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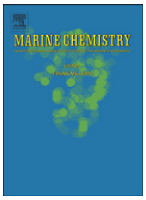

Behavior of dissolved redox sensitive elements (U, Mo and Re) in the water column of the Bay of Bengal

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ABSTRACT

The dissolved concentrations of redox sensitive elements, U, Mo and Re have been measured in the water column of the Bay of Bengal (BoB) to track their distributions and behavior in its suboxic layers at the intermediate depths. The dissolved oxygen content in the intermediate waters (200–800 m) north of ~11°N decreases to values as low as ~3 μmol/ℓ. The distribution of U, Mo and Re in the surface waters along the 87°E transect shows a north–south gradient with significant correlation with salinity, underscoring the dominant influence of the Ganga–Brahmaputra (G–B) Rivers in controlling the geochemical budgets of these three elements. The concentrations of these three elements in surface and deep waters of the BoB are governed by salinity suggestive of their conservative behavior. On a macroscale, there is no discernable removal of U, Mo, or Re from the suboxic layer in the BoB water column, consistent with earlier studies in the suboxic zones of other oceanic regions. Further, their conservative behavior in the bay, suggest that the annual delivery of ~10^9 tons of suspended matter rich in organic matter by G–B and other rivers do not have any measurable impact in determining their distributions. This study suggests that the suboxic conditions and high particulate flux prevailing in the water column of the Bay of Bengal do not affect the conservative behavior of U, Mo and Re. The dissolved Re concentrations in the upper layers in the central BoB seem to be marginally higher compared to that expected based on their salinities. This seems to be contributed from the Godavari River, which drains into the BoB and has dissolved Re three times higher than seawater. The higher Re concentrations in the central Bay of Bengal suggest that mixing process by local gyre and/or eddies in the BoB transports riverine dissolved material to ~400 km offshore. More detailed transects of Re from the Godavari coast to central bay are needed to confirm this.

1. Introduction

The concentrations and the distributions of redox sensitive elements (RSEs), Fe, Mn, U, Mo, Re and V in sediments, have been used extensively to investigate contemporary and paleo-oceanographic conditions (Calvert and Pedersen, 1993; Crusius et al., 1999; Morford et al., 2001; Nameroff et al., 2002; Nameroff et al., 2004; Pattan and Pearce, 2009; Sarkar et al., 1993; Schenau et al., 2002). The growing interest on the applications of these elements as paleo-redox indicators of oceans requires better understanding of their geochemistry, which includes their sources, transport, internal cycling and sinks. Among the various RSEs, the behavior of U, Mo and Re has been investigated in greater detail as these elements get enriched to a greater extent in sediments compared to many other RSEs due to their higher $[\text{metal}]_{\text{seawater}}/[\text{metal}]_{\text{crust}}$ ratio; this has led to their preferential exploitation in paleo-oceanographic research. In the case of Mo, in addition to studies on its abundance, its isotope systematics have provided better insight into its oceanic budget (Neubert et al., 2008; Poulson et al., 2006; Siebert et al., 2006; Voegelin et al., 2009). Mo isotopes fractionate significantly during their removal from sea water onto Fe–Mn nodules (i.e. oxic sinks), compared to minor or no fractionation from Mo isotope composition of sea water during their removal into euxinic sediments (i.e. anoxic sinks) (Anbar, 2004; Barling and Anbar, 2004; Barling et al., 2001; McManus et al., 2002). Investigations on the isotopic composition of Mo holds promise for the reconstructions of global ocean paleo-anoxicity and assessing the areal extent of reducing conditions in the oceans on million year time scales (Anbar, 2004; Arnold et al., 2004; Siebert et al., 2003).

The distributions of dissolved U, Mo and Re in well oxygenated oceanic regions show their conservative behavior. In these regions, they occur in their higher oxidation states, $U^{VI}O_2(CO_3)_3^{4-}$, $Mo^{VI}O_4^{2-}$, and $Re^{VII}O_4^{-}$. The relatively passive nature of these oxy-anions in oxic seawater is reflected in their long residence times, estimated to be in the range of ~10^5–10^6 y (Colodner et al., 1993; Dunk et al., 2002; Emerson and Huested, 1991; Rahaman and Singh, 2010). The onset of reducing conditions, particularly anoxic conditions can lower their oxidation states to U^{IV}, Mo^{IV}, and Re^{IV} which are amenable for

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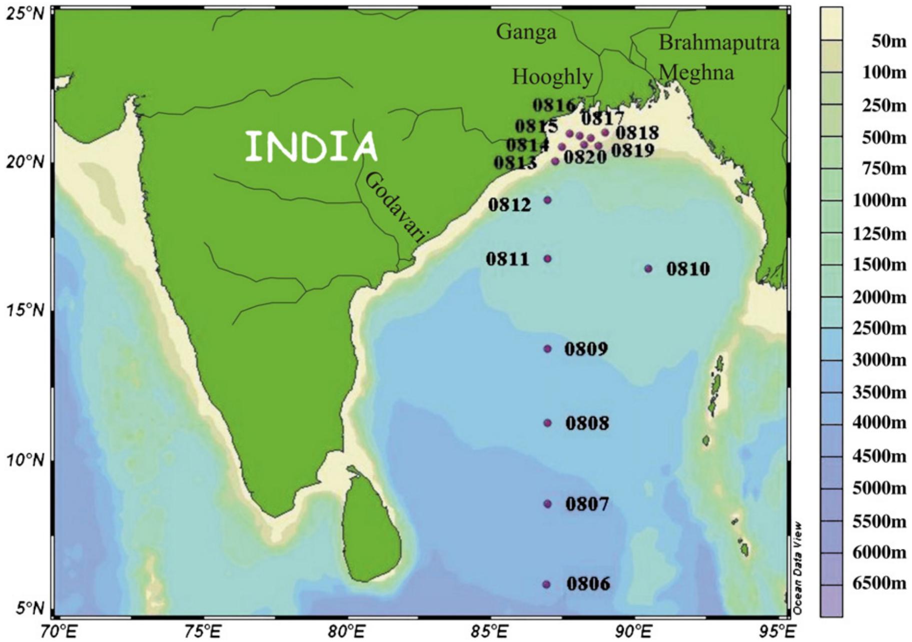

Fig. 1. Sampling locations for dissolved U, Mo and Re in the Bay of Bengal during the cruise SS-259 onboard FORV Sagar Sampada. Please Note: All the contours in this and subsequent figures are plotted in ODV4 software (Schlitzer, 2010). Whereas Bathymetry data for section contours was taken along the cruise track using GMRT grid (http://www.geomapapp.org; Ryan et al., 2009).

sequestrations from dissolved to particulate phases (Bertine, 1972; Colodner et al., 1995; Colodner et al., 1993; Emerson and Huested, 1991; Klinkhammer and Palmer, 1991; Nameroff et al., 2002). Such reducing conditions are generally associated with oceanic regions that do not meet the oxygen demand for combustion of organic matter such as land locked seas/channels or continental margins with restricted ventilation. The chemical speciation of U, Mo and Re in reducing oceanic water column is not well constrained compared to that in oxygenated waters and the processes promoting their removal from such regions are still debated. Among these three elements, Mo actively participates in bio-geochemical processes, being a cofactor in enzymes (Falkowski, 1983), however its distribution in the water column does not seem to be affected by its involvement in these processes (Bruland et al., 2003). In contrast, there is no evidence to suggest active participation of U and Re in bio-geochemical processes; though, U is known to form organo-metallic complexes. These complexes can contribute to its authigenic deposition in coastal and margin environments, the preservation of which depends on bottom water oxygen concentration (Anderson, 1982; Chappaz et al., 2010; Zheng et al., 2002).

Table 1
Details of sampling locations in the Bay of Bengal.

Station	Latitude (°N)	Longitude (°E)	Sampling depth (m)	No. of samples
SS259-0806	5.813	86.997	5–3800	21
SS259-08-S1	6.990	86.938	Surface	1
SS259-08-S2	8.021	86.990	Surface	1
SS259-0807	8.494	87.007	5–3550	16
SS259-08-S3	9.974	86.805	Surface	1
SS259-0808	11.270	86.990	5–3200	15
SS259-08-S4	12.405	86.994	Surface	1
SS259-0809	13.769	87.004	5–2900	15
SS259-08-S5	14.572	88.066	Surface	1
SS259-08-S6	15.373	89.104	Surface	1
SS259-0810	16.420	90.498	5–2350	17
SS259-08-S7	16.457	89.471	Surface	1
SS259-08-S8	16.697	87.420	Surface	1
SS259-0811	16.759	86.993	5–2500	18
SS259-0812	18.759	86.997	5–2000	14
SS259-0813	20.047	87.262	5–640	8
SS259-0814	20.537	87.476	4–45	2
SS259-0815	20.975	87.778	4–30	2
SS259-0816	20.571	88.107	4–30	2
SS259-0817	20.836	88.492	5–70	2
SS259-0818	21.003	88.996	5–60	2
SS259-0819	20.576	88.753	5–110	2
SS259-0820	20.585	88.249	5	1

There have been studies on the removal of these three redox sensitive elements from the seawater to sediments, particularly to sediments underlying suboxic/anoxic waters, such as the Arabian Sea, Black Sea, Cariaco Trench, Saanich Inlet and the eastern tropical North Pacific (Anderson et al., 1989b; Barnes and Cochran, 1990; Colodner et al., 1995; Colodner et al., 1993; Crusius et al., 1996; Emerson and Huested, 1991; Klinkhammer and Palmer, 1991; Nameroff et al., 2002). These studies have brought out the role of diffusion in pore waters and various carrier phases (Dellwig et al., 2010; Nealson et al., 1991; Tebo, 1991) in sequestering these elements to sediments. Some of these studies also have underscored the importance of element dependent microbial processes in their reduction and sequestration, for example in the reduction of U compared to that of Mo and Re (McKee and Todd, 1993; Morford et al., 2009).

Studies in the Black Sea (Anderson et al., 1989a; Colodner et al., 1995; Emerson and Huested, 1991), demonstrated that all these three elements are depleted in the euxinic deeper waters; suggesting their removal from the water column. The mechanism(s) and sites of their removal, however, remain to be fully established. In case of Mo, inter-conversion of molybdates to more particle reactive intermediate thio-molybdates when H_2S exceeds a threshold value has been suggested as a mechanism for its removal in sediments (Erickson and Helz, 2000; Vorlicek and Helz, 2002; Vorlicek et al., 2004). In contrast to investigation of these elements in sediments, there are, however only limited studies on their behavior in suboxic/reducing water columns. Study in the Cariaco Trench (Anderson, 1987) does not indicate any measurable variation of U concentration in oxygen minimum zone (OMZ) compared to that in oxygenated waters. However, uranium distribution in the water columns of the Arabian Sea and Framvaren Fjord and sediment trap studies in BoB (Bay of Bengal) hinted towards its possible removal from the OMZ (McKee and Todd, 1993; Rengarajan et al., 2003; Sarin et al., 2000). Studies pertaining to Mo and Re distribution in the water columns associated with OMZ are limited.