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MINERAL CHARACTERIZATION OF NATURALLY RADIOACTIVE BRAZILIAN BEACH SANDS

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ABSTRACT

The Espírito Santo coast is known for its beautiful nature and beaches, especially Guarapari, which has naturally radioactive beach sands. The presence of thorium and uranium is mostly due to the presence of monazite (Ce, La, Nd, Th)PO_4 and its secondary products – ilmenite, zircon, and rutile – forming black sand beaches. In this study, sand samples were collected from five different beaches in Guarapari and subjected to a morphology characterization using the scanning electron microscopy (SEM) technique and an elemental composition analysis through energy-dispersive X-ray spectroscopy (EDS). Subsequently, another aliquot was finely ground, and its mineral composition was investigated using X-ray diffraction (XRD). Morphology analysis indicated the presence of three main types of grains: extremely porous, rounded, and flat. When comparing the samples, the grain size was mostly homogeneous, ranging from 200 to 400 micrometers, except for Praia de Setiba, which contains larger grains around 900 micrometers. As expected, the chemical element analysis showed the dominance of oxygen and silicon, mostly forming SiO_2 grains. The presence of calcium, iron, and titanium suggested the formation of calcite ($CaCO_3$) and ilmenite ($FeTiO_3$). Due to their extremely low count percentages, heavier elements such as cerium, lanthanum, thorium, and neodymium appeared in limited amounts. Notably, a monazite grain was found inside a small fissure in a quartz (SiO_2) grain at Praia da Bacutia. Indeed, the XRD analysis confirmed that the quartz is dominant and conceals the presence of other compounds.

1. INTRODUCTION

The village of Guarapari is a coastal city in the Brazilian state of Espírito Santo, known for its naturally radioactive beaches. The natural radioactivity comes from the U-238, Th-232 e U-235 series present in erosion deposits from when these sands were formed [1]. In Guarapari, the mineral that forms the sand is monazite, a group of phosphate minerals containing rare earth elements (REE) such as cerium, lanthanum, and neodymium. Monazite also contains thorium (2% to 14%) and uranium (0.05% to 0.3%), making it valuable for potential applications [2]. For instance, extracted uranium and thorium could be used in nuclear fuels, while neodymium could be used in high-strength magnets.

It is also important to study the presence of monazite in these areas due to its contribution to the annual effective dose rates, which impact the population and inform public management decisions. A 2005 study found that the radium equivalent activities in Guarapari and ten other coastal locations in Brazil exceeded the annual effective dose recommended by the Organization for Economic Co-operation and Development (OECD) [2]. According to OECD guidelines, the effective dose from natural radioactivity in building materials should generally not surpass 1 millisievert (mSv) per year. Of all the locations studied, Guarapari exhibited the highest radium equivalent activity [2].

Thus, it is important to assess these areas not only for their potential commercial value due to the presence of rare earth elements, uranium, and thorium, but also for the implications of natural radiation exposure on public health. This study provides an analysis of the elemental and mineral compositions of five beaches in Guarapari – *Praia do Morro, Praia da Areia Preta, Praia das Castanheiras, Praia de Setiba*, and *Praia da Bacuti*a – using scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), and X-ray diffraction (XRD) techniques.

2. METHODS

2.1. Sampling

This study collected six sand samples from five beaches in Guarapari, Espírito Santo. The collection points are shown in Tab. 1. The samples (Fig. 1) were collected from random points within an area of 4 m² in the middle of the available sand strip at each beach. They were then dried, homogenized, and subjected to a quartering process to ensure representativeness.

Tab. 1. Sample collection points.

Sample	Location
1	Praia do Morro
2	Praia da Areia Preta
3	Praia das Castanheiras
4	Praia de Setiba
5	Praia da Bacutia (location 1)
6	Praia da Bacutia (location 2)

1 2 3 4 5 6

Fig. 1. Samples are numbered according to Table 1. After the quartering process, one aliquot from each sample was separated for each technique.

2.2. Scanning electron microscopy and energy-dispersive X-ray spectroscopy

One aliquot from each sample was used for scanning electron microscopy and energy-dispersive X-ray spectroscopy analysis, performed using a ZEISS ULTRA 55 Field Emission Scanning Electron Microscope equipped with an Oxford Instruments detector. Scanning electron microscopy (SEM) was utilized to obtain high-resolution images due to its ability to reconstruct the sample's topography from secondary electrons and other products resulting from the interaction between the primary electron beam and the material [3]. Subsequently, the elemental composition was investigated using energy-dispersive X-ray spectroscopy (EDS), which identifies chemical elements by the characteristic photons produced when the sample is excited by electrons [4]. Approximately eleven EDS spectra were acquired from each sample, varying among grains that appeared distinct from one another.

Fig. 2. Samples prepared for SEM and EDS analysis.

2.3. X-ray diffraction

Lastly, another aliquot was finely ground using a 200-mesh sieve, and its mineral composition was analyzed by X-ray diffraction using an Empyrean system from Malvern PANalytical, equipped with a copper X-ray tube. This equipment can detect crystalline phases with a weight percentage greater than 5% in the analyzed sample. This technique was employed to determine the mineral composition, as it distinguishes compounds based on interference peaks at specific diffraction angles [5]. The conditions for obtaining the X-ray diffractograms were as follows: the copper tube operated at 45 kV and 40 mA. The scanning mode used was theta-two theta (θ-2θ), with 2θ varying from 10° to 90°, in increments of 0.05°, and a continuous mode with 82 seconds per step. The sample was rotated with a dwell time of 4 seconds to minimize the effects of preferred orientation

3. RESULTS

3.1. Morphology

The morphology assessment revealed the presence of three types of grains: extremely porous, rounded, and flat (see Fig. 3). In all samples, the predominant shape exhibited rounded corners, as shown in Fig. 1d. All grain types displayed signs of weathering, including holes, lines, and irregular excavations. Additionally, mineral deposition on the surface was observed, particularly on the rounded grains (Fig. 3b). The mean grain size values are presented in Tab. 2. In some samples, the high standard deviation indicates significant variability among individual grains. However, overall, the mean size was mostly homogeneous, ranging from 300 to 400 micrometers, except for *Praia de Setiba*, which contained larger grains averaging around 880 micrometers.

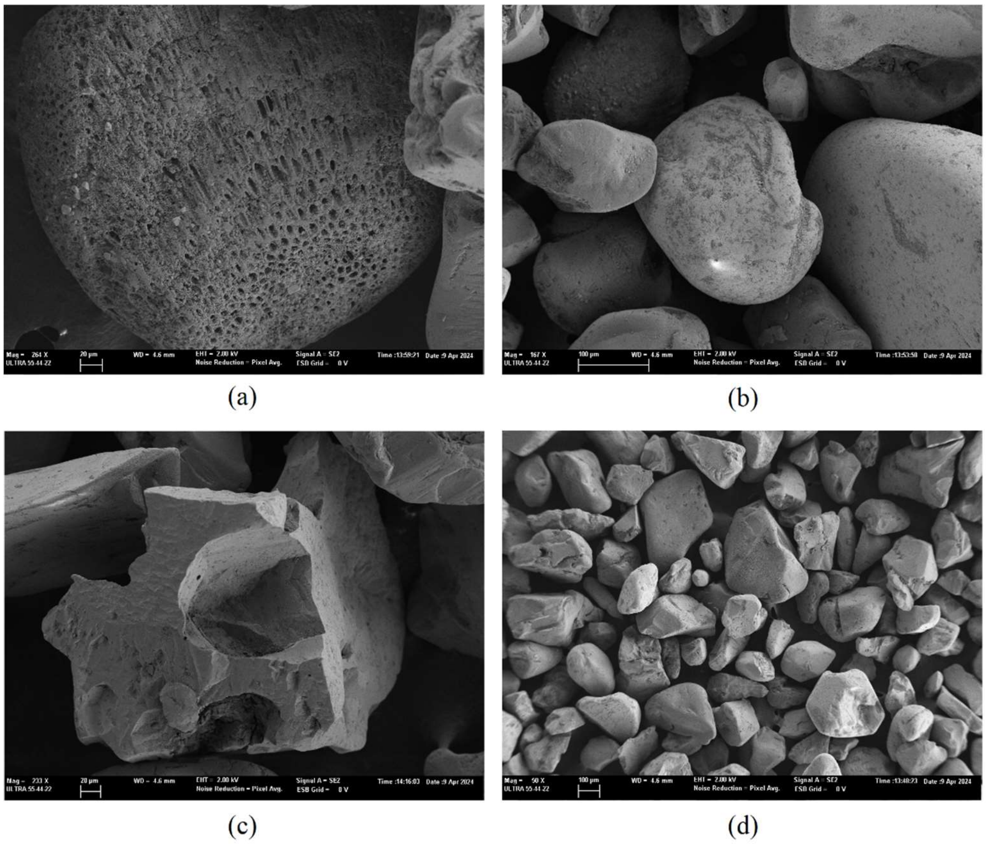


Fig. 3. SEM images show three main types of grains: (a) porous, (b) round, and (c) flat sides. (d) Sample 2 shows the predominance of grains with rounded features.

Tab. 2. Mean grain size obtained from 20 measurements of SEM photos.

Sample	**Mean grain size**
1	(310 ± 82) μm
2	(334 ± 67) μm
3	(413 ± 118) μm
4	(882 ± 216) μm
5	(291 ± 67) μm
6	(357 ± 168) μm

3.2. Elemental composition

As expected, the most abundant elements in all samples are oxygen and silicon, indicating the presence of quartz (SiO_2). Sample 1 exhibited the highest homogeneity, containing almost exclusively oxygen, silicon, carbon, and calcium. These elements can form calcium carbonate ($CaCO_3$), which accounts for the porous texture observed in some of the rocks.

At Areia Preta Beach (sample 2), other expected elements were detected, as the beach is renowned for its black sand. For instance, the presence of titanium and iron suggests the formation of ilmenite ($FeTiO_3$), an oxide rich in titanium that contributes to the sand coloration [6]. However, naturally radioactive elements were observed in only two spectra. Cerium, lanthanum, thorium, and neodymium were detected alongside oxygen and phosphorus, indicating the presence of monazite-(Ce): (Ce, La, Nd, Th)PO_4. These two rocks are highlighted in Fig. 4.

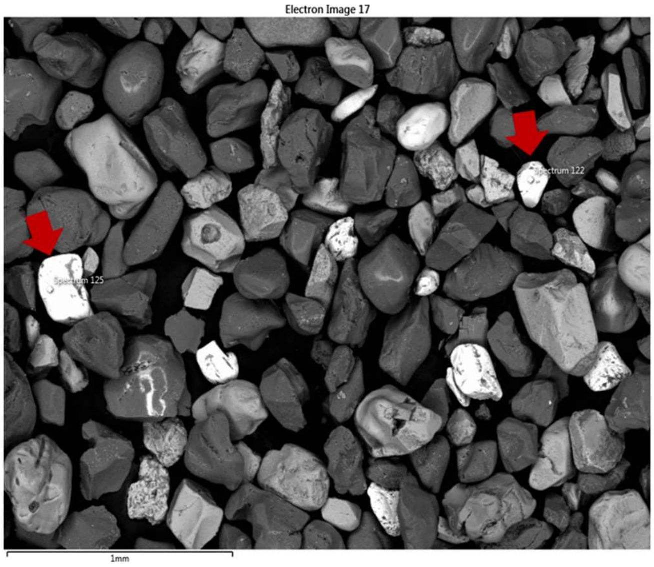
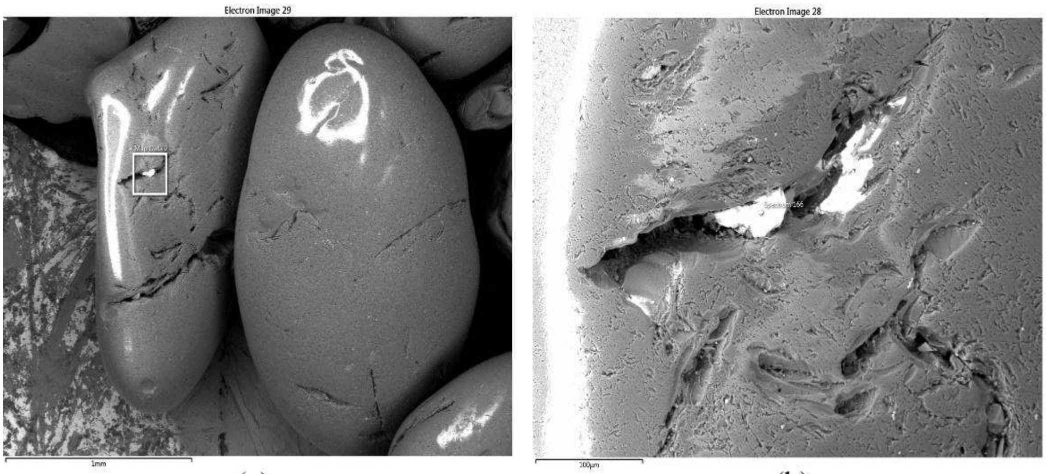


Fig. 4. Two spectrums (122 and 125) indicated the presence of monazite grains in sample 2.

Samples 3, 4, and 5 did not reveal any new elements or noteworthy combinations, except for trace amounts of aluminum, manganese, and zirconium. Additionally, occasional traces of sodium and chlorine were observed, suggesting the presence of NaCl, which aligns with the nature of the samples.

In sample 6, the final spectrum confirms the presence of monazite-(Ce). Notably, this grain was found within a fissure of a rock primarily composed of oxygen and silicon. Figure 5 displays images of the grain, while Figure 6 presents the EDS MAP spectra for the elements identified in this grain. Each color corresponds to a specific chemical element; for example, orange represents silicon, and the intensity of the color indicates the strength of the signal. Consequently, the outer rock exhibits a high concentration of silicon and oxygen, whereas the concentration of rare earth elements (REE) and radioactive elements is primarily located within the internal fragment.



(a) (b)

Fig. 5. SEM micrograph of the Sample 6 (a) entire grain, and (b) slit that contains the monazite grain.

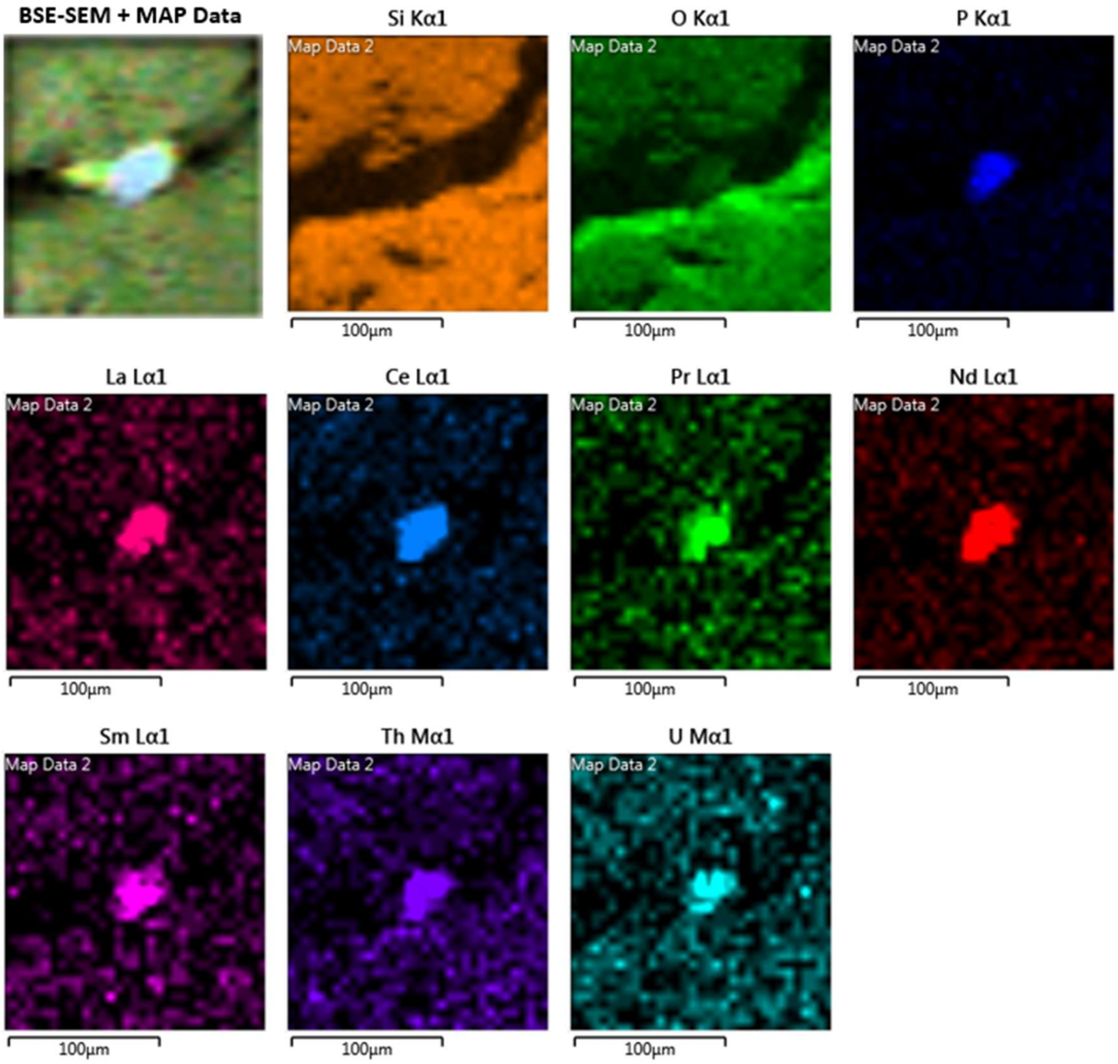


Fig. 6. EDS mapping of the composition of sample 6 shows the REE (La, Ce, Pr, Nd, Sm), quartz elements (Si, O), and radioactive elements (Th, U).

3.3. Mineral composition

The analysis of the diffraction peaks revealed the exclusive presence of quartz. This is illustrated in Fig. 7, which compares the quartz peaks (AMCSD 789) [7] with the XRD patterns of the samples. Although the SEM/EDS analysis identified monazite grains and other chemical elements indicative of calcium carbonate and ilmenite, the identification of additional minerals by XRD was limited. This limitation arose from the inability to detect crystalline phases with a mass percentage below 5%.

Over the years, numerous studies have reported on the effective dose rates in Guarapari, highlighting the challenges in identifying radioactive elements [8]. The results presented here confirm, through XRD analysis, that other minerals constitute only a small fraction of the total mass of the samples. Nevertheless, even at low concentrations, these minerals may contribute to the high effective annual dose observed in Guarapari. This suggests that both the composition and dose rate data should be monitored simultaneously in the coming years to assess their evolution and correlation.

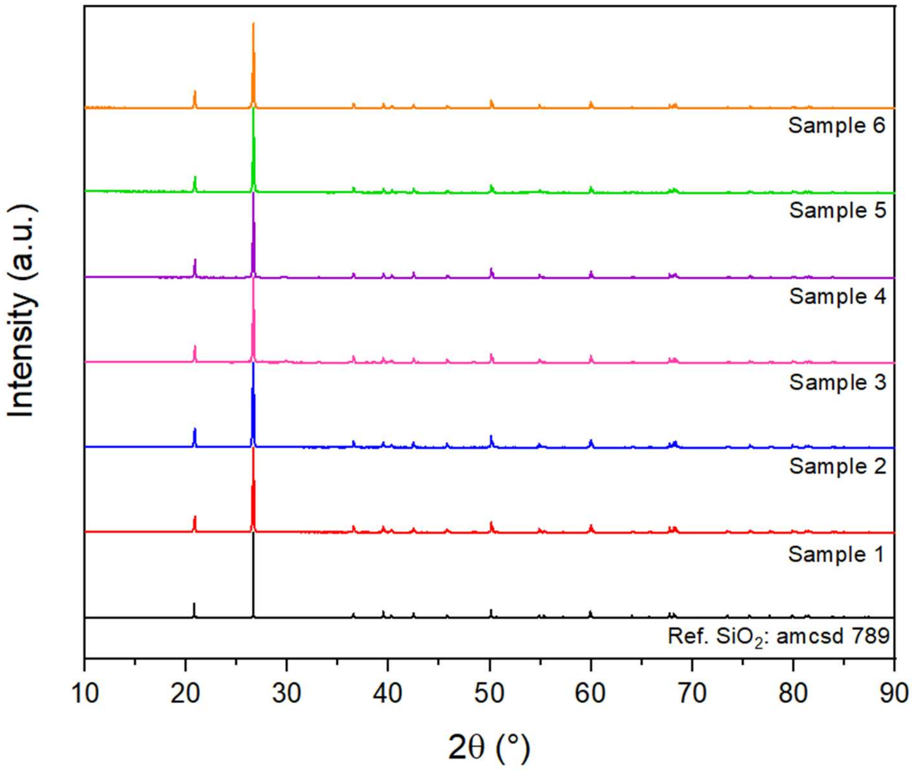


Fig. 7. Comparison between samples XRD and quartz XRD pattern from American Mineralogist Crystal Structure Database.

4. CONCLUSION

This study investigated six sand samples from the coastline of Espírito Santo, Brazil, focusing on grain morphology and size through scanning electron microscopy (SEM). The analysis revealed a predominance of grains with rounded features and a homogeneous size of approximately 400 µm, except at *Praia de Setiba*, which contained larger grains. Energy-dispersive spectroscopy (EDS) allowed for the identification of the elemental composition, which included Si, O, Fe, Ti, La, Ce, Pr, Nd, Sm, Na, and Cl. This composition suggests the presence of minerals such as quartz, ilmenite, monazite-(Ce), and sodium chloride. To validate the EDS analysis, further studies are essential to accurately ascertain the presence of these elements. Techniques such as inductively coupled plasma mass spectrometry (ICP-MS) could be employed to evaluate trace levels effectively. X-ray diffraction (XRD) results confirmed that quartz is the most abundant mineral in the samples, while radioactive phases constituted less than 5% of the total mass, rendering them undetectable in the XRD measurements.

Future research should also focus on characterizing the radioactivity of these samples, particularly evaluating thorium and uranium content through alpha spectrometry. Moreover, a long-term correlation between mineral composition and dose rate data should be established to better understand the origins of radiation and its implications for the effective dose affecting the local population.

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