Early diagenesis of organic matter in two lacustrine evaporitic environments in Brazil

Introduction

Most organic matter in lakes originates from a mixture of lipids, carbohydrates, proteins, and other organic matter produced mostly by plants growing in and around the lake. Molecular biomarkers are compounds that characterize certain biotic sources and are low susceptible to microbial degradation, retaining their source information after burial in sediments (MEYERS, 1997). They have been widely used in recent paleoenvironmental studies as a tracer to a particular process and reveals more specific contributions from different organisms groups providing more information regarding past environmental conditions in comparison to bulk geochemical analyses.

The Lagoa Vermelha (LV) and Brejo do Espinho (LBE) hypersaline coastal lagoons have been widely used as natural laboratories to investigate the interaction of climate conditions, microbial mediation, and mineral precipitation due to the modern dolomite formation associated to the seasonal coastal upwelling. Since the discovery of the microbial mediation of modern dolomite precipitation at Lagoa Vermelha (Brazil) (VASCONCELOS et al., 1995), many in situ and laboratory culture experiments have been done using different microbial consortium (e.g. halophilic, sulfate-reducers) to understand how the bacteria act to induce/mediate the mineral precipitation (SÁNCHEZ-ROMÁN et al., 2009; VAN LITH et al., 2002) and many other studies conducted to understand these deposits (BAHNIUK et al., 2015; NASCIMENTO et al., 2019; SPADAFORA et al., 2010; VAN LITH et al., 2002; WARTHMANN et al., 2000).

Methods

The LBE and LV are neighboring shallow hypersaline lagoons, located along the coast, 100 km east of Rio de Janeiro, Brazil. These lagoons are part of a large barrier/lagoonal system bordering the South Atlantic, formed as a result of the sea-level oscillations since Pleistocene (TURCQ et al., 1999). After the sea-level regression around 3.6 kyr B.P. the lagoons became isolated from the large Lagoa de Araruama and the Atlantic Ocean, causing changes in the lacustrine sedimentation patterns, with deposits rich in carbonate mud (BARBOSA, 1997). The lagoons are one of the few places in the world with the modern formation of dolomite minerals. The high salinity, sulfate-reducing bacterial activity, and sulfide oxidation are most likely to be the controls on dolomite formation (VASCONCELOS et al., 2006).

Two sedimentary cores from LV (154 cm) and LBE (100 cm) were analyzed for their radiocarbon ages, organic and inorganic carbon content, carbonate mineralogy (XRD), the stable isotopic composition of bulk carbonates (δ18O and δ13C) and n-alkanes stratigraphy. These analyses were done to better understand the process involved in the deposition of the carbonate mud and the organic matter diagenesis.

Results and Discussion

The LV core is formed by two sedimentary facies, the marine (aphanitic) and lacustrine (laminated) facies, covered by a thin (1 cm) microbial mat and comprises the last ~6.1 cal kyr BP (Figure 1). The upper interval from 39 cm to the top of the core is composed of the modern deposition, which means formed after 1950 AD. The interval from 6.1 to 3.6 cal kyr BP is mainly composed of very fine dark mud deposited during the Holocene marine transgression (CASTRO et al., 2014). The lacustrine facies deposited after the sea-level regression, ~3.6 cal kyr BP (AREIAS et al., 2020), is characterized by an alternation of aphanitic (pallet) and laminated facies, with a large increase in the carbonate content, mostly high Mg-Calcite. Laminated and aphanitic facies observed at LV and LBE sediments differ due to the transition from dry/wet episodes. High saline conditions generated during drought periods prevent the growth of eukaryotic organisms and lead to the remain of carbonate laminas (BAHNIUK et al., 2015). Wet conditions decrease salinity which allows grazing organisms to invade and feed on the organic matter in the mats (DELFINO et al., 2012). The exposure of the sediment during the following
dry episode leads to degradation of the remaining organic matter, and the carbonate mud is preserved as homogeneous aphanitic facies (BAHNIUK et al., 2015).

The sediment core LBE18-1 recovered the last ~1.6 cal kyr, and the first 13 cm represents modern deposition and is also characterized by the two, aphanitic and laminated facies. Stratigraphically both lagoons are complementary, the dolomite concretion in LV correlates with the concretion in LBE which was formed after 2.0 cal kyr BP (Figure 1 - yellow bars). The LBE core is mainly formed by dolomite (average 49.3 %) and high-Mg-calcite (average 35.3%) with low portions of calcite (average 14.2%). The LV core shows a different trend relative to carbonate minerals composition with high-Mg-calcite (average 41.6%) and aragonite (average 20.1%) as the main minerals, but Ca-dolomite (average 12.8%) and dolomite (average 11.6%) have been detected in all layers. One lithified layer deposited between 0.85 and 2.1 kyr BP, consists of a mixture of aragonite (9.75%), high Mg-calcite (33.54%), and Ca-dolomite (56.71%), some samples often retain some high Mg-calcite that has not been diagenetically altered, which seems to be the case of the LV concretion.

The values of the stable carbon and oxygen isotopes data measured on bulk sediments from LV varied between -10.55 and +0.74 ‰ for carbon and -1.20 and +4.55‰ for oxygen. The δ¹³C and δ¹⁸O values of LBE varied from -8.73 to -0.84‰ and from -0.05 to +5.70‰, respectively. The stable isotope measurements showed a similar trend, the most depleted δ¹³C values (-10.5 and -8.73‰, respectively for LV and LBE) and enriched δ¹⁸O values (+4.55 and +5.70‰, respectively for LV and LBE) are associated with the dolomite rich layers, suggesting very dry conditions during the dolomite formation. This condition is related to the exposition of the surface sediments where the microbial mats form and consequently, the organic matter is degraded leading to the incorporation of the ¹²C into the carbonates precipitate. NASCIMENTO et al. (2019) have related the intensification of the coastal upwelling events at the ocean to the increase in stoichiometric dolomite precipitation.

The n-alkane stratigraphy of LV core can be summarized as follows: the C₃₁ and C₃₃ are the most abundant compound during the marine phase (from ~6.1 to 3.6 cal kyr BP) together with the C₂₁, which is largely detected from ~5.0 to 3.6 cal kyr BP, with a sharp decrease towards the top. The large presence of C₁₇ at the interval ~3.9 cal kyr BP suggest the replacement of the C₂₁ organisms to the production of short-chain ones at this microenvironment. Afterwards, the profile changes and the long-chain n-alkanes, C₃₁ and C₃₃ and C₃₅ dominates, the longer-chain n-alkanes (C₃₃, C₃₅) are abundant in C4 grasses (FREEMAN; PANCOST, 2014), suggesting the establishment of a vegetation more efficient to respond to arid conditions. At the youngest part of the record, from 15 cm to the top, the C₁₇ reestablish its abundance. The n-alkane stratigraphy of LBE displays large abundance of the long-chain n-alkanes (C₃₁ and C₃₃) at the entire profile. At the interval ~1.0 kyr cal BP the C₁₇ compound increases to around 8.4 µg/g, however this compound is not detected for the upcoming interval, ~150 yrs. Afterwards, the long-chain n-alkanes decreases in the meantime that short-chain increases its dominance. The C₂₇ and C₃₀ are diagnostic of waxes from trees and shrubs while the n-C₃₁ is diagnostic of grass waxes (JENG, 2006).

The carbon preference index (CPI), is a numerical approach to represent the predominance of odd-over-even n-alkanes in one given sample and can indicate the n-alkane source (JENG, 2006). CPI values for long-chain (CPI(C₂₇-C₃₃)) homologs at LV displayed the wider range (3.6 to 7.1) compared to LBE, in which the values varied between 2.5 to 5.8. The CPI values of ~5 to 10 have been described for terrestrial plants (PEARSON; EGLINTON, 2000), values approximately 1.0 are derived from petrogenic sources, low CPI values can be due to degradation of organic matter, microbial activity or algal inputs (CRANWELL; EGLINTON; ROBINSON, 1987). The CPI values suggest a mixed origin for the organic matter in the sediments of the lagoons whereas part is fed by terrestrial organic matter inputs from rain and wind action along with microbial activity responsible for the autochthonous organic matter production.
Figure 1. Geochemical record from Lagoa Vermelha and Brejo do Espinho depicting in blue the marine like facies and in brown the lacustrine facies. Yellow bars represent the dolomite rich intervals on both lagoons. Red dashed (vertical) lines indicate the transition between facies and the black dashed square in LV marks the interval that correlates with LBE. The gray dashed line (horizontal) represents the limit to distinguish vascular land plants from microbial CPI.

Conclusion

Studies on the ecological functioning of Lagoa Vermelha and Brejo do Espinho using a multiproxy approach are essential to better understand the responses of these vulnerable aquatic systems to environmental changes along the Holocene and to better constrain the close association of dolomite formation with environmental conditions. The usage of n-alkanes together with inorganic proxies ($\delta^{13}$C and $\delta^{18}$O) suggest the formation of dolomite/carbonate-rich intervals under the influence of dry weather and intense organic matter degradation by microbial activity.

References


