka (Fig.2 a) are associated with high Mn which could be a result of oxic diagenesis and is similar to other observations made concerning MnO_2 rich sediments (Crusius et al., 1996). In oxic pelagic sediments, Mo is associated with sedimentary Mn-oxides (Morford and Emerson, 1999), Mn-containing particulate material and ferromanganese nodules by adsorption (Shimmield and Price 1986). Ferromanganese nodules and sediments rich in a MnO_2 phase from the Central Indian Ocean Basin, have

average Mo contents of 570 ppm and up to 22 ppm respectively (Jauhari and Pattan, 2000; Pattan unpublished data) indicative of their oxic nature (Pattan et al., 2005b). A high Mo content in oxic sediments is typically positively correlated with high Mn contents (Shimmiel and Price, 1986). In the studied core, between 5 ka to 140 ka, sediment Mo contents are almost uniform at an average content of 0.8 ppm (Fig. 2), slightly lower than the average crustal abundance of 1.0 ppm (Taylor and McLennan, 1985). Similarly, Mn contents are low (average ~0.016 %) and almost uniform. Piper (1994) and Crusius et al. (1996) proposed that increased Mo concentrations (between 5 to 40 ppm) can be used as an indicator of sediment deposition in reducing conditions, where concentrations are greatly increased over those of detrital material (~ 1 ppm). In the sediment core from the southeastern Arabian Sea there is no enrichment of Mo (except 0-5 ka) throughout the entire 140 ka record, which suggests that sediments never attained truly anoxic conditions during this time. In modern anoxic environments Mo shows strong positive correlation with organic carbon (Algeo and Lyons, 2006), but this is not seen in the studied core ($r = -0.093$). The small increase in Mo content observed at ~ 74 ka is associated with the presence of rhyolitic glass shards of Youngest Toba Tuff origin (Pattan et al., 2001).

4.4 Vanadium

In oxic sea waters, V is present as V(V) vanadate oxyanions. Vanadate rapidly adsorbs to both Fe-Mn oxyhydroxides (Calvert and Piper, 1984). In reducing conditions, V(V) is reduced to V(IV) and forms vanadyl ions (VO^{2+}), related hydroxyl species and insoluble hydroxides. In the marine environment V(V) may be removed to the sediment by surface adsorption or by the formation of organometallic ligands (Emerson and Huested, 1991). Vanadium is relatively unreactive in seawater and is preferentially concentrated in sediments deposited in anoxic conditions (Temple and Cave, 1992). The mean V content of the sediment core (204 ppm) is slightly lower than average crustal abundance of 230 ppm (Taylor and McLennan, 1985). This, like the data for Mo, suggests that the sediments never experienced anoxic conditions at any time during the last 140 ka.

4.5 Cadmium

Unlike the other redox sensitive elements described above (U, Mo, V and Re), Cd has only one naturally oxidised state (Cd^{2+}). Cadmium exhibits nutrient-like distribution in oxygenated seawater and is enriched in sulphidic sediments. Its removal in anoxic, sulfide-bearing sediments is related to the formation of insoluble sulphides in the presence of H_2S (see Rosenthal et al., 1995 b). The Cd content in the analysed sediment core varies from 0.27 – 2.7 ppm, indicating that Cd is enriched relative to average crust (0.1 ppm) and average shale (0.13 ppm) (Taylor and McLennan, 1985). Cadmium contents are higher at the LGM, 46.5 ka, 55.4 ka, stadials of MIS-5 and GT-II, and these high concentrations suggest suboxic conditions (Fig.2 b). During the early stages of sulfate reduction, the generated sulfide reacts to form iron sulfide in the sediment, maintaining H_2S below detectable limits (Thamdrup et al., 1994). A similar mechanism has been suggested for the precipitation of Cd in suboxic sediments, where CdS may form in the presence of trace levels of H_2S (Rosenthal et al., 1995b). In contrast, the low Cd contents during MIS-I and interstadials of MIS-5 probably suggest sediment deposition in oxic conditions. The highest Cd content, at ~75 ka, may be a result of the presence of glass shards of Youngest Toba Tuff origin (Pattan et al., 2001).

4.6 Antimony and Thallium

The behaviour of Sb and Tl has not been studied in detail in marine sediments, but these elements appear to be sensitive to redox gradients (Grzetic and Zemmann, 1993) and are usually found concentrated in suboxic/anoxic sediments (Brumsack, 1980; Thomson et al., 1995). Thallium behaves conservatively in oxic seawater (Flegal and Patterson, 1985) and can accumulate in pyrite and in strongly reduced materials (Heinrichs et al., 1980; Brumsack, 1980). The mechanisms responsible for the enrichment of Tl are still poorly understood, but this is likely to be incorporated into any sulfide minerals particularly pyrite which form in the sediment, (see above, Crookes, 1863, Turgeon and Brumsack, 2006). In the sediment core from the southeastern Arabian Sea, Tl varies from 0.61 – 1.21 ppm, with an average of 0.87 ppm (Table 2, Fig.2 b). Turgeon and Brumsack (2006) suggested that Tl content above 2 ppm suggest the presence of sulphidic (anoxic) conditions, and thus, the low concentrations of Tl here throughout the

last 140 ka further support the hypothesis that the southeastern Arabian Sea never endured sulphidic (anoxic) conditions. Antimony behaves similarly to Cd in the sediment core and Sb and Tl have an average concentration of 3.3 ppm and 3.12 ppm respectively, higher than their average crustal abundance of 0.2 ppm and 0.1 ppm respectively (Fig.2 b). Antimony, Tl and Cd all show enrichment during LGM and GT-II. Further, these elements exhibit strong positive inter-correlations (see Table 3) which may be related to the formation of sulfide phase(s) (possibly sphalerite, see above, or stibnite?) at low H₂S (Fig.5).

4.7 Ratios of Re/Mo, U/Th and Re/TOC

Because of their contrasting behaviours, the Re/Mo ratio has been used to distinguish between anoxic and suboxic sedimentary depositional conditions (Crusius et al., 1996). However, Nameroff et al. (2002) warned that these ratios sometimes do not adequately distinguish suboxic depositional environments based on sediments from the Mexican margin. A Re/Mo (ppm/ppm) ratio in sediments close to that of present-day seawater (0.8×10^{-3}) indicates deposition in anoxic conditions, with higher values indicative of suboxic conditions. Re/Mo ratios in the sediment core studied here average 18.2×10^{-3} with maximum values during the LGM, the interstadials of MIS-5 and GT-II (Fig.3) suggesting deposition at these times in suboxic conditions. During LGM and GT-II the Re/Mo ratio (ppm/ppm) was as high as 86×10^{-3} and 72×10^{-3} whereas during MIS-1 this ratio drops to a minimum of 0.37×10^{-3} , close to crustal ratio of 0.4×10^{-3} (Fig.3). This suggests that Re in MIS-1 is mostly derived from a detrital source. Elsewhere in the core the Re/Mo ratio does not fall below 4.6×10^{-3} (i.e. always considerably above the present day seawater Re/Mo ratio) indicating the absence of anoxic conditions during the last 140 ka (cf. Crusius et al., 1996). Black-shales from the Atlantic have mean Re/Mo ratio of 0.76×10^{-3} suggesting their formation under anoxic conditions (Warning and Brumsack, 2000). The Re/TOC ratio behaves in a similar manner to Re/Mo, and is again indicative of suboxic to oxic conditions over the last 140 ka (Fig. 3).

In oxygen-deficient or reducing environments U(VI) is reduced to U(IV), which is particle reactive and becomes fixed onto sediments (Mangini, 1978; Klinkhammer and

Palmer, 1991). In contrast, Th is relatively immobile (Nozaki et al., 1981; Anderson et al., 1983) and is associated mostly with the detrital clay fraction (Myers and Wignall, 1987). Thorium concentrations in the sediment core, with the exception of the sediment around ~ 74.5 ka, are relatively constant at between ~ 8 -12 ppm (average of 10 ppm). The Th concentration in the sample at ~ 74.5 ka suggests this is a mixture of \sim two-thirds lithogenic material and one-third Youngest Toba Tuff which contains between 28-33 ppm of Th (Westgate et al., 1998; Pattan et al., 2001). Because of their differential behaviour, the U/Th ratio can be used as a redox indicator where higher values in sediments (>1.25) indicate deposition in anoxic conditions, and lower values (<0.75) result from deposition in oxic environments (Jones and Manning, 1994). In the present sediment core, the U/Th ratio varies from 0.23 - 1.75 indicating deposition in both oxic and suboxic environments. The presence of suboxic conditions is identified in the core by moderate U/Th ratios (~ 1) during the LGM, 46.5 ka, 55.4 ka, stadials of MIS-5 and GT – II (Fig. 3). In the Arabian Sea, surface sediments beneath the oxygen minimum zone have higher U/Th ratio (1.25) suggesting suboxic depositional conditions (Nath et al., 1997). A very low U/Th ratio (0.1) reported in a sediment core from the Central Indian Ocean Basin suggested deposition in oxic conditions (Pattan et al., 2005), and in the current study U/Th ratios of 0.2 and 0.4 respectively in sediments from MIS-1 and interstadials may suggest deposition in near-oxic conditions.

4.8. Redox-timing and productivity proxies

Based on a number of productivity proxies (calcium carbonate, biogenic opal and biogenic Ba), Pattan et al. (2003; 2005a) suggested that the interglacials (MIS-1,3 & 5) had higher paleoproductivity than the glacial (MIS-2, 4 & 6), and that terrigenous input was greater during the glacial than the interglacials. However, total organic carbon did not show any relationship to the glacial-interglacial time scale. The enrichments of Re and U during the LGM, the stadials of MIS-5 and GT-II, caused by the reduction in bottom water oxygen content, do not exhibit any relationships with the productivity proxies such as calcium carbonate, biogenic opal and biogenic Ba. Further, the near oxic conditions observed during MIS-1 and 3 are associated with higher productivity proxies but MIS-4, although it had near oxic conditions, was associated with low productivity. In

contrast, MIS-5 had higher productivity and there were no distinct variations during the stadials and interstadials. The suboxic conditions recorded during the stadials of MIS-5 and GT-II do not exhibit any relationships with palaeoproductivity. Therefore, redox timing and productivity proxies such as carbonate, opal and biogenic Ba do not exhibit any clear interrelationships. This contrasts with the clear relationships between high total organic carbon content and reduced bottom water conditions during the LGM, the stadials of MIS-5 and GT-II. Furthermore, the association of terrestrially derived organic carbon with a low supply of terrigenous material (i.e. low Al content) during the interstadials of MIS-5 could result from the supply of organic carbon by wind from the continent.

4.9. Bottom water oxygen and circulation

Organic carbon and bottom-water oxygen concentrations determine sediment redox conditions. A decrease in bottom-water oxygen may enhance authigenic U concentrations independent of an increase in organic carbon (Chase et al., 2001). It is evident from the redox-sensitive elements described from sediment core SK-129/CR-05, that suboxic conditions occurred in the bottom water during the LGM, stadials of MIS-5 and GT-II and that near-oxic conditions prevailed during MIS-1, 3, 4 and the interstadials of MIS-5. Sarkar et al. (1993) reported near anoxic conditions in the southeastern Arabian Sea during MIS 2, 3 and 4 and they inferred that anoxic conditions occurred during the last glacial period evidenced by the relatively high organic C and authigenic U contents. In comparison to the compared to sediment core studied here, the sediments studied by Sarkar et al. (1993) came from a greater depth (2523m), were deposited at an order of magnitude slower sedimentation rate and were away from the margin of an upwelling zone. These differences may have resulted in a difference in redox conditions between the two cores. In the present sediment core, high U (10 ppm), Re (54 ppb) and total organic carbon (0.8 %, Pattan et al., 2003) are observed in sediments deposited during the LGM (17.48 ka), all suggesting suboxic bottom water conditions. Concentrations below average crustal abundances of the redox-sensitive elements Mo (0.82 ppm) and V (230 ppm) indicate that during the LGM there was no possibility that anoxic conditions existed during the deposition of sediments in the present core, which is

in contrast to the suggestions of Sarkar et al. (1993). Under anoxic conditions these elements should all be relatively enriched, (Calvert and Price, 1993). Therefore, it is suggested that sedimentation during the LGM occurred under suboxic, rather than anoxic, conditions. Similarly GT-II and the stadials of MIS-5 were also associated with suboxic conditions. Sediment chemistry here indicates that MIS-1, 3 and 4 were associated with near-oxic conditions, which again differs from the observations of Sarkar et al. (1993), who noted that MIS 2, 3 and 4 were associated with near-anoxic conditions. In the core studied here, high TOC during MIS-5 (the penultimate interglacial) and in stadials (5b and 5d) could be a result of suboxic conditions where enough dissolved oxygen is not available for C oxidation. In contrast, MIS-1 (Holocene) had oxic conditions which resulted in the oxidation of organic C, resulting in sediments now containing low contents of organic C (Figure 2). There is however a notable mismatch between the variation of U and Re to the enrichment of organic C during the stadials of MIS-5 (Fig. 2). Low (~0.5 %) and high (~1.5%) organic C respectively during the interstadials and stadials of MIS-5 correspond to inputs of marine and terrigenous derived C indicated by carbon/nitrogen (C/N) ratios of ~ 7 and 25 (Pattan et al., 2003). High organic C occurs at 93 ka and 111 ka (stadials-5b and 5d) whereas, high Re and U occur at 84.87 ka and 105.7 ka. This mismatch could be due to the dominance of terrigenous organic C during the stadials (93 ka and 111 ka). Furthermore, such a disparity is not observed during the LGM and near GT-II where U, Re and organic C all show enrichment because, at these times, organic C is completely marine in origin (C/N ratio ~ 7, Pattan et al., 2003). Marine organic C may be more labile and more susceptible to microbial activity, which in turn would promote a higher rate of oxidant use, causing more pronounced changes in redox than would be the case with more recalcitrant, terrigenous organic C. It is thus necessary to recognize the source of organic C before relationships between TOC, Re and U can be established.

Ocean circulation driven by the formation of deep water and role of Southern-sourced deep water formation in the Northern Indian Ocean is poorly understood. Ocean circulation and climate are strongly interconnected and changes in bottom-water oxygen concentrations could result from alterations to deep- water circulation. During the

LGM, Indian Ocean deep water was cooler by at least 1.5°C than it is today, more depleted in $^{13}\delta\text{C}$ and poorly oxygenated (Kallel et al., 1988). Below 2000m, deep Indian Ocean water originates from the Southern Ocean (Mantyla and Reid, 1983). The present sediment core was raised at a water depth of 2300 m and outside the oxygen minimum zone (OMZ). Based on large changes in $^{13}\delta\text{C}$ during the LGM a weak ventilation of Southern Ocean deep waters has been suggested by Kallel et al. (1988) and Curry et al. (1988) suggested decreased ventilation of deep water in the glacial Southern Ocean at this time. Therefore, the suboxic conditions which occurred during the LGM, stadials of MIS-5 in the southeastern Arabian Sea could have resulted from changes in the circulation of deep water originating from the Southern Ocean which was weakly ventilated. Recent data (Piotrowski et al., submitted), on the Nd isotope composition of leached authigenic ferromanganese oxides, and $\delta^{13}\text{C}$ of benthic foraminifera in a sediment core from the equatorial Indian Ocean at a water depth of 3800 m, showed a relatively increased proportion of North Atlantic Deep water (NADW) during the interglacials (MIS-1 and 5) and a reduced proportion of NADW during the glacials (MIS-2 and 4). Further, Piotrowski et al. also observed a decreased proportion of NADW during the LGM and GT-II. Therefore, it seems likely that the suboxic conditions which developed during the LGM and GT-II in the southeastern Arabian Sea might have been the result of a decreased proportion of NADW. However, this needs to be confirmed by the Nd isotope studies in the southeastern Arabian Sea.

5. Conclusions

The results of the present study allow the following conclusions to be drawn regarding conditions in the southeastern Arabian Sea over the last 140 ka.

1. Sedimentation during Marine Isotope Stages 1, 3, 4 and the interstadials of Stage 5 (5a, 5c and 5e) occurred in near oxic conditions. In contrast, sedimentation during Marine Isotope Stage -2 (Last Glacial Maxima), the stadials of MIS- 5 (5b and 5d) and GT-II occurred in suboxic conditions. Sedimentation during MIS-1 (Holocene) occurred in more near-oxic conditions when compared to all other isotope stages during the past 140 ka. Sediments deposited during the Last Glacial Maxima, the stadials of MIS-5 and GT-

II have very high Re contents and would appear to be the major sink for Re in global mass balance estimations.

2. Generally, high organic C is associated with high Re and U contents in the sediments. During the stadials of MIS-5 and MIS-1, high and low TOC result from suboxic and near-oxic conditions where the availability of dissolved oxygen varied from relatively low to moderate levels respectively. During the stadials of MIS-5, high organic C is not mirrored by high Re and U contents. This occurs because the organic C present in these stadial sediments was derived from terrigenous sources and, as a result of its resistance to microbial reactivity, strongly reducing conditions do not develop, in turn generating lower contents of Re and U in the sediments. In contrast, high Re and U contents are associated with lower contents of more reactive organic carbon derived from marine sources. Therefore, it is essential to understand the source of organic C before being able to confirm interrelationships and correlations with other elements.

3. Molybdenum and V are generally enriched in sediments deposited in strongly reducing conditions (i.e. sediments where H₂S is present), but a lack of enrichment of these elements over the last 140 ka suggests that Southeastern Arabian Sea sediments never contained free H₂S. This is further confirmed by the higher Re/Mo ratio of $> 1.26 \times 10^{-3}$ which is again indicative of an absence of H₂S in the sediment. However, generation of small amounts of H₂S in the sediment, may have occurred at times during the early diagenesis, with this being more or less immediately consumed by the formation of some sulphide phase.

4. Similar to the Last Glacial Maxima, there may have been changes in deep-water circulation patterns during the stadials of MIS-5 and at GT-II, where redox-sensitive element variations suggest oxygen depleted deep water from the Southern Ocean moved northwards into the southeastern Arabian Sea.

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Tables

Table 1. Analyte isotope(s) and acquisition method used for ICP-MS analysis, with a comparison of trace elements data obtained for reference material QLO-1 in the present study with reported values (USGS,2006) and calculated detection limits (LLD,3 σ) in the solid (see text).

Element	Isotope(s) used for analysis	ICP-MS method	QLO-1, this study	QLO-1 Reference concentrations (USGS,2006)	Element certification status	Equivalent LLD in 0.2g solid (see text)
All concentrations in ppm						
V	51	Scanning	55.7	54 \pm 6	Recommended	0.044
Mo	95	Peak Jumping	2.58	2.6 \pm 0.3	Recommended	0.0066
Cd	111, 114	Scanning	0.24	0.05	<i>Provisional</i>	0.055
Sb	121	Scanning	2.13	2.1 \pm 0.4	Recommended	0.026
Re	185, 187	Peak Jumping	0.0033	<10	<i>Provisional</i>	0.0006
Tl	203, 205	Scanning	0.20	0.22 \pm 0.04	<i>Provisional</i>	0.027
Th	232	Scanning	4.18	4.5 \pm 0.5	Recommended	0.038
U	238	Scanning	1.82	1.94 \pm 0.12	Certified	0.003

Table. 2. Redox-sensitive elements concentration (ppm) **on carbonate free basis** and TOC, Calcium Carbonate and Al content in a sediment core (SK-129/CR-05) from southeastern Arabian Sea .

Age (Ka)	Core Dep. cm	V	Mo	Cd	Sb	Re	Tl	Th	U	TOC (%)#	CaCO ₃ (%) #	Al (%)\$
1.36	06-08	186	5.56	0.89	3.22	0.0070	0.73	8.23	2.06	0.400	63.50	2.25
4.07	18-20	185	14.9	0.74	2.52	0.0056	0.62	9.78	2.25	0.445	66.30	2.25
6.79	30-32	204	1.10	0.70	1.93	0.0078	0.63	9.69	2.20	0.378	60.85	2.80
8.60	38-40	215	1.32	0.59	3.14	0.0065	0.66	10.48	2.24	0.304	54.38	3.37
11.32	50-52	199	0.94	0.99	2.96	0.0060	0.75	10.58	3.34	0.363	45.31	3.79

13.30	58-60	181	0.47	0.76	2.40	0.0052	0.77	10.47	7.49	0.432	41.82	4.27
15.39	66-68	199	0.47	0.67	3.23	0.0190	0.75	10.03	8.84	0.673	45.33	4.12
17.48	74-76	201	0.62	1.00	4.57	0.0536	0.79	9.88	10.2	0.734	42.79	4.41
19.57	82-84	240	0.50	1.29	4.53	0.0157	1.05	10.98	9.03	0.718	44.05	4.41
21.65	90-92	229	0.78	1.08	4.48	0.0190	1.00	9.07	7.87	0.697	41.81	4.54
25.39	104-106	206	0.51	0.68	2.54	0.0062	0.76	9.70	4.37	0.549	37.58	4.78
28.72	116-118	193	0.55	0.52	2.00	0.0058	0.77	9.68	4.55	0.542	43.75	4.42
33.72	134-136	182	0.53	0.69	2.66	0.0071	0.82	11.9	5.35	0.583	45.85	4.07
39.83	156-158	222	0.64	0.72	3.89	0.0098	0.87	11.7	5.38	0.502	52.61	3.67
42.06	164-168	216	0.47	0.80	2.28	0.0035	0.66	9.68	4.19	0.400	47.64	3.97
46.50	180-182	241	0.79	1.74	5.40	0.0237	0.95	9.20	9.85	0.635	49.49	4.10
52.06	200-202	214	0.42	0.66	2.42	0.0074	0.86	9.81	5.98	0.538	45.55	3.88
55.39	212-214	213	0.72	1.45	3.74	0.0133	0.92	10.2	10.7	0.598	51.41	3.57
61.12	236-238	219	0.62	0.60	2.90	0.0108	0.86	9.72	5.84	0.571	40.39	3.85
65.73	260-262	202	0.50	0.59	2.79	0.0074	0.71	10.5	4.68	0.455	34.27	4.25
68.58	280-282	179	0.97	0.73	3.27	0.0111	0.83	9.88	6.17	0.636	29.82	5.44
72.65	296-298	188	1.28	0.97	4.63	0.0111	1.05	12.6	8.42	0.813	36.06	4.63
74.71	308-310	147	1.30	0.70	2.75	0.0140	1.01	17.12	6.23	0.540	31.30	4.65
75.84	316-318	233	1.24	2.38	3.61	0.0219	1.05	11.0	7.48	0.622	41.14	4.21
78.68	336-338	236	0.69	1.35	2.40	0.0059	1.00	9.39	6.31	0.883	51.64	3.40
82.06	352-354	164	0.49	0.27	1.48	0.0056	0.68	9.88	3.47	0.286	41.78	4.54
84.87	364-366	283	1.04	2.67	4.90	0.0545	1.21	11.2	13.4	0.817	51.61	3.55
87.67	376-378	218	1.10	1.21	4.32	0.0281	1.14	9.56	10.5	1.364	52.46	3.19
90.48	388-390	175	1.06	1.26	4.04	0.0204	1.03	8.67	9.27	1.716	51.03	2.96
93.06	400-402	170	1.30	0.94	4.15	0.0176	0.98	8.79	9.11	1.765	49.29	2.86
95.59	412-414	183	0.91	0.85	2.92	0.0069	1.03	9.58	6.21	0.840	51.32	3.25
99.95	432-434	203	0.69	0.67	2.72	0.0062	0.74	10.4	3.93	0.283	46.54	4.10
105.65	452-454	215	1.56	1.06	5.77	0.0425	1.11	11.7	16.4	0.716	53.79	3.25
110.22	468-470	194	1.11	1.20	4.25	0.0212	1.15	9.67	9.41	1.404	50.21	3.41
113.91	476-478	198	1.13	0.78	4.20	0.0118	1.13	11.1	9.65	0.983	54.17	3.37
118.07	484-486	198	0.93	1.52	3.31	0.0097	0.84	8.15	6.92	0.881	55.06	3.05
120.16	488-490	218	0.99	1.10	2.33	0.0098	0.88	9.99	5.46	0.338	64.44	4.80
128.48	504-506	161	0.44	0.47	1.38	0.0059	0.61	9.29	3.68	0.855	48.81	3.67
133	520-522	235	0.70	1.94	5.39	0.0502	0.82	9.38	16.4	0.973	52.64	3.60
137.22	536-538	201	0.66	0.90	2.58	0.0068	0.73	8.96	5.37	0.364	43.15	4.71
141	550-552	232	0.62	0.80	2.84	0.0065	0.76	10.2	4.24	0.343	43.70	4.57
T&M		230	1.00	0.10	0.20	0.0040	0.36	3.50	0.91	-	-	-
*												

#- Pattan et al., 2003; \$- Pattan et al., 2005. – data not available.

T & M *-Crustal values from Taylor and McLennan, 1985 and 1995.

Table 3. Correlation matrix for redox-sensitive element based on their carbonate-free concentrations, TOC, calcium carbonate and Al content in sediment core (SK-129/CR-05) from the southeastern Arabian Sea

	V	Mo	Cd	Sb	Re	Tl	Th	U	TOC %	CaCO ₃ %	Al%
V	1.000										
Mo	-0.155	1.000									
Cd	0.652	-0.050	1.000								

Sb	0.444	-0.060	0.608	1.000							
Re	0.432	-0.098	0.638	0.762	1.000						
Tl	0.310	-0.204	0.571	0.676	0.480	1.000					
Th	-0.143	-0.072	-0.059	0.071	0.059	0.261	1.000				
U	0.372	-0.236	0.617	0.829	0.831	0.687	0.089	1.000			
TOC%	-0.102	-0.093	0.317	0.481	0.388	0.609	-0.205	0.545	1.000		
CaCO3%	0.185	0.469	0.180	0.061	0.062	-0.036	-0.387	-0.001	0.091	1.000	
Al%	0.027	-0.495	-0.140	-0.132	-0.075	-0.062	0.315	-0.042	-0.369	-0.764	1.000

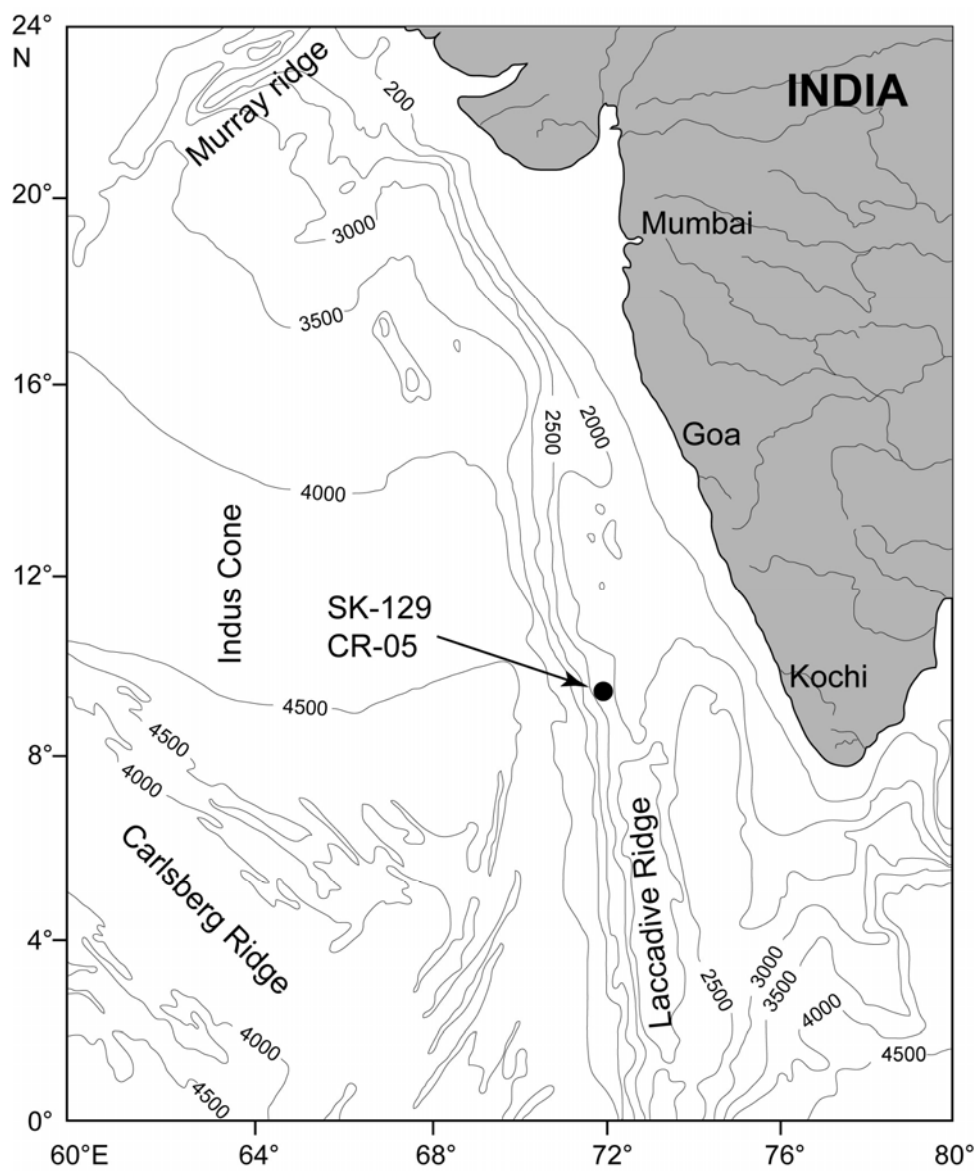


Fig.1. Location of sediment core from southeastern Arabian Sea.

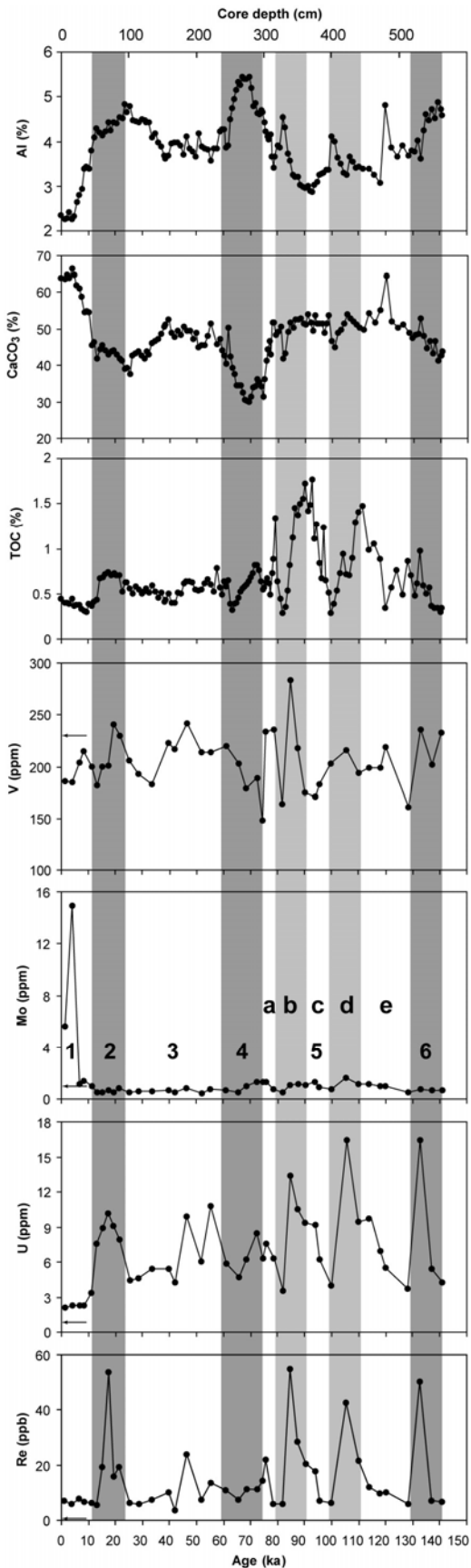


Fig.2a. Concentrations of Re, U, Mo, V on **carbonate free basis** and TOC, CaCO₃ (Pattan et al., 2003) and Al (Pattan et al., 2005) in a sediment core. Dark shade represents glacial and light shade during MIS-5) represents stadials. Arrow indicates average crustal value (Taylor and McLennan, 1985,1995).

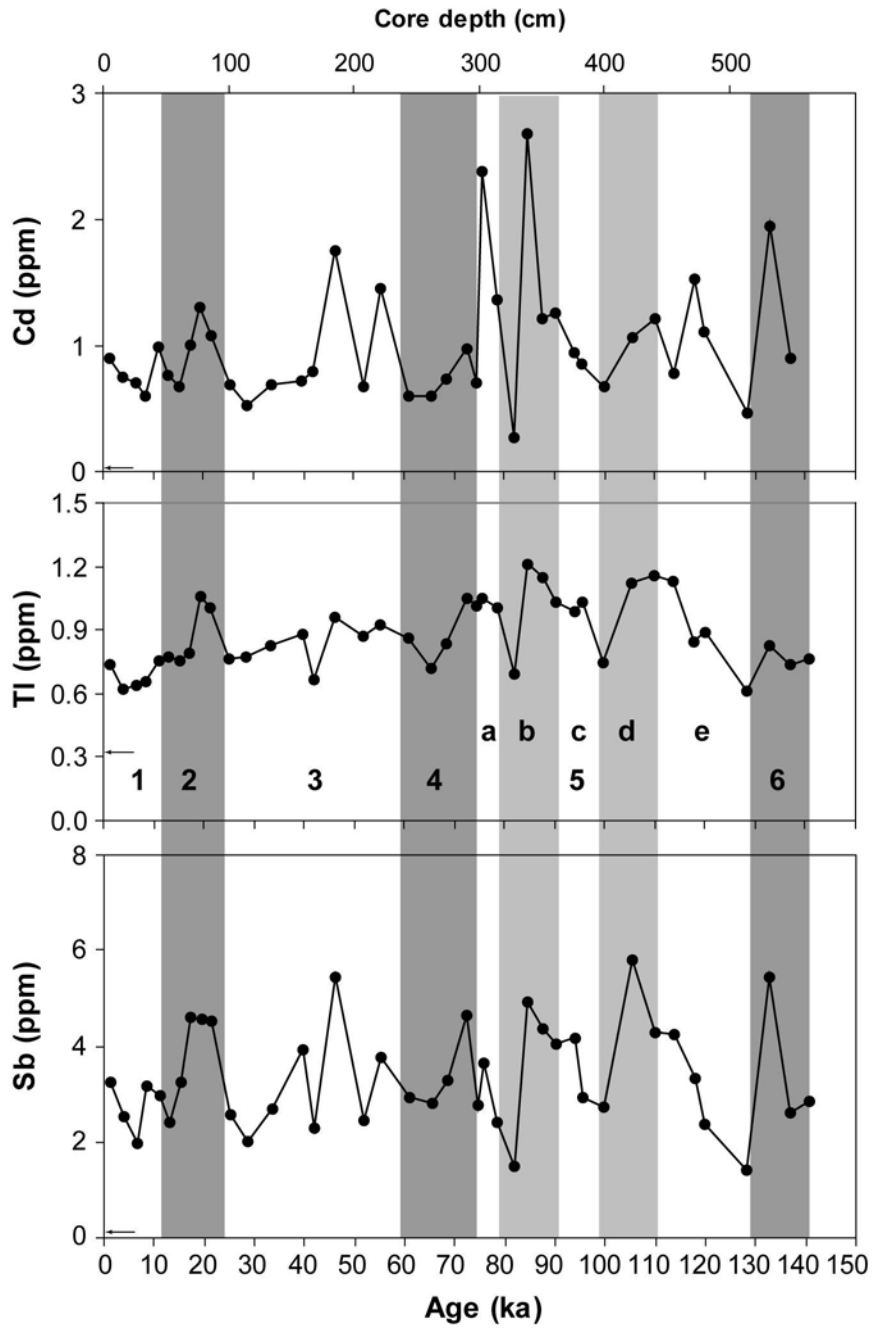


Fig.2b. Concentrations of Sb, Tl and Cd (carbonate free) in a sediment core from southeastern Arabian Sea. Dark shade represents glacial and light shade in MIS-5 represents stadials. Arrow indicates average crustal value.

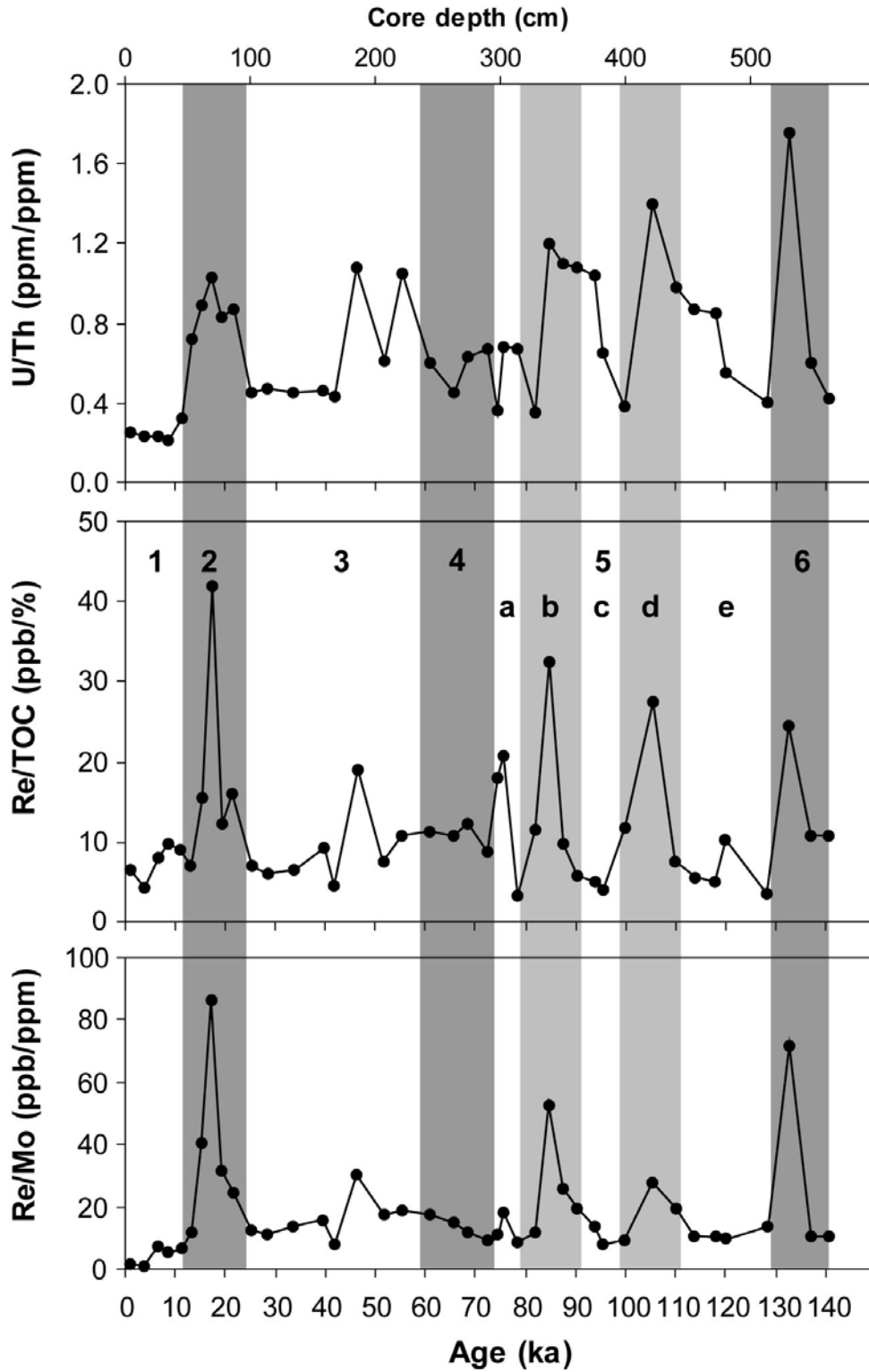


Fig.3. Ratios Re/Mo, Re/TOC and U/Th (carbonate free) in a sediment core from southeastern Arabian Sea.

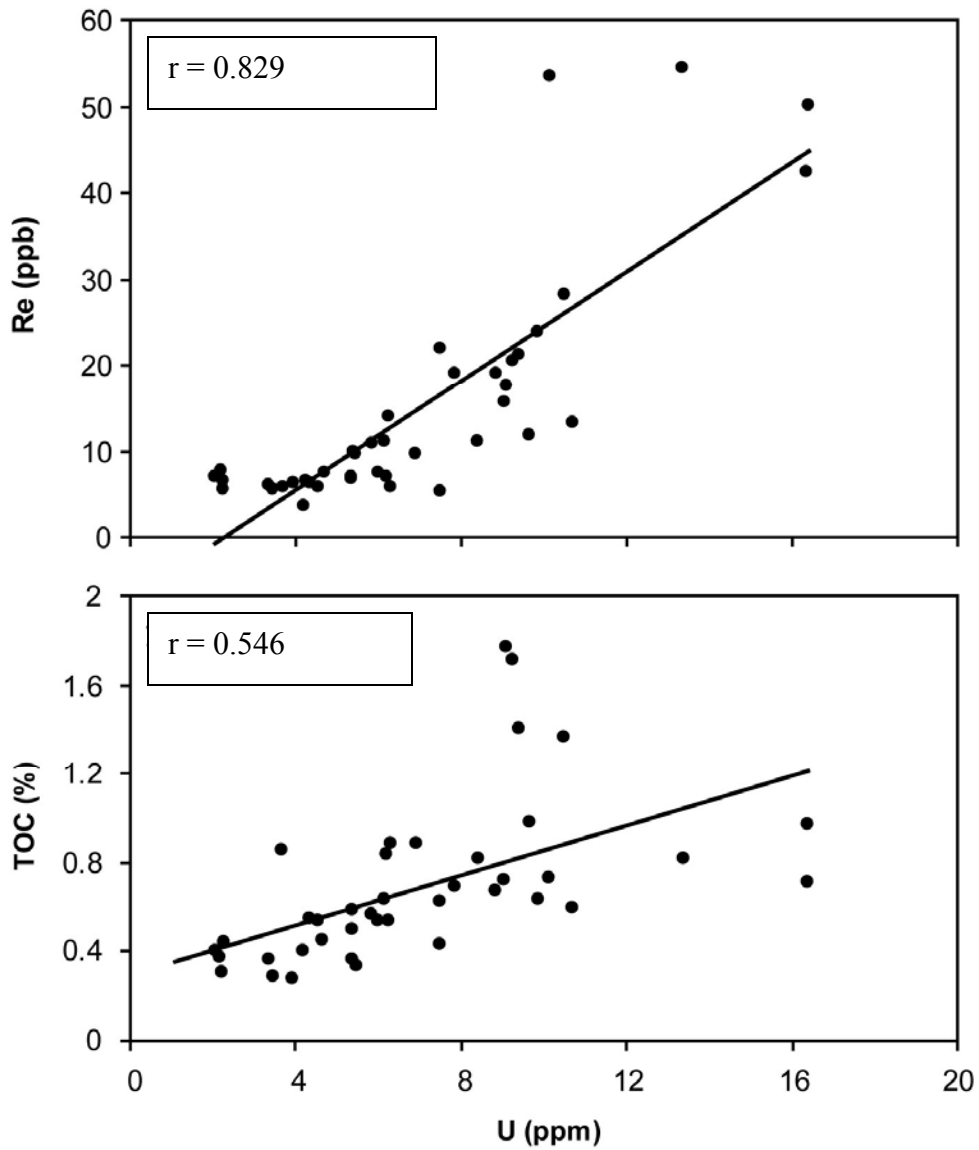


Fig.4. Scatter plots of U ppm (carbonate free) with TOC (%) and Re ppm (carbonate free) in a sediment core.

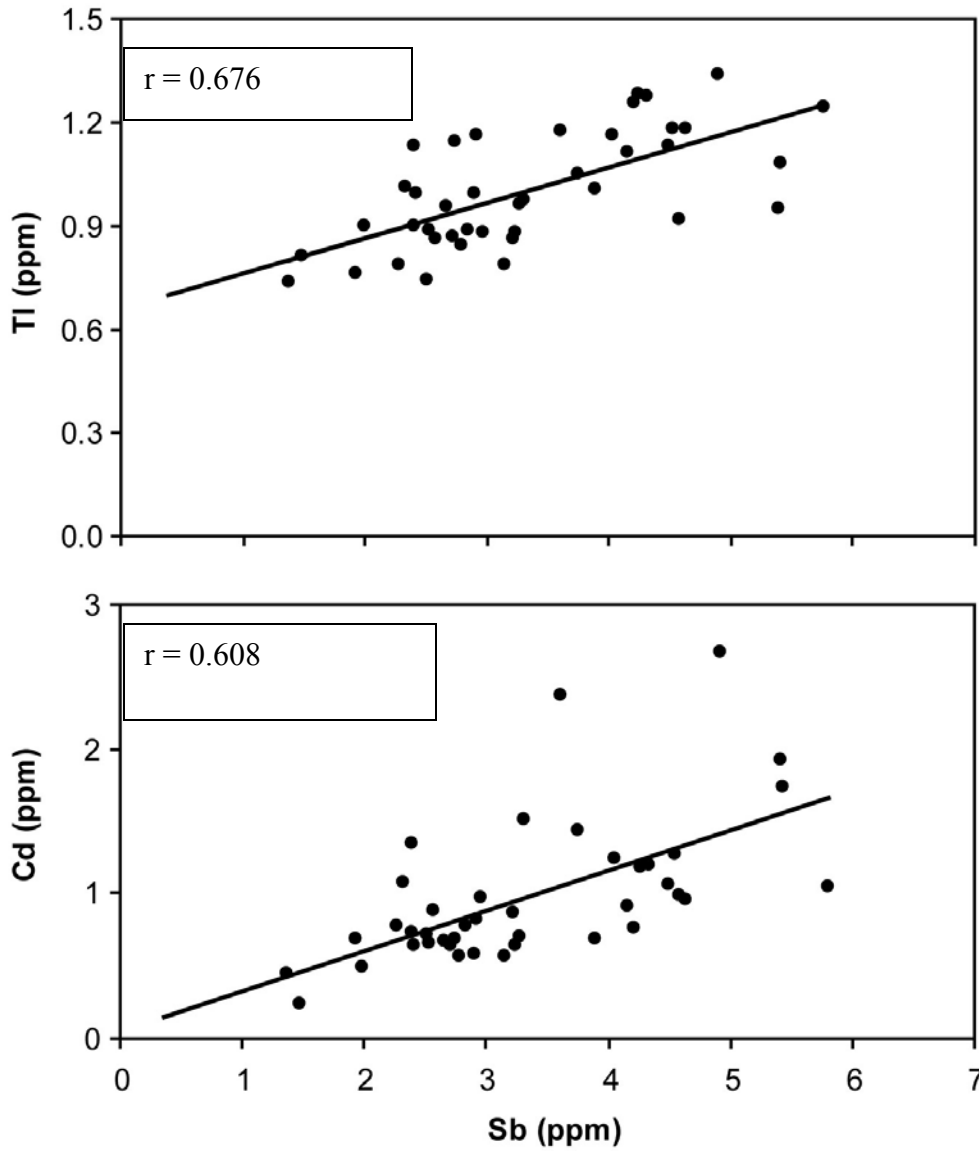


Fig.5. Scatter plots of Sb ppm(carbonate free) with Cd ppm (carbonate free) and Tl ppm (carbonate free) in a sediment core.

