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# Petrographical and geochemical study of modern lacustrine sedimentary organic matter (Lagoa do Caçò, Maranhão, Brazil): Relations between early diagenesis, organic sedimentation and lacustrine filling.

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## **Abstract**

Lagoa do Caçò is an equatorial lake in northeast Brazil, where the Inter-Tropical Convergence Zone (ITCZ) enters the South-American continent, and so at a key position for deciphering Quaternary climatic variation. Preliminary results have shown that the sedimentary organic matter (OM) in lake records the shifts ITCZ since the Last Glacial Maximum. The nature and fate of the OM have been determined by studying surface sediments and potential OM sources. We present here the results of organic petrographic and Rock-Eval pyrolysis analytical assessments of the biological origin and preservation state of the OM in modern sediments from two deep transects of the lake. These results lead us to understand how an oligotrophic lake has accumulated 6 m of OM-rich sediment during the last 20 kyr. Paleoenvironmental studies have shown that the lake level fluctuated during this time. Our results explain the influence of lake bathymetric variation on early diagenetic processes and enable interpretation of the corresponding sedimentary OM record, which is dependent on the bathymetric variation.

*Key words:* Brazil, Caço Lake, organic sedimentation, early diagenesis, palynofacies, organic geochemistry.

## 1. Introduction

Paleoenvironmental records in lacustrine sediments depend strongly on physicochemical and biological parameters of ecosystems and thus on climatic variation. The time resolution of paleoenvironmental reconstruction depends essentially on the capacity of sedimentary markers to record rapid environmental evolution under the influence of climate and/or anthropogenic activity. Lacustrine sediments contain fundamental information on the temporal evolution of sedimentary fluxes from the basin. Studies have shown that global organic proxy is especially sensitive to environmental variation, both natural and anthropogenic causes. They provide good parameters for reconstructing the ecological and sedimentological evolution of lake basins in old sedimentary records (Martín-Closasa et al., 2005 and references there in; Carvalho et al., 2006a, b) during the Quaternary (Meyers and Lallier-Vergès, 1999; Wilkes et al., 1999; Talbot and Lærdal 2000; Meyers 2003) and especially during the Holocene (Lallier-Vergès et al., 1993; Hui et al., 1995; Ariztegui et al., 1996, 2001; Sifeddine *et al.*, 1996; Abbott *et al.*, 2003). For example, Noël (2002) showed that trophic level of Lake Annecy (France) had notably evolved during the last few centuries, not only under human influence, but also owing to climate variation during this period.

These studies demonstrate that organic geochemical and petrographical investigation of lacustrine sediments can provide key information on the impact of early diagenesis on labile organic matter and its subsequent re-deposition within a lake. The conception of a complete model aimed at understanding the preservation and the accumulation of the Organic Matter (OM) in a lacustrine basin remains a challenge. This can be accomplished by studying its origin and the processes leading to its fossilization in present day lacustrine systems. This allows filtering out of diagenetic disturbances affecting the original (biological) organic signal. It also allows determining the processes leading to differential modes of degradation and preservation in order to finally fully understand the significance of organic markers. One approach to achieving these challenges is to study the spatial distribution of modern lacustrine sedimentary OM and to compare it with the potential source organisms in the lake and its surrounding area. The approach should allow, for example, a better understanding of the

influence of lake level fluctuation on the type of fossilized OM, and improve deciphering of the recorded signals and their variability in the sedimentary column.

The most important climate factor in the tropical region is the precipitation, which have an impact on the lake level changes. Any changes in the precipitation/evaporation balance can lead changes in lake level and consequently in its lacustrine ecosystems. To understand the behavior of modern sedimentary organic matter in tropical lacustrine ecosystems can help to better interpret changes in lake level during the past and consequently the paleoclimate variations.

The objective of this study was to determine the origin, nature and preservation state of sedimentary OM in an equatorial lacustrine basin through organic geochemical and organic petrographical analyses. Previous works showed that the 4 to 6 m thick sediments of Lagoa do Caçò (Fig. 1) consist of abundant but poorly preserved OM but nevertheless record environmental and climatic variation over the last 20 kyr (Jacob et al., 2004, 2005). Through these studies, a preliminary question arose as to how an oligotrophic lake, such as Lagoa do Caçò, could accumulate 4 to 6 m of organic sediments in less than 20 kyr and to identify the possible OM of this infill. In addition, the study aimed at assessing the early diagenetic transformations that might bias the organic sedimentary record from initial production to final deposition.

Here, we characterize the nature, structure and internal texture of the OM in surficial sediments from two depths transects (longitudinal and transverse) in order to establish relationships between bathymetry and OM quality and to provide clues for using OM in palaeoenvironmental and palaeoclimatic reconstruction over long time scales.

## **2. Material and methods**

### *2.1 Setting*

Lagoa do Caçò (Fig. 1) is in the state of Maranhão (northeastern Brazil), close to the equator (2°58S, 43°25 W, 80m of altitude). The region, displays a large zonation of vegetation ranging from *Restinga* (steppe grass) near the Atlantic coast, to *Cerrado* (shrub savannas) inland that gives place to *Cerradao* (woody savanna) in humid zones (Ledru *et al.*,

2001, 2002). The climate is tropical humid with a rainy season (1500 to 1750 mm/yr) from November to May and 26 °C mean annual temperature. The studied lake is ca. 5 km x 0.5 km and 12 m in depth during wet seasons (austral summer) and 10 m during dry seasons (austral winter). A bathymetric map shows that the lake is divided into several sub-basins separated by ridges (Fig. 1). The ridges are probably related to the installation of a secondary SE-NW group of dunes distinguished on the geomorphology of the longitudinal-transect (transverse dunes, Fig. 1).

Opposing directions of the lacustrine water flow (from SW to NE) and the prevailing trade winds (N-S) are responsible for constant mixing of the water column. A detailed physicochemical investigation identifies the lake as polymictic with unstable water column stratification (Sifeddine et al., 2003). It is presently oligotrophic to meso-oligotrophic with only very small phytoplanktonic growth in the water column.

This lake margin ecosystem (Fig. 2) is a protective area constituting an environment very rich in biologic and mineral nutrients. The shallow water macrophytes constitute a barrier that prevents most or even all the mineral discharge from the sandy margins of the lake but exports part of its own production to the lake center. A > 2 m thick floating meadow occupies the lake entrance and filters most of the mineral and organic influx from the small tributary. Thus, inorganic sedimentation consists of mostly eolian particles and authigenic minerals.

The lake is situated (Fig. 1) at the present mean annual position of the Intertropical Convergence Zone (ITCZ). The zone is defined as the meteorological equator, which is determined by way of the meeting of the air masses from the two hemispheres (Labeyrie, 2000). Its position fluctuates seasonally and has varied considerably in the past. It is considered to control the humidity in the region, and to be responsible for the alternation of dry and humid seasons. Previous studies (e.g., Martin et al., 1997) have retraced fluctuation in the ITCZ since the beginning of the Holocene. It was hoped that a study of the lake sediments would contribute to improving our understanding of the role of the ITCZ in low latitude paleoclimatic phenomena.

## 2.2. Sampling

Sediment samples (Table 1) were collected at the water/sediment interface (i.e. 0-2 cm) along two depth transects, one longitudinal and the other one transverse (Fig. 1). The longitudinal transect (SW-NE) was sampled in the deepest part of the lake from the entrance (0.5 m depth) to the exit (7 m). A total of 11 samples were collected along the 5 km length of the lake. The 0.5 km transverse transect was sampled at higher resolution. Sampling began at 0.5 m depth on the SE border (sample 1 at 0 m reference of the transect distance) and finished at same depth on the NW border of the basin (sample 21, at 493 m of the transect distance).

In order to determine the nature of the original OM, 16 source organisms situated on the lake borders (e.g., rushes, gramineae, sponges, and associated epiphytes,) were also collected (Fig. 2). A total of 48 samples of the 16 species were studied (Table 2).

## 2-3 Methods

The samples were collected in a cylindrical tube and stored in a cold room before lyophilization and grinding in an agate mortar to provide a homogeneous powder.

### - Organic petrography

Palynofacies observations allow petrographical characterisation of the particulate organic constituents and their quantification (Combaz, 1980; Tyson, 1995). Ca. 1 g sediment was subjected to acid treatment (HCl and HF) to remove the mineral matrix. The resulting organic residue was then examined and a description of the different fractions made using transmitted light and reflected light microscopy. Observation under UV excitation was then performed. This permits identification of phytoplanktonic material, which is sometimes invisible in transmitted white light, from fluorescence of hydrocarbon-rich fractions. Counting of > 1000 surface units was then performed to estimate the proportion of each organic fraction.

- *Bulk organic geochemistry*

Rock-Eval pyrolysis is a classical method for determining the amount and quality of OM preserved in (source) rocks and sediments, with applications recently expanded to soil and peat studies (Disnar and Trichet, 1984; Di-Giovanni *et al.*, 1988, 1999; Sebag *et al.*, 2006, Zaconne *et al.*, 2011).

Depending on the estimated OM content, 50 to 100 mg of dried sediment was used for Rock-Eval6<sup>®</sup> (Vinci Technologies, Rueil Malmaison) analysis. The pyrolysis program started with an isothermal stage (2 min. 200°C). Then, the oven temperature was raised at 30 °C. min<sup>-1</sup> to 650 °C (held 3 min). The oxidation phase corresponds to an isothermal stage at 400 °C then a ramp at 30 °C min<sup>-1</sup> to 850 °C, (held 5 min).

The significance of classical Rock-Eval parameters was explained by Espitalié *et al.* (1977, 1985a, b). The specific parameters given by the new Rock-Eval 6 device were presented by Lafargue *et al.* (1998). The Rock-Eval parameters used here were: (i) mineral carbon (MinC) representing the amount of inorganic carbon, (ii) total organic carbon (TOC, %), which express the quantity of the organic matter (iii) the hydrogen index (HI, mg HC g<sup>-1</sup> TOC), is the amount of hydrocarbon (HC) produced during the pyrolysis (S<sub>2</sub>) and expressed relative to TOC content, the general shape of the curve vs the pyrolysis temperature also reflecting the type of refractory or labile OM (Langford and Blanc-Valleron, 1990; Sebag *et al.*, 2006); (iv) T<sub>max</sub> is a well-established OM maturity indicator for ancient sediments (Espitalié *et al.*, 1985a,b). Unlike previous instruments, Rock-Eval 6 measures the exact temperature experienced by the sample (Behar *et al.*, 2001). The value determined at the top of the S<sub>2</sub> peak is called TpS<sub>2</sub>; because T<sub>max</sub> defined with previous Rock-Eval show ca. 40°C differences with the Rock-Eval 6 TpS<sub>2</sub>, and has no significance in terms of maturity for modern sediments (Disnar *et al.*, 2000, Manalt *et al.*, 2001; Lüniger and Schwark, 2002), we elected to use TpS<sub>2</sub> values; (v) oxygen Index OI (mg O<sub>2</sub> g<sup>-1</sup> TOC), a measure of the oxygen content of the OM, is calculated from the amounts of CO and CO<sub>2</sub> released during pyrolysis, normalized to TOC.

The amounts of sulfur, nitrogen and total carbon (TC) were determined with a LECO

elemental analyser. TC was compared to the TOC provided by Rock-Eval pyrolysis to confirm the results and check the mineral contribution in TOC analysis.

### **3. Results and discussion**

#### *3.1. Bulk geochemistry*

TOC concentrations of the shallow lake entrance samples from the longitudinal transect (Fig. 4a) range between 10% and 16%. The values decrease in the deepest part (2%), and then increase again toward the lake outlet. The TOC concentrations in the transverse transect ranges between 8 and 15%. The values also decrease in the deepest part of the basin. In the samples from the borders of the lake, high TOC values reaching 25% are observed. This pattern shows a high OM accumulation close to highly productive margins. The decrease in TOC values in the deepest part of the lake may result from a combination of several factors: weak export of organic sediment; increased degradation in the deepest parts of the lake and greater dilution of OM content by mineral input.

The LECO results afford measurements of the concentration of organic carbon that are similar to those obtained with Rock-Eval (Fig. 3). Low sulfur content (between 0 and 0.4%) was recorded along the two studied transect. Higher values (close to 1%) were observed on the longitudinal transect (samples 6 and 9). These low values suggesting the non-participation of the natural sulfurization in the preservation of the sedimentary OM of the lake. The longitudinal transect is characterized by values  $< 0.5\%$ , decreasing progressively from SW to NE. Nitrogen is relatively high in lake margin samples (maximum of 1.7%) and low (0.3 to 0.9%) in the deepest area. The atomic C/N ratio varies between 8 and 22. In the longitudinal transect the C/N ratio increases progressively toward the lake center. This evolution is not observed in the transverse transect. The C/N ratio allows identifying the sources of organic matter (Meyers, 1994; Kunz et al., 2011). This ratio distinguishes between terrestrial and aquatic sources. The nitrogen content is relatively the same in terrestrial and aquatic organic matter, but the carbon content varies between the two. Vascular terrestrial material contains lignin and cellulose and has higher C/N values of 20 or greater; aquatic algae do not include

these, and has lower C/N values, usually  $< 10$ . The average values of C/N ratio is about 15.33 with a maximum of 24.40 in the sample 3 of the transvers transect and a minimum of 8,31 in sample PL2 of the longitudinal transect. These values demonstrate a significant influence in terrestrial plants to the surface sediments of Lagoa do Caçò and a very low contribution of phytoplankton and epiphytes. Degradation and aquatic diagenesis of phytoplankton and epiphytes materials also increase the C/N ratio.

The Rock-Eval  $TpS_2$  values range between 320 and 440 °C, i.e. typical values for recent sediment. In both transects, these parameters cluster around 440°C (Table 1). However, few samples show lower values (around 320 °C) that would indicate the presence of especially well preserved OM. A reverse correlation between the  $S_2$  and  $TpS_2$  signals can be noted: decrease in temperature being systematically accompanied by an increase in  $S_2$ . This indicates that easily pyrolysable rich hydrocarbon particles with similar Rock-Eval parameters for producing organisms (Table 2). This feature suggests the delivery of fresh and or slightly weathered organic particles to the sediments.

The pyrolysed “hydrocarbonaceous” fraction ( $S_2$ ) shows a very close variability with TOC, indicating that the hydrogen-rich organic fraction decreases progressively from SW to NE in the longitudinal transect. This tendency is similar in the transverse transect, with a progressive decrease in  $S_2$  and TOC toward the deepest part of the basin. The results indicate a significant participation of pyrolysed hydrocarbon ( $S_2$ ) in the TOC and not a contribution of allochthonous refractory material. TOC variation is related to both quantitative and qualitative autochthonous organic sedimentation.

HI values (Fig. 4) range between 50 and 500 mg HC  $g^{-1}TOC$ , decreasing progressively in the transverse transect from the margins (ca. 400 mg HC  $g^{-1} TOC$ ) towards the interior (100-200 mg HC  $g^{-1}TOC$ ). The longitudinal transect shows a progressive decrease in HI from the lake entry (south basin) toward the exit, with the exception of sample 6 situated on the water current sheltered area. The two transects show high HI values for sediment from the borders and lower HI values toward the center of the lake.

Generally the fluctuations in HI suggest variation in the quality of the sedimentary OM. Indeed, in our samples this fluctuation reflects variation in the initial input of phytoplanktonic

OM to the sediment or variation in the degradation of total OM. The decrease in HI in the deepest part of the basin can be explained by the relative increase in the resistant woody fraction due to more extensive diagenetic degradation of the phytoplanktonic OM toward the central part of the lake.

The OI values at the lake entrance are between 150 and 250 mg CO<sub>2</sub> g<sup>-1</sup> TOC and increase in the north basin sediments before decreasing toward the lake exit.

The interrelation between TOC and HI is characterized by a small difference between transverse and longitudinal transects, but the two transects show a positive correlation between these quantitative and qualitative OM parameters.

### 3.2. *Palynofacies observations*

In addition to pyrite, thirteen classes of organic constituents were described according to texture and morphology (Fig. 4).

Three types of amorphous OM (AOM) were defined:

(i) Granular AOM (gAOM) that is orange to reddish according to the particle thickness,

(ii) greyish flaky AOM (fAOM) that is translucent gray or brown depending on thickness. So called grayish AOM has been considered as phytoplanktonic in origin (Lallier-Vergès et al., 1993; Patience et al., 1995; Noël, 2002). This origin is valid if the petrographic analysis is supported by geochemical and molecular studies or by previous verification via fluorescence. The fAOM in Lagoa do Caçò sediments has no fluorescence and is poor in hydrocarbonaceous products. It may originate from the “amorphisation” of higher plant particles (degradation residue, leaves, petals or sepals), or from highly degraded phytoplanktonic material.

(iii) Gellified AOM. In the lake, gAOM is characterized by its resinous aspect. Geochemical and petrographical studies of Tritrivakely Lake (Madagascar) showed that gAOM derives from the gelification of vascular plant tissue in early diagenesis (Bourdon, 1999; Bourdon et al., 2001). For our sediments two possible origins can be proposed: (i)

gelification of woody residue transported from the catchment basin and (ii) autochthonous “amorphisation” of fragments derived from grass and reed stems produced in the lake borders. Eleven types of organic material with visible structures were also defined.

The ligno-cellulosic fractions are debris derived from higher plants and are easily recognizable by a characteristic woody shape. Six types of woody remnants were distinguished according to their texture and their state of degradation:

(i) Translucent ligno-cellulose debris (tLCD): Many types of structures depending on botanical origin were observed. These particles are considered as a marker of well-preserved fresh organic input to the sediment.

(ii) Slightly amorphized ligno-cellulose debris (saLCD) is the first stage of degradation, starting within the internal structures. The cell walls and ducts remain identifiable.

(iii) Amorphized ligno-cellulose debris (aLCD).

(iv) Gellified ligno-cellulosic debris (gLCD).

(v) Opaque ligno-cellulose debris (oLCD) described in Fig. 6. Identification of oLCD is important because these particles indicate long exposure to a subaerial environment (subaerial oxidation) or re-mobilization of fossil organic material from soil and rocks.

(vi) Pyrofusinite “burnt wood fragments” (Pyro) display opaque vascular shapes in transmitted light. They present a very jagged aspect that differentiates them from the opaque LCD and indicate a plant combustion origin. Their presence in the lacustrine basin is a good indicator of fires, revealing either a dry climate (natural fires) or human impact on the catchment (deforestation). During their transport, these remnants can undergo fragmentation that diminishes particles size, like the oLCD. To avoid confusing the two types of particles, further observations in incident light were performed.

(vii) Spores and pollen (SP) are characterized by a high variability in types. Nevertheless they are easily recognizable by way of their circular or elliptic shape (2 to 5  $\mu\text{m}$ ) and yellow fluorescence under UV excitation. The spores are distinguishable from pollen owing to their large size (10 to 200  $\mu\text{m}$ ). The presence of this group in the lake sediment is due to transport by wind, water or insects. They may come from distant areas and therefore give information about regional environments.

(viii) Membranes and cuticles (MC; Fig. 5); these are thin layer and large particles that are translucent white or yellow and often have a rolled up shape. When they show internal ornamentation they are assigned a zooclastic origin. Layers of cutin that cover the cellulose epiderm of higher plants represent the cuticles. The presence of these particles in the sediments indicates an autochthonous source when they come from plants on the lake borders or an allochthonous origin when they derive from plants developed in the catchment.

(ix) Phytoplanktonic OM is a purely algal fraction (AlgOM in Fig. 5) representing the production in the lake. It appears as very thin and grayish flakes corresponding to the degraded residues of phytoplankton and can be easily confused with flaky amorphous OM. Discrimination between both particles requires systematic verification under fluorescent light since AlgOM displays yellow fluorescence in this mode. In Lake Caçó, diatoms and sponges that are confined to the margins of the lake and associated with the aquatic macrophytes constitute most of the plankton productivity.

(x) Zooclasts which are remnants of the insects that lived in the surrounding basin and in the lake. They are minor components of the particulate OM.

(xi) Pyrite, a small contribution (1%) being only detected in sample 8 of the transverse transect.

### 3.3. Quantitative survey

The palynofacies composition is dominated by amorphous particles. Except for the three types of AOM, the proportions of all the fractions decrease from borders toward the center of the lake (Fig. 6 and 7).

In the longitudinal transect (Fig. 6), the proportion of reddish gAOM is between 2.5 and 5% of the particulate OM at the entrance to the south basin and more than 15% at the lake center. These particles increase to 35% of the material at the northeast exit of the lake. In the northern basin, the reddish AOM represents a very small proportion (< 5%).

The grayish flaky AOM is more abundant (9% in the first bathymetric sillentry samples and 42% in samples from the north basin). This amorphous fraction is present in all the

samples of the longitudinal transect, with little decrease in the values toward the SW of the lake.

The gelified AOM is less abundant in the south basin (17 to 23%) than in the north basin (>50%). The greatest proportion of the gelified particles is in the deepest zones.

The ligno-cellulose debris is more abundant in the entrance and exit of the lake. We also note more important proportions on both sides of the hinge zone joining the two basins. We also note the presence of amorphised and gelified plant debris with more important proportions in the internal part of the north basin.

The longitudinal contribution of lignocellulose debris is small, probably because particulate contributions from the river are filtered out by the dense floating meadow and by the blockage of sediment at the different bathymetric sills of the lake.

The distribution of opaque particles (pyrofusinite and DLCO) shows in general a proportion of 4% to 5% in the two transects. The large particles are concentrated in samples representing the entrance to the lake

The distribution of the SP fraction represented by very small proportions is localized essentially at the borders of the lake (< 2%). The membranes and the cuticles have a more elevated frequency and vary between 5 and 25%. Their distribution is similar to the ligno-cellulose fragments. This contribution is high at the lake entrance and in the samples from the first bathymetric sill, a zone of concentrated accumulation of this type of particle.

In the transverse transect (Fig. 7) the contribution of AOM increases from the borders toward the middle of the lake. An important qualitative difference exists between the samples from the SE border and those from the NW border. We found a predominance of the flaky AOM on the east border (weak slope) with a relative increase in this type of AOM toward the central area of the lake. In contrast, the reddish AOM is relatively more abundant on the west border (steeper slope) of the lake (ca. 50%). At this border, we observe an absence of the flaky AOM and an increase in the granular AOM abundance towards the central part.

Gellified AOM increases in proportion from 2 m of depth and reaches ca. 50% at 3 and 4 m depth on the two slopes of the lake.

The evolution of the woody particles nicely reflects the role of early diagenesis in an aquatic environment. The TLCD is concentrated in the area of production (2 m depth). It decreases in proportion while the amorphized debris increases. However, the more gelified fractions are largely concentrated on the NW border, where organic productivity is less than at the SE border. This pattern shows that the organic fraction produced at the SE border nourishes the other border via gelified particles. These particles are likely transported under the action of the lake currents driven by wind action.

SP contributes < 5% to OM particles. Sample 19 (from the extreme NW border) has a higher value (15%). This high value reflects the wind action that drives the pollen deposited on the water surface and accumulates it on the west side of the transect.

The membranes and the cuticles are more important in the border samples (30%) and are little represented in the central part. The distribution of these particles is similar to that of the DLCT.

#### **4. Organic matter delivery and deposition**

TOC content, HI and OI values show a symmetrical evolution along the two transects (Fig. 4), indicating a loss of OM content and a decrease in the degree of hydrogenation which are associated with an increase in the degree of OM oxygenation from the margins toward the middle of the lake. In view of the lack of carbonate in our samples, the high OI values are therefore related either to the incorporation of oxygen during oxidative diagenesis of the OM or to the preservation of naturally oxygenated OM.

The high HI values for the margin samples are related to occurrence of strongly hydrogenated OM. These sites have important epiphytonic activity. In contrast, the lower HI values in the central part are associated with the degradation and progressive oxidation of the different organic fragments, particularly the lignocellulose fractions, during their transport.

The HI vs. OI plot of these samples on a pseudo Van Krevelen diagram (Fig. 8) reveals the general dominant type of OM (Vandenbroucke and Behar, 1988). The OM in the surface sediments is intermediate between Type II and Type III. However, the OM signature seems to

approach the continental Type III. Two major groups can be separated with respect to the following samples:

- (i) A group corresponding to highly hydrogenated OM with low OI values (50 and 100 mg O<sub>2</sub>/g TOC). This OM is produced at the margins of the lake where the epiphytonic contribution is important.
- (ii) A group of samples dispersed in the diagram, with variable OI values and HI values scattered between 150 and 500 mgHC/gTOC.

Inclusion of the plant source data enables assessment of the different plants that might contribute organic material. The gramineae *Brachiaria* and spongiacae, which have HI/OI distributions distant from those of the sediments, can be excluded as important sources of the sediment OM.

In the longitudinal transect, the low amount of TOC (2%) in sample 7 is related to the presence on the lake floor of a channel that would constitute either a zone of non-deposition or perhaps a zone of erosion. In contrast, the zones favorable for OM accumulation are located close to the borders of the lake. To these topographical zones, we can add two very distinct zones located on the bathymetric sills of the longitudinal transect and well protected from the wind action. These zones can be considered as protected areas that accumulate a high amount of sedimentary OM.

Thus, OM in sediments from the NW margin, the entrance to the lake and the bathymetric sill contain an important fraction of labile biologic compounds. The margin is characterized by a more important contribution of lignin and cellulose. In the center of the lake, the labile compounds and lignocellulose fractions disappear whereas more resistant and certainly more complex geopolymeric compounds appear. This material is probably early diagenetic residue from the transformation via biodegradation and progressive oxidization of the OM produced on the margins and transported and deposited in progressively deeper areas of the lake.

In summary, elevated S<sub>2</sub> and lower TpS<sub>2</sub> values always correspond to high TOC concentration and HI values, and low OI values. Towards the center of the lake, TOC and HI decrease whereas OI increases. The samples characterised by higher TOC and HI values and also lower TpS<sub>2</sub> and OI values, indicate sediments rich in fresh and/or well-preserved OM.

The petrographical investigations showed the existence of granular AOM (reddish), flaky AOM (grayish) and gelified AOM. The distribution of these 3 fractions is different in the two transects. The most elevated contents of these different fractions are located in the north part of the longitudinal transect. The granular AOM is more abundant in the south part of the lake, whereas the flaky AOM is best represented in the north part of the basin. This distribution can reflect a variation in OM source, associated with variation in preservation/degradation conditions. The phytoplanktonic AOM is at a low level in the sediments from the margins and is absent from the central part of the lake. Because the lake is oligotrophic, the major part of the autochthonous phytoplanktonic production comes from epiphytes on the rushes in the margins of the lake. The amount of structured OM shows a dramatic decrease northwards (longitudinal transect) and from SE toward the NW (transverse transect), with progressive degradation of the ligno-cellulosic fragments from the translucent (LCD) toward amorphized LCD, that later form AOM. From these various results, we can summarize the spatial evolution of the degradation of the OM in Lagoa do Caçò as follows.

The main physical factors influencing degradation are wind, the topography of the lake bed, and the variation of the water depth, so:

- Wind influences directly the distribution of organic fractions in the lake by driving lake circulation. It also provides mixing that encourages permanent oxygenation of the open water of the lake and thus oxidative degradation of OM.
- The topography gives some very favorable places for sedimentation and/or degradation of OM transported along the slopes.
- The third factor – variation in water depth – is presumably the essential factor for the differentiation of amorphisation mode of the principal OM source (rushes). We find a direct relationship between the amorphisation of OM and lake depth (Fig. 9).

During the seasonal dry period, the small (2 m) decrease in water level permits sub-aerial degradation of a large part of the OM produced by the epiphytes. The increase in water level during the humid season permits mobilization of a large part of this degraded phytoplanktonic OM. This process can probably explain the origin of the grayish flaky AOM and would also explain the non-fluorescence of this AOM derived from the phytoplankton.

The combination of petrographical data with Rock-Eval pyrolysis allows us to propose that the decrease in TpS<sub>2</sub> temperature results from the abundance of tLCD and therefore to the proportion of well preserved OM. However, it appears contradictory to the analysis of the modern plant source material that revealed values of more elevated TpS<sub>2</sub> values despite the freshness of the material.

The abundance of membranes and well-preserved cuticles (samples 2 and 18 of the transverse transect) seems to have little influence on the maximum temperature of cracking. This finding appears especially clear with regard to sample 3 of the transverse transect, where the proportions of membranes and cuticles reach > 30 %. According to these observations, we can affirm that advanced decomposition by way of biodegradation enables separation of some easily pyrolysable organic substances. Consequently, diagenesis simplifies and weakens part of organic material, allowing pyrolysis at lower temperatures than for the pyrolysis of organic sources.

The plant belt that edges the lake constitutes a filter for allochthonous contributions. This feature, added to the high productivity in the margins, confirms that this belt is the principal source of the plant contribution of OM in the lake. The contribution of organic particles by wind exists but is very low.

The assignment of a given organic fragment to a specific kind of plant is not simple. Identification is heavily influenced by the degradation state. The comparison of palynofacies of plant sources with the studied samples permitted recognition of a certain number of well-preserved constituents. In some cases, it was even possible to determine their botanical origin, notably the woody fragments of rushes and grasses and some cuticles from spongy plants.

Previous work showed that the proportion of land plant components in the OM of lake sediments typically decreases with greater distance from the shore (Talbot and Lærdal, 2000). This simple observation has been combined with the bulk organic geochemical indicators of OM sources to reconstruct climate induced changes in water levels of tropical lakes during the last 20 kyr (Talbot and Lærdal, 2000; Jacob et al., 2004). The differences in surface sediment OM elemental and isotopic composition among the depth related zones in this lake

(Siffeddine et al., 2011) suggest that changes in lake level can leave an imprint on the sediment record. Our studies on organic signal gives same conclusion describing for the first time in detail the organic geochemical and petrographical content of potential plant sources and identifying clear changes in the texture of modern sedimentary OM delivered to different water depth parts of a lake. OM origins, as inferred from this study, show that the major source of OM is macrophytes and their associated epiphytes, with high productivity in the shallow waters of the lake margins. A portion of this OM having experienced diagenetic amorphisation and oxidation is transferred to the deeper water of the open lake. This transfer explains how this oligotrophic lake has accumulated 6 m of OM rich sediments. Changes in water level have a significant influence on the OM production and deposition. The evolution of the amorphisation index (Fig. 9) with water depth is a new parameter that should be operated and calibrated for palaeoenvironmental studies using well established paleohydrological lake records. This strong correlation between the geochemical and textural palynofaciès information and the water depth of the lacustrine environment must be tested in other lake surface sediments. We have also to test these parameters on the sedimentary records of Lagoa do Caçò and other lakes.

## **5. Conclusions**

Petrographical and bulk geochemical analysis of surface sediments sampled along two transects (one transverse and one longitudinal) constrains the main OM suppliers and the fate of their remains during early diagenesis. The approach reveals heterogeneous spatial distribution of the OM in the surface sediments. OM distribution depends largely on the topography of the lake, which favors important sedimentation on its borders and in areas sheltered from water currents generated by the trade winds, especially in the vicinity of bathymetric sills. The petrographic investigation shows that the main part of the gelified OM is located in the deepest zones. Indeed, the evolution of the lignocellulose remnants reflects the role of early diagenesis in aquatic environments.

Shallow water macrophytes are important contributors to sediment OM in the lake. Because

the macrophyte population in Caço Lake is highly produced mainly in water < 4 m depth, the translucent ligno-cellulose debris is concentrated in this area of organic production. Its proportion decreases when the frequency of amorphous debris increases. Amorphous OM shows a general increase from the margins toward the deepest part of the lake. These petrographic observations allow us to propose a relationship between a gelification index (defined as the ratio of amorphous fraction vs figured and non amorphised fractions) and the depth of the water column.

The main suppliers of OM to the sediments are the higher plants that grow near the lake border, especially *Juncus juncus*. To the lignocellulose debris derived from the post mortem biodegradation of these plants is added some phytoplanktonic OM. A form of amorphous OM that may be underestimated due to rather rapid and extensive biodegradation represents this latter source. However, this phytoplanktonic OM could be responsible for the local increase of HI values on the margins of the lake. The major effect of water column variations is sub-aerial degradation on the margins of the lake. The variation could be responsible for the differentiation of various types of AOM. The annually 2 m fluctuation in water column depth is probably responsible for the oxidative degradation of the epiphyte phytoplanktonic material, explaining the non-fluorescent properties of grayish AOM in spite of its likely planktonic origin, explaining the source of OM delivery in this oligotrophic lake.

Comparison of the S<sub>2</sub> pyrolysis curves with the TpS<sub>2</sub> values reveals the presence of three types of pyrolytic compounds. OM in sediment from the NW margin, the entrance to the lake and the bathymetric sills contains an important amount of labile biologic compounds. A more important proportion of lignin and cellulose characterizes the SE margin. Toward the lake center, the labile compounds and lignocellulose fractions disappear, whereas the amount of residual consolidated compounds increases. This latter material originates from transformation by way of progressive biodegradation and oxidation of OM produced on the margins, transported and deposited progressively in the deeper parts of the lake.

In summary, the increase in qualitative (HI) and quantitative (TOC) parameters on the lake margins reveals high organic productivity mainly from higher plants and to a lesser

extent from phytoplankton. The OM is then progressively transported from the lake borders towards the center, where it undergoes extensive oxidative degradation in oxygenated waters mixed well by the trade winds. Water column variation between the humid and dry seasons could be responsible for the differentiation of the AOM and most probably for the non-fluorescent AOM that appears to be derived from algae. This sedimentary process, allowing the transfer of OM from the edges toward the center of the lake helps explain how this oligotrophic lake, having low or non-existent photic zone bioproduction, has encouraged the deposition and preservation of sediments rich in OM.

### **Acknowledgments**

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### **Table captions:**

#### Table 1

Rock-Eval and EA LECO geochemical data for surface sediments from the two transects of Lagoa do Caço. Replicate analyses of surface sediment samples show excellent TOC reproducibility, with an analytical error lower than 2% \*TOC value (c.a. 0,02 each 1%). The standard deviation on the other main parameters are:  $T_{\text{peak}}$ :  $\pm 5$  °C;  $\pm 6\%$  of HI values;  $\pm 10\%$  of OI values. RSD analysis precision of LECO EA is  $\pm 0.4$  for C, and  $\pm 0.02$  for S and N.

#### Table 2

Rock-Eval geochemical data of the produced organisms of Lagoa do Caço. The standard deviation on Rock-eval6 parameters are: TOC:  $\pm 2\%$  ;  $T_{\text{peak}}$ :  $\pm 5$  °C ; HI:  $\pm 6\%$ ; OI:  $\pm 10\%$ .

### Figure captions:

Fig. 1. Location, bathymetric map of Lagoa do Caçò and sample locations along two transects “L: longitudinal and T: transverse”. The lake formation is due to the installation of late Pleistocene dunes oriented NW-SE (longitudinal dunes) responsible for the actual hydrographic geomorphology of the region. A second generation of dunes, perpendicular to the previous ones (transverse dunes), is responsible for the establishment of many lakes in Maranhao State. The bathymetric map provides better highlighting of the geometry of the basin. It shows that a flat bottom and steep margins characterize the lake. The transverse transect reveals an asymmetry between the slopes of the margins; the northeast margin is more abrupt than the southwest one.

Fig. 2. Disposition of aquatic plant, macrophyte and epiphyte production along the southeast margin of the transverse transect. Most of the organic production originates from semi-submerged plants (highly dominant *Eleocharis* sp.) that colonize the marginal zone growing around the lake in water 1 to 3m deep and from submerged plants. From 2 to 4 m depth, the lake margin is colonized by macrophytes with abundant epiphytic algae dominated by diatoms and a unique species of sponge (*Metania spirata*).

Fig. 3. Correlation between TOC contents (%) determined by RE6 pyrolysis with Total carbon contents determined by classical combustion with a Leco CNS-2000 analyzer. The absence of carbonates in the samples allows for the direct comparison of Total carbon Leco determinations with RE6 TOC measurements. The samples of produced organisms have not been taken into account for this comparison.

Fig. 4. Evolution of OI, HI and TOC of Rock-Eval parameters along two transects: longitudinal (a) and transverse (b)

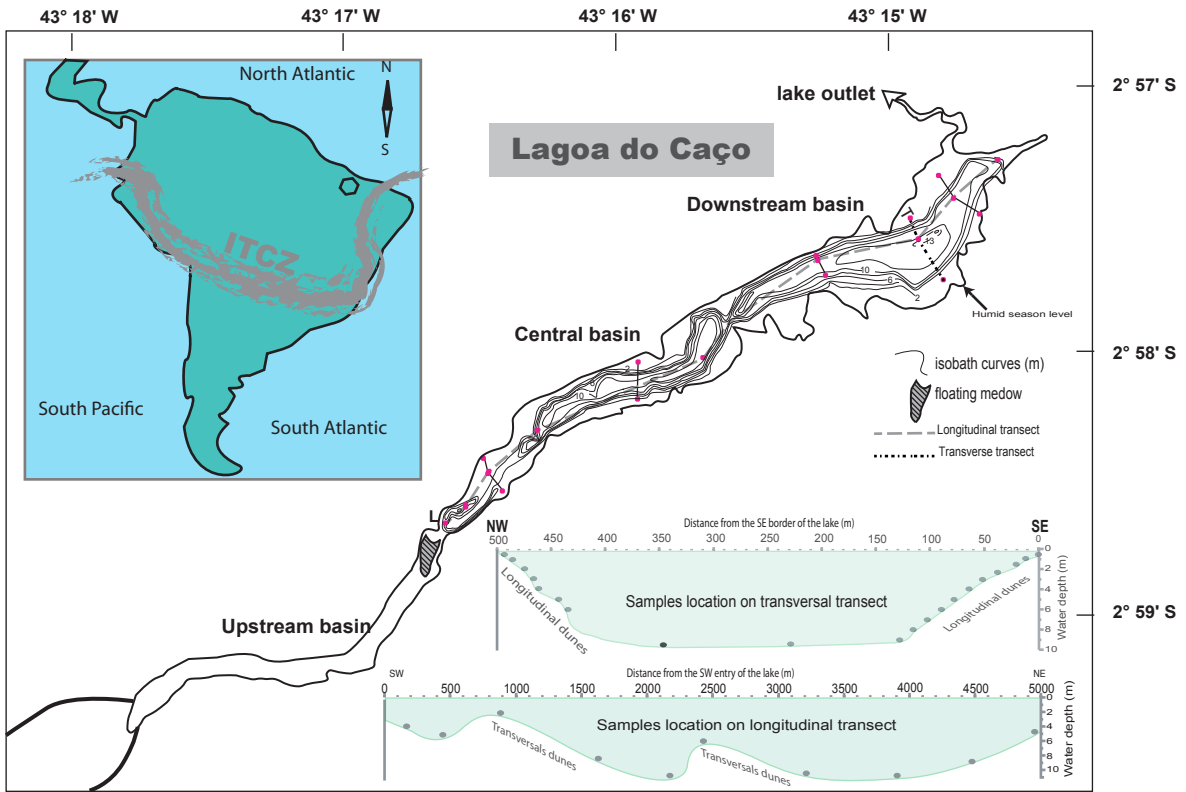
Fig. 5. Main palynofacies fractions in surface sediments of Lagoa do Caçò: descriptions, possible origin and main depositional environment.

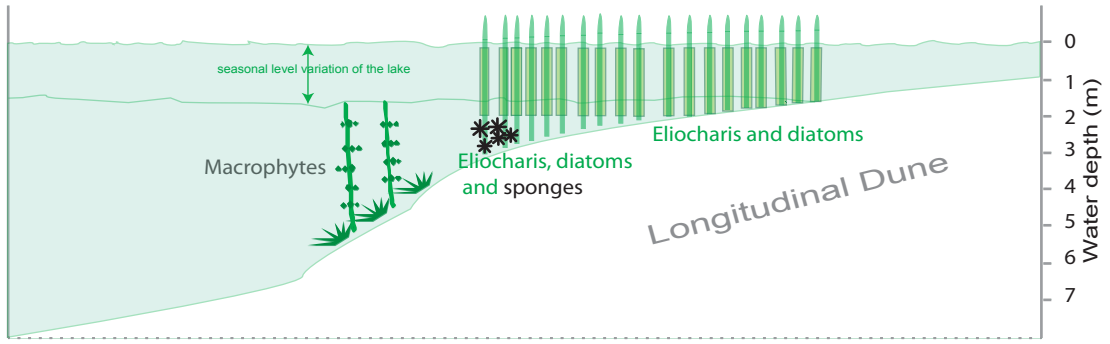
Fig. 6. Relative abundance of palynofacies of longitudinal transect surface sediments.

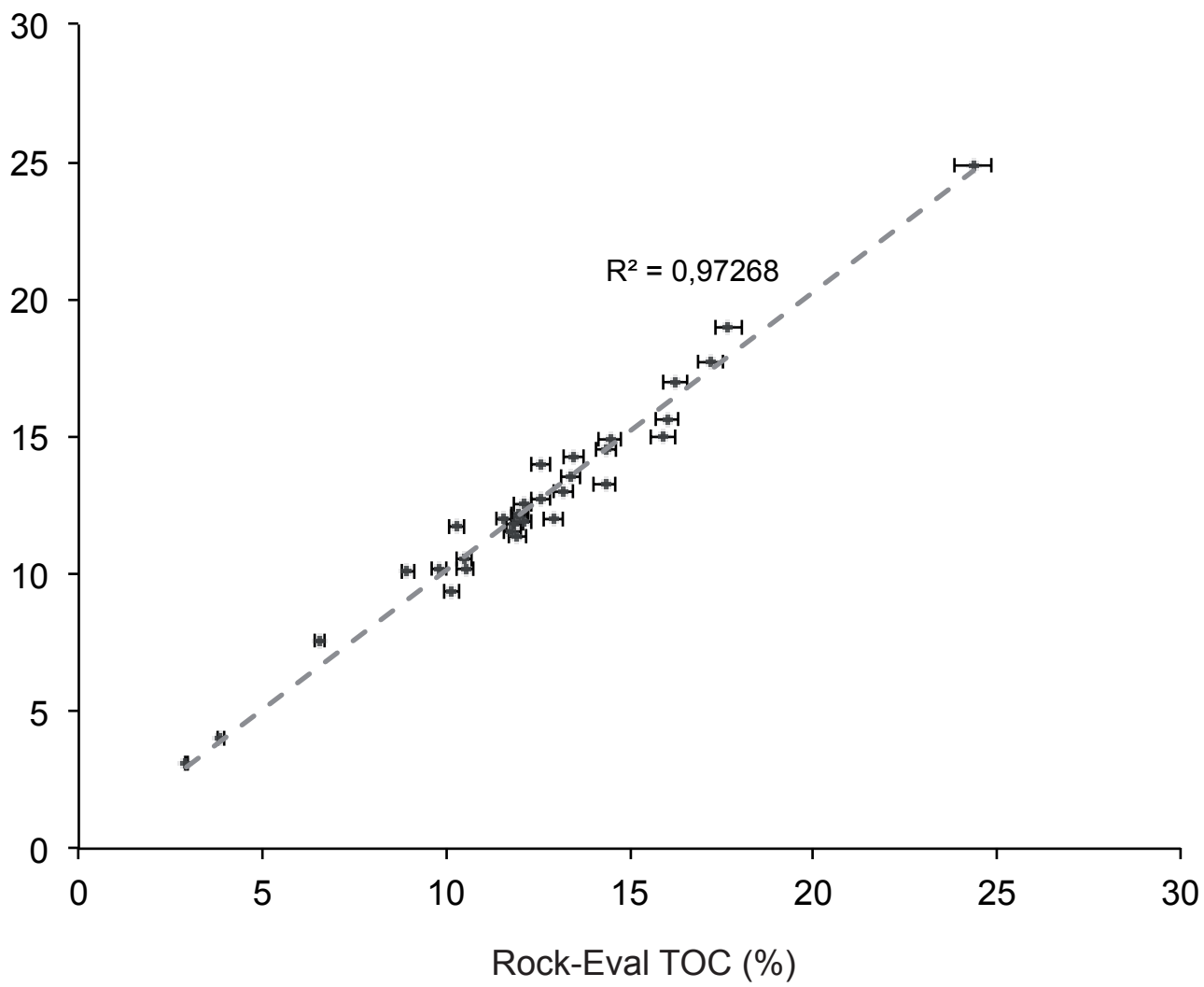
Fig. 7. Relative abundance of palynofacies of transversal transect surface sediments.

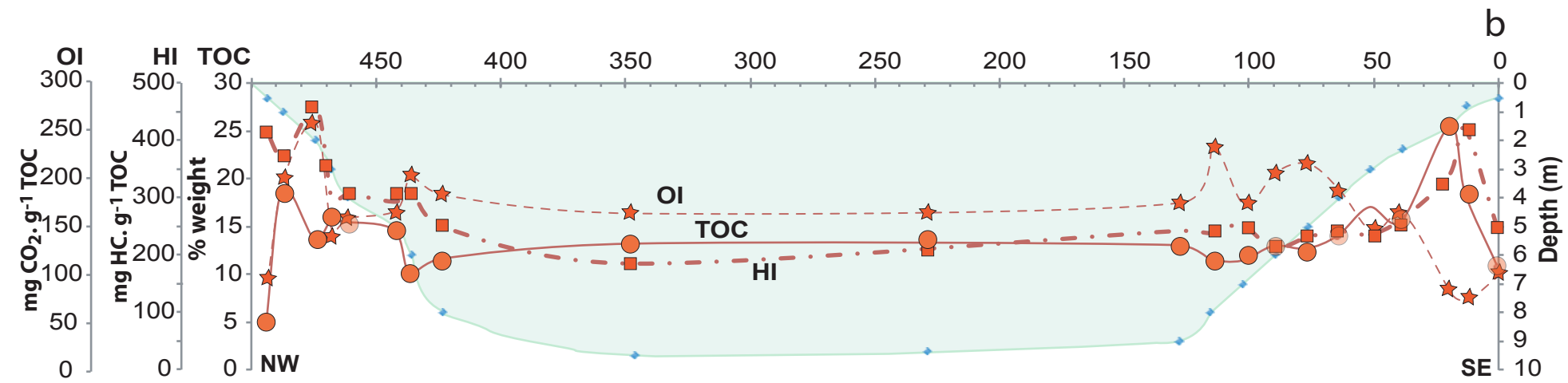
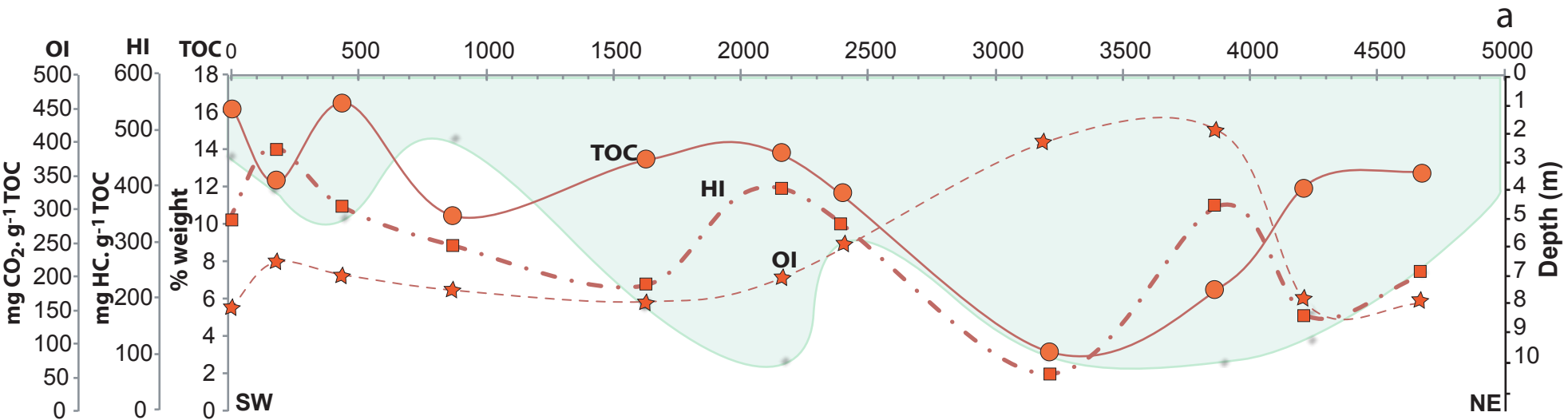
Fig. 8. HI vs OI pseudo-Van Krevelen diagram of sediment surface samples and producer organisms in Lagoa do Caçó



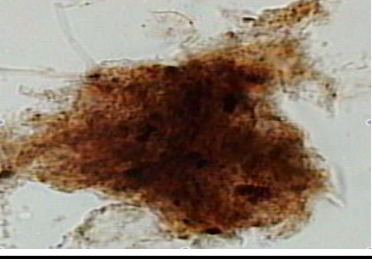






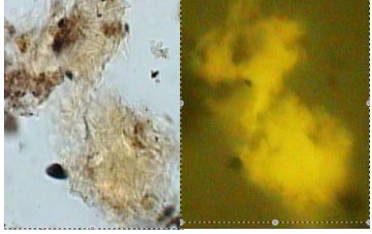
Fig. 9. Gelification index vs. depth of Lagoa do Caçó revealing good correlation between “amorphization” and depth.

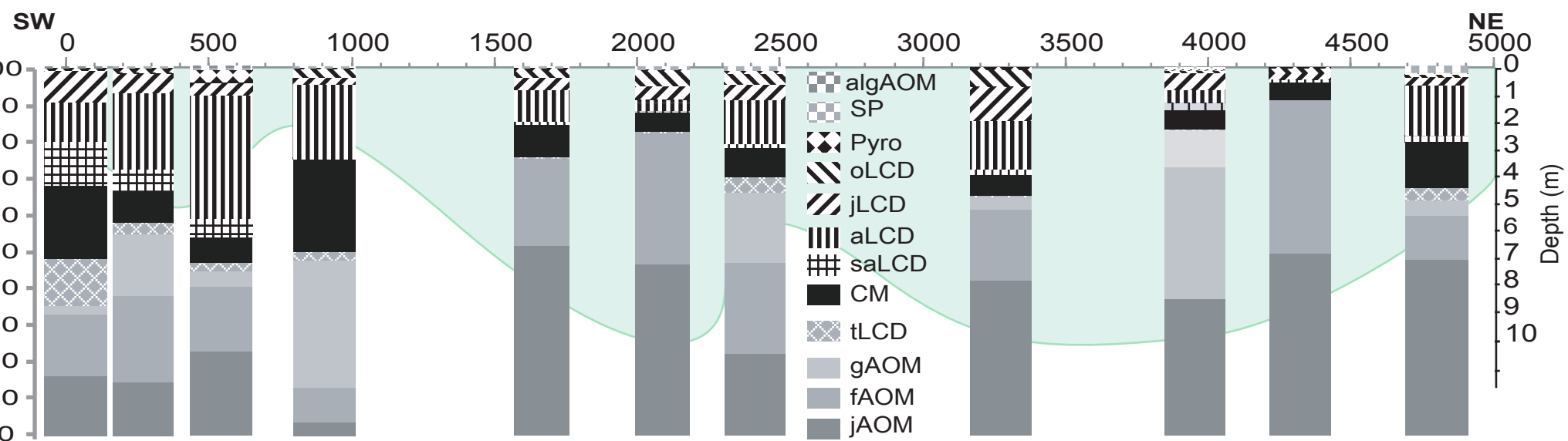


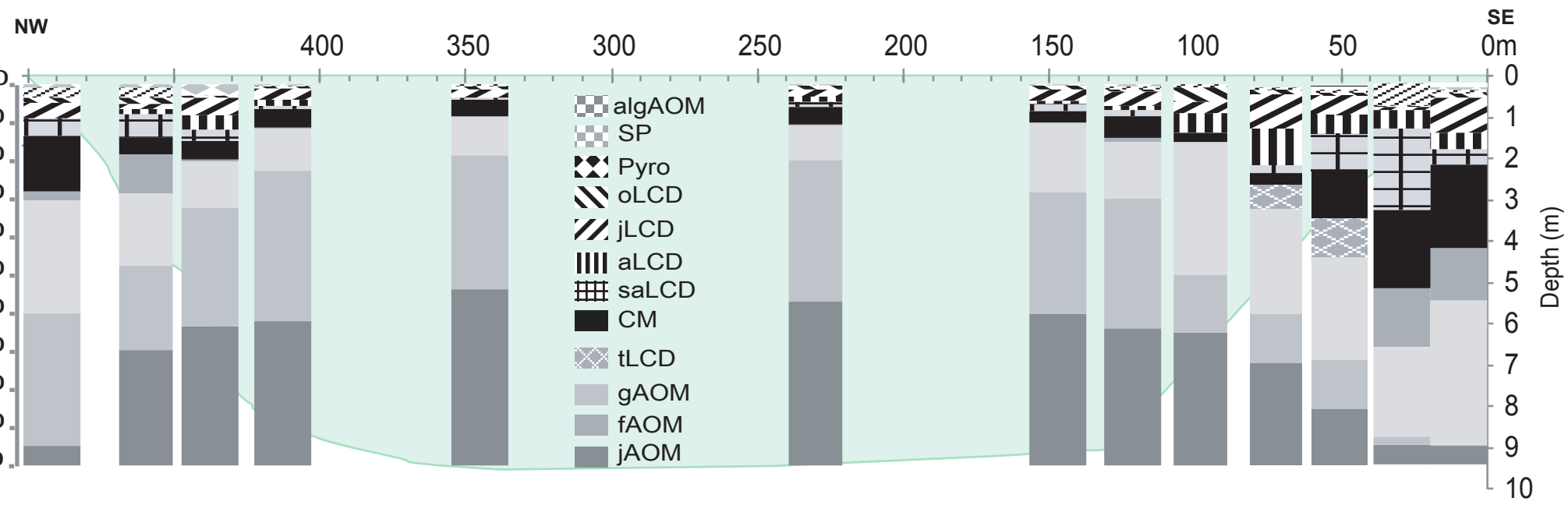


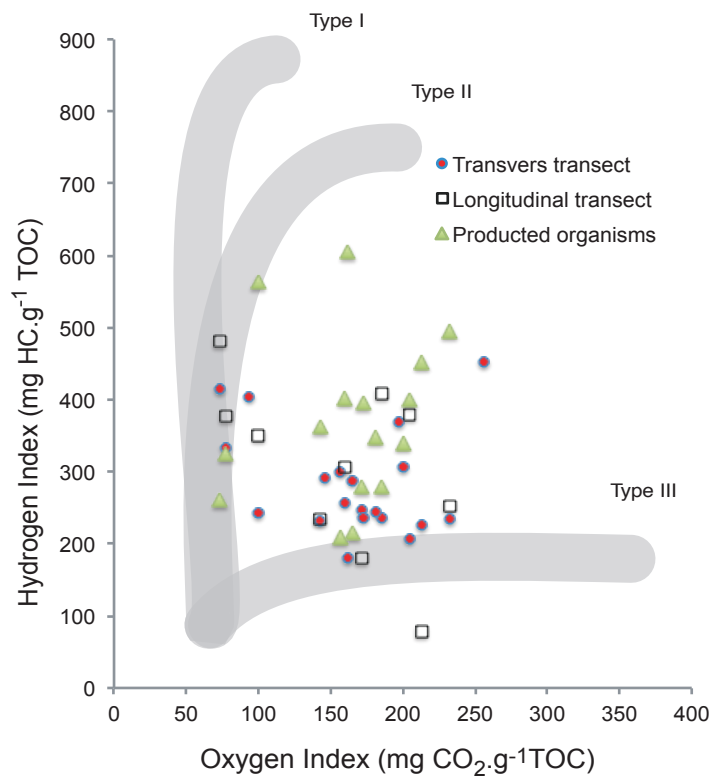


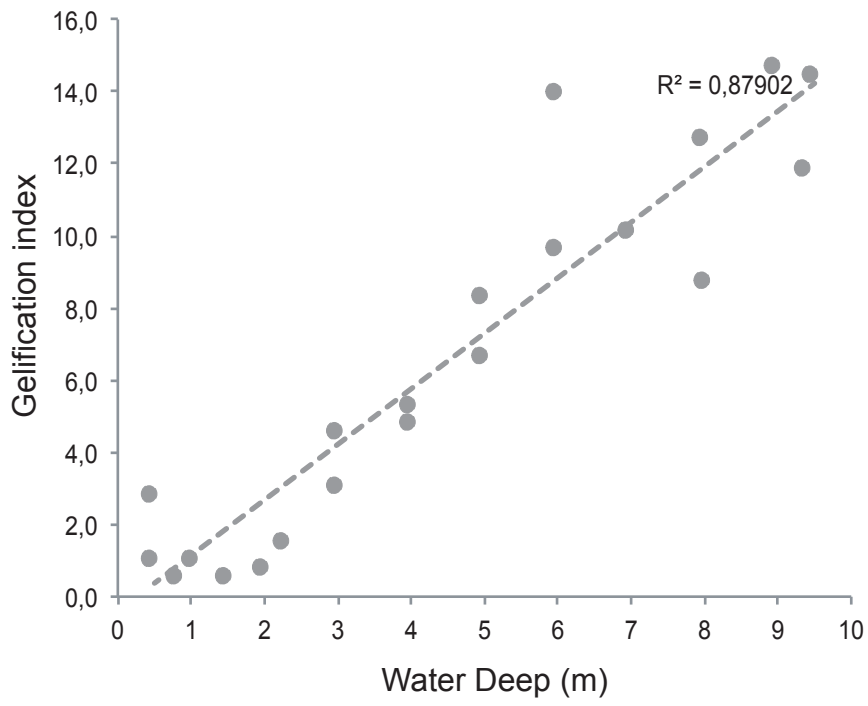


Type of OM constituent	Illustration	Description	Possible origin	Main depositional environment
<b>granular Amorphous Organic Matter (gAOM)</b>		Globular shape with reddish/orange small scraps and innumerable granules in their internal textures	Degradation and amorphisation of OM in oxygenated aquatic condition	Lacustrine
<b>Greyish flaky AOM (fAOM)</b>		Blurred aspect with neither clear shape nor specific internal structure and no fluorescence. It is heterogeneous with flocculated texture	Originate from the amorphisation of some non lignocellulosic part of higher plant particles or from highly degraded phytoplanktonic material.	Lacustrine
<b>jellified AOM (jAOM)</b>		Totally homogeneous in texture and orange to dark brown with a sub-rounded shape .	Gellification of woody residues transported from the catchment basin or autochthonous amorphisation of fragments derived from grasses and reed stems produced in the lake borders.	Palustrine and lacustrine
<b>The translucent Ligno-Cellulosic Debris (tLCD)</b>		Lengthy particles with very clear outlines and apparent vascular structures. Many types of structures depending on botanical origin are observed.	These particles are considered as a marker of well preserved fresh organic input in the sediment.	Paludal fresh OM input
<b>slightly Amorphised Ligno-Cellulosic Debris (sALCD)</b>		Ligno--cellulosic particles with a structural loss and beginnings of amorphisation	First stage of degradation of higher plant debris starting within the internal structures. The cell walls and ducts remain identifiable.	Palustrine input in lacustrine sedimentation with beginning of gelification in hydromorphous or lacustrine environments
<b>Amorphised Ligno-Cellulosic Debris (aLCD)</b>		Brown woody particles without any internal structures. similar texture to jAOM and are difficult to distinguish from it. characterized by their inherited lengthiness as well as the presence of straight borders and jagged woody	Final stage of LCD degradation The cell walls and ducts are non identifiable. It could be the last stage of degradation, before the complete amorphisation. (AOM stage)	Paludal apport
<b>jellified Ligno-Cellulosic Debris (jLCD)</b>		Has a sub-oblong morphology and brown to reddish color with vitreous texture without apparent internal structures	May have resinous or gel plant secretion of origins	Terrestrial and soil OM
<b>The opaque Ligno-Cellulosic Debris (oLCD)</b>		Appears as black and opaque particles in transmitted light observation, with clean contours They show a high reflectance on incident-light observation.	Ultimate stage of oxidative degradation. they indicate a long exposure to a subaerial environment (subaerial oxidization) or re-mobilization of organic material from soil	Paludal or aquatic higher plants
<b>Membranes and Cuticles (MC)</b>		Are thin large particles that are translucent white or yellow and often have a rolled up shape.	The cuticles are represented by layers of cutin that cover the cellulosic epiderm of higher plants. Submerged (autochthonous) or emergent (allochthonous) higher plants	Paludal or aquatic higher plants
<b>Algal Organic Matter (AlgAOM)</b>		Purely Well preserved algal fraction representing the production in the lake. It appears as very thin and greyish flakes under natural transmitted light (left) and fluorescent under UV excitation (right)	In Lake Caço, phytoplanktonic productivity is mostly represented by diatoms and sponges that are confined to the margins of the lake and associated with the aquatic macrophytes.	Lacustrine









	Samples N°	Deep (m)	Distance (m)	TOC %	OI mg O2/g TOC	HI mg HC/g TOC	TPS2 °C	TC %	S %	N%	C/N
<b>Transvers transect</b>	T01	0.5	0.00	9.81	99	242	455	10.21	0.11	0.60	19.85
	T02	0.8	12.82	17.22	73	414	444	17.75	0.21	1.09	19.00
	T03	1.5	19.23	24.36	77	333	430	24.89	0.31	1.19	24.40
	T04	2.3	38.46	14.47	160	257	439	14.91	0.27	1.05	16.57
	T05	3.0	51.28	15.92	143	231	441	14.98	0.18	0.98	17.83
	T06	4.0	64.10	12.92	185	237	442	12.00	0.96	0.94	14.89
	T07	5.0	76.72	11.58	213	225	437	12.04	0.08	0.18	78.04
	T08	6.0	89.74	11.86	205	207	439	11.85	0.07	0.79	17.50
	T09	7.0	102.56	10.31	171	247	437	11.68	0.67	0.74	18.41
	T10	8.0	115.38	10.49	232	233	441	10.52	0.08	0.83	14.79
	T11	9.0	128.20	11.94	173	237	439	11.39	0.05	0.74	17.96
	T12	9.4	228.70	12.00	164	175	440	12.20	0.07	0.81	17.57
	T13	9.5	346.15	12.10	162	180	440	12.50	0.06	0.75	19.44
	T14	8.0	423.07	10.53	181	244	441	10.20	0.07	0.85	14.00
	T15	6.0	435.89	8.96	200	307	441	10.07	0.05	0.74	15.88
	T16	5.0	442.30	13.50	165	288	435	14.22	0.15	1.13	14.68
	T17	4.0	461.53	14.36	157	301	440	14.50	0.12	1.18	14.34
	T18	3.0	467.94	14.32	146	292	440	13.23	0.08	1.08	14.29
	T19	2.0	474.35	12.58	256	452	320	13.97	0.12	1.53	10.65
	T20	1.0	487.17	17.70	197	368	313	18.96	0.22	1.63	13.57
	T21	0.5	493.58	3.88	93	404	456	4.00	0.03	0.32	14.58
<b>Longitudinal transect</b>	PL01	2.8	0.00	16.03	158	351	303	15.66	0.03	1.41	12.96
	PL02	4.0	172.72	11.99	229	482	429	12.11	0.15	1.70	8.31
	PL03	5.0	445.45	16.24	211	377	325	16.96	0.16	1.51	13.10
	PL04	2.0	881.81	10.16	188	307	440	9.36	0.03	0.96	11.38
	PL05	8.0	1627.27	13.19	171	235	439	13.03	0.09	0.98	15.51
	PL06	10.0	2172.72	13.38	207	409	303	13.50	0.07	0.88	17.90
	PL07	5.8	2400.00	11.80	325	385	425	11.52	0.09	0.79	17.01
	PL08	10.0	3209.09	2.93	409	78	440	3.07	0.02	0.34	10.53
	PL09	10.0	3900.00	6.56	421	379	444	7.60	0.07	0.80	11.08
	PL10	9.5	4245.45	12.10	162	180	440	11.88	0.07	0.81	17.11
	PL11	7	4681.81	12.58	169	253	439	12.76	0.06	0.90	16.54

<b>Rock – Eval Parameters</b>		<b>TOC %</b>	<b>OI mg O2/g TOC</b>	<b>HI mg HC/g TOC</b>	<b>TPS2 °C</b>
<b>Produced organisms</b>	Sponges	30.28	69	563	359
	Stems of red macrophytes	39.31	157	260	329
	Grasses from the lake edges	46.37	112	325	340
	Leaves of submerged macrophytes (cabomba)	42.45	181	402	341
	Pistia emersa	38.91	154	362	338
	Epiphytes under Katayif	18.26	180	280	428
	Brachiaria submersa	37.37	105	452	365
	Fresh Katayif	43.50	147	400	334
	Gelified biodegraded Katayif	34.55	150	280	346
	Leaves of Motrychardia	44.19	178	496	333
	Eliocharis	43.72	202	396	339
	Brachiaria emersa	34.20	199	605	366
	Grasses from the lake entry	28.32	213	348	338
	Sponge Plants	39.50	310	339	306
	Stems of water Lilies	42.94	294	215	321
	Leaves of water Lilies	46.59	244	210	339