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Onocerane testifies to dry climatic events during the Quaternary in the Tropics

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Abstract

An unusual molecular fossil (onocerane I) has been detected for the first time in Quaternary lacustrine sediments (Lagoa do Caçó, NE Brazil). This molecule was initially thought to attest to the former presence of ferns or club mosses. According to possible plant precursors of onocerane-related molecules recorded in the literature and by comparison with palynological results and palaeoclimatic data, we here provide evidence that club mosses and ferns cannot account as sources of onocerane I in this setting. Onocerane I is abundant in the lipid extracts of sediments deposited during the two driest periods recorded in Northern Brazil (Last Glacial Maximum and Younger Dryas). This molecule is therefore suspected to be diagnostic of the development of plants adapted to dry or semi-arid conditions in this region.

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1. Introduction

The interpretation of terrestrial biomarker fingerprints in sediments is highly dependent on our understanding of present day plant-molecule relationships. Intensive research of new molecules in living plants has greatly contributed to our knowledge of the taxonomical and ecological significance of fossil molecules. Nevertheless, despite the large amount of presently available data, uncertainties remain about the significance of some molecules. Therefore, there is a crucial need to more closely relate these molecules to their living precursors by calibration with recent sedimentary series.

The present work was carried out in the framework of a multidisciplinary research project conducted on Lagoa do Caçó (a small oligotrophic lake located in Northern Brazil, Fig. 1) and its surroundings, in order to detect paleoenvironmental changes that affected the area during the Late Quaternary (Ledru et al., 2001; 2002; Sifeddine et al., 2003; Jacob et al., accepted). This scientific context is highly relevant to terrestrial biomarker studies since the sedimentary organic matter mostly consists of higher plant remains (Jacob et al., accepted). Indeed, several methyl ethers of pentacyclic triterpenes with oleanane, ursane, taraxerane, fernane and arborane structures have been identified in the lake sediments (Jacob et al., 2002). Here we compare the variations of onocerane I abundance along a 6m core covering a 20,000 yrs record with independent results (especially palynology) and discuss the possible plant precursors of this compound as well as the paleoenvironmental significance of its occurrence.

2. Experimental

2.1. Sample handling

Core 98-3 (6m long) was collected with a vibra-corer (Martin et al., 1995) under 12m of water, in the deepest part of the lake in the southernmost basin (Fig. 1). Core 97-1 (3m long) was drilled with the same method as described above in the northern sub-basin of the

lake (Fig. 1) and has been the subject of previous publications (Ledru et al., 2001; 2002; Sifeddine et al., 2003).

2.2. Chronology

Six radiocarbon ages have been measured within the core 98-3 by acceleration mass spectrometry (AMS) at the Beta Analytic Laboratory and at the University of Arizona Tucson Laboratory, USA. Radiocarbon ages younger than 18,000 yrs B.P. were calibrated using the intercept of the mean of conventional ages with the calibration curve of ^{14}C (CALIB version 4.3; Stuiver et al., 1998). These data are summarized in Table 1.

2.3. Palynology

Pollen determinations in core 97-1 are according to Ledru (1993). The detailed methodology for pollen analysis is described in Ledru et al. (2001). Except for data on Ferns and Lycophyta spores which were not previously published, pollen results have been published in Ledru et al. (2001, 2002) and Sifeddine et al. (2003). Detailed pollen countings are available on the Latin American Pollen Database website (www.ngdc.noaa.gov/paleo/lapd.html).

2.4. Extraction and separation of free lipids

Twenty two samples were selected from core 98-3 for detailed lipid analyses, following preliminary screening by Rock-Eval6 (RE6) of 300 regularly spaced samples (Jacob et al., accepted). One gram of dried sediment was ultrasonically extracted with acetone-pentane 1:1. The mixture was then separated according to the procedure described by Logan and Eglinton (1994). The neutral and acidic fractions were separated by Solid Phase Extraction (SPE) using AminoPropyl Bond Elute© cartridges with DCM-MeOH (1:1) for the

elution of neutrals and acetic acid and ether for acidic compounds. The neutral fraction was then submitted to further fractionation on activated Florisil® to yield (i) aliphatic hydrocarbons (eluted with heptane), (ii) aromatic hydrocarbons and methyl ethers (DCM) and (iii) polar compounds (DCM-MeOH). 5α-Cholestane was added as an internal standard prior to analysis by gas chromatography/mass spectrometry.

2.5. Gas chromatography/Mass spectrometry

Analyses were performed on a Thermofinnigan TRACE-GCQ gas chromatograph-mass spectrometer (GC-MS). The gas chromatograph was fitted with a Rtx®-5Sil MS capillary column (30m x 0.32 mm i.d., 0.25µm film) with 5m of guard column. The injector was set at 280°C and helium was the carrier gas. The temperature program used was 1 min isothermal at 40°C, then 40-120°C at 30°C.min^{-1}, 120-300°C at 3°C.min^{-1} and finally 30min hold at 300°C. The mass spectrometer was operated in the electron ionisation (EI) mode on a m/z 50-650 amu range with a scan time of 0.55s and an electron energy of 70eV. Onocerane I was identified by comparison with published mass spectra and relative retention times. We further certified the identification of onocerane I by comparison with a sample of Nigerian oil that has been proven to contain onocerane I (sample DA14, Pearson and Obaje, 1999) (see paragraph 3.1.).

In order to avoid any co-elution, onocerane I relative abundance was determined by comparison of the peak area of onocerane I on the m/z 123+191 mass chromatogram with the peak area of 5α-cholestane (internal standard) on the Total Ion Current (TIC).

3. Results

3.1. Identification of onocerane I

On the m/z 191 mass chromatogram of sample 254 (520cm), onocerane I elutes at 56.82min under our chromatographic conditions, between $C_{29}\alpha\beta$ and $C_{29}\beta\alpha$ hopanes (Fig. 2). This is in agreement with previous observations (Pearson and Obaje, 1999) on the elution position of onocerane I. This compound displays mass spectroscopic features that are also consistent with an onocerane I structure: (i) a molecular ion M^+ 414; (ii) a base peak at m/z 123; (iii) another important fragment at m/z 191 (Fig. 3a). This fragmentation pattern is encountered in onoceranes (8,14-seco-gammaceranes) where breaking of the C(9)-C(11) or C(12)-C(13) bonds produces fragments of m/z 191, whereas the ion at m/z 123 results from the rupture of bonds C(9)-C(10) and C(5)-C(6) or C(13)-C(18) and C(16)-C(17) (Fig. 3b). Five-membered E-ring triterpenoids (hopanes, lupanes, fernanes, arboranes, adiananes) with the 8,14-seco structure can display similar fragmentation patterns (Schmitter et al., 1982). However, the lack of an ion at m/z 371 in the mass spectrum of the considered compound excludes the presence of any isopropyl group and hence any of the latter structures. Three onocerane isomers have been reported previously (Kimble et al., 1974). Structural changes between these compounds occur at positions C(8) and C(14). The compounds labelled onoceranes I, II and III have the configuration 8β(H),14α(H), 8α(H),14α(H) and 8α(H),14β(H), respectively. The relative abundances of ions m/z 191 and m/z 193 are diagnostic of this isomerism (Henderson et al., 1969; Kimble et al., 1974). In onocerane I, m/z 191 is far more abundant than m/z 193, in good agreement with the mass spectrum of the compound eluting at 56.82min in our GC/MS analysis. Finally, comparison of the retention time of this compound with that of onocerane I previously identified within a Nigerian oil sample (Fig. 2, sample DA14; Pearson and Obaje, 1999) and comparison of the mass spectra further confirm this identification.

3.2. Sedimentology and organic matter composition

Five main sedimentary units, labelled U1 to U5 from bottom to top, have been described in the core 98-3 (Jacob et al., accepted). Unit U1 corresponds to the Pleistocene sandy substratum and will not be discussed further. Units U2 and U3 (ca. 1.5m thick each), which consist of fine sands and silts (quartz and kaolinite), respectively, were deposited rapidly at the end of the Last Glacial Maximum (LGM). The two uppermost units U4 and U5, made up of brownish and black organic silts, respectively, exhibit lower sedimentation rates. This is consistent with a mineral input restricted to authigenic minerals (goethite and siderite) and biogenic silica, in these two latter units. Combination of Rock-Eval pyrolysis, palynofacies, bulk and isotopic analyses (C/N, $\delta^{13}C$ and ^{15}N) allowed us to attribute a highly predominant higher plant origin to the OM of the entire section of the core (Jacob et al., accepted). Only unit U3 could contain small amounts of phytoplanktonic OM. Concerning the preservation of the OM, units U2 and U3 are composed of well-preserved OM as a consequence of the rapid burial of higher plant remains. Conversely, units U4 and U5 contain degraded OM that suffered strong reworking in highly oxygenated waters.

The sedimentological, geochemical and palynological results obtained on core 97-1 have been published elsewhere (Ledru et al., 2001; 2002; Sifeddine et al., 2003) and will not be further discussed here. In this core, the marked transition from clastic material to organic silts is also recorded, around 14,000 ^{14}C yrs B.P.

3.3. Quantitation of onocerane I

The variation in the relative abundance of onocerane I down core 98-3 is shown in Figure 4. The highest amounts of this compound are found between 580 and 430cm in the bottom sandy unit (U2). The abundance of onocerane then decreases upcore before increasing again in the organic silts (U4), between 230 and 200cm depth.

4. Discussion

4.1. Onocerane in sediments

Compared to other terrestrial biomarkers (oleanane, ursane, lupane), onoceranes are among the most uncommon biomarkers in the sedimentary record. Since the first description of three onocerane isomers (I, II, III; Kimble et al., 1974) there have only been few reported examples of these molecules in the sedimentary record. Figure 5 illustrates the preceding reports of onocerane-type molecules in the geological record. Onoceranes II and III have been reported back to the Carboniferous (Tieguan et al., 1988), in association with serratanoids. As demonstrated by Tsuda et al. (1964), onoceranes II and III can be produced by isomerisation of serratane-type compounds (serratandiols), these latter compounds being exclusively produced by ferns. Therefore, the occurrence of onocerane II and III in rocks and oils older than the Upper Cretaceous can be attributed to ferns via serratane-type molecules. In contrast, onocerane I has only been reported in Upper Cretaceous (Tieguan et al., 1988) and Tertiary sediments (Giannasi and Niklas, 1981; Curiale, 1988 and Fu Jiamo et al., 1988). This evidence claims for an angiospermal origin of onocerane I, in contrast with the previous hypothesis (Pearson and Obaje, 1999). However, all previous studies point to the deposition of onoceranes in continental settings, including fluvial and lacustrine series in intramontane basins or in lagoonal-brackish contexts (Pearson and Obaje, 1999).

4.2. Onocerane-related compounds in living plants

The origin of onocerane in sediments is still debated because the possible plant sources (although not numerous) are distributed in very different taxa. Pteridophyta and Lycophyta have been proposed as plant producers of the onoceranes recorded in Upper Cretaceous sediments (Pearson and Obaje, 1999) because possible precursors were isolated

from these taxa (Tsuda et al., 1964; Ageta et al., 1982a; Ageta et al., 1982b and Masuda et al., 1989; Table 2). This interpretation is questionable since hop-22(29)-ene and neohop-13(18)-ene, also isolated from the same taxa, were absent in the studied sediments. The only undisputed source-product relationship in geological samples was ascertained by Giannasi and Niklas (1985) who isolated onocerane II and III from *Pseudofagus sp*. (Fagaceae) fossil leaves in the Clarkia deposit (Idaho, USA).

Onocerin, the alcohol derivative of onocerane, was first isolated from leaves and roots of *Ononis sp*. (Fabaceae; Barton and Overton, 1955; Henderson et al., 1969; Rowan and Dean, 1972) and from club mosses (Tsuda et al., 1964 and Masuda et al., 1989). Other onocerane-related molecules have also been isolated from *Lansium domesticum* (Meliaceae; Habaguchi et al., 1968 and Nishizawa et al., 1983) and *Cissus quadrangularis* (Vitaceae; Bhutani et al., 1984; Table 2). Contrary to most of the pentacyclic triterpenes that are biosynthesized from squalene monoepoxide (e.g. α- and β-amyrin), in *Ononis spinosa* α-onocerin synthesis involves the both-ends cyclisation of a bis-epoxy-squalene (Rowan et al., 1971). The term onoceroid has been proposed (Ageta et al., 1982b) for all the compounds produced by this pathway (i.e. serratane, ambreane and onocerane), which is uncommon in nature and might explain why onocerane-type molecules have been reported in such a limited number of species. However, the occurrence of such compounds in plant taxa as diverse as ferns, club mosses and angiosperms certainly denotes adaptative convergence.

The physiological role of onocerane-related molecules is uncertain but should strongly differ depending on the associated functional group(s). In the roots of Ononis sp., onocerin (onocera-8,14-dien-3α,21β-diol) is thought to permit the colonization of water-deficient environments (Dean and Mayes, pers. com.). The role of onocerin in *Lycopodium clavatum* and of onoceradienes, onoceranoxide and other related molecules in ferns and club mosses must be very different since these taxa are well adapted to humid environments.

4.3. Comparison of onocerane abundance with palynology and other studies

For the purpose of comparison between cores 98-3 and 97-1, radiocarbon ages measured on samples from core 98-3 were converted into calendar ages, which were then interpolated by linear regression (Fig. 6). The age model for core 97-1 was previously established by Sifeddine et al. (2003).

The LGM (ca. 21,000 years ago) has proven to be difficult to describe in the Tropics because of the frequent hiatus observed in lowland tropical records (Ledru et al., 1998 and Turcq et al., 2002). Lagoa do Caçó paleoenvironmental history started at ca. 20,000 cal yrs BP, immediately after the peak of the glaciation, when a steppe-type environment is indicated, mainly by high frequencies of Poaceae, *Richardia sp*. (Rubiaceae), *Ceratosanthes sp*. (Cucurbitaceae) and various Amaranthaceae (Ledru et al., 2001) responsible for a low ratio between arboreal and non-arboreal pollen (AP/NAP, Fig. 7). Concordantly, a dry environment is also observed at the end of the LGM in marine sediments from Northern Brazil (Behling et al., 2000). These relatively dry climatic conditions are likely to have prevented the development of ferns or club moss taxa in the Lagoa do Caçó watershed, which is supported by the absence of their spores at that time in core 97-1. Therefore, these taxa cannot have been the sources of onocerane I between ca. 20,000 and 19,000 cal yrs BP.

The evidence for onocerane producers in the upper half of core 98-3 can also be deciphered by comparison with palynological data obtained from core 97-1 (Fig. 7). Spores from Adiantaceae, Polypodiaceae, *Cyathea sp*. and Lycophyta are abundant between 17,000 and 14,000 cal yrs BP. Ferns are generally related to rather humid environments. In the sediments deposited during the considered period, when such conditions prevailed as attested also by high AP/NAP ratio and other palynological evidence (Ledru et al., 2001; Sifeddine et al., 2003), only low levels of onocerane I were detected (Fig. 7).

Higher levels of onocerane I are once again recorded around ca. 13,000 cal yrs BP in core 98-3 (Fig. 7). As attested by palynological results from core 97-1, ferns and club mosses were not present around the lake at this time and thus cannot account for onocerane I production. At the same time, core 97-1 records lower AP/NAP values than before, denoting the regression of moist forest in favour of more open vegetation, and an increase in frequencies of *Cecropia sp.*, a pioneer species that colonizes areas left vacant after the reduction of humid forest. This drastic destruction of the forest is interpreted as the consequence of a dry and abrupt climatic change, correlated with the North Atlantic climatic reversal, specifically the Younger Dryas event (Ledru et al., 2002).

As the *Ononis* genus has not yet been described in NE Brazil, an unknown source of onocerane must certainly be considered here. From this evidence and in general agreement with the previous interpretation (Pearson and Obaje, 1999), onocerane I can be proposed as an indicator of dry to semi-arid conditions in post-Cretaceous sediments where fern remains are absent.

5. Conclusion

According to a literature review of possible plant precursors of onocerane-type molecules, with regard to the physiological role of onocerin in some plants, and by comparison with palynological evidence, the onocerane I reported in sediments deposited in Lagoa do Caçó indicates the presence of a plant that lived in dry to semi-arid conditions, at the end of LGM and during the Younger Dryas, in NE Brazil. The specific plant precursor of this compound found in Lagoa do Caçó sediments remains unknown but could be closely related to the *Ononis* genus. Because pollens from Fabaceae are very fragile and poorly specific, onocerane I could be the only recognizable remnant of its producer.

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Table captions:

Table 1: Radiocarbon and calendar ages of Total Organic Matter (TOM) from core 98-3.

Depth (cm)	Measured ages (^{14}C yrs BP)	$^{13}C/^{12}C$	Conventional ages (^{14}C yrs BP)	Age range* (cal yrs BP)	Intercept (cal yrs BP)
			Core 98-3		
73 - 75	4930 ± 50	-27.2 ‰	4890 ± 50	5720 - 5580	5610
196 - 198	9850 ± 60	-28.9 ‰	9790 ± 70	11,270 - 11,120	11200
286 - 288	14,450 ± 80	-27.8 ‰	14,400 ± 80	17,680 - 16,830	17250
354 - 356	15,620 ± 80	-19.9 ‰	15,700 ± 80	19,230 - 18,290	18750
426 - 428	16,100 ± 80	-22.9 ‰	16,130 ± 80	19,740 - 18,770	19240
574 - 576	16,670 ± 100	-24.3 ‰	16,670 ± 100	20,410 - 19,330	19850

*Range at two standard deviations with error multiplier of 1.0.

Table 2: Onocerane-related molecules and plant species from which they have been isolated.

Product	Plant precursor	Reference
colysanoxide	*Colysis sp.* (Polypodiophyta, Polypodiaceae)	Ageta et al., 1982a.
onoceradienes onoceranoxide	*Lemmaphyllum microphyllum* (Polypodiophyta)	Ageta et al., 1982b Masuda et al., 1989.
α-onocerin	*Ononis sp.* (Fabaceae)	Barton & Overton, 1955 Rowan & Dean, 1972 Henderson et al., 1969.
onocer-7-ene-3,21-diol	*Cissus quadrangularis* (Rhamnales, Vitaceae)	Bhutani et al., 1984.
Lansiosides lansic acid onoceradienedione	*Lansium domesticum* (Sapindales, Meliaceae)	Nishizawa et al., 1983 Habaguchi et al., 1968.
onocerane II and III	*Pseudofagus sp.* (Fagaceae)	Giannasi & Niklas, 1985 Niklas & Giannasi, 1985.
α-onocerin	*Lycopodium clavatum, L. obseurum, L. deuterodensum* (Lycopodiophyta)	Tsuda et al., 1964.

Figure captions:

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

Figure 2: m/z 191 chromatograms for a Nigerian crude oil extract (DA14; Pearson and Obaje, 1999) and for sample 254 collected from core 98-3 at 520cm depth. Onocerane I is indicated as ON1. Other peaks are hopanoids as indicated in the key.

Figure 3: a- Mass spectrum of onocerane I identified in the sediments of Lagoa do Caçó; b- Structure of onocerane I, carbon numbering and major fragments.

Figure 4: Variations of onocerane I relative abundance in core 98-3. The values of onocerane abundance correspond to the ratio between the areas of the peak eluting at 56.82min in the m/z 123 + 191 mass chromatogram normalized to the areas of the internal standard (5α cholestane) in the Total Ion Current (TIC).

Figure 5: Preceding records of onoceranoids in sediments and oils. References: a;f: Wang Tieguan et al., 1988; b: Pearson and Obaje, 1999; c: Fu Jiamo et al., 1988; d: Curiale, 1988; e: Giannasi and Niklas, 1981; g: this study.

Figure 6: Age model for core 98-3.

Figure 7: Comparison of onocerane I relative abundance from core 98-3 with palynological results from core 97-1. AP represents the percentage of arborel pollens compared to the total pollens. Ferns and Lycophyta spores comprise the spores of Adiantaceae, Polypodiaceae, *Cyathea sp*. and Lycophyta normalized to total pollen grains. Pollen results are from Ledru et al. (2001 and 2002) and Sifeddine et al. (2003). Ferns and Lycophyta were not previously published but result from the same study.

Figure 1

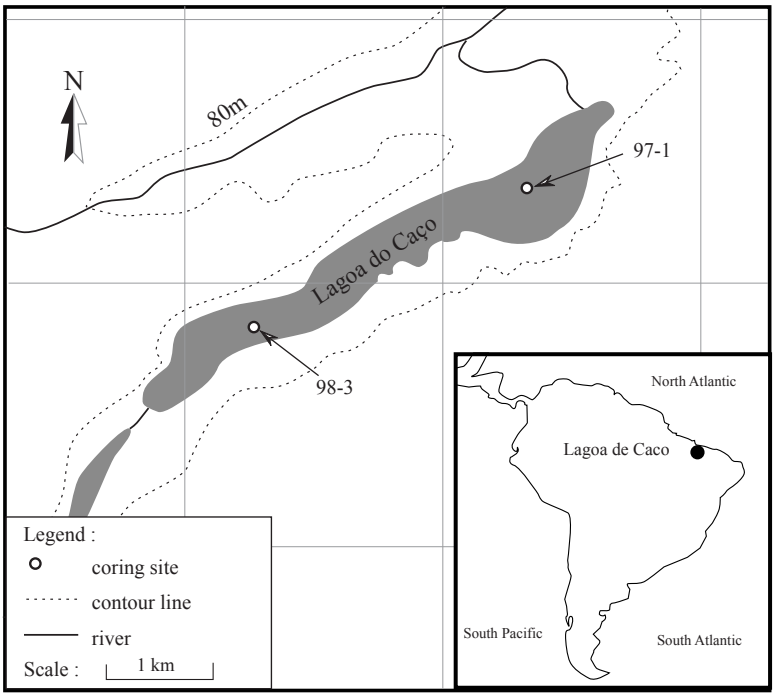
N
80m
97-1
Lagoa do Caço
98-3
Legend :
coring site
contour line
river
Scale :
1 km
North Atlantic
Lagoa de Caco
South Pacific
South Atlantic

Figure 2

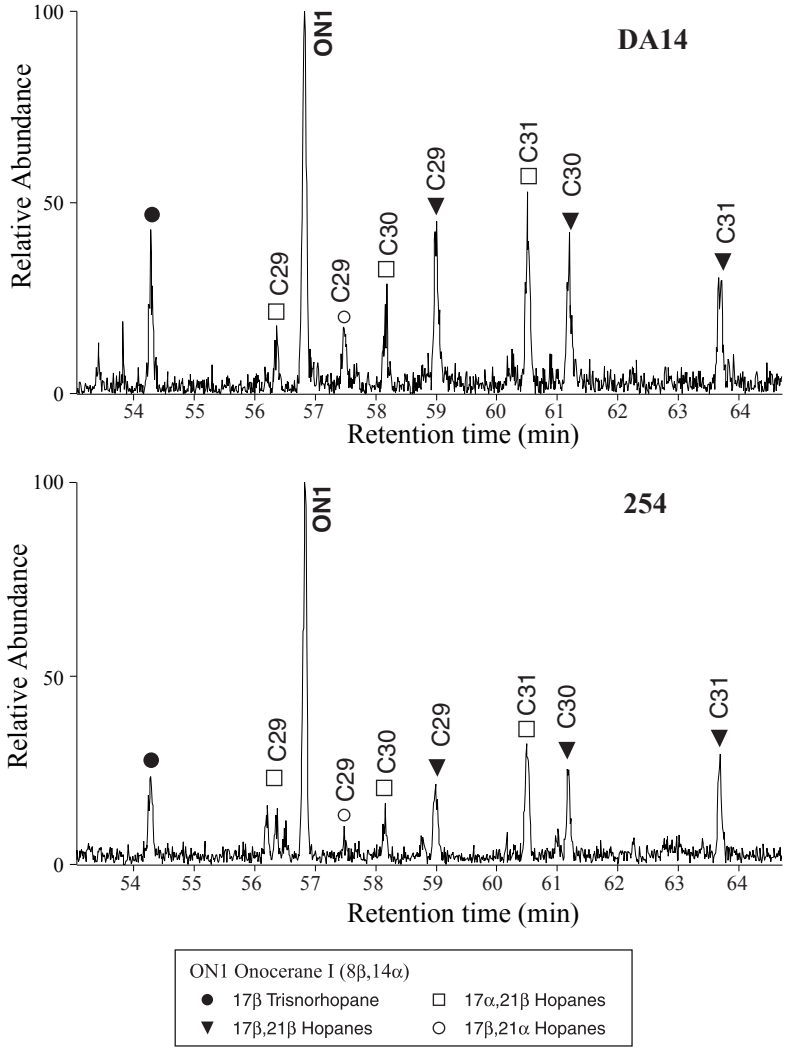

Figure 3

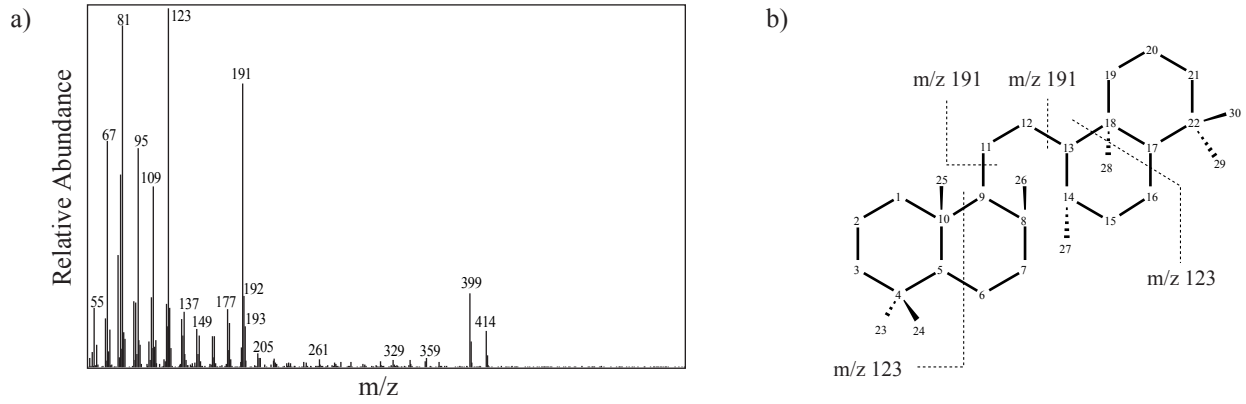

Figure 4

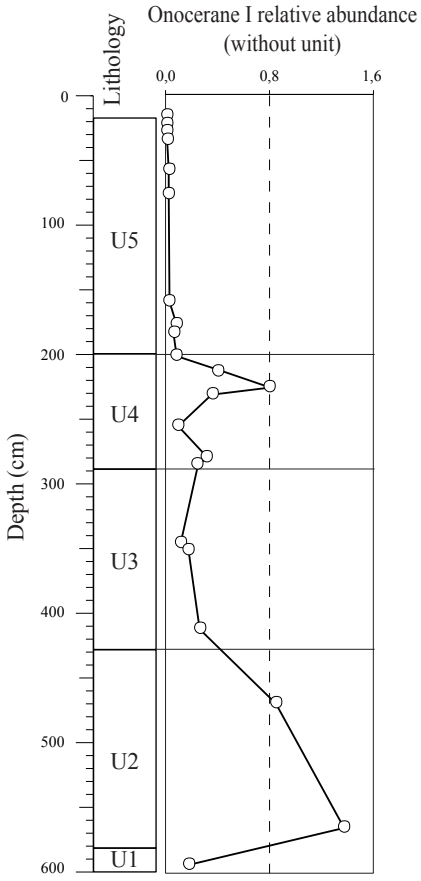

Figure 5

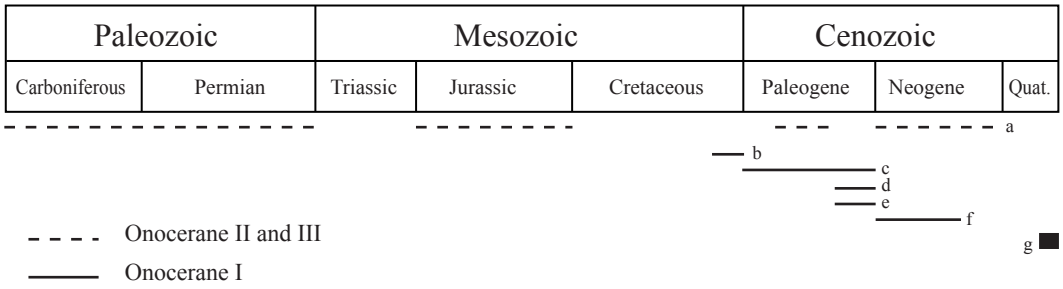

Figure 6

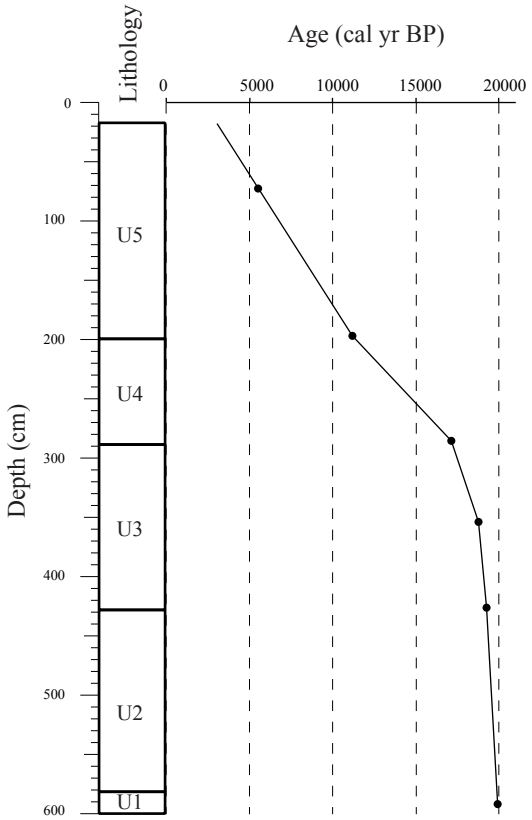
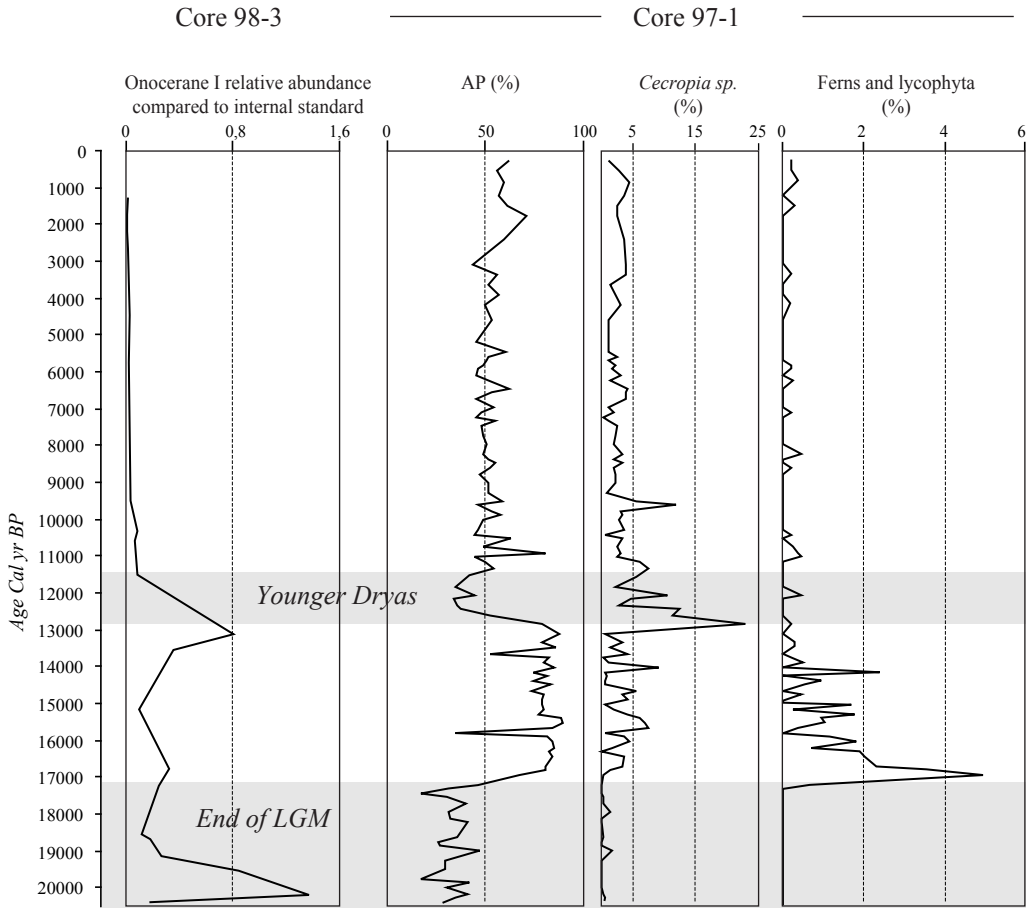
Figure 7