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Coupling between suboxic condition in sediments of the western Bay of Bengal and southwest monsoon intensification: A geochemical study

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ABSTRACT

Reconstruction of paleo-redox conditions in a radiocarbon (^{14}C) dated sediment core (SK-218/1), covering the past 45 ka (thousand calendar years), collected from the western Bay of Bengal (Lat: 14° 02′N; Long: 82° 00′E) at a water depth of 3307 m, has been made based on redox-sensitive element geochemistry. The high U/Th ratio, Mo enrichment, Mo/U enrichment factor ratio, Ce/Ce*<1 and lower Mn/Al and Fe/Al ratios, compared to upper continental crust are all indicative of prevalence of suboxic condition in the benthic environment from 15.2 ka to 4.5 ka, peaking around 9.5 ka. The suboxic condition around 9.5 ka corresponds to the previously recorded southwest (SW) monsoon intensification in response to the increase in northern hemisphere summer insulation. However, productivity proxies – organic carbon and nitrogen contents – do not indicate marked increase in productivity at this time. It is proposed that as a result of large increase in lithogenic material supplied from land due to SW monsoon intensification, which is evident by the very high concentration of Al, Zr and Hf, the flux of fresh labile organic matter and these might have formed dense mineral matter — biogenic aggregates which sinks rapidly to the seafloor, and the degradation of labile organic matter might have led to the development of suboxic condition in the benthic environment. There exists a strong positive correlation (r = 0.98) between Mo and Zr during 15.2 ka to 4.5 ka suggesting a coupling between suboxic condition and lithogenic flux supply by the intensified SW monsoon. Our results suggest that temporal variability of the ballasting effect of the terrestrially-derived material could play a key role in benthic biogeochemistry and ecology of the Bay of Bengal.

We also provide the first record of the nitrogen isotopic composition ($\delta^{15}N$) of sedimentary organic matter in the western Bay of Bengal, a region where the mesopelagic oxygen minimum zone (OMZ) is just short of being suboxic (denitrifying) today. The sedimentary $\delta^{15}N$ fluctuated considerably in the past, especially during the Marine Isotope Stage 3. Oscillations in $\delta^{15}N$ were apparently in concert with those in organic carbon and nitrogen contents and could be related to climatic changes (Heinrich and Dansgaard–Oeschger events) in the North Atlantic. The Dansgaard–Oeschger 12 event appears to have exerted the most intense effect on Bay of Bengal biogeochemistry when surface productivity, as inferred from the organic carbon and nitrogen contents, was the highest recorded in the core, and the $\delta^{15}N$ reached up to 6.3‰. Considering the probable dilution by isotopically light terrigenous organic matter, it would appear that OMZ of the Bay of Bengal had turned denitrifying. However, the absence of suboxic conditions in the sediments at this time suggests a decoupling of the benthic processes with those in the mesopelagic water column.

1. Introduction

The Bay of Bengal (BoB) receives a large quantity of suspended particulate matter (2.1×10^{12} kg a^{-1}) and fresh water discharge (1887 km^3 a^{-1}) from the Himalayas and Indian peninsula by major rivers like Ganges–Brahmaputra, Mahanadi, Krishna–Godavari, Cauvery, and Irrawaddy–Salween (Bird et al., 2008). The northern part of BoB receives maximum particle flux during the SW monsoon that coincides with discharge maxima of the Ganges–Brahmaputra rivers (Ittekkot et al., 1991, 1992). This discharge reduces the surface water salinity by 7‰ (La Violette, 1967), and also supplies nutrients which may enhance primary productivity (Ramaswamy and Nair, 1994) and cause strong stratification during the SW monsoon (Ostlund et al., 1980). The waters of the BoB have very low (<5 μM) dissolved oxygen content at intermediate depths (200–800 m) resulting in a pronounced oxygen minimum zone (OMZ) (Wyrtki, 1971; Rao et al., 1994; Sardessai et al., 2007). A model study revealed that oxygen levels within the OMZ are controlled by a combination of physical and biological processes (Sarma, 2002).

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Singh et al. (2011a) measured concentrations of dissolved U. Mo and Re in the water column of BoB and found little variations in these redox-sensitive elements within the OMZ indicating their conservative behavior, i.e. these elements co-vary with salinity and are not affected by the large quantity of organic-rich suspended load brought by the rivers. The sediments in the Krishna–Godavari basin supplied by the Krishna–Godavari river systems in the western BoB have smectite as the dominant clay mineral (Subramanian, 1987; Kolla and Rao, 1990) and have silty clay texture (Pattan et al., 2008). Rashid et al. (2007) suggested that the SW monsoon was stronger in the BoB during the Bolling/Allerod event, early Holocene and weaker during the Younger Dryas, and deglacial warming that began around 19 ka was contemporary with deglaciation warming in Antarctica, indicating a strong connection through Indonesian throughflow or Subantarctic mode water (Naidu and Govil, 2010). Sediments in the western BoB were mainly derived from the Himalayas during the last glacial maximum (LGM) (Tripathy et al., 2011) and there occurred a change in the sedimentary depositional environment around 12 ka (Kessarkar et al., 2005; Prakash Babu et al., 2010). Galy et al. (2007) showed that the amount of terrestrial organic carbon deposited in the Bengal Basin is 10 to 20% of the total terrestrial organic carbon buried in the oceanic sediments and the removal of carbon to the seafloor is mostly through continentally derived material (Ittekkot et al., 1991, 1992).

The past depositional environmental conditions and processes involved within marine sediments can be reconstructed by using multiple proxies such as bioturbation index, sediment laminations, trace and ultra-trace metal concentrations, and stable isotope abundances. Trace metals, particularly redox-sensitive elements, in the sediments have been used extensively to reconstruct redox conditions in the bottom water at the time of deposition (Brumsack, 1980; Wignall and Myers, 1988; Calvert and Pedersen, 1993; Dean et al., 1999; Tribovillard et al., 2006, 2008; Pattan and Pearce, 2009; Algeo and Tribovillard, 2009; Algeo et al., 2012 and reference therein). In the marine environment, the depositional conditions can be oxic, suboxic/dysoxic and anoxic/euxinic depending upon the presence or absence of oxygen and H_2S. Algeo and Ingall (2007) showed that redox conditions can be highly variable over short time scales and consequently the effects on redox-sensitive trace metals can be rather complex and such effects on the trace metal uptake by sediments are still incompletely understood. The BoB receives large quantity of suspended particulate matter and fresh water discharge mainly from the Himalayan and Indian peninsular rivers which supply nutrients and also reduce the surface water salinity. Therefore, it is necessary to understand the implications of these parameters on behavior and distribution of redox-sensitive elements with time. Till now variations in redox-sensitive elements such as U, Mo, Ce, Mn and Fe have not been studied in sediment cores from the BoB. Therefore, in the present study, we make the first attempt to reconstruct the past depositional environmental conditions in the BoB based on redox-sensitive element geochemistry using a radiocarbon (^{14}C) dated sediment core that provides insights into factors responsible for the formation of reducing conditions during the past 45 ka.

2. Material and methods

A 8.2 m long sediment core (SK-218/1) was raised from a water depth of 3307 m (Lat: 14° 02′ 01″N; Long: 82° 00′ 12″E) off Krishna–Godavari basin, western Bay of Bengal (BoB), onboard *ORV Sagar Kanya* cruise (SK-218) on 19th March, 2005 (Fig. 1). The core site is well below the present day OMZ in the water column (Wyrtki, 1971; Olson et al., 1993; Rao et al., 1994). A total of 100 sub-samples from the sediment core were analyzed in the present study. Sediment sub-samples were made salt free, dried and powdered. For the chemical analysis, about 50 mg of sediment was weighed in a Teflon beaker. To this 10 ml of acid mixture of $HF + HNO_3 + HClO_4$ (7:3:1 ratio) was added and the contents were concentrated to a paste by placing the beaker on a hot plate. To this paste 4 ml of 1:1 HNO_3 was added. After heating for 5 min the material was diluted with ultrapure (18.2 MΩ) water to a final volume of 100 ml. Similar digestion procedure was followed for standard reference materials (MAG-1, SGR-1) and blanks. These solutions were analyzed for a few major, trace and rare earth elements on an inductively coupled plasma-mass spectrometer (*Thermo X Series 2*). The accuracy compared to the standard reference material and the precision of the data based on duplicate analysis were better than ±6%. The calcium carbonate content was determined with a coulometer (UIC, Inc-CM5130 acidification module). Analytical grade calcium carbonate was used as the standard reference material. The accuracy and precision of measurements based on analysis of duplicate samples and standard reference material were within ±2%.

Aliquots of sediment sub-samples were made carbonate free by treating with 0.1 N HCl. For the analyses of total organic carbon (TOC), total nitrogen (TN) and their isotopes ($\delta^{13}C$ and $\delta^{15}N$), carbonate-free sediments (residue) were weighed in tin cups and combusted in a *Euro-Vector* Elemental Analyzer (EA) coupled with a *Delta V plus* stable isotope mass spectrometer (*Thermo*®) in a continuous flow mode. Working standard ε-Amino-n-Caproic Acid (ACA) supplied by Prof. Mark Altabet (SMAST, UMASS) whose reported values for $\delta^{15}N$ and $\delta^{13}C$ are 4.6‰ and −25.3‰ and internal sedimentary standard COD whose long term average values are 7.38‰ and −21.01‰, respectively, were used to check the precision of the measurements. Standard deviation for both $\delta^{15}N$ and $\delta^{13}C$ was less than 0.2‰.

3. Results

Uranium and Mo are among the most useful redox sensitive trace elements used as proxies to investigate paleo-redox conditions in the marine environment. The U and Mo concentrations in our sediment core reached maximum values of 9.4 ppm and 36 ppm around 9.5 ka respectively. Cerium is one of the unique members of rare earth element group due to its occurrence in two valence states (III & IV). The Ce-anomaly has been represented as Ce/Ce* ratio and is also used as one of the parameters to trace the paleo-bottom water redox condition. The Ce/Ce* values generally exceed 1 in the entire sediment core (1.2) except from 10.5 ka to 7 ka where the ratio is <1. The lowest Ce/Ce* value of 0.71 is recorded at 8.89 ka. Terrigenous elements such as Al, Zr and Hf also showed their highest concentration of 18%, 0.8% and 180 ppm around 9.5 ka, respectively, in the sediment core. The productivity indicators such as total organic carbon and total nitrogen varied from 02. % to 2.85%, and from 0.3% to 0.22%, respectively. However, their highest concentrations occurred at 42 ka. The $\delta^{13}C$ and $\delta^{15}N$ values fluctuate from −20.26‰ to −13.4‰, and from 2.44‰ to 6.31‰, respectively. The highest $\delta^{15}N$ value of 6.33‰ is recorded at 42 ka.

4. Discussion

4.1. Sedimentation rates

Based on eight ^{14}C dates, the 8.2 m long sediment core (SK-218/1) covers the past 45,000 calendar years. The detailed age model for the core is shown in Fig. 2 (Naidu and Govil, 2010; Govil and Naidu, 2011). In the core last glacial maximum (LGM) is located between 20 ka and 15 ka (Govil and Naidu, 2011). The sedimentation rate in the last 45 ka varied from 7.08 $cm(ka)^{-1}$ to 27.3 $cm(ka)^{-1}$. During the Marine Isotope Stage (MIS) 1, sediment accumulation rate varied from 15.1 $cm(ka)^{-1}$ to 27.3 $cm(ka)^{-1}$ with an average of 21 $cm(ka)^{-1}$; during MIS 2 the sedimentation rate ranged from 9.9 $cm(ka)^{-1}$ to 11.2 $cm(ka)^{-1}$ with an average of 10.5 $cm(ka)^{-1}$; and during MIS 3, it varied from 7 $cm(ka)^{-1}$ to 22 $cm(ka)^{-1}$ with an average of 17 $cm(ka)^{-1}$. These data suggest higher sedimentation rates during the interglacial as compared to the glacial periods. The mean sedimentation rate in the sediment core during the last 45 ka was 15.6 $cm(ka)^{-1}$.