

Mineralogy and Sr-Nd isotopes of SPM and sediment from the Mandovi and Zuari estuaries: influence of weathering and anthropogenic contribution

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Abstract

Clay minerals and Sr-Nd isotopes of suspended particulate matter (SPM) and bottom sediment were investigated along transect stations of the Mandovi and Zuari estuaries, western India to determine the provenance and role of estuarine processes on their distribution. Kaolinite and illite, followed by minor goethite, gibbsite and chlorite were present in SPM and bottom sediment at all stations, both during monsoon and pre-monsoon. Smectite occurred in traces at river end stations but its contents increased downstream in both estuaries. Smectite contents were much higher in Zuari than in Mandovi estuary. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and ϵNd of SPM were higher than those in hinterland rocks and laterite soils. The Sr ratios were highest at river end stations of both estuaries and decreased sharply seaward. The Sm/Nd ratios of SPM and sediment were close to that of iron ore material flushed into the estuaries. The mean ϵNd of SPM and sediment were similar in both estuaries. It is suggested that the smectite is formed in coastal plains and its distribution downstream is controlled by lithology and drainage basin of rivers. Abundant kaolinite and high Sr ratios reflect chemical weathering and lateritization of source rocks. Sr isotopic ratios along transects are influenced by changes in salinity, organic matter and turbidity. High and near identical ϵNd values along transect stations of both estuaries suggest that the Nd isotopic compositions are influenced by the lateritization of source rocks and anthropogenic contribution of ore material.

Introduction

Clay minerals are the weathering products of continental rocks and are transported to the oceans largely by rivers. The composition of clay minerals primarily depends on source rock composition, climate and topography of the drainage basin of the river (Grim, 1968). The parent rocks in the humid, tropical and sub-tropical regions have extensively been lateritized and undergo very large geochemical fractionation during lateritization. Moreover, the clay minerals transported by rivers pass through estuaries before reaching the seas. In estuaries they are modified by the physical and bio-geochemical processes (Gibbs, 1977; Hedges, 1978). Therefore, the relative abundance of clay minerals reaching the sea depends on source rock composition, primary and secondary processes associated with laterites and estuarine processes. On the other hand, the Sr and Nd isotopic compositions of continental rocks depend on the Rb/Sr and Sm/Nd ratios and their ages. The sediments of the rivers draining older crust have relatively more radiogenic Sr and non-radiogenic Nd than rivers draining younger crust (Dasch, 1969; Biscaye et al., 1974; Goldstein et al., 1984; Grousset et al., 1988; Innocent et al., 1997). The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of particulates detached from the rocks remains unchanged. Moreover, the ^{87}Sr and ^{86}Sr are not fractionated by processes such as phase separation, evaporation or biological assimilation (Peterman et al., 1992). The only change to the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in the sedimentary environment will be due to mixing of Sr from different sources. Therefore, the Sr isotope signatures are excellent tracers for understanding processes such as water-rock interactions, the mixing of isotopically distinct water masses and the influence of geology on the composition of river water (Douglas et al., 1995). Studies on SPM of the rivers and estuaries indicated that small variations in $^{87}\text{Sr}/^{86}\text{Sr}$ ratio could be due to degree of weathering on lithological formations and influence of organic matter, grain size of sediments and anthropogenic inputs of Ca (and hence Sr) from fertilizers (Douglas et al., 1995). Recent studies have also shown that the Sr-Nd isotopic composition of the weathering products have extensively been modified during lateritization (Brimhall et al., 1991; Viers and Wasserburg, 2004). Therefore, it is important to determine the sources of clay minerals and Sr-Nd isotopic composition of SPM and sediment in rivers and estuaries to understand the controls affecting their variations in space and time. The purpose of this paper is to report the spatial distribution of clay minerals and Sr-Nd isotopes in suspended and bottom sediments of the Mandovi and Zuari (Ma-Zu) estuaries, both during monsoon and pre-monsoon to better understand their sources and factors controlling their distribution.

Subramanian (1980) studied mineralogy of the suspended matter for major Indian rivers. Several workers reported clay minerals in SPM and bottom sediment of the Ma-Zu estuaries (Bukari and Nayak, 1996; Kessarkar et al., 2010 and 2013) and shelf sediments off western India (Nair et al., 1982; Rao and Rao, 1995). The Sr-Nd isotopes of the igneous and metamorphic rocks in the southern Indian

Peninsula (Peucat et al., 1989; Lightfoot et al., 1990; Harris et al., 1994), river sediments (Goswami et al., 2012) and shelf sediments off western India (Kessarkar et al., 2003) have been reported. However, there are no systematic studies on Sr-Nd isotopes of the suspended and bottom sediments in Indian estuaries.

Study area

The Mandovi and Zuari (Ma-Zu) rivers are two major rivers of Goa in the central west coast of India (Fig. 1A), adjacent to each other and share some common features. Both rivers originate in the Western Ghats (mountain regions) and drain through a narrow coastal plain with nearly identical length (~50 km each) of estuaries. The hinterland rocks are subjected to intense chemical weathering under humid, tropical climate conditions and capped by ferruginized laterites (Fig. 1B). Laterites are considered to represent the weathering residuum that remains after intensive *in situ* chemical alteration of a “protolith” bedrock under tropical weathering conditions. The rivers drain through rocks of the Goa Group belonging to the Dharwar Super Group of the Archaean–Proterozoic age (Gokul et al., 1985). The Bicholim Formations (schists, phyllites, limestones, banded-iron formations, and manganiferous cherts) and Sanvordem Formations (metagreywacke, conglomerate, and argillites) covered by ferruginized laterites occurring in the drainage basins of both rivers. The Bicholim Formations occupy a large area in the upstream of Mandovi River, whereas the Sanvordem Formations occupy a large area in the downstream of Zuari River basin (Mascarenhas and Kalavampara, 2009).

The estuaries of both rivers are classified as ‘monsoonal estuaries’ (Vijith et al., 2009) which receive abundant river discharge only during the monsoon (June–September). The river runoff of Mandovi measured at the head during June–October is $\sim 258 \text{ m}^3\text{s}^{-1}$ and during November–May is $\sim 6 \text{ m}^3\text{s}^{-1}$ (Vijith et al., 2009). The Zuari River was dammed upstream and the runoff measured at Sanguem and Kushavati tributaries (Fig. 1A) during the monsoon (June–September) and pre-monsoon (February–May) are ~ 147 and $0.8 \text{ m}^3\text{s}^{-1}$, respectively. These estuaries are meso-tidal and the tidal ranges are ~ 2.3 and 1.5 m during the spring and neap tides, respectively (Shetye et al., 2007). The currents in the estuaries are tide-dominated. Tidal oscillations have been observed and saline waters penetrate ~ 45 km upstream from the river mouth during the dry season (October to May; Shetye et al., 2007). Several big open cast iron and manganese ore mines operate in the drainage basins of the rivers. As Fe and Mn ores brought from the mines are stored on the shores of the estuaries (Fig. 1C), abundant ore material is being flushed into the estuaries during heavy monsoon rains. Since ore handling (loading of ore onto barges, transport through river channel, and reloading at the port or midstream onto giant ships for export) is done in an open system one would expect abundant spilled-over ore material into the estuaries.

Materials and Methods

Fig. 1A shows the location of samples in the Ma-Zu estuaries. SPM and sediment samples collected in August (representative month of monsoon) and April (pre-monsoon) along transect stations of estuaries were investigated. For clay mineral studies a total of 31 samples of SPM, including 14 from Mandovi ((M1 to M7)_{monsoon}+(M1 to M7)_{pre-monsoon}) and 17 from Zuari estuary ((Z1 to Z7)_{monsoon}+(Z0 to Z9)_{pre-monsoon}) and 31 samples of surface sediment, including 14 from Mandovi ((M1 to M7)_{monsoon}+(M1 to M7)_{pre-monsoon}) and 17 from Zuari estuary ((Z1 to Z7)_{monsoon}+(Z0 to Z9)_{pre-monsoon}) were analyzed. Detailed procedure for analyzing clay minerals in SPM, given in Kessarkar et al. (2010) was followed. Representative X-ray diffractograms along transect stations of the Ma-Zu estuaries are shown in Figs. 3 and 4. As monthly data on clay mineralogy of SPM along transect stations are available with the authors (see Kessarkar et al. 2010), the mean percentage of clay minerals and standard deviation for each mineral on a seasonal basis are given in Table 1. The sediments were dried at <50°C and analyzed for their sand, silt and clay content (Table 1), following Folk (1968). The <2 µm fraction of sediment was used for clay mineralogy and procedure for their mineralogy mentioned in Rao and Rao (1995) was followed. Representative X-ray diffractograms of sediments are given in Figs. 6 and 7. As clay mineralogy of sediments for two months in each season (July and August for monsoon and March and April for pre-monsoon) are available with the authors, the mean percentages of clay minerals and their standard deviations at each station are given in Table 1.

For Sr-Nd isotopic studies a total number of 10 SPM samples, including 4 from Mandovi (M1, M4 and M7 during monsoon and M4 during pre-monsoon) and 6 from Zuari (Z1, Z4 and Z7 during monsoon and pre-monsoon) estuary were analyzed. Six sediment samples, including 3 each from Mandovi (M1, M4 and M7) and Zuari (Z1, Z4 and Z7) estuaries and 2 surface sediments collected at 18 m and 54 m depth from the shelf were also investigated (Table 2).

The SPM from the filter paper was carefully removed, dried and powdered. For sediments, the < 2 µm fraction of the sediment was separated and used for isotope measurements. Sr and Nd isotopic analyses were made on carbonate and organic matter free fraction of the sediments (Singh et al., 2008). The powdered sediment samples were first decarbonated by leaching with 0.6 N HCl at 80°C for ~ 30 min with ultrasonic treatment. The slurry was centrifuged, residue washed with Milli-Q water, dried and ashed at ~ 600°C to oxidize organic matter. A known weight (~100 mg) of the carbonate and organic matter free fraction of sediment was transferred to Savillex® vial and digested repeatedly with HF-HNO₃-HCl at ~ 120°C to bring the sediment to complete solution. The acid digestion step was repeated as needed to ensure that the entire sample was brought to complete solution. The < 2 µm fraction of sediments was digested in presence of ⁸⁴Sr and ¹⁵⁰Nd spikes. Pure Sr and Nd fractions were

separated from the solution following standard ion exchange procedures (Rahaman et al., 2009; Goswami et al., 2012). Sr and Nd concentrations and $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ of sediments were measured on a Finnigan Neptune Multiple collector – Inductively Coupled Plasma – Mass Spectrometry (MC-ICP-MS) at Physical Research Laboratory, Ahmedabad. The analyses were made in static multi-collection mode. Mass fractionation corrections for Sr and Nd were made by normalizing $^{86}\text{Sr}/^{88}\text{Sr}$ to 0.1194 and $^{146}\text{Nd}/^{144}\text{Nd}$ to 0.7219, respectively. During the course of analyses, NBS987 Sr standard was measured, these yielded values of 0.710287 ± 0.000020 (1σ , $n = 15$) for $^{86}\text{Sr}/^{88}\text{Sr}$. For Nd, JMC-321 standard was measured on MC-ICP-MS, this yielded an average value of 0.511095 ± 0.000007 (1σ , $n = 13$) (Goswami et al., 2012). The internal reproducibility was better than 10 ppm for both Sr and Nd isotopic measurements. Following the formula of DePaolo and Wasserburg (1976), the Nd isotopic data was expressed in terms of ' ϵNd '. Several total procedural blanks for Sr and Nd were also processed during the analysis. These blanks are several orders of magnitude lower than typical total Sr and Nd loads analyzed and hence no corrections for blanks were made. Average and standard deviations of Rb/Sr, Sm/Nd ratios and ΣREE of SPM and sediment at each station on seasonal basis and $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios and their standard errors (SE) are shown in Table 2.

Results

(i) Clay minerals and Sr-Nd isotopes in suspended matter

A water sample collected during peak monsoon in the Mandovi estuary showed very high SPM concentration and low salinity (0.01). The particulate matter of this sample showed abundant kaolinite content followed goethite and gibbsite and traces of smectite (Fig. 2A). Kaolinite was the most abundant mineral, followed by illite and chlorite in SPM along transect stations of the Mandovi estuary both during monsoon and pre-monsoon (Fig. 2B and 2C). Smectite occurred in traces at most stations landward and increased to a maximum of 15% and 23% at sea end stations during the monsoon and pre-monsoon, respectively (Fig. 2B and 2C; Table 1). Smectite content increased with increasing SPM content at sea end stations, despite salinity variations along transect were minor during the monsoon (0.02 to 0.42; Fig. 2B) and major during pre-monsoon (8.4 to 31.3; Fig. 2C). Gibbsite, goethite and quartz are also present in all samples.

A water sample collected during peak monsoon in Zuari estuary showed low salinity (0.01) and high SPM concentrations. The SPM of this sample showed high kaolinite content followed by goethite, gibbsite and traces of smectite (see Fig. 3A). Kaolinite followed by illite and chlorite were highest at landward stations and their contents decreased seaward with increasing smectite, both during monsoon and pre-monsoon (Fig. 3B-C). Although the smectite distribution along transects was similar

in both estuaries, smectite content was much higher in Zuari than in Mandovi (Table 1). Smectite showed no distinct variations with salinity at river end stations during monsoon, but its high concentrations were associated with salinity between 3.4 and 15.1 at sea end stations (Fig. 3).

The Rb/Sr and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of SPM were high at river end stations of Mandovi (M7) and Zuari (Z7) estuaries during monsoon and decreased seaward (Fig. 4). The Rb/Sr ratios were lower in both estuaries during the pre-monsoon than in monsoon (Table 2). In Zuari, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios at each station were lower during pre-monsoon than in monsoon. The seaward decrease of Sr isotopes coincided with increase in salinity, smectite and SPM concentrations in both estuaries (Fig. 4). The Sm/Nd ratios of SPM were slightly higher in Mandovi than in Zuari estuary. Although the $\epsilon\text{Nd}(0)$ showed a range of values in Ma-Zu estuaries during monsoon (Table 2), the mean $\epsilon\text{Nd}(0)$ in Mandovi (-14.42) was close to that of Zuari (-13.66). The Sm/Nd ratios and $\epsilon\text{Nd}(0)$ values of SPM during pre-monsoon were within the range as that of monsoon (Table 2). The mean $\epsilon\text{Nd}(0)$ of SPM in Zuari (-15.02) was same as that of Mandovi (-15.37, only one value) during pre-monsoon (Table 2).

(ii) Clay minerals and Sr-Nd isotopes in bottom sediments

The sediments of the Mandovi estuary were sandy at mid-stations and clayey silts or silty sands at other stations, both during monsoon and pre-monsoon. While in Zuari the sediments were sandy in the upper estuary and clayey silts at mid-stations and sandy silts in the bay (Table 1). The clay mineral variations in sediments along transect of both estuaries were same as that of SPM (Figs. 6 and 7). Kaolinite and illite contents were high at river end stations and decreased seaward with increasing smectite content in these estuaries, both during monsoon and pre-monsoon. The smectite content was higher in sediments than in SPM in both estuaries. It was also higher in Zuari sediments than in Mandovi (Table 1).

The Rb/Sr ratios of sediments were higher than in SPM in both estuaries. The ratios increased seaward in the Mandovi estuary, but in Zuari estuary high ratio occurred at mid-station (Z4). As in SPM the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of sediments were highest at river end stations of both estuaries, but Sr ratios of sediments were lower than in SPM (Table 2). The Sm/Nd ratios of sediments were similar (0.215) at all stations in the Mandovi estuary but ranged from 0.178 to 0.207 in Zuari estuary with highest value at mid-station (Z4; Fig. 8). The mean $\epsilon\text{Nd}(0)$ of sediments in Mandovi estuary (-14.20) was the same as that of Zuari (-14.15). The Rb/Sr ratios decreased and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios increased seaward in shelf sediments (Table 2). The Sm/Nd values were similar at both stations on the shelf and $\epsilon\text{Nd}(0)$ of sediment at 18 m depth was less radiogenic (-15.32) than at 54 m depth (-12.45; Table 2).

Discussion

A. Sources of Clay minerals

The rocks in the drainage basins of rivers weather in tropical conditions and are capped by laterites. Kaolinite is expected to be the most dominant mineral along with gibbsite and goethite in laterites (see Chamley, 1989). Since the basic rocks are Pre-cambrian metamorphosed gneisses and schists and are exposed at places on slopes of mountains, minor proportions of residual minerals like illite and chlorite would also be delivered to the clay fraction from them. Chlorite gets destroyed easily in tropical climatic conditions. As abundant kaolinite and illite together with minor gibbsite, goethite and chlorite are present in SPM of the Ma-Zu estuaries, these minerals reflect their source from the hinterland and indicate weathering products of laterites. Several workers reported abundant kaolinite, illite, gibbsite and goethite in Ma-Zu estuaries (Bukari and Nayak, 1996; Kessarkar et al., 2010 and 2013)

Traces of smectite in SPM of water delivered to the estuaries during peak monsoon (Figs. 2A and 3A) suggest that the rivers contributed little smectite to the estuary during peak discharges. As the rivers take sediment load largely from mountainous regions during heavy rainfall, it appears that the river load from upstream contains abundant kaolinite and traces of smectite. This statement is also supported by the SPM at river end stations of both estuaries (M7 and Z7), which showed high kaolinite and illite and traces of smectite during monsoon and pre-monsoon (Figs. 2B-C and 3B-C). However, one needs to explain the sources and increase of smectite from river end to sea end stations of both estuaries and also higher smectite in Zuari than in Mandovi estuary (Table 1). Four plausible factors that contribute smectite are: (a) geomorphology and lithology of the drainage basin, (b) estuarine processes, (c) smectite transported from offshore and (d) influence of salinity on size and characteristics of clay minerals.

B. Sources and factors influencing spatial variations of smectite in SPM

(i) Geomorphology and composition of rocks in the drainage basin: Smectite content increases seaward, marginally in the Mandovi and more distinctly in Zuari estuary. Although both rivers receive sediment load from mountainous regions the geomorphology and lithological formations vary along their drainage basins: For example, (a) the drainage basin of the Zuari River is largely located in coastal plains, whereas that of Mandovi is largely in elevated and mountainous regions with narrow coastal plain in the downstream. (b) The river run off into the Mandovi estuary ($258 \text{ m}^3 \text{ s}^{-1}$) is much higher than that of Zuari ($147 \text{ m}^3 \text{ s}^{-1}$) during the monsoon. (c) There is no dam on the main channel of Mandovi River, whereas the Zuari River is dammed upstream. In view of large river basin in uplands and high discharge into the Mandovi estuary, the sediment load into this estuary would dominantly be

characteristic of rocks from mountain regions upstream, with chemical (kaolinite) and to some extent physical (illite) weathering products. In view of the dam on Zuari River, discharge into its estuary was low compared to the Mandovi estuary. Since the Zuari River has large river basin in coastal plains, the sediment load delivered into the lower estuary of Zuari is expected to be more from coastal plain than from upstream during the monsoon. Moreover, the Bicholim Formations in the upstream laterally change to the Sanvordem Formations in the coastal plain downstream areas and the latter are predominantly widespread in the drainage basin of Zuari River. Since smectite variations are seen only in the lower estuary it may have formed in coastal plains and processes for its formation are as follows: In coastal plains and in less permeable argillite-covered (Sanvordem Formations) regions, the leaching solutions with more and more dissolved elements released from hydrolysis are not entirely evacuated by running water, but tend to be stored and concentrated in soil profiles. During dry conditions, these elements combine and form new minerals such as smectite. In regions where groundwater levels are high, the smectites thus formed may migrate upwards and replace formerly well-drained kaolinite soils through a progressive ionic saturation of weathering profiles (Chamley, 1989). Thus, the soils in the coastal plain, downstream areas are enriched with more smectite and in turn transported into the estuary during heavy monsoon rains. More stations showing distinct smectite in the lower estuary of Zuari than in Mandovi (Table 1) may be due to the large drainage basin in coastal plains for the Zuari River. Smectite, therefore, is a weathering product of the lithological formations in coastal plains and transported into the estuary during monsoon (see Kessarkar et al., 2013).

(ii) Estuarine processes: Estuarine turbidity maximum (ETM) is a consistent feature and located downstream of both estuaries. The zone of ETM with high SPM concentrations is caused by re-suspension of bottom sediments (Rao et al., 2011). Since the seaward increase of smectite coincides with increase in SPM concentrations (Fig. 4), smectite re-suspended from bottom sediment by turbidity may have contributed to the water column and partly increased its concentrations in SPM.

(iii) Smectite transported from offshore: High smectite at sea end stations and its decrease landward (Figs. 2 and 3) suggests offshore source of smectite. This source of smectite is suggested because the inner shelf sediments contain abundant smectite and low kaolinite (Rao and Rao, 1995), transported from the Deccan Trap Basalts in the hinterland, located north of the study area. If smectite is sourced from Basalts and transported into the estuary by the prevailing southerly surface (Shetye et al., 1990) and, tidal and wind-induced currents from offshore, its Sr-Nd isotopic signatures would be distinctly different from that of Pre-Cambrian gneisses and schists in the hinterland. The Sr-Nd isotopes of SPM and sediment (Table 2), however, do not confirm that smectite is transported from offshore (see discussion below).

(iv) Influence of salinity on size and characteristics of clay minerals: The grain size of smectite is smaller than that of kaolinite and illite (Whitehouse et al., 1960). Kaolinite and illite respond rapidly and flocculate abundantly at very low salinities. Keeping these in view, Gibbs (1977) proposed early flocculation of kaolinite and illite and winnowing of smectite away from the source. Segregation of clay minerals due to salinity change may not explain smectite variations, because the salinity variations are minor at M7 to M3 stations in the Mandovi estuary (Fig. 2) but large at Z9 to Z7 stations in the Zuari estuary (Fig. 3) during monsoon. The smectite content, however, is always in traces at these stations. In other words, instead of salinity, the sediment load characteristic of upland (kaolinite-dominated) influenced clay minerals in such a way that more stations in Mandovi and only a few stations in Zuari estuary (due to the dam upstream) are affected by upland sediment load. Degens and Ittekkot (1984) suggested that because of greater surface area and smaller size of smectite, it bonds with organic compounds with greater intensity and flocculates in a wide range of salinity and organic matter (OM) conditions. The organic matter content of SPM at river end stations varies during monsoon and pre-monsoon (see Fig. 4), but the smectite content of SPM is always in traces at these stations. In other words, smectite variations at river end stations may not have been influenced by changes in grain size of clay minerals, salinity and OM.

High smectite content coincides with high salinity and high SPM concentrations at several sea end stations (Figs. 2 and 3). OM content is high and type of OM also changes from river end to sea end stations (see Fig. 4). It is not clear which factor contributed high smectite, but it is likely that apart from coastal plain origin of smectite, turbidity maximum favoured smectite to remain in solution and therefore high smectite is seen in SPM at sea end stations.

C. Correspondence between Sr-Nd isotopes and clay minerals in SPM

(i) River end stations during monsoon: High Rb/Sr and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios correspond with high kaolinite at river end stations (M7 and Z7) of both estuaries (Table 1 and 2; Figs. 2 and 3). During lateritic weathering less resistant and mobile elements (Si, Na, K, Mg, Ca, Sr) are continuously stripped away leaving secondary minerals enriched in Fe_2O_3 and Al_2O_3 . Rb is enriched in older rocks and ^{87}Rb produces radiogenic ^{87}Sr through radioactive decay. During chemical weathering Sr is more mobile than Rb and Sr going into solution is much less radiogenic (^{86}Sr) (Tripathy et al., 2012). Therefore, high Rb/Sr and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are expected from the weathering products of older rocks. Parent rocks (Pre-Cambrian gneisses and schists) in the study area are lateritized (Fig. 1B). High $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (M7: 0.7470; Z7: 0.7686; Table 2) than those of parent rocks (0.7103 to 0.7344; Jayananda et al., 2004) indicate intense chemical weathering and laterite alteration. Wimpenny et al. (2007) suggested that the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio becomes more radiogenic during laterite alteration. Mao et al. (2011) reported high

$^{87}\text{Sr}/^{86}\text{Sr}$ ratios with kaolinite-rich soils. High $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and abundant kaolinite at river end stations thus indicate intense chemical weathering and laterite alteration.

The ϵNd of SPM at M7 (-15.07) and Z7 (-15.09) are much higher than that of Upper Continental Crust (-17; Goldstein and Jacobsen, 1988), Pre-Cambrian gneisses and schists (-41 to -29; Jayananda et al., 2000) or sediments of the rivers (Netravati: -40.8 to -32.6; Periyar: -26.2 to -28.2; Goswami et al., 2012) that drain through Pre-Cambrian formations, weathered granites (-37.7 to -37.5) or granodiorite gneisses (-27.3 to -26.8; Deepthy, 2008). This suggests that even the Nd isotopic composition of SPM (see Fig. 5) is more radiogenic and does not reflect parent rock composition. Brimhall et al. (1991) suggested the increase in Sr and Nd isotopic ratios could be due to altered laterites in the hinterland and dust deposited in the laterites. Viers and Wasserburg (2004) measured ϵNd of the laterite soil profile developed on late Archean crust in the Cameroon and reported a regular increase in ϵNd from -36 of the parent rock to -18 near the top of the laterite profile. They suggested that the increase in ϵNd towards the top is related to differential weathering of constituent minerals, and the redeposition of REE in phosphate and a significant contribution of radiogenic Nd from dust. Removal of less susceptible minerals like feldspar (with low Sm/Nd) would grossly increase the value of ϵNd of the bulk rock at the early stage of weathering. Thus the bulk Nd isotopic composition of the soils represents a mixture of residual primary phases and secondary phases produced during transformation from rock to a soil layer. Deepthy (2008) reported different $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and ϵNd of the laterites developed on Pre-cambrian gneissic rocks at 2 locations in Mangalore (see Fig. 5). In one locality the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (0.7126 to 0.7166) are close to the parent rock but ϵNd values (-11.2 to -19.8) are much more radiogenic. In another locality the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (0.7239 to 0.8121) are higher but ϵNd values (-32.9 to -41.5) are the same as that of the parent rock. The distinct variations in Sr and Nd isotopes associated with laterites indicate different degrees of lateritization and weathering of minerals in parent rocks. The more radiogenic ϵNd of SPM may therefore represent soil material from laterites.

The Sm/Nd ratios of SPM in the Mandovi (0.210-0.227) and Zuari (0.208-0.212; Table 2) estuaries are, however, much higher than the lateritic soils (0.093-0.104; Viers and Wasserburg, 2004) or laterite profiles (0.143-0.175; Deepthy, 2008). This implies some Sm-Nd from other sources may have also contributed to the total SPM. Goethite is a minor component in SPM (Figs. 2-3). Rare earth elements (REE) exhibit stronger affinity for Fe, Mn oxy-hydroxides. Some Sm-Nd may have been incorporated during ferruginization of laterites. Gingele and De Deckker (2005), however, indicated that the iron (oxy-) hydroxides (haematite and goethite), if present in small amounts in the clay fraction, do not significantly influence the Nd isotopic composition. Pulverized, fine-grained Fe-Mn ore deposits are stored on the shores of both estuaries (Fig. 1C). Ore handling is an important activity throughout the

year in both estuaries. Therefore, the particulate ore material flushed into the estuary during heavy monsoon rains and ore material spilled into the estuary from barges carrying ore deposits would contribute significantly to the total SPM. Since the Sm/Nd ratios of SPM in the Ma-Zu estuaries (0.208- to 0.227; Table 2) are close to that of ore material (0.277) we suggest that the ore dust influenced Nd isotopic composition of SPM. Shynu et al. (2011 and 2013) reported the REE patterns of SPM in Ma-Zu estuaries (MREE- and HREE enriched patterns with positive Ce and Eu anomalies) are similar to those of ore material. In other words, the Nd isotopic composition of SPM is not only influenced by altered laterites from hinterland but also by the anthropogenic contribution of ore material flushed into the estuaries from time to time.

(ii) Spatial variations of $^{87}\text{Sr}/^{86}\text{Sr}$ and ϵNd in SPM during monsoon: The seaward decrease of Rb/Sr and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios corresponds with marginal increase in salinity in both estuaries (Fig. 4). Salinity variations of surface water along transect (0.02 at M7, 0.05 at M4 and 7.0 at M1) are marginal in Mandovi but large in Zuari estuary (0.28 at Z7; 3.45 at Z4 and 15.1 at Z1 - see Fig. 4). It appears that the initial changes in salinity and flocculation and aggregation processes at the mixing zone of fresh and seawater may have influenced to decrease Sr isotopic ratio sharply. Since Sr ratios are similar with low smectite as well as high smectite content of SPM at sea end stations (Fig. 4), smectite may not have significantly influenced Sr ratios. On the other hand, organic matter (OM) content of SPM increases seaward or, type of organic matter changed from terrigenous to marine in Mandovi estuary and terrigenous to brackish-marine in Zuari estuary (see $\delta^{13}\text{C}$ values of OC in Fig. 4). As OM takes up soluble Sr (which is largely non-radiogenic ^{86}Sr), the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of SPM decreases with increase in OM content. Douglas et al. (1995) reported the small amount of increase in natural OM (algal material) significantly lowered the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of SPM in the Murray-Darling River system. Moreover, the sharp decrease in $^{87}\text{Sr}/^{86}\text{Sr}$ ratio from M4 to M1 and from Z7 to Z4 coincides with increase in total SPM concentrations at M1 and Z4 stations (see Fig. 4). Since the high SPM at these stations was due to re-suspension of bottom sediments, the Sr isotopic ratios may have been diluted by high SPM (with few particles with distinctly different Sr isotopic ratio) and therefore decreased the values.

The ϵNd values (-15.07 to -14.06) along transect of the Mandovi estuary indicate little change in provenance of source material. Although the ϵNd of SPM at the river end (-15.09) and sea end stations (-13.9) are not different in Zuari estuary, station Z4 shows more radiogenic ϵNd (-11.98) and corresponds with peak high SPM concentration, Fe, ΣREE content and marginal increase in Sm/Nd (see Fig. 4). As station Z4 is located in the zone of estuarine turbidity maximum (ETM) it is likely that the repeated re-suspension may have favoured more fine-grained, Sm-Nd associated material (ore material) in suspension resulting in high ϵNd . In other words, the variations in Nd isotopes of SPM

along transect may be due to the admixtures of different proportions of laterite-derived material and ore dust and re-suspended material from the bottom.

(iii) Variations in $^{87}\text{Sr}/^{86}\text{Sr}$ and ϵNd of SPM in Zuari estuary during pre-monsoon: During pre-monsoon, the Ma-Zu estuaries are characterized by negligible river runoff and high productivity. Ore handling activity takes prominence. ETM occurs in the lower estuary (Rao et al., 2011). Therefore, particulates from ore and those re-suspended from bottom sediment and marine organic matter would be important components of SPM. Despite Rb/Sr ratios maintaining more or less similar values along transect (Table 2), the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio decreased sharply at mid station (Z4) and this decrease coincides with high SPM and marine organic carbon, suggesting that dilution due to particulates and, adsorption of ^{86}Sr onto organic matter may have depleted the Sr ratio. Similarly, the Sm/Nd ratios, ϵNd values and SPM concentrations showed no significant change at river end and sea end stations of the Zuari estuary, but high ϵNd value at mid-station (Z4) is associated with high SPM, ΣREE and Fe indicating that the radiogenic Nd may be due to the fine-grained particulates re-suspended from bottom sediment and ore material.

(iv) Synthesis of discussion on clay minerals and Sr-Nd isotopes in SPM: Abundant kaolinite with gibbsite and highest Sr ratios corresponding with high kaolinite percentages at river end stations suggest intense chemical weathering of laterites. Decrease of kaolinite with increasing smectite seaward is characteristic of both estuaries despite significant variations in river discharges during monsoon and pre-monsoon. This suggests lithology of the coastal plains and estuarine turbidity played major roles in the distribution of clay minerals in SPM. The sharp decrease in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios at the mixing zone indicates that the flocculation and precipitation processes probably favoured strong sorption of dissolved ^{86}Sr affected the Sr ratio. Changes in the proportions of clay minerals along transect contributed little to the ϵNd of SPM. However, very high Fe (9-16%; Fig. 4) and (high) Sm/Nd ratios and REE patterns similar to that of iron ore indicate REE contribution from ore material affected ϵNd of SPM in both estuaries. The iron ore material spilled over into the estuaries mostly because of anthropogenic activities at shore stations and during transport of ore through the estuary throughout the year. Therefore, the ϵNd of SPM is controlled both by lateritic weathering and ore material that introduced into the estuaries because of human activities at the shore.

D. Clay minerals and Sr-Nd isotopes in bottom sediments

Clay minerals are similar in SPM and sediments of both estuaries. Smectite contents are consistently low in sediments at the river end stations even if the total clay (< 4 μm fraction) content of sediment is high (see M7 and Z8 stations in Figs. 6 and 7). High smectite content is associated with high clay content in sediments at sea end stations of both estuaries. Moreover, smectite content is low in

sediments with low clay as well as with high clay content (Figs. 6 and 7; Table 1). These indicate that the smectite distribution is unaffected by total clay content of the sediment. As explained for SPM, smectite is a product of sediments in coastal plains and transported into the estuaries during monsoon.

The sediments at Z3 and Z4 stations are associated with high clay, smectite and OM (Fig. 7). Since finer grain size and high OM contribute to the cohesiveness of sediment, the clay minerals once settled at the bottom may prevent their erosion and transportation due to its cohesive nature. Innocent et al. (1997) suggested that the fine fraction ($< 10 \mu\text{m}$) behaves cohesively in seawater and cannot be winnowed easily by currents after deposition. More clay ($< 4 \mu\text{m}$ fraction) and more smectite at different stations in Zuari estuary than in Mandovi (Table 1) may be because the coastal plains of Zuari have a larger river basin. In view of low river discharge into the Zuari estuary (because of the dam in upper reaches) fine-grained clay and smectite from coastal plains contributed abundantly to the lower estuary of Zuari. While in the case of Mandovi, the sediments from uplands dominated the estuary because of high river discharge and smaller river basin in coastal plains and therefore less smectite.

Variations in Rb/Sr ratios along transect follow that of Mg, Al and total clay content of sediments in the Mandovi and, Al and smectite contents of sediments in Zuari estuary (Fig. 8). The preferential adsorption of Rb onto clays explains the relationship of Rb/Sr ratios with detrital clays. As in SPM, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of sediments decrease sharply seaward. Since depleted $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are associated with low clay / low smectite content (stations M4 and Z4) as well as high clay / high smectite content (stations M1 and Z1), flocculation and aggregation in response to salinity, organic matter and turbidity played important roles for decreasing Sr ratios along transect rather than total clay or smectite content.

The variations in Sm/Nd, $\epsilon\text{Nd}(0)$ and ΣREE in sediments along transect of Mandovi estuary are marginal implying that there is no change in provenance. As variations in Sr and Nd isotope ratios of sediments resemble that of SPM along transect, processes and factors explained for their variations in SPM work even for sediments. Lower Fe content and Sm/Nd ratios in Zuari estuary than that of Mandovi estuary (Fig. 8; Table 2) may be due to the fact that more ore is being transported through the Mandovi estuary and therefore more ore material to the sediments. The $\epsilon\text{Nd}(0)$ of sediments, however, are remarkably similar from river end to sea end stations of the estuaries. Unlike SPM, which represent contemporary processes, the bottom sediments in estuaries may reflect cumulative processes over a period of time, modified by physico-chemical conditions. Greater uniformity in Nd isotopes of sediment along transect of both estuaries indicates (a) the provenance of sediments is similar, (b) variations in total clay or clay minerals along transect have not influenced their isotopic ratios and (c) repeated re-suspension of bottom sediments due to consistent turbidity maximum in both estuaries may have triggered uniformity in their ratios. The dominant factors that determined the Nd isotopic composition

are most probably lateritic soils from the hinterland and iron dust transported into the estuary from time to time. The geomorphology of the river basins in coastal plains simply affected the clay minerals, but laterites in the hinterland and man-made (mining and transport) activities along the estuary largely affected the Sr-Nd isotopes.

High $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the shelf sediments (Table 2) could be due to the fine-grained particulates transported to the shelf and, high isotopic ratios usually coincide with finer particulates. The more radiogenic ϵNd (0) in sediment at 54 m depth on the shelf could be due to admixture of different sources of clays, i.e., clay transported from basalts and from Pre-Cambrian gneisses in the shelf region.

Synthesis of discussion on clay minerals and Sr-Nd isotopes in sediments: Distribution of clay minerals in sediments along transect is same as that of SPM in both estuaries. More clay ($< 4 \mu\text{m}$) content and higher proportions of clay minerals in the sediments of Zuari estuary than in Mandovi may be due to the existence of larger drainage basin in coastal plains of Zuari, which in turn transported more fine sediment into the lower estuary. The Sr ratios of sediments are much lower than in SPM at each station. As bottom sediments represent sediment accumulation over a period of time it is likely that flocculation and aggregation processes allowed to sorb more dissolved ^{86}Sr onto settling particulates that reduced the Sr ratios of bottom sediments. High Fe, ΣREE and Sm/Nd ratios, and uniform ϵNd of sediments along transect suggest strong iron ore contribution because of anthropogenic activity during mining and transportation of ore to the port modified the ϵNd of sediments. We therefore suggest that the drainage basin of rivers in coastal plains, lateritic weathering and anthropogenic iron ore determined the sources of clay minerals and Sr-Nd of the particulates, whereas the estuarine processes determined their distribution.

Conclusions

- Kaolinite and illite followed by minor gibbsite, goethite and chlorite in SPM and sediment of Ma-Zu estuaries in both seasons suggest that these are the intense chemical weathering products of laterites in the hinterland.
- Traces of smectite in SPM and sediment at river end stations and its seaward increase in both estuaries suggest that smectite may have formed in coastal plains. Smectite distribution is controlled by the lithology and drainage basin of the rivers in coastal plains.
- High $^{87}\text{Sr}/^{86}\text{Sr}$ ratios at river end stations of both estuaries indicate intense chemical weathering of laterites. The seaward decrease of Sr isotopic ratio may be due to changes in salinity, organic matter and total SPM concentrations.

- High ϵNd and near uniform values of ϵNd along transect stations of both estuaries indicate the influence of lateritic weathering and anthropogenic contribution of ore material to the SPM and bottom sediments of both estuaries.

Acknowledgments

Shynu thanks CSIR, New Delhi for awarding research fellowship. This is NIO contribution

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Figure captions

- Fig. 1. (A). Location of the samples in the Mandovi and Zuari estuaries. Approximate locations of the shelf samples are given in the insert figure. (B) Photograph showing laterite profile developed on bed rock (after Mascarnenhas and Kalavampara, 2009); (C) Photograph showing iron ore deposit on the shore of the estuary.
- Fig. 2. X-ray diffractograms of SPM collected at the regular station during peak monsoon (A), transect stations during monsoon (B), and pre-monsoon (C) from the Mandovi estuary. M1 - M7 are sampling stations. SPM concentrations (mg/l) and salinity at each station are also shown in brackets. S-smectite, K-kaolinite, Ch-chlorite, I-illite, Gi-gibbsite, Go-goethite.
- Fig. 3. X-ray diffractograms of SPM collected at the regular station during peak monsoon (A), transect stations during monsoon (B), and pre-monsoon (C) from the Zuari estuary. Z0 - Z9 are sampling stations. SPM concentrations (mg/l) and salinity at each station are also shown in brackets. S-smectite, K-kaolinite, Ch-chlorite, I-illite, Gi-gibbsite, Go-goethite
- Fig. 4. Variations in the mean salinity, SPM, smectite content, Mg and Fe content, organic matter (OM) content, REE content and Rb/Sr, $^{87}\text{Sr}/^{86}\text{Sr}$, Sm/Nd and $\epsilon\text{Nd}(0)$ along transect stations of the Mandovi (A) and Zuari (B) estuaries during monsoon.
- Fig. 5. The plot of $^{87}\text{Sr}/^{86}\text{Sr}$ ratio versus $\epsilon\text{Nd}(0)$ of the suspended matter and bottom sediment in the Mandovi-Zuari estuaries and adjacent shelf (present study). Published values on the Sr and Nd isotopes of Deccan Basalts, laterites developed on gneisses from Mangalore region, peninsular gneiss/granites, metabasalt, sediment from the Netravathi and Periyar Rivers are also shown.
- Fig. 6. X-ray diffractograms of sediments collected along transect stations of the Mandovi estuary during monsoon (A) and pre-monsoon (B). M1 - M7 are sampling stations. Clay fraction ($<4\ \mu\text{m}$) of sediment (%) is also shown in brackets. S-smectite, K-kaolinite, Ch-chlorite, I-illite, Gi-gibbsite, Go-goethite.
- Fig. 7. X-ray diffractograms of the sediments collected along transect stations of the Zuari estuary during monsoon (A) and pre-monsoon (B). Z0 - Z9 are sampling stations. Percentage of clay fraction ($<4\ \mu\text{m}$) of sediment is also shown in brackets. S-smectite, K-kaolinite, Ch-chlorite, I-illite, Gi-gibbsite, Go-goethite.
- Fig. 8. Variations in $^{87}\text{Sr}/^{86}\text{Sr}$ and $\epsilon\text{Nd}(0)$ of surface sediment with other parameters such as clay ($<4\ \mu\text{m}$), smectite, Al, Fe, Mg, ΣREE and OM content of sediments along transect stations of the Mandovi estuary (A) and Zuari (B) estuaries during monsoon.

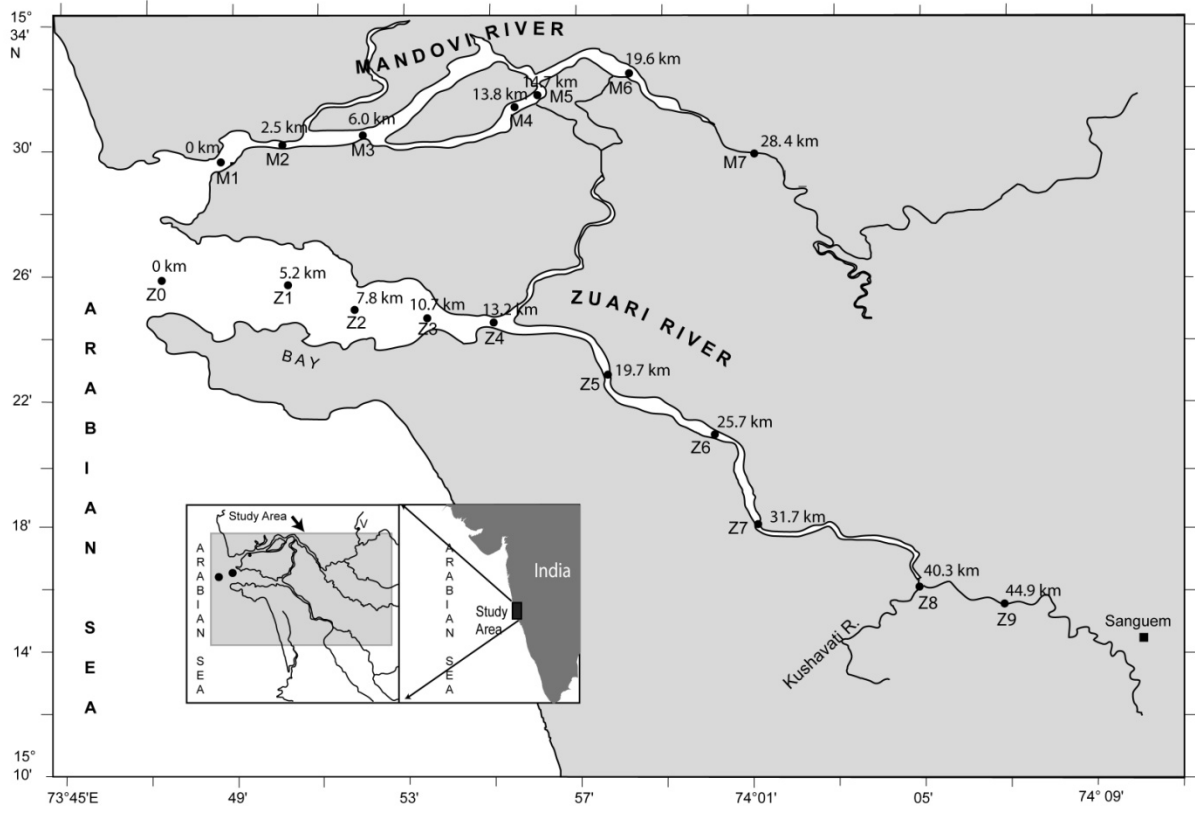


Fig. 1A



Fig. 1B



Fig. 1C

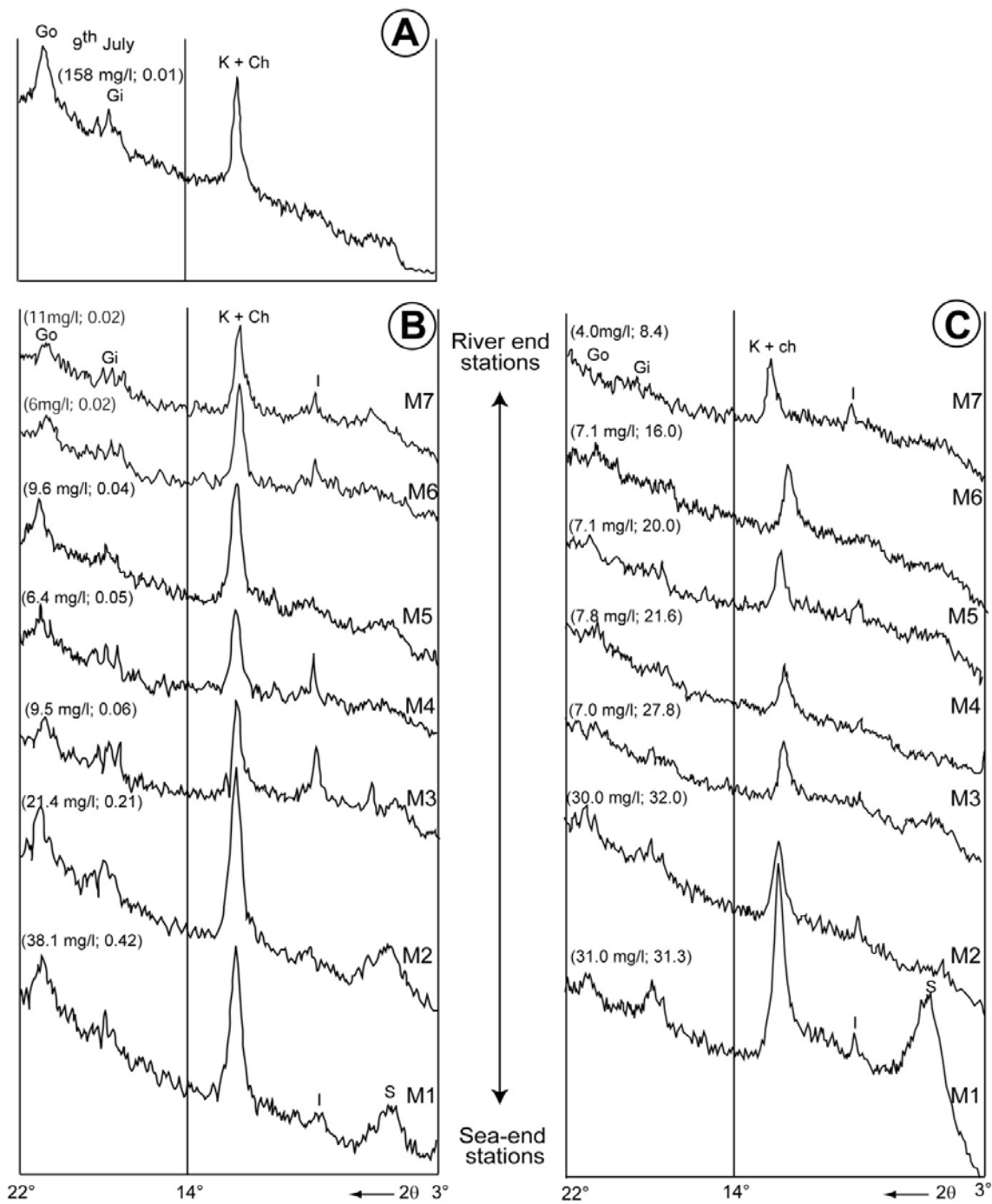


Fig. 2

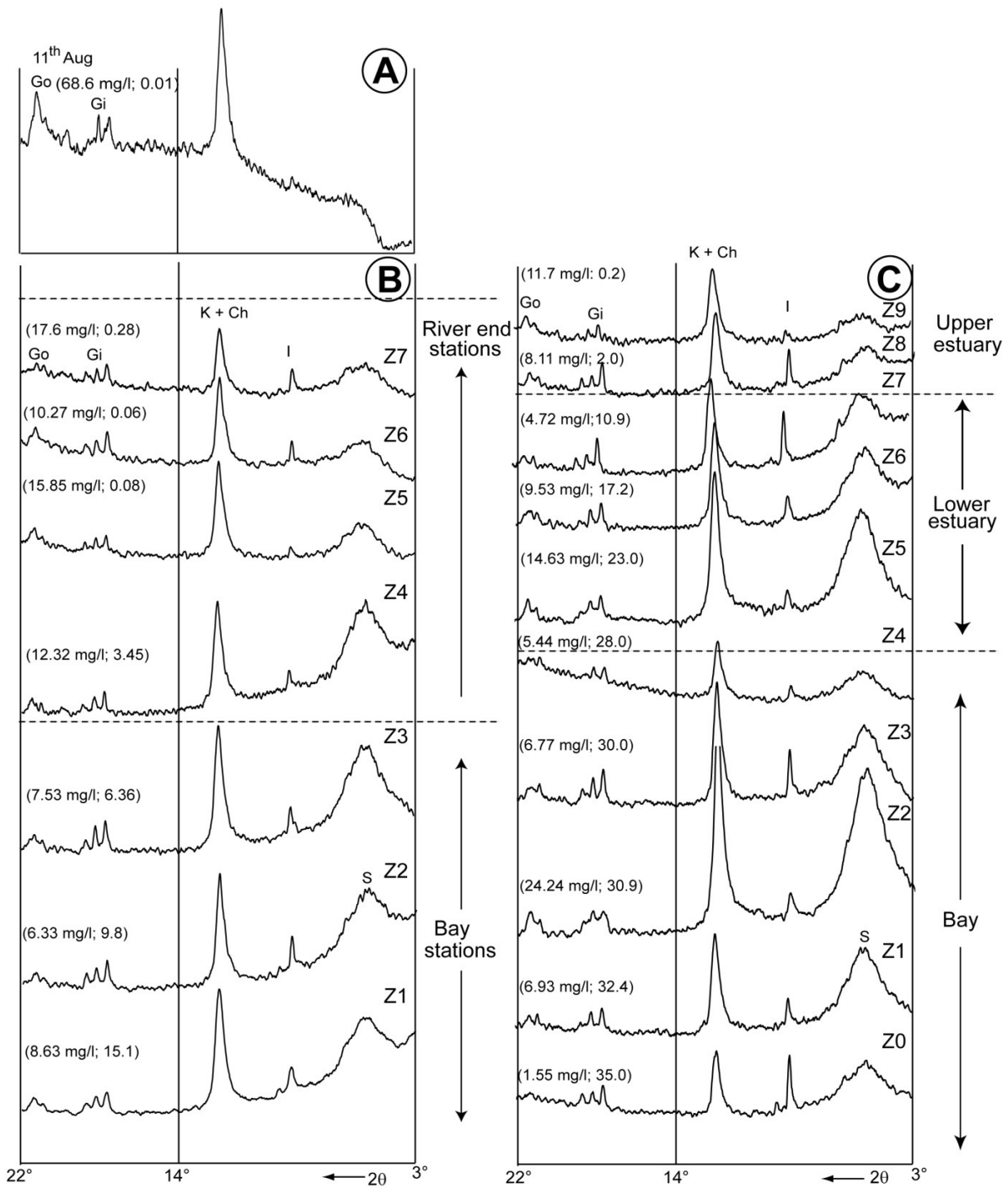


Fig. 3

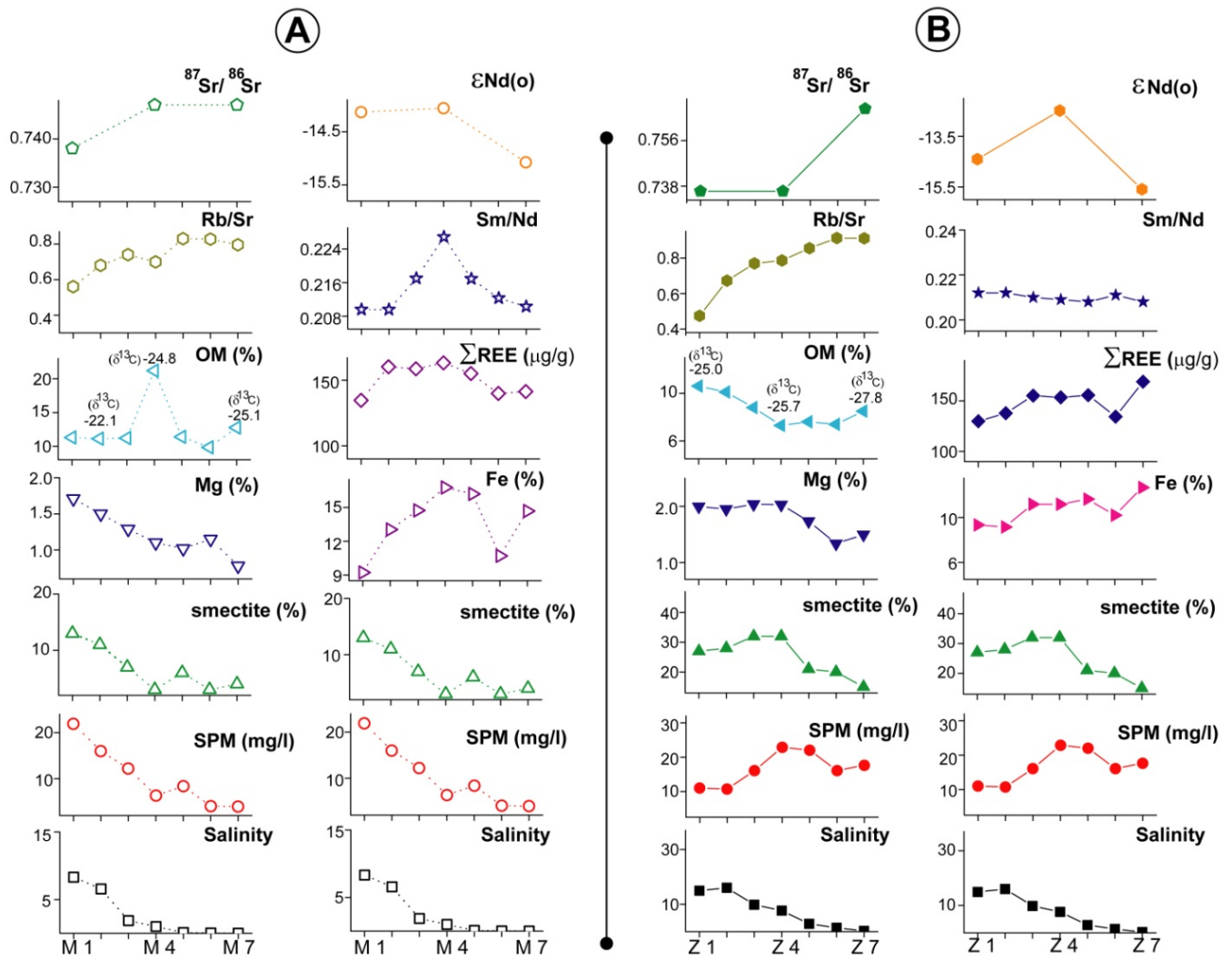
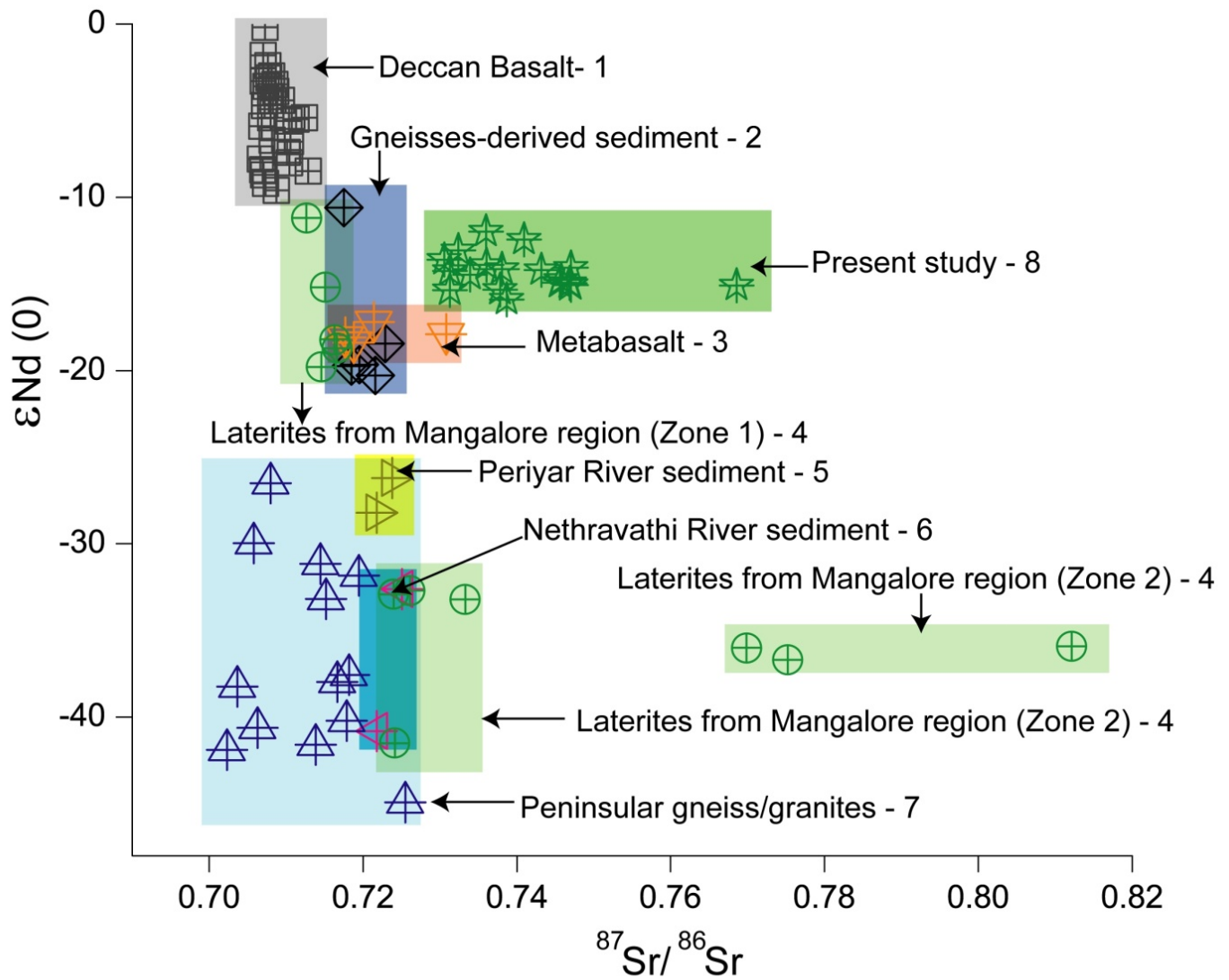


Fig. 4



1- Deccan Basalt (Peng et al., 1994); 2- Gneisses-derived sediment from off-shore (Kessarkar et al., 2003); 3- Metabasalt (Deepthy, 2008); 4- Laterites from Mangalore region zone 1 and zone 2 (Deepthy, 2008); 5- Periyar River sediment (Vineet et al., 2012); 6- Nethravathi River sediment (Vineet et al., 2012); 7- Peninsular gneisses/granites (Pauca et al., 1989); 8- Present study.

Fig. 5

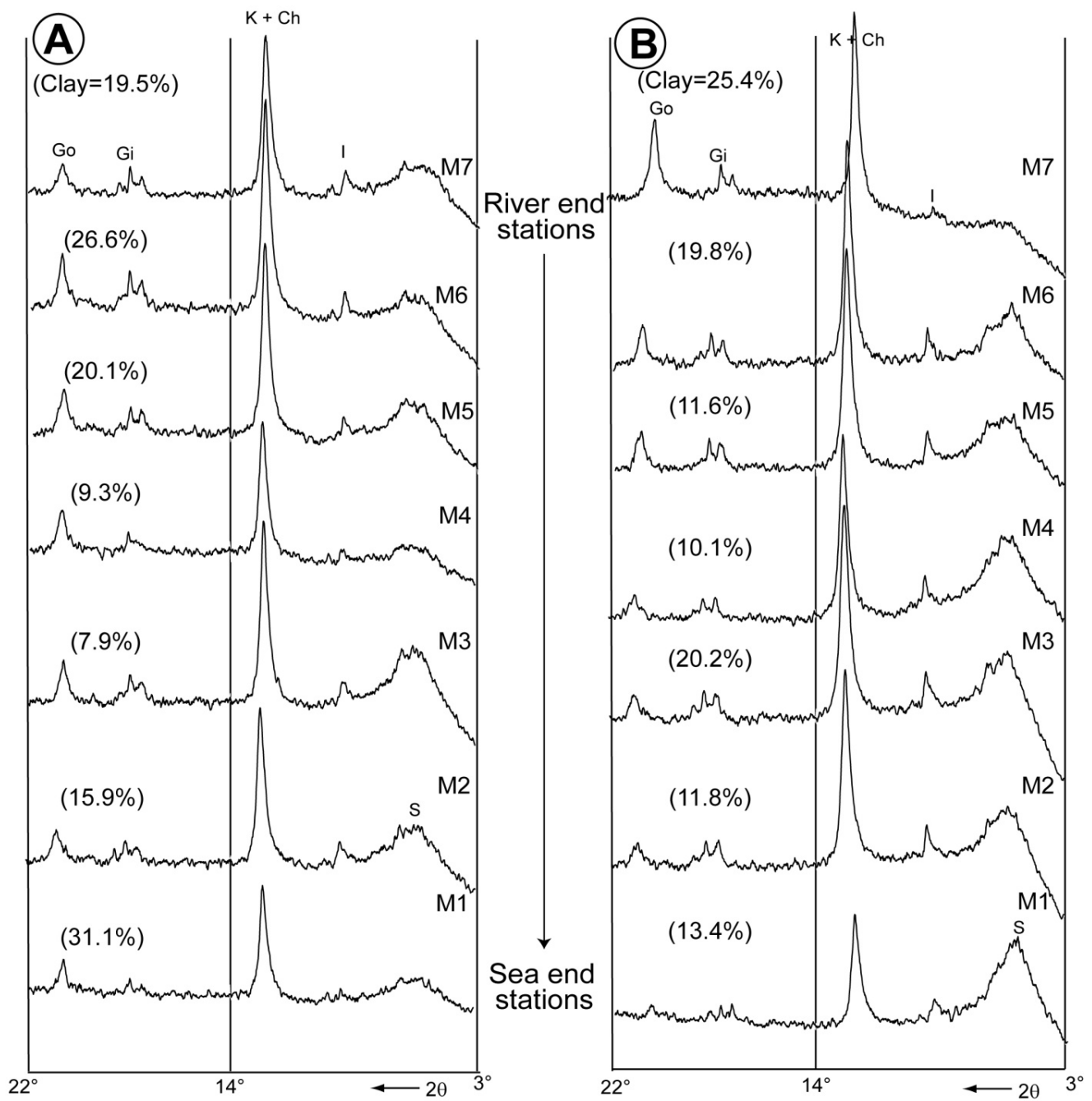


Fig. 6

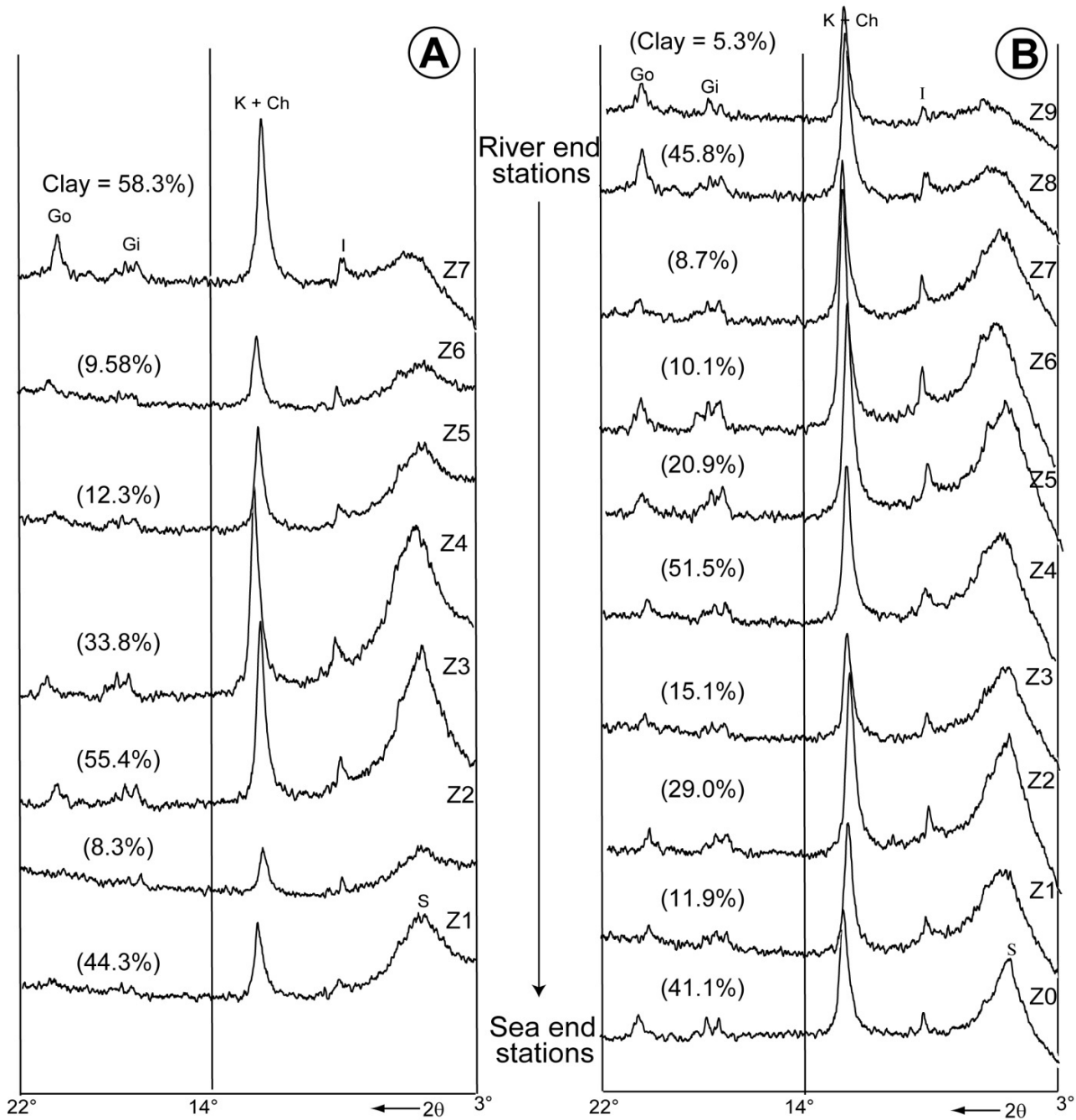


Fig. 7

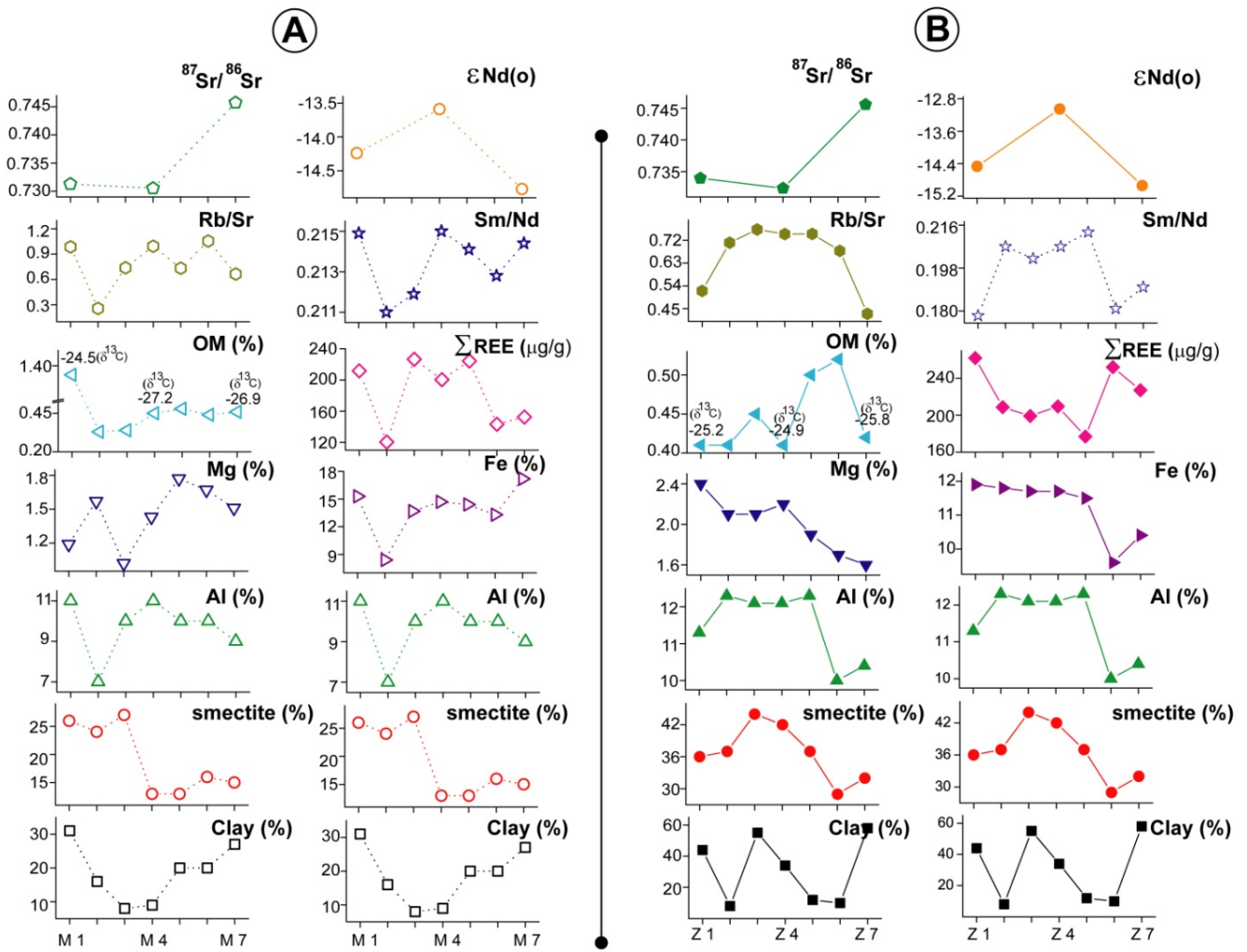


Fig. 8

Table 2 Isotope (Sr-Nd) chemistry of the SPM during monsoon and pre-monsoon and sediment during monsoon at transect stations of the Mandovi and Zuari estuaries.

Stations	Rb/Sr	⁸⁷ Sr/ ⁸⁶ Sr	S.E. σ _μ (%)	ΣREE	Sm/Nd	¹⁴³ Nd/ ¹⁴⁴ Nd	S.E. σ _μ (%)	εNd	S.E. σ _μ (%)	Remarks	
Monsoon SPM											
M1	0.56 ± 0.13	0.7381 ± 0.0011		134.6 ± 58.5	0.210 ± 0.005	0.51191 ± 0.0027		-14.13 ± 0.2668			
M4	0.70 ± 0.18	0.7470 ± 0.001		163.0 ± 29.2	0.227 ± 0.008	0.51192 ± 0.0016		-14.06 ± 0.1638			
M7	0.83 ± 0.09	0.7470 ± 0.001		155.0 ± 27.4	0.217 ± 0.003	0.51187 ± 0.0014		-15.07 ± 0.1424			
Z1	0.47 ± 0.23	0.7360 ± 0.0011		129.9 ± 12.9	0.212 ± 0.004	0.51193 ± 0.0017		-13.90 ± 0.1735			
Z4	0.79 ± 0.08	0.7360 ± 0.0012		153.4 ± 8.1	0.209 ± 0.002	0.51202 ± 0.0026		-11.98 ± 0.2612			
Z7	0.91	0.7686 ± 0.0016		168.9	0.208	0.51186 ± 0.0014		-15.09 ± 0.1440			
Pre-monsoon SPM											
M1	0.37 ± 0.05	NA		127.6 ± 12.7	0.209 ± 0.003	NA		NA			
M4	0.37 ± 0.14	0.7313 ± 0.0011		114.8 ± 30.4	0.210 ± 0.004	0.51185 ± 0.0026		-15.37 ± 0.2590			
M7	0.22 ± 0.09	NA		83.7 ± 42.6	0.212 ± 0.004	NA		NA			
Z1	0.48 ± 0.08	0.7387 ± 0.0011		137.2 ± 21.6	0.215 ± 0.002	0.51182 ± 0.0038		-15.91 ± 0.3830			
Z4	0.60 ± 0.01	0.7432 ± 0.001		151.0 ± 14.9	0.210 ± 0.005	0.51191 ± 0.002		-14.20 ± 0.1947			
Z7	0.57 ± 0.09	0.7469 ± 0.0027		175.2 ± 26.7	0.208 ± 0.003	0.51187 ± 0.0037		-14.96 ± 0.3671			
Monsoon Sediments											
M1	0.99 ± 0.08	0.7313 ± 0.0008		211.7 ± 3.9	0.215 ± 0.005	0.51191 ± 0.0023		-14.24 ± 0.2263			
M4	0.99 ± 0.08	0.7305 ± 0.0008		200.3 ± 28.4	0.215 ± 0.005	0.51194 ± 0.0013		-13.59 ± 0.1343			
M7	0.73 ± 0.45	0.7457 ± 0.0006		224.3 ± 97.5	0.215 ± 0.005	0.51188 ± 0.0015		-14.77 ± 0.1465			
Z1	0.52 ± 0.1	0.7339 ± 0.0007		262.0 ± 101.5	0.178 ± 0.002	0.51190 ± 0.0022		-14.47 ± 0.2160			
Z4	0.74 ± 0.16	0.7324 ± 0.0007		209.6 ± 1.2	0.207 ± 0.007	0.51197 ± 0.0022		-13.05 ± 0.2178			
Z7	0.68 ± 0.21	0.7456 ± 0.0006		252.2 ± 146.2	0.181 ± 0.004	0.51187 ± 0.0016		-14.94 ± 0.1573			
Off-shore sediments											
18 m	0.40	0.7378 ± 0.0016		169.8	0.215	0.51185 ± 0.0034		-15.32 ± 0.3420			
54 m	0.22	0.7409 ± 0.0012		131.1	0.217	0.51200 ± 0.0028		-12.45 ± 0.2803			
Laterite (Zone 1)	0.672	0.7150			0.155	0.51179		-16.62	Deepthy, 2008		
Laterite (Zone 2)	1.198	0.7521			0.184	0.51082		-35.56	Deepthy, 2008		
Granitic gneisses	0.166	0.7196			0.114	0.51058		-40.17	Paucat et al., 1989		
Charnockites	0.054	0.7080			0.143	0.51085		-34.88	Paucat et al., 1989		
UCC	0.281	0.7160			0.190			-17.00	Goldstein et al., 1988		

NA-Not analysed UCC- Upper continental crust S.E. σ_μ Standard error on the measurements (internal precision).