Gammaspectrometry and mineralogy of carbonate sediments of Brejo do Espinho Lake (RJ) during the Holocene

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Abstract

The Brejo do Espinho Lake is, located in Costa do Sol Park in the state of Rio de Janeiro - Brazil, is one of the few places in the world where dolomite currently precipitates. The site is characterized by the deposition of calcareous sediments with high magnesium content and the presence of a semi-arid microclimate due to the upwelling zone around the Cabo Frio region. Previous studies have shown that the microbial activity supports the formation of sinsedimentary dolomite and significantly influences the isotopic composition of the sulfur and the concentration of sulfate dissolved in the water of the lake. These characteristics and modern dolomites are considered rare in the world, and important, since it is a mineral widely found in the geological record, especially in Precambrian carbonate rocks, commonly associated to microbial structures, and also as important rock analogues of oil reservoirs and in paleolimnological studies.

This study is part of a project of the Department of Geochemistry of Universidade Federal Fluminense (UFF) in partnership with ETH-Zürich and Université de Genève, Switzerland, with the specific objective of evaluating the sedimentary evolution of Brejo do Espinho Lake through stratigraphy and physico-chemical properties of the sediments during the Holocene. The methodology of the characterization of the stratigraphy, geochemistry, physical properties, and mineralogy applied to the sedimentary succession is effective as a tool in the reconstruction of paleoenvironmental evolution.

Introduction

In the coastal region of the state of Rio de Janeiro, between the cities of Guaratiba and Cabo Frio, sedimentary plains occur, with two lagoonal sequences separated by sandy barriers of different ages (Martin et al., 1997; Turcq et al., 1999; Villwock et al., 2005). The internal sand bar sequence is formed by large and rounded lagoons, such as Araruama, Jacarepaguá, and Rodrigo de Freitas, of Pleistocene ages. Smaller, thinly elongated lagoons and lakes, such as the Marapendi, Vermelha, Brejo do Espinho and Pernambuca (Turcq et al., 1999), form the outer sequence, with Holocene age.

The Brejo do Espinho lake (Figure 1), is located approximately 100 km east of the Rio de Janeiro city, near the Praia Seca village (Saquarema municipality), between coordinates 22°55'47.6" S, 42°20'58.52" W, with an area of 1 km² and a water column that varies between 2 cm and 1.5m (Anjos et al., 2003). Furthermore, according to Vasconcelos & Mackenzie (1997), the lake is also controlled by climatic variations, where during rainy seasons, the input of meteoric water increases, raising the level of the water, while during in the dry season, the lake is controlled mainly by water percolation of the Araruama lagoon and the Atlantic Ocean.

The environment is characterized by the presence of microbial mats and precipitation of primary dolomite. Dolomite is a mineral widely found in the geological record, especially in pre-Cambrian carbonate rocks, commonly associated with microbial structures. However, their scarcity in modern environments and inability to be synthesized at low temperatures in laboratory, hamper the understanding of the environmental variables associated with their formation and diagenesis. One of the fundamental factors for the occurrence of microbialites associated with dolomite is the microclimate of the Cabo Frio region due to the semi-arid characteristics imposed by the oceanographic upwelling of cold and nutrient rich South Atlantic Central Water (SACW), favoring a high evaporation on the coastal hypersaline environments (Valentin, 1984).

In the 80's, when the formation of primary dolomite was discovered in the hypersaline environment of the neighbor Vermelha lake (Hohn et al., 1986; Vasconcelos, 1988), it was observed that microorganisms, specially the sulfate reducing bacteria, had a fundamental role in the formation of dolomite precipitation (Van Lith et al., 2002). Vasconcelos & McKenzie (1997) proposed a model for the formation of dolomite through microbiological action, in association with geochemical and climatic factors, advancing the studies of dolomite's precipitation problem.

The microbialites, carbonate rocks formed by microbial action and their environment of formation have been relevant for understanding the evolutionary history of the Earth and related paleoenvironments. Microbialites are currently found in the hypersaline lagoons in the state of

Rio de Janeiro, and may be associated with the microbial origin of the carbonates that can constitute the pre-salt reservoirs, which include dolomitic carbonate rocks.

This study investigates the sedimentary paleoenvironment of Brejo do Espinho Lake through stratigraphy and geochemistry, based on total count gamma-spectrometric analysis, also carried of the most common radioactive elements: Potassium (K), Uranium (U), and Thorium (Th), and others physical properties such as grain size, mineralogy, magnetic susceptibility and p-wave velocity. We expect to understand the paleolimnological evolution of this environment, which represents a modern analogue of one of the largest oil discoveries int Brazil, the pre-salt.
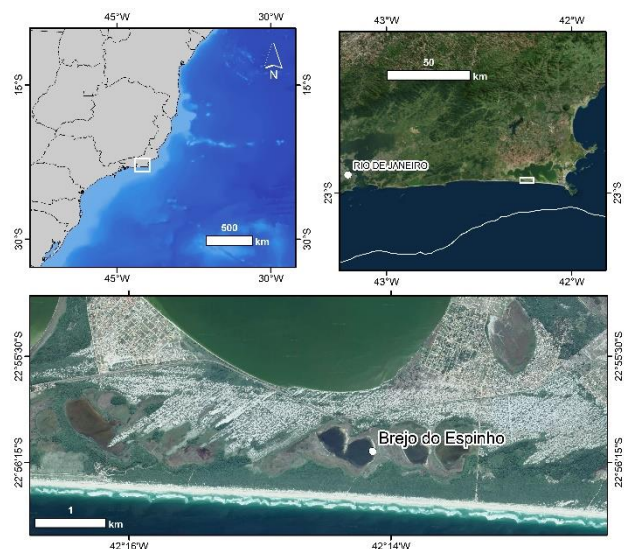

Figure 1 – Study site of Brejo do Espinho Lake in the southeast Brazil on the east coast of Rio de Janeiro state.

Method

The sedimentary core was obtained in June 2018 using PVC tube manually pushed into the sediment as deep as possible and then withdrawn. The core was identified as LBE18-1 and has a length of 100 cm.

To analyze the physical properties, the core was examined with a Multi-Sensor Core Logger (MSCL) manufactured by GEOTEK, in the Physical Geography Laboratory (LAGEF) at the Department of Geology and Geophysics of the Universidade Federal Fluminense (UFF). The sampling resolution for these analyses was 0.5 cm with 250 kHz, in order to obtain the p-wave velocity, gamma-density and porosity.

In the laboratory of sedimentology of the Geochemistry Department (UFF) the core was cut longitudinally in two halves, described in detail and photographed. One half was stored as an archive, the other was used for the physical, and sedimentary analyzes. After that, the gamma spectrometric analysis was made using the model RS-230-BGO by Radiation Solution with measurements in intervals of 2.5 cm. This analysis allowed us to detect the total radiation emitted, as well as that emitted by

Potassium (K), Uranium (U), and Thorium (Th), in order to identify clay contents of different geological units using chemical stratigraphy and the relation between the influence of marine and continental sedimentation.

The core was sliced into 2 cm thick segments, identified, closed in zip lock bags and stored in a freezer at + 4 ºC, and then slplit into aliquots for additional analysis.

For the grain size analysis, each 2 g aliquot was decarbonated using HCl (1 N) and placed on a vibrating platform until the end of the reaction, washed with distilled water and centrifuged to remove excess acid. After this, the organic matter was removed with hydrogen peroxide (H_2O_2) and, after the end of the reaction, the sample was washed again. Sodium hydroxide (40 %) was added to disaggregate the particles present in the sample. The grain-size measurements were performed using a laser particle analyzer (CILAS ® 1064), which has a detection range of 0.02-2000 µm, using the grain size statistics method of Folk and Ward (1957) performed in GRADISTAT software version 8.0 (Blott and Pye, 2001) to interpret the results.

Other 2 g aliquots were used for mineralogical analysis after the removal of the organic matter with hydrogen peroxide (H_2O_2) and homogenization through maceration. In the X-ray diffraction laboratory at UFF, the aliquots were placed on the sample tray and the material smoothed to avoid the presence of surface imperfections, as these would interfere in the acquisition of the diffraction data, changing diffraction peaks, and generating unsatisfactory responses with a high probability of significant errors (Langford, 1996). X-ray diffractograms were obtained in the BRUKER D8 ADVANCE equipment, with LYNXEYE detector using Bragg-Brentano geometry, under the following conditions: angular range (2θ) between 5º and 100º, angular pitch of 0.02º and time of collection by 0.8 s step. The measurements of the interplanar distances and the relative intensities of the peaks in the diffractogram were obtained by the program PowderCell 2.4 (PCW), where the interplanar spacing was compared with the values presented in the book "Crystal structures of clay minerals and the x-ray identification" by Brindley & Brown (1980) to identify minerals in the aliquots.

Results

The LBE 18-1 core presented grain size alternation, with the predominance of sand in the samples closest to the top, while at greater depths silt predominates. The percentages varied from 0% to 99.45% (mean of 49.87% and standard deviation of 41.95%) for the sand content, from 0.13% to 97.25% (mean of 46.11% and standard deviation of 39.14%) for the silt content and from 0.20% to 14.06% (mean of 4.02% and standard deviation of 3.96%) for clay (Figure 2).

The grain size ranged from 5.69 µm to 205.61 µm (mean of 97.60 µm and standard deviation of 87.71 µm).Several characteristics of marine sediments, such as density, porosity, interstitial fluid and confinement pressure, are factors that interfere with the p-wave velocity (AYRES-

NETO, 1998). The Vp profile obtained from LBE18-1 showed variations between 1376.15 m / s and 1673.53 m / s (average of 1605.9 m / s and standard deviation of 33.14 m / s). At 25 cm and 55.5 cm depths, a decrease in grain
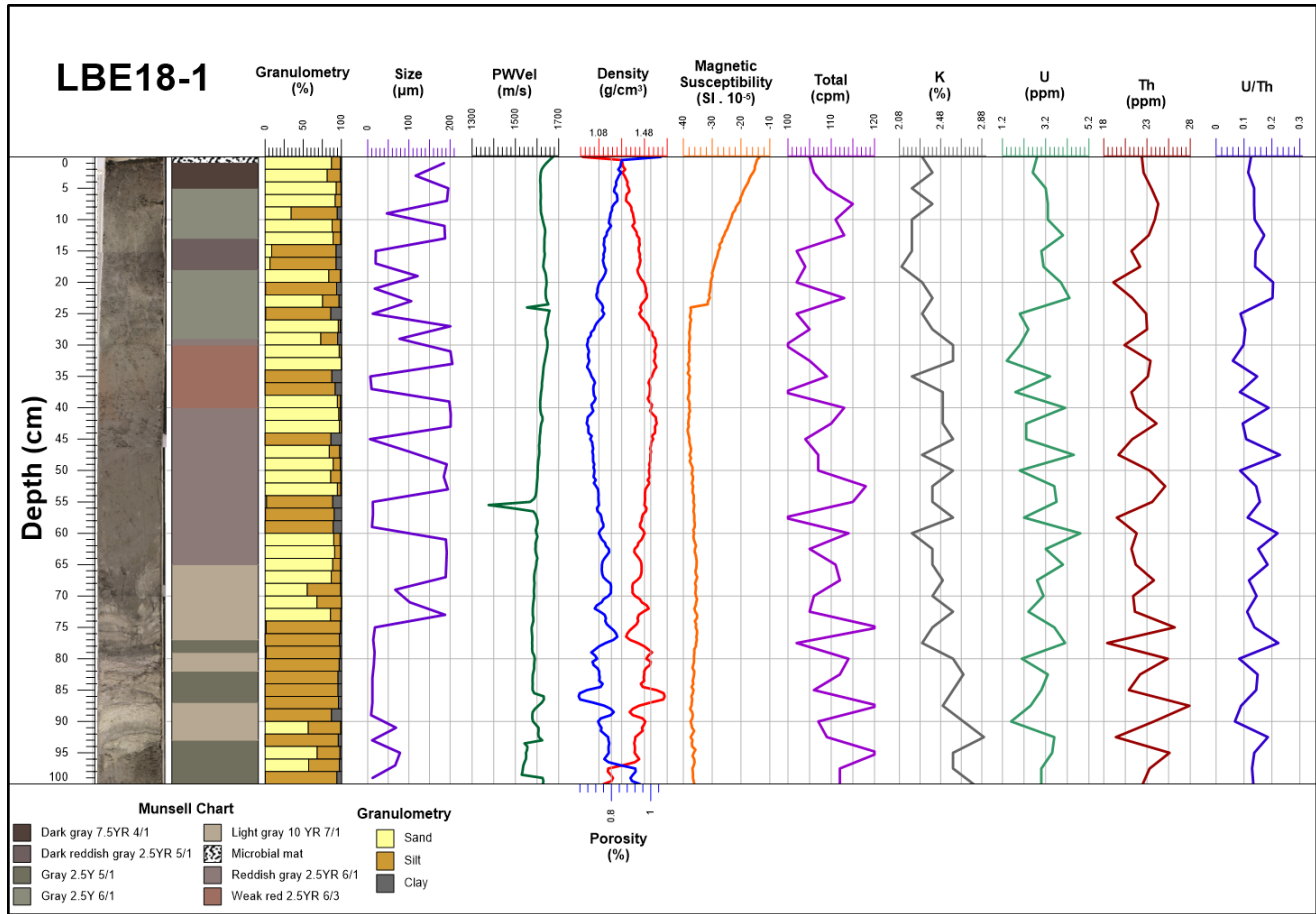

Figure 2 – *Representation of particle size analysis in percentage and µm, seismic profiling and gamma spectrometry of the core LBE18-1 at Brejo do Espinho Lake.*

size was observed (12.17 µm and 12.44 µm respectively) along the highest percentages of clay (14.06% and 11.66%, respectively) corroborating the inferred Vp decrease.

In addition, close to the base of the core, between 85 cm and 95 cm, a predominance of sandy sediments with large amounts of silt and clay was observed, in which the finer sediment filled the pores between coarse grains, decreasing porosity. These results corroborate those found by Hamilton (1979); Kim et al. (2001), Macedo (2006), who verified that the higher velocities are related to sediments of greater grain size.

Porosity is defined as the volume of the empty space between the grains occupied by the water, in gas-free sediments (HAMILTON, 1976) and has a relation inversely proportional to grain size. The porosity values varied from 0.6% to 1.0% (mean of 0.7% and standard deviation 0.05%). In samples where there is a sand grain domain, but with the presence of silt and clay, the porosity reduction was verified. The density parameter is a mirror

image of the porosity and thus the parameters described above occurred inversely with the density data. Information on the magnetic and mineralogical composition of the sediments was obtained by means of the magnetic susceptibility curve, since it is calculated for the ability of a material to magnetize itself, when exposed to an induced magnetic field (CHANNEL et al., 2006; Schultheiss et al., 2011). The core showed a change from -38.47 x 10^{-5} to -13.54 x 10^{-5} SI (mean of -33.80 x 10^{-5} SI and standard deviation of 6.09 x 10^{-5} SI) (Figure 2).

Higher values of magnetic susceptibility close to the top of the core indicate the presence of diamagnetic minerals, such as calcite and quartz, while lower values point to the presence of clay and dolomite minerals. Magnetic susceptibility signal could have been attenuated due to the PVC tube coating of the cores (CHANNEL et al., 2006) (Figure 2).

Gammaspectrometry for the LBE18-1 core showed coherent values of the radiation emitted by the elements

Uranium (U), Potassium (K) and Thorium (Th). Potassium presented a variation between 2.1% and 2.9% (mean of 2.4% and standard deviation 0.1%), where its occurrence is directly associated with variations in the amount of micas, k-feldspars, and weathered clay minerals (Serra et al., 1980). The uranium element presented a variation between 1.4 ppm to 4.8 ppm (average of 3.0 ppm and standard deviation of 0.8 ppm), where high concentrations in carbonate rocks are not related only to the clay fraction, but also can be associated to organic sources. For thorium values between 18.4 ppm to 27.9 ppm (mean of 22.5 ppm and standard deviation 1.9 ppm) were observed. Significant concentrations of thorium are interpreted as radioactive clays and heavy minerals present in sediments such as monazite, torite, zircon, titanite and allanite (Durrance, 1986). In the total count graph, a variation from 99.1 to 121.0 (mean of 108.8 and standard deviation of 5.8) was verified, being an important factor for the calculation of the amount of clay within a carbonate. The U / Th ratio shows a relationship between the two radioactive elements during deposition in the Brejo do Espinho Lake, allowing the visualization of the marine and continental influence, since they are related to the predominance of U and Th concentrations, respectively (Figure 2).

In order to evaluate the mineralogy, XRD analysis was performed for different samples. The values of the most intense peaks were verified and compared with standards according to the literature BRINDLEY & BROWN, 1980. Minerals such as calcite ($CaCO_3$), magnesian calcite (($Ca,Mg)CO_3$), dolomite ($CaMg(CO_3)_2$), quartz (SiO_2), weddellite ($Ca(CO_2)_2 . 2(H_2O)$), gypsum ($CaSO_4 . 2 H_2O$), aragonite ($CaCO_3$) and ankerite ($Ca(Fe,Mg,Mn)(CO_3)_2$), present significant variation in quantity through the core LBE18-1 (Figure 3).
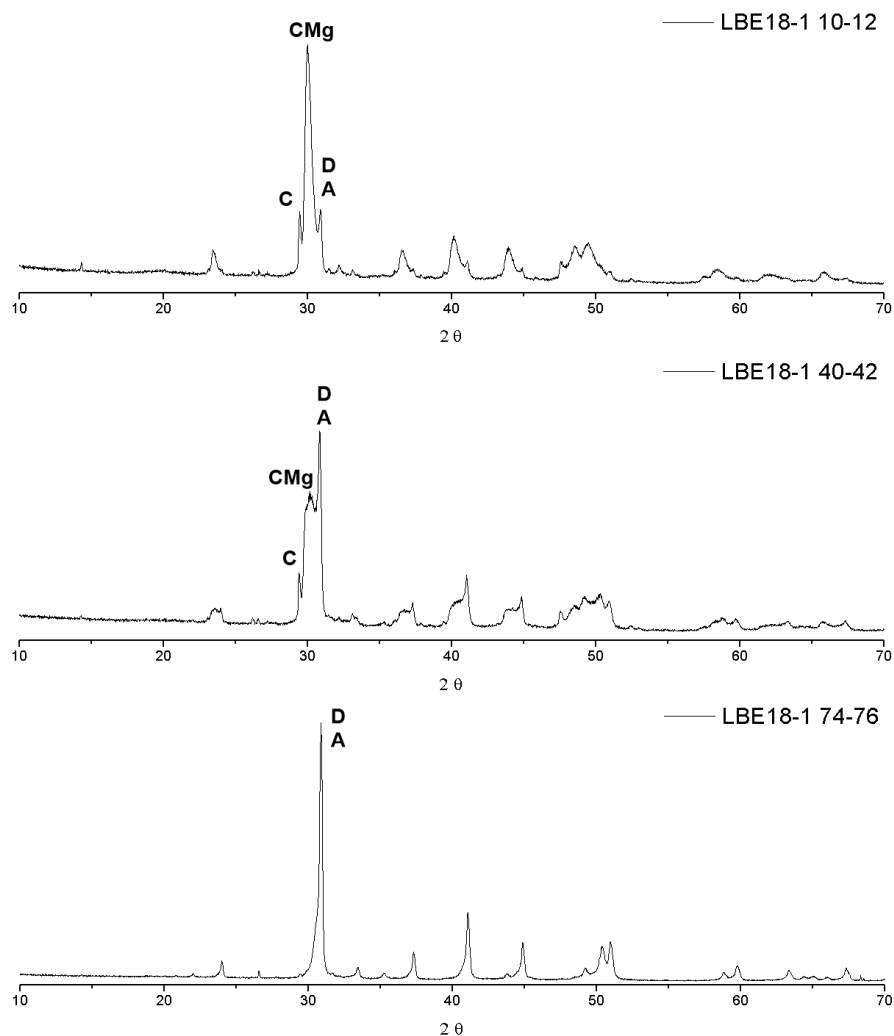

Figure 3 – *XRD analysis of representative selected samples from the LBE18-1core. C means calcite, CMg means magnesian calcite, D means dolomite and A is ankerite.*

Conclusion

The analysis of grain size, seismic profiling, gammaspectrometry and x-ray diffraction, allowed the identification and study of the carbonate sediment of the Brejo do Espinho Lake, in which three geological units were observed along the LBE18-1 core (Figure 4):

- At the base, the first unit is represented between depths of 100 cm to 72.5 cm, with dominant grain size of medium and coarse silt, showing a lighter color and porosity and density curves following grain size variation. The XRD analysis showed a predominance of ankerite, with smaller amounts of dolomite, whereas the magnesian calcite had the lowest values on the core. Thus, these minerals influence the magnetic susceptibility curve, presenting the lowest values found in LBE18-1;

- The second unit is limited between depths 73 cm to 26 cm, with predominantly fine sand, with important clay percentages. Mineralogy showed a predominance of ankerite and dolomite. The magnetic susceptibility presented similar values with the first unit;

- The third unit, between depths 25cm to 0cm, presented variable grain size between fine sand and coarse silt, resulting in an increase in density and a decrease in porosity. Significant amounts of magnesian calcite and dolomite were observed in these samples, closer to the top of the core. The high magnetic susceptibility, when compared to the rest of the core, can be explained due to the predominance of this magnesian calcite.

The different physical analyzes carried out in the LBE18-1 core showed good contrasting responses, demonstrating that the characterization of a sedimentary succession through chemical stratigraphy, physical and mineralogical properties is effective as a tool in the reconstruction of the paleoenvironmental evolution of Brejo do Espinho Lake.
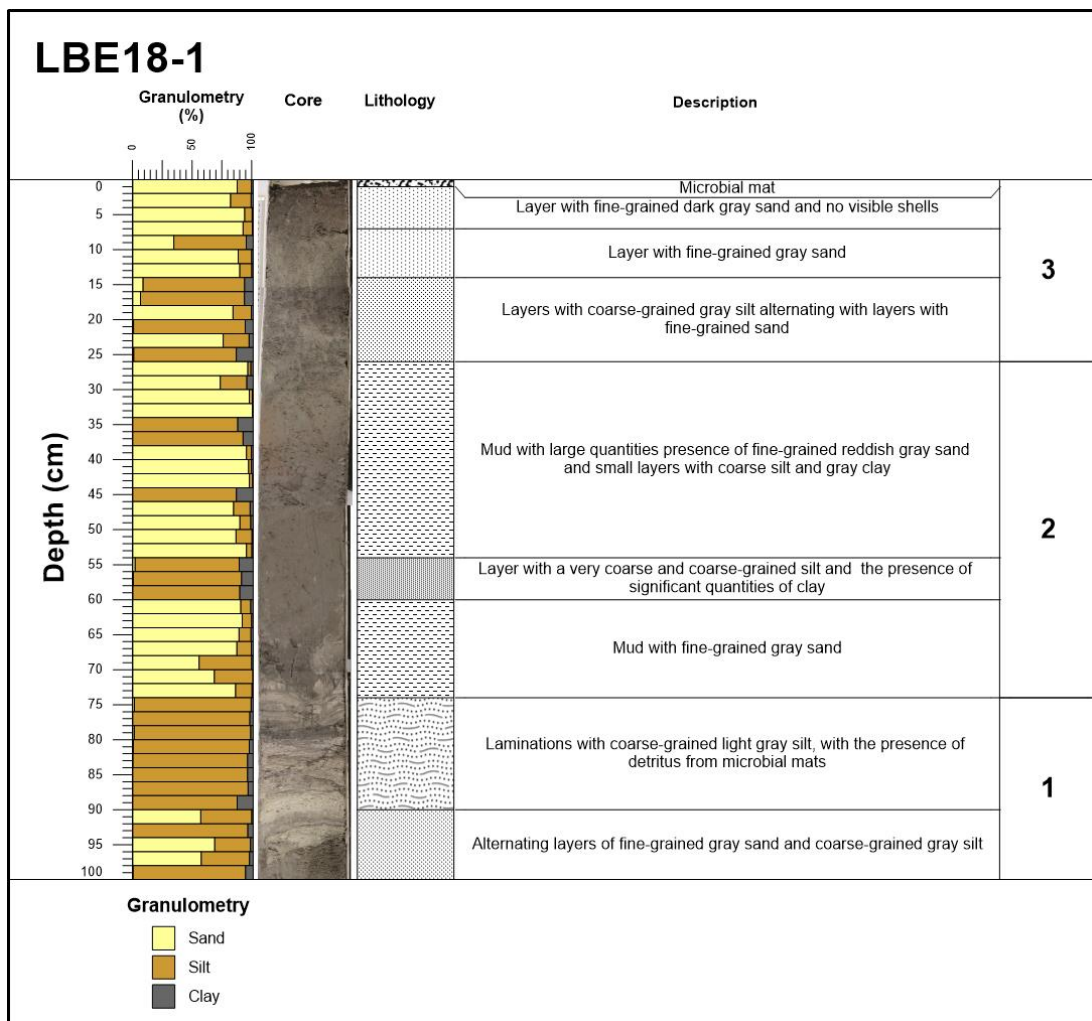

Figure 4 – Summary of the lithology and grain size found in core LBE18-1.

Acknowledgements

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