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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 ∼ 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