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Research paper

Speciation of phosphorus in the continental shelf sediments in the Eastern Arabian Sea

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ABSTRACT

The distributions of various forms of phosphorus (P) and their relation with sediment geochemistry in two core sediments near Karwar and Mangalore offshore have been studied through the modified SEDEX procedure (Ruttenberg et al., 2009) and bulk chemical analysis. The present study provides the first quantitative analysis of complete phosphorus speciation in the core sediments of the Eastern Arabian shelf. The chemical index of alteration (CIA), chemical Index of Weathering (CIW) and Al–Ti–Zr ternary diagram suggest low to moderate source area weathering of granodioritic to tonalitic source rock composition, despite the intense orographic rainfall in the source area. Due to the presence of same source rock and identical oxic depositional environment, the studied sediments show the same range of variation of total phosphorus (24 to 83 $\mu\text{mol/g}$) with a down-depth depleting trend. Organic bound P and detrital P are the two major chemical forms followed by iron-bound P, exchangeable/loosely bound P and authigenic P. The authigenic P content in the sediments near Mangalore coast varies linearly with calcium ($r=0.88$) unlike that of Karwar coast. The different reactive-phosphorus pools exhibit identical depleting trend with depth. This indicates that the phosphorus released from the organic matter and Fe bound fractions are prevented from precipitating as authigenic phosphates in the deeper parts of the sediment column. The low concentration of total P, dominance of detrital non-reactive fraction of P and inhibition of formation of authigenic phosphate result in the absence of active phosphatization in the Eastern Arabian Shelf in the studied region. High sedimentation rate (35–58 cm/kyr) and absence of winnowing effect appear to be the dominant factor controlling the P-speciation in the studied sediments.

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1. Introduction

Phosphorus (P) is believed to be the ultimate limiting nutrient whose availability drives the primary productivity of ocean on geological timescales (Howarth et al., 1995; Tyrrell, 1999). The continental weathering processes primarily control the supply of P into the marine realm (Paytan and McLaughlin, 2007), because of the negligible mobility of the element in the gaseous form (Jahnke, 2000). In contrast, the increasing demand for the other major nutrient, Nitrogen (N), can be fulfilled by cyanobacteria through N-fixation from the vast atmospheric N reservoir (Howarth et al., 1995; Tyrrell, 1999). Thus, organic carbon burial in marine sediments is primarily controlled by the availability of dissolved P in seawater. The change in the amount of burial of organic carbon in

marine sediments controls the formation of pyrite (Berner, 1989) and regulates the atmospheric oxygen and CO₂ concentration (Berner, 1989; Berner and Canfield, 1989). Hence, detailed knowledge of P geochemistry in the marine system ultimately helps to understand the C, N, S and O cycles in the ocean.

The cycling of P in marine sediments is highly dynamic in nature and involves the geochemical and biological transformation of the different P-bearing phases. Phosphorus is delivered to the sediments primarily in association with organic carbon (Anderson et al., 2001). Microbial degradation of organic matter and reduction of Fe-oxides result in the release of P to the pore waters of sediments (Paytan and McLaughlin, 2007). Depending on the environmental conditions (viz. redox condition of seawater, sedimentation rate, sediment grain size, availability of metal-oxyhydroxides phases) this released P may be adsorbed onto the grain surfaces, bound to iron-oxyhydroxides, diffuse back to the bottom water or eventually transform into the most stable authigenic mineral, that is carbonate fluorapatite (CFA). The sediments having high authigenic phosphorus content are known as

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phosphorite where P_2O_5 concentration exceeds 5 wt% (Cook, 1984). Occurrence of phosphorites have been reported in widely varied marine settings such as deep-sea sediments of equatorial Pacific (Filippelli and Delaney, 1996), upwelling-dominated Oman margin (Schenau et al., 2000), continental margin sediments of Peru (Froelich et al., 1988), and shelf sediments of Namibia (Thomson et al., 1984). Besides these upwelling-dominated systems, phosphorite has also been reported in the low productive regions and shallow continental margin sediments (e.g. Slomp et al., 1996; Louchouart et al., 1997).

The Eastern Arabian Shelf (EAS) is a monsoon-dominated system characterized by an intense upwelling phenomenon which makes this zone as one of the highly productive region of the world (Qasim, 1982) and a zone of high rate of consumption of oxygen in the surface water. High surficial oxygen demand in combination with the circulation of oxygen-poor source water from the southern Indian Ocean results in massive mid-water (150–1000 m) oxygen minimum zone (OMZ) (e.g. see Pattan et al., 2005 and references therein). Although, studies on pore water and phosphorus-bearing phases in sediments from Oman and Karachi margin have clearly indicated the active phosphorite formation within OMZ (Schenau et al., 2000), the EAS is poorly understood in terms of its P geochemistry.

Murty et al. (1966), Setty and Rao (1972), Rao et al. (1978, 1987), and Paropkari (1990) have studied the total P variation in the surface sediments of the western coast of India. These studies give a preliminary idea on P distribution and its mode of incorporation within the surface sediments. The variations in the distributions of total P reported by these workers are in close agreement with the distribution of dissolved P in seawater and the abundance of sea fish (Murty et al., 1966). The similarity in the distributions of total P in surface sediments and that of organic carbon concentration (Babu et al., 1999) reveals that the variation of P is dependent on the upwelling in the EAS. Babu and Nath (2005) applied modified SEDEX (Ruttenberg, 1992) P-speciation method on the surface sediments of EAS and demonstrated that authigenic P is the dominant phase in the sediments lying within the OMZ of Arabian Sea. The latitudinal decrease of detrital P in the above speciation reflects the importance of terrigenous supply in P concentration in the surface sediments. Rao et al. (1995) through visual inspection during sectioning of thirty gravity cores along the western continental shelf of India, reported phosphorite nodules in only three gravity cores collected from the topographic highs in the continental slope off Goa. Despite the favorable environment for the formation of phosphorite in the EAS (e.g. intense seasonal upwelling, high organic carbon in the surface sediments and OMZ), no trace of it was observed in top one meter of those sediment cores. Although, Rao et al. (1995) broadly suggested the interplay between high calcium content in pore waters and sedimentation rate as the cause of the absence of phosphorites in those sediments, they did not furnish any information about the different P-pools in core sediments that is essential to explain such a hiatus. In the present study, a modified P extraction procedure SEDEX proposed by Ruttenberg et al. (2009) along with bulk geochemistry were adopted for the sediments of two gravity cores retrieved from the Karwar and Mangalore coast. The present work aims to explain (i) the sediments characteristics of cores (Section 4.1), (ii) the down-depth variation of phosphorus species and the factors influencing the distribution of P forms (Section 4.2) in core sediments giving particular attention to the major elements. Finally, we compare phosphorus distribution in the EAS with different global shelf settings (Section 4.3) to understand the difference/similarity in the geochemical and physical parameters with reference to P distribution. The present documentation of P speciation is expected to improve the perception of the phosphorite formation in marine sediments.

2. Materials and methods

Two gravity cores (SK-291/GC-10 and SK-291/GC-13) were raised from the shelf region of southeastern Arabian Sea during ORV Sagar-Kanya cruise 291 (Fig. 1(a), Table 1). The dissolved oxygen concentration measured by the SBE 9plus CTD measuring instrument equipped with SBE 43 dissolved oxygen sensor in December, 2011, shows that the sampling sites are overlain by completely oxic water columns (Fig. 1(b)) ($O_2 > 2$ ml/l, Tribouillard et al., 2006). A total of 34 samples were analyzed from these cores at a regular interval of 25 cm to study the P speciation and bulk sediment characteristics in EAS.

The bulk chemical compositions of sediments were determined by using X-ray fluorescence spectrometry (Philips PW2404 WD X-Ray Fluorescence Spectrometer). Sediment samples were made salt-free, dried at 60 °C for 36 h and pulverized for bulk chemical analysis. The powdered samples of 4 g each were made into pellets by mixing thoroughly with 2 g of boric acid and subjecting to a pressure of 15 t for 4 min in a hydraulic press. Major element oxides and trace elements were measured through quantitative program SUPERQ of PANalytical using 8 International reference standards for calibration. The precision and accuracy were checked by the parallel analysis of international reference materials (STSD-1, Till-4, and MAG-1). The accuracy for the major elements were better than 3% variation (except Na, < 5%) and for minor elements the accuracy was within 4%.

Total carbon (TC) and nitrogen (TN) were measured with an elemental analyzer (Eurovector EA3000), using helium as a carrier gas. For this analysis, about 20 mg of dried, pulverized sediments were combusted at a temperature of 1010 °C in a stream of high-purity oxygen. The gaseous combustion products were chemically reduced and then separated by a gas chromatography column and quantified with a thermal conductivity detector (TCD). Different weights of Sulphanilamide (CHNS grade standard) were used for calibration. Analytical precision was within 2% for both TC and TN.

Total inorganic carbon (TIC) of the sediment was determined after treatment with ortho-phosphoric acid in a Shimadzu TOC-5000A analyzer with SSM-5000A Solid Sample Module. Total organic carbon (TOC) was determined by the difference between TC and TIC. Carbonate content was calculated using the TIC concentration, assuming that calcite was the only carbonate-bearing mineral and according to the formula: $CaCO_3 = TIC \times 8.33$.

Detailed P speciation was obtained using the SEDEX sequential extraction procedure slightly modified from the method of Ruttenberg et al. (2009) (Table 2). The five sedimentary P phases separated by this technique are (i) exchangeable or loosely adsorbed P, (ii) P bound to Fe-(oxy)hydroxides, (iii) authigenic apatite, (iv) detrital apatite of igneous and metamorphic origin, and (v) organic P. Fe-bound P fraction was determined by the bicarbonate-dithionite (BD) reagent as recommended by Jensen and Thamdrup (1993), instead of citrate-bicarbonate-dithionite (CBD) reagent as proposed by Ruttenberg (1992). This modification was considered because of the two reasons: (i) due to the presence of chelating citrate ion, CBD reagent dissolves calcium bound P which will overestimate this fraction of P and (ii) use of BD instead of CBD decreases the interference with the molybdate complex during the measurement of P. The orthophosphate concentrations in all extracted solutions were analyzed by the molybdenum-blue method (Murphy and Riley, 1962) with a Varian Cary 50 UV-vis spectrophotometer. In the case of the BD-extractant, molybdenum-blue complex was extracted by a mixture of 95% hexanol and 5% isopropanol and the absorbance was measured at 690 nm. Triplicate extractions and analyses were performed on two samples from each core to test the reproducibility of the applied extraction method. The resulting relative standard deviations (RSD) range from 1 to 9% depending on the targeted P fraction (Table 2).

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