

Minor and rare earth elements as paleoenvironmental markers of late quaternary sediments in Marajo Island, Northern Brazil

Dilce de Fátima Rossetti¹*
Casimiro Sepúlveda Munita²
Paulo Meira Silva Oliveira²

¹Instituto Nacional de Pesquisas Espaciais-INPE,
Rua dos Astronautas 1758
CP 515, 12245-970
São José dos Campos-SP, Brazil
rossetti@dsr.inpe.br

²Instituto de Pesquisas Energéticas Nucleares - IPEN - CNEN/SP,
Av. Prof. Lineu Prestes 2242,
05508-000, São Paulo, SP, Brazil

Abstract

The recognition of estuarine deposits in the ancient record is problematic if based only on sedimentological studies due to the difficult assessment of both sedimentary processes and body geometry, particularly where only cores are available. Exploring proxies that can be used in combination with sedimentary parameters can improve the reconstruction of estuarine systems in the geological record. Geochemical tracers have good potential as paleoenvironmental proxies. However, additional studies are needed to further demonstrate their application for discriminating various estuarine environments. This approach was applied to a late Quaternary estuarine succession in northern Brazil. Multivariate analysis of trace and rare earth elements allowed distinguish five geochemical groups in agreement with previous interpretations of depositional environments consisting of fluvial, outer estuary, central estuarine basin, tidal flat, and lagoon. Statistical analyses allowed a clear distinction between fluvial-influenced and marine-influenced deposits. The distribution of geochemical tracers had strong effect of variations in salinity and pH that typify these depositional environments, though some of the changes also might be related to other processes, such as adsorption due to the influence of colloidal material, mineralogical influence, airborne deposition, and burrowing. The results lead to suggest that trace and rare earth elements are useful tools to distinguish depositional environments associated with ancient estuarine systems.

Keywords: estuary, geochemical proxies, paleoenvironments.

1. Introduction

The volume of publications aiming the recognition of estuarine deposits in the ancient record has progressively increased in these last decades (e.g., Shanley *et al.* 1992, Anderson *et al.* 1996, Miall & Arush 2001, Wellner & Bartek 2003). This is mostly due to their occurrence within incised valleys, which are depositional systems of great interest for hydrocarbon exploration (Zaitlin & Shultz 1984, 1990, Dalrymple *et al.* 1992), as well as for studies emphasizing sea level (e.g., several papers in Dalrymple *et al.* 1994, Blum & Törnqvist 2000), climate and tectonic reconstructions (e.g., Schumm *et al.* 1987, Blum & Price 1998, Ardies *et al.* 2002, Lukie *et al.* 2002, Zaitlin *et al.* 2002, Carr *et al.* 2003).

Due to the fact that estuaries are elongated, semi-enclosed water bodies with mixed fluvial and marine processes (Boyd *et al.* 2006), their recognition in the geological record is difficult due to rapid lateral and vertical changes in sedimentary facies characteristics. This problem is particularly enhanced where only core data are available, when the determination of lateral facies relationships is difficult. Taking this in account, it is important to analyze estuarine deposits with basis on different approaches to help interpreting the various environments within this system.

The complex interplay of fluvial and marine contributions into estuaries controls geochemical characteristics of sediments in a predictable way. This is due to changes in pH, redox, and adsorption/desorption reactions in the water system, which might be associated with variation in depositional conditions, as well as discharge provenance and weathering (Nath *et al.* 2000). Geochemical analyses of trace elements (TE) and rare earth elements (REE) of fine-grained particles are potentially useful for helping distinguishing among various depositional

environments associated with estuarine settings, improving their recognition in the ancient record. This is because many of these elements, in particular the REE, are regarded as generally immobile during weathering, transport, and sedimentation (e.g. McLennan 1989), though fractionation due to diagenesis (Milodowski & Zalasiewicz 1991, Ohr *et al.* 1991, Bock *et al.* 1994) and weathering (Nesbitt 1979, Banfield & Eggleton 1989, McDaniel *et al.* 1994, Hannigan & Sholkovitz 2001) has been also documented.

Most of elemental analyses undertaken on estuaries have emphasized dissolved and particulate phases (e.g., Goldstein & Jacobsen 1988, Sholkovitz & Elderfield 1988, Sholkovitz 1992). A number of studies have also undertaken analysis of TE in estuarine and adjacent marine and fluvial sediments (e.g., Zhu *et al.* 1997, Nozaki *et al.* 2000, Singh & Rajamani 2001, Borrego *et al.* 2004, López-González *et al.* 2006, Dubrulle *et al.* 2007).

The present work contains the results of geochemical analysis of TE and REE from a sedimentary succession formed during the late Quaternary at the mouth of Amazon River, northern Brazil. An estuarine interpretation is well constrained for these deposits with basis on an integrated approach consisting of geomorphological characterization of remote sensing imagery, sedimentary facies analysis, and carbon and nitrogen isotopic data derived from organic matter preserved on sediments (Miranda *et al.* 2009). Our focus now is to determine if the elements analyzed herein could be used as markers for characterizing the various estuarine depositional paleoenvironments previously interpreted in this study area, verifying their potential for the interpretation of estuarine environments in the ancient record.

2. Geological background

The study area is located in the western margin of Arari Lake, eastern Marajó Island, at the mouth of Amazon River, Brazil (Fig. 1). An increasing volume of publication was presented in these last years concerning the paleoenvironmental reconstruction of Quaternary deposits in this region. This is because this area contains the best core data of Quaternary strata from the Brazilian Amazonia, where other type of information is problematic due to the overall scarcity of natural geological exposures. The study area is located in a poorly-known geological setting referred as the Pará Platform, a structure bounded by the Marajó Graben System to the northwest and southwest, and the Pará-Maranhão Basin to the southeast. The origin of the Marajó Graben System is due to crustal stretching associated with the opening of the South Atlantic Ocean, initiated in the Jurassic-Cretaceous boundary.

Rather than a tectonically stable area among sedimentary basins, the Pará Platform displays small, but deep, tectonic troughs with still poorly-known sedimentary fills. Adjacent areas of the Marajó Graben System contain siliciclastic deposits of the Breves/Jacarezinho (Aptian-Cenomanian), Anajás (early Cretaceous), and Limoeiro (late Cretaceous) Formations, which formed in depositional settings ranging from alluvial fan, fluvial to shallow marine (Azevedo 1991). These deposits are overlain by a shallow

marine, mixed siliclastic-carbonatic unit related to the Marajó Formation (Paleocene-Eocene), and a fluvial to transitional siliciclastic unit related to the Tucunaré/Pirarucu Formations (Quaternary) (Azevedo 1991). In surface, there are late Cenozoic, mostly estuarine sandy and muddy deposits of the Barreiras Formation and Post-Barreiras Sediments (Rossetti 2004).

The Post-Barreiras Sediments around the Arari Lake occur within an elongate, funnel-shaped morphology up to 25 km wide and 50 km long (Fig. 2), which records an estuarine system that became abandoned in the Marajó landscape during the Holocene, previously to the lake establishment (Rossetti *et al.* 2007, Rossetti *et al.* 2008 a,b). A 124 m-thick continuous core recording these estuarine deposits revealed six facies associations (Tab. 1), including: facies association A (fluvial channel), facies association B (outer estuary), facies association C (central estuarine basin), facies association D (tidal flat), facies association E (estuarine channel), and facies association F (lagoon) (Miranda *et al.* 2009). Interpretation of depositional environments was based on a detailed study integrating facies analysis, $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, and C/N, already published elsewhere (see details on the paleoenvironmental interpretation in Miranda *et al.* 2009). Therefore, only a summary of the main facies characteristics is presented in Table 1.

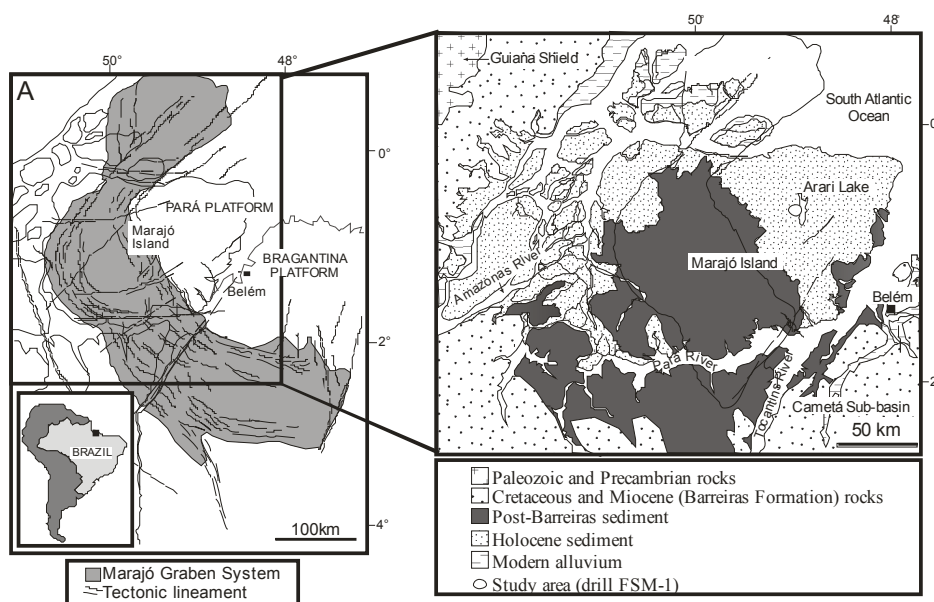


Fig. 1

A) Location of the study area in eastern Marajó Basin, Pará Platform, northern Brazil. Note the studied well at the western margin of Arari Lake.

B) Simplified chart summarizing the stratigraphy of the study area. (A and C, modified from Villegas 1994; B modified from Rossetti & Valeriano 2007).

Age		Lithostratigraphy				
		Subsurface	Surface			
CRETACEOUS	Late	Maastrichtian	Pirarucu/Tucunaré Formations	Post-Barreiras Sediments		
					Tertiary	Marajó Formation
		Campanian	Limoeiro Formation			
				Santonian		
	Early	Albian	Breves/Jacarezinho Formations			
				Cenomanian	Anajás Formation	
						Aptian

3. Methods

3.1. Sampling

The TE and REE analyses were carried out on a total of 113 samples of mud and streaky and lenticular heterolithic deposits derived from continuous core acquired with a LONGYAR 40 rotating drilling system. The samples were collected aiming to record the various facies association described above. Only facies association E was not analyzed,

because its dominantly sandy nature was not of interest to run the present geochemical analyses. Samples were collected at different stratigraphic horizons up to a depth of 120 m. The precise coordinate sampling point was determined during the sampling by using a GPS device. Figure 2 shows sampling location.

3.2. Analytical procedures

The samples were prepared by manually grinding them into an agate mortar and pestle until a thin enough grain size was obtained. The grounded samples were then sieved using a 100 mesh sieve. The sieved parcels were dried in an oven for 24 h, at 105°C and stored in a desiccator.

The Constituent Elements in Coal Fly Ash (NIST-SRM-1633b), and the International Atomic Energy Agency – IAEA Soil 7 (Trace Elements in Soil) standards were used to check the samples throughout the analysis. These standards were dried in an oven for 2 h at 105°C, and stored in a desiccator. About 120 mg of soil samples, one standard (NIST-SRM-1633b), and one IAEA-Soil 7 were weighted in polyethylene bags and wrapped

in aluminum foil. Groups of 10 samples and one reference material were packed in aluminum foil. These were irradiated in the research reactor's pool IEA-R1 of the IPEN-CNEN/SP, Brazil. The analyses were performed with a thermal neutron flux of about $5 \times 10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$ for 8h.

Two measurement series were carried out, using a Ge (Hyperpure) detector, model GX 2519 from Canberra, with a resolution of 1.90 keV, 1332.49 keV gamma peak of ^{60}Co , and an S-100 MCA from Canberra. This contained 8,192 channels. Potassium, La, Lu, Na, Nd, Sm, U, and Yb were measured after 7 days cooling time, while Ce, Co, Cr, Cs, Eu, Fe, Hf, Rb, Sc, Ta, Th, and Zn after 25-30 days. Gamma ray spectra

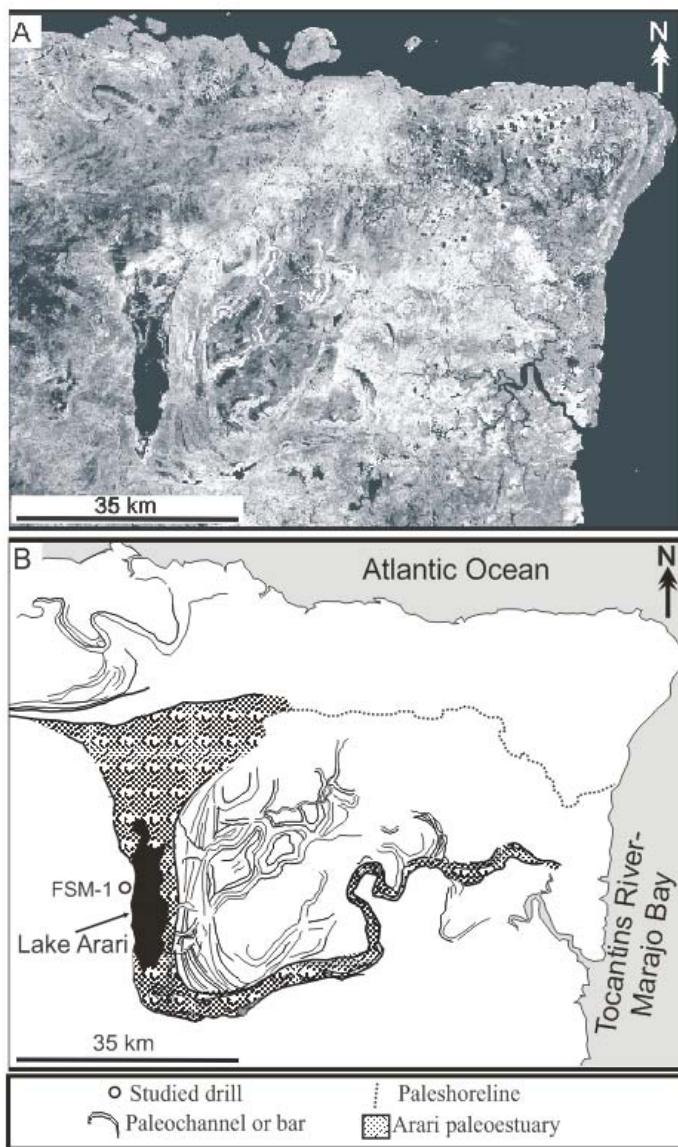


Fig. 2
 A) Landsat image.
 B) Drawing over the image illustrating the Arari paleoestuarine system in eastern Marajó Island. When this estuarine system was active, the paleoshoreline was located nearly 45 km southward of its modern position. Note that Arari Lake occurs inside the inner paleoestuary area, which is also surrounded by numerous paleochannels.

Facies Association	Interpreted Paleoenvironment	Description	Main Source of Organic Matter (interpreted from $\delta^{13}C$, $\delta^{15}N$ and C/N)
A	Fluvial Channel	Moderately sorted, fine- to coarse-grained, locally conglomeratic, massive sand (facies Sm), with only subordinate parallel laminated mud (facies Mp). These lithotypes are typically arranged into several fining upward cycles, which vary in thickness from 0.1 m to 8 m. The base of these cycles, sharp and usually erosive, is locally marked by mud intraclasts. A few mud intraclasts, as well as quartz granules, are dispersed within the sands, as are plant debris	Terrigenous origin, with organic carbon derived mainly from C ₃ vascular vegetation
B	Outer Estuarine Basin to shallow marine	Dominantly muddy, consisting mostly of parallel mud and streaky heterolithic bedded deposits (facies Mp/Hs). Interbedded with numerous packages of lenticular and wavy to flaser heterolithic deposits, corresponding to facies Hl and Hw/f, respectively. The sandier heterolithic packages vary from 0.2 m to 2 m thick, and grade upward from facies Mp/Hs, forming coarsening upward successions. Thicker sand layers locally display combined flow cross lamination. Plant debris is dispersed throughout this facies association, as are mud intraclasts.	Terrestrial (both C ₃ and C ₄ plants), phytoplankton (marine and freshwater), and mixed organic matter sources
C	Inner Estuarine Basin	Facies characteristics as association B, though thinner (up to 10 m thick). Coarsening and fining upward cycles	Freshwater phytoplankton, as well as C ₃ and C ₄ vascular vegetation
D	Tidal flat	Lenticular and wavy to flaser heterolithic deposits (facies Hl and Hw/f), which are locally interbedded with packages of massive sands (facies Sm) up to 1 m thick. These strata are typically intergraded, forming sharp based, fining upward cycles up to 4 m thick. Plant debris are locally present in this facies association	Marine or freshwater phytoplankton source, or even a mixture of both. Contributions of C ₃ and C ₄ land plants are also recorded
E	Estuarine Channel	Sharp-based unit up to 15 m thick, consisting of coarse- to fine-grained sand and, secondarily, heterolithic deposits arranged into fining and thinning upward cycles. Reactivation surfaces, mud drapes and mud clasts are abundant	C ₃ terrestrial plants, but with episodes of either marine phytoplankton or mixed marine and land plant inputs
F	Lagoon	An 18 m-thick unit located at the top of the studied section. Sandier at the base and muddier upward, and arranged into fining and coarsening upward cycles. Muddier cycles prevail upward in the section. Dispersed plant debris	Strong marine influence, except for a few intervals, where mixed marine and terrigenous sources are evident.

Tab. 1
 Summary of facies associations with the corresponding interpretation of the organic matter sources and paleoenvironments (After Miranda *et al.* 2009).

concentration analyses were carried out using the Genie-2000 Neutron Activation Analysis (INAA) from Canberra. The program calculates elemental concentrations by comparing

3.3. Statistical treatment of dataset

By means of INAA, it is possible to determine several elements simultaneously. The volume of data is considerable when a large number of samples is analyzed. Then, the associations between elements and samples are so complex that multivariate statistical methods are generally used to data handling and evaluating. In this paper, the dataset were studied by means of three multivariate statistical methods: cluster analysis (CA), discriminate analysis (DA), and principal component analysis (PCA).

Cluster analysis is a statistical technique for examining the relations between the samples that attempts to allocate the individual samples to groups. This is based on dissimilarity matrix, which calculates the distance between all pairs of samples being analyzed. This procedure distinguishes each group of samples from every other group. DA constructs a series of discriminate functions that maximize the differences between two or more groups. This is based on the assumption that pooled variance-covariance matrix is an accurate representation of the total variance and covariance. The transformation of dataset based on eigenvector methods is performed in PCA to determine the direction and magnitude of maximum variance in the dataset in hyperspace. The first principal component (PC) is a linear combination of the original variables, and it is

4. Results

The mean and standard deviations of TE, ME and REE from muds and sands representative of the five depositional groups analyzed in this study are given in Table 2. Individual groups correspond to the depositional facies associations A to D and F. The NASC values are also given in this table for comparison. Considering all the studied groups, the abundance patterns of TE and REE varies relative to the NASC values, being either higher, as for Ce, Eu, La, Lu, Nd, Sm, Th, and U, or lower, as for Co, Cr, and Ta. The major element K is also lower than the NASC value. The remaining elements (i.e., Cs, Hf, Na, Rb, Sc, Yb, and Zn) display variable values: Zn is higher in A, B and F, and lower in C and D; Hf is higher in A, C and D, and lower in B and F; Cs is higher in B and F, and lower in A, C and D; Na and Yb are, in general, higher, except in the A and F groups, respectively, where these values are lower than NASC; Rb is lower in all groups, except in B and F; and Sc is lower in A, C and D and higher in B and F. Zinc, Hf, Cs and Rb display the most significant gradients among the analyzed groups.

The elemental patterns normalized to NASC were plotted considering the minimum and maximum concentration for all samples (Fig. 3), and the mean concentration for each group (i.e., facies associations) representative of the individual depositional environments (Fig. 4). As expected, these data revealed elemental distribution with comparable patterns among the analyzed groups. In general, the values increase from left to right, which is consistent with TE and REE crustal distribution. A few elements, such as Rb, K, and Na are too low, and Nd too high; the reason for these anomalous values in the study area

integrated peak areas in the samples and standards. Analytical details and the precision attained with this analytical method have been published elsewhere (Munita *et al.* 2000).

oriented in the direction of maximum variance. The second PC is perpendicular to the first PC, and is calculated to lie in the direction of maximum remaining variance (e.g., Swan 1995).

All the chemical elements were measured and quantified (Munita *et al.* 2004) in order to make corrections before applying the method to real samples. The concentration of chemical elements measured in the IAEA Soil 7 reference material was statistically compared with certified values to evaluate the accuracy and precision of the analytical procedures. The elements, with an accurate and relative standard deviation (RSD) of less than 10%, were Co, Cr, Cs, Hf, Rb, Sc, Ta, U, Th, and Zn (TE); Fe, K, Na (Major Elements-ME); and La, Ce, Nd, Sm, Eu, Yb, and Lu (REE). Afterwards, these elements were analyzed in the investigated samples. In order to minimize the effect of variation in TR, ME, and REE due to their natural abundance in fine-grained sediments, the values were compared to those from a shale reference considered to be representative of the theoretical geochemical composition of particulate material exported to the ocean. This was made through normalization to NASC (North American Shale Composite), a procedure that has been applied when dealing with marine influenced deposits (Taylor & McLennan 1985).

needs further investigation. The graphics also show differences in behavior when individual elements are compared among the five studied groups (Fig. 4). Hence, depositional environments with higher salinity, corresponding to the B, D, and F groups, display higher concentrations in Cs, Rb, U, Sm, K, Na, Yb, Eu, and Sc, and lower concentration in Hf, Co, and Cr relatively to more continental influenced deposits (A and C groups). Cesium concentration peaks in the B and F groups (almost the double of NASC concentration), while Hf shows the lowest concentration in these facies associations. On the other hand, group A, and eventually C, contains higher concentration in Th, La, Ce, Nd, and Cr, and lower concentration in Cs, Rb, U, K, Na, and Yb relative to the more marine-influenced depositional environments. Among these elements, La, and Th have the highest peaks, while K and Na the lowest ones.

The dendrogram depicting the total samples for all groups (Fig. 5) revealed elemental concentrations forming two major clusters (I and II). Cluster designated as I encompasses all samples from the two depositional environments with higher continental influence. It includes all samples from group A, which form an individual smaller cluster (Ia), and all samples from group C plus two samples from group D, which are concentrated in a separate sub-cluster (Ib). The other major cluster (II) joins all samples representative of the depositional environments with higher marine influence. It comprises a larger set of samples representative of the B, D, and F groups, which similarly form two small clusters (IIa and IIb). In general, the largest sub-cluster (IIa) contains all samples from group B that are mixed with many samples from group F, and only one

*	Mean	S.D.	mean	S.D.	mean	S.D.	mean	S.D.	mean	S.D.	NASC
Co	120.10	13.29	106.29	4.65	100.38	17.89	86.77	8.79	103.00	9.00	66.70
Cr	113.28	14.94	88.51	11.10	94.90	15.16	68.06	8.72	83.06	9.20	124.50
Cs	5.24	0.84	10.94	1.10	4.77	1.11	6.15	1.45	9.64	1.41	5.16
Hf	9.10	2.37	4.88	0.60	9.99	2.61	11.66	3.84	6.59	1.86	6.3
Rb	64.30	36.80	143.78	19.70	93.15	20.35	100.94	18.83	134.45	24.38	125.00
Sc	14.64	1.90	18.42	0.58	14.91	2.98	12.89	1.98	17.06	1.80	14.90
Ta	1.34	0.19	1.29	0.15	1.35	0.22	1.41	0.20	1.47	0.23	1.12
U	2.82	0.22	3.94	0.40	3.73	0.45	3.76	0.43	3.67	0.40	2.66
Th	23.32	2.98	16.95	0.83	15.21	2.19	13.57	1.37	16.52	1.53	12.30
Zn	112.42	16.77	115.47	11.5	68.15	18.05	77.40	13.80	107.26	14.53	100
Fe	5.36	2.01	5.33	0.32	5.03	6.01	3.46	0.58	5.00	0.72	4.40
K	1.52	0.79	2.19	0.29	1.60	0.22	1.76	0.27	2.17	0.35	3.20
Na	0.05	0.04	0.65	0.13	0.26	0.06	0.68	0.06	0.84	0.10	0.75
Ce	120.10	13.29	106.29	4.65	100.38	17.89	86.77	8.79	103.88	9.80	66.70
Eu	1.66	0.17	1.84	0.1	1.66	0.32	1.49	0.14	1.79	0.15	1.18
La	62.18	7.62	55.58	2.08	51.13	8.91	45.66	4.57	54.16	4.70	31.10
Nd	49.50	7.32	48.37	17.60	38.06	9.49	35.21	9.04	45.73	10.42	27.40
Sm	9.02	0.95	9.69	0.32	8.52	1.47	7.96	0.76	9.37	0.76	5.59
Lu	0.48	0.04	0.59	0.04	0.58	0.06	0.62	0.06	0.61	0.04	0.46
Yb	2.88	16.77	115.47	11.50	68.15	18.05	77.40	13.80	107.26	14.53	100.00

* (All values= $\mu\text{g/g}$, except for the major elements Fe, K, Na(‰)); S.D.=standard deviation; NASC= North American Shale Composite (Taylor & McLennan 1985).

Tab. 2 Means and standard deviations (S.D.) of TE, ME, and REE representative of the five depositional groups analyzed in this study.

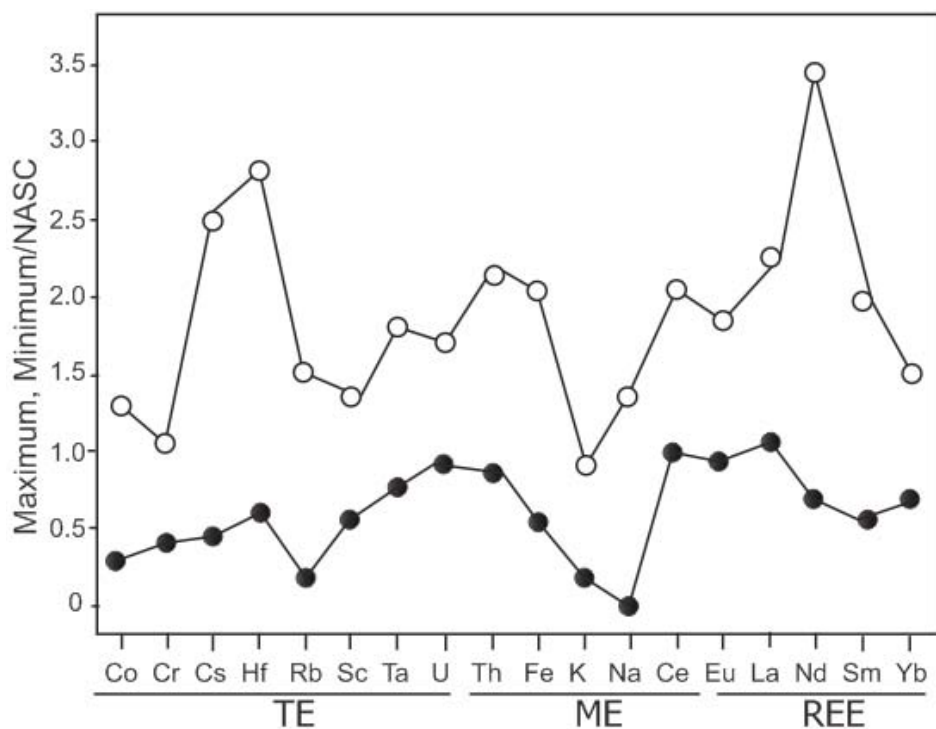


Fig. 3 TE, ME, and REE concentrations considering all groups (facies associations A, B, C, D, and F) of the study area, with data normalized to NASC composition.

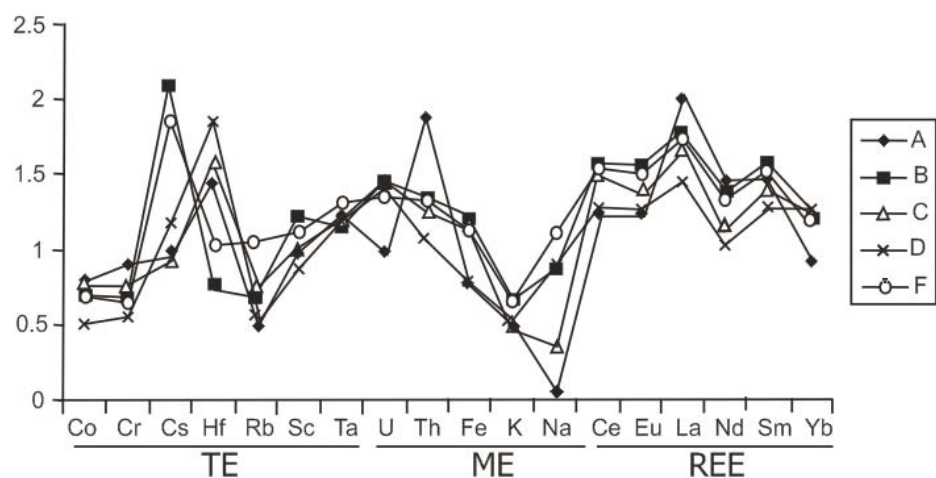


Fig. 4 Mean concentration of TE, ME, REE (normalized to NASC) for each group representative of the individual depositional environments. A=fluvial; B=outer estuary; C=central estuarine basin; D=tidal flat; F=lagoon.

sample from group D. The smaller sub-cluster (IIb) contains the bulk of samples from group D, as well as the remaining samples from group F.

Multivariate analysis consisting of discriminating functions (Fig.6) depicts the continental-influenced deposits organized into two clusters, with one including all samples from group A and another one with all samples from group C. All the other samples derived from marine-influenced deposits were

plotted together far from the A and C groups. Among these, samples from B and F groups are closely related, while samples from group D are roughly discriminated, though there are also several samples overlapping those of the B and F groups. Noteworthy is that group C, related to the central estuarine basin, is located half way between the fully continental (i.e., group A) and the outer estuarine, tidal flat, and lagoon deposits (group F).

Fig. 5

Dendrogram of the total samples for all groups of samples. Note that the samples are organized into two major clusters, each presenting two sub-clusters (Ia=total of samples from group A-fluvial; Ib=total of samples from group C-central estuarine basin, in addition to 2 samples from group D-tidal flat; IIa=group B-outer estuary+part of samples from group F-lagoon+one sample from group D-tidal flat; IIb=group D-tidal flat+group F-lagoon).

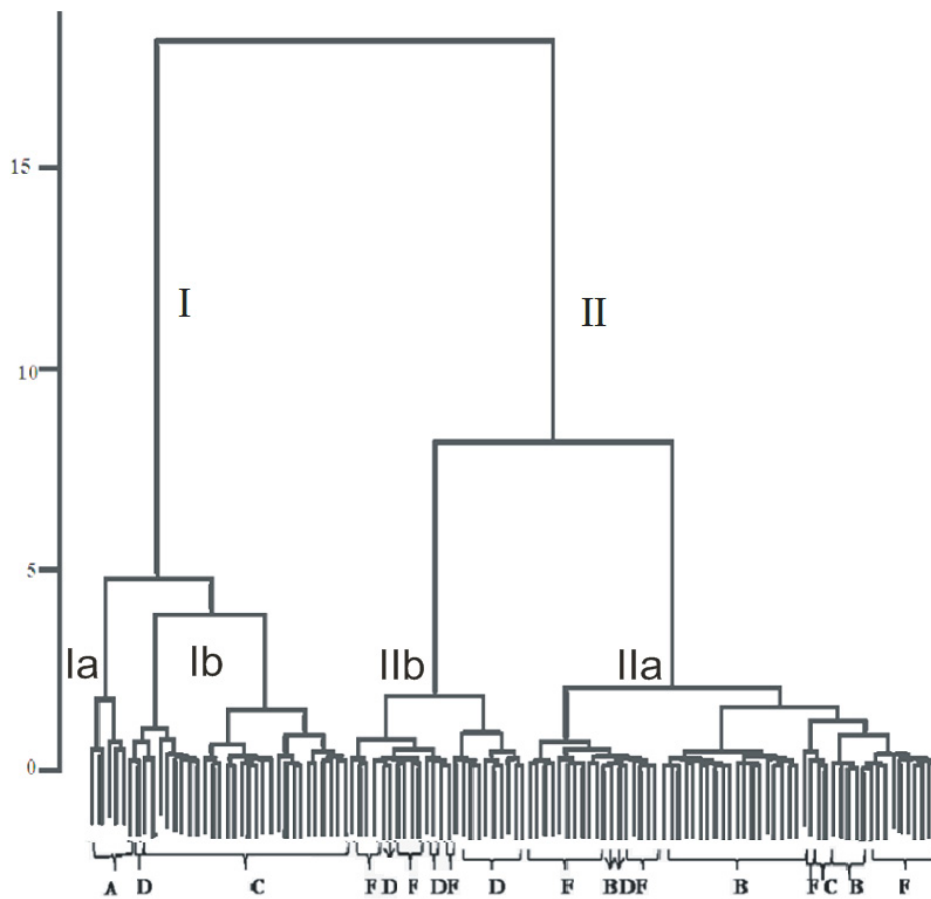
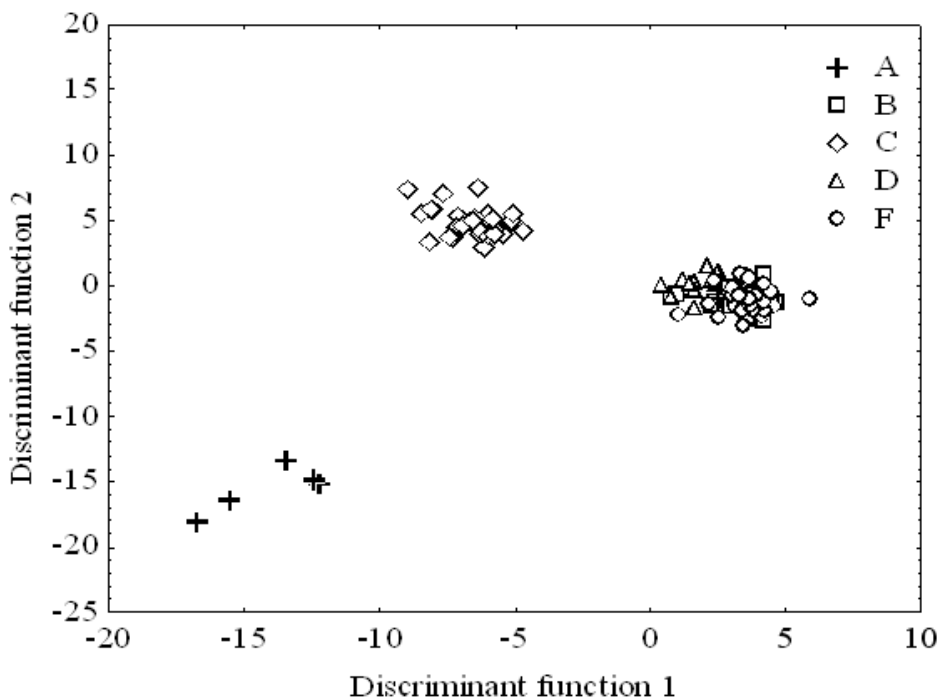


Fig. 6

Graphic with the discriminating functions, where group A (fluvial) and group C (central estuarine basin) are plotted as two distinctive clusters far from the remaining groups (B, D, and F). The samples related to more marine-influenced deposits from the B (outer estuary), D (tidal flat), and F (lagoon) groups are closely related, with only a rough discrimination of group D.



Results slightly better were reached with the PCA (Fig. 7), which also plotted all samples from the A and C groups within two well-defined clusters concentrated in the same side of the diagram. In addition, all samples from group D were joined in a separate cluster in the intermediate part of the diagram. The B and F groups show samples with the highest degree of mixture, with the first overlapping the latter in its central part.

Table 3 displays the ratios between selected elements of interest, with values normalized to NASC. It also shows the K+Na, as well as the mean concentrations of total rare earth elements (TREE), total light rare earth elements (TLREE), and total heavy rare earth elements (THREE). In general, most of the ratios indicate higher values in group A, except La/Th, which is lower in this group, and constant in the remaining ones. Following group A, Th/U decreases from the C to F, and B and D groups; La/Yb decreases from the B to F, C and D groups; K/Na decreases from the C to B, D and F groups, being

relatively similar in the three latter ones, while K+Na are higher in the group F, decreasing toward the B, D, C and A groups. It seems that K+Na shows a better contrast between continental-related facies association (A and C groups) and marine-related ones (B, D, and F groups). The TREE and TLREE are higher in A, decreasing toward the B, F, C, and D groups, while THREE is higher in D, increasing from the F to C, B, and A groups.

Because the relation between K and Rb has been used as good weathering indicator (Fedó *et al.* 1996, Xu *et al.* 2010), a diagram with the plot of log K versus log Rb is shown in Figure 8. It illustrates that all deposits are slightly depleted in K with respect to the upper continental crust, except in group A (fluvial deposits), which falls on the line of K/Rb=230 (upper crust). Additionally, both elements increase in the following direction: A, C, D, F, and B groups, with the two latter ones (i.e., representative of more marine-influenced, outer estuary and lagoon deposits) being plotted in closer proximity.

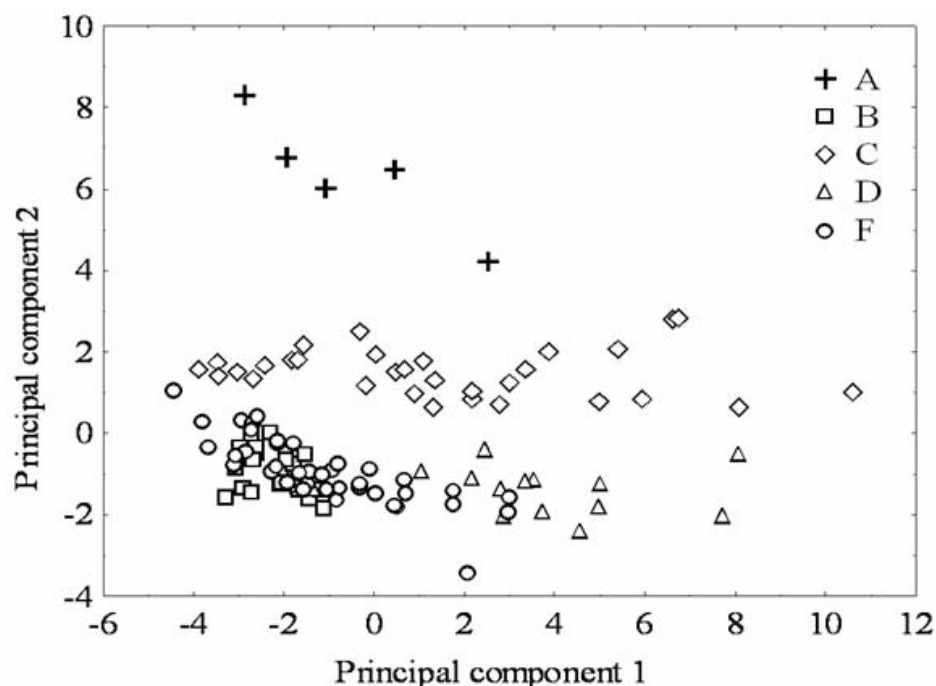


Fig. 7
Graphic with the principal components (PC), where all groups are distinguished, except B and F.

	A	B	C	D	F
$(\text{La/Yb})_{\text{NASC}}$	2.16	1.51	1.36	1.20	1.45
$(\text{La/Th})_{\text{NASC}}$	1.06	1.30	1.33	1.33	1.30
$(\text{Th/U})_{\text{NASC}}$	1.83	1.23	1.43	0.79	0.84
$(\text{K/Na})_{\text{NASC}}$	6.71	0.79	1.43	0.61	0.61
K+Na	1.57	2.85	1.86	2.44	3.00
TREE	245.74	226.04	204.08	181.55	219.24
TLREE	242.38	221.77	199.75	117.09	214.90
THREE	3.36	4.27	4.33	4.46	4.34

Table 3
Ratios between selected elements of interest (values normalized to NASC), K+Na values, and mean concentrations of TREE, TLREE), and THREE for the five analyzed groups.

5. Discussion

Due to their relatively immobile nature during weathering, transport, and sedimentation, many of the TE (e.g., Cs, Th, Sc, Hf, Cr, Co) and all REE (La, Ce, Nd, Sm, Eu, Yb, and Lu) analyzed in this study have been regarded as useful indicators to approach geological processes (see several references in Varga & Szakmány 2004). These elements are analyzed herein

in order to verify their relationship to changes in geochemical conditions in the various depositional environments of the studied estuarine setting.

The sedimentary cycle encompassing weathering, erosion, transport, and deposition tends to promote an overall homogenization of sediment chemical composition due to mixing of

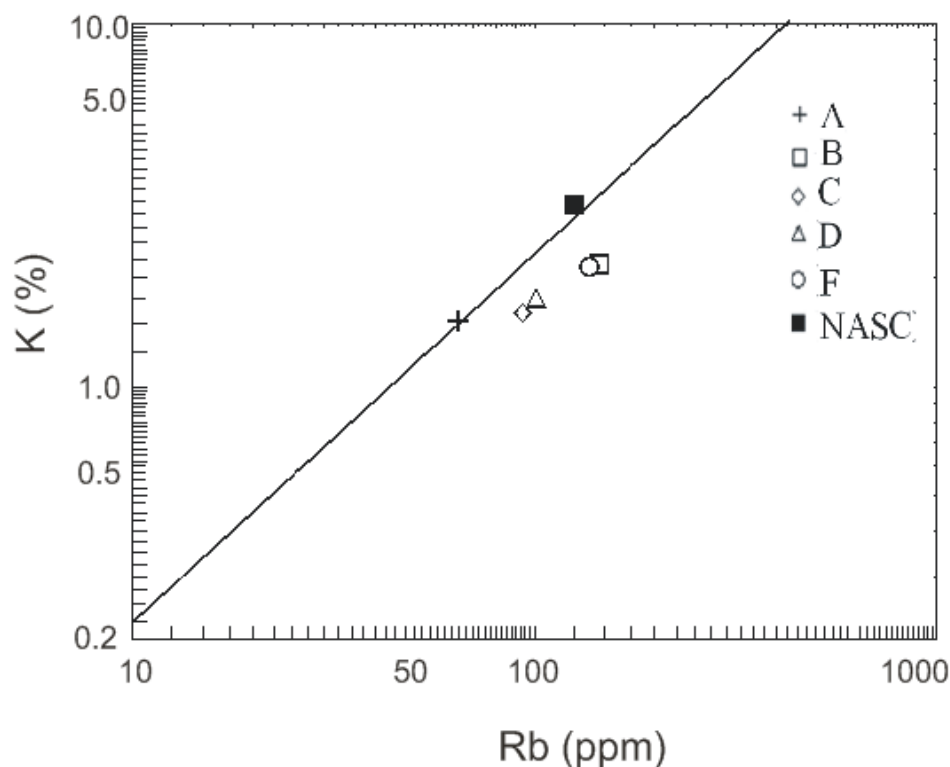


Fig. 8

Graphic with log K versus log Rb, considering the mean concentration for all groups established in this work. Note that group A (fluvial) overlaps the K/Rb line for the upper continental crust (K/Rb=230). The other groups display K/Rb lower than this value. The $[K/Rb]_{NASC}$ is from Gromet *et al.* (1984).

material derived from diverse source areas, rock types, and ages (e.g., Taylor & McLennan 1985, McLennan *et al.* 1993). As a result, sediment geochemistry tends to approach the elemental distribution of the upper continental crust. However, the sediment geochemistry varies when deposits from different environments within a single depositional system are compared.

Several studies have demonstrated that grain size variation due to sediment hydrodynamics in the estuarine, as well as adjacent fluvial and shallow marine settings, might play a major role on controlling element composition in sediments (Shajan 2001, Machado *et al.* 2005). In general, finer-grained, marine and estuarine settings favor concentration of most TE and REE in comparison with sandier fluvial deposits. A number of studies have also demonstrated that important chemical reactions are caused by riverine inflows into estuaries, with significant impacts on the concentration of TE and REE of estuarine sediments and/or of sediments delivered into the marine realm (Martin and Meybeck 1979, Sholkovitz & Elderfield 1988, Nath *et al.* 2000, Nozaki *et al.* 2000, Borgeo *et al.* 2005). Understanding these variations is critical to analyze the potential use of these proxies for the purpose of reconstructing these sedimentary environments.

Grain size could not justify the elemental changes recorded in Table 1, which leads to suggest more complex processes taking place in the environmental setting. The concentration patterns of some elements relative to NASC, as well as the described variations in geochemical composition comparing all analyzed groups (reflecting facies associations), vary significantly.

Although concentration patterns for some of the analyzed elements are difficult to be explained, the bulk concentration taking into account all the elements together can be related to differences in geochemical conditions inherent of individual depositional environments. This is revealed by the efficient grouping of samples in the dendrogram, as well as in the discriminating and PC graphics, where fluvial deposits were

plotted distant from all the other deposits, indicating that group A is geochemically unrelated to any of the other more marine-influenced groups. Furthermore, these graphics were efficient to distinguish the central estuarine basin deposits (group C), positioning all the samples representative of these deposits in a unique cluster situated in an intermediate position between the fluvial and the remaining saline water related deposits. These data, together with the fact that samples from the A and C groups compose two sub-clusters within a major cluster (I) in the dendrogram, sustain their geochemical affinity. Similarly, the major cluster II encompasses all samples representative of deposits formed under higher influence of saline waters, i.e., the B, D and F groups. Although cluster II also contains two sub-clusters (IIa and IIb), the high degree of confusion amongst their samples precludes the use of the analyzed elements to discriminate among the depositional environments formed under influence of saline waters.

On the other hand, the DA was efficient to distinguish the two facies associations more affected by fluvial inflows (i.e., A and C groups), separating them from deposits formed under relatively higher marine influence (B, D, and F groups). The samples derived from tidal flat deposits (group D) display a certain degree of geochemical differentiation when contrasted to the outer estuarine and lagoon deposits (B and F groups, respectively). This might indicate that part of the samples record deposits formed in high intertidal and supratidal areas, which might be affected by freshwater runoffs, and part might be related to deposits formed in more marine influenced subtidal and low intertidal areas. The fact that the PCA plotted group D (tidal flat) in a separate cluster between the A/C and B/F groups sustains its slightly different geochemical nature.

The foregoing discussion led to conclude that the various depositional environments of the studied estuarine setting display significant differences in geochemical signatures that can help their differentiation in the geological record. The results indicated by the dendrogram, DA, and PCA derive from

significant contrasts in elemental concentrations, which are discussed in more detail in the following.

The upper continental crust composition is regarded as similar to the composition of marine shales (e.g., Taylor & McLennan 1985, Johannesson *et al.* 2006). Indeed, the plot of minimum and maximum concentration of TE, ME, and REE (Fig. 3) relative to NASC in the study area follows an overall similar pattern of variation of the upper continental crust. However, the increased concentration of all light REE (i.e., La, Ce, Nd, Sm, Eu) relative to NASC concentrations is taken as evidence of deposition in a coastal to fluvial setting. This variation is readily related to deposition in environments displaying lower salinity relative to the fully marine shale concentration used as comparison.

In general, freshwater-dominated and high energy environments with high terrigenous sources, as occur in fluvial and central estuarine settings, have an increased concentration of REE (Machado *et al.* 2005) relative to marine waters (Dubrulle *et al.* 2007). There is an overall agreement, however, that these elements are intensely removed due to changes in physicochemical conditions within the estuary, which is mainly due to colloid coagulation under influence of saline waters (Martin *et al.* 1976, Hoyle *et al.* 1984, Goldstein & Jacobsen 1988, Shokovitz 1993, Byrne & Liu 1998). Other important controls on this budget are pH variations (Johannesson *et al.* 2004), biological processes (Wyndham *et al.* 2004), and co-precipitation with iron oxydes-hydroxides (Martin *et al.* 1976). These processes within the estuarine saline mixing zone contribute particularly to remove THREE (Nozaki *et al.* 2000, Borrego *et al.* 2005).

REE concentration follows a predictable pattern in the study area, where the most fluvial-influenced deposits (group A) are compared with the most marine-influenced deposits (B and F groups). This is indicated by the higher TREE, higher TLREE with consequent lower THREE, and higher La/Yb recorded in the former group. However, instead of having intermediate values, the lowest values for all these parameters in the central estuarine basin (group C) and tidal flat (group D) point to a more significant loss of TLREE. The exception is the THREE, which is higher in these two groups. Therefore, in addition to salinity and pH changes, other unknown additional processes must have contributed to the increased fractionation of REE in deposits of the C and D groups.

The decreased concentration of K+Na towards the group sequence F-B-D-C-A is consistent with the proposed depositional interpretation. These elements have the highest concentration in the two marine-influenced strata (i.e., B and F groups), with a peak in the most restricted setting, which is probably due to evaporation of saline waters within the lagoon. Despite the lower K+Na values in relatively more fluvial influenced deposits, the high K/Na indicates that the fluvial inflow acted as a preferential source of K than Na. The comparable K/Rb in fluvial deposits relative to the crustal ratio leads to suggest that K was derived directly from this crustal material into the drainage systems. Additional K and Na were provided from the marine realm. The increased K/Rb from the C to D, B, and F groups is consistent with additional contribution from marine waters. The highest Rb concentration in the B and F groups sustains a marine influence, which is also consistent with the lowest Rb concentration in group A (fluvial). Rubidium is strongly adsorbed on the surface of and into clay minerals (Grim 1968). Hence, its concentration might be enhanced in

natural marine settings due to surface water in contact with the solution and high residence time (Neal *et al.* 1996).

The increased Th values from marine- to fluvial-influenced deposits, with an almost duplication in group A relative to NASC concentration, followed by an increase in Th/U values, conforms to the proposed paleoenvironmental settings. Th/U ratios are higher in oxidizing fluvial environments, where U removal is favored (McLennan & Taylor 1980).

The lower Zn concentration in the central estuarine basin (group C), and tidal flat (Group D) deposits might be due to biochemical changes. As opposed to most of the other elements analyzed herein, Zn is a mobile element that enters the aquatic systems as solute through either aerial deposition or surface runoff due to the association with organic matter, as well as iron and manganese oxides (Campbell & Tessier 1996). Its concentration in the continental crust is of 70 µg/g (James 1991), but much higher values are recorded in many modern ocean waters, which have been related to Zn derived from the atmosphere (Helz *et al.* 1985). Following this pattern, it would be expected to have a progressive increased distribution in Zn concentration from the fluvial to the outer estuarine areas, which was not observed in this study (Table 2). However, Zn concentration in estuaries might change according to sediment redox potential (Guo *et al.* 1997, Ibhaddon *et al.* 2004), pH (Mohammed *et al.* 2009), large insoluble molecular humic material and sulfides with precipitation as ZnS and co-precipitation with FeS (Bertine 1970), and bacterial reworking (Pomeroy *et al.* 1966, Lowman *et al.* 1971). The central estuarine basin is an area of low energy that might be affected by intense sediment reworking due to the activity of marine bacteria. It has been reported that burrowing by polychaete worms might decrease 3 to 7 times the Zn values in sediments (Renfro 1973). One hypothesis is that sediment burrowing, which is common in central estuarine basin and tidal flat areas, was responsible for selectively decreasing the Zn value relative to the other deposits.

The lowest Hf concentration in more marine-influenced deposits (B and F groups) is more promptly explained. The main carrier of this element is the mineralogical group of zircon (Nath *et al.* 2000, Randle & Al-Jundi 2001). Because zircon is a stable mineral, its Hf content, in general, does not change during the sedimentary cycle (Vervoort *et al.* 1999). Ongoing studies of heavy mineral assemblages in the study area indicate an increased percentage of this mineral in deposits with higher fluvial influence, with values up to 32.3% against 21.4% for marine-influenced strata. Thus, the highest volume of zircon in fluvial-influenced sediments might explain correlation with higher Hf concentration.

Cesium is one of the least mobile radioactive metals in natural environments. Its occurrence in the continental crust is 1.9 µg/kg, and in the sea water is 0.5 µg/kg. This element adheres quite well to soil and sediments, being 280 times higher than in interstitial waters. Thus, a certain amount of Cs occurs in sediments, and it is expected that its distribution decreases with a seaward shift in depositional environments. The highest Cs concentration in the more marine-influenced deposits (B and F groups; Table 2) of the study area is in conflict with this general statement. In fact, several factors might have influence on Cs distribution, including pH, element concentration, presence and concentration of competing ions, temperature and time for equilibrium (Hakem *et al.* 1997). The mixing of marine and freshwaters within the estuary could have

contributed to modify the decreasing seaward pattern of Cs concentration. However, because the major change is centered in the two more marine-influenced environments, a more likely hypothesis is that this element was slightly increased in seawaters due to airborne deposition. Noteworthy is that Cs concentration in the B and F groups duplicates with respect to NASC concentration, which leads to invoke that an additional unknown source (i.e., airborne deposition) might have been active during sediment deposition.

The highest Cr concentration in the A and C groups was

6. Conclusion

Applying sediment geochemistry for identifying the paleoenvironmental nature of sedimentary deposits associated with estuarine settings might be problematic, because of the complex interplay of processes that result in sediment mixture in different time-scales. The elemental analyses discussed herein lead to suggest that TE and REE might be a useful tool for characterizing depositional environments associated with estuaries. Shifts in depositional conditions, caused mostly by salinity and pH gradients along the proximal to outer estuarine environments, seem to be responsible for the main recorded elemental changes. Multivariate analysis including dendrogram, graphics with discriminating and PC, revealed to be efficient for differentiating between marine and fluvial influenced deposits in the estuarine system studied. In particular, PCA revealed to be the most powerful to discriminate sample clusters, which had good correspondence to the interpreted depositional environments. This last statistical treatment indicates significant contrasts in elemental concentrations of the water in the various estuarine environments, which are reflected in the geochemical composition of the sediments coming from different facies associations.

The results also revealed that concentrations of TE and REE for the studied samples display an overall similar pattern when compared to the composition of the standard marine shale (NASC). Significant changes in concentration of REE do

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expected, because the occurrence of this element is favored in freshwater-influenced environments due to its preferential association with organic and colloidal material (Mayer *et al.* 1984). Under low salinity in fluvial to central estuarine areas, dissolved trivalent and hexavalent Cr is either flocculated or adsorbed onto these particulate matters (Campbell & Yeats 1984). The lowest concentration of this element is recorded in the lagoon setting. This is probably due to high salinity added to reduced oxygen, which also might contributed to Cr removal (Nieboer & Jusys 1988).

occur, which seems to have been controlled mainly by salinity and pH changes in water of the depositional environment. Hence, sediments formed in fluvial-influenced environments display higher TREE, higher LREE with consequent lower HREE than marine-influenced deposits. As opposed to the expected intermediate values, the sediments derived from tidal flat and central estuarine basin displayed the lowest concentration in TREE and LREE and the highest concentration in HREE, which led to suggest that other processes (e.g., airborne deposition) inherent from these settings might have contributed to removal of light LREE.

Other important changes in geochemical parameters included higher K+Na, Rb, Th/U, Cs, and lower Th, Hf and Cr in marine-influenced settings relative to fluvial ones, which is due to a combination of processes mostly related to natural distribution of these elements along a continental to marine transect, adsorption due to the influence of colloidal material, mineralogical influence, and airborne deposition. For instance, an important found of this contribution was that the lower Zn concentration in central estuarine basin and tidal flat settings is probably due Zn removal during burrowing. Combination of all these processes was important to create a geochemical signature that shows good correspondence with changes in depositional environments within the studied estuarine setting.

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