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Controls on the distribution and fractionation of yttrium and rare earth elements in core sediments from the Mandovi estuary, western India

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ABSTRACT

Mineralogy, major elements (Fe, Mn and Al), rare earths and yttrium (REY) of bulk sediments were analyzed in four gravity cores recovered along the main channel of the Mandovi estuary, western India, to determine the sources and controls on REY distribution. The accelerator mass spectrometer (AMS) ages of total organic carbon indicated modern age for the sediments of the upper estuary and, maximum mean ages of 1588 years AD and 539 years AD for the bottom sediments of the cores in the lower estuary and bay, respectively. The sediments of the upper/middle estuary showed abundant hematite, magnetite and goethite and high Fe, Mn, total-REE (ΣREE) and Y, while those in the lower estuary/bay showed abundant silicate minerals and relatively low Fe, Mn, ΣREE and Y. ΣREE showed significant correlation with clay and silt fractions and Y, Al and organic carbon (OC) content of the sediments. The light to heavy REE ratios (LREE/HREE) of sediments were lower than in Post-Archean Australian Shale (PAAS). The PAAS-normalized rare earths and yttrium (REY; Y inserted between Dy and Ho) patterns of sediments showed middle REE (MREE)- and HREE-enrichment with positive Eu anomaly (Eu/Eu*) and variable Ce anomaly (Ce/Ce*). The REY of sediments is primarily controlled by its texture and REE of source sediment, which is ore material-dominated in the upper/middle estuary and silicate material-dominated in the lower estuary/bay. Low LREE/HREE ratios suggest that very fine-grained sediments were carried away from the estuary because of high-energy conditions. Fractionations of REY (Y/Ho, Sm/Nd, Ce/Ce* and Eu/Eu*) are controlled by different mechanisms. High Y/Ho ratios in clayey silts are due to redistribution of Y and Ho by adsorption onto organic-rich, clays. Variations in Sm/Nd ratios are similar to that of Eu/Eu* in cores from the lower estuary/bay and are controlled by mineral constituents of the sediments. Positive Ce and Eu anomalies are inherited from ore material, and ore material and source rocks, respectively. Negative Ce anomaly is related to source rock material and influenced by lanthanum enrichment at certain sediment intervals.

1. Introduction

The rare-earth elements (REE), La to Lu, are widely used as tracers of geochemical processes in a wide variety of sedimentary environments. REE are useful for determining petrogenetic histories of rocks (Shields and Stille, 2001). Several investigators reported dissolved and particulate REE in fluvial systems and identified the influence of weathering on fractionation of REE and yttrium (Nesbitt, 1979; Goldstein and Jacobson, 1988; Nesbitt et al., 1990; Nozaki et al., 1997; Andersson et al., 2006; Ma et al., 2007) and control of source rock composition on REE of sediments (Singh and Rajamani, 2001; Yang et al., 2002). The dissolved and particulate REE are affected by both flocculation and precipitation processes at the mixing zone of fluvial and seawater. Geochemical processes identified at this stage are large scale removal of dissolved fluvial REE (in particular light REE) (Sholkovitz and Szymezak, 2000; Nozaki et al., 2000), salt-induced coagulation of river colloids (Elderfield et al., 1990) and REE adsorption on Fe-organic colloids (Sholkovitz and Elderfield, 1988; Sholkovitz, 1993) and particulate organic carbon (Byrne and Kim, 1990; Sholkovitz, 1992; Schijf et al., 1995; Arraes-Mescoff et al., 2001; Haley et al., 2004). Fractionation of REE, especially light to heavy REE and Ce relative to other REE develops in a river-estuarine system. Although Y and Ho have similar ionic radii, the seawater ratios of Y/Ho are approximately 2 times higher than the crustal values (Nozaki et al., 1997; Zhang et al. 1994), suggesting fractionation of Y and Ho must take place during weathering and riverine transport or in marine conditions. Bau et al. (1995) suggested fractionation of Y to Ho takes place largely in rivers and estuaries, whereas Nozaki et al. (1997, 2000) suggested most prominent fractionation in estuaries and seawater. Although both Sm and Nd are mobile during weathering, REE-bearing minerals and

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differential weathering of constituent minerals, for instance removal of less susceptible minerals like feldspar, would grossly change the Sm/Nd ratio. Therefore the Sm/Nd ratio of the weathered soil depends on primary residual phases and secondary phases produced during transformation of rock to a soil layer (Viers and Wassenburg, 2004; Bau and Zhao, 2008; Feng, 2010). Several investigators identified the factors (source rock composition, grain size and mineralogy) that control REE distribution in surficial sediments (Cullers et al., 1987; Klaver and van Weering, 1993; Yang et al., 2002; Borrego et al., 2005; Censi et al., 2007; Prego et al., 2009; Jung et al., 2012). There are a few studies on cycling of REE during early diagenetic decay of organic matter in estuarine sediments (López-González et al., 2012; Morgan et al., 2012). Investigations on marine sediments have revealed the REE patterns in sedimentary systems are influenced by both depositional environment (Murray et al., 1990, 1992) and diagenetic processes (Milodowski and Zalasiewicz, 1991; Murray et al., 1992). Nozaki et al. (2000) suggested Nd and other REE are released back to seawater from sediments in high salinity regions of estuaries. Therefore, the REE that reach the oceans are the products of source rock composition, fractionation during weathering and sum of geochemical (depositional and diagenetic) processes in estuaries. Investigations on bottom sediments of the estuaries help us to understand the processes involved in controlling the distribution and fractionation of REE. The purpose of this paper is to report the down core distribution of REE and Y in four sediment cores collected along transect of the Mandovi estuary, western India (Fig. 1) and to determine the factors controlling their distribution and fractionation.

1.1. Study area

The Mandovi River is a major river in the state of Goa. The Mandovi estuary (Fig. 1) is ~50 km in length and experiences two extreme conditions: It receives abundant river run off (~258 $m^3 s^{-1}$; Vijith et al., 2009) during the wet monsoon period (June – September) and negligible runoff (~6 $m^3 s^{-1}$) during dry period (October–May). As a consequence, this estuary acts largely as an extension of river during wet period and an extension of sea during dry period. This estuary is mesotidal and the tidal ranges are 2.3 and 1.5 m during the spring and neap tides, respectively (Manoj and Unnikrishnan, 2009). Circulation in this estuary during dry period is dominated by tidal and wind-induced currents and intrusion of saline water was reported as far as 45 km from the mouth of the estuary (Manoj and Unnikrishnan, 2009). High-energy conditions are prevailed in the lower estuary/bay both during monsoon and pre-monsoon because of consistent estuarine turbidity maximum (Rao et al., 2011). Mangroves are abundant on the shores of the estuary. Productivity in the estuary is low during wet period and abundant during dry period. Mining of ore deposits is an important industrial activity in the state of Goa. Fe – Mn ores brought from the mines are stored on the shores of the estuary. Ore deposits are loaded on to barges at several shore stations in the upper/middle estuary, transported through the estuary to the port for export. Several investigators reported the concentrations and composition of the suspended particulate matter (SPM) and bottom sediments in the Mandovi estuary (Kessarkar et al., 2010, 2013; Rao et al., 2011; 2014; Shynu et al., 2011, 2012, 2013). In this study we report the REE of sediments in gravity cores collected along the main channel of the Mandovi estuary and Aguada Bay (Fig. 1). Prajith et al. (2015) reported magnetic properties of sediments in these cores.

The entire territory of Goa is covered by rocks of the Goa Group belonging to the Dharwar-Super Group (Western Dharwar Craton – WDC) of the Archean-Proterozoic age, except for a narrow strip in the northeastern corner of the territory which is covered by Deccan Traps of the Upper Cretaceous-Lower Eocene age (Gokul et al., 1985). The WDC is predominantly made up of green schist of metamorphic rocks and Tonalite-Trondhjemite Gniesses (TTG), and are characterized by high-Mg basalts and komatiites with metavolcanics and meta-sedimentary rocks (Naqvi, 2005). The Mandovi River and its tributaries largely drain through the Bicholim formation of the Goa group in the hilly region and Al- and Fe-laterites formed by deferrification of Pre-cambrian rocks at the low level (Fig. 1). The Bicholim formation is represented by quartz-chlorite-amphibole schists, metapyroclasts and tuff with calcareous, manganeferous and ferruginous (banded-iron formations – BIF) ore deposits (Gokul et al., 1985).

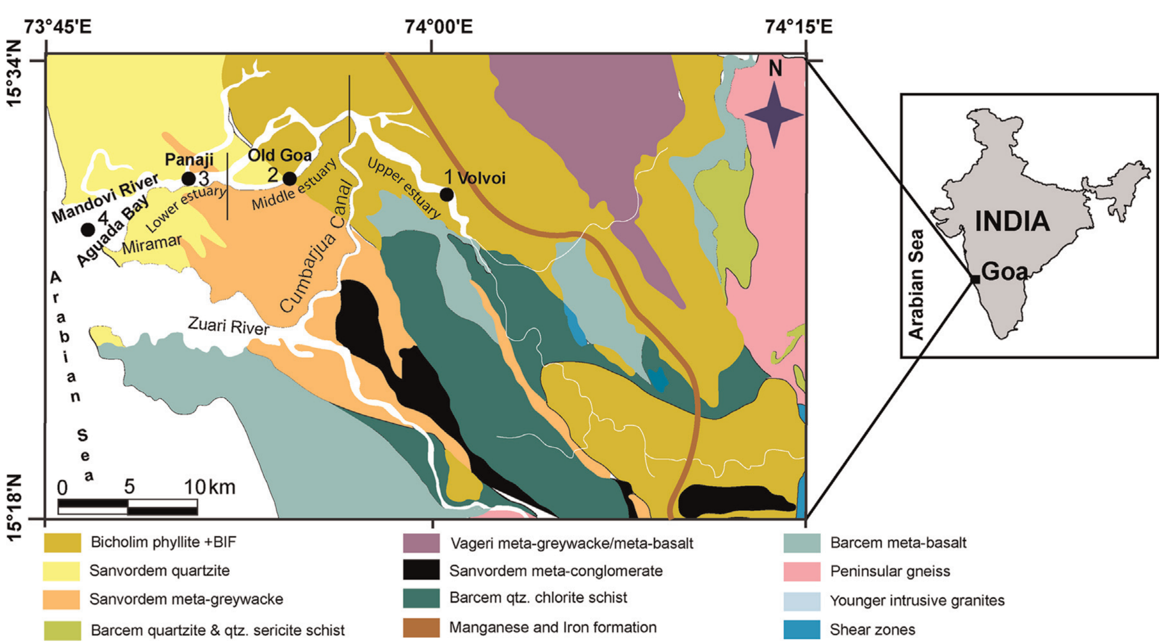

Fig. 1. Map showing the location of sediment cores in the Mandovi estuary, western India. Upper estuary, middle estuary and lower estuary and bay are also marked in the figure. Geology of the Mandovi River basin (modified after Mascarenhas and Kalavampara, 2009) is also shown.