

**MINOR AND RARE EARTH ELEMENTS AS PALEOENVIRONMENTAL
MARKERS OF LATE QUATERNARY SEDIMENTS IN MARAJÓ ISLAND,
NORTHERN BRAZIL**

**Dilce de Fátima Rossetti^{1*}, Casimiro Sepúlveda Munita², Paulo Meira Silva
Oliveira²**

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

²*Instituto de Pesquisas Energéticas Nucleares - IPEN - CNEN/SP, Av. Prof. Lineu Prestes 2242, 05508-
000, São Paulo, SP, Brazil
(rossetti@dsr.inpe.br)*

*** Corresponding Author**

**MINOR AND RARE EARTH ELEMENTS AS PALEOENVIRONMENTAL
MARKERS OF LATE QUATERNARY SEDIMENTS IN MARAJO ISLAND,
NORTHERN BRAZIL**

**Dilce de Fátima Rossetti^{1*}, 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

Estuaries are characterized by high lateral and vertical facies variability that results from complex interaction of fluvial and marine processes. Where only core data are available, the recognition of estuarine deposits in the ancient record is problematic based on sedimentological studies due to the difficult assessment of sedimentary processes and body geometry. Exploring proxies that can be used in combination with sedimentary parameters is important for helping reconstructing estuarine paleoenvironments. Geochemical tracers including Ce, Co, Cr, Cs, Eu, Fe, Hf, K, La, Lu, Na, Nd, Rb, Sm, Sc, Ta, Th, U, Yb, and Zn have good potential for paleoenvironmental purposes. However, additional studies are needed in order to further demonstrate the success of these proxies to interpret various depositional environments formed within estuaries. This type of approach was applied to a late Quaternary succession in northern Brazil, where available studies integrating morphological analysis, sedimentary facies and isotope data had led to distinguish among several estuarine depositional environments. Multivariate analysis of trace and REE allowed distinguishing five geochemical groups, which conform to previously reconstructed fluvial, outer estuarine, central estuarine basin, tidal flat and

lagoon deposits. In particular, the dendrogram, as well as principal components (PCA) and discriminating (DA) analysis allowed a clear distinction between fluvial influenced (i.e., fluvial and central estuarine basin) and relatively more marine influenced (outer estuarine, central estuarine basin and tidal flat) deposits. The distribution of geochemical tracers in the analysed deposits had a strong influence of variations in salinity and pH that typify these depositional environments, though concentration some of the changes might have also responded to other processes as adsorption due to the influence of colloidal material, mineralogical influence, airborne deposition and burrowing. The results of the present study lead to suggest that the trace and rare earth elements analysed herein might be a useful tool for helping distinguishing depositional environments associated to ancient estuarine deposits.

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; Zaitlin et al., 1994; Anderson et al., 1996; Miall and Arush, 2001; Wellner and Bartek, 2003; see also several papers in Dalrymple et al., 2006). This is mostly due to their occurrence within incised valleys, which are depositional systems of great interest for hydrocarbon exploration (Zaitlin and Shultz, 1984, 1990; Dalrymple et al., 1992, 1994), as well as for studies emphasizing sea-level (e.g., several papers in Dalrymple et al., 1994; Blum and Törnqvist, 2000), climate and tectonic reconstructions (e.g., Schumm et

al., 1987; Blum and 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 bodies of water with a mixture of fluvial and marine processes (Boyd et al., 1992), their recognition in the geological record is difficult due to rapid lateral and vertical changes in sedimentary facies characteristics. This problem is particularly enhanced when only core data are available, which precludes determination of lateral facies relationships. Taking this into account, it is important to analyse estuarine deposits through a larger variety of approaches that can be used 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 processes (Nath et al., 2000). Therefore, geochemical analyses of trace 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 REEs, are regarded as generally immobile during weathering, transport and sedimentation (e.g. McLennan, 1989), though fractionation due to diagenesis has been also documented (Milodowski and Zalasiewicz, 1991; Ohr et al., 1991; Bock et al., 1994) and weathering (Nesbitt, 1979; Banfield and Eggleton, 1989; McDaniel et al., 1994; Hannigan and Sholkovitz, 2001).

Most of the elemental analysis undertaken on estuaries have emphasized dissolved and particulate phases (e.g., Goldstein and Jacobsen, 1988; Sholkovitz and Elderfield, 1988; Sholkovitz, 1992; Nozaki et al., 2000). A few studies have undertaken analysis of trace elements in estuarine and adjacent marine and fluvial sediments (e.g., Zhu et al., 1997; Singh and Rajamani, 2001; Dubruelle et al., 2007). Perhaps due to the lack of understanding on the behavior of some rare elements in the various depositional settings and also during burial, there is still a lack of studies applying geochemical analysis for reconstructing ancient estuarine settings.

The present work contains the results of geochemical analysis of trace and rare earth elements 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 by an integrated approach based on geomorphological characterization of remote sensing imagery, sedimentary facies analysis, as well as carbon and nitrogen isotopic data derived from organic matter preserved on sediments (Miranda et al., 2009). The focus is to determine if the elements analysed herein could be used as markers for characterizing the various estuarine depositional paleoenvironments previously interpreted in this study area.

2. GEOLOGICAL BACKGROUND

The study area is located at the western margin of Lake Arari in eastern Marajó Island, mouth of Amazon River, Brazil (Fig. 1). An increasing volume of publication has been presented in these last years concerning to the paleoenvironmental reconstruction of

Quaternary deposits in this area. This is because this area contains the best record of core data recording Quaternary strata from the Brazilian Amazonia, where other type of information is problematic due to the lack 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 this 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, whose sediment fill is still poorly known. 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 Marajó (Paleocene-Eocene) Formation, and fluvial to transitional siliciclastic unit related to Tucunaré/Pirarucu (Quaternary) Formations (Azevedo, 1991). In surface, there are late Cenozoic, mostly estuarine sandy and muddy deposits related to Barreiras Formation and Post-Barreiras Sediments (Rossetti, 2004).

The Post-Barreiras Sediments around the Lake Arari area occur within an elongate, funnel-shaped morphology up to 25 km wide and 50 km long (Fig. 2), which record an estuarine system that became abandoned in Marajó landscape during the Holocene, previously to lake establishment (Rossetti et al., 2007; Rossetti et al., 2008

a,b). An 124 m-thick continuous core recording these estuarine deposits revealed six facies associations (Tab. 1) attributed to fluvial channel (facies association A), outer estuary (facies association B), central estuarine basin (facies association C), tidal flat (facies association D), estuarine channel (facies association E) and lagoon (facies association F) depositional settings (Miranda and Rossetti 2009). These interpretations were made 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 are presented in the following.

The fluvial channel deposits (association A) consist of moderately sorted, fine to coarse-grained, locally conglomeratic, massive sand, with only subordinate parallel laminated mud. These lithotypes are typically arranged into several fining upward cycles, that are sharply based and usually erosive, and marked by mud intraclasts. This association is dominated by organic carbon derived mainly from C_3 vascular vegetation.

The outer estuarine (association B) and central estuarine basin (association C) comprise parallel-laminated mud and streaky heterolithic bedded deposits that are interbedded with numerous packages of lenticular and wavy to flaser heterolithic sands and muds. Sediments in this association contain terrestrial (both C_3 and C_4 plants), phytoplankton (marine and freshwater), and mixed sourced organic matter, while association C contains organic matter derived only from freshwater phytoplankton and vascular plants.

The tidal flat (association D) is represented by lenticular and wavy to flaser heterolithic deposits, which are locally interbedded with packages of massive sands.

These strata are typically intergraded, forming sharp based, fining upward cycles. The organic matter from these sediments is marine or freshwater phytoplankton, C₃ and C₄ land plants, or a mixture of both.

The estuarine channel (association E) strata are sharp based and consist 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. The organic matter is represented by C₃ terrestrial plants, but with episodes of either marine phytoplankton or mixed marine and land plant inputs.

The lagoon deposits (association F) correspond to a succession that is sandier at the base and muddier upward, and arranged into fining and coarsening upward cycles. These deposits show prevalence of organic matter derived from the marine realm, except for a few intervals, where mixed marine and terrigenous sources are evident, particularly in the uppermost portion of the succession, where the sediments grade into the modern Lake Arari deposits. After estuarine development, the depositional system graded into a lagoonal phase, when fluvial influx into the area was cut off due to the opening of Marajó Bay by fault reactivation (Rossetti et al., 2007, 2008a.b).

3. METHODS

3.1. Sampling

The analysis was carried out on a total of 113 samples of mud and streaky and lenticular heterolithic deposits derived from continuous core drilled 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 sampled given the

dominantly sandy nature of its deposits. 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 granulometry was obtained. This was done in order to pass in through a 100 mesh sieve. These materials were dried in an oven for 24 h, at 105°C and stored in a desiccator.

Constituent Elements in Coal Fly Ash (NIST-SRM-1633b) were used as a standard and the International Atomic Energy Agency – IAEA Soil 7 (Trace Elements in Soil) were used to check the samples throughout the analysis. These materials were dried in an oven for 2 h at 105°C and stored in a desiccator until weighing. About 120 mg of soil samples, one standard (NIST-SRM-1633b) and one IAEA-Soil 7 were weighed in polyethylene bags and wrapped in aluminum foil. Groups of 10 samples and one reference material were packed in aluminum foil and irradiated in the research reactor's pool, IEA-R1, located at IPEN-CNEN/SP, Brazil. It was 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, using a 1332.49 keV gamma peak of ^{60}Co and an S-100 MCA from Canberra. This contained 8192 channels. K, La, Lu, Na, Nd, Sm, U, and Yb were measured after 7 days cooling time and Ce, Co, Cr, Cs, Eu, Fe, Hf, Rb, Sc, Ta, Th, and Zn after 25-30 days. Gamma ray spectra analysis

and the concentrations were carried out using the Genie-2000 Neutron Activation Analysis Processing Procedure from Canberra. The program calculates elemental concentrations by comparing integrated peak areas in the samples and the standards. Analytical details and the precision attained have been published elsewhere (Munita et al., 2000).

3.3. Statistical Treatment of Dataset

By means of INAA, it is possible to determine several elements simultaneously and the volume of data is considerable when a large number of samples is analysed. Then, the associations between elements and samples are so complex that multivariate statistical methods are generally used to data handling and evaluating (Oliveira et al., 2009). In this paper, the dataset were studied by means of three multivariate statistical methods: cluster analysis (CA), discriminant 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 analysed. This procedure distinguishes each group of samples from every other group (Johnson and Wichern, 2007).

DA constructs a series of discriminant functions that maximize the differences between two or more groups. Is based on the assumption that pooled variance-covariance matrix is an accurate representation of the total variance and covariance (Johnson and Wichern, 2007).

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 (Johnson and Wichern, 2007). The first principal component (PC) is a linear combination of the original variables and it is 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.

Throughout this paper, a determination of all parameters in the analyses were measured and quantified (Munita et al., 2004.), in order to make corrections before applying the method to real samples. In order to evaluate the accuracy and the precision of the analytical process, the IAEA Soil 7 reference material elemental concentrations were statistically compared with the certifies values. The elements, with an accurate and relative standard deviation (RSD) of less than 10%, were Ce, Co, Cr, Cs, Eu, Fe, Hf, K, La, Lu, Na, Nd, Rb, Sm, Sc, Ta, Th, U, Yb, and Zn. Afterwards, these elements were used in the subsequent data analyses.

In order to minimize the effect of variation in trace and rare earth elements due to their natural abundance, 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 and McLennan, 1985).

4. RESULTS

The mean and standard deviations of minor and rare earth elements from shales and sands representative of the five depositional groups analysed in this study are given in Table 2. Individual groups correspond to the previously described depositional facies associations. Group E was not analysed, due to the reduced number of samples. The NASC values are also given in this table for comparison. Considering all the analysed groups, the abundance patterns of minor and rare earth elements vary relative to the NASC values, being either higher, as for La, Ce, Nd, Sm, Eu, Lu, U, Th, or lower, as for K, Cr, Co, Ta. The remaining elements (i.e., Zn, Hf, Cs, Na, Yb, Rb and Sc) 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 groups F and A, 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. Zn, Hf, Cs and Rb display the most significant gradients amongst the analysed 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 representative of the individual depositional environments (Fig. 4). The elements were organized in these graphics following their decreasing order of abundance in the upper continental crust. As expected, these data revealed elemental distribution with comparable patterns among the analysed groups, in general with values decreasing from left to right, which is consistent with minor and rare earth element crustal distribution. However, these graphics also show differences in behavior when individual elements are compared among the five groups. Hence, depositional

environments with higher salinity, corresponding to groups B, E, and eventually D, 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 (groups A and C). Cs concentration peaks in groups B and F (almost the double of NASC concentration), while Hf shows the lowest concentration in these deposits. On the other hand, groups A, and eventually C, contain higher concentration in Th, La, Ce, Nd and Cr, and lower concentration in Cs, Rb, U, K, Na and Yb. Among these elements, La and Th have the highest peak, while K and Na the lowest one.

The dendrogram depicting the total samples for all groups (Fig. 5) revealed sample concentration 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 groups B, D, and F, 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 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 groups A and C. Among these, samples from groups B and F are closely related, while samples from group D are roughly discriminated, though there is also several sample overlapping. 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.

Results slightly better were reached with the PCA (Fig. 7), which also plotted all samples from groups A and C within two well defined clusters that are 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. Groups B and F shows 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), light rare earth elements (LREE) and heavy rare earth elements (HREE) total rare earth elements. 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 groups C to F, B and D; La/Yb decreases from B to F, C and D; K/Na decreases from C to B, D and F, being relatively similar in the three latter ones, while Na+K are higher in group F, decreasing toward groups B, D, C and A. The TREE and LREE are higher in A, decreasing toward groups B, F, C and D, while HREE is higher in D, increasing from F to C, B and A.

Because the relation between K and Rb has been used as good weathering indicator, a diagram with the plot of log K versus log Rb is shown in Figure 8. It

illustrates that all deposits are 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, with the two latter ones being plotted in closer proximity.

5. DISCUSSION

Due to their relatively immobile nature during weathering, transport and sedimentation, many of the rare elements (e.g., Cs, Th, Sc, Hf, Cr, Co) and all rare earth elements analysed in this study have been regarded as useful indicators to approach geological processes (see several references in Varga and Szakmány, 2004). These elements are analysed 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 erosion, weathering, transport and deposition tends to promote an overall homogenization of sediment chemical composition due to mixing of material derived from diverse source areas, rock types and ages (e.g., Taylor and McLennan, 1985; McLennan et al., 1993). As a result, sediment geochemistry tends to approach the elemental distribution of the upper continental crust. However, 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 and 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 trace and rare earth elements 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 concentration of trace and rare earth elements of estuarine sediments or of sediments delivered into the marine realm (Martin and Meybeck, 1979; Sholkovitz and Elderfield, 1988; Nath et al., 2000; Nozaki et al., 2000; Borrego et al., 2005). Understanding these variations is critical to analyse 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 call upon 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 analysed groups, vary significantly.

Although concentration patterns for some of the analysed 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 to 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 groups. Furthermore, these graphics were efficient to distinguish the central estuarine basin (group C), positioning all the samples representative of these deposits in a unique cluster situated in an intermediate position between fluvial and the remaining

deposits. These data, together with the fact that samples from groups A and C compose two sub-clusters within a major cluster (I) in the dendrogram, sustain their geochemical affinity. Likewise, the major cluster II encompasses all samples representative of deposits formed under higher influence of saline waters, i.e., groups B, E and D. Although cluster II also contains two sub-clusters (IIa and IIb), the high degree of confusion amongst their samples precludes the use of the analysed elements to discriminate amongst the depositional environments formed under influence of saline waters.

On the other hand, the DA was efficient to distinguish the two facies associations that were more affected by fluvial inflows (i.e., groups A and C), separating them from deposits formed under relatively higher marine influence (groups B, D and F). The group of samples derived from tidal flat deposits (group D) displays a certain degree of geochemical differentiation when contrasted to the outer estuarine and lagoon deposits. 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 in a separate cluster between groups A/C and E/F sustains its slightly different geochemical nature.

The foregoing discussion led to conclude that the various depositional environments of the studied estuarine setting display significant geochemical signatures that can help their differentiation in the geological record. The results indicated by the dendrogram, DA e 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 (Johannesson et al., 2006). Indeed, the plot of minimum and maximum concentration of trace and rare earth elements (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 rare earth elements (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 energetic environments with high terrigenous sources, as occur in fluvial and central estuarine settings, have an increased concentration of rare earth elements (Dubrulle et al., 2007) relative to marine waters (Machado et al., 2005; Lim et al., 2006). There is an overall agreement, however, that these elements are profoundly removed due to changes in physicochemical conditions within the estuary mainly due to colloid coagulation under influence of saline waters (Martin et al., 1976; Hoyle et al., 1984; Goldstein and Jacobsen, 1988; Shokovitz, 1993; Byrne and Liu, 1998). Other important controls on this budget are pH variations (Johannesson and Zhou, 1999), biological processes (Wyndham et al., 2004), and co-precipitation with iron hydroxides (Martin et al., 1976). These processes within the estuarine saline mixing zone contribute particularly to removal of heavy rare earth elements (Nozaki et al., 2000; Yang et al., 2002; Borrego et al., 2005).

REE concentration follows the predictable pattern in the study area, where the most fluvial-influenced deposits (group A) are compared with the most marine influenced deposits (groups B and F). This is indicated by the higher TREE, higher LREE with

consequent lower HREE, 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), except for the HREE, which is higher in these two groups, point to a more significant loss of LREE. In addition, this also indicates the HREE concentration in environments with mixed saline and freshwater inputs, without affecting the concentration of these elements in the outer estuary. Therefore, in addition to salinity and pH changes, other unknown additional processes must have contributed to the increased fractionation of REE in deposits of groups C and D.

The increased concentration of K+Na towards the group sequence F-B-D-C-A is consistent with the proposed depositional interpretation. These elements have highest concentration in the two marine-influenced strata, 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 for these strata 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 material into the drainage systems. Additional K and Na were provided from the marine realm. Therefore, the slight K depletion with respect to Rb in the other deposits indicates that as K was added to the more marine-influenced sediments, so was Rb. This is shown by the increased K/Rb from groups C to D, F and B. The highest Rb concentration in groups B and F sustains a marine influence, which is also consistent with its lowest peak in group A. Rb 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 greater 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 the decreasing Th/U values, conforms to the proposed paleoenvironmental settings. Th/U ratios are higher in oxidizing environments, where U removal is favored (McLennan and Taylor, 1980).

The high concentration of Zn in the most fluvial influenced (Group A) and saline influenced sediments (groups B and F) suggests important biochemical changes taking place in the central estuarine basin (group C) and tidal flat (Group D) settings, which was responsible for lowering significantly the concentration of this element. As opposed to most of the other elements analysed herein, Zn is a mobile element that enters the aquatic systems as solute through aerial deposition or surface runoff due to association with organic matter, as well as iron and manganese oxides (Campbell and Tessier, 1996). Its concentration in the continental crust is of 70 $\mu\text{g/g}$ (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.

However, Zn concentration in estuaries might change, being controlled by sediment redox potential (Guo et al., 1997; Ibadon 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 (Lowman et al., 1971;

Pomeroy et al., 1996). 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). Sediment burrowing was possibly responsible for selectively decreasing the Zn value in central estuarine basin and tidal flat areas relative to the associated fluvial setting.

The lowest Hf concentration in more marine influenced deposits (groups B and F) is more promptly explained. The main carrier of this element is the mineralogical group of zircon (Nath et al., 2000; Randle and Al-Jundi, 2001). Because zircon is a stable mineral, its Hf content in general does not change during the sedimentary cycle (Vervoort, 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.

Cs is one of the least mobile radioactive metals in natural environments. Its occurrence in the continental crust is 1.9 mg/kg and in the sea water is 0.5 mg/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 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 groups B and F duplicates with respect to NASC concentration, which leads to invoke that an additional unknown source might have been active during sediment deposition.

The highest Cr concentration in groups A and C was 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; Steinberg, 1980). Under low salinity in fluvial to central estuarine areas, dissolved trivalent and hexavalent Cr is either flocculated or adsorbed onto these particulate matters (Campbell and 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 favor Cr removal (Nieboer and Jusys, 1988).

6. CONCLUSION

Applying sediment geochemistry for identifying the paleoenvironmental nature of sedimentary deposits formed in association 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 trace and rare

earth elements might be a useful tool for characterizing depositional environments associated to estuaries. Shifts in depositional conditions, caused mostly by salinity and pH gradients along the proximal to outer estuarine environments, seem to respond 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 particular, PCA revealed to be the most powerful to discriminate sample clusters, which had good correspondence to the interpreted depositional environments. This indicates significant contrasts in elemental concentrations of the water in the various estuarine environments, which are reflected in sediment geochemistry.

The results also revealed that concentrations of trace and rare earth elements 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 rare earth elements do occur, which seems to have been controlled mainly by salinity and pH changes. Hence, sediments formed in fluvial-influenced environments display higher TREE, higher LREE with consequent lower HREE, and higher La/Yb than the sediments deposited in marine-influenced environments. Instead of 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 inherent from these settings might have contributed to removal of light rare earth elements.

Other important changes 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. The relative 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.

ACKNOWLEDGMENTS

This work was funded by FAPESP (Project # 004/15518-6), with the logistic contribution of the Goeldi Museum and the Mayor of the town of Santa Cruz do Arari.

REFERENCES

- Anderson J.B., Abdulah K., Sarzalejo S., Siringin F. and Thomas M.A. (1996) Late Quaternary sedimentation and high-resolution sequence stratigraphy of the East Texas Shelf. In *Geology of Siliclastic Shelf Seas* (eds. M. Batist and P. Jacobs). Geol. Soc. London Special Publication 117, pp. 95-124.
- Ardies G.W., Dalrymple R.W. and Zaitlin B.A. (2002) Controls on the geometry of incised valleys in the Basal Quartz unit (Lower Cretaceous), Western Canada Sedimentary Basin. *J. Sed. Res.* **72**, 602-618.

- Azevedo R.P. (1991) Tectonic Evolution of Brazilian Equatorial Continental Margin Basins. Ph.D. Thesis, Royal School of Mines Imperial College, London.
- Banfield J.F. and Eggleton R.A. (1989) Apatite replacement and rare earth mobilization, fractionation, and fixation during weathering. *Clays Clay Min.* **37**, 113-127.
- Bertine K.K. (1970) The marine geochemical cycle of chromium and molybdenum. Ph.D. Thesis, Yale University.
- Blum, M.D., and Price, D.M. (1998) Quaternary alluvial plain construction in response of glacio-eustatic and climatic controls, Texas Gulf Coast Coastal Plain. In *Relative Role of Eustasy, Climate, and Tectonism in Continental Rocks* (eds. K. Shanley and P. McCabe). SEPM Special Publication 59, pp. 31-48.
- Blum M.D. and Törnqvist T.E. (2000) Fluvial responses to climate and sea-level change: a review and look forward. *Sedimentology* **47**, 2-48.
- Bock B., Hurowitz J. A., McLennan S. M. and Hanson G. N. (2004) Scale and timing of Rare Earth Element redistribution in the Taconian foreland of New England. *Sedimentology* **51**, 885-897.
- Borrego J., López-González N., Carro B. and Lozano-Soria O. (2005) Geochemistry of rare-earth elements in Holocene sediments of an acidic estuary. Environmental markers (Tinto River Estuary, South-Western Spain). *J. Geochem. Explor.* **86**, 119-129.
- Boyd R., Dalrymple R.W., Zaitilin B.A. (2006) Estuary and incised valley facies models. In *Facies Models Revisited* (eds. H.W. Posamentier and R.G. Walker). SEPM Special Publication 84, pp. 171-234.

- Byrne, R.H. and Liu, X. (1998) A coupled riverine-marine fractionation model for dissolved rare earths and yttrium. *Aquatic Geochem.* **4**, 103-121.
- Campbell, P.G.C. and Tessier, A. (1996) Ecotoxicology of metals in aquatic environments: Geochemical aspects. In *Ecotoxicology: A hierarchical treatment* (eds. M.C. Newman and C.H. Jagoe). Lewis Publishers, Boca Raton, Florida.
- Carr I.D., Gawthorpe R.L., Jackson C.A. L., Sharp I.R. and Sadek A. (2003) Sedimentology and sequence stratigraphy of early syn-rift tidal sediments: the Nukhul Formation, Suez Rift, Egypt. *J. Sed. Res.* **73**, 407-420.
- Dalrymple R.W., Boyd R., and Leckie D. (1994) The stratigraphic organization of incised valley systems: implications to hydrocarbon exploration and production- with examples from the Western Canada Sedimentary Basin. Calgary, Alberta, Canadian Society of Petroleum Geologists, 260 pp.
- Dalrymple R.W., Zaitlin B.A. and Boyd, R. (1992) Estuarine facies models: conceptual basis and stratigraphic implications. *J. Sed. Petrol.* **62**, 1130-1146.
- Dalrymple R.W., Boyd R. and Zaitlin B.A. (1994) *Incised-Valley Systems: Origin, and Sedimentary Sequences*. SEPM Special Publication 51, 399 pp.
- Dalrymple R.W., Leckie D.A. and Tillman R. (2006) *Incised Valleys in Time and Space*. SEPM Special Publication 85, Oklahoma.
- Dubruelle C., Lesueur P., Boust D., Dugué O., Poupinet N. and Lafite R. (2007) Source discrimination of fine-grained deposits occurring on marine beaches: The Calvados beaches (eastern Bay of the Seine, France). *Estuar. Coast. Shelf Sci.* **72**, 138-154.
- Goldstein S.L and Jacobsen, S.B. (1988) Rare earth elements in river waters. *Earth Planet. Sci. Lett.* **89**, 35-47.

- Guo T., DeLaune R. D. and Patrick Jr., W.H. (1997) The influence of sediment redox chemistry on chemically active forms of arsenic, cadmium, chromium, and zinc in estuarine sediment. *Environ. Internat.* **23**, 305-316.
- Grim R.E. (1968) *Clay Mineralogy*. 2nd ed. McGraw Hill, New York.
- Gromet, L.P., Dymek, R.F., Haskin L.A. and Korotev R.L. (1984) The “North American Shale Composite”: its compilation, major and trace element characteristics. *Geochim. Cosmochim. Acta* **48**, 2469-2482.
- Hannigan R.E. and Sholkovitz E. (2001). The development of middle rare earth element enrichments in freshwaters: weathering of phosphate minerals. *Chem. Geol.* **175**, 495-508.
- Hakem N., Al Mohamed I., Apps J. and Moridis G. (1997) Sorption of cesium and strontium on savannah river soils impregnated with colloidal silica. Ernest Orlando Lawrence Berkeley National Laboratory, University of California, Berkeley, California. Report 94720, 7 pp.
- Helz G.R., Sinex S.A., Ferri K.L. and Nichols M. (1985) Processes controlling Fe, Mn and Zn in sediments of northern Chesapeake Bay. *Estuar. Coast. Shelf Sci.* **21**, 1-16.
- Hoyle E.J., Elderfeld H., Gledhill A. and Greaves M. (1984) The behavior of the rare earth elements during mixing of river and sea waters. *Geochim. Cosmochim. Acta* **48**, 143-149.
- Ibhadon A.O., Wright P. and Daniels R. (2004) Trace metal speciation and contamination in an intertidal estuary. *J. Environ. Monit.* **6**, 679-683.

- James W.M. (1991) *Inorganic Contaminants of Surface Water, Research and monitoring Priorities*. New York, Berlin, Heidelberg, London, Paris, Tokyo, Hong Kong, Barcelona. Springer-Verlag.
- Johannesson K.H., Hawkins D.L. and Cortés A. (2006) Do Archean chemical sediments record ancient seawater rare earth element patterns? *Geochim. Cosmochim. Acta* **70**, 871-890.
- Johnson R.A., Wichern D.W. (2007) *Applied multivariate statistical analysis*. Pearson Prentice Hall, 773 pp.
- Lim D.I., Jung H.S., Choi J.Y., Yang S. and Ahn K.S. (2006) Geochemical compositions of river and shelf sediments in the Yellow Sea: Grain-size normalization and sediment provenance. *Cont. Shelf Res.* **26**, 15-24.
- Lukie T.D., Ardies G.W., Dalrymple R.W. and Zaitlin B.A. (2002) Alluvial architecture of the Horsefly unit (Basal Quartz) in southern Alberta and northern Montana. Influence of accommodation changes and contemporaneous faulting. *Bull. Can. Pet. Geol.* **50**, 73-91.
- Machado A., Rocha F., Gomes C., Dias J.A., Araújo M.F. and Gouveia, A. (2005) Mineralogical and geochemical characterisation of surficial sediments from the Southwestern Iberian Continental Shelf. *Thalassas.* **21**, 67-76.
- Martin J.M. and Meybeck M. (1979) Elemental mass balance of material carried by major world rivers. *Mar. Chem.* **7**, 173-206.
- Martin J.M., Hogdahl O. and Phillipot J.C. (1976) Rare earth element supply to the ocean. *J. Geophys. Res.* **81**, 3119-3124.

- Mayer L.M. Schick L.L. and Chang C.A. (1984) Incorporation of trivalent chromium into riverine and estuarine colloidal material. *Geochim. Cosmochim. Acta* **48**, 1717–1722.
- McDaniel D.K., Hemming S.R., McLennan S.M. and Hanson G.N. (1994) Resetting of neodymium isotopes and redistribution of REEs during sedimentary processes: The Early Proterozoic Chelmsford Formation, Sudbury Basin, Ontario, Canada. *Geochim. Cosmochim. Acta* **58**, 931-941.
- McLennan S.M. (1989) REE in sedimentary rocks: influence of provenance and sedimentary processes. *Rev.Min.* **21**, 170-199.
- McLennan S.M., Hemming S., McDaniel D.K. and Hanson G.N. (1993) Geochemical approaches to sedimentation, provenance and tectonics. In *Processes Controlling the Composition of Clastic Sediments* (eds. M.J. Johnsson and A. Basu). GSA Special Paper 284, pp. 21-40.
- Miall A. D. and Arush, M. (2001) The Castlegate Sandstone of the Book Cliff, Utah: Sequence stratigraphy , palaeogeography, and tectonic controls. *J. Sed. Res.* **71**, 537-548.
- Milodowski A.E. and Zalasiewicz J.A. (1991) Redistribution of rare earth elements during diagenesis of turbidite/hemipelagite mudrock sequences of Llandovery age from central Wales. In *Developments in Sedimentary Provenance Studies* (eds. A.C. Morton, S.P. Todd, and P.W. Haughton). Geol. Soc. London Special Publication 57, pp. 101-124.
- Miranda M.C.C., Rossetti, D.F. and Pessenda, L.C.R. (2009) Quaternary paleoenvironments and relative sea-level changes in Marajó Island (Northern Brazil): Facies, $\delta^{13}\text{C}$, $\delta^{15}\text{N}$ and C/N. *Palaeog. Palaeocl. Palaeoecol* **282**, 19-31.

- Mohammed S.A.S., Naik M. and Tanveeruddin, S. (2009) Influence of additives on the retention of metal ions in a soil of Bangalore, India. *Rev. Amb. Água-An Interdisciplinary J. App. Sci.* **2**, 20-36.
- Munita C.S., Nascimento A., Schreiber S.B., Luna S., Oliveira P.M.S. (2004) Chemical study of some ceramics from Brazilian Northeast. *J. Radioanal. Nucl. Chem.* **259**, 305-309.
- Munita C.S., Paiva R.P., Alves M.A., Momose E.F., Saiki, M. (2000) Chemical characterization by INAA of Brazilian ceramics and cultural implications. *J. Radioanal. Nucl. Chem.* **244**, 575-578.
- Nath B.N., Kunzendorf H. and Plüger W.L. (2000) Influence of provenance, weathering, and sedimentary processes on the elemental ratios of the fine-grained fraction of the bedload sediments from the Vembanad Lake and the adjoining continental shelf. Southwest coast of India. *J. Sed. Res.* **70**, 1081-1094.
- Neal C.J., Smith H.A., Jeffrey H., Jarvie, P. and Robson, A.J. (1996) Trace element concentrations in the major rivers entering the Humber Estuary, NE England. *J. Hydrol.* **182**, 37-64.
- Nesbitt H.W. (1979) Mobility and fractionation of rare earth elements during weathering of a granodiorite. *Nature* **279**, 206-210.
- Nieboer E., Jusys A.A. (1988) Biologic chemistry of chromium. In *Chromium in the Natural and Human Environments* (eds. J.O. Nriagu and E. Nieboer). Adv. Environ. Sci. Technol. Wiley Series, v. 20, 572 pp.

- Nozaki Y., Lerche D., Alibo D.S. and Tsutsumi M. (2000) Dissolved indium and rare earth elements in three Japanese rivers and Tokyo Bay: Evidence for anthropogenic Gd and In. *Geochim. Cosmochim. Acta* **64**, 3975-3982.
- Ohr, M., Halliday, A.N. and Peacor, D.R. (1991) Sr and Nd isotopic evidence for punctuated clay diagenesis, Texas Gulf Coast. *Earth Planet. Sci. Lett.* **105**, 110–126.
- Oliveira P.M.S., Munita C.S., Hazenfratz R. (2009) Comparative study between three methods of outlying detection on experimental results. *J. Radioanal. Nucl. Chem.* in press.
- Pomeroy L.R., Odum E.P., Johannes E.R., Roffxian D.B. (1966) Flux of ^{32}P and Zn through a salt-marsh ecosystem. Disposal of radioactive wastes into seas, oceans and surface waters. *Geochim. Cosmochim. Acta* **19**, 244-260.
- Randle K. and Al-Jundi J. (2001) Instrumental neutron activation analysis (INAA) of estuarine sediments. *J. Radioanal. Nucl. Chem.* **249**, 361–367.
- Renfro W. C. (1973).. Transfer of ^{65}Zn from Sediments by Marine Polychaete Worms. *Mar. Biol.* **21**, 305-316.
- Rossetti, D.F. (2004) Paleosurfaces from northeastern Amazonia as a key for reconstructing paleolandscapes and understanding weathering products. *Sed. Geol.* **169**, 151-174.
- Rossetti D.F., Valeriano M.M. and Thalles M. (2007) An abandoned estuary within Marajó Island: implications for Late Quaternary paleogeography of northern Brazil. *Est. and Coast.* **30**, 813-826.

- Rossetti D.F., Valeriano M.M., Góes A.M. and Thalles M. (2008a) Palaeodrainage on Marajó Island, northern Brazil, in relation to Holocene relative sea-level dynamics. *The Holoc.* **18**, 923-934.
- Rossetti D.F., Góes A.M., Valeriano M.M., Miranda M.C.C. (2008b) Quaternary tectonics in a passive margin: Marajó Island, northern Brazil. *J. Quat. Sci.* **23**, 121-135.
- Schumm S.A., Mosley M.P. and Weaver W.W. (1987) *Experimental Fluvial Geomorphology*. New York, Wiley, 413 pp.
- Shajan K.P. (2001) Geochemistry of bottom sediments from a river-estuary-shelf mixing zone on the tropical southwest coast of India. *Bull. Geol. Surv. Jpn.* **52**, 371-382.
- Singh P. and Rajamani V. (2001) Geochemistry of the floodplain sediments of the Kaveri river, Southern India. *J. Sed. Res.* **71**, 50-60.
- Shanley K.W., McCabe P.J. and Hettinger R.D. (1992) Tidal influence in Cretaceous fluvial strata from Utah: a key to sequence stratigraphic interpretation. *Sedimentology* **39**, 905-930.
- Sholkovitz E.R. (1993) The geochemistry of rare earth elements in the Amazon River estuary. *Geochim. Cosmochim. Acta* **57**, 2181-2190.
- Sholkovitz E.R. (1992) Chemical evolution of Rare Earth Elements: fractionation between colloidal and solution phases of filtered river water. *Earth Planet. Sci. Lett.* **114**, 77-84.
- Sholkovitz E.R., and Elderfield H. (1988) The cycling of dissolved rare earth elements in Chesapeake Bay. *Global Biogeochem. Cycles* **2**, 157-176.

- Sholkovitz E.R. and Szymezak R. (2000) The estuarine chemistry of rare earth elements: comparison of the Amazon, Fly, Sepik and Gulf of Papua systems. *Earth Planet. Sci. Lett.* **178**, 299-309.
- Taylor S.R. and McLennan S.M. (1985) *The Continental Crust: its Composition and Evolution*. Blackwell Scientific Publications, pp. 307.
- Wellner R.W. and Bartek L.R. (2003) The effect of sea level, climate, and shelf physiography on the development of incised-valley complexes: a modern example from the East China Sea. *J. Sed. Res.* **73**, 926-940.
- Wyndham T., McCulloch M., Fallon S. and Alibert C. (2004) High-resolution coral records of rare earth elements in coastal seawater: biogeochemical cycling and a new environmental proxy. *Geochim. Cosmochim. Acta* **68**, 2067-2080.
- Varga A.R. and Szakmány G. (2004) Geochemistry and provenance of the Upper Carboniferous sandstones from borehole Diósvizsló-3 (Téseny Sandstone Formation, SW Hungary). *Act. Miner. Petr.*, **45**, 7-14.
- Vervoort J.D., Patchett P.J., Blichert-Toft J. and Albarède F. (1999) Relationships between Lu-Hf and Sm-Nd isotopic systems in the global sedimentary systems. *Earth Planet. Sci. Lett.* **168**, 79-99.
- Zaitlin B.A. and Shultz B.C. (1984) An estuarine embayment fill model from the Lower Cretaceous Mannville Group, west-central Saskatchewan. In *The Mesozoic of Middle North America* (eds. D.F. Stott and D.J. Glass). *Can. Soc. Pet. Geol. Mem.* **9**, 455-469.
- Zaitlin B.A. and Shultz B.C. (1990) Wave-influenced estuarine sand body, Senlac heavy oil pool, Saskatchewan, Canada. In *Sandstone Petroleum Reservoirs* (eds. J.H.

Barwis, J.G. McPherson and R.J. Studlick). New York, Springer-Verlag, pp. 363-387.

Zaitlin B.A., Warrern M.J. and Potocki D. (2002) Depositional styles in a low accommodation foreland basin setting: an example from the Basal Quartz (Lower Cretaceous), southern Alberta. *Bull. Can. Pet. Geol.* **50**, 31-72.

Zhu W., Kennedy M., de Leer E.W.B., Zhou H., Alaerts G.J.F.R. (1997) Distribution and modelling of rare earth elements in Chinese river sediments. *Sci. Tot. Environ.* **204**, 233-243.

FIGURE CAPTIONS

Fig. 1: A) Location map of the study area in eastern Marajó Basin, Pará Platform, northern Brazil. Note the studied well at the western margin of Lake Arari. B) Simplified chart summarizing the stratigraphy of the study area.

Fig. 2: A) Landsat image and 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 Lake Arari occurs inside the inner paleoestuary area, which is also surrounded by numerous paleochannels.

Fig. 3: Minimum and maximum minor and rare earth element concentrations considering all groups, with data normalized to NASC. The elements were organized in this

graphic according to their decreasing abundance in the upper continental crust following Taylor and McLennan (1985).

Fig. 4: Mean concentration of minor and rare earth elements (normalized do NASC) for each group representative of the individual depositional environments. A=fluvial; B=outer estuary; C=central estuarine basin; D=tidal flat; F=lagoon.

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; 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. The samples related to more marine influenced deposits (groups B=outer estuary; D=tidal flat; F=lagoon) are closely related, with only a rough discrimination of group D.

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

Fig. 8: Graphic with log K versus log Rb, considering the mean concentration for all groups. 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).

TABLE CAPTIONS

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

Tab. 2: Means and standard deviation of minor and rare earth elements representative of the five depositional groups analysed in this study. NASC values are also presented for comparison. The values are in $\mu\text{g/g}$, unless otherwise indicated.

Tab. 3: Ratios between selected elements of interest (values normalized to NASC) and mean concentrations of total rare earth elements (TREE), light rare elements (LREE) and heavy rare elements (HREE) for the five analysed groups. K+Na values are also included in this table.

Table 1

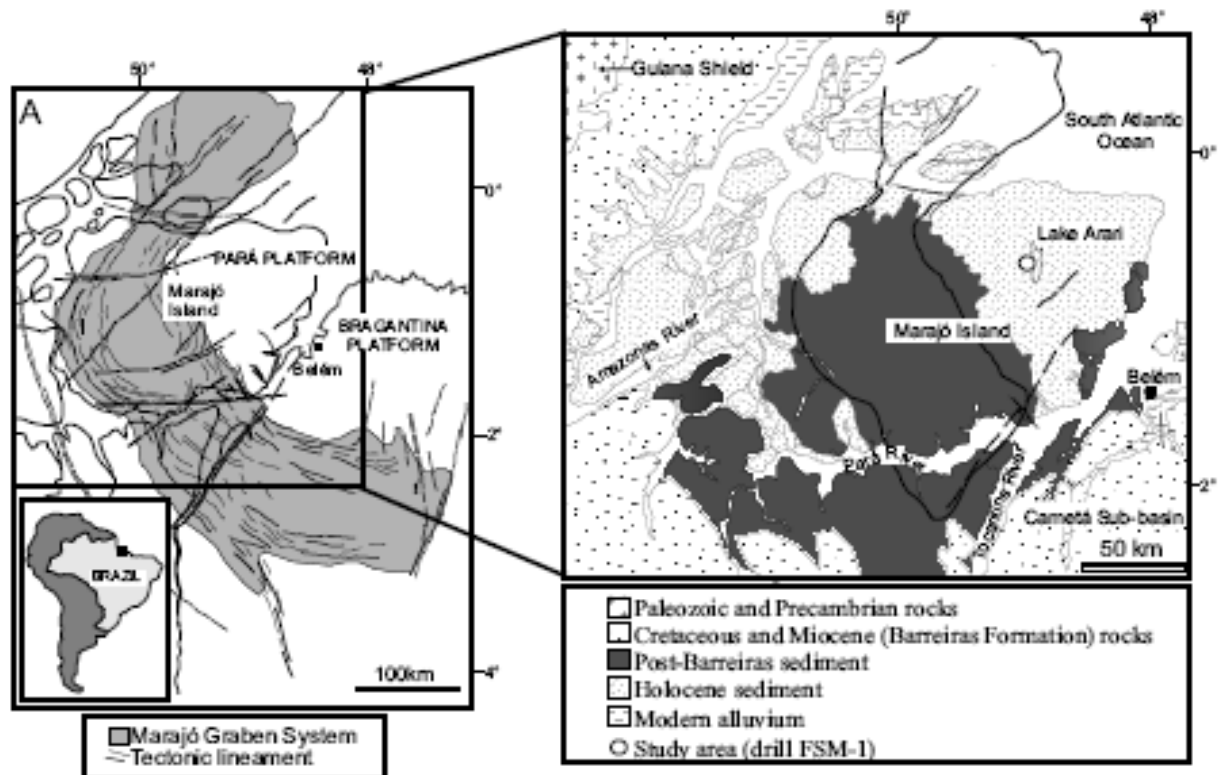
Facies Assoc.	Interpreted Paleoenvironment	Description	Main Source of Organic Matter (interpreted from $\delta^{13}\text{C}$, $\delta^{15}\text{N}$ and C/N)
A	Fluvial Channel	Moderately sorted, fine to coarse-grained, locally conglomeratic, massive sand (facies Sm), with only subordinate parallel laminated 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 Hwf, 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, particularly in the uppermost portion of the succession

Table 2

	A		B		C		D		F		NASC ^a
	mean	S.D.	mean	S.D.	mean	S.D.	mean	S.D.	mean	S.D.	
Ce	120.1	13.29	106.29	4.65	100.38	17.89	86.77	8.79	103.88	9.8	66.7
Co	20.78	5.47	18.29	0.75	20.14	4.94	13.24	1.97	17.46	3.58	25.7
Cr	113.28	14.94	88.51	11.1	94.9	15.16	68.06	8.72	83.06	9.2	124.5
Cs	5.24	0.84	10.94	1.1	4.77	1.11	6.15	1.45	9.64	1.41	5.16
Eu	1.66	0.17	1.84	0.1	1.66	0.32	1.49	0.14	1.79	0.15	1.18
Fe(%)	5.36	2.01	5.33	0.32	5.03	6.01	3.46	0.58	5	0.72	4.4
Hf	9.1	2.37	4.88	0.6	9.99	2.61	11.66	3.84	6.59	1.86	6.3
K(%)	1.52	0.79	2.19	0.29	1.6	0.22	1.76	0.27	2.17	0.35	3.2
La	62.18	7.62	55.58	2.08	51.13	8.91	45.66	4.57	54.16	4.7	31.1
Lu	0.48	0.04	0.59	0.04	0.58	0.06	0.62	0.06	0.61	0.04	0.46
Na(%)	0.05	0.04	0.65	0.13	0.26	0.06	0.68	0.06	0.84	0.1	0.75
Nd	49.5	7.32	48.37	17.6	38.06	9.49	35.21	9.04	45.73	10.42	27.4
Rb	64.3	36.8	143.78	19.7	93.15	20.35	100.94	18.83	134.45	24.38	125
Sc	14.64	1.9	18.42	0.58	14.91	2.98	12.89	1.98	17.06	1.8	14.9
Sm	9.02	0.95	9.69	0.32	8.52	1.47	7.96	0.76	9.37	0.76	5.59
Ta	1.34	0.19	1.29	0.15	1.35	0.22	1.41	0.2	1.47	0.23	1.12
Th	23.32	2.98	16.95	0.83	15.21	2.19	13.57	1.37	16.52	1.53	12.3
U	2.82	0.22	3.94	0.4	3.73	0.45	3.76	0.43	3.67	0.4	2.66
Yb	2.88	0.52	3.68	0.16	3.75	0.33	3.84	0.31	3.73	0.2	3.06
Zn	112.42	16.77	115.47	11.5	68.15	18.05	77.4	13.8	107.26	14.53	100

Table 3

	A	B	C	D	F
[La/Yb] _{NASC}	2.16	1.51	1.36	1.2	1.45
[La/Th] _{NASC}	1.06	1.3	1.33	1.33	1.3
[Th/U] _{NASC}	1.83	1.23	1.43	0.79	0.84
[K/Na] _{NASC}	6.71	0.79	1.43	0.61	0.61
K+Na	1.57	2.85	1.86	2.44	3
TREE	245.74	226.04	204.08	181.55	219.24
LREE	242.38	221.77	199.75	177.09	214.9
HREE	3.36	4.27	4.33	4.46	4.34



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

Fig. 1

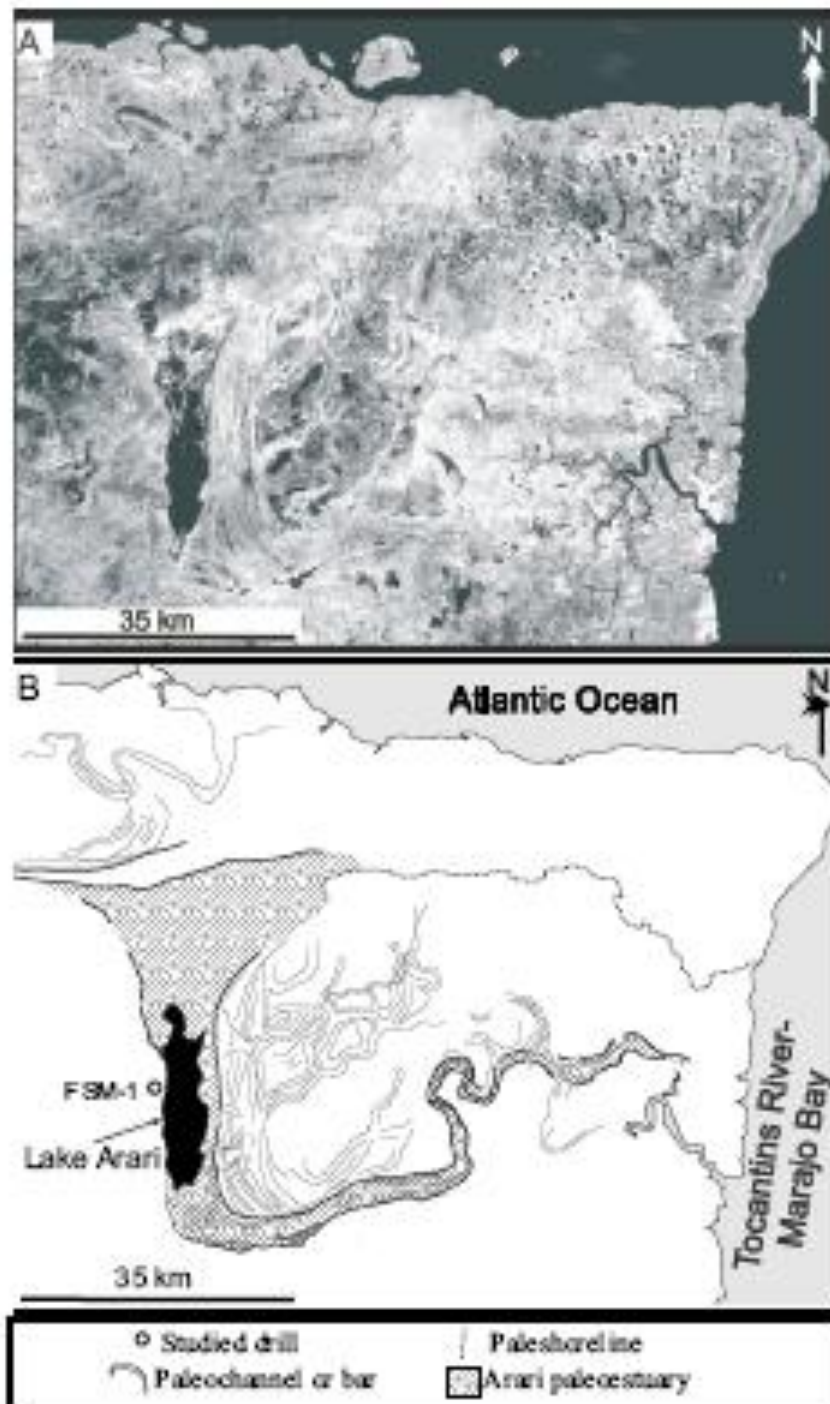


Fig. 2

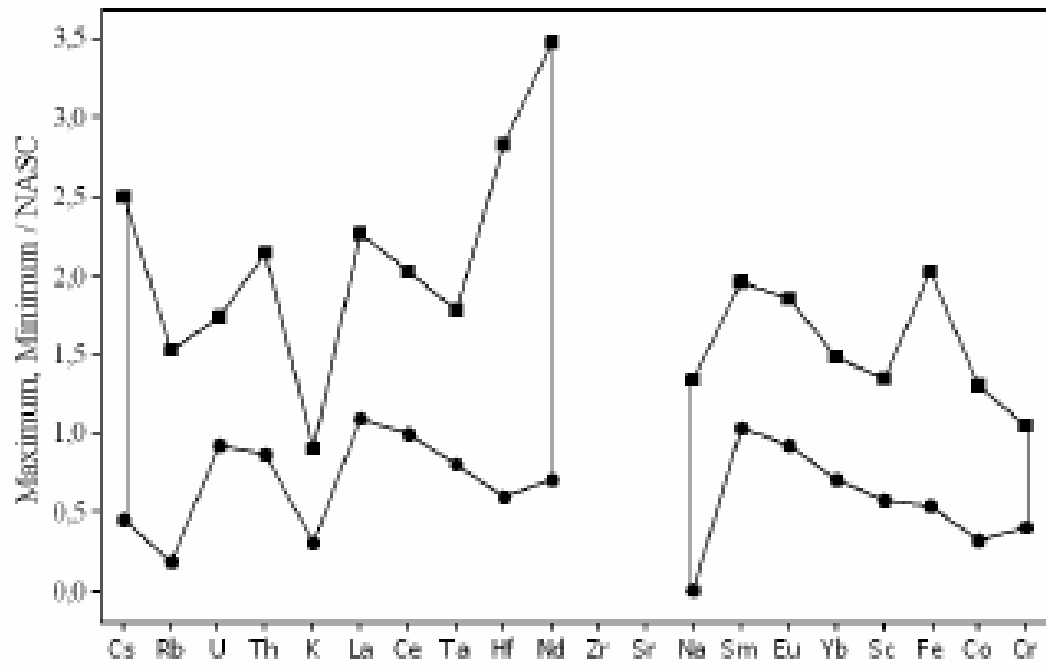


Fig. 3

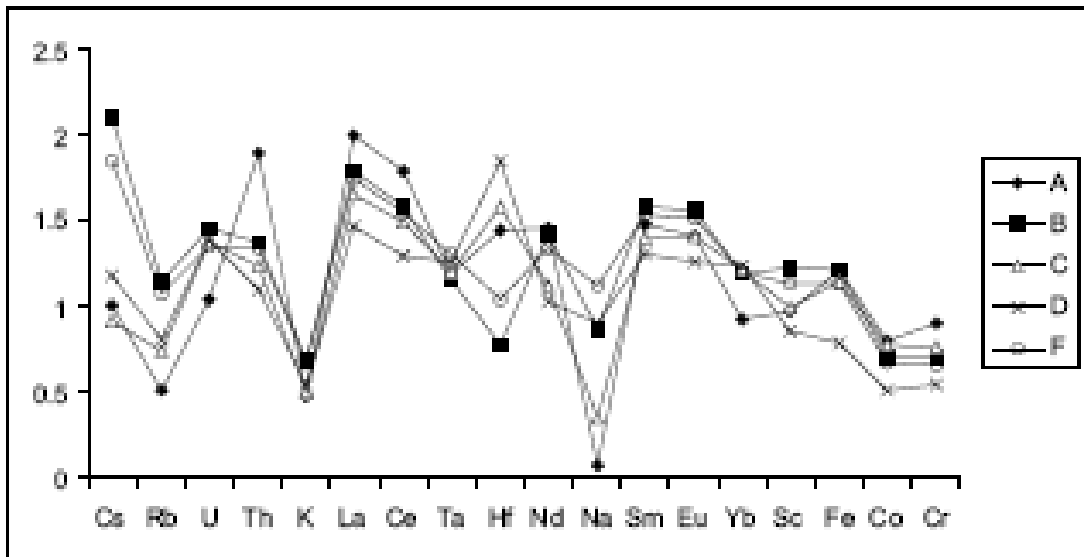


Fig. 4

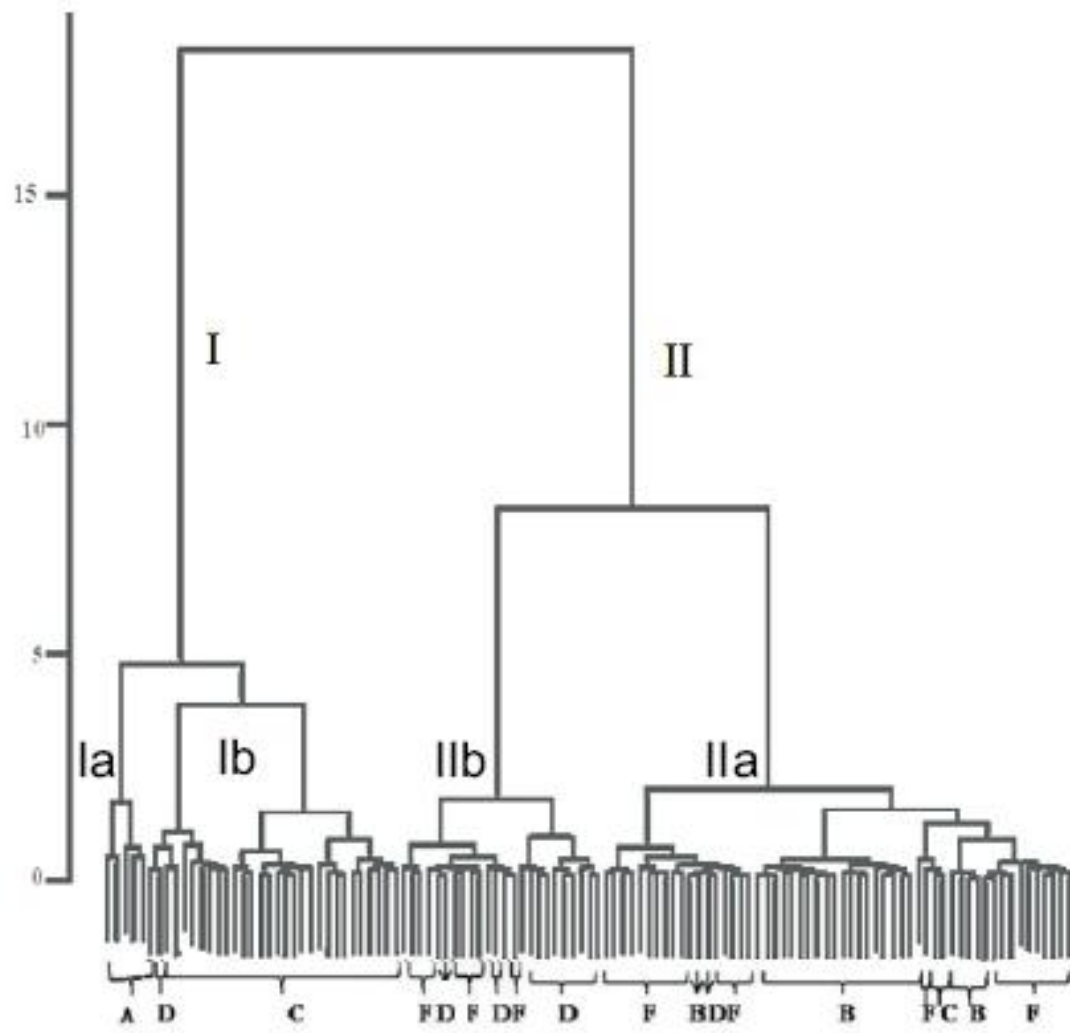


Fig. 5

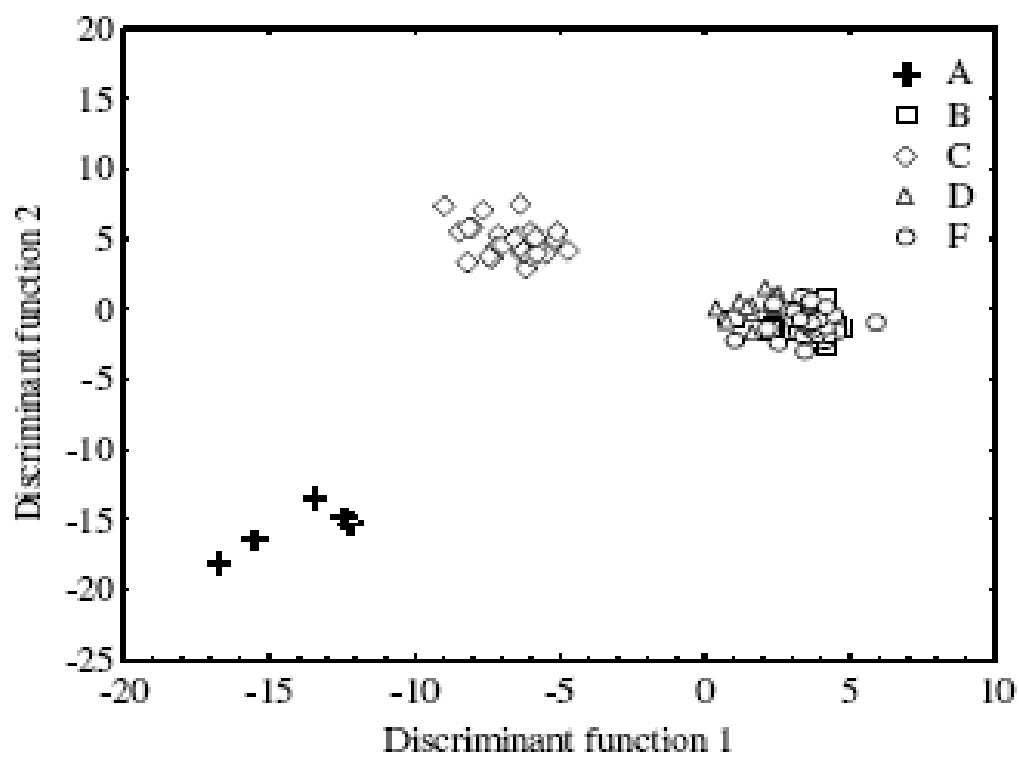


Fig. 6

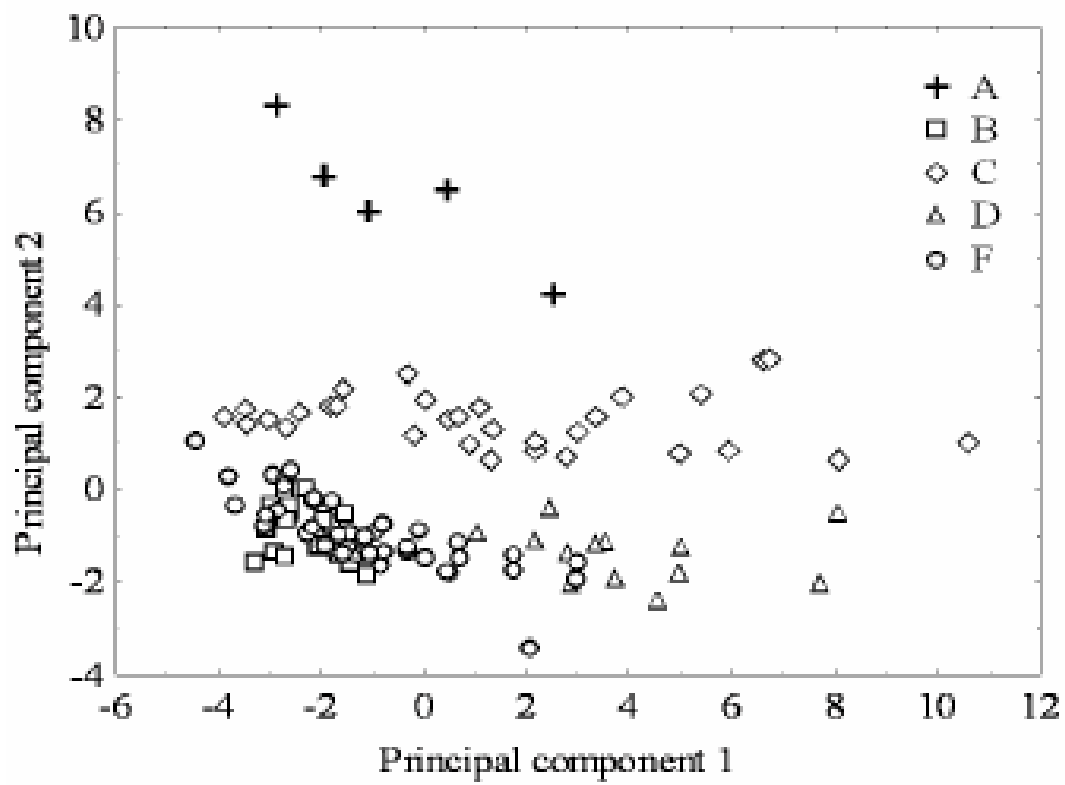


Fig. 7

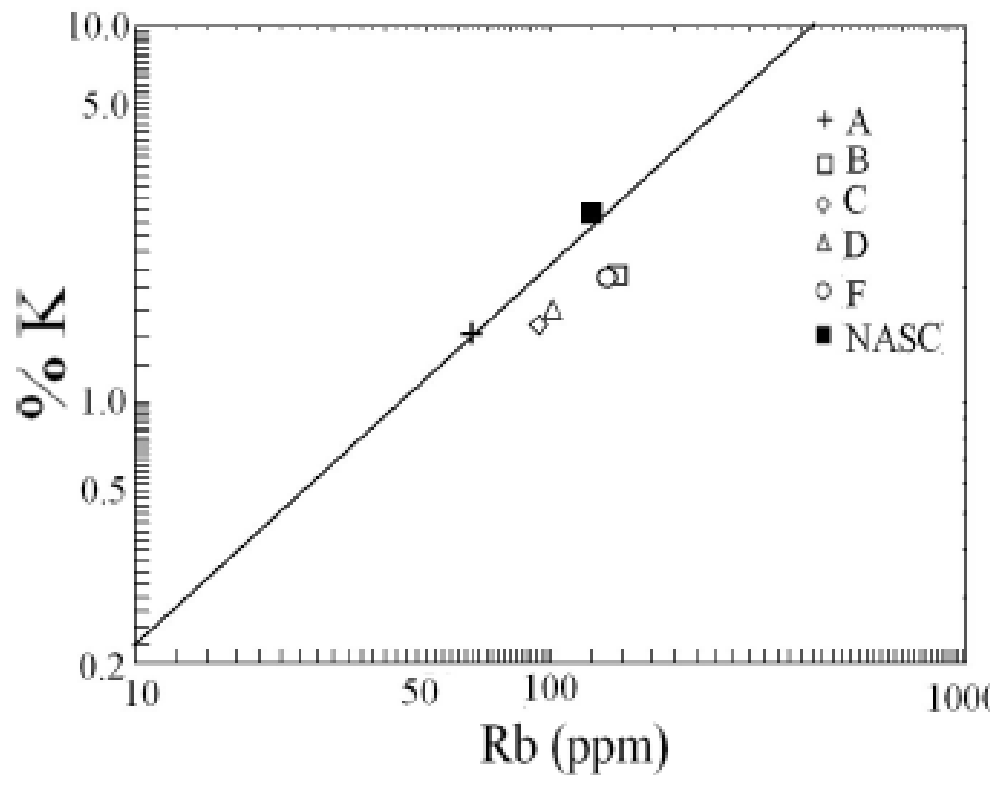


Fig. 8