

# **Major environmental changes recorded by lacustrine sedimentary organic matter since the Last Glacial Maximum near the Equator (Lagoa do Caçó, NE Brazil).**

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## **Abstract**

Sediment samples collected along a six-meter core, drilled in the deepest part of the Lagoa do Caçó (NE Brazil), have been investigated in order to determine source(s) and degradation conditions of the organic matter (OM) with special emphasis on paleoenvironmental implications. Bulk organic geochemistry (Rock-Eval pyrolysis, C/N determination,  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  measurement) and petrography combined with sedimentological evidence and radiocarbon dates allowed to identify four major intervals documenting major environmental changes that occurred during the last 20,000 years. The first interval, dating back to the end of the Last Glacial Maximum (LGM), contains well preserved OM derived from higher plants. This material was most probably produced in an ephemeral palustrine system and rapidly buried by sands. This level is thought to have been deposited under relatively arid climate conditions associated with strong but episodic rainfalls. Between 19,240 and 17,250 Cal yrs BP, the climate appears to have been more humid and seasonality more pronounced as suggested by the presence of a permanent lake. After a drastic environmental change dating back to 17,250 Cal yrs BP, the sediment became truly lacustrine with restricted mineral input and highly-degraded higher plant-derived organic matter. After that, a stepwise improvement in the preservation of OM occurred, as revealed by several pronounced shifts in the Rock-Eval TpS2 signal. These changes could document abrupt climatically driven changes during the Lateglacial. Finally, around 5610 Cal yrs BP, environmental conditions, approaching those prevailing today were established. Minor climatic changes during the Holocene were

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probably buffered by a high water table which might explain the lack of paleoenvironmental fluctuations.

*Keywords* – Brazil, lacustrine organic matter, paleoenvironments, paleoclimate, Rock Eval, organic petrography

## **1. Introduction**

Recent studies in tropical South America (Sifeddine *et al.*, 1998; 2001; Colinvaux *et al.*, 1996; Behling *et al.*, 2000; Ledru *et al.*, 2001; 2002) have improved our knowledge of past environmental changes and their driving mechanisms in this area. Nevertheless, major controversies still remain, for example on the respective contribution of the Intertropical Convergence Zone (ITCZ) and Polar Advections on regional climate variability (Ledru *et al.*, 2002). These controversies emphasize the need to better document the climatic fluctuations that affected this area since the Last Glacial Maximum (LGM). New analytical approaches applied on new records are needed in order to enhance our understanding of the nature, the extent and the origin of past paleoclimatic fluctuations. OM analyses have now proven their utility for paleoenvironmental reconstructions, in particular in lacustrine sedimentary records in temperate areas (Lallier-Vergès *et al.*, 1993; Meyers and Lallier-Vergès, 1999; Manalt *et al.*, 2001; Sifeddine *et al.*, 1996), but rarely in tropical settings (Talbot and Livingstone, 1989; Street-Perrott *et al.*, 1997; Sifeddine *et al.*, 1998; 2001; Ficken *et al.*, 1998; Huang *et al.*, 1999). Sedimentary lacustrine series are attractive targets to document paleoenvironmental changes because they generally offer high temporal resolution due to high sedimentation rates. In addition and in contrast to high latitudinal settings which receive little or almost no organic input during glacial times, tropical settings might have benefited of a more favourable climate during such periods leading to a more continuous record of vegetation change in the drainage area. Located at the present southernmost limit of seasonal displacement of the ITCZ, near the Atlantic and on the border of the Amazon Basin, Lagoa do Caçó is in a key area to document paleoclimatic changes that affected the tropical South America. The lake record also lends itself especially well to record sedimentary OM. This study presents the results obtained from OM analyses carried out on a 6m long core covering nearly 20,000 years of sedimentation. Abundance, origin and quality of the OM are discussed and temporal fluctuations interpreted in terms of paleoenvironmental changes.

## 2. Study site

Lagoa do Caçó is located in north-eastern Brazil (Maranhão State), about 80km from the Atlantic coast and close to the Equator (2°58'S, 43°25'W and 120 m above sea-level). The local present-day climate is tropical humid with pronounced seasonality. Precipitation, which annually reaches 1750mm on average, mostly occurs during the rainy season, from November to May. The mean annual temperature is 26°C. Located on the edge of the Amazon Basin, the vegetation in this region displays a strong zonation ranging from *Restinga* (grass steppe) near the coast, to *Cerrado* (shrub savanna) inland followed by *Cerradao* (woody savanna) in the more humid regions (Ledru *et al.*, 2002). The lake (ca. 2.5 km<sup>2</sup> surface area) is enclosed in an SW-NE oriented former river valley within a dune field dating back to Pleistocene times. The maximum water depth is 10m during the wet season (austral summer) and 9m during the dry season (austral winter). The opposite flow direction of the tributary river (from SW) and the trade winds (from N) results in a constant mixing of the water column. Today the lake is oligotrophic to meso-oligotrophic. In fact, only few phytoplankton taxa live in the water column. Most of the organic production originates from semi-emerged plants (*Juncus sp.* highly dominant) growing around the lake at about 1 to 3m water depth and from submerged plants. Attached to the rushes, some diatoms can be found as well as a unique species of sponge (*Metania spirata*; Volkmer-Ribeiro, pers. comm.). The rushes prevent almost all mineral transport from the sandy banks into the lake but export a part of their own production to the lake. A more than 2m thick floating meadow occupies the river inflow and filters most of mineral and organic influx from the small tributary. Thus, inorganic sedimentation is primarily derived from aeolian particles and authigenic minerals.

## 3. Sampling and methods

### 3.1. Sampling

Twin sedimentary cores 98-3 and 98-4 (6m each) have been drilled with a vibracorer (Martin *et al.*, 1995), less than 1m distance apart, in the deepest part of the lake (Fig. 1). Samples were taken every 2cm from 17 to 594cm depth on core 98-3 and from 0 to 583cm on core 98-4. The samples were dried at 40°C in an oven and then crushed and stored.

### 3.2. Organic Petrography

About 1g of sediment was treated with HCl and HF to remove the mineral matrix. The resulting organic residues were then observed by natural transmitted light microscopy. Over 1000 surface units of particles were counted to estimate the relative proportions of each

organic fraction. Distinction of hydrocarbon-rich fractions was achieved under UV excitation and iron sulphides were recognized under natural reflected light.

### 3.3. Bulk Organic Geochemistry

*Rock-Eval pyrolysis:* Between 50 and 100mg of dried sediments from core 98-3 were used for Rock-Eval6 (RE6) analysis, depending on the estimated OM content. The pyrolysis program starts with an isothermal stage of 2 min at 200°C. Then, the pyrolysis oven temperature was raised at 30°C/min to 650°C, and held for 3 minutes at this temperature. The oxidation phase, performed in a second oven under an air stream, starts at an isothermal stage at 400°C, followed by an increase to 850°C at 30°C/min and held at final temperature for 5 minutes.

Rock-Eval parameters have been described by Espitalié *et al.* (1977). Specific parameters provided by the new RE6 device are presented by Lafargue *et al.* (1998). The Rock-Eval parameters we used for this study are the following ones: (i) mineral carbon (Minc) which represents the amount of inorganic carbon (from carbonates) released during pyrolysis and oxidation; (ii) Total Organic Carbon (TOC, %) accounts for the quantity of organic matter present in the sediment; (iii) Hydrogen Index (HI, in mg HC/g TOC) is the amount of hydrocarbonaceous (HC) products released during pyrolysis (integrated from the S2 peak, in mg HC/g dry sediment) normalized to TOC; (iv) Tmax is a well-known OM maturity indicator in ancient sediments (Espitalié *et al.*, 1985b). It is the temperature of the pyrolysis oven recorded at the top of peak S2, which thus corresponds to the maximum release of hydrocarbonaceous products during pyrolysis, carried at 25°C/min in previous Rock-Eval devices. However, this temperature is 30 to 40°C lower than that effectively experienced by the sample (Espitalié *et al.*, 1985a). As opposed to previous devices, RE 6 measures the exact temperature experienced by the sample. The temperature determined at the top of the S2 peak is called TpS2. Because Tmax has no significance in term of thermal maturity for recent OM (Manalt *et al.*, 2001; Lüniger and Schwark, 2002; Disnar *et al.*, 2003), we here used TpS2 values; (v) Oxygen Index OIRe6 (in mg O<sub>2</sub>/g TOC), which gives the oxygen content of the OM. It is calculated from the amounts of CO (S3CO) and CO<sub>2</sub> (S3CO<sub>2</sub>) released during pyrolysis, normalized to TOC.

*C/N,  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$ :* Total Carbon and Nitrogen as well as their stable isotopes ratios ( $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$ ) were measured on core 98-4 by combustion with a Shimadzu CHN analyser coupled to a Prism mass spectrometer. Because carbonates (siderite) were only found in a well defined interval (Sifeddine *et al.* 2003), and because of the geological and hydrological context (sand dunes and ferralsols; acidic lake waters), these analyses were realized on bulk sediments, thus avoiding any artefact due to acid attacks. Accordingly, C/N ratios are expressed as total carbon over total nitrogen.

### 3.4. Dating

Six radiocarbon dates have been performed on bulk OM on core 98-3 by acceleration mass spectrometry (AMS) at the Beta Analytic Laboratory (Florida, USA). Interpolated ages

were calculated using the intercept of the mean conventional age interval with the calibration curve of  $^{14}\text{C}$  (CALIB version 4.3, Stuiver and Reimer, 1993; Stuiver *et al.*, 1998).

## 4. Results

### 4.1. Lithology and mineralogy (Fig. 2)

The lowermost unit of the core (U1) consists of sands of the Pleistocene substratum that will not be further discussed. The remaining part of the core of about 6m length has been subdivided in two parts of equal length according to mineral content and granulometric criteria. The lower part, which mainly comprises detritic material, has been further divided into fine-grained sands (U2) and silts (U3). U2 contains between 60 and 80% of quartz whereas unit U3 contains 50% of quartz and 50% of kaolinite. The upper half of the core consists of fine-grained OM-rich sediments. It has also been subdivided into two units related to their colour, i.e. brown-green silts (U4) and black silts (U5). Mineralogy of unit U4 strongly differs from the underlying sediments by its high content in goethite (0-26%), amorphous silica (4-20%) and, at specific levels, in siderite (35%). The inorganic assemblage of U5 is mainly composed of amorphous silica (sponge spicules and diatoms).

### 4.2. Organic Petrography (Table 2 and Fig. 2)

In addition to pyrite, eleven classes of organic constituents have been distinguished according to morphological and textural criteria. The first of these criteria is the presence of recognizable biological structures. The structureless material is called "amorphous". A description of the constituents is given in Table 2. The variations of the relative proportions of the different organic classes are plotted against depth in Figure 2. Amorphous constituents are largely dominant (60 to 90%) along the core. The upper half-core contains primarily Flaky Amorphous OM (FlAOM) while the lower half is dominated by Gelified Amorphous OM (GelAOM). More or less well preserved ligno-cellulosic debris (TLC, GelLC and AmLC) account for 20 to 40% of the organic constituents in U2 sands. These particles strongly decrease in the upper intervals, notably at the base of the greenish-brown organic silts in U4. Opaque debris (OD), which are sparse or even absent in the lower half of the profile, increase slightly upcore in U4 to reach 10% at 3m depth. In the upper unit U5, OD represent 20-30% of the organic constituents. Authentic phytoplanktonic OM constitutes only 5% of the total OM. Pyrite is recorded in U3 silts (7%) and, in lower proportions, in U4 greenish-brown organic silts. No trace of this mineral was identified in the lower and upper units U2 and U5.

#### 4.3. $\delta^{15}\text{N}$ , $\delta^{13}\text{C}$ and C/N (Fig. 3)

$\delta^{15}\text{N}$  is around 10‰ in U2 and U3 units and around 3-4‰ in U4 and U5 units after a strong decrease at the U3/U4 boundary.  $\delta^{13}\text{C}$  values average -25‰ in U2, then increase to -20‰ in U3 and remain stable at ca. -27‰ in U4 and U5 except for the 2.6-2.3m interval (-15‰) due to siderite concretions. C/N is high in U2 (ca. 40), and much lower in U3, U4 and U5. The siderite concretions are again responsible for high C/N in U4.

#### 4.4. Rock-Eval pyrolysis (Fig. 4)

The main occurrence of mineral carbon (Minc), reaching 2 to 3% is recorded at 2.3m depth and can be ascribed to siderite concretions. TOC varies from ca. 1% in the Pleistocene sands of unit U1, to ca. 15% at the base of unit U5. TOC values increase slightly from the base of U2 to reach 6-7 % at the top of this unit before decreasing to 5% at the U2/U3 limit, the boundary between sands and silts. Values then decrease from ca. 10 to 5% in U3 and increase again in the upper part of the unit U3 to reach more than 15% at 2.2m depth, before slightly decreasing again. From 1.4m towards the top, TOC finally stabilizes at 10%. Two levels at 2.1 and 1.8m depth have lower TOC values deviating from the general trend. In general, HI values range from 50 to 600 mg HC/g TOC. The lower half of the core exhibits relatively high HI values ranging from 200 to 755 mg HC/g TOC. After a strong decrease at 2.9m, HI values remain between 50 and 250 mg HC/g TOC in the organic silts of units U4 and U5. The generally low TpS2 values, all in the 385-472°C range (i.e. Tmax from ca. 345 to 432°C), are typical for immature OM (i.e. Tmax < 435°C, Espitalié *et al.*, 1985a). Extremely low Tps2 values (< 400°C) have been determined in some levels in U2 sands. Above this unit, TpS2 remains relatively constant around 470°C, before showing again marked variability in the 430-460°C range in U4. TpS2 values then decrease slightly from 460 to ca. 450°C towards the top of the core. OIRe6 values, that average 100 mg O<sub>2</sub>/g TOC in the lower part of the core, increase strongly at 2.9m to reach 400 mg O<sub>2</sub>/g TOC. Subsequently, the values of this index decrease linearly up to 1.7m depth, except for some levels around 2.3, 2.5 and 1.8m depth. Finally, OIRe6 increases towards the top of the core to reach a value of about 200 mg O<sub>2</sub>/g TOC.

### 5. Discussion

#### 5.1. Sediment fill

Sedimentological analyses supplemented by dating the boundaries of the different units of core 98-3, confirm that Lagoa do Caçó recorded an apparently continuous sedimentation from 19,860 to 5610 Cal yrs BP and, by extrapolation, until Present. If one excepts the lowermost

core unit of Pleistocene age sands (U1), the sediment fill can be divided into two main units of comparable length. The lower segment, which consists mainly of detritic sediments, sands (U2) and silts (U3), was deposited rapidly (ca. 1.15 mm/yr), at the end of the LGM. The upper section is fine-grained, deposited under lower sedimentation rates (ca. 0.2mm.yr<sup>-1</sup>), from Lateglacial times to Present. These low sedimentation rates result from limited inorganic input, which preferentially consists of authigenic and bio-induced minerals (goethite, siderite and amorphous silica) with an important organic contribution.

## 5.2. Abundance and quality of OM

The lithological and dynamic contrast between the lower and the upper portions of the core, reveals a major environmental change, also recorded by sedimentary OM. TOC values are always lower than 5% in U2 and U3, and much higher in U4 and U5. The distinction between the two major sections is even more pronounced when considering the  $\delta^{15}\text{N}$  and the Hydrogen Index (HI).  $\delta^{15}\text{N}$  values that first depend on the source of nitrogen used for biosynthesis (dissolved  $\text{NO}_3^-$  for phytoplankton and atmospheric  $\text{N}_2$  for land plants) can also be affected by diagenesis through bond rupture (Macko et al., 1993). Thus, the very high  $\delta^{15}\text{N}$  values (>10‰) found in units U2 and U3, can either be due to residual OM enriched in  $^{14}\text{N}$  by deamination or hydrolysis reactions (Macko et al., 1993) or to the assimilation of nitrates previously enriched in  $^{15}\text{N}$  by denitrification (as it might arrive for plants throwing in swampy environments; Muzuka, 1999). In contrast,  $\delta^{15}\text{N}$  values ranging from 3 to 5‰ in units U4 and U5 might indicate an assimilation of nitrates by plants, without any significant N-nitrate fractionation (Meyers and Lallier-Vergès, 1999). HI which represents the degree of OM hydrogenation first depends on the balance between phytoplanktonic (highly hydrogenated) and terrestrial contributions (e.g. Talbot and Livingstone, 1989), and second on the extent of biodegradation of the original material before burial (Espitalié et al., 1985a). HI values are greater than 250 mg HC/g TOC (and sometimes higher than 500 mg HC/g TOC) in sands and silts, but always smaller than this value in organic silts. This distinction between U2-U3 on one hand and U4-U5 on the other hand, corroborates that already established by  $\delta^{15}\text{N}$  values. Slightly lower C/N values in U4-U5 than in U2-U3 can be attributed to the preferential degradation of labile, higher plant, carbohydrates. The change in sedimentation is also recorded by OIR<sub>6</sub> which increases from values lower than 100 mg O<sub>2</sub>/g TOC in U2 and U3, towards 400 mg O<sub>2</sub>/g TOC at the U3/U4 limit. These shifts coincide with a significant lowering of TpS<sub>2</sub> that is not accompanied by any notable TOC change.

The HI values of 250-350 mgHC/g TOC recorded in U2 are typical of well preserved higher-plant OM, further supported by the presence of well recognisable higher plant debris

(sometimes more than 1cm long). In the absence of carbonates, rather high C/N values of 30 to 40 are also indicative of a good preservation of nitrogen-depleted biopolymers, like polysaccharides and lignin. Low TpS2 values (ca. 380°C) are also observed in several levels in this interval, typical of unaltered higher plant biopolymers usually present in high proportions in upper soil horizons (Disnar *et al.*, 2003). The saw tooth pattern of TpS2 values (between 380 and 460°C) is attributed to the heterogeneity of the samples and depends on the amount of well-preserved higher plant debris in the sample.

In U3 silts, HI values of up to 500 mg HC/g TOC can be tentatively explained by a higher contribution of planktonic or microbial OM. This explanation is consistent with lower C/N and  $\delta^{13}\text{C}$  values (−20‰) that effectively document a contribution of planktonic material, which is richer in hydrogen, nitrogen and heavy carbon isotope than C3 higher plants. A C4 higher plant contribution, shifting  $\delta^{13}\text{C}$  to more positive numbers in U3, can also be evoked. U3 silts also contain pyrite that indicates deposition and/or early diagenesis under reducing conditions.

The OIR<sub>6</sub> values recorded in the lower half of the core are consistent with those of well-preserved modern lacustrine OM, but exceptionally high values in U4 (exceeding 300mg O<sub>2</sub>/g TOC) are uncommon in recent lacustrine sediments and point to a highly oxidized OM. This is corroborated by the low HI values found in this unit (<200mg HC/g TOC). Covariant low HI and TOC values indicate extensive reworking during deposition and/or diagenesis. Furthermore, background values of about 1% of Minc recorded in the upper half-core appear to be an analytical artefact related to the presence of refractory OM which decomposes lately into CO and CO<sub>2</sub> during pyrolysis. The decrease of OIR<sub>6</sub> with increasing TOC towards the top of U4 could reflect better preservation. In U4 and U5 units, TOC and HI display similar trends, but opposite to OIR<sub>6</sub> (Fig. 4b). The presence of siderite at 2.2m depth is responsible for high Minc (Fig. 4) and OIR<sub>6</sub> values as a result of early decomposition of this carbonate during pyrolysis (Espitalié *et al.*, 1977). Three comparable siderite occurrences recorded in nearby cores (97-1 and 97-3) were interpreted as indicative of reducing conditions (Sifeddine *et al.*, 2001). TpS2 values, fluctuating between 430 and 460°C, coincide with high OIR<sub>6</sub> values and cannot be attributed to well-preserved higher plant OM as discussed above for U2 unit. In contrast, these fluctuations could be due to variable but extensive degradation of the OM in this unit. Because the S2 signals are of low intensity in U4, slight variations in the shape of peak S2 leads to exaggerated shifts of TpS2. Consistently, TpS2 fluctuations decrease upcore with decreasing OM degradation.

Finally, high TOC and HI values observed immediately after the siderite interval in U4 could mark an improvement in OM quantity and quality under more reducing conditions. The



last feature for unit U4 arise from petrographical investigations that indicate an increase of OD, probably resulting from an increase of forest fires.

In U5, OM appears homogeneous both from a quantitative and qualitative point of view. Only a slight decrease in TOC (15 to 10%) is recorded from the base of this unit to its top. HI values remain rather low (around 200mg HC/g TOC) but OIRe6 increases slightly. These features are consistent with the accumulation of moderately preserved type III OM and limited dilution by mineral input as presently occurring. Larger amounts of OD in U5 (up to 25%) than in U4 point to a net intensification of forest fires.

To summarize these results, the Rock-Eval data from core 98-3 have been plotted in the diagrams shown in Fig. 5. In a classical pseudo-Van Krevelen HI-OI diagram (Fig. 5-a), samples show a continuum between hydrogen-rich (represented by U2 and U3) and oxygen-rich end-members (U4 and U5). This diagram distinguishes three main types of OM (Espitalié *et al.*, 1977): (i) type I is attributed to a hydrogen-rich and oxygen-depleted lacustrine algal OM; (ii) type III is typical of an oxygen-rich and hydrogen-poor OM derived from lignin-rich parts of higher plants; (iii) intermediate type II corresponds to lacustrine or marine algal OM. In addition to these presumably pure materials, other (sub-) types arise from mixing of the above mentioned materials in various proportions and as a consequence of degradation upon sediment transport and/or deposition. For example, type IV OM corresponds to higher plant OM that suffered extensive oxidation therefore exhibiting very low HI and high OI values. There are exceptions to these rules. Surficial soil horizons can have HI consistent with type II OM (Disnar *et al.*, 2003). Hydrogen-rich epicuticular waxes of terrestrial plants can yield HI values similar to those of phytoplanktonic OM (Lüniger and Schwark, 2002). The distribution of core 98-3 samples, in a large part of the HI-OI diagram, therefore indicates both changes in the contribution of biological sources (phytoplanktonic and terrestrial) but mostly drastic changes in depositional conditions and early diagenesis of this OM. The distinction between the lower detritic units (U2 and U3) and the upper organic silts (U4 and U5) becomes more obvious when plotted in a  $S_2=f(\text{TOC})$  diagram. While U2 and U3 data display a good correlation between  $S_2$  and TOC, U5 and especially U4 ones always show lower  $S_2$  values than expected from the preceding correlation. A similar pattern has been interpreted by Langford and Blanc-Valleron (1990) as the reflection of a mineral matrix effect. This effect is enhanced for OM-poor samples and results from the ability that some minerals, like clays (e.g. illite), have to retain hydrocarbons during pyrolysis (Espitalié *et al.*, 1985b). This effect is negligible in our case because of the high TOC contents of the samples and the absence of active mineral species. Another notable difference between the upper and lower units is sensible in the  $S_3\text{CO}_2$  vs. TOC diagram (Fig. 5c). Similarly to the  $S_2$  vs TOC diagram, a good

correlation is observed between these two parameters for the U2 and U3 samples, whereas most of the U4 and U5 samples have unusually high S3CO<sub>2</sub> values with regard to TOC. The conclusion that can be drawn from these two diagrams is that, in contrast to U2 and U3 units, that contain a rather well preserved OM of predominant type III, the upper U4 and U5 units contain refractory OM, depleted in hydrogenated compounds and enriched in oxygenated constituents. The transition between the lower and upper parts of the core occurs in several successive stages, all recorded in U4. This transition apparently ends with the formation of siderite. The first drastic change is confined to no more than 4 samples (stage 1 in Figs. 4b-c) and corresponds to a rapid degradation of OM shown by a marked decrease of S2 (and TOC) and a S3CO<sub>2</sub> increase. The second stage is mainly characterized by a major increase of TOC reflecting increased organic input, with only a slight improvement in OM quality, as depicted by a slight increase of S2. If one excludes the peak of siderite recorded at 2.4m, the simultaneous upcore decrease of IORE6 and increase of TOC recorded in U4 (Fig. 4) indicate increasing preservation of the original organic input to the sediment. This interpretation is strengthened by higher HI values in the top unit samples than in those from the base. Input of a different OM, richer in compounds producing CO<sub>2</sub> upon pyrolysis but also poorer in S2 may account for this difference. This OM is probably of higher-plant origin and owe its refractory nature to the highly degrading conditions that existed during U4 deposition. The relative continuity of the TOC record at the U3/U4 transition is undoubtedly a coincidence, the dilution of the well-preserved OM by the mineral matrix in U3 being compensated by the considerable degradation of OM-rich input at the base of U4.

From a petrographical point of view and except for opaque debris, the distinction between the lower and upper sections is marked by the relative amounts of GelaOM and FlaOM. An organic fraction similar to GelaOM has been described in the Tritrivakely (Madagascar) peaty marsh and was attributed to sub-aerial degradation of herbaceous plant remains (Bourdon *et al.*, 2000). In addition, lacustrine sediment samples from the Siberia record (Bolivia) contain a similar reddish amorphous OM (Sifeddine *et al.*, 1998) of pedogenic origin. In contrast, FlaOM appears as a degradation product of higher plants under a relatively constant water depth (Bourdon *et al.*, 2000). Information from organic petrography can be summarized as follows: in the lower half core, organic constituents such as TLC, GelLC and GelaOM, document the degradation of higher plant remains in a palustrine context. In contrast, in the upper core interval, FlaOM documents sub-aquatic degradation of higher plant OM. An alternative explanation for such a distribution of plant remains could be different OM sources. For example, terrestrial higher plants with aerial vascular tissues could have lead to the formation of GelaOM associated with TLC and GelLC in the lower interval,

while dominant FLAOM might derive from soft submerged or emergent aquatic macrophytes (e.g. *Juncus sp.*). Nevertheless, these two hypotheses on the respective origin of the amorphous fractions lead to identical paleoenvironmental interpretations. With reference to the discussion on the interpretation of Rock Eval parameters, the submerged/emergent origin and/or degradation of higher plants could be partly responsible for the high IOR<sub>6</sub> and weak HI recorded in the upper interval (U4-U5).

### 5.3. Paleoenvironmental implications

#### 5.3.1. Phase I (19,860 to 19,240 Cal yrs BP): unit U2

This phase is characterized by the rapid sedimentation of coarse-grain sediment with well-preserved and dispersed ligno-cellulosic OM. The relative abundance and good preservation of this material, which comprises numerous centimetre-size plant remains, imply short transport distances. The OM would thus originate from higher plants that grew within the basin or in its immediate vicinity. However, the local plant cover was sparse enough to allow mobilisation of sands. A semi-arid environment is supposed to have prevailed at the end of the LGM in the study area (Ledru *et al.*, 2001; 2002). River flow might have been temporarily fed by sporadic and heavy precipitation. The good preservation of the OM may thus result from rapid burial as well as the persistence of standing water in a swampy depression where fluvial sediments accumulated. During the same period, at the end of the LGM, several other South American sites also recorded comparable detritic intervals reflecting the erosion in the catchment areas (Turcq *et al.*, 1997; 2002). The authors concluded that these deposits were formed under the influence of severe but scarce rainfall events while the vegetation had not yet stabilized soils.

#### 5.3.2. Phase II (19,240 to 17,250 Cal yrs BP): unit U3

The deposition of silts (U3) may indicate the occurrence of erosive rainfall in a landscape with denser vegetation and soil development. A more humid climate and a more pronounced seasonality than during the previous period have probably favoured these environmental changes. The presence of notable proportions of kaolinite in unit U3 could point to an effective soil development, unless this mineral originates from the erosion/weathering of the Pleistocene substratum. The hypothesis of a more pronounced seasonality seems corroborated by sediment laminations, expressing depositional rhythmicity (Sifeddine *et al.*, 2003). The top of unit U3 is also characterized by higher HI and  $\delta^{13}\text{C}$  values and amorphous silica content. These features are consistent with a higher contribution of the phytoplanktonic biomass in a

perennial lake resulting from regionally wetter conditions than those that prevailed during the preceding phase.

These interpretations on phases I and II are in good agreement with palynological data showing sparse and residual vegetation at the end of the LGM (Ledru *et al.*, 2002). Our results are also consistent with Stute *et al.* (1995) who hypothesized that the LGM was cooler but also more arid than presently, as demonstrated by the partial replacement of the Amazonian rainforest by savanna (van der Hammen and Absy, 1994; Colinvaux *et al.*, 1996). Few records of sedimentary lacustrine deposits support our assumptions. As a matter of fact, during LGM, sedimentary records often display hiatuses due to dessication or intense subsequent erosion (Ledru *et al.*, 1998). In contrast to other lacustrine records, Lagoa do Caçó appears to have recorded these erosive episodes, at least in core 98-3. Nevertheless, the remaining questions on the environmental setting during the deposition of U2 and most of U3 do not allow determining the true lacustrine nature of the basin.

#### 5.3.3. Phase III (17,250 to 11,200 Cal yrs BP): unit U4

The major change in the detritic input and in the sedimentary regime that intervenes at mid-core, points to a major modification of the local environmental conditions. These changes most likely became close to those that still prevail at present, i.e. an oligotrophic lake where the primary production is mostly confined to margins. The drastic lowering of the mineral input to the sediment suggests a stabilization of the surrounding soils, thus restricting aeolian erosion and river input transport. Apparently, the lateral and tributary-controlled mineral fluxes became very limited or even hindered by the *Juncus sp.* belt around the lake and by the floating meadow that developed upstream. If the mechanisms leading to the oxygen-rich organic matter that accumulated during much of this time interval remain unclear, the data indicate oxidising conditions due to the mixing of waters by the trade winds. As demonstrated by the presence of siderite at one level and by repeated TpS2 fluctuations, reducing conditions might have occurred from time to time, possibly caused by abrupt climatic changes. From this point of view, core 98-3 appears less responsive than core 97-1, drilled downstream in shallower waters, where siderite is recorded in three levels in unit U4 (Sifeddine *et al.*, 2003). Palynological results on the lake sediment filling (Ledru *et al.*, 2001; 2002) reveal that a rapid reforestation occurred around 14,000 <sup>14</sup>C yrs BP, at the level where the sedimentary change occurs. The development of the plant cover is suggested by the presence and expansion of gallery forest taxa, representative of cooler and more humid climates than at present. These observations are also consistent with marine data showing a phase that is considered the most humid phase in the area since LGM, between 15,500 and 11,800 <sup>14</sup>C yrs BP (Behling *et al.*,

2000). A subsequent important change that occurred between 11,000 and 10,000  $^{14}\text{C}$  yrs BP lead to the decline of humid forests, the expansion of savannas and the increase of fires (Ledru *et al.*, 2001).

#### 5.3.4. Phase IV (11,200 to 5610 Cal yrs BP): unit U5

Similar to the preceding unit, this latter phase is characterized by very low sedimentation rates that indicate efficient filtering of mineral input by the belt of rushes and by the floating meadow. In addition, the surrounding dense vegetation (cerrado/cerradao; i.e. shrub and woody savannas) prevents erosion. In this context, the sediment only consists of degraded and refractory OM with some biogenic minerals namely, silica from sponge spicules and diatom valves. The decrease of OM contents and quality from 2 to 1m depth, is probably due to a lateral migration of the macrophyte belt in response to water level rise. This rise would result from an increase distance between the OM production and the deposition centre, with a subsequent increase of the residence time of the OM in oxygenated water column. In contrast, the slight increase in TOC recorded above 1m could reflect progradation and aggradation of the *Juncus sp.* belt. The substantial increase of charcoal-like OD particles in this interval indicates an intensification of forest fires after 11,200 Cal yrs B.P. In unit U5, the deposition of the sediments in the center of a permanent lake, under relatively deep water, could have substantially buffered the sensitivity to paleoenvironmental changes, under a relative climatic stability during the Holocene.

## 6. Conclusions

Our study of Lagoa do Caçó sediments allowed to complement earlier paleoenvironmental findings (Ledru *et al.*, 2001; 2002; Sifeddine *et al.*, 2003) through a better understanding of depositional conditions and related environmental changes. From the sedimentary OM data, we could distinguish at least four major climatic phases since the end of the LGM: (i) phase I: arid or semi-arid climate with strong but episodic rainfall. The precipitation allowed the development of ephemeral vegetation in the depression. Plant remains were rapidly buried and preserved under sands eroded from a poorly vegetated landscape; (ii) phase II: generally more humid conditions which favoured the development of a dense plant cover and soils, and the formation of a permanent lake; (iii) phase III: after a drastic environmental and climatic change, lake sediments indicate abrupt climatic events evolving towards conditions approaching those prevailing today; (iv) phase IV: environmental and depositional conditions appear more stable and similar to present. In its deepest part, the lake did not record any notable change during the Holocene.

In addition to these paleoenvironmental conclusions, other aspects arise from the OM composition in this lacustrine setting. The detritic units (U2 and U3) contain scarce but well preserved OM, unexpected in such deposits. This contrasts with strongly reworked OM deposited at the beginning of Lateglacial times (U4 and U5) after a longer residence time in a highly-oxygenated water column. Lagoa do Caçó therefore exhibits a peculiar OM lacustrine record consisting exclusively of higher-plant remains, where conventional geochemical parameters based on autochthonous versus terrestrial OM cannot be applied.

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### **References**

- Behling, H., Arz, H. W., Pätzold, J. and Wefer, G., 2000. Late Quaternary vegetational and climate dynamics in northeastern Brazil, inferences from marine core GeoB 3104-1. *Quat. Sci. Rev.* 19, 981-994.
- Bourdon, S. Laggoun-Défarge, F., Disnar, J.R., Maman, O., Guillet, B., Derenne, S. and Largeau, C., 2000. Organic matter sources and early diagenetic degradation in a tropical peaty marsh (Tritrivakely, Madagascar). Implications for environmental reconstruction during the Sub-Atlantic. *Org. Geochem.* 31, 421-438.
- Colinvaux, P.A., de Oliveira, P.E., Moreno, J.E., Miller, M.C. and Bush, M.C., 1996. A long pollen record from lowland Amazonia: forest cooling in glacial times. *Science* 274, 85-88.
- Disnar, J. R., Guillet, B., Kéravis, D., Di-Giovanni, C. and Sebag, D., 2003. Soil organic matter (SOM) characterisation by Rock-Eval pyrolysis: scope and limitations. *Org. Geochem.* 34, 327-343.
- Espitalié, J., Laporte, J.L., Madec, M., Marquis, F., Leplat, P., Paulet, J., Boutefeu, A., 1977. Méthode rapide de caractérisation des roches mères, de leur potentiel pétrolier et de leur degré d'évolution. *Rev. Inst. Fr. Pét.* 32/1, 23-42.
- Espitalié, J., Deroo, G., Marquis, F., 1985a. La pyrolyse Rock-Eval et ses applications; première partie. *Rev. Inst. Fr. Pét.* 40, 563-579.

- Espitalié, J., Deroo, G., Marquis, F., 1985b. La pyrolyse Rock-Eval et ses applications; deuxième partie. *Rev. Inst. Fr. Pét.* 40, 755-784.
- Ficken, K.J., Street-Perrott F.A., Perrott, R.A., Swain, D.L., Olago, D.O. and Eglinton, G., 1998. Glacial/interglacial variations in carbon cycling revealed by molecular and isotope stratigraphy of Lake Nkunga, Mt. Kenya, East Africa. *Org. Geochem.* 29/5-7, 1701-1719.
- Huang, Y., Street-Perrott, F.A., Perrott, R.A., Metzger, P. and Eglinton, G., 1999. Glacial-interglacial environmental changes inferred from molecular and compound-specific  $\delta^{13}\text{C}$  analyses of sediments from Sacred Lake, Mt. Kenya - Examples from Antarctic lakes. *Geochim. et Cosmochim. Acta* 63/9, 1383-1400.
- Lafargue, E., Marquis, F., Pillot, D., 1998. Rock-Eval 6 applications in hydrocarbon exploration, production, and soil contamination studies. *Rev. Inst. Fr. Pét.* 53/4, 421– 437.
- Lallier-Vergès, E., Sifeddine, A., Beaulieu, J.L. de, Reille, M., Tribovillard, N., Bertrand, P., Mongenot, T., Thouveny, N., Disnar, J.R. and Guillet, B., 1993. Sensibilité de la sédimentation organique aux variations climatiques du Tardi-Würm et de l'Holocène – Lac du Bouchet (Haute Loire, France). *Bull. Soc. Géol. Fr.* 164, 661-673.
- Langford, F.F. and Blanc-Valleron, M.M., 1990. Interpreting Rock-Eval pyrolysis data using graphs of pyrolysable hydrocarbons vs. total organic carbon. *AAPG Bull.* 74, 799-804.
- Ledru, M.P., Bertaux, J., Sifeddine, A. and Suguio, K., 1998. Absence of last glacial maximum record in lowland tropical forest. *Quat. Res.* 49, 233-237.
- Ledru, M.P., Cordeiro, R.C., Dominguez, J.M.L, Martin, L., Mourguiart, P., Sifeddine, A. and Turcq, B., 2001. Late-glacial cooling in Amazonia as inferred from pollen at Lagoa do Caçó, Northern Brazil. *Quat. Res.* 55, 47-56.
- Ledru, M.P., Mourguiart, P., Ceccantini, G., Turcq, B. and Sifeddine, A., 2002. Tropical climates in the game of two hemispheres revealed by abrupt climatic change. *Geology* 30/3, 275-278.
- Lüniger, G. and Schwark, L., 2002. Characterisation of sedimentary organic matter by bulk and molecular geochemical proxies: an example from an Oligocene maar-type Lake Enspel, Germany. *Sed. Geol.* 148, 275-288.
- Macko, S. A., Engel, M. H. and Parker, P. L., 1993. Early diagenesis of organic matter in sediments. Assessment of mechanisms and preservation by the use of isotopic molecular approaches. In: Engel, M. H. and Macko, S. A. (Eds.), *Organic Geochemistry. Principles and applications*. Plenum Press, New York, pp. 211-224.
- Muzuka, A. N. N., 1999. Isotopic compositions of tropical East African flora and their potential as source indicators of organic matter in coastal marine sediments. *J. African Earth Sci.* 26, 757-766.

- Manalt, F., Beck, C., Disnar, J.R., Deconninck, J.-F. and Recourt, P., 2001. Evolution of clay mineral assemblages and organic matter in the Lateglacial-Holocene sedimentary infill of Lake Annecy (Northwestern Alps): paleoenvironmental implications. *J. Paleolim.* 25, 179-192.
- Martin, L., Flexor, J.M. and Suguio, K., 1995. Vibrotestemunhador leve. Construção, utilização e potencialidades. *Rev. IG. Sao Paulo*, 16, 59-66.
- Meyers, P.A. and Lallier-Vergès, E., 1999. Lacustrine sedimentary organic matter records of Late Quaternary paleoclimates. *J. Paleolim.* 21, 345-372.
- Noël, H., 2002. Caractérisation et calibration des flux organiques sédimentaires dérivant du bassin versant et de la production aquatique (Annecy, le Petit Lac) – Rôles respectifs de l'Homme et du Climat sur l'évolution des flux organiques au cours des 6000 dernières années. PhD dissertation. University of Orléans, France. pp. 273. [http://tel.ccsd.cnrs.fr/documents/archives0/00/00/16/35/index\\_fr.html](http://tel.ccsd.cnrs.fr/documents/archives0/00/00/16/35/index_fr.html)
- Sifeddine, A., Bertrand, Ph., Lallier-Vergès, E. and Patience, A., 1996. The relationships between lacustrine organic sedimentation and palaeoclimatic variations. Lac du Bouchet, Massif Central, France. *Quat. Sci. Rev.* 15, 203-211.
- Sifeddine, A., Bertaux, J., Mourguiart, Ph., Disnar, J.R. and Laggoun-Défarge, F., 1998. Etude de la sédimentation lacustre d'un site de forêt d'altitude des Andes centrales (Bolivie). Implications Paléoclimatiques. *Bull. Soc. Géol. Fr.* 169, 395-402.
- Sifeddine, A., Martin, L., Turcq, B., Volkmer-Ribeiro, C., Soubiès, F., Campello Cordeiro, R. and Suguio, K., 2001. Variations of the Amazonian rainforest environment: a sedimentological record covering 30,000 years. *Palaeogeogr., Palaeoclimatol., Palaeoecol.* 168, 221-235.
- Sifeddine, A., Albuquerque, A.L.S., Ledru, M-P., Turcq, B., Knoppers, B., Martin, L., Zamboni de Mello, W., Passenau, H., Landim Dominguez, J.M., Campello Cordeiro, R., Abrao, J.J. and Carlos da Silva Pinto Bittencourt, A.C., 2003. A 21000 cal years paleoclimatic record from Caçó Lake, northern Brazil: evidence from sedimentary and pollen analyses. *Palaeogeogr., Palaeoclimatol., Palaeoecol.* 189, 25-34.
- Street-Perrott, F.A., Huang, Y., Perrott, R.A., Eglinton, G., Barker, P., Ben Khelifa, L., Harkness, D.D. and Olago, D.O., 1997. Impact of lower atmospheric carbon dioxide on tropical mountain ecosystems. *Science* 278, 1422-1426.
- Stuiver, M. and Reimer, P.J., 1993. Extended  $^{14}\text{C}$  database and revised CALIB 3.0.  $^{14}\text{C}$  age calibration program. *Radiocarbon* 35, 215-230.
- Stuiver, M., Reimer, P.J. and Braziunas, T.F., 1998. High-precision radiocarbon age calibration for terrestrial and marine samples. *Radiocarbon* 40, 1127-1151.

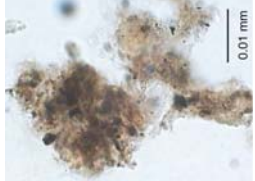
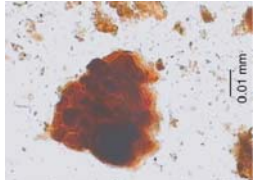


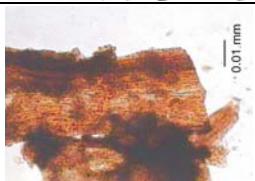

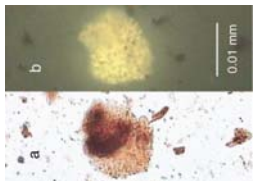


- Stute, M., Forster, M., Frischkorn, H., Serejo, A., Clark, J.F., Schlosser, P., Broecker, W.S. and Bonani, G., 1995. Cooling of tropical Brazil (5 °C) during the last glacial maximum. *Science* 269, 379-383.
- Talbot, M.R. and Livingstone, D.A., 1989. Hydrogen index and carbon isotopes of lacustrine organic matter as lake level indicators. *Pal. Pal. Pal.* 70, 121-137.
- Thompson, L.G., Mosely-Thompson, E., Davis, M.E., Lin, P.-E., Henderson, K.A., Cole-Dai, B., Liu, K.B., 1995. Late glacial stage and Holocene tropical ice core records from Huascaren, Peru. *Science* 269, 46-50.
- Turcq, B., Pressinnoti, M.M.N. & Martin, L., 1997. Paleohydrology and paleoclimate of the past 33,000 years at the Tamandua River, Central Brazil. *Quat. Res.* 47, 284-294.
- Turcq, B., Cordeiro, R.C., Sifeddine, A. Simoes Filho, F.F. Abrao, J.J., Oliveira, F.B.O., Silva, A.O., Capitaneo, J.L. and Lima, F.A K, 2002. Carbon storage in Amazonia during the LGM: data and uncertainties. *Chemosphere* 49, 821-835.
- van der Hammen, T. and Absy, M.L., 1994. Amazonia during the last glacial. *Palaeogeogr., Palaeoclimatol., Palaeoecol.* 109, 247-261.
- Volkmer-Ribeiro, C. 2002. pers. comm.

Table 1: Radiocarbon ages from Lagoa do Caçó sediments.

Code	Sample	Measured ages <sup>14</sup> C yrs BP	<sup>13</sup> C/ <sup>12</sup> C	Conventionnal ages <sup>14</sup> C BP	Calibrated ages yrs BP	Intercept Yrs BP
Beta - 162661	MA98/3/73-75	4930±50	-27.2 ‰	4890±50	5720 to 5580	5610
Beta - 162662	MA98/3/196-198	9850±70	-28.9 ‰	9790±70	11270 to 11120	11200
Beta - 162663	MA98/3/286-288	14450±80	-27.8 ‰	14400±80	17680 to 16830	17250
Beta - 162664	MA98/3/354-356	15620±80	-19.9 ‰	15700±80	19230 to 18290	18750
Beta - 162665	MA98/3/426-428	16100±80	-22.9 ‰	16130±80	19740 to 18770	19240
Beta - 162666	MA98/3/574-576	16670±100	-24.3 ‰	16670±100	20410 to 19330	19860

Table 2: Description of the main organic classes identified in the palynofacies of Lagoa do Caçó sediments.

Type of organic constituent	Abbreviation	Illustration	Description - main features	Possible origin	Main depositional environment
Flaky Amorphous OM	FlAOM		Diffuse edge - heterogeneous texture	Submerged or emergent higher plants	Lacustrine
Gelified Amorphous OM	GelAOM		Sharp edges - homogeneous texture	Terrestrial higher plants	Palustrine
Translucent Ligno-Cellulosic debris	TrLC		Vascular structures still present - translucent texture	Higher plants	Paludal  Increasing degradation
Amorphized Ligno-Cellulosic debris	AmLC		Progressive destruction of biological structures	Higher plants	
Gelified Ligno-Cellulosic debris	GelLC		Phytoclast morphology - homogeneous texture	Higher plants	
Opaque debris	OD		Opaque up to edge - ± biostructures - devolatilisation features	Higher plants	Allochthonous: - aerial degradation - fossil OM - charcoal
Algal OM	Alg		a- algal micro-colonies - b- fluorescent under U.V excitation	Phyto-planctonic	Essentially lacustrine

**Figure captions :**

Figure 1: Map of study area with location of coring sites.

Figure 2: Core 98-3 with radiocarbon chronology and results from organic petrography. a- chronology, showing  $^{14}\text{C}$  conventional and calibrated (cal yr BP) ages; b-proportions of organic constituents in the palynofacies.

Figure 3: Bulk organic geochemistry ( $\delta^{15}\text{N}$ ,  $\delta^{13}\text{C}$  and C/N) along core 98-4.

Figure 4: a- Downcore variations of OM abundance and composition deduced from RockEval analyses (core 98-3); b- Evolution of TOC, HI and IORE6 (values inverted) in the upper section of core 98-3.

Figure 5: Correlation of Rock-Eval parameters. a-  $\text{IH}=\text{f}(\text{IORe6})$ ; Pseudo Van Krevelen diagram; b-  $\text{S2}=\text{f}(\text{TOC})$ ; c-  $\text{S3CO}_2=\text{f}(\text{TOC})$ .

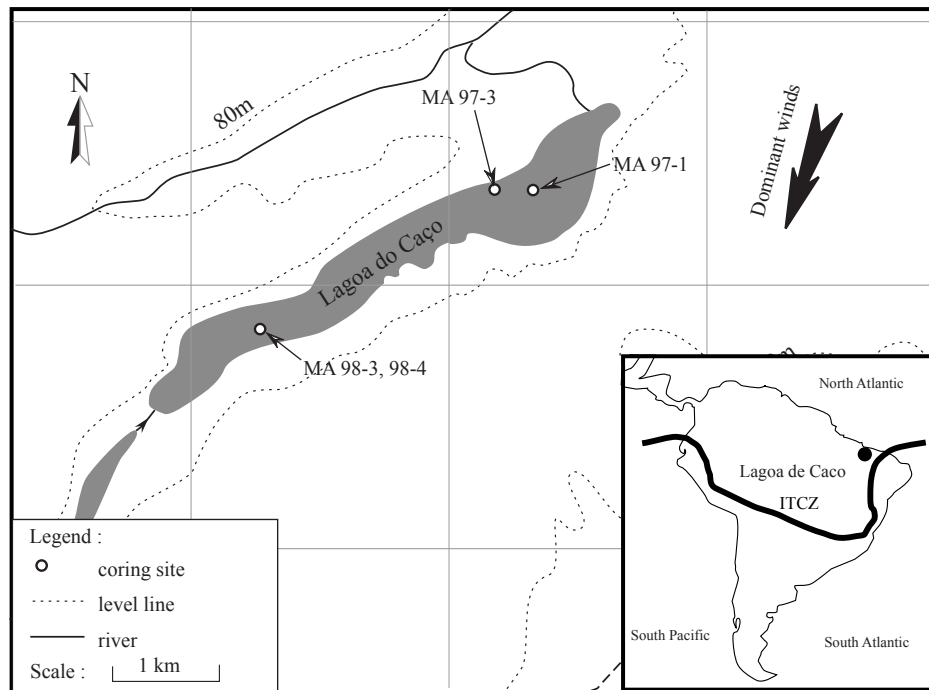


Figure 1: Map of study area with indication of coring sites.

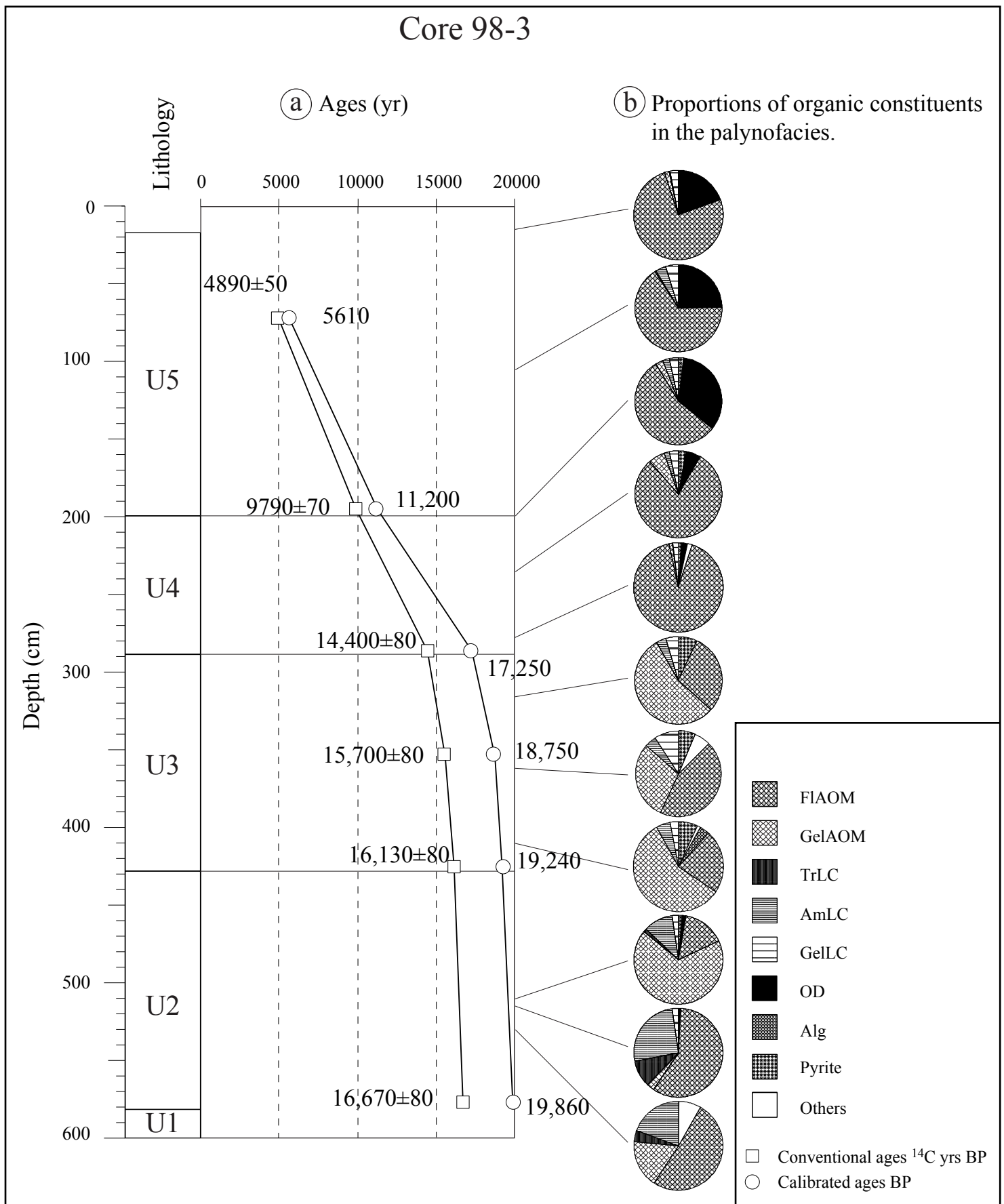


Figure 2: Core 98-3 with radiocarbon chronology and results from organic petrography.

a- Chronology, showing  $^{14}\text{C}$  conventional and calibrated (cal yr BP) ages.

b- Proportions of organic constituents in the palynofacies.

Abbreviations: FIAOM: Flaky Amorphous OM, GelAOM: Gelified Amorphous OM, TrLC: Translucent Ligno-Cellulosic debris, AmLC: Amorphous Ligno-Cellulosic debris, GelLC: Gelified Ligno-Cellulosic debris, OD: Opaque debris, Alg: Algae, Pyrite, Others: spores, pollens, zooclasts.

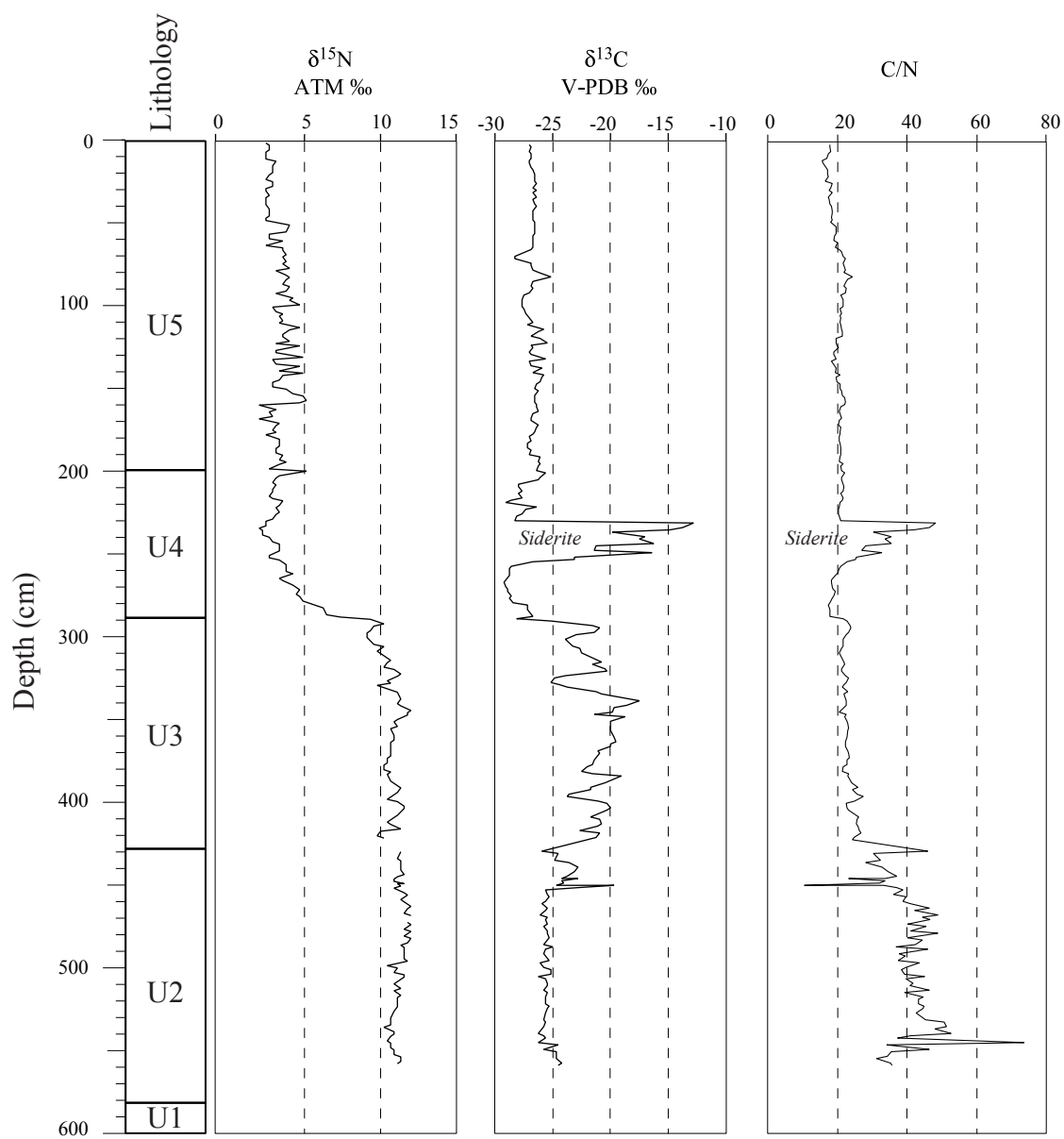
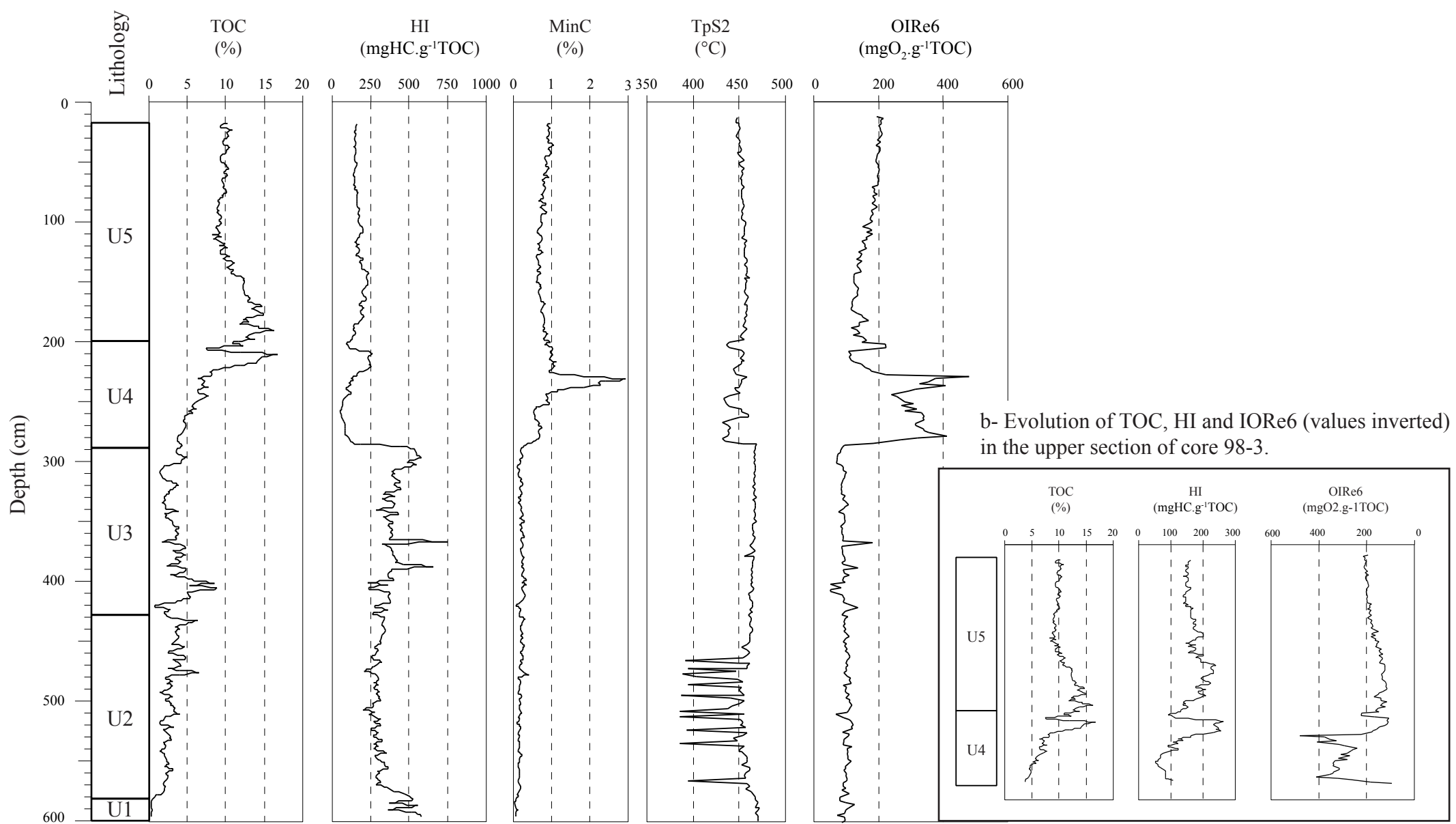


Figure 3: Bulk organic geochemistry (δ<sup>15</sup>N, δ<sup>13</sup>C and C/N) along core 98-4.

Figure 4: a- Downcore variation of OM composition extracted from RockEval analyses (core 98-3).





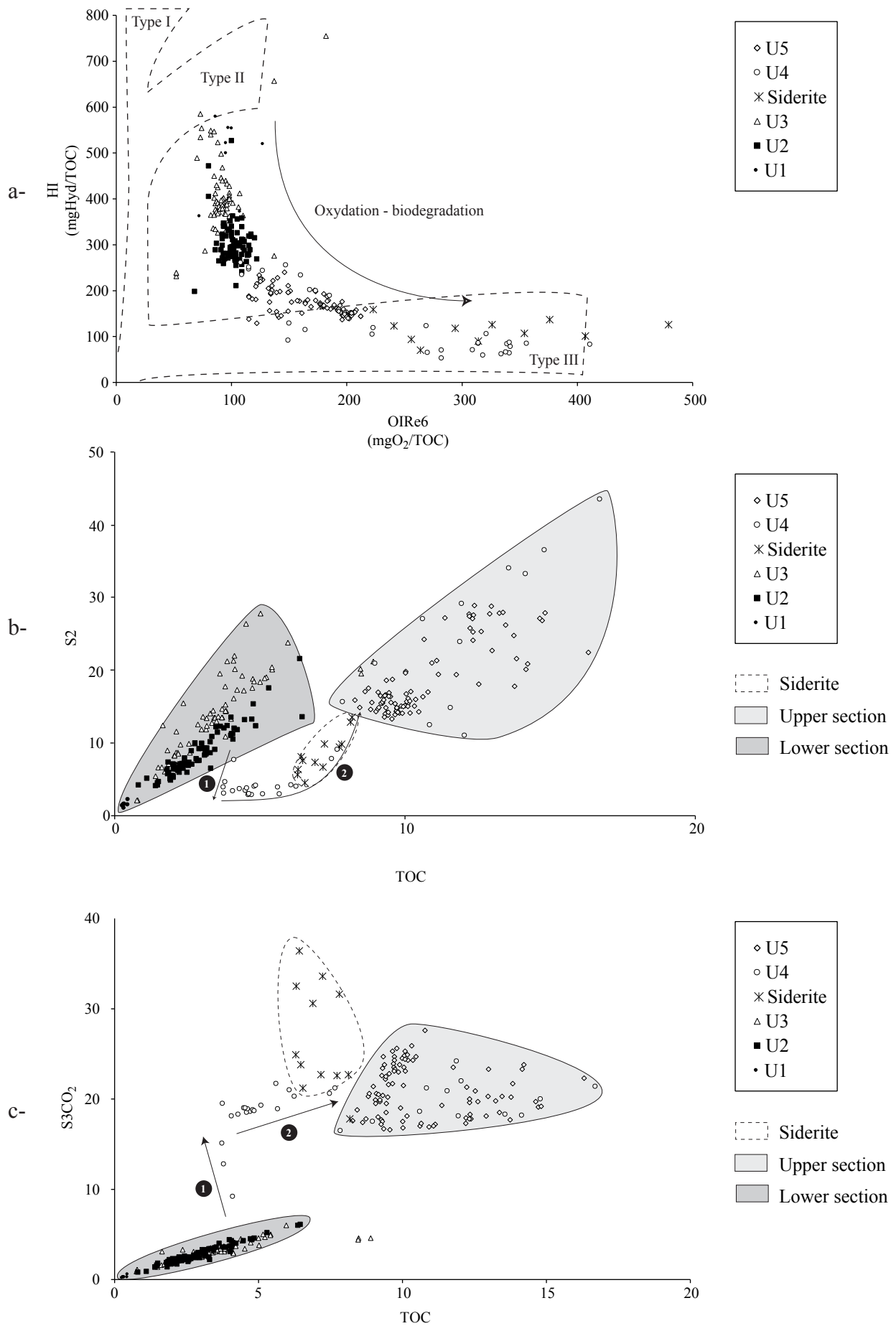


Figure 5: Correlation of Rock-Eval parameters:  
 □ a-  $IH=f(OIRe6)$ ; Pseudo Van Krevelen diagram,  
 □ b-  $S_2=f(TOC)$ ,  
 □ c-  $S_3CO_2=f(TOC)$ .