The geostatistics of the metal concentrations in sediments from the eastern Brazilian continental shelf in areas of gas and oil production

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ABSTRACT

Geostatistical techniques were used to evaluate the differences in the geochemistry of metals in the marine sediments along the Eastern Brazilian continental margin along the states of Ceará and Rio Grande do Norte (Northeastern sector) and Espírito Santo (Southeastern sector). The concentrations of Al, Fe, Mn, Ba, Cd, Cu, Cr, Ni, Pb, V, Hg, and Zn were obtained from acid digestion and quantified using flame atomic absorption spectrometry (AAS), inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma atomic emission spectrometry (ICP-AES). The metals showed a similar order of concentration: $Al > Fe > Ba > Mn > V > Ni > Pb > Cr > Zn > Cu$, in both the Ceará; and Rio Grande do Norte shelf regions but different in the Espírito Santo shelf ($Fe > Al > Mn > Ba > Zn > V > Cr > Ni > Pb > Cu$. The concentrations of Hg and Cd were below the detection limit in all areas. A multivariate analysis revealed that the metals of siliciclastic origin on the continental shelf of Ceará are carried by Al. In addition, a large portion of metal deposits is connected to the iron and manganese oxides on the continental margin of Rio Grande do Norte. The metals from the continental supply on the coast of Espírito Santo (Cu, Ni, Ba, and Mn) are associated with Al; whereas Cr, Pb, V, and Zn are associated with iron in this southern area. Geochemical evaluations are needed to distinguish the origin and mineralogical differences of marine sediments within the regions. Scanning electron microscopy/energy dispersive spectrometry (SEM/EDS) applied to the sediments from the coast of Ceará showed the morphological diversity of sediment grains: biological fragments, multifaceted particles, aggregates, and crystals occurred in the three regions analyzed. Among these grains, calcite, Mg-calcite, and aragonite were predominant in the northeastern sector, whereas silicates and other minerals were predominant the southeastern sector. Mg, K, Ti, and Zr as well as the lanthanides La and Ce were identified using SEM/EDS and added to the geochemical analysis of the data.

1. Introduction

Continental shelves consist of a submerged extension of the continents with a small slope toward the high sea that occupy approximately 7% of the ocean floor surface, with an average global depth of 130 m. They extend from the shallow areas, which are dominated by coastal processes, to the edge of the continental slope, which is dominated by oceanic processes. In general, marine sediments originate from various sources, such as terrigenous materials transported by rivers, biogenic compounds originating from marine organisms, and antigenic minerals, which are the product of salt precipitation from sea water (Tessler and Mahiques, 2000).

Depending on the acting sedimentary processes, continental shelves can be divided into autochthonous, such as those in northeastern Brazil, which receive a small supply of modern continental sediments resulting in geochemical characteristics highly influenced by the in situ reworking of old deposits (relic deposits); and allochthonous continental shelves, whose sediments are mostly supplied by modern sources (e.g., in the northern and southern Brazil) brought primarily from the adjacent continent. With regard to the composition of sediments, the continental shelves can be further divided into siliciclastic continental shelves, where siliceous sediments are predominant (e.g., southern Brazil), and carbonaceous continental shelves, where

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carbonate sediments predominate (e.g., northeastern Brazil) (Vital et al., 2005).

The discovery of various oil and gas fields in the Brazilian continental shelf brought new challenges to environmental monitoring; thereby enhancing the need for increasing the knowledge of the geochemical distribution of elements in the continental shelf. Motivated by the need to increase production and meet the demands of the Brazilian environmental legislation, the petroleum industry initiated a series of site-specific evaluations to determine the geochemical base levels and anomalies of metals in the continental shelf and to evaluate the potential effect of this activity. Although the sampling strategy of these evaluations is not uniform along the continental shelf, a review of the data obtained from different sectors of the Brazilian coast, using the same geostatistical criteria can clarify existing differences between the compositions of the sediments from different regions of the continental shelf and indicate the need to define a geochemical criteria of these Brazilian continental shelf sectors. The knowledge of regional variability can also aid in the definition of the sampling grids that are necessary to supply information to identify geochemical anomalies as well as distinguish between natural anomalies and those caused by anthropogenic activities.

1.1. General physiography of the Brazilian coast

Brazil has one of the largest coastal areas of the Americas (approximately 5900 km long). When the contours of the islands, bays, and estuaries are considered, the coastal area extends for more than 9200 km long. In general, a succession of coastal plains alternating with cliffs and rocky shores, that border an ancient continental area composed of Pre-Cambrian polymetamorphic igneous rocks, is observed along the Brazilian coast. The coastal plains, which consist of tertiary and quaternary sediments accumulated in continental, transitional, and marine environments, are more developed around the mouths of the major rivers, where a larger sedimentary supply of terrigenous clastic sediments has been found (Villwock et al., 2005).

The continental shelf investigated this study harbors most of the country's offshore gas and oil production and are enclosed in the region surrounding the South Equatorial Current (SEC) bifurcation, which is one of the least well researched regions in the South Atlantic Ocean. The southernmost branch of the South Equatorial Current (sSEC) arrives and bifurcates between 10 and 20°S originating the Brazil Current (BC), initially carrying about $4 \sim$ Sv to the south, and the North Brazil Current (NBC), carrying the remainder northwestward along the northern coastline of Brazil. Southwards, the sSEC bifurcation signal near the continental margin shows velocity fields dominated by mesoscale eddies suggesting a flow strongly influenced by topography and probably very unstable (Soutelino et al., 2011). Further south, at approximately 36−38°S, the Malvinas Current encounters the Brazil Current, forming the Brazil−Malvinas Confluence. Northward the NBC crosses the equator, carrying approximately 12 Sv into the northern hemisphere (Peterson and Stramma, 1991).

Different classifications of the Brazilian coastal zone exist based on various criteria (e.g., morphology, climate, oceanographic parameters, sedimentary cover, shelf width, geology, mineralogy, and hydrological regime) (Revizee, 1995; Muller et al., 1999; Knoppers et al., 1999). In the current study adopted the Large Marine Ecosystem (LME) typology proposed by Ekau and Knoppers (1999). This typology divides the Brazilian coast into three regions based on bathymetry, productivity, and trophic levels: North, East (where this study was developed), and South. The importance of the geochemical criteria will be evaluated in this context to determine the contributions and processes associated with the geochemical

partitioning of metals with regard to the different sedimentary facies present on two distinct sectors of the eastern Brazilian continental shelf (EBCS), the northeastern under the dominium of the NBC and the southern, under the influence of the BC.

1.2. Metals in marine sediments

Marine sediments generally show low concentrations of trace metals. Marine carbonates are depleted in the majority of trace elements compared with clays in the marine environment (Chester, 1990). Li and Schoonmaker (2003) studied the mineralogy and geochemistry of the pelagic sediments of the Equatorial Pacific and identified various types of sediments. The Enrichment Factor (EF) and a factor analysis were used to determine the major components and predominant mineralogical phases of marine sediments. The major pelagic marine sediment components were (i) aluminum silicates primarily derived from the weathering of shale, wind deposition, and river transportation and containing Al, Si, Ti, Th, Zr, K, Rb, Fe, As, and Mg; (ii) manganese oxides containing Mn, Ni, Co, Mo, Pd, Cu, and Zn; and (iii) phosphates and fluorapatite associated with carbonates composed of Ca, Sr, P, and Y.

Karageorgis et al. (2005) studied the geochemistry of Al, Si, Fe, Ca, Sr, V, Cr, Mn, Co, Ni, Cu, Zn, As, Mo, and Pb in the surface sediments of the Aegean Sea. The authors classified Al, Si, and Fe as lithogenic metals, Ca and Sr as biogenic metals, and Cu, Zn, and As as anthropogenic metals. Moreover, the oxides and hydroxides of Fe and Mn were classified as minerals that control the deposition of V, Cr, Co, Ni, Zn, As, Mo, and Pb via exogenous sedimentary processes.

Ohta et al. (2007) evaluated the geochemical distribution of V, Cr, Ni, Cu, Zn, Ba, and Pb along the coast of Japan. The authors concluded that the grain size of the sediments and the regional geology control the sedimentary deposition of these metals in the marine sediments. The composition of these sediments is similar to that of the sediments from the continental areas adjacent to the coast. Anthropogenic contributions of Zn, Cd, Mo, Sn, Pb, and Bi were observed among the marine sediments of certain sectors of the coastal region.

On the inner continental shelf of the Bay of Bengal southeast of India, the geochemical processes that influence the distribution of Al, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, Si, and Zn were studied. The sediments of this region were poorly selected, with concentrations of sand greater than 90% and organic matter (OM) below 0.4%. The authors concluded that Cd, Co, Cr, Ni, and Pb were from anthropogenic sources, whereas the other elements were derived from the existing regional lithology (Selvaraj et al., 2004). Thus, studies in different marine environments have shown that the major process controlling the geochemistry of metals in marine sediments are the allochtonous contribution from continents, including both natural and anthropogenic sources, and the autigenic interactions with different mineralogical matrix, including biological activity.

1.3. Metal concentrations in the sediments of the Brazilian continental shelf

Studies on the geochemical distribution of metals on the Brazilian continental shelf are concentrated in the southeastern region, the most industrialized area of the country. These studies are more concentrated in the coastal zones, primarily in the estuaries of the major rivers in the eastern and northern regions. A review of the most relevant prior studies on the geochemistry of metals performed along the Brazilian continental shelf provides extremely important information regarding the geochemistry of metals in the marine sediments of the Brazilian coast. However, they are

inadequate to accurately determine sedimentation processes, identify origins, or monitor the areas potentially affected by contaminants.

Several studies (Abílio et al., 2004; Lacerda et al., 2005, 2013; Campos et al., 2005; Marins et al., 2005; Lacerda and Marins, 2006; Rezende et al., 2002, 2004) discussed the impacts of the petroleum activity on the Brazilian coast in relation to metal distribution in sediments. All concluded that natural drivers such as continental runoff (Molisani et al., 1999) and autigenic minerals precipitation were the major processes controlling metal distribution in shelf sediments.

Consistent studies regarding the chronological markers of the sedimentation regime are scarce for the EBCS; thus, Arz et al. (1999) study on the sedimentary profiles sampled along the continental shelf of Ceará, Rio Grande do Norte, and Paraíba is worth emphasizing. These authors obtained sedimentation rates, using ^{14}C dating, of 8 cm/1000 years, 30 cm/1000 years, and 100 cm/1000 years in Ceará, Rio Grande do Norte, and Paraíba Basins, respectively. Furthermore, the Ti/Ca and Fe/Ca ratios revealed an increase of siliciclastic inflow on the EBCS across different periods. These results suggests that the continental contribution is 3—10 times greater in the Paraíba Basin in the southern extreme of the Eastern Brazilian shelf, compared to the northeastern extreme, represented by the Ceará and Rio Grande do Norte.

The results obtained in the surface sediments on the continental shelf of Ceará using $Ti/CaCO_3$ ratios revealed periods of sedimentary deposition processes controlled by the inflow of continental materials, autochthonous marine processes, or both (Aguiar et al., 2008). Sedimentation rates of 0.1—0.8 cm/year were obtained using ^{210}Pb dating in the southeastern portion of the Brazilian coast on the inner continental shelf between the Pardo and Doce Rivers (Patchineelam and Smoak, 1999).

2. Study area

According to Ekau and Knoppers (1999), the EBCS corresponds to the region between the Parnaíba River Delta and the Cape of São Tomé. Previous studies defined the sedimentary cover and the boundaries of the Brazilian continental shelf (Revizee, 1995; Cavalcanti, 2011). Recent studies have examined the morphology and described the major sedimentary facies of the northern portion of the EBCS (Freire, 1985; Rocha and Martins, 1998; Freire et al., 2004; Vital et al., 2005). The relief of this coastal region is composed of a 50—100 km band of coarse tertiary siliciclastic sediments (i.e., the Barreiras Formation; Lacerda, 2002; Villwock et al., 2005). Extensive fields of dunes, coastal lakes, and swamps occupy the estuary regions that characterize the coastline. The climate of the northern region is predominantly semiarid with irregular rainfall precipitations that vary from 500 to 1200 mm/year. The climatic seasonality of the region strongly influences the rivers. In general, the rivers are small and intermittent except for the Parnaíba, the Jaguaribe, the northern portion of the Capibaribe/Mundaú, and the central portion the São Francisco Rivers, which have perennial flow rates of 741 m³/s, 20 m³/s, 4.5 m³/s, and 1403 m³/s, respectively (ANA, 2011; Dias et al., 2011).

In contrast, the inner portion of the coastal plain adjacent to the continental shelf of the southeastern coast of Brazil is bounded by the granitic-gneissic massif of the Serra do Mar and remains partially covered by the Atlantic Forest (Mata Atlântica). This plain is in a wet, tropical climate with annual precipitation ranging from 1100 to 1500 mm, with localized areas of up to 2000 and 3000 mm of precipitation in the Serra do Mar and the southern coastal region of Bahia (Sei, 1988). Extensive quaternary sandy plains and approximately 60 coastal lagoons are located between south Bahia and north Rio de Janeiro. The adjacent continental shelf is narrow

and varies in length from 15 to 90 km, with the exception of Abrolhos, where the shelf extends up to 220 km (Ekau and Knoppers, 1999). This region is subject to strong erosion and soil movement as well as characterized by perennial drainage. The major rivers of this area are the Paraguaçu, Contas, Pardo, and Paraíba Rivers with average flow rates of 149 m³/s, 100 m³/s, 93 m³/s, and 292 m³/s, respectively (CRA, 2001; Paula et al., 2010; ANA, 2011).

3. Materials and methods

3.1. Sampling

The surface sediment samples analyzed in this study were collected along the east coast of Brazil, specifically on the continental shelf corresponding to Ceará, Rio Grande do Norte, and Espírito Santo, while PETROBRAS Oil Company performed monitoring studies in areas of oil and gas production (Fig. 1). On the continental shelf of Ceará, 25 sampling stations were distributed along the coastline. Three launchings of the sampler were conducted per station to collect 75 sediment samples. Forty-three stations were sampled on the continental shelf of Rio Grande do Norte with three launchings of the sampler per station, totaling 129 samples. Samples were collected from 23 stations on the continental shelf of Espírito Santo. After sampling, the sediments were refrigerated at 4 °C and packed in the laboratory at −20 °C in a polypropylene flask until the tests were performed.

3.2. Chemical analysis

The concentration of metals in the sediments from the EBCS was determined in <2 mm fractions and expressed in mg/kg (average ± standard deviation and concentration range). The laboratories of the UFC-CE and PUC-RJ analyzed the samples collected along the coasts of Ceará and Rio Grande do Norte, respectively. A laboratory contracted by PETROBRAS analyzed the samples from the continental shelf of Espírito Santo.

Samples digestion used hydrochloric and nitric acid (HCl/HNO_3) to determine the concentrations of Al, Cr, Cu, Ba, Cd, Fe, Mn, Ni, Pb, V, Zn, and Hg in the sediments of the continental shelf of Ceará (Aguiar et al., 2007). To determine the concentrations of Al, Fe, Mn, Ba, Cd, Cu, Cr, Ni, Pb, V, Zn, and Hg in the samples from the coast of Espírito Santo, a digestion was performed using a mixture of HCl, HNO_3, and hydrogen peroxide (H_2O_2; EPA, 6010B). HNO_3 and hydrofluoric acid (HF) were used to determine the concentrations of Al, Fe, Mn, Ba, Cd, Cu, Cr, Ni, Pb, V, Zn, and Hg in the sediments from the continental shelf of Rio Grande do Norte (Campos et al., 2005).

Digestion procedures employing HCl/HNO_3 have a distinct oxidizing power and are capable of promoting the release of metals from all labile (i.e., adsorbed, exchangeable, oxidizable, and reduced) fractions, leaving only the detritic fraction and the metal associated with the mineralogical structure of lithogenic silicates that do not characterize anthropogenic contamination (Sutherland, 2002). In turn, mixtures of HCl, HNO_3, and HF are capable of solubilizing chemicals that are associated with all phases or geochemical fractions, the labile fractions, and the residuals (Sastre et al., 2002). Studies performed using HCl/HNO_3 and HNO_3/HF in the marine sediments from the coast of Ceará showed differences only with regard to concentration. However, the different digestion methods did not alter the geochemical interpretation of the data (Aguiar et al., 2007).

The limit of detection (LD) for the concentrations of the analyzed metals was determined using the standard deviations of the respective analysis blanks via the equation LD = 3 s/S, where s = the standard deviation of 10 sample blank readings according to Miller and Miller (1994). A gravimetric analysis was used to
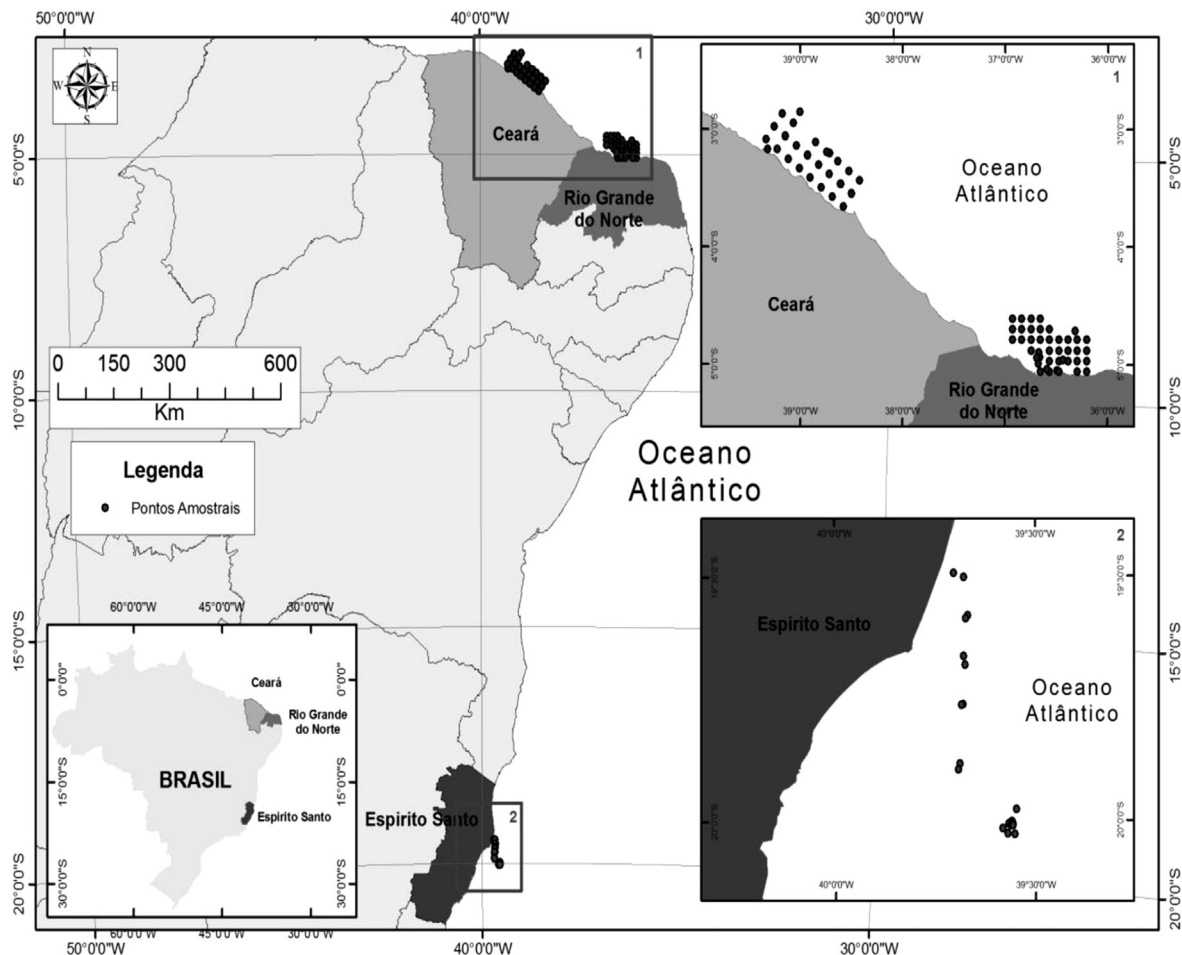
Fig. 1. Location of sampling stations in the three areas of the Brazilian continental shelf.

determine the OM and carbonate contents (Loring and Rantala, 1992). Two certified reference materials were analyzed for the accuracy of the methodologies used: "Marine Sediment Reference Materials for Trace Metals and other Constituents" (MESS-2) from the Canadian National Research Council (CNRC) and Inorganics in Marine Sediment (SRM 2702) from the National Institute of Standards and Technology (NIST, Gaithersburg, USA).

The quantification of Al, Fe, Mn, Ba, Cd, Cu, Cr, Ni, Pb, V, and Zn among the sediments from the EBCS were obtained using flame atomic absorption spectrometry (AAS), inductively coupled plasma mass spectrometry (ICP-MS), and inductively coupled plasma atomic emission spectrometry (ICP-AES). Hg was quantified using hydride generation atomic absorption spectrometry (HG AAS). Importantly, AAS measures concentrations in mg/kg, whereas, ICP-MS, ICP-AES, and Hg AAS quantifies metal in μg/kg.

3.3. Data analyses

Multivariate techniques including a grouping analysis, cluster analysis (CA), and principal component analysis (PCA) were applied to the dataset using the ESTATÍSTICA 8 program. CA and PCA are appropriate to evaluate relationships between variables and the general behavior of the data. LD values were used for concentration values equal to zero in the CA and PCA; the data matrix was standardized using Z-scores, and the Ward's Amalgamation method and the quadratic Euclidean distance were employed. CA and PCA enable evaluations of the concentration of metals by station sampled. These techniques were recently applied to interpret the

data from marine sediment metals (Landim, 2000; Aguiar et al., 2008; Abílio et al., 2004; Mendonça, 2006; Hortellani et al., 2008) along the east and south coast of Brazil as well as those for sediments from the coast of the United States (Simeonov et al., 2001).

3.4. Analytical microscopy (SEM/EDS)

Lyophilized sediments from three stations on the continental shelf of Ceará were adhered to two-sided carbon adhesive tape over an Al support; the sediments were then covered with an approximately 5-nm layer of platinum using BALTEC 050 sputter. The morphological data and x-ray microanalysis results were obtained using a scanning electron microscope (ZEISS XVP EVO 40; Carl Zeiss SMT AG) coupled to an IXRF dispersive energy spectrometer (IXRF System, Inc.) equipped with an Si (Li) detector with an ultrafine window (0.3 μm) of beryllium, operating with ZAF correction. Morphological data (i.e., secondary electron images [SE images] and back-scattered electron images [BSE images]) were obtained with equipment operating in a high-vacuum mode with a voltage acceleration of 25 KeV. Dispersive energy spectra and chemical element distribution maps were obtained using the electron beam with a current varying between 500 pA and 1.0 nA, 90 s of acquisition time, an 8.5 mm working distance, and a 35° x-ray detection angle using the afore mentioned conditions. The presence of carbonates was retested using the deposition of sediments on Au supports with analyses performed on samples kept at −20 °C using Pt with a temperature-controlled DEßEN stage-cooler (Miguens et al., 2010). The sampling stations were selected based on the

Table 1
Metal concentrations (mg kg^{-1}) in bottom sediments (Ø < 2 mm) in three sectors of the Eastern Brazilian continental shelf.

| Metal	Ceará*	Rio Grande do Norte*	Espirito Santo*
Fe	1250 ± 1069 (20–2868)	1330 ± 1761 (120–7133)	35,948 ± 14,876 (16,799–73,260)
Mn	42 ± 57 (5–177)	26 ± 29 (5–147)	1003 ± 534 (171–2073)
Al	1389 ± 1129 (202–4669)	2854 ± 3988 (78–13,362)	28,058 ± 10,470 (4797–42,396)
Ba	945 ± 1398 (8.3–5997)	66 ± 77 (6–332)	134 ± 68 (8–219)
V	19 ± 26 (5.6–78)	7.8 ± 7.3 (2.1–40)	69 ± 21 (42–129)
Cr	5.3 ± 1.6 (2.6–9.5)	8.0 ± 5.6 (2.4–23)	60 ± 22 (17–104)
Ni	6.0 ± 6.6 (0.2–23)	0.9 ± 1.6 (<0.1–7)	26 ± 9.5 (5.0–38)
Cu	0.9 ± 0.6 (0.18–2.2)	0.6 ± 1.3 (<0.1 ± 6.6)	17 ± 6.0 (2.8–22)
Zn	2.5 ± 2.0 (0.2–7.0)	1.5 ± 3.1 (<0.1–13)	58 ± 30 (12–171)
Pb	6.0 ± 5.0 (0.6–17)	1.5 ± 2.0 (<0.1–7.1)	11 ± 5.3 (2.4–26)

results from the previously obtained sedimentary chemical analyses (Aguiar et al., 2007). Mineralogy was determined using dispersive energy spectroscopy and a semi-quantitative analysis of sediment grains with an axis at least 20 μm-n = 100/station.

4. Results and discussion

4.1. The concentrations of metals in sediments from the EBCS

Metals concentrations in sediments from the EBCS are shown in Table 1. In general, the data showed that the relative abundance of major and trace elements were similar in the continental shelves of Ceará and Rio Grande do Norte, with abundance of the different metals following: Al > Fe > Ba > Mn > Cr > V; a small difference in trace elements abundance was found between the two areas, while in the Ceará shelf relative abundance was: Ni > Pb > Zn > Cu; in the Rio Grande do Norte shelf the relative abundance among trace elements was: Zn = Pb > Ni > Cu. Abundance of major and trace elements was different in the Espírito Santo shelf with Fe dominating over Al concentrations and Mn over Ba. Trace elements relative abundance was, V, Cr, and Zn with similar concentrations followed by Ni > Cu > Pb. The concentrations of Cd and Hg in
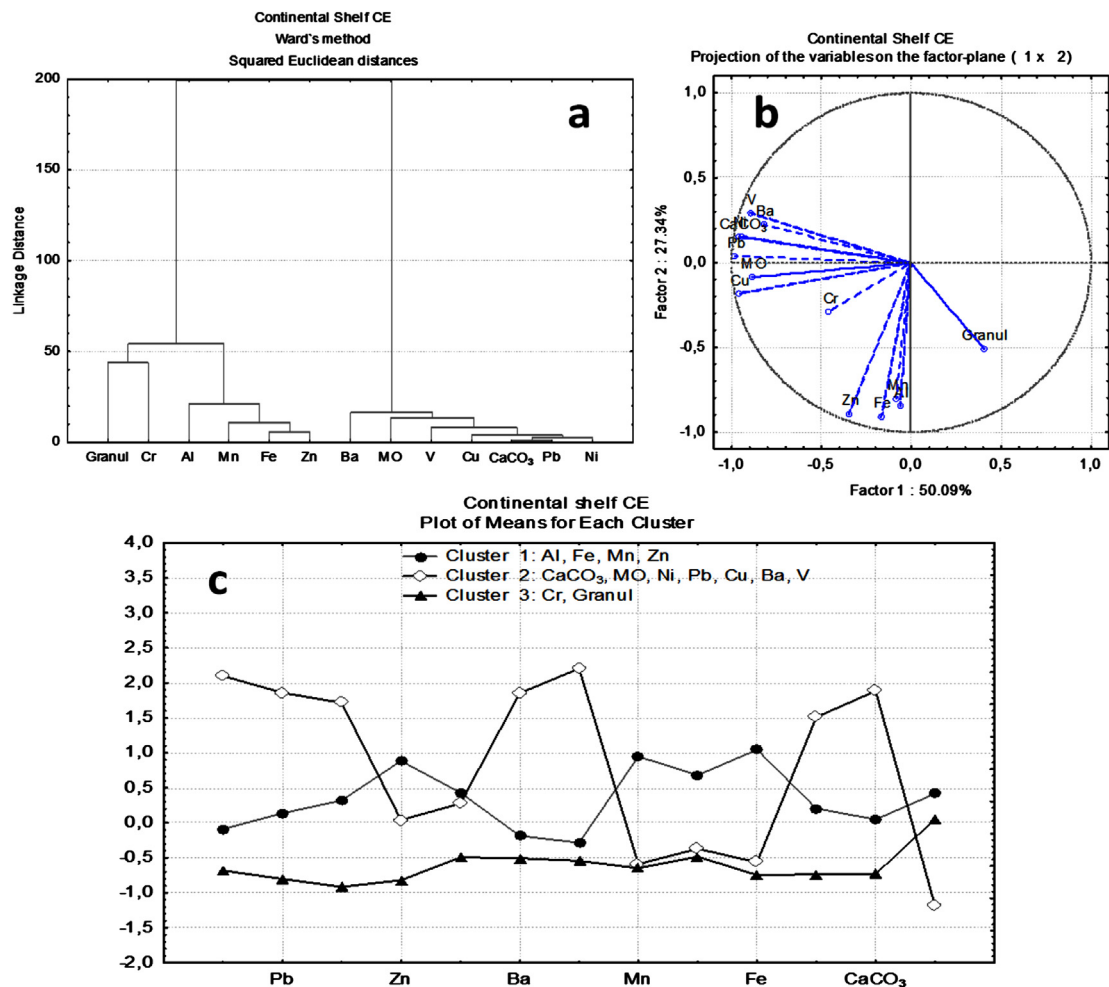
Fig. 2. Cluster Analysis (a), Principal Component Analysis (PCA) applied to Z normalized and varimax rotated metal concentrations (b) and K-means Cluster Analysis (c), applied to the different elements measured in shelf sediments from the Ceará Continental Shelf.

almost all of samples from the EBCS were below the LD using the employed methodology. These results follow the same sequence reported in the literature for the EBCS (Freire et al., 2004; Marins et al., 2005; Campos et al., 2005; Lacerda and Marins, 2006; Aguiar et al., 2007).

The concentrations of Cu and Zn were quantified in fewer than 30% of the stations on the continental shelves of Ceará and Rio Grande do Norte. The concentrations of Pb were smaller than 1.0 mg/kg in approximately 70% of the samples analyzed. Therefore, these metals were evaluated with certain restrictions concerning geochemical interpretations.

The concentrations of all metals measured in the southern continental shelf of Espírito Santo were higher or at the upper limit of the range reported for sediments from other two northern areas of the EBCS. In that southern region, the higher inflow of continental materials is marked with decreased concentrations of carbonates as well as increased concentrations of fine sediments, silt–clay, and organic matter (Carvalho et al., 1993; Knoppers et al., 1999; Rezende et al., 2004; Nascimento et al., 2010). The concentrations of Al and Fe in sediments from the continental shelves of Ceará and Rio Grande do Norte were in the same order of magnitude, but lower than the concentrations found in the Espírito Santo shelf sediments (Table 1). Previous studies in this region have observed an increase in the concentrations of Al and Fe near the coastline and a decrease with the distance away from the coastal zone (Freire et al., 2004; Lacerda et al., 2005; Lacerda and Marins, 2006; Aguiar et al., 2007). The geochemical distribution of these metals is most likely associated with the inflow of materials transported from the hydrographic basins of the region.

The Ba and Mn in the sediments from the EBCS showed marked concentration differences with Ba showing higher concentration in sediments from the continental shelf of Ceará, whereas Mn highest concentrations were observed in Espírito Santo shelf sediments (Table 1). Ni, Zn, Pb, Cu, Zn, Cr, and V showed lower and similar concentration ranges in the sediments from the northeastern Brazilian shelf, compared to the southern sector of the EBCS, where much higher concentrations of these trace metals were observed. Studies on the distribution of metals in the sediments from the southern portion of the EBCS have suggested that the largest concentrations of metals are associated with fine sediment fractions (Rezende et al., 2004). The addition of silt and clay fractions to the sedimentary substrate from the continental margin of Espírito Santo, resultant from a larger continental input, is most likely one of the dominant factors leading to higher trace elements concentrations in the southern sector of the EBCS.

4.2. Geochemical similarities among metals in the sediments from the Brazilian east coast

The normalization of the data using conservative elements is frequently used to interpret geochemical studies of metals given that the proportions of concentrations between lithogenic metals and their conservative elements are relatively constant (Hortellani et al., 2008). In the current study, Al, Fe, and Mn were used as
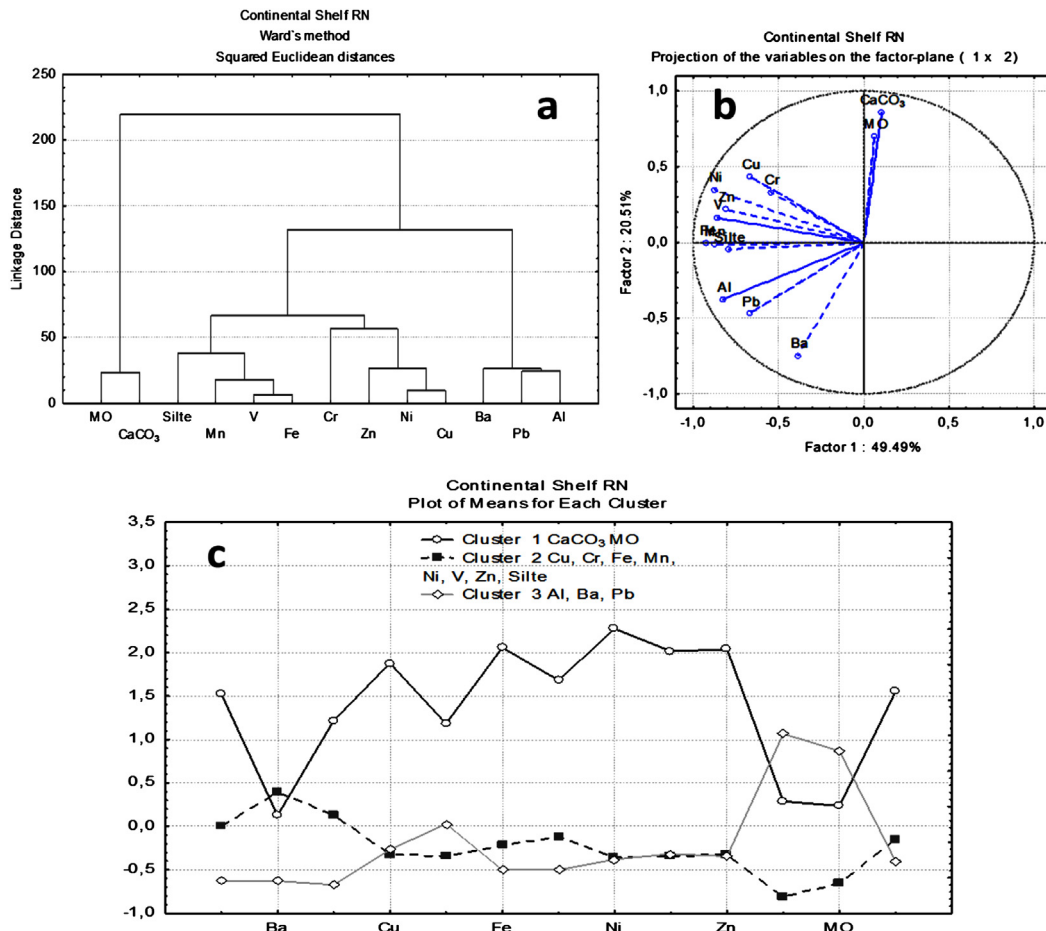

Fig. 3. Cluster Analysis (a), Principal Component Analysis (PCA) applied to Z normalized and varimax rotated metal concentrations (b) and K-means Cluster Analysis (c), applied to the different elements measured in shelf sediments from the Rio Grande do Norte Continental Shelf.

tracers of continental sources, and the concentrations of carbonates were used as indicators of marine sedimentary processes. These elements are present in the chemical constitution of the regional lithology and show relatively constant concentrations in the lithogenic matrix during transport and sedimentation. Furthermore, they are not influenced by radioactive decay, atmospheric exchange, coastal water pH and oxidation-reduction potential variations, or diagenetic processes (Schiff and Weisberg, 1999; Chester, 1990).

The multivariate analyses (Ward's Amalgamation Method and the Euclidean Quadratic Distance) applied to the interpretation of the metals distribution in the sediments revealed two major groups of metals in the continental shelf of Ceará (Fig. 2a). The first group was composed by the small grain-sized fraction, Fe, Al, Mn, Cr, and Zn. The second group consisted of $CaCO_3$, organic matter (OM), Ni, Pb, Ba, and Cu. This finding suggests that different sources and sedimentation processes exist for these groups of metals. The first group most likely originated from the alteration of silicate materials (e.g. feldspars) whose source rocks are the Pre-Cambrian granites typical of the geological foundation of the region adjacent to the coastal zone. Tertiary sediments from the Barreiras Formation, whose formation is the primary source of Fe, Mn, Ti, Zn, and Cr, among others, covers the foundation of the areas closest to the coast (Freire et al., 2004). Ancient sediments might be an additional source of these metals, whose existence in the extensive bands is

common on the EBCS including the coastal regions of Ceará and Rio Grande do Norte (Freire and Cavalcanti, 1998; Villwock et al., 2005). The results also show a strong connection between Cr and the grain size of the sediments. The dominant sedimentary processes for Fe, Al, Mn, Cr, and Zn, therefofe, are related to the transport associated with terrigenous materials and sedimentary deposition on the shelf (Aguiar et al., 2007).

Pb, Ni, V, Ba, and Cu were related to carbonates and OM. Carbonate deposits strongly influence the metals in the sediments from the continental shelf of Ceará. The continental inflow through the hydrographic basins might be a geogenic source of Ni and Cu along the eastern and northeastern coasts (Muller et al., 1999). However, strong correlations were obtained between Ni, Ca, Mg, and Sr, which are dominant natural constituents of the sedimentary deposits in marine areas on the inner continental shelf of northeast Brazil. The results obtained in the present study suggest that the deposition of antigenic carbonates controls the distribution of Ni and Cu, thereby corroborating previous studies in the region (Freire et al., 2004).

The deposition of Pb, V, and Ba also accompanied the group of carbonates. Torres et al. (2005) suggested that relevant contributions of Pb in Brazilian urban areas are due to the burning of fossil fuels. Chester et al. (2000) analyzed samples of rainwater along the coasts of France and the United Kingdom and obtained significant concentrations of Pb near large urban centers suggesting that
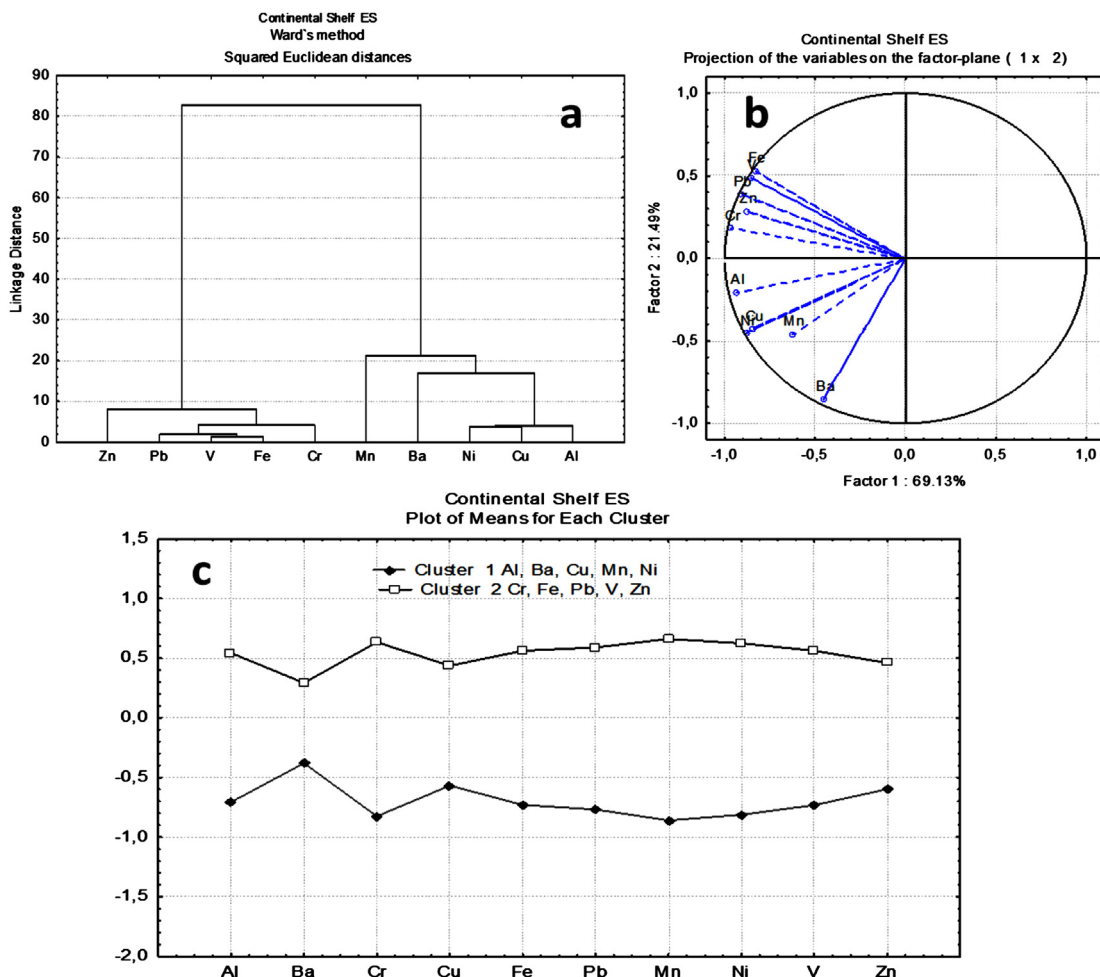

Fig. 4. Cluster Analysis (a), Principal Component Analysis (PCA) applied to Z normalized and varimax rotated metal concentrations (b) and K-means Cluster Analysis (c), applied to the different elements measured in shelf sediments from the Espírtrito Santo Continental Shelf.

atmospheric deposition is a significant source of this metal. This deposition process most likely contributes with Pb present in sediments in this sector of the Brazilian continental shelf, and the final destination of these atmospheric inputs might be found in the carbonate deposits. The relationship between V and the carbonates indicates that this metal was adsorbed to the marine sediments after weathering processes. However, studies on the geochemical behavior of V along the east coast of Brazil remain non-existent. Nevertheless, Marins et al. (2005) suggested that continental sources of this metal exist. Sulfate minerals, especially barite, area natural source of Ba. Carvalho (1995) suggested the strong adsorption of Ba by clays and sediments that are enriched in the Fe and Mn from the ocean floor. However, petroleum exploration, might have also contributed to the Ba concentrations observed in this study. Ba is one of the major constituents of petroleum production effluents in the open sea, and it has been used as an environmental indicator of waters in which petroleum is produced (Lacerda et al., 2013; Hartley, 1994).

The multivariate PCA determined the major factors that explained 77% of the total variance (Fig. 2b). The first component is responsible for 50% of the total variance, with the largest contributions coming from the carbonate, OM, Pb, Ni, V, Ba, and Cu variables. The second component explains 27% of the variance, with the largest contributions coming from the Fe, Al, Mn, Cr, Zn, and grain-size variables. Although they are a part of the second component, the grain-size and Cr variables were plotted separately from the other variables. To show the distinct behavior of these two variables using PCA, a K-means CA was performed to examine the measurements for each group obtained from the CA that created uniform or distinct groups. These results suggest that Cr is deposited in the form of a heavy mineral in marine sediments from the EBCS (Fig. 2c). Significant concentrations of heavy minerals were identified in sediments from the continental shelf of Ceará, including ilmenite, rutile, magnetite and chromite (Cavalcanti et al., 1993).

The cluster analysis identified three groups on the continental shelf of Rio Grande do Norte (Fig. 3a). The first was composed by Al, Pb, and Ba; the second group consisted of Cr, Zn, Ni, Cu, Fe, grain size, Mn, and V; and the third group was composed of $CaCO_3$ and OM.

The results obtained in the sediments on the continental shelf of Rio Grande do Norte showed some different geochemical properties compared with those observed on the continental margin of Ceará. The change in groupings between the evaluated variables along this portion of the Brazilian east coast is most likely related to regional lithological differences. The coastal plain, which is adjacent to the continental shelf of Ceará, is constituted of tertiary sediments from the Barreiras Formation that rest on pre-Cambrian crystalline rocks. In turn, the Barreiras Formation is superimposed on calcareous rocks in the lithological context of the Potiguar basin in the coastal region of Rio Grande do Norte (Vital et al., 2010). In contrast to the results observed from the sediments from the coast of Ceará; Pb and Ba were associated with Al, which suggests the presence of continental lithological sources, most likely from the alteration of minerals such as barite, anglesite, and cerussite. Studies on metals geochemistry in sediments from the continental
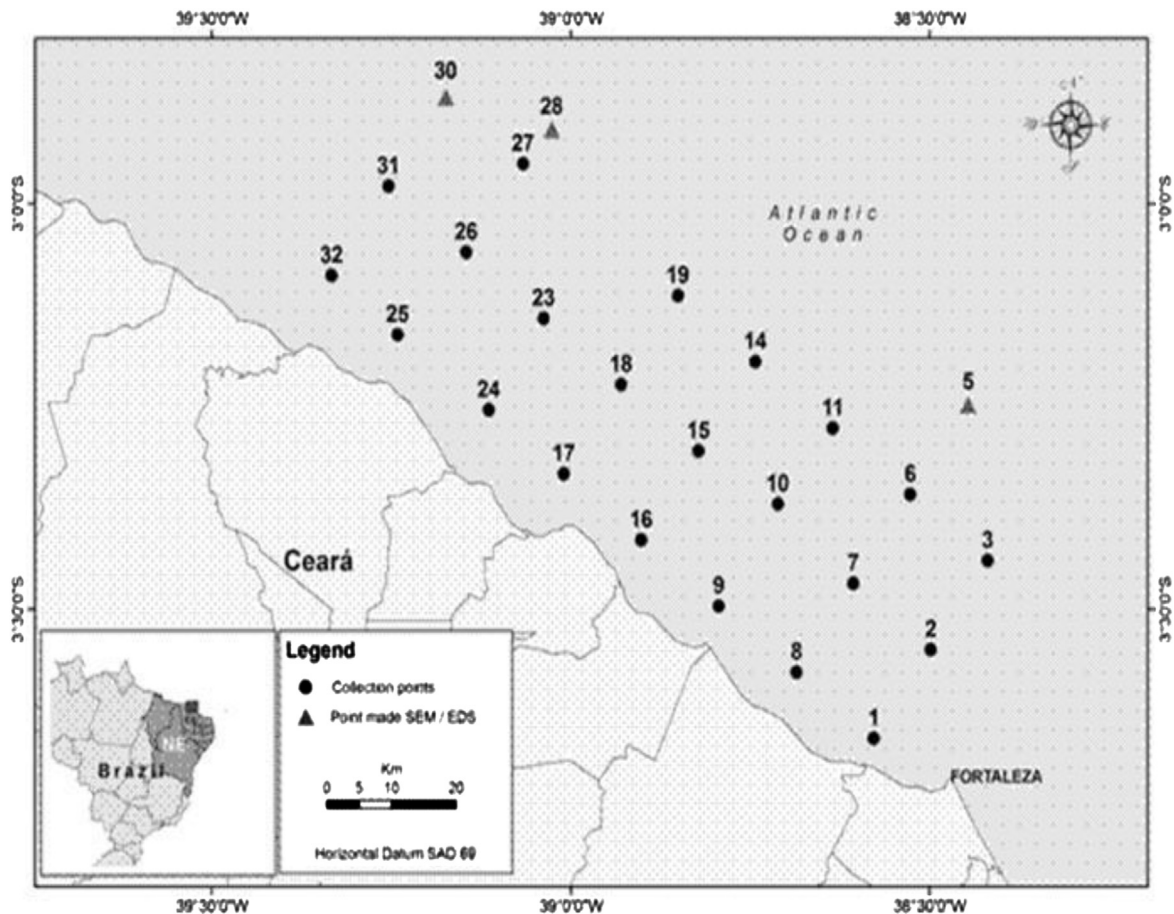
Fig. 5. A Map of the surface sediment sampling stations on the continental shelf of Ceará. The triangles above highlight Stations 005, 028, and 030 as evaluated by SEM/EDS. Adapted from Aguiar et al. (2007).

shelf of Rio Grande do Norte corroborate these results (Lacerda et al., 2013).

The second group can be divided into four subgroups: Cr, Zn, Ni, and Cu and suggests the importance of sulfide minerals, at least for Zn, Ni and Cu. Thus, these elements can be incorporated into sediments associated with sulfide minerals. The concentrations of silt, Mn, V, and Fe were associated with deposits of Fe and Mn oxides. The similarity between the second group of metals and Fe and Mn indicates the presence of continental sources for this set of variables. This group of metals likely originates from the scheelite and pegmatite of the Seridó province located along the upper basin of the Piranhas Açu River. The mineralogy of this river consists of scheelite, chalcopyrite, molybdenite, rhodochrosite, and cassiterite (Angelin, 2007), which are the primary natural sources of Cu, Mo, Mn, and Cr. The third group most likely originates from the predominant autochthonous sedimentation regime in the northern sector of the Brazilian east coast.

The PCA results revealed two major factors that explained 70% of the total variance (Fig. 3b). The first factor explained 49.5% of the total variance, with the largest contributions coming from the carbonate and OM variables. The second component accounted for 20.5% of the variance, with the largest contributions coming from the silt, Mn, and Fe, followed by Ni, Cr, Cu, V, Zn, Al, Pb, and Ba.

To determine the distinct behavior of the variables using PCA, a K-means cluster analysis, performed to examine the average for each group obtained from the CA, demonstrated distinct groups. The results suggested that carbonates are the major constituents of the autochthonous sedimentation regime of this region (Fig. 3c). Unlike the coast of Ceará, however, the group of continental, geogenic elements was more clearly defined by similarities with Al, Fe, and Mn in the sediments from the Potiguar Basin.

The cluster analysis (using Ward's Amalgamation method and the Euclidean quadratic distance) applied to the results from the continental margin of Espírito Santo identified two groups (Fig. 4a). The first was composed of the variables Al, Cu, Ni, Mn, and Ba. The second group consisted of Cr, Fe, Pb, V, and Zn. The similarities between the metals from the first group and Al strongly suggest that these elements originate from the continent, which differentiates them from the other results observed in the north sector of the Brazilian east coast, where sediments from the continental shelf of Ceará were strongly associated with carbonate deposits (Lacerda and Marins, 2006; Aguiar et al., 2007). In turn, these results corroborate previous studies reported in the literature of the EBCS (Rezende et al., 2004; Mendonça, 2006) and Carvalho et al. (1993) in a study of the southeast coast of the Brazilian continental margin that also demonstrated that Cu is strongly related to Al, Fe, Mn, and Ti.

The group composed of Cr, Fe, Pb, V, and Zn suggests that these metals have different origins. Unlike the northern portion of the EBCS, where the continental inflow is putatively insignificant, the coast of Espírito Santo receives a significant volume of sediments through the hydrographic basins of the region, which are characterized by perennial drainage and significant river discharge (CRA, 2001; ANA, 2011). However, the results from the multivariate analysis indicated that continental sources appear to be unimportant with regard to the southern portion of the EBCS. Studies performed on the sediments of the Bacia de Campos (Campos Bay) show that these metals can be adsorbed to iron hydroxide (Mendonça, 2006). This result reveals Fe to be a geochemical tracer of the sedimentary deposition of metals in this sector of the Brazilian coast. On the other hand, mineral deposits from sulfides were identified near Abrolhos, which is located between 60 and 70 km from the coast and at a depth of approximately 30 m.

The multivariate PCA determined two major factors that explained 90% of the total variance (Fig. 4b). The first component explained 69% of the total variance, with the major contributions from the variables Al, Cu, Ni, Mn, and Ba. The second component explained 21.5% of the variance, with major contributions from the variables Fe, V, Pb, Cr, and Zn. These results must be interpreted with caution given the limited number of variables measured and the small sample size. The lack of measurements of important geochemical carriers (e.g., the concentrations of carbonates, OM, and grain size) used to determine the metal deposits on the Brazilian continental shelf did not allow for stronger conclusions regarding the geochemistry of metals evaluated along the continental shelf of Espírito Santo.

The K-means CA revealed homogeneous groups that differed from the results of the continental margin of Ceará and Rio Grande
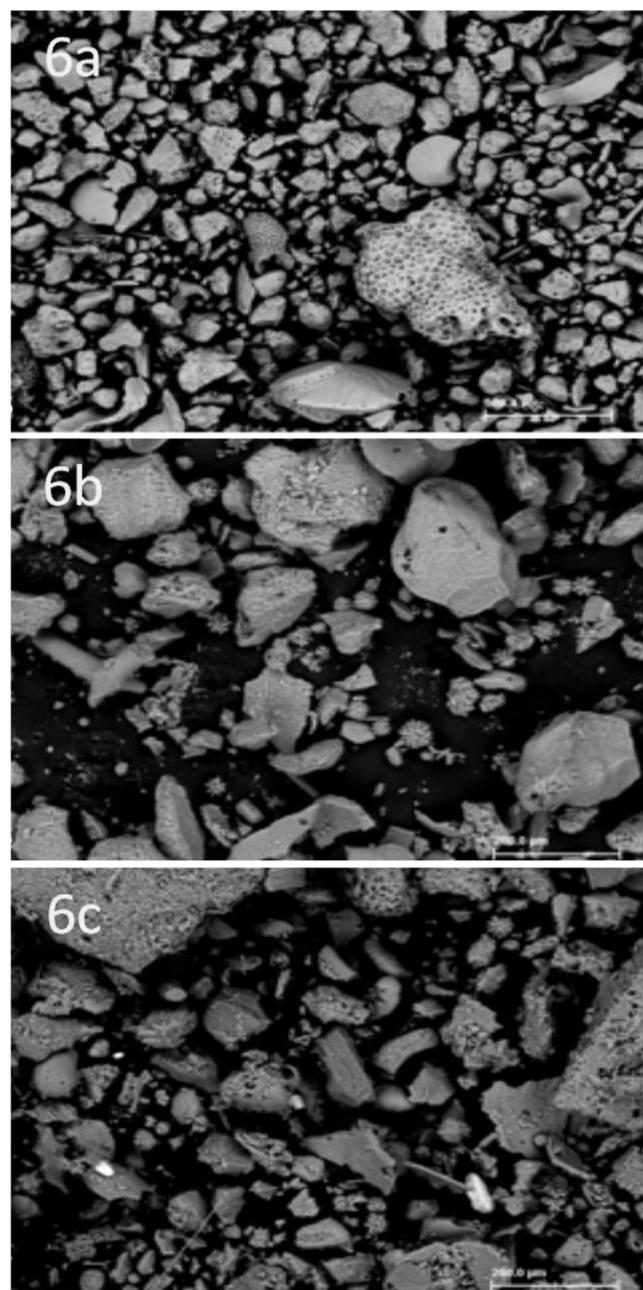
Fig. 6. Panoramic images from Scanning Electronic Microscopy in sediments from the Ceará continental shelf from stations 005 (6a); 028 (6b) and 030 (6c). Note the similarity in grain morphology constituted by biogenic fragments, amorphous structures and crystals and angled forms.

do Norte, which suggests the presence of a recent, large and continuous sedimentary deposit on the continental margin of Espírito Santo (Fig. 4c).

4.3. SEM/EDS

The sediments from Stations #05, #28, and #30 at the Ceará shelf (Fig. 5), were studied with regard to the geochemistry of the metals via AAS (Aguiar et al., 2007). These authors found an increase in the concentration of Ba in these sediments with regard to the other stations and a strong correlation with the concentration of $CaCO_3$. SEM/EDS analysis was applied to the evaluation of these sediments to identify mineralogy and its possible associations with the high Ba concentrations observed.

The morphologies of the sediments collected on the continental shelf of Ceará (Fig. 6) were similar, consisting of fragments of biological material, amorphous agglomerates, multifaceted particles, and crystals. The dimensions of these structures varied from nm to mm in length, but micrometric structures predominated. The major advantages of using SEM with morphological analysis instruments in geology are its spatial resolution to scale, field depth, simple preparation of samples, and the conservative character of the crystallites. SEM generates images of individual sediment grains and information about the formation, habit, porosity, and growth of minerals (Reed, 2005).

Crystals of calcite (Fig. 7a) and aragonite (Fig. 7b) as well as amorphous calcite and Mg-calcite were identified in the three sampling stations. The association of morphology, electron dispersive energy spectroscopy, and element distribution maps identified these crystals. Calcite and aragonite polymorphs were
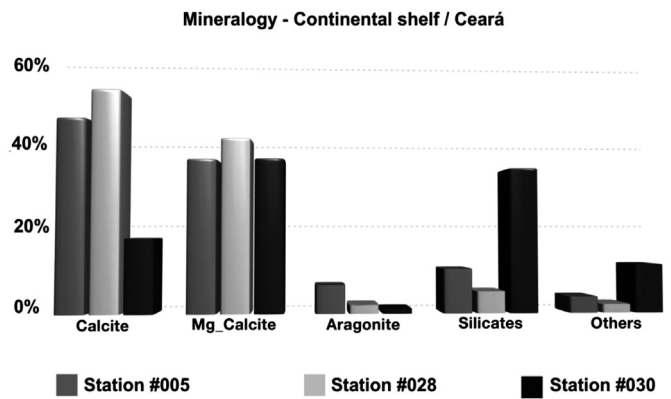

Fig. 8. Relative distribution of major minerals detected in sediments grains with diameter larger than 20 µm ($n = 100$) from the Ceará shelf.

the primary mineral phases found in modern carbonaceous marine sediments (Morse et al., 2007). The use of an x-ray detector with an ultrafine window of Be allowed for C and O to be detected in the spectra, and distribution maps of these elements can be generated (Reed, 2005; Severin, 2004). Furthermore, the analysis of sediment grains deposited directly on the conducting surface (Au) suppressed the spurious signal of C, thereby confirming the structure composition (Miguens et al., 2010).

The minerals identified by x-ray microanalysis (electron energy dispersive spectra and semi-quantitative analysis [wt%]) in structures with a major axis larger than 20 µm varied considerably between the analyzed sampling stations (Fig. 8). Calcium carbonates
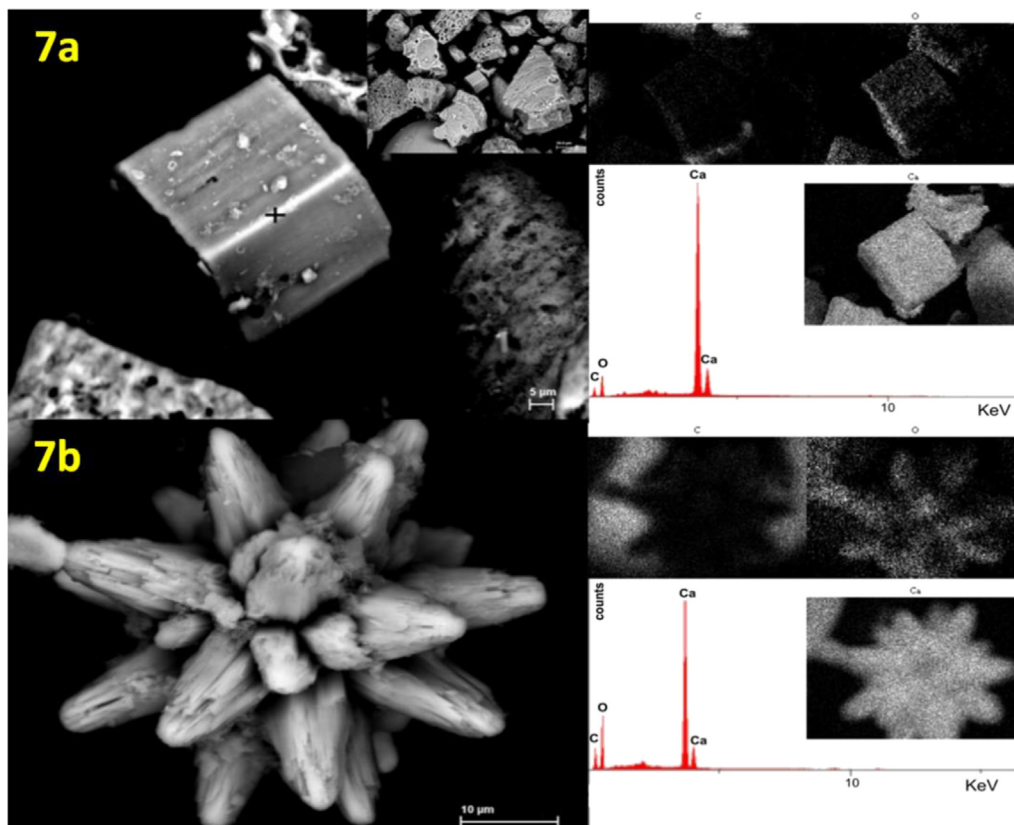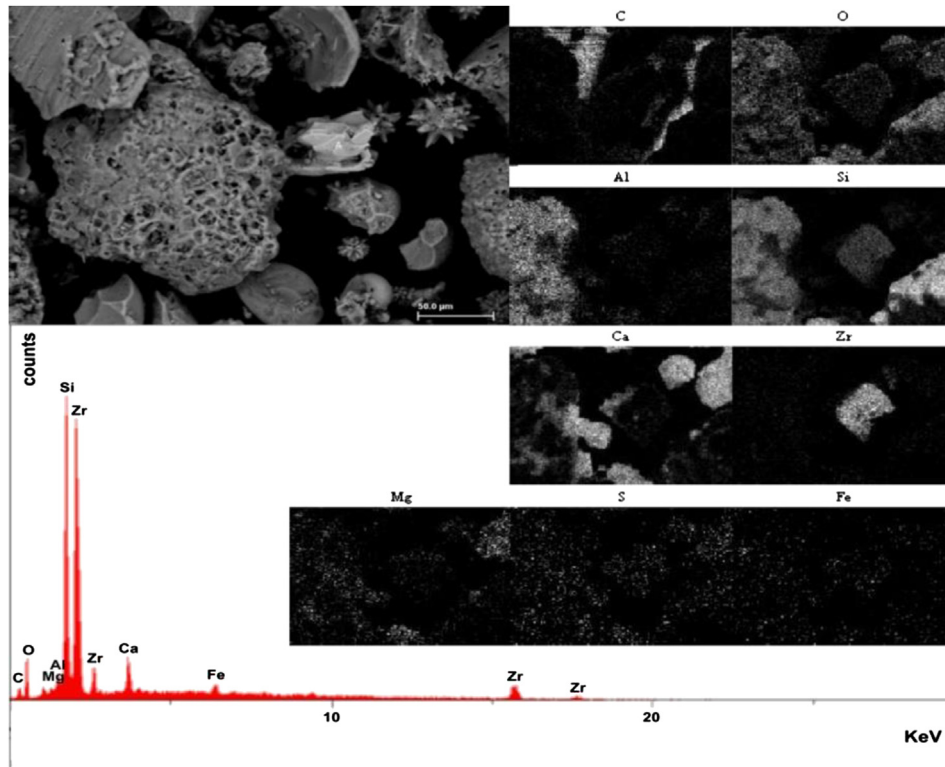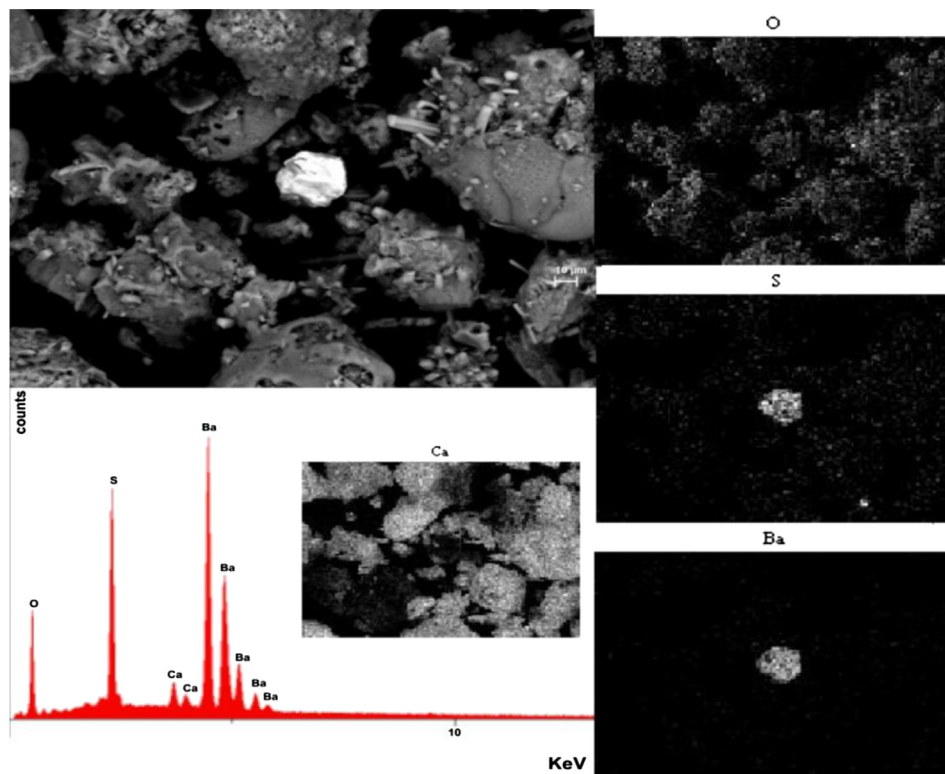

Fig. 7. Detailed images from Scanning Electronic Microscopy in sediments from the Ceará continental shelf; an euedric calcite crystal from station 005 (7a); diverging radiated aragonite from station 028 (7b). Disperse energy spectra show C, O and Ca as major elements; spatial distribution maps of elements match with the structure of polymorph carbonates.

Fig. 9. Scanning Electronic Microscopy images from station 030 in the Ceará shelf sediments; disperse energy spectra show Si, Zr, O and Ca as major elements; C and Fe as minor elements and Mg, Al and S as trace elements.

Fig. 10. Scanning Electronic Microscopy images from station 030 in the Ceará shelf sediments; disperse energy spectra show O, S, Ba and Ca as major elements; distribution maps of elements suggest barite (barium sulfate). Random Ca signals are from scattered adjacent carbonate crystals.

(i.e., calcite, Mg-calcite, and aragonite) represented approximately 86% of Station #05, 93% of Station #28, and 53% of Station #30, whereas silicates represented approximately 10%, 5%, and 33% of these stations, respectively. Other minerals, mostly oxides, constituted approximately 3.7%, 2%, and 11% of the sediment grains collected at Stations #05, #28, and #30, respectively. A comparative SEM/EDS study with ICP-AES revealed similarities in qualitative and quantitative analyses, thereby establishing differences between particles. In this study, 100 particles per sample with an axis greater than 20 μm were analyzed via SEM/EDS for mineral identification, as recommended in the literature (Haley et al., 2006; Severin, 2004).

Mg, Al, K, Ca, and silica as well as silicates of K, Ca/Mg, and Ca/K were detected at Station #05. Calcium sulfate, Mg, Al, K, Ca, Ti, Mn, and Fe as well as silica, silicates of Ca, Mg/Ca, K, and Fe, and oxides of Fe, Ti, Fe/Ti, and Fe/Mn were identified at Station #28. Mg, Al, K, Ca, Ti, Mn, Fe, Zr, Ba, and the lanthanides La and Ce were identified at Station #30. However, Zr was identified mainly in connection with the silicates (Fig. 9), Ba in sulfates (Fig. 10), and La and Ce (Fig. 11).

The morphology associated with SEM/EDS allowed various minerals on the continental shelf of Ceará to be identified. Despite the existence of the mineral classification keys that employ this methodology (Severin, 2004), the morphological characteristics, especially the superposition of the structures (Figs. 6, 9 and 10) and particles immersed in amorphous agglomerates (Fig. 11), hindered precise mineralogical identification. SEM/EDS identified a structure with hemispherical morphology and a diameter of 1.35 mm whose

chemical constituents were in the following proportions: C, 8.26 wt %; O, 48.5 wt%; Mg, 2.53 wt%; Al, 2.15 wt%; Si, 3.4 wt%; S, 4.4 wt%, and Ca, 28.14 wt%. The elemental distribution map shows that although the proportions of S were diffuse along the structure, its distribution was associated with Ca, which was a major constituent of this crystallite (Fig. 12).

The SEM/EDS results corroborate the literature regarding the metals found on the eastern continental shelf and add the chemical analysis data obtained on Mg, K, Ti, Zr, and the lanthanides La and Ce to what has been learned using other analytical techniques. Despite having analyzed a satisfactory number of crystallites (Haley et al., 2006), various trace metals previously quantified using AAS were not identified by SEM/EDS due to their low concentrations in the sediments from the coast of Ceará, as discussed above.

5. Conclusions

In general, the findings demonstrate that the EBCS shows similar characteristics with regard to the geochemical distribution of metals, with higher concentrations located in the coastal zone. However, differences in the geochemical properties were significant in this sector and are most likely influenced by the different climatic, geological, and geomorphological conditions between the northern and southern portions of the EBCS. These differences justify a new geochemical categorization of the eastern continental shelf, and the different base levels of these components should be determined. This information will allow changes in the pelagic medium (either due to petroleum-based or other types of activities)
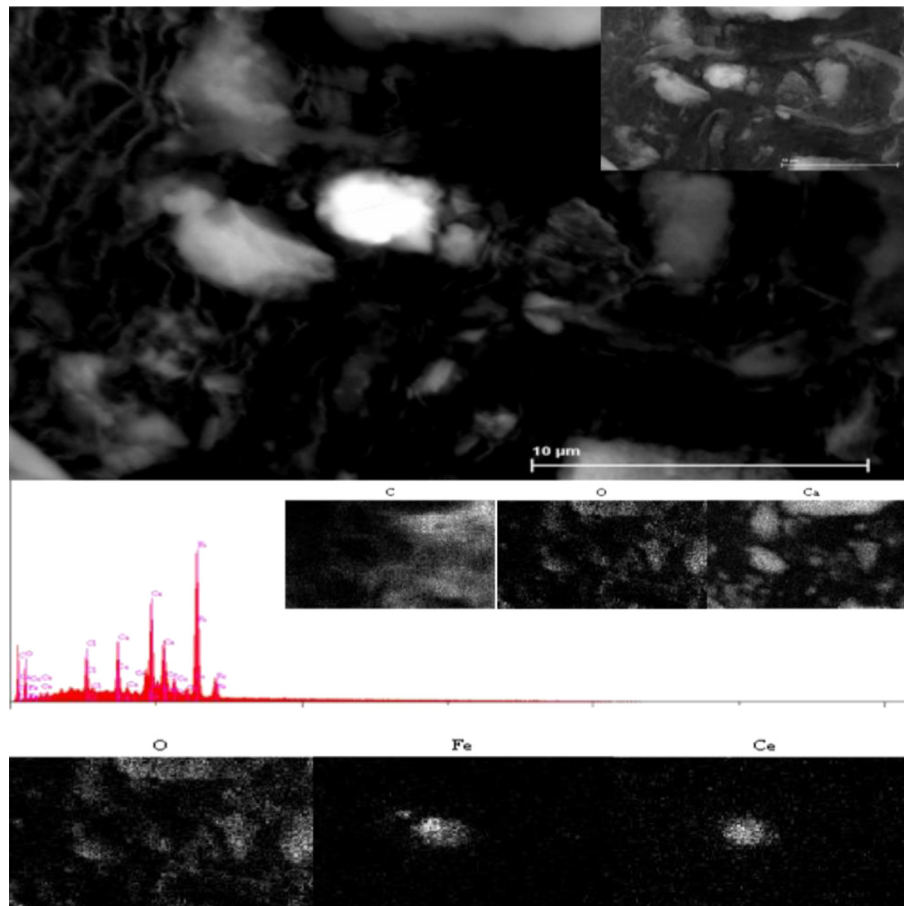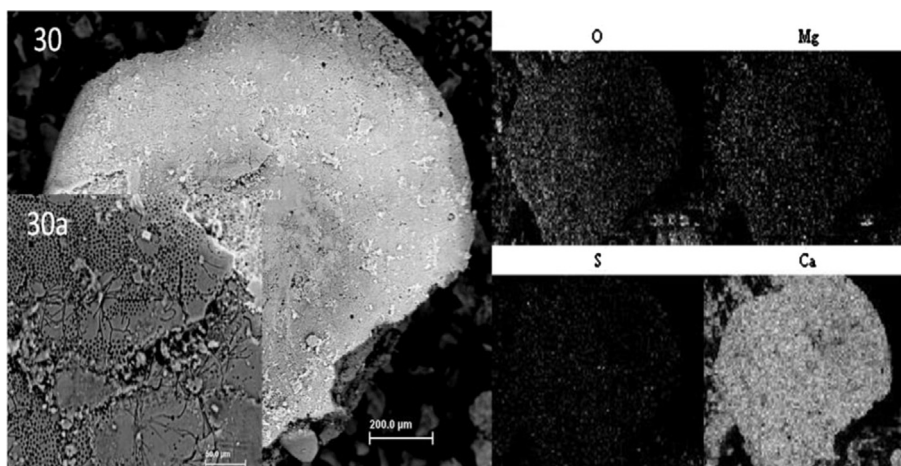

Fig. 11. Scanning Electronic Microscopy images from station 030 in the Ceará shelf sediments; disperse energy spectra show a differentiated signal from a central agglomerate showing internal particles with C, O, Fe and Ce as major elements. Distribution maps of individual elements suggest Fe/Ce oxides.

Fig. 12. Scanning Electronic Microscopy images from station 030 in the Ceará shelf sediments; showing a biological fragment of 1.35 mm of individual elements show O, Mg, S and Ca as major elements.

to be more easily detected and monitored, thereby minimizing deleterious effects.

The identification of two major factors distinguished two sectors of the continental shelf of Ceará: The first consisted of Fe, Al, Mn, Cr, and Zn from predominantly continental sources, and the second was controlled by autochthonous marine deposits characterized by similarities between the carbonates formed with Ni, Pb, Ba, and Cu.

The SEM/EDS x-ray microanalysis in the sediments from the continental shelf of Ceará identified silicates, oxides, carbonates, and sulfates. At the same time, this method increased the quantification of metals in the sediments from the east coast of Brazil. The $BaSO_4$ present in the sediments from Station #30 matches the high Ba concentrations obtained using AAS as discussed above. Although SEM/EDS was applied to a limited set of samples in the present study, this tool is indisputably important in the geochemical evaluation of marine sediments, given that it reveals the habits of the minerals present in the sediments and the location of the chemical elements that comprise the structure of particles or crystalline aggregates in micrometric dimensions.

Three major groups were identified along the coast of Rio Grande do Norte with distinct geochemical properties. Al had less influence on the metal deposits and was associated with Ba and Pb. Fe and Mn oxides were predominant in the depositions of most metals from the continental inflow. Carbonates, which are major constituents of the autochthonous marine deposition regime, did not influence the metal depositions in the sediments on the continental shelf of Rio Grande do Norte. The two-dimensional factoring via the PCA ordered the stations into three groups. These results will allow more detailed evaluations in future studies in sectors with different characteristics.

The metal concentrations obtained on the continental margin of Espírito Santo showed significant increases compared with those observed along the coasts of Ceará and Rio Grande do Norte. The results obtained from the multivariate analysis demonstrated the presence of contributions from the continental inflow of Cu, Ni, Ba, and Mn due to their similarities with Al, Cr, Pb, V, and Zn were associated with Fe, which suggests that this group of metals has different sedimentary processes. These results also characterized Fe as a geochemical tracer of the sedimentary deposits in the southern portion of the east coast of Brazil. The interaction between the metal concentration results and the existing mineralogy in marine sediments will allow for a more conclusive analysis concerning the continental signature of the metal deposits along the Brazilian continental shelf.

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