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A multi-proxy evidence for the transition from estuarine mangroves to deltaic freshwater marshes, Southeastern Brazil, due to climatic and sea-level changes during the late Holocene

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ABSTRACT

The present study investigates a paleo-estuary at the Doce River Delta, southeastern Brazil, through a multi-proxy approach that links palynology, diatoms, sedimentology and geochemistry analyses (i.e., Total C, Total N, $\delta^{13}C$ and $\delta^{15}N$). These analyses, temporally synchronized with five radiocarbon ages, revealed environmental changes from marine to continental over the last ~7550 years. The studied sedimentary succession recorded the upward transition from estuarine channel (until ~7550 cal yr BP) to estuarine central basin (>~7550 to ~5250 cal yr BP) deposits, the latter containing increased mangrove vegetation, marine and marine/brackish water diatoms. The range of geochemical values ($\delta^{13}C = -30$–-10‰, $\delta^{15}N = 2 - 8$‰ and C/N = 4–40) also indicate marine/estuarine organic matter and C_3 terrestrial plants to that time interval. A following period recorded two phases: lake/ria (~5250 to ~400 cal yr BP) and fluvial channel (~400 cal yr BP until modern age). During this stage, mangroves were replaced by trees/shrubs and herbs/grasses due to the disconnection with the marine realm. As a result, the corresponding sediments contain only organic matter sourced from freshwater and C_3 terrestrial plants ($\delta^{13}C = -29$–-26‰, $\delta^{15}N = 0 - 8$‰ and C/N = 10–45). The equilibrium between fluvial sediment supply and relative sea-level changes during the Holocene controlled the morphologic and vegetation changes in the studied littoral. The estuary became established during the early Holocene as a resulted of a eustatic sea-level rise, when the fluvial sediment supply to the coast was relatively lower due to a dry period. However, during the late Holocene, the climatic force was more significant to the development of coastal morphology due to a wet period that caused an increase in sandy sediment supply to coastal system. Then, the increase of fluvial discharge associated to a relative sea-level fall caused a marine regression and shrinkage of mangroves during the late Holocene. The evaluation of mangrove dynamics according to climatic and sea-level changes mainly during the late Holocene is essential for the understanding of their survival ability under future scenarios, with a probable accelerated sea-level rise and intensification of extreme climatic events in southeastern Brazil for the next century.

1. Introduction

Climate changes and sea-level oscillations have caused significant impacts on coastal sedimentary dynamics and ecosystems along the Brazilian littoral during the late Quaternary (Suguio et al., 1985; Dominguez et al., 1992; Ledru et al., 1996; Angulo and Lessa, 1997; Behling et al., 1998b; Grimm et al., 2001; Bezerra et al., 2003; Martin et al., 2003; Cohen et al., 2005a,b; Angulo et al., 2006; Vedel et al., 2006; Behling et al., 2007; Sawakuchi et al., 2008; Lara and Cohen, 2009; Zular et al., 2013; Guimarães et al., 2012, 2013; Buso Junior et al., 2013; França et al., 2012, 2013, 2014).

It is well known that the dominant depositional systems under sea-level rise are estuaries (Swift, 1975). It evolves as the result of the interaction between geomorphological structures and dynamic processes that are marine and riverine; this interaction adds up to processes that are inherently estuarine (Jackson, 2013). Their response to sea-level changes is affected by tidal range, nearshore wave climate and river inflow, as well as by the nature and supply of sediments. All estuaries

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assumed their present form during the rise of sea-level that followed the Last Glacial Maximum (LGM), about 20 thousand years ago (Chappell and Woodroffe, 1994). However, the sea-level fall creates highly unfavorable conditions for the genesis and maintenance of this coastal system. A continued river sediment supply may result in shoreline progradation, and it can generate a delta (Suter, 1994).

Considering the relative sea-level changes during the Holocene, it crossed above the present one at 7000 BP (Suguio et al., 1985), reaching 4 to 6 m above the present one in many areas of the Brazilian coast (Martin and Suguio, 1992; Angulo et al., 2006; Rossetti et al., 2008; Reis et al., 2013), with a subsequent fall to the present time (e.g., Angulo et al., 2006). In terms of climatic changes, significant rainfall variations occurred in the Brazilian central region, and consequently it affected the volume of the rivers. Then, during the drier periods of the early and mid-Holocene (Ledru, 1993; Ledru et al., 1996; Behling, 1995; Behling and Lichte, 1997; Behling et al., 1998b; Pessenda et al., 2009), the river inflow may have been severely reduced, and it affected the salinity gradients and the sediment supply to the coastal system. In contrast, in the mid- to late Holocene, the climate was marked by wetter conditions (Ledru, 1993; Ledru et al., 1998; Salgado-Labouriau, 1997; Salgado-Labouriau et al., 1998; Ledru et al., 2009; Pessenda et al., 2004, 2009). Therefore, the interaction between the sea-level and climatic changes have affected significantly the evolution of coastal systems.

Several paleoenvironmental indicators, such as sedimentological features (Suguio et al., 1985; Giannini et al., 2007; Rossetti et al., 2012), isotopes and geochemical data (Freitas et al., 2003; Pessenda et al., 2010), pollen (Behling et al., 2001, 2004; Cohen et al., 2005a,b, 2008, 2012; França et al., 2012) and diatoms (Round et al., 1990; Bennion, 1995; Hillebrand and Sommer, 2000; Rivera and Diaz, 2004; Hassan et al., 2006; Korhola, 2007; Zong and Horton, 1998; Zong et al., 2010; Castro et al., 2013) have been used individually to investigate the past climate and the sea level fluctuations, as well as local environmental changes.

In this context, this paper integrates lithology, diatom and pollen data previously published by Castro et al. (2013) and Cohen et al. (2014) with Total Organic Carbon (TOC), Nitrogen (N), stable isotopes ($\delta^{13}C$ and $\delta^{15}N$), C/N and radiocarbon date in order to present an evolutionary model for the State of Espírito Santo littoral, southeastern Brazil, according to the interplay between climatic changes and relative sea-level oscillations during the Holocene.

2. Study area

The study site is located in the deltaic plain of the Doce River (Fig. 1). This is a feature with a maximum width of about 40 km and length of about 150 km (Suguio et al., 1982; Bittencourt et al., 2007) that occurs near the town of Linhares (around 30 km), State of Espírito Santo, Southeastern Brazil. The Doce River Delta occurs within an incised valley that cut down into Miocene strata (Dominguez et al., 1981).

2.1. Geological setting

The area is composed of a Miocene plateau constituted by continental deposits of the Barreiras Formation, whose surface is slightly sloping to the ocean. Four geomorphological units are recognized in the area: (1) a mountainous province of Precambrian rock; (2) a tableland with the Barreiras Formation (Neogene) (Arai, 2006; Dominguez, 2009); (3) a coastal plain (Martin et al., 1987; Cohen et al., 2014); and (4) an inner continental shelf (Asmus et al., 1971).

Currently, the Doce River shows a mostly W–E trending “straight” pattern, and it flows over basement crystalline rocks into the littoral plain through a low valley with Holocene terraces. The terraces consist of a mixture of sediments from the Barreiras Formation, which were transported by rivers originated in mountainous areas and Neogene tablelands. The Barreiras Formation is constituted by sandstones, conglomerates and mudstones attributed mainly to Neogene fluvial and alluvial fan deposits, but possibly including deposits originating from a coastal overlap associated with Neogene marine transgressions (Arai, 2006; Dominguez, 2009). The delta plain deposits are composed mainly of moderately sorted, coarse- to very-coarse grained sands of beach ridges distributed along the coastline. Downstream, sandy silts of the Doce River spread over floodplains. Residual and very poorly-preserved mangrove vegetation close to marine influence occurs at the margin of coastal lagoon systems. Elongated coastal sand barrier occurs parallel to the shore and are separated from the mainland by a lagoon. It displays 37 and 3.6 km in length and width, respectively, and presents multiple beach ridges. These likely represent successive shoreline positions formed during the coastline progradation associated with the RSL fall (Otvos, 2000).

The studied delta plain covers an area of ~2700 km^2. It displays fluvial channels and an extensive network of paleochannels. The abandoned channels are straight to meandering, and they maintain the shape and typical concavity of the original channel, resulting lakes. Avulsion may have been responsible for the partial or complete abandonment of several channels due to rapid sand accumulation (Cohen et al., 2014).

2.2. Climate

Southeastern Brazil is characterized by a warm and humid tropical climate, with annual precipitation averaging 1400 mm (Peixoto and Gentry, 1990). Seasonal climate is controlled by position of the South Atlantic Convergence Zone (SACZ), which controls moisture at this latitude and Inter Tropical Convergence Zone (ITCZ) or meteorological equator that divides the year into a rainy (austral summer) and a dry season (austral winter) (Carvalho et al., 2004). The SACZ is evident along the year, but more intense during the summer, when it is connected with the area of convection over the central part of the continent, causing episodes of intense rainfall over much of southeastern South America (Liebmann et al., 1999). The ITCZ corresponds to the belt of minimum pressure and intense low-level convergence of the trade winds over the equatorial oceans which reaches the northeast Brazil, producing the rainy season of northern State of Espírito Santo — Brazil (Garreaud et al., 2009). The rainy season occurs between November and January, with a drier period between May and September. The average temperature ranges between 20° and 26 °C (Carvalho et al., 2004).

2.3. Modern vegetation

The vegetation is characterized by tropical rainforest, with plant families such as Fabaceae, Myrtaceae, Sapotaceae, Bignoniaceae, Lauraceae, Hippocrateaceae, Euphorbiaceae, Annonaceae and Apocynaceae (Peixoto and Gentry, 1990). An herbaceous plain, mainly represented by Cyperaceae and Poaceae with some trees and shrubs, occurs at the edges of the proximal delta plain. The transition from the distal deltaic plain to the shoreline is dominated by *restinga* vegetation with tolerance the stresses of sand mobility and salt spray (Moreno-Casasola, 1986), represented by shrub vegetation and coastal herbs over sand plains and dunes without tidal influence colonized by *Ipomoea pescaprae* (Convolvulaceae), *Hancornia speciosa* (Apocynaceae), *Chrysobalanus icaco* (Chrysobalanaceae), *Hirtella Americana* (Chrysobalanaceae), *Cereus fernambucensis* (Cactaceae), *Anacardium occidentale* (Anacardiaceae) and *Byrsonima crassifolia* (Malpighiaceae). Palm trees, as well as orchids and bromeliads growing on trunks and branches of larger trees, are also present along the shoreline. The vegetation inside the lakes and at their margins comprises *Tabebuia cassinoides*, *Alchornea triplinervia* and *Cecropia sp*., and emergent, submerged, floating-leaved and floating plants, such as *Typha* sp., Cyperaceae, Poaceae, *Salvinia* sp., *Cabomba* sp., *Utricularia* sp. and *Tonina* sp. The marine and fluvial marine areas are colonized by mangroves. These, located around 60 km

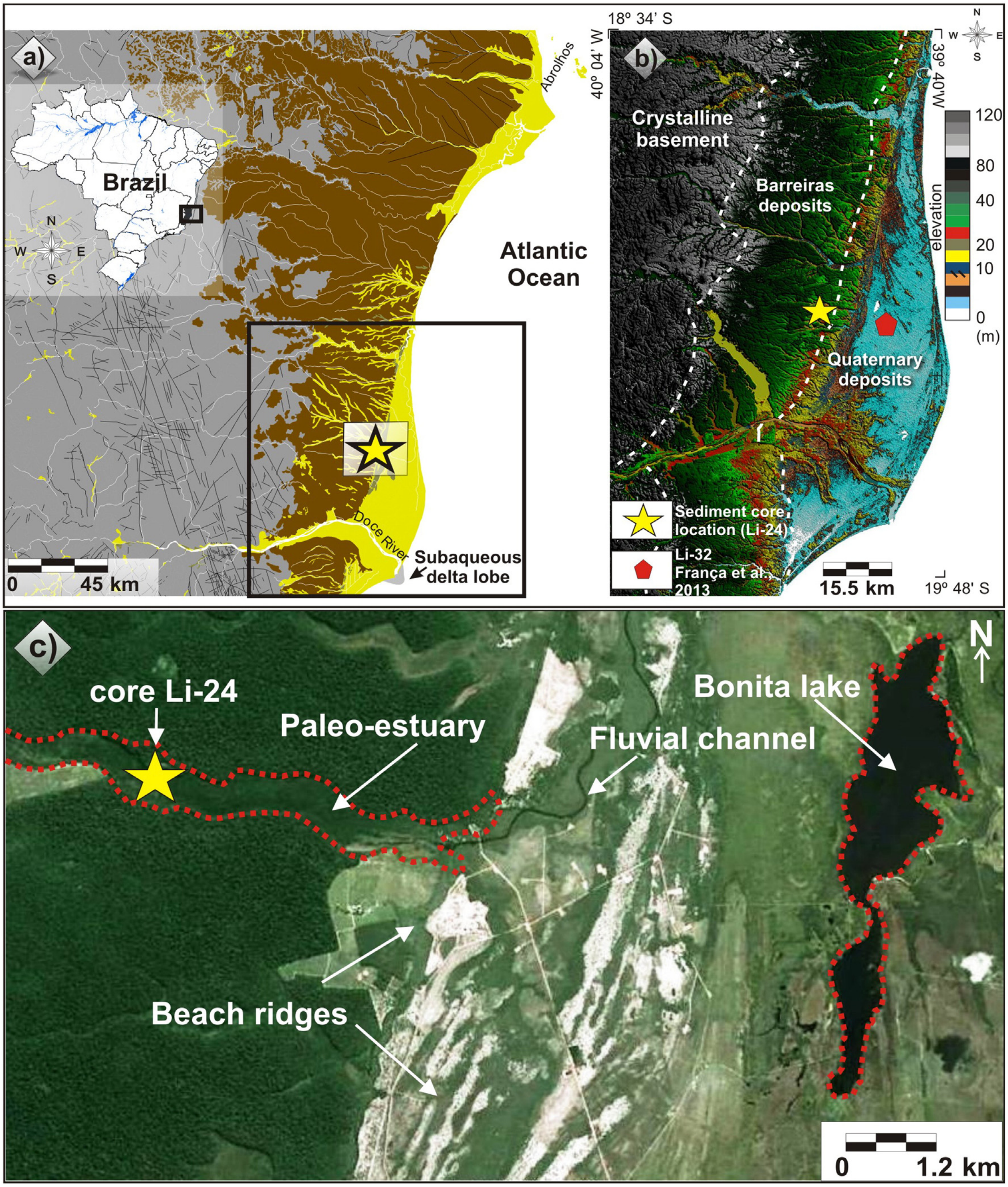

Fig. 1. a) Location of the study area and sampling site; b) view of the study area on DEM-SRTM data showing the position of the cores Li-24 and Li-32 (França et al., 2013) and; c) RGB Landsat images with the paleodrainage networks, paleo-estuary, beach ridges, fluvial channel and lake system.

from the studied core, are characterized by *Avicennia germinans* (L.) Stearn. (Avicenniaceae), *Laguncularia racemosa* (L.) Gaertn. f. (Combretaceae) and *Rhizophora mangle* L. (Rhizophoraceae). The mangroves are currently restricted to the northern and southern littoral of the delta plain (Bernini et al., 2006).

3. Materials and methods

3.1. Field work and sample processing

An 11-m deep sediment core (Li-24) located on the deltaic plain of the Doce River was collected with a percussion drilling Robotic Key System (RKS), model COBRA mk1 (COBRA Directional Drilling Ltd., Darlington, UK) during the dry season of November 2009 (S 19° 9′ 8.5″/ W 39° 55′ 47.5″). The site was selected because it records the history of a paleo-estuary located ca. 5 km upstream from the Doce River Delta paleoshoreline and almost 20 km from the modern coastline (Castro et al., 2013). The multi-proxy analysis included description of features such lithology, grain size, sedimentary structure, diatoms, pollen and spore analysis, geochemical analyses ($\delta^{13}C$, $\delta^{15}N$ and C/N) and radiocarbon dating.

3.2. Stratigraphic analysis

Samples were taken at 10 cm intervals for grain size analysis at the Chemical Oceanography Laboratory of the Federal University of Pará (UFPA). This analysis made use of a laser particle size analyzer (SHIMADZU SALD 2101). Grain size graphics were obtained using the Sysgran Program (Camargo, 1999). Grain size distribution followed Wentworth (1922), with separation of sand (2–0.0625 mm), silt (62.5–3.9 μm) and clay (3.9–0.12 μm) fractions. Facies analysis included descriptions of color (Munsell Color, 2009), lithology, texture and structure (Harper, 1984; Walker, 1992). The sedimentary facies were codified according to Miall (1978).

3.3. Pollen and spore analysis

The sediment core was sub-sampled with 44 total samples at different downcore intervals with muddy sediments since the sandy sediments are not favorable to pollen preservation (Havinga, 1967). 1 cm^3 of sediment was taken for palynological analysis (Cohen et al., 2014). All samples were prepared using standard analytical techniques for pollen including acetolysis (Faegri and Iversen, 1989). Sample residues were placed in Eppendorf microtubes and kept in a glycerol gelatin medium. Reference morphological descriptions (Roubik and Moreno, 1991; Herrera and Urrego, 1996; Colinvaux et al., 1999) were consulted for identification of pollen grains and spores. A minimum of 300 pollen grains were counted in each sample. Software packages TILIA and TILIAGRAPH were used to calculate and plot pollen diagrams (Grimm, 1990). The pollen diagrams were statistically subdivided into zones of pollen and spore assemblages using a square-root transformation of the percentage data, followed by stratigraphically constrained cluster analysis (Grimm, 1987).

3.4. Diatoms

Diatoms data were extracted from a total of 65 samples obtained from Castro et al. (2013). Samples (1 cm^3 each) were pretreated with 30% H_2O_2 and 10% HCl, and mounted on standard microscope slides using Naphrax. Diatom identification was based on several published diatom morphological descriptions (Round et al., 1990; De Oliveira and Steinitz-Kannan, 1992; Houk, 2003; Bigunas, 2005). The counting included 200–500 valves for each slide, depending on the concentration. Identification and counting were undertaken using a Carl Zeiss Axioskop 40 microscope. Diatoms were identified according to frustule patterns and ornamentations, with the sum and percentage calculated by TILIA and TILIAGRAPH (Grimm, 1990). These softwares were also used for establishing the zonation of diatoms and the constrained incremental sums of squares (CONISS) diagram. Data are presented in diagrams as percentages of the total sum of diatoms.

3.5. $\delta^{13}C$, $\delta^{15}N$ and C/N

A total of 144 samples (6–50 mg) were collected at 10 cm intervals from the core for geochemical analyses (e.g., Pessenda et al., 2010). Samples were separated and treated with 4% HCl to eliminate carbonates, washed with distilled water until at pH ~ 6, dried at 50 °C, and homogenized. $\delta^{13}C$, $\delta^{15}N$ and elemental C and N concentrations were analyzed at the Stable Isotopes Laboratory (CENA/USP) using a Continuous Flow Isotopic Ratio Mass Spectrometer (CF-IRMS). Organic carbon and nitrogen results (C/N ratio) are expressed as percentages of dry weight. Results of isotope ratios ($\delta^{13}C$ and $\delta^{15}N$) are expressed in delta per mil notation with an analytical precision greater than 0.2‰, with respect to the VPDB standard and atmospheric air, respectively.

The relationship between $\delta^{13}C$, $\delta^{15}N$ and C/N was used to provide information about the origin of organic matter preserved in the coastal environment (Fry et al., 1977; Peterson and Howarth, 1987; Schidlowski et al., 1983; Meyers, 1997, 2003; Wilson et al., 2005; Lamb et al., 2006).

3.6. Radiocarbon dating

Five bulk samples of ~10 g each were used for radiocarbon dating obtained from Castro et al. (2013). Samples were checked and physically cleaned (no roots) under the stereo microscope. The residual material for each sample was then extracted with 2% HCl at 60 °C for 4 h, washed with distilled water until neutral pH was reached, at 50 °C and dried (Pessenda et al., 2010, 2012). The organic matter from the sediment was analyzed by Accelerator Mass Spectrometry (AMS) at the Center for Applied Isotope Studies (Athens, Georgia, USA). Radiocarbon ages are reported in years before AD 1950 (yr BP) normalized to $\delta^{13}C$ of −25‰VPDB and in cal yr BP, 2σ (Reimer et al., 2009) and use the median of the range for discussing our and other authors data in the text.

4. Results and discussion

4.1. Radiocarbon dates and sedimentation rates

Radiocarbon dates for this core (Castro et al., 2013) and sedimentation rates are presented in Fig. 2. The sedimentation rates were based on the ratio between the depth intervals (mm) and the time range. The calculated sedimentation rates are 7.71 mm/yr (9.5–6.7 m), 0.97 mm/yr (6.7–5 m), 0.53 mm/yr (5–3 m) and 1.34 mm/yr (3–1 m). Higher sedimentation rates were obtained near the base (between ~7550 and ~7200 cal yr BP), probably due to the formation of estuarine central basin during the relative sea-level rise. From ~7200 cal yr BP to ~1355 cal yr BP a decrease of the sedimentation rates, probably, a consequence of the stabilization of the relative sea-level during the middle Holocene occurred. It was followed by an increase in the sedimentation rate until the modern period, which it may be caused by the change on depositional environment from lake/ria to fluvial channel.

4.2. Organic matter source

In order to identify the source of sedimentary organic matter, our geochemical data are presented as a profile along the studied core (Fig. 2) and binary diagram between $\delta^{13}C \times C/N$ and $\delta^{15}N \times \delta^{13}C$ (Fig. 3a). The last one reveals the different organic matter influence, considering the C_3 and C_4 terrestrial plants, marine and freshwater algae, marine and freshwater/estuarine Dissolved Organic Matter (DOC) and marine Particulate Organic Matter (POC) (Deines, 1980; Meyers, 1994; Tyson, 1995) (Fig. 3). In addition, Figs. 2 and 3b present the $\delta^{15}N$ values and the binary $\delta^{15}N$ x $\delta^{13}C$, respectively, where atmospheric nitrogen has a $\delta^{15}N$ value of zero, and terrestrial plants tend to have $\delta^{15}N$ values close to 0‰. However, *Spartina* sp. and nearshore plankton have $\delta^{15}N$ values around +6‰ and from +6 to +10‰, respectively (Wada, 1980; Macko et al., 1984; Altabet and McCarthy, 1985).

Regarding these ranges of values to each environment, between >7550 and ~5250 cal yr BP the geochemical values ($\delta^{13}C = -30$–-10‰, $\delta^{15}N = 2 - 8$‰ and C/N = 4–40) indicate marine/estuarine organic matter and C_3 terrestrial plants. During the last ~5250 cal yr BP the corresponding sediments contain only organic matter sourced from freshwater and C_3 terrestrial plants ($\delta^{13}C = -29$–-26‰, $\delta^{15}N = 0 - 8$‰ and C/N = 10–45).

4.3. Facies association

The integration of lithologies, diatoms (Castro et al., 2013), pollen (Cohen et al., 2014) and geochemical data allowed define four facies associations representative of estuarine channel, estuarine central basin, lake/ria and fluvial channel (Fig. 3).

4.3.1. Estuarine channel facies association

The bottom (11–9.7 m; until at least ~7550 cal yr BP) of the studied core presents massive mud to coarse-grained sands that are organized

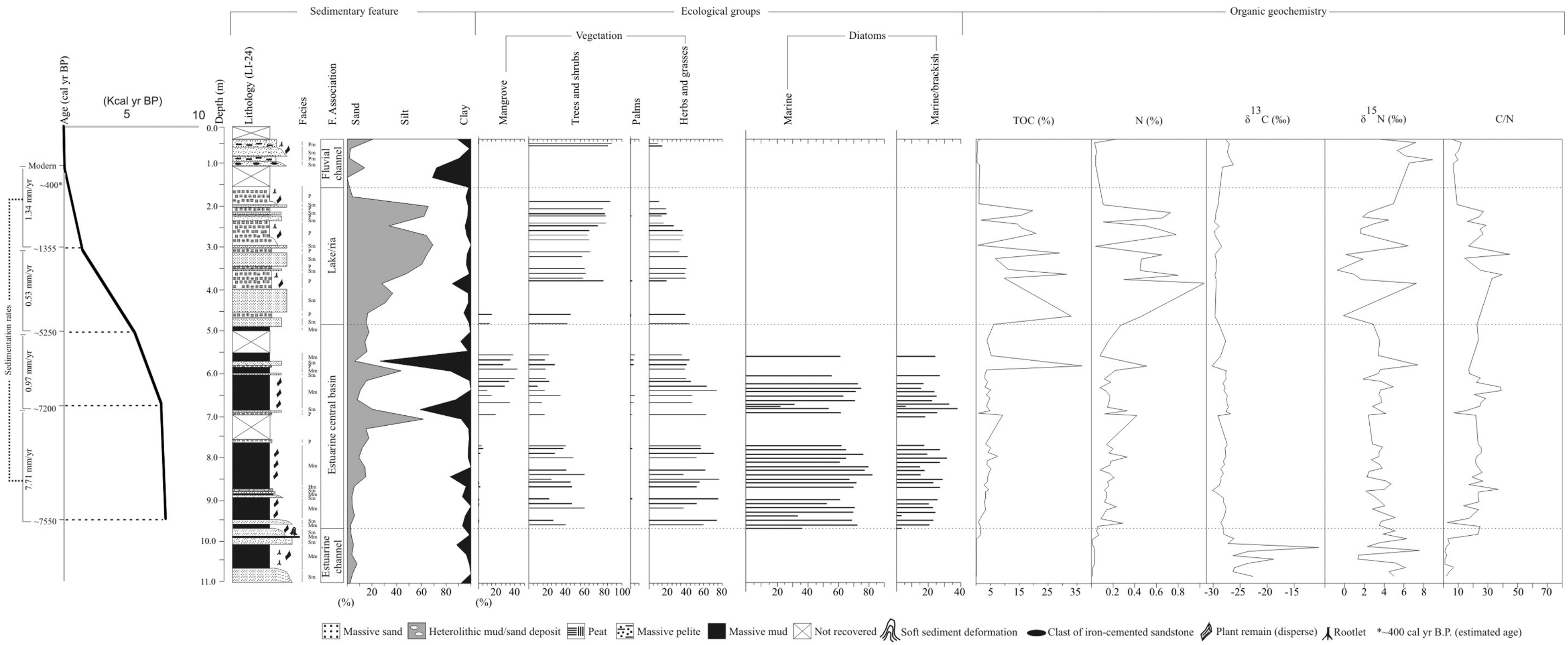

Fig. 2. Summary of the pollen and geochemistry results for the studied sediment core, plotted with sedimentation rates, facies, diatom and ^{14}C ages published elsewhere (i.e., Castro et al., 2013). Pollen and diatoms data are presented as percentages of the total sum.

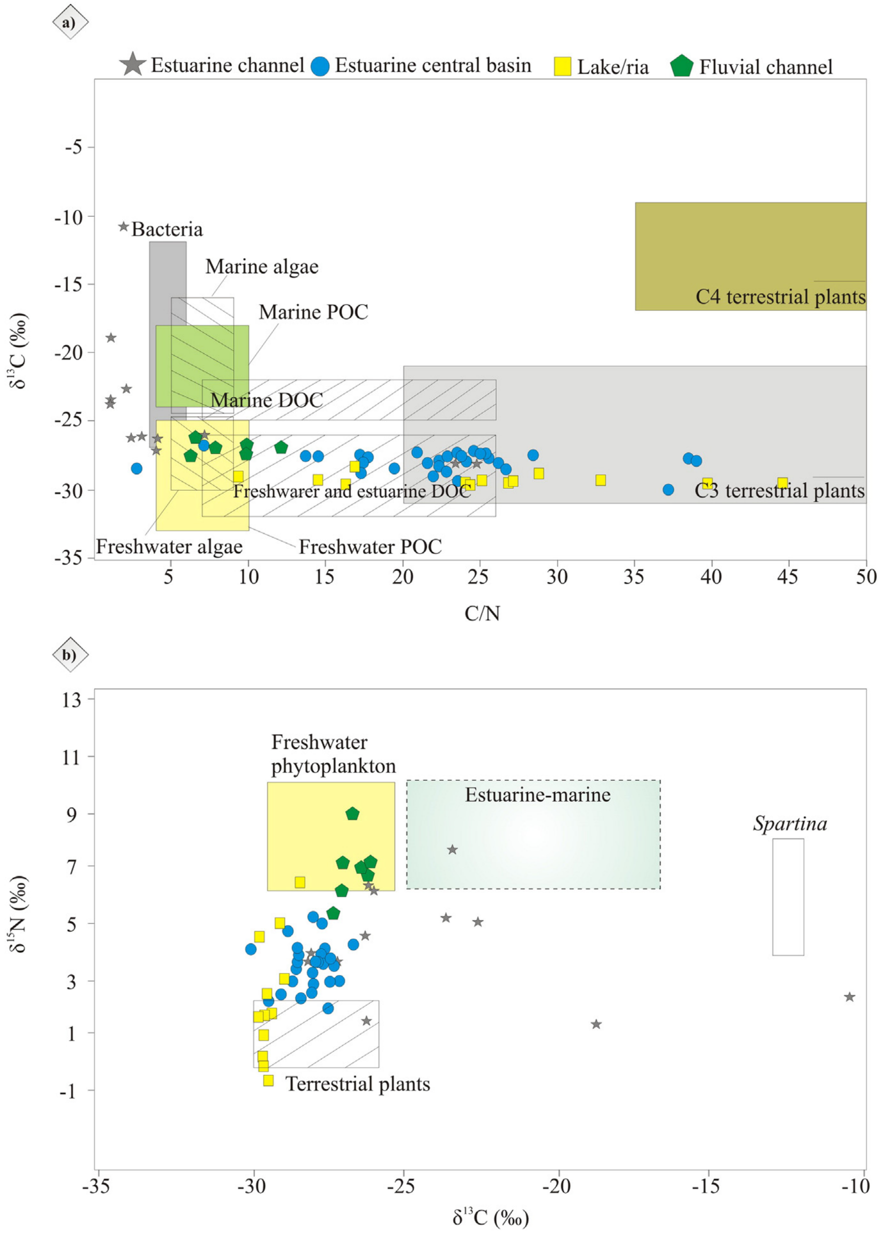

Fig. 3. a) Diagram illustrating the relationship between $\delta^{13}C$ and C/N ratio for the different sedimentary facies, according to Lamb et al. (2006), Meyers (2003) and Wilson et al. (2005). b) $\delta^{15}N$ vs. $\delta^{13}C$ values for the different sedimentary facies, according to Cloern et al. (2002) and Ogrinc et al. (2005).

into fining upward successions with sharp erosional bases. The geochemical results indicate total organic carbon values (TOC) around 0–1.6% (mean = 0.2%), low nitrogen results (N) < 0.07%, $\delta^{13}C$ values between −28.1 and −10.5‰ (mean = −23.9‰), and $\delta^{15}N$ values between 1.3 and 7.5‰ (mean = 4.3‰). The C/N values showed considerable variation between 4 and 24 (mean = 6.2). Therefore, the data suggest a mixture between marine and freshwater organic matter influence (Figs. 2 and 3) such as typically obtained from estuarine system.

These deposits do not present pollen grains and diatoms valves for statistical analysis. It may be caused by various external factors such as sediment grain size, pollen oxidation and mechanical forces (Havinga, 1967) and low nutrient supply, as well as low silica and iron availability for diatoms, where dissolution of the frustules occurs rapidly (Brezezinski et al., 1999; Martin et al., 1999).

4.3.2. Estuary central basin facies association

This facies association occurs between 9.7 and 4.8 m depth (between ~7550 and 5250 cal yr BP), and it is mainly represented by massive mud with thin layers of massive fine to medium-grained sand. The pollen content is characterized by mangrove (5–45%), trees and shrubs (10–60%), palms (<5%), herbs and grasses (35–75%) and marine elements (<5%, micro-faminifera). The diatoms are represented mainly by marine (22–83%) and marine/brackish (3–38%) organisms with the local occurrence of freshwater diatoms.

The geochemical results for this facies association (Fig. 2) are characterized by TOC around 0.7–36.7% (mean = 4.8%), N values of 0.08–0.5% (mean = 0.2%), $\delta^{13}C$ values between −30.2 and −26.7‰ (mean = −28.1‰), $\delta^{15}N$ records show values between 1.8 and 7.4‰ (mean = 3.5‰) and the C/N results between 4 and 38 (mean = 26.2).

In this context, the pollen data suggest mangrove predominance (Fig. 2) and according to binary $\delta^{13}C$ and C/N values a dominance of C_3 terrestrial plant organic matter occurred with some influence of freshwater and estuarine organic matter in an estuarine central basin (Fig. 3).

4.3.3. Lake/ria facies association

These deposits consist of massive sand, muddy peat and pure peat layers between 4.8 and 1.5 m depth (~5250 to ~400 cal yr BP). The pollen assembly of this facies association is mainly characterized by two ecological groups, defined by the presence of trees/shrubs (40–90%) and herbs/grasses (12–41%). Along these sediments were recorded whole and fragmented valves of freshwater diatoms and some fragments of marine and brackish water species.

The TOC results were around 1.0–31.6% (mean = 15.0%), N values of 0.04–1.04% (mean = 0.5%), $\delta^{13}C$ values between −29.7 and −28.4‰ (mean = −29.4‰), $\delta^{15}N$ records show values between 0.7 and 7.2‰ (mean = 2.5‰) and the C/N values showed results between 9.2 and 45 (mean = 28.6) (Fig. 2). It is noteworthy that high value of $\delta^{15}N$ around 7‰ in 3.8 m depth indicates an increase in aquatic organic matter influence, while the C/N values about 32 suggest an increase in terrestrial organic matter in the same depth. This was caused by mixture of organic matter source, as it may be also evidenced by the oscillation of C/N and $\delta^{15}N$ values along this facies association. However, the mean value of these parameters (C/N = 28 and $\delta^{15}N$ = 2.5‰) consistently indicate an increase in the terrestrial organic matter influence (Fig. 2). In this way, the binary diagram between $\delta^{13}C$ and C/N (Fig. 3) reveals the influence of C_3 terrestrial plants organic matter followed by an upward increase of freshwater influence (Fig. 3).

4.3.4. Fluvial channel

The fluvial channel facies association is found at the top of the sediment core (~400 cal yr BP to the present) and it presents several thin fining upward successions of massive, cross-stratified or cross-laminated, fine- to coarse-grained sands. The pollen and spore analysis revealed two ecological groups represented by arboreal (85–90%) and herbaceous elements (10–20%). For this facies association were not recovered diatoms valves.

The organic geochemistry results showed for TOC between 0.2 and 1.3% (mean = 0.62%), N results between 0.03 and 0.2% (mean = 0.07%), $\delta^{13}C$ values between −28.2 and −26.7‰ (mean = −27.2‰), $\delta^{15}N$ values range between 3.6 and 8.8‰ (mean = 6.3‰) and the C/N values from 6.1 to 12.0 (mean = 8.6) indicating an increase in freshwater influence (Figs. 2 and 3).

4.4. Paleoenvironmental history

The integration of lithology, diatoms, pollen and geochemical data confirms a transition from marine to continental influence during the Holocene in the study site. The estuarine system recorded in the early and middle Holocene was followed by an increase in continental influence that caused the establishment of lakes/rias and fluvial channels.

4.4.1. Early to middle Holocene

This period was initially marked by an estuarine channel facies association (> ~7550 cal yr BP). The binary diagrams of $\delta^{13}C$ vs. C/N and $\delta^{15}N$ vs. $\delta^{13}C$ confirm the influence of marine organic matter (Fig. 3a,b). The trend of more depleted $\delta^{13}C$ values upward (10–9.7 m depth) suggests a mixture of marine and freshwater organic matter. Similar values were also related to equivalent mixing of organic matter by Meyers (1994). The mean $\delta^{15}N$ value of 4‰ also supports this interpretation (Fig. 2). Aquatics plants normally use dissolved inorganic nitrogen, which is isotopically enriched in ^{15}N by 7‰ to 10‰ relative to atmospheric N (0‰). Thus terrestrial plants, which use N_2 derived from the atmosphere, have $\delta^{15}N$ values ranging from 0‰ to 2‰ (Thornton and McManus, 1994; Meyers, 2003). The C/N values (mean = 6.2) also indicate an influence of organic matter from algae. In general, C/N values < 10 indicate algae dominance and C/N values > 12 indicate vascular plants (e.g., Meyers, 1994; Tyson, 1995).

From ~7550 cal yr BP to ~5250 cal yr BP, estuarine channel deposits were overlain by estuarine central basin deposits (Fig. 2). The latter is a setting dominated by low-energy subtidal conditions. As commented in Castro et al. (2013), "the central part of an estuary is a zone of maximum turbidity, where flow energy is at a minimum and mud deposition from suspension reaches its highest values due to the seaward decreasing riverine inflow added to the landward decreasing wave and tidal inflow (Dalrymple et al., 1992)". The pollen record is in agreement with mangrove development (5–45%) associated with herbs, grasses, trees and shrubs. The diatom analysis showed marine and marine/brackish species. These data altogether are consistent with the estuarine central basin setting previously. Mud and organic matter accumulation into the estuarine central basin caused an increase of TOC and N values, i.e., 0.7–36.7% and 0.08–0.5%, respectively. Furthermore, the results of geochemistry analysis allowed the identification of an increase of C_3 plants, as attested by values between −30.2‰ and −26.7‰, which are comparable to the C_3 plant values of −32‰ to −21‰ presented by Deines (1980). The $\delta^{15}N$ values exhibit a fluctuation between 2‰ and 7.4‰, suggesting an influence of aquatic and terrestrial organic matter (see also Peterson and Howarth, 1987; Fellerhoff et al., 2003). The mean C/N ratio of 26 indicates organic matter from vascular plants that have colonized the margins of the estuary. Values > 12 were reported for vascular plants elsewhere (Meyers, 1994; Tyson, 1995). The binary diagrams of $\delta^{13}C$ vs. C/N and $\delta^{15}N$ vs. $\delta^{13}C$ confirm the contribution of C_3 terrestrial plants and freshwater phytoplankton (Fig. 3a,b).

During this phase in a distal position of the studied coastal plain (Li32, Fig. 1b), a transition from a foreshore to lagoon phase occurred (Fig. 4b). The tidal flat in the margin of this lagoon was occupied by mangroves, herbs, palms, trees and shrubs. The $\delta^{13}C$ and C/N values of the sedimentary organic matter indicated a mixture of C_3, C_4 (probably marine herbs) plants and aquatic organic matter, while the $\delta^{15}N$ values (mean = 5.2‰) suggested a mixture of terrestrial plants and aquatic organic matter (França et al., 2013) (Fig. 4b).

4.4.2. Middle to late Holocene

Since about 5250 cal yr BP, the estuarine system has been replaced by a lake/ria environment, with the closure of the estuary, the mangrove ecosystem became extinct at the study site, but it remained in a distal position with lower topographies (core Li32), as showed by França et al. (2013) (Fig. 4b). The loss of mangrove area during this period indicates unfavorable conditions for the development of this ecosystem, which may be related to lower porewater salinity, which may be caused by a sea-level fall. The lower salinity allowed the expansion of herbs, trees and shrub vegetation in the study site. Besides, along the lake/ria stage was recorded sandy sediments accumulation, it indicates a relatively higher energy environment that is unfavorable to the establishment of mangroves (Fig. 2).

The TOC and N values are close to 1% and 0.1%, respectively, at the top of this phase (~5250 to ~400 cal yr BP) (Fig. 2), that show a decrease trend, probably due to increase of grain size accumulation. The $\delta^{13}C$ values from −23‰ to −28‰ indicate an expansion of arboreal vegetation (−32‰ to −21‰; Deines, 1980). The $\delta^{15}N$ values show an oscillation between 0.7 and 7.2‰ (mean = 2.8‰), indicating a mixture of terrestrial and aquatic organic matter influence. Additionally, the C/N values show a decrease trend upward from 35 to 9, showing a transition from the continental to aquatic organic matter influence. The binary diagrams of $\delta^{13}C$ vs. C/N and $\delta^{15}N$ vs. $\delta^{13}C$ indicate an influence of algae freshwater, freshwater POC and C_3 terrestrial influence (Figs. 3a,b and 4). This tendency is also supported by the occurrence of a few whole and fragmented valves of freshwater diatoms, consisting of *Eunotia zygodon*, *Eunotia didyma*, and species of *Desmogorium* Ehrenberg and *Pinnularia* Ehrenberg (Castro et al., 2013).

The fourth phase (~400 cal yr B.P. to modern) is represented by the development of small fluvial channels, with no preservation of diatom

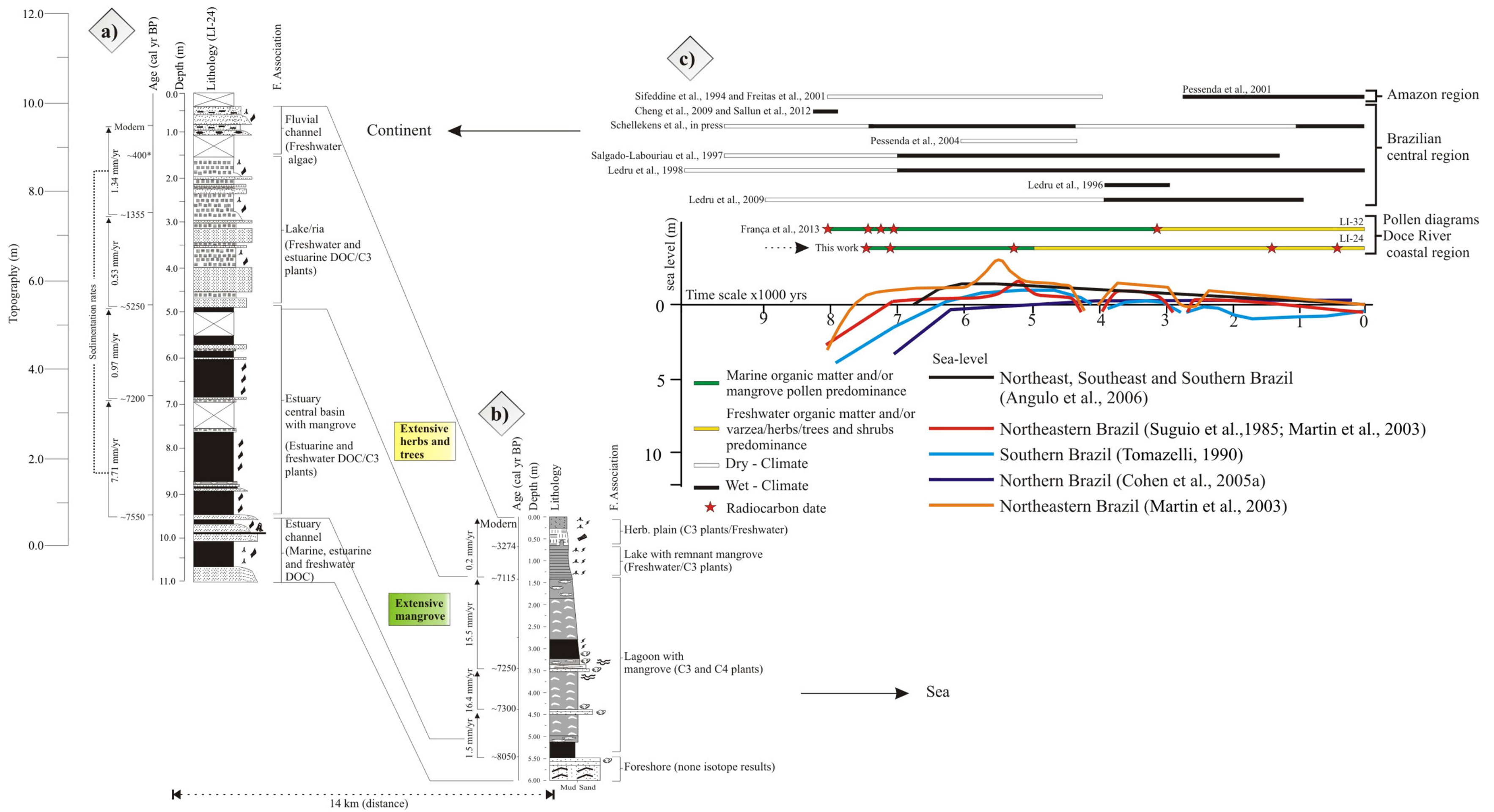

Fig. 4. Topographic and facies associations correlation between Li-24 a) and Li-32 b) (França et al., 2013) and c) comparative diagram of climatic changes records in the Brazilian central region and Amazon basin, sea-level fluctuations in eastern South America during the Holocene and pollen diagrams from Doce River coastal region.

valves (Castro et al., 2013). This interpretation is compatible with pollen analysis, which shows an increase of trees and shrubs, while there was a decrease of herbs (Fig. 2). The $\delta^{13}C$ values also indicated an influence of C_3 plants with mean results around −27‰. The results for TOC (0.2–1.3%) and N (0.03–0.2%) were lower, probably due to oxidation of the organic matter. Likely, the sediments were exposed to the atmosphere and/or they have been transported by high flow energy. The $\delta^{15}N$ values between 3.6 and 8.8‰ indicate an aquatic influence. The relations $\delta^{13}C$ vs. C/N and $\delta^{15}N$ vs. $\delta^{13}C$ indicate a strong influence of freshwater organic matter (Fig. 3a,b).

From the middle to late Holocene in the distal position of the studied coastal plain (core Li32, Fig. 1b) a transition from a lagoon system to lake/herbaceous flat occurred (França et al., 2013). The mangrove area shrunk and the vegetation was characterized mainly by herbs, trees, and shrubs in this zone. According to $\delta^{13}C$ and C/N values the environment was marked by a mixture of continental and aquatic organic matter, which was dominantly composed of C_3 plants (França et al., 2013) (Fig. 4b).

4.5. RSL fluctuations at the Southeastern Brazil during the Holocene

This multi-proxy study is in accordance with the establishment of a paleo-estuary during the early and middle Holocene, as previously proposed by Castro et al. (2013). This coastal system was colonized by mangrove vegetation with diatom assemblages from marine and marine/brackish environment. The sedimentary organic matter was sourced from marine and estuarine DOC. The marine influence during the early and middle Holocene attests a RSL rise, as recorded by Buso Junior et al. (2013), Castro et al. (2013) and França et al. (2013).

Between ~5250 and ~1355 cal yr BP, the lake/ria environment was established. Mangroves were largely replaced by other arboreal and herbaceous vegetation, and freshwater diatoms were recorded. This phase is marked by an increased trend of freshwater organic matter. After ~400 cal yr BP (estimated age) the margin of a fluvial channel was colonized by trees, shrubs, herbs and grasses. Freshwater organic matter accumulated during this phase.

Therefore, all data available from the studied core are consistent with a RSL rise during the early and middle Holocene, as also proposed for other Brazilian coastal areas (Martin et al., 2003; Angulo et al., 2006). In addition, this sea-level rise is coherent with various sea-level studies summarized by Murray-Wallace (2007), who indicated a worldwide sea-level rise reaching an early- to mid-Holocene highstand at around 7000 cal yr BP. This high RSL led to the reactivation of paleo-estuaries, formed during the penultimate marine transgression (120 k yr BP), and formation of numerous lagoons along the coast of southeastern Brazil. Thus, the early to middle Holocene transgression reported in the present study, and also in other recent studies (Buso Junior et al., 2013; Castro et al., 2013; França et al., 2013), agrees with the overall eustatic behavior. After this sea-level maximum, the sea-level dropped to the present level time (Angulo et al., 2006). In this context, the relative drop in sea level causes a coastal progradation. This process gave rise to the closure of the studied estuary mouth and its replacement by a lake/ria and fluvial channel. The marine connection was reduced and ultimately interrupted due to the development of sandy beach ridges and barriers associated with the establishment of the wave-dominated delta system (Castro et al., 2013).

4.6. Climatic changes

The recorded late Holocene marine regression observed on geological setting, biomarkers and organic matter source may be mainly attributed to the action of RSL fall and additionally to the wetter climatic conditions that might have increased the sediment supplied to the coastal system, and it contributed to the development of a deltaic system. This is proposed based on previous claims that RSL fall and increased sedimentary supply by river discharges, during the late Holocene, may have affected the relative position of the shoreline along the Brazilian coast, and, consequently, the characteristics of coastal stratigraphy and vegetation dynamics (Scheel-Ybert, 2000; Cohen et al., 2005a,b; Buso Junior et al., 2013; Guimarães et al., 2012; Smith et al., 2012; França et al., 2012; Cohen et al., 2012, 2014).

A previous study (i.e., Prado et al., 2013) suggested a mid-Holocene water deficit scenario in South-eastern of South America compared to the late Holocene one. Low mid-Holocene austral summer insolation caused a reduced land–sea temperature contrast and hence a weakened South American monsoon system circulation. This scenario is represented by a decrease in precipitation over the South Atlantic Convergence Zone area, saltier conditions along the South American continental margin, and lower lake levels. In addition, other paleoenvironmental studies in Brazil indicate relatively drier climatic conditions during the early Holocene in central (Ferraz-Vicentini, 1993; Ferraz-Vicentini and Salgado-Labouriau, 1996; Barberi et al., 2000), southeastern (Ledru, 1993; Ledru et al., 1996; Behling, 1995; Behling and Lichte, 1997; Behling et al., 1998a,b; Pessenda et al., 2009) and southern regions (Roth and Lorscheitter, 1993; Neves and Lorscheitter, 1995; Lorscheitter and Mattoso, 1995; Behling, 1995; Behling and Lichte, 1997; Stevaux, 1994, 2000). The middle to late holocenic climate was marked by wetter conditions (Ledru, 1993; Ledru et al., 1998, 2009; Salgado-Labouriau, 1997; Salgado-Labouriau et al., 1998; Pessenda et al., 2004, 2009). During this period, higher rainfall generated increased river discharges and more intensified continental conditions.

In this context, climate fluctuations (Molodkov and Bolikhovskaya, 2002), which influenced the rainfall (e.g., Absy et al., 1991; Pessenda et al., 1998a,b, 2001, 2004; Behling and Costa, 2000; Freitas et al., 2001; Maslin and Burns, 2000), and consequently caused changes in fluvial discharge and estuarine salinity gradients (Lara and Cohen, 2006) affected the mangrove dynamics (Cohen et al., 2012). Therefore, during a humid climate in the region, the greater discharge of the rivers promoted the progressive reduction of water salinity that favors the development of freshwater vegetation followed by retreat of mangroves. After the shrink of mangroves on Li-24 site, they remained on Li-32 site (Figs. 1b and 4b). Probably, this is caused by the sea level fall (Suguio et al., 1985; Martin et al., 2003; Angulo et al., 2006), associated to a wet period (Salgado-Labouriau, 1997; Ledru et al., 1998; Schellekens et al., 2014). This change may be evidenced in the source of organic matter. During the early Holocene the environment was mainly influenced by marine organic matter, followed by estuarine and freshwater algae influence during the middle and late Holocene, which was corroborated by the presence of mangrove replaced by trees and grasses typically of the freshwater influence (Figs. 2–4).

4.7. Sea-level and climatic change controlling the depositional environment

The equilibrium between fluvial sediment supply and relative sea-level changes during the Holocene might have controlled the changes in the depositional environment identified in this work. In this context, the larger range of changes in relative sea-level or river discharge, the greater the expression of their respective effects on the littoral. During the early Holocene, the post glacial sea-level rise and drier climatic conditions seem to have promoted the development of estuarine conditions along the Doce River coastal plain (Fig. 4). During this phase, fluvial sediment supply to the coast might have been also reduced due to a drier climatic episode, which contributed to the transgressive nature of this coast. However, during the late Holocene, the depositional system evolved from an estuary to a deltaic plain having superimposed lake/ria and fluvial channels. This was a response of a sea-level drop that followed the early to middle Holocene transgression. Additionally, the tendency to a wet period during the late Holocene may have caused an increased sediment supply to the coast. Hence, from the middle Holocene, the Doce River coastal plain has experienced a sufficient supply of sediment that have overwhelmed the amount of space available, with a consequent marine regression. This process contributed to delta development and to the downward of the shoreline. However, further studies are still needed in order to determine whether the Doce River Delta initiated its development from this time, as proposed in several previous publications (e.g., Bandeira et al., 1975; Suguio et al., 1982; Dominguez et al., 1981, 1992, 2006; Martin et al., 1996), or if it is an older morphology developed in the studied coast that was only reactivated following an intermediate transgressive phase.

5. Conclusions

The post glacial sea-level rise, during the early and middle Holocene, caused a marine transgression with the reactivation of paleo-estuaries along the littoral of the Espírito Santo State, formed during the penultimate marine transgression. Probably, it has been intensified by decreased fluvial sediment supply to the coast due to a dry period. In the studied site, this phase is recorded by estuarine channel (> ~ 7550 cal yr BP), and estuarine central basin (~7550 to ~5250 cal yr BP) deposits, the latter with pollen and geochemical signatures of mangrove and marine and/or brackish water organic matter.

The early to middle Holocene transgression was followed by a drop in sea-level that continued up to the present time, which produced coastal progradation. This event was combined with wetter climatic conditions, which increased sediment input to coastal system and enhanced the continentality. This regressive phase is documented by the establishment of lake/ria (~5250 to ~400 cal yr BP) and fluvial channel (~400 cal yr BP until modern age) deposits in the uppermost part of the studied core. Probably, the relative sea-level fall and increase of sediment supply to coastal system during the late Holocene contributed to delta development. Consequently, the marine influence decreased, causing the loss of mangrove areas and the expansion of freshwater organic matter and freshwater diatoms.

The assessment of coastal wetland dynamics according to climatic and sea-level changes during the Holocene is crucial for the understanding of their survival ability under future scenarios, with a probable accelerated SLR rates between 0.18 mm/yr (Bindoff et al., 2007) and 13 mm/yr (Grinsted et al., 2009), as well as the intensification of extreme climatic events for the next century (Marengo, 2006; Cavalcanti and Shimizu, 2012; Marengo et al., 2013).

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