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# SPATIAL DISTRIBUTION OF CLAY MINERALS IN GUANABARA BAY SEDIMENTS AND ITS RELATIONSHIP WITH THE ESTUARY HYDRODYNAMICS

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## ABSTRACT

Ninety-two samples were collected in the Guanabara Bay bottom sediments. After grainsize analyses, clay mineral identification was performed in twenty-five samples located in the inner section of the bay where fine sediment deposition predominates. Kaolinites (mean=73%), illites (mean=16%) and smectites (mean=11%) were the group of clay minerals identified. The clay minerals identified showed detrital characteristics which indicate an absence of recent authigenic processes within the surface sediments of the bay. Smectites showed a preferential setting towards the region of higher salinity values. Its lowest abundance (0.15%) was observed near the rivers where the average salinity was 14 whereas its highest abundance (17%) was observed at the most downstream station with average salinity of 32. An inverse relationship between kaolinites and smectites relative abundance was also observed from the inner region towards the more saline region of the bay.

#### RESUMO

Noventa e duas amostras de sedimentos foram coletadas na Baía de Guanabara, Rio de Janeiro. Após analises granulométricas, grupos de argilominerais foram identificados em vinte e cinco amostras localizadas na região interna da baía, onde predomina a deposição de sedimentos finos. Os grupos de argilominerais identificados ocorreram em todas as amostras e seus teores relativos foram: caulinitas (média=73%), seguido de ilitas (média=16) e esmectitas (média=11%). Através do MEV se observou que todos os argilominerais apresentavam um caráter detritico, o que indica a ausência de processos autigênicos recentes de formação de argilominerais nos sedimentos superficiais da baía. Não se observou correlação entre a deposição dos argilominerais e a granulometria. Porém, uma deposição preferencial de esmectitas foi observada em regiões mais salinas enquanto que maiores teores de caulinitas foram observados na região menos salina por se situar perto da desembocadura dos rios. Uma relação inversa negativa foi observada entre os teores relativos de caulinitas e esmectitas em um eixo NS desde a região mais interna e menos salina até a região mais próxima a entrada da baía, onde os valores de salinidade se aproximam dos valores oceânicos.

#### **INTRODUCTION**

The study of clay mineral distribution in recent sediments of estuaries and deltas can

provide information about the processes that control their deposition at the continent-ocean interface. Clay minerals have been widely used in studies dealing with sedimentary provenance as well as an oceanographic tool within estuarine environments (Allen, 1991; Bukhari & Navak, 1996; Feuillet & Fleischer, 1980; Gutierrez-Mas et al., 1997; Li et al;. 1999). Besides presenting a general correspondence between clay mineral assemblage in coastal ecosystems and the mineral composition of nearby continental rocks, they also show a differential settling pattern in estuarine waters. Kaolinites and illites usually are deposited in the estuary head as a consequence of variations in water salinity whereas smectites remain in suspension due to their smaller size and lower density. Therefore, smectites settle preferentially on distal areas of an estuary where the rate of flocculation increases due to higher salinity values (Whitehouse et al., 1960; Gibbs, 1983; Chamley, 1989).

It is our goal to identify and quantify the relative abundance (%) of the main clay mineral groups in Guanabara Bay sediments. We also intend to identify and relate any trend in the clay minerals spatial distribution with the oceanographic characteristics of the bay. This is an important because it provides information on the variability in the salinity values.

# **STUDY AREA**

Guanabara Bay is characterized by tectonic control and also by recent sedimentary processes. It presents features of a coastal plain estuary such as gravitational and residual tidal circulation. According to Kjerfve (1994), the Guanabara Bay can be included in the estuarine geomorphic type coastal bay. The bay is localized at latitude 22°50'S and longitude 43°10'W and has a superficial area of 328 km<sup>2</sup> (Figure 1). A total population of 11 million inhabitants populated several and important cities located along its border. The sediment discharge into the bay has increased due to human activities such as deforestation, river canalization and landfill. Such anthropogenic pressure has increased the average sedimentary accumulation rate from 0.24 cm per century (1849-1922) to 0.81 cm per century (1938-1962) (Amador, 1980). However, according to Godoy et al. (1998) in the last 100 years the human activities were responsible for a huge increase in the rates of sediment transfer to the bay. Consequently the average rates of sedimentation increased to 1 to 2 cm year<sup>-1</sup>. Bottom sediments are composed mostly by clay and silt in the area between the Rio-Niterói Bridge and the innermost reaches of the north of the bay. Sandy sediments predominate near the bay mouth, a region dominated by waves and tidal currents. In this region, the higher velocities during flood tides build sand wave deposits, which indicate the importance of marine sands transport into the bay (Kjerfve *et al.*, 1997; Camargo *et al.*, 2004).

## METHODOLOGY

Ninety two surficial sediment samples were collected using a Van Veen drag during four cruises in November 1999 (Figure 2). The samples were homogenized immediately after the sample collection. A portion of there samples was dried for all the parameters measurements. Carbonatic content, organic carbon, nitrogen, sulfur contents and grain-size distribution were already determined Cantazaro et al. (2004) in all samples following the procedures in Gingele and Leipe (1997). For the clay mineral preparation, bulk samples were treated with 10% hydrogen peroxide solution and 10% acetic acid for disaggregating and removal of organic carbon and carbonate. Separation of the clay fraction (< 2 mm) was performed in twenty-five samples (Figure 1) being achieved after repeated centrifugation steps. A solution of 50% MgCl, was added to clay suspensions to accelerate the sedimentation of the clay particles as well as to provide a uniform cation charging. Preparation of preferentially oriented clay mounts followed the procedure described by Petschick et al. (1996). X-ray diffratometry-measurements were performed on a Philips PW 1830 device, using CoKa radiation (40 kV, 40 mA). Scans were run between 1° and 18° 2q with a step size of 0.02° in the air-dry state and between  $2^{\circ} - 40^{\circ}$  2g after ethylene glycol solvation. Evaluation of scans followed the procedures in Petschick et al. (1996). The particle investigation was realized by morphological and chemical investigation with scanning electron microscopy (SEM) and energy dispersive X-ray microanalysis (EDX). The



Figure 1: Guanabara Bay



Figure 2: Localization of sampling stations. Bold triangles indicate samples which were subject to DRX analyses.

samples for SEM and EDX analysis were filtered through 0.45  $\mu$ m nucleopore filters. Thereafter, salt was removed by filtering 0.5 l distilled water, and filters were dried at 60 °C for 3 h and stored for later analysis. In the laboratory, the filters were placed on a carrier and covered with elemental carbon to ensure electric conductivity. An automated system (NX-Chem) was employed to distinguish particles on the filter by image processing and analyses of the individual chemical composition of 500-1000 particles per filter. The elements selected for processing were Si, Ti, Al, K, Ca, Mg, Mn, Fe, P, and S, because they represent the main elements of minerals and inorganic particles in the SPM and are not problematic for EDX analyses.

# **RESULTS AND DISCUSSION**

At the inner section of bay, from the Ilha do Fundão (Fundão Island) (station #46) towards the north portion of the bay, fine grainsize sediment predominated (mean=63%), followed by silt (mean=35%), and sand (mean=2%). This region undergoes intense sediment deposition due to the decrease in the tidal currents velocity (Quaresma, 1997). On the northeast sector, clay size sediments predominates due to lower energy and also the presence of mangrove vegetation, which act as a trap for finer particles (Catanzaro et al., 2004)

Clay size sediments showed high concentration of organic matter (OM), where the highest value was found in the inner section of the bay while the lowest values were found near the bay entrance and within the central channel. The high values can be explained by the high-no treated daily sewage discharge into the bay (Catanzaro et al., 2004). According to these authors, the mean concentration of OM within Guanabara Bay fine sediments is 4,74% whereas the mean concentration of OM with the coarse sediments is only 0,81%.

Kaolinites, illites and smectites were the main groups of clay minerals identified in the sediment samples located close the Fundão Island (station 46) towards the inner section of bay. In all samples, kaolinites were the most abundant clay mineral (mean=73 %), followed by illites (mean=16%) and smectites (mean-11%). Other authors have determined clay mineral assemblage in the drainage basin For example, Amador (1997) have identified kaolinite, illite, vermiculite, gibbsite and illite-vermiculite mixed layer on the sediments of Macacu River and Faria & Sanchez (2001) have identified kaolinite, illite and illite-smectite mixed layer on the sediments of Caceribu River and kaolinite, illite, vermiculite, illite-vermiculite and illitesmectite mixed layers on the northeastern



**Figure 3:** MEV photos of an illite identified on the bottom sediments of Guanabara Bay. The mineral shows rounded borders which are characteristics of transportation.

sediments of Guanabara Bay. According to them, these clay mineral assemblage show a general correspondence with the lithological units of the catchment area. Mixed layer clays were not covered by the methods used in this study.

Through MEV analysis, it was observed that the clay minerals show rounded borders which indicate their detrital origin (Figure 3). This characteristic together with the mineralogical homogeneity of the samples suggests that no authigenic process such as neo formation of clays is currently taking place within the superficial sediments of the bay. Also, correlation between clay mineral relative abundance and grain-size was low, indicating that the deposition of the clay minerals is not related with granulometric sorting. All these data support our hypothesis that the clay mineral distribution in the bottom sediments is indeed related to the Guanabara Bay oceanographic processes such as variation of the salinity intrusion.

Kaolinites show preferential accumulation near the rivers mouth (station #8, 84%), region where the mean salinity was 14%0. Its abundance decreases towards the entrance of the bay (station #46, 63%), region



**Figure 4:** a) Differential settling of kaolinites and smectites on a NS axis. b) Inverse relationship between kaolinites and smectites within Guanabara Bay bottom sediments.

where the salinity values approach marine values (32%0). On the other hand, smectites showed preferential accumulation in the bay entrance. At station 8, near the rivers mouth smectites abundance was observed to be about 0.15% (station #8, 0.15%) whereas the highest abundance values were observed in the region of higher salinity (represented at the station #46, 17%) (Figure 4a). An inverse relationship ( $r^2 = -0.74$ ) was also observed between smectites and kaolinites relative abundances in the studied samples of bottom sediments. For example, sediment samples with high content of kaolinites showed a low content of smectites and vice-versa (Figure 4b). These results agree with those observed in the Nile River Delta (Stanley and Liyanage 1986), in the Amazon River shelf (Patchineelam & Figueiredo 2000), and in the Zaire Fan River sediments (Gingele et al., 1998).

The preferential settling of smectites in environments associated with high salinity values is related to the smaller size of the grains and low density which makes them flocculate gradually with increasing salinity (Whitehouse *et al.*, 1960; Gibbs, 1983). This characteristic is very useful because one can identify ancient sedimentary environments such as estuaries and deltas through the clay mineral assemblage and distribution.

## CONCLUSIONS

The twenty-five sediment samples analyzed showed a homogeneous mineralogical assemblage, where all identified clay minerals - kaolinites, illites and smectites - were present in all samples and show a detrital character. Kaolinites and smectites showed an inverse relationship in their relative abundance in the Guanabara Bay sediments. A preferential settling of kaolinites was observed at the inner region of the bay near the river mouths where salinity values are low. On the other hand, smectites showed a preferential settling at the distal region where the salinity approaches oceanic values The differential accumulation of kaolinites and smectites is related to the salinity gradient in the Guanabara Bay caused by water circulation.

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