



Research papers

Response of trace metal redox proxies in continental shelf environment: The Eastern Arabian Sea scenario

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ABSTRACT

Major and trace elements (viz. Al, Si, Ca, Na, Fe, Ti, K, S, Mn, V, Cu, Zn, Mo, Ni, Th and U) along with organic carbon and nitrogen content were analyzed in the sediment samples of a gravity core (GC-08/SK-291; 12°34'N; 74°11.47'E) which lies within the upper edge of intense oxygen minimum zone (OMZ) of Eastern Arabian Sea. The aim was to determine how the geochemistry of the redox-sensitive elements (viz. V, Cu, Zn, Mo, Ni, and U) was influenced by the suboxic water column and bottom water condition and whether the sediments show a unique signature of such redox condition. The weathering intensity was also determined and the provenance of sediments has been inferred to discern the uniformity in sediment supply in the studied location.

The chemical index of alteration (CIA), Chemical Index of Weathering (CIW) and Al–Ti–Zr ternary diagrams suggest low to moderate source area weathering of granodioritic to tonalitic source rock composition, which is similar to the regional geology of the continental mass nearby. The relative variations of major elements such as Si, Al and Ca suggest that the terrigenous fractions in the studied sediments are diluted by marine carbonates, unlike by biogenic opal, which is the case for most shelf regions of the world experiencing upwelling. The relative distributions of total organic carbon (TOC), total sulfur (TS) and total nitrogen (TN) suggest that the organic matter in the studied sediments is primarily of terrestrial origin irrespective of its presence in the deeper part of the shelf. We adopted the multi-proxy procedure for analyzing the redox condition prevalent during the deposition of sediments (e.g., enrichment of redox-sensitive elements, authigenic U, and ratios of trace metals such as U/Th, V/Cr, V/Mo, Ni/Co and (Cu + Mo)/Zn). The most striking result is a fully oxic signature reflected consistently by all redox proxies despite the occurrence of studied location within the OMZ of Arabian Sea. The redox proxies estimated from the bulk composition as well as the marine fraction of trace metals, do not reveal any significant difference in the depositional condition. The seasonal variation of O₂ concentration seems to be the dominant factor which controls the response of the trace metals to the water column anoxia in the studied location. The major implication of the present study is that the trace element redox proxies alone are not always suitable to discern the redox condition of deposition in continental shelf sediments which are characterized by high sediment input from continents and significant seasonal variation of O₂ concentration in the water column.

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1. Introduction

The redox environment prevalent during the deposition of marine sediments is reconstructed using the geochemical behavior of redox-sensitive trace metals such as V, Cu, Zn, Mo, Ni, and U (Jones and Manning 1994; Tribouillard et al., 2006). Studies on

behavior of these metals in suboxic and anoxic bottom water condition have been conducted in several sedimentary records, such as for the gulf of California (Brumsack, 1989), Black Sea (Anderson et al., 1989; Brumsack, 1989; Colodner et al., 1995), Cariaco Basin (Lyons et al., 2003; Piper and Dean, 2003), Gulf of Mexico (Swarzenski et al., 2008), Peru and Chilean Margins (Böning et al., 2004, 2005), Arabian Sea (van der Weijden et al., 2006; Pattan and Pearce, 2009) and Bay of Bengal (Pattan et al., 2013). A number of geochemical techniques have been used as indices of redox condition in recent sediments and sedimentary rocks. In general, they can be divided into three groups: (i) those based on formation of pyrite during early diagenesis (degree of pyritization (DOP)) and the relation between pyritic sulfur and

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organic carbon (e.g. Berner and Raiswell, 1983); (ii) those using the enrichment or depletion of authigenic trace metals in different depositional environment (e.g. Morford and Emerson, 1999); and (iii) those employing threshold values for various trace metal ratios such as U/Th, V/Cr, V/Mo, and Ni/Co (e.g. Riquier et al., 2006). Uncertainties still remain in the interpretation of these redox proxies in marine sedimentary records. The trace metal redox responses often get superimposed by the diagenetic signatures after sediment burial and also get affected by the changes in organic matter export to the sea floor. The growing evidence suggests that these trace metal redox proxies are not consistent in all environments of deposition. Nameroff et al. (2002) studied trace metal distribution in water column, settling particulate matters and sediment samples from eastern tropical north pacific and showed that redox-sensitive trace metals (Re, Mo, Cd, and U) signature in sediments does not reflect the bottom water redox condition. Similarly, McKay et al. (2007) studied the distribution of Re, U, Cd, Mn and Mo along with Iodine/organic carbon ratio in continental margin sediments of N.E. Pacific and showed that the response of these redox-sensitive proxies are not always reliable in environments characterized by high sedimentation rates and/or low sedimentation rates in combination with deep bioturbation. Therefore, a wide range of marine settings and environmental conditions need to be investigated to further develop our understanding in the responses of these trace metals to various redox conditions. Although the sediment columns from deeper basin of Arabian Sea were studied previously for trace metal responses (van der Weijden et al., 2006; Pattan and Pearce, 2009), the redox behavior of trace elements has not been studied in Eastern Arabian shelf sediments. Arabian Sea is characterized by intense upwelling which results in a high phytoplankton production that in return, enhances the consumption of dissolved oxygen. This high oxygen consumption in combination with a moderate rate of thermocline ventilation by Indian Ocean central water, Red Sea water and Persian Gulf water result in massive mid-water (150–1500 m) oxygen minimum zone (OMZ) (Wyrtki, 1971; Naqvi, 1987; Helly and Levin, 2004; Kurian et al., 2013). This prominent OMZ along with high organic input are likely to modify the geochemistry of the redox-sensitive metals in sediments.

To address these problems, we studied the geochemistry of sediments of a gravity core retrieved from the eastern Arabian Shelf (12°34'N; 74°11.47'E), which is overlain by the suboxic water

column. The objectives of the present study are (i) to work out the geochemistry of redox-sensitive elements and (ii) to identify whether this 'known suboxic' nature of water column can be traced from the redox proxies of the sediments. Besides, deciphering the provenance and weathering intensity through major element geochemistry has also been one of the objectives of the present work. We believe that the present study will put better constraints on the applicability of trace metal redox proxies, especially in the shelf sediments which are dominated by terrigenous inputs.

2. Samples and analytical methods

A gravity core (SK-291/GC-8) was raised from the shelf region (water depth of 180 m; 12°34'N and 74°11.47'E) of southeastern Arabian Sea during ORV Sagar-Kanya cruise 291 in December 2011 (Fig. 1(a)). The dissolved oxygen concentration measured by the SBE 9plus CTD measuring instrument equipped with SBE 43 dissolved oxygen sensor, shows that the core site is overlain by a suboxic water column (Fig. 1(b)) ($0.2 < \text{dissolved O}_2 < 2 \text{ ml/l}$, Tribouillard et al., 2006). The accuracy of the SBE 43 is specified as 2% of saturation, which is 0.14 ml/l for a solubility of 7.05 ml/l at 32 ppt and 6° C, or 0.11 ml/l for a solubility of 5.27 ml/l at 32 ppt and 20° C (Martini et al., 2007 and reference therein). The chemical composition of GC-8 core sediments (34 samples) were analyzed at 5 cm intervals up to 50 cm and 10 cm intervals beyond that up to 300 cm. Sediment samples were made salt free, dried at 60 °C for 36 h and pulverized for chemical analysis.

Total carbon (TC), nitrogen (TN) and sulfur (TS) (CNS) were measured with a Eurovector elemental analyzer EA3000, using helium as a carrier gas. For CNS analysis, about 20 mg of pulverized sediment sample was combusted at a temperature of 1010 °C in a stream of high-purity oxygen. The gaseous combustion products were chemically reduced and were separated by gas chromatography and quantified with a thermal conductivity detector (TCD). Analytical precision as checked by parallel analysis of Sulfanilamide (CHNS grade standard), was within 2% for TC and TN and 4% for TS.

Total inorganic carbon (TIC) was determined after treatment of the sediment with orthophosphoric acid in a Shimadzu TOC-5000A analyzer with SSM-5000A Solid Sample Module. Total

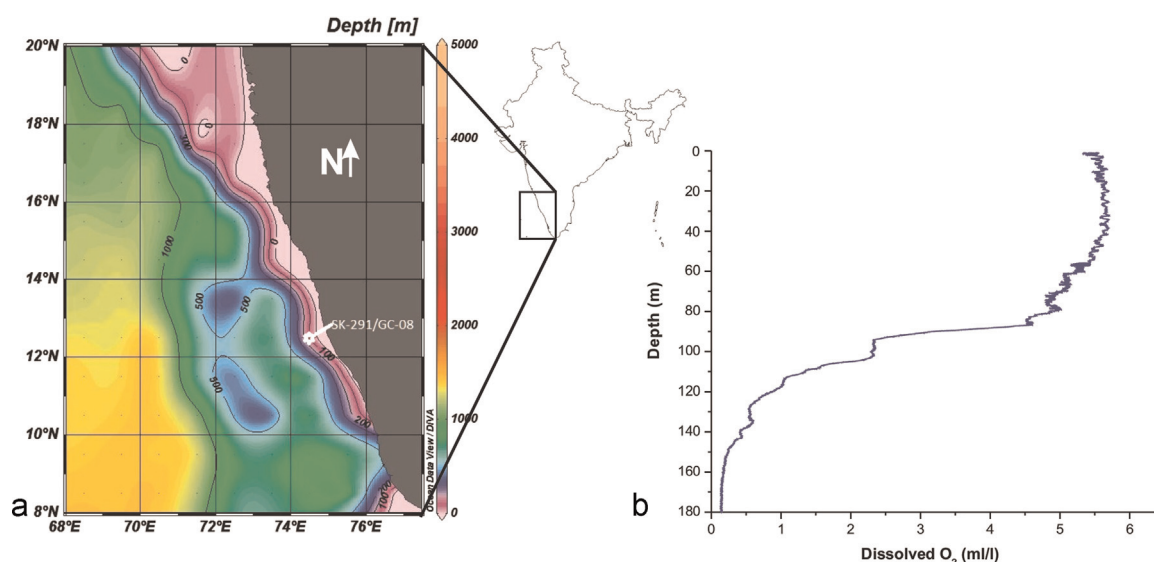


Fig. 1. (a) Bathymetric map of SE Arabian sea having the sample location plotted by Ocean Data View software (ODV4. 6. 2, Schlitzer, 2015). (b) Dissolved oxygen in seawater measured through SBE 9plus CTD measuring instrument equipped with SBE43 dissolved oxygen sensor.

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