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Derivatives of triterpenes formed during diagenesis in tropical lacustrine recent sediments (Lake Caçó, Brazil).

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Abstract

Hydrocarbon fractions extracted from sediment layers deposited in a small Brazilian lake during the last 20,000 yrs, were investigated by gas chromatography-mass spectrometry. Considerable differences in the distribution and the amount of triterpene derivatives in the aliphatic as well as in the aromatic fraction were observed all along the series. The largest compound diversity was found in the lowest levels of the series where good preservation of terrestrial plant debris was ensured by rapid burial. There, the aliphatic fractions comprise des-A-triterpenes, onocerane I and hopanoids and the aromatics mono and triaromatic triterpenes. A third series of compounds was tentatively identified as diaromatic derivatives of tetracyclic triterpenes. The distinct dynamics of des-A and aromatic triterpenes

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derivatives under variable medium conditions led us to hypothesise that these two families of compounds derive from distinct pools that contributed differently to the sediment depending on the environmental context. Des-A-lupane was most probably produced in subaquatic conditions within a belt of *Eleocharis sp.* that developed between 1 and 3m water depth around the lake. Reversely, aromatic derivatives of triterpenes could have resulted from the degradation of their biological precursors within reducing micro-environments in the catchment basin.

1. Introduction

Pentacyclic triterpenes constitute a highly diversified family of molecules that are mostly produced by higher plants (Pant and Rastogi, 1979; Das and Mahato, 1983; Mahato et al., 1988; 1992; Mahato and Sen, 1997). Their extensive study for medicinal and pharmaceutical purposes provided abundant, but still disputed information that can be used for taxonomical purposes. Despite the high potentialities they thus offer for reconstructing past depositional environments, neither these compounds nor their diagenetic transformation products are frequently used for such a purpose, especially in recent sedimentary records (Cranwell, 1984; Hauke, 1994; Jaffé and Hausman, 1995; Prartono and Wolff, 1998). In addition to the supplementary information that they can provide on botanical assemblages, the degradation products of triterpenes also can put some constraints on medium conditions during sediment deposition and early diagenesis. Indeed, the negative consequences that diagenesis can have by reducing structural specificities (Rullkötter et al., 1994, van Aarssen et al., 2000), can be counterbalanced by allowing to trace back the physico-chemical conditions that prevailed when molecular transformations occurred. Numerous studies were carried out on the diagenesis of triterpenes (Corbet, 1980;

Spyckerelle, 1975; Lohmann, 1988; Trendel et al., 1989; ten Haven and Rullkötter, 1988; ten Haven et al., 1991; Hauke, 1994; Rullkötter et al., 1994) but the compound transformation routes and the identification of intermediates are still incomplete. In addition, all that previous work was carried out on organic rich sediments, especially lignites and brown coals that were deposited under oxygen deficient conditions. This study intends to contribute to our understanding of terrestrial triterpene diagenesis by comparing the distributions of triterpene derivatives in samples deposited under different environmental conditions. The studied samples were collected in the sedimentary infill of a small oligotrophic lake located in Northern Brazil, almost under the Equator (Figure 1). The major paleoenvironmental changes that have affected the area since the end of the Last Glacial Maximum (LGM) have been assessed from the detailed study of a sedimentary core (Jacob, 2003; Jacob et al., 2004a). The almost exclusive contribution of higher plant material to the sediment and contrasting conditions of degradation offer an interesting context to monitor the diagenetic fate of higher plant triterpenes and other biomolecules. In previous reports on the biomarker content of these sediments, we discussed on the presence and the significance of onocerane I and of a series of pentacyclic triterpene methyl ethers (Jacob et al., 2004b; Jacob et al., 2005). The numerous types of molecular skeletons that have so far been detected in these sediments (namely oleanane, ursane, taraxerane, bauerane, fernane, arborane and onocerane) strengthen the interest of biomarker studies to apprehend the different routes followed by triterpenes during degradation depending on (paleo)environmental conditions.

2. Materials and methods

2.1. Sample selection

Sixteen samples were selected on a 6m core drilled in the sediments of Lake Caçó, located almost under the equator, in north eastern Brazil (Figure 1). They are representative of the five main sedimentary units defined by sedimentology, organic petrography and bulk geochemistry (Jacob et al., 2004-a; see § 5).

2.2. Extraction and separation of free lipids

The method for lipid extraction and separation was described elsewhere (Jacob et al., 2005). One gram of dried sediment was ultrasonically extracted with acetone-pentane 1:1. The mixture was then separated into a neutral and an acidic fraction by solid phase extraction using AminoPropyl Bond Elute© cartridges. Neutral compounds were eluted with CH₂Cl₂:CH₃OH (1:1) and acidic compounds with ether after acidification of the medium with ether:formic acid 9:1. The neutral fraction was submitted to further fractionation on activated Florisil® to give aliphatic hydrocarbons (eluted with heptane), aromatic hydrocarbons and ethers (CH₂Cl₂) and polar compounds (CH₂Cl₂:CH₃OH 1:1). 5 α -Cholestane and *n*C₂₈ alkane were added as internal standards prior to injection.

2.3. GC-MS analysis

GC-MS analyses were performed on a ThermoFinnigan TRACE-PolarisGCQ gas chromatograph-mass spectrometer. The gas chromatograph was fitted with an Rtx®-5Sil MS capillary column (30 m x 0.32 mm i.d., 0.25 μ m film thickness) with 5 m of guard column. The GC operating conditions were as follows: temperature hold at 40°C for 1 min, then increase from 40 to 120°C at 30°C.min⁻¹, 120 to 300°C at 3°C.min⁻¹ with final isothermal hold at 300°C over 30 min. The sample was injected splitless, with the injector

temperature set at 280°C. Helium was the carrier gas. The mass spectrometer was operated in the electron ionisation (EI) mode at 70 eV ionization energy and scanned from 50 to 650 Dalton. Compounds were identified by comparison with published mass spectra and relative retention times or the structures were tentatively assigned according to comparative interpretation of mass spectra. The mass spectra of several compounds discussed in the text are given in Appendix together with the proposed structures. Due to frequent coelutions, quantitations were performed by GC-MS using ion specific chromatograms. The areas of the resulting peaks were compared with the area of the peak of 5 α -Cholestane on the TIC. The specific ions used for calculation correspond to the three most abundant fragments in the mass spectra of the compounds. They are listed in Table 1.

3. Results

3.1. Aliphatic hydrocarbons

Seven compounds eluting between nC_{23} and nC_{25} alkanes (Figure 2) in the GC-trace of the aliphatic hydrocarbon fraction of sample 229 (470 cm depth) comprise a series of seven des-A-triterpenes (numbered 1 to 7 after their elution order). Their mass spectral characteristics are summarized in Table 1. Compounds 1 to 4 plus 6 that have a molecular mass of 328 amu ($C_{24}H_{40}$) were identified as unsaturated des-A-triterpenes. Compounds 5 and 7 that exhibit a molecular ion at m/z 330 ($C_{24}H_{42}$) are most certainly saturated counterparts. The mass spectra of compounds 1 to 4 do not display any fragment characteristic of the loss of an isopropyl group $[M-43]^+$. They are interpreted as des-A-structures containing a six-membered ring E. Abundant fragments at m/z 189, 203, 204 and 218 are typical for C-ring cleavage in oleanene and ursene structures, followed by retro-Diels Alder rearrangement (Djerassi et al., 1962; Budzikiewicz et al., 1962). According to

relative retention times of oleanane and ursane-type triterpenes and mass spectral resemblance with already proposed structures (Logan and Eglinton, 1994; Corbet, 1980), compound 1 was identified as des-A-olean-13(18)-ene, compound 2 as des-A-olean-12-ene, compound 3 as des-A-urs-13(18)-ene and compound 4 as des-A-urs-12-ene. Compound 5 was identified as 10 β -des-A-lupane according to Corbet (1980), Philp (1985), Trendel et al. (1989) and Woolhouse et al. (1992). The mass spectrum of compound 6 displays intense fragments at m/z 175, 161 and 149 that are common in D:C or E:C-friedo triterpenes (Shiojima et al., 1992). According to Jaffé and Hausmann (1995), compound 6 is 10 β -des-A-arbor-9(11)-ene. The mass spectrum of compound 7 displays a molecular ion at 330 amu, consistent with a des-A-triterpane structure (C₂₄H₄₂). It is tentatively identified as des-A-oleanane/ursane by comparison with a published spectrum (Woolhouse et al., 1992).

3.2. Aromatic hydrocarbons

In the aromatic fractions, 20 compounds are interpreted as aromatic derivatives of triterpenes. They are divided into three main groups with regard to their mass spectra, the most significant fragments of which are listed in Table 1. The mass spectra of compounds from the first group exhibit prominent fragments at m/z 145, 158, 172. The mass spectra of those from the second group show abundant ions at m/z 195, 207 and 221. The compounds of the third group are characterized by spectra displaying molecular ions at m/z 340 or 342. The chromatographic distributions of these molecules on ion-specific chromatograms are displayed in Figure 3 and their mass spectra are displayed in Appendix.

3.2.1. Ring A monoaromatic pentacyclic triterpenes

The mass spectra of these compounds exhibit molecular ions at m/z 336 (compound 8), m/z 380 (compounds 9 and 10), m/z 378 (compounds 15 and 22), m/z 376 (compounds 11, 12 and 13) and m/z 374 (compound 26). The mass spectra of compounds 8 to 13, 15, 22 and 26 show intense ions at m/z 145, 157, 158, 170 and 172 that is consistent with/for A-ring monoaromatic triterpanes with oleanane, ursane or lupane skeletons (Laflamme and Hites, 1978; Wakeham et al., 1980; Chaffee et al., 1984; Hazai et al., 1986; Chaffe and Fookes, 1988; Loureiro and Cardoso, 1990; Stout et al., 1992). The relative intensities of ions m/z 145, 157, 158, 170 and 172 depend on whether additional unsaturations are located on rings B, C, D or E. As demonstrated by several authors (Lohmann, 1988; Loureiro and Cardoso, 1990), the double bond position in natural product precursors is often preserved in diagenetic derivatives. For example, Δ^{12} oleanenes are transformed into aromatic oleanoids in which the Δ^{12} double bond is preserved as long as aromatisation does not affect ring C.

The mass spectra of compounds 15 and 22 display an intense ion at m/z 145 and minor ions at m/z 157 and 172. Their molecular weight of 378 amu is consistent with a $C_{28}H_{42}$ formula. Comparable spectra have been described in Hazai et al. (1986), Wolff et al. (1989), ten Haven et al. (1992) and Stout (1992) where they were attributed to ring A monoaromatic triterpenes with oleanane, ursane or lupane structures. Compounds 15 and 22 are tentatively identified as dinor-oleana(ursa)-1,3,5(10)-triene and dinor-lupa-1,3,5(10)-triene, respectively.

The mass spectra of compounds 11, 12 and 13 display a molecular ion at m/z 376 that denotes ring A monoaromatic structures with one additional double bond ($C_{28}H_{40}$). Compounds displaying resembling mass spectra have been reported in sub-bituminous coals (Hazai et al., 1986), in Tertiary angiospermous lignite (Stout, 1992) and identified

with synthetic standards (Wolff et al., 1989). According to spectral and relative retention times, compounds 11, 12 and 13 are identified as dinor-oleana(ursa)-1,3,5(10),13(18)-tetraene isomers.

The molecular ion of compound 26 (374 amu) is consistent with a $C_{28}H_{40}$ formula. Abundant fragments at m/z 145, 157 and 172 attest to a A-ring monoaromatic structure. No isopropyl loss is expressed by any $[M-43]^+$ ion. As suggested by the preservation of the already mentioned ions m/z 145, 157 and 172, the two additional double bonds cannot be both located on rings B or C since this latter configuration would lead to dominant m/z 221 (Stout, 1992). Therefore an A-aromatic pentacyclic structure derived from oleanane or ursane and bearing two additional double bonds in Δ^{12} and Δ^{18} positions is proposed for compound 26. The molecular ion at $M+ 336$ of compound 8 differs from 42 amu from that of compound 22. This difference could be taken as an evidence that compound 8 is the 22,29,30-trisnor- derivative of compound 22. Therefore, the structure of pentanor-lupa-1,3,5(10)-triene is proposed for compound 8.

The identification of compounds 9 and 10 is more difficult since the mass spectrum of both these molecules shows a fragmentation pattern similar to those discussed above (prominent fragments at m/z 145, 157, 159, 172 and 173 in the mass spectra) but a molecular weight of 380 amu ($C_{28}H_{44}$). Such a molecular weight supposes the addition of two hydrogen atoms on the already discussed compounds that exhibit a molecular weight of 378 amu, but without affecting the double bonds that participate to ring aromatisation. Therefore, compounds 9 and 10 could be A-monoaromatic derivatives of seco-triterpenes or of tetracyclic triterpenes possessing a lateral chain. This latter assumption is corroborated by the presence of an abundant fragment at m/z 351 in the mass spectra of compound 9 that

attests to the loss of an ethyl moiety.

3.2.2. Triaromatics

The mass spectra of compounds 20, 23 and 24 all exhibit a molecular ion at m/z 342 and a strong fragment at m/z 257 that characterise rings A,B,C triaromatic triterpenes (Wakeham et al., 1980; Chaffee and Fookes, 1988; Stout, 1992). Comparison of mass spectral data allowed us to identify compounds 20 and 23 as tetranor-oleana(ursa)-1,3,5(10),6,8,11,13-heptaene isomers and compound 24 as tetranor-lupa-1,3,5(10),6,8,11,13-heptaene, respectively, with undefined stereochemistry at the D/E ring junction (Chaffee and Fookes, 1988). The mass spectra of two other compounds (16 and 19) resemble the previous ones, but with a molecular ion at m/z 340 and a prominent ion at m/z 255. Compounds 16 and 19 are therefore interpreted as rings A,B,C-triaromatic triterpenes with an additional double bond, probably with oleanane and ursane structures, respectively.

3.2.3. Rings A,B diaromatic tetracyclic triterpenes

The mass spectra of compounds from the third group (compounds 14, 17, 18, 21, 25 and 27) often exhibit prominent fragments at m/z 181, 195, 207 and 221 and a molecular mass of 360, 374 and 376 amu. To our knowledge, few reports of such mass spectra have been published (Hazai et al., 1986; Stout et al., 1992; Killops et al., 1995 and Hauke, 1994). According to this latter author, ions at m/z 195, 207 and 221 with a molecular ion at m/z 374 correspond to the A,B-diaromatic 24,25-dinor-arbora-1,3,5,7,9-pentaene. In contrast, in the mass spectra of 24,25-dinor-arbora-1,3,5(10),9(11)-tetraene (molecular ion at m/z 376), major fragments are recorded at m/z 209, 219 and 187. Therefore, one can hypothesize that m/z 181, 195, 207 and 221 fragments characterise rings A,B diaromatic structures with

methyl groups located at the rings C,D junction. This assumption cannot account for compounds 14 and 18. The mass spectra of these compounds both have base peak at m/z 195 but a molecular ion at m/z 376 ($C_{28}H_{40}$), thus requiring two hydrogen atoms more than in the compound with a molecular ion at m/z 374, that is incompatible with a structure of diaromatic pentacyclic triterpene. According to these observations, the considered compounds could be rings A,B diaromatic derivatives of tetracyclic triterpenes with methyl groups located at C(13) and C(14) positions (e.g. lanostane, tirucallane or euphane structures) for which a proposed fragmentation mechanism is reported in Figure 4. Because the fragmentation pattern is rather similar for compounds with a molecular ion at m/z 376 and those with a molecular ion at m/z 374, the additional double bond in these later cannot occur in the vicinity of rings C and D but is most probably located on the lateral chain. According to these observations, compounds 14 and 18 are tentatively identified as rings A,B diaromatic derivatives of lanostane, euphane or tirucallane type compounds. Differences in the spectral signature of these molecules could arise from different configuration at C(13) and C(14) positions. Compounds 21, 25 and 27 appear as possible derivatives of compounds 14 and 18 with one additional double bond. In addition to the isomerism at C(13) and C(14) positions, the position of the double bond on the lateral chain could participate in the diversity of fragmentation patterns. Finally, compound 17, of which the molecular ion is 360, is assumed to correspond to a similar structure with the reduction of the lateral chain length.

4. Discussion

4.1. Sedimentation and early diagenesis in Lake Caçó

The Pleistocene sand dunes and the laterites that are the only outcropping geological

formations in the region exclude any possibility of contamination of Lake Caçó sediments by fossil organic matter. The lacustrine sedimentary infill has been divided into 5 units according to lithofacies, organic petrography and Rock Eval parameters (Figure 6; Jacob et al., 2004a). The lower unit (U1) consists of fine grained sands of the Pleistocene substratum that will not be discussed further. Unit 2 presents rather low contents of organic matter (TOC < 5 %) but consisting in exceptionally well preserved higher plant debris. The high preservation of this material is in particular depicted by low TpS2 values attributable to the presence of fresh biopolymers in the samples (Disnar et al., 2003). This remarkable organic matter preservation is thought to result from the rapid burial of higher plant detritus by episodic but strong mineral inputs in an ephemeral lake (Jacob et al., 2004a). At this time, soils developing on the sand dunes were poorly vegetalized due to a harsh climate with a long dry season. Sparse vegetation developed in wet hollows. During the short rainy season, sand that was mobilized by heavy showers allowed the burial of OM in hollows. During unit U3 deposition the climate was slightly more humid than during the previous period. There were still erosive rainfalls but soils were more developed and there was a denser plant cover. The U3-U4 transition marks a drastic change in environmental conditions as depicted by a sudden decrease in HI values and a change in lithology from silts to clays. These changes were attributed to an increase in the precipitation regime especially with a longer rain season. These rather humid conditions allowed forest development around the lake (Ledru et al., 2001) that became perennial with a notable water level. Nevertheless the lake waters were well oxygenated as a result of a strong mixing by the westerlies. A belt of *Eleocharis sp.* (spikerush) that developed on the lake border hindered any mineral and organic input from the watershed. The sedimentary organic matter, which was still mainly derived from higher plants, was highly degraded as a

result of a rather long stay in oxygenated waters and a very slow burial consequential to low inorganic input (Jacob et al., 2004-a). Despite these conditions unfavourable to OM preservation, but thanks to very low allochthonous (watershed) and autochthonous (e.g. diatom frustules) inorganic inputs, samples from U4 and U5 present high TOC values, reaching up to 15 %. At ca. 2.2 m depth, the presence of siderite attests to the development of more reducing conditions during diagenesis. The organic matter preserved in the sediments is hence essentially derived from terrestrial plants that suffered distinct environmental and diagenetic histories along the record. These highly contrasted conditions during sedimentation and early diagenesis are also depicted by triterpene derivative distributions.

4.2. Diagenesis of higher-plant triterpenes

Transformation processes initiating the early diagenesis of higher plants pentacyclic triterpenes are thought to already begin during leaves senescence (Corbet, 1980; Trendel, 1985; Lohmann, 1988 and references therein), the mechanisms involved in such transformations being possibly microbially or photochemically mediated (Corbet, 1980). The main degradation routes that pass by the loss or the aromatisation of ring A, have already been summarized by various authors [Carruthers and Watkins (1964), Jarolim et al. (1965), Chaffee and Fookes (1988), Trendel et al. (1989), Wolff et al. (1989), Stout (1992) and Rullkötter et al. (1994)]. Basically, the first step in higher plant pentacyclic triterpenes degradation is the loss of an oxygenated function at C(3) functionalized position from unsaturated compounds such as α and β -amyrins. This leads to corresponding di-unsaturated counterparts such as ursadienes and oleanadiene (ten Haven et al., 1992). After

this primary transformation, various pathways lead to (i) the formation of Δ^2 triterpenes, $\Delta^{2,x}$ triterpadienes or ring A contracted triterpenes (Elgamal et al., 1969; Ekweozor et al., 1979; ten Haven et al., 1992); (ii) the progressive aromatisation of the skeleton from ring A to finally produce fully aromatised pentacyclic moieties (Laflamme and Hites, 1978; Wakeham et al., 1980; Wolff et al., 1989); (iii) the loss of ring A (des-A-compounds), followed by the progressive aromatisation towards ring E (Hussler et al., 1984). The loss of ring A is initiated by its opening leading to the formation of A-seco- intermediates, a phenomenon that readily occurs in plant leaves under photochemical/photomimetic control (Corbet, 1980).

4.3. Triterpene fingerprint

The various triterpene derivatives found in Lake Caçó sediments are listed in Table 1 with their main mass spectral data. The variety of these compounds highlights the large contribution of higher plant OM to the sediments. This is fully consistent with the botanical richness of the study area and the wide diversity of triterpenes already discussed in previous studies (onocerane: Jacob et al., 2004b; “PTME”: Jacob et al., 2005). If one excludes onocerane and some hopanoids, the only triterpenes found in the non-aromatic fractions of Lake Caçó sediments were des-A derivatives. No saturated tetra- or pentacyclic triterpane nor Δ^2 triterpenes or $\Delta^{2,x}$ triterpadienes was found in sample extracts. In contrast to unsaturated and fully saturated compounds which require several reaction steps to be formed from, say a triterpenenol, the corresponding triterpadiene only requires the loss of the alcoholic functional group of the same precursor. Thus, the absence of such compounds is explained by the fact that these olefinic compounds only acted as transitory intermediates in the degradation of original triterpenes into aromatics and/or des-A-

triterpenes, depending on medium conditions. For triterpenes, another reaction path would be the direct reduction of the oxygenated function of natural triterpenes together with their double bond. Such a reaction would require much more reducing conditions than those which developed in Lake Caçó sediments. Finally, the absence of triterpanes and of their mono- and di-unsaturated counterparts is consistent with Spyckerelle (1975) conclusion that, in contrast to hopanoids, the early diagenetic transformation of higher plant triterpenes preferentially leads to aromatics or des-A-triterpenes rather than to unsaturated or saturated pentacyclic compounds.

The fingerprints of aromatic derivatives depicted for samples taken at 1.6 and 4.7 m depth globally resemble those described by Stout (1992) and Hazai et al. (1986) for a lignite and a sub-bituminous coal, respectively. They comprise a series of monoaromatic pentacyclic compounds with various structures and degrees of unsaturation, a series of pentacyclic triaromatics and diaromatic derivatives of tetracyclic triterpenes. Concerning these latter ones, Stout (1992) and Hazai et al. (1986) also detected compounds the mass spectra of which displayed a m/z 195 ion as dominant peak. We here propose a first tentative identification of this series of compounds as diaromatic tetracyclic triterpenes of the lanostane/euphane series. This tentative identification is substantiated by the presence, in the considered samples, firstly of a methyl ether having such a structure (Jacob et al., 2005), and secondly by the presence of a ketone and an alcohol derivative in more polar fractions (Jacob, J., unpublished results). No ring A,B diaromatic triterpene derivative, fully aromatised triterpene or aromatic derivative of des-A-triterpene was either detected in the studied aromatic fractions. The absence of ring A,B diaromatic derivatives could be explained by the pre-existence of one or two double bonds on the rings C or D of molecular precursors (β - and α -amyrin). As suggested by Lohmann (1988), little additional energy is

necessary to aromatise ring C following rings A and B when one or two double bonds already exist on ring C. This explains the sole occurrence of mono- and triaromatic derivatives of pentacyclic triterpenes. Such an absence of A-B diaromatic derivatives of pentacyclic triterpenes was also noted by Stout (1992) who did not either detect any aromatic derivative of des-A-triterpene in the Brandon lignite. The co-occurrence of des-A-triterpenes and mono- and triaromatic derivatives of triterpenes in our samples, without any des-A-triterpene aromatic derivative, indicates that the aromatisation of des-A-triterpenes was hindered or that adventitious aromatic des-A-triterpenes were rapidly degraded once formed. Because the aromatisation of triterpene biomolecules is unlikely to occur in oxygenated waters (Jaffé et al., 1995), this phenomenon most probably occurred before functionalized triterpenes entered the water column and the sediment. Finally, no fully aromatised triterpene was found in the selected samples. This highlights that more drastic diagenetic conditions or longer times (Jaffé and Hausmann, 1995) are required to further aromatise the precursor compounds. In summary, the coexistence of des-A-triterpenes and triterpenes derivatives with various degrees of unsaturation/aromatization substantiates the possibility that there were distinct pools of triterpene precursors and/or that it existed different diagenetic pathways in the studied system (i.e. lake surroundings plus water column and sediment) through out the lake history.

4.4. Variations in abundance along the record

As shown in Figure 6, the distribution of triterpene derivatives in the sediment record allows distinguishing three sections differing in the abundance and/or the nature of such compounds. Section 1 coincides with unit U2. Section 2 corresponds to U3, the base of U4

and the uppermost recent part of the series that belong to U5. Section 3 extends from c.a. 2.4 up to 0.6 m depth.

4.4.1. Section 1

The samples from this section reveal a great diversity of triterpene derivatives that consists of monounsaturated des-A-triterpenes, saturated des-A-triterpenes (des-A-lupane and compound 7), mono and triaromatic derivatives of pentacyclic triterpenes and diaromatic derivatives of tetracyclic triterpenes. Such compound distribution is very comparable to those described in previous studies, especially on brown coals and lignite (Stout, 1992; Hazai et al., 1986). This compound distribution is consistent with the conditions of OM deposition and the diagenesis of the considered section, at the end of the Last Glacial Maximum (c.a. 18,000 yrs cal BP), namely, fresh higher plant debris that were rapidly buried in an ephemeral lake by sands mobilized from the denuded substratum by rare but abundant tropical rainfalls. This compound distribution is also fully consistent with the well-admitted ideas on triterpenes diagenesis: (i) a very early transformation of original triterpenes that can steadily occurs in senescent leaves and thus does not require intense diagenesis; (ii) two main diagenetic pathways that prevail under dysoxic conditions and lead to des-A-triterpenes and mono- and triaromatic derivatives of triterpenes, respectively. The co-occurrence of des-A-triterpenes and aromatic derivatives of triterpenes in the same samples indicates that the diagenetic pathways leading to both compound classes occurred synchronously, or so. The alternation of a long dry season and the short raining season during which the ephemeral lake developed (Jacob, 2004) could straightforwardly substantiate two distinct degradation modes of triterpene biomolecules: (i) firstly, the formation of aromatic derivatives during the dry season, in aerial conditions; (ii) secondly,

the production of des-A-triterpenes from their triterpene precursors in sub-aquatic conditions, in the/an ephemeral lake, during the rainy season. This latter conclusion is in agreement with the assumptions of Trendel (1985) when he remarked that the formation of des-A-triterpenes is favoured in soils or sediments that are at least temporarily submerged.

4.4.2. Section 2

In contrast to Section 1, des-A-lupane is by far the dominant triterpene derivative in Section 2 that comprises U3, the lower levels of unit U4 and the upper most core levels. In all Section 2 des-A-lupane can represent up to 80% of the total amounts of des-A-triterpenes. Other des-A-triterpenes with oleanane, ursane or arborane structures were only detected in low amounts in some levels around 2m depth (see § 5.4.1.). In addition, there are very few or even no aromatic derivatives in the different intervals of Section 2. Such a low molecular diversity and the high predominance of des-A-lupane can be interpreted as resulting from (i) a higher sensibility to degradation into the water column or the sediment of other des-A-triterpenes and aromatic derivatives, in comparison to des-A-lupane; (ii) environmental changes leading to changing sources (vegetation) and transportation modalities. The almost uniqueness of des-A-lupane in the specified samples can at least partly result from its preferential formation and a peculiar resistance of this compound to diagenetic transformations, as compared to other triterpene derivatives. In contrast to the most common higher plant pentacyclic triterpenes (α - and β -amyrins for example), biomolecules with a lupane structure often own an external double bond on the isopropyl group. In favourable conditions the external location of the double bond would favour the reduction of lupenes rather than the initiation of aromatisation that is facilitated by an internal double

bond (in Δ^{12} position for example in α - and β -amyrins). Des-A-lupane, as other des-A-triterpenes, is relatively stable to diagenesis. Therefore, the exclusiveness of des-A-lupane in Section 2 could indicate intense diagenesis whereas its co-occurrence with other des-A-triterpenes in Section 1 and at c.a. 2m depth (Figure 5) would result from better preservation conditions. However, this hypothesis is somewhat weakened by a detailed study of Section 2. A sharp decrease in HI values is recorded at c.a. 2.9m. Below this drastic change, high HI values are interpreted as reflecting a notable phytoplanktonic contribution, the rather fast burial of which by silts, entailing good OM preservation. Reversely, low HI values associated to high Oxygen Index in the lower levels of U4 attest to a strong degradation due to a long residence time of higher plant remains in oxygenated waters. Because triterpene fingerprints are similar on both sides of U3/U4 limit, diagenesis conditions cannot alone account for the distribution of triterpene derivatives in the considered section. Alternatively, the present day Lake Caçó setting obliges us to attribute the dominance of des-A-lupane to environmental changes, leading to varying sources and transportation. Presently, the lake is bordered by a belt of *Eleocharis sp.* (from 1 to 3m depth, Figure 7a) that prevents any organic input from the watershed. This peculiar environment is characterized by a relatively high productivity in the protected medium that constitutes the belt, leading there to more reducing conditions than in the open basin (under oligotrophic conditions). The distribution of pentacyclic triterpenes in this species of *Eleocharis* has not been determined. Nevertheless, phytochemical investigations on *Eleocharis sp.* show that the only pentacyclic triterpenes this plant synthesizes are of the lupane type (betulinic acid, betulin and lup-20(29)-en-3 β ,16 β -diol with minor contributions from neohop-13(18)-en-3 α -ol and fern-9(11)-en-3 α -ol (Miles et al., 1994; Amaral et al.,

2004). Similarly, geochemical investigations on surficial sediments from a marsh covered with *Eleocharis sp.* and developing within a mangrove system did not show any pentacyclic triterpene but lupeol (Koch et al., 2003). Accordingly, it can be hypothesized that des-A-lupane could originate from lupane-type precursors synthesized by *Eleocharis sp.*, whereas other triterpenes are subordinates. The sub-aerial and reducing conditions that prevail(ed) within the *Eleocharis sp.* belt could favour the transformation of lupane-type precursors into des-A-lupane, again in agreement with the observations of Trendel (1985). Then, des-A-lupane would be exported to the open basin to be buried with no or only limited degradation. As previously assumed in § 5.3., aromatisation processes cannot occur in the water column or even in the sediment. Therefore, aromatic derivatives must have been produced in the watershed, before reaching the lake. For sediments belonging to Section 2, these compounds were most probably filtered by the *Eleocharis sp.* belt as non lupane-type des-A-triterpenes. Altogether, the predominance of des-A-lupane over other triterpene derivatives in Section 2 could attest to the settling of the *Eleocharis sp.* belt around the lake, first, during the deposition of the sediments that are presently found at c.a. 4.5m depth, i.e. earlier than it was previously thought from bulk geochemistry (Jacob et al., 2004a), and secondly, in recent times.

4.4.3. Section 3

The short episode depicted by high amounts of des-A-lupane between 2.3 and 3 m is interpreted as resulting from the destruction of the *Eleocharis sp.* belt, entailing a strong influx of *Eleocharis sp.*-derived material (and especially des-A-lupane) to the sediment. Subsequently, this major environmental change also allowed the strong discharge of aromatic derivatives to the sediment (Figure 6). The destruction/erosion of the *Eleocharis*

sp. belt was probably favoured by a lowering of the lake level. As a matter of fact, and according to our age model, this episode corresponds to the equivalent of the Northern Hemisphere Younger Dryas episode, which is found dry in the region (Ledru et al., 2002; Jacob, 2004).

4.5 *Paleoenvironmental scenario*

The scenario leading to the distinct triterpene derivatives fingerprints found along the sedimentary record is resumed in Figure 7. In Section 1, the degradation of triterpene biomolecules produced during the long dry season is realized in reducing conditions due to burial by a strong input of sand originating from the denuded substratum. During the short wet season, the development of ephemeral lakes with a low water level, allows the (sub-)aquatic degradation of triterpene biomolecules into des-A derivatives. More seasonal precipitations during the deposition of Section 2 sediments are responsible for the development of true lacustrine conditions in hollow(s). Because the lake level remains constant or so, a belt of *Eleocharis sp.* build up around the lake. This belt is the site of production of lupane-type molecules that give des-A-lupane that is exported to the sediment. In the meantime, the input of organic products from the catchment is hindered by the *Eleocharis sp.* belt. Under more arid climate conditions (due to shorter wet seasons and longer dry seasons) during the deposition of Section 3 sediments, the lake level drops. The *Eleocharis sp.* belt is destabilized and the organic matter that had accumulated within this environment is exported towards the centre of the lake, with a strong contribution of des-A-lupane (Step 1). Then, the organic material that accumulated in more or less reducing micro-environments within the watershed, and/or that could not reach the lake because of the presence of the *Eleocharis sp.* belt, is leached and transported to the sediment (Step 2).

When the *Eleocharis sp.* belt builds up again under more stable climatic conditions (Section 2 in upper most levels of the core), detrital material from the watershed with associated aromatic derivatives cannot be exported to the basin. Then, only the organic matter produced within the *Eleocharis sp.* belt (i.e. des-A-lupane) contributes to the sediment.

5. Conclusions

The detection of various by-products of biological triterpenes (des-A-triterpenes, aromatic derivatives of triterpenes) and their quantitation in the hydrocarbon extracts of sediments pertaining to a 6 m long core, allowed us to get an insight into the origin and the dynamics of these compounds depending on environmental conditions. Presumably, des-A-triterpenes and aromatic derivatives of triterpenes are both produced in anoxic or at least dysaerobic environments. Nevertheless, their respective dynamics depend on distinct early diagenetic transformation pathways that probably occurred within distinct (micro-) environments. Although this hypothesis would require further investigations, the relative abundance of des-A-triterpenes and aromatic derivatives of pentacyclic triterpenes could provide an index of the degree of hydromorphism of the ecosystems where the sedimentary organic matter is produced, within the watershed of lacustrine systems. We also tentatively identified a new class of compounds that would result from the aromatisation of higher plant tetracyclic triterpenes with euphane/lanostane basic structures.

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Table captions

Table 1: List of compounds discussed in the text with retention times, mass spectral data, tentative identification and references.

Figure captions

Figure 1: a- Map of study area with location of the coring site. b- Location of samples selected for lipid analyses.

Figure 2: Distribution of des-A-triterpenes in the partial selected ion chromatogram (m/z 163+177+189+203+218) of the aliphatic hydrocarbon fraction extracted from sample 229. The mass spectral data, retention times and identity of compounds 1 to 7 is given in Table 1.

Figure 3: Distribution of aromatic triterpenes depicted on the Total Ion Chromatogram, m/z 145, m/z 195 and m/z 340+342 GC traces of samples 073 (a) and 229 (b). The mass spectral data, retention times and identity of compounds 8 to 27 is given in Table 1.

Figure 4: Fragmentation mechanism for 24,25-dinor-arbora-1,3,5,7,9-pentaene (adapted from Hauke, 1994) and proposed mechanism for ring A-B diaromatic derivatives of tetracyclic triterpenes with euphane or lanostane structure.

Figure 5: Evolution of the distribution of des-A-triterpenes illustrated on the m/z 163+177+189+203+218 GC traces in selected samples from core 98-3.

Figure 6: Evolution of the abundance of des-A-triterpenes and aromatic derivatives of triterpenes as compared to Rock Eval parameters along core 98-3. a- Total Organic Carbon (TOC; %), b- Hydrogen Index (HI, mgHC.g⁻¹TOC), c- Mineral Inorganic Carbon (MINC, %), d- True temperature of maximum release of hydrocarbonaceous compounds during pyrolysis (TpS2; °C), e- abundance of des-A-triterpenes (arbitrary unit), f- relative abundance of des-A-lupane as compared to other des-A-triterpenes (arbitrary unit), g- abundance of aromatic derivatives of triterpenes (arbitrary unit).

Figure 7: a- Picture of the lake margins illustrating the development of a belt of *Eleocharis sp.* around the lake, between 1 and 3 m depth; b- Schematic scenario of the

paleoenvironmental changes that occurred around Lake Caçó during the last 20,000 yrs explaining the evolution of triterpene derivative fingerprint in the sediments.

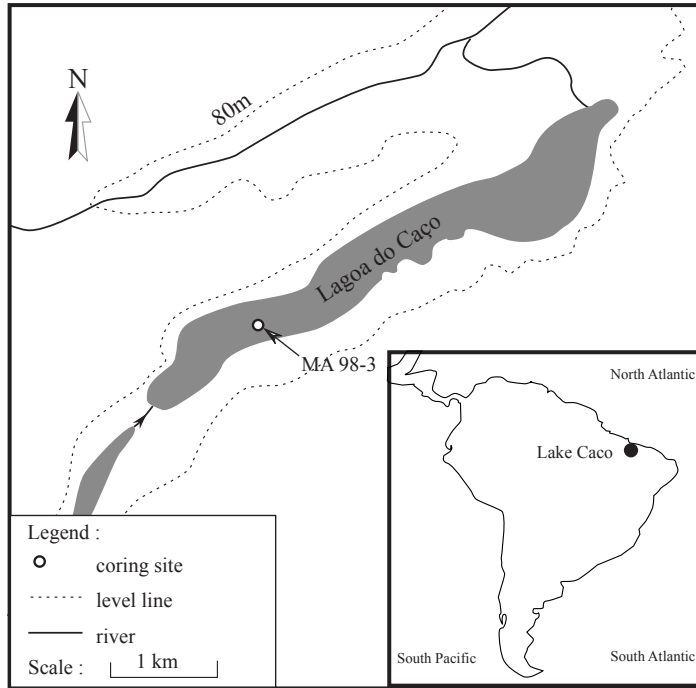
Peak N°	Ret. time	Molecular mass	Most significant ions (by decreasing relative abundance order)	Formula	Tentative identification	References
Des-A-triterpenes						
1	37.83	328	189,204,313,161,328,161,218	C ₂₄ H ₄₀	des-A-olean-13(18)-ene	A, B
2	37.99	328	203,218,189,231,313,161,175,328,243	C ₂₄ H ₄₀	des-A-olean-12-ene	A, B
3	38.28	328	313,189,161,175,204,328,218	C ₂₄ H ₄₀	des-A-urs-13(18)-ene	A, B
4	39.07	328	218,313,189,231,203,243,328	C ₂₄ H ₄₀	des-A-urs-12-ene	A, B
5	39.83	330	163,149,191,177,206,287,217,315,330	C ₂₄ H ₄₂	des-A-lupane	B, C (235), D, E
6	41.92	328	161,313,175,149,191,328,231,257,243	C ₂₄ H ₄₀	des-A-arbor-9(11)-ene	F
7	42.07	330	191,177,206,315,330,219,233	C ₂₄ H ₄₂	des-A-oleanane/ursane	E
Aromatics						
8	50.82	336	145,157,172,336,285,217	C ₂₅ H ₃₆	pentanor-lupa-1,3,5(10)-triene	
9	52.02	380	145,351,173,380,213	C ₂₈ H ₄₄	Unknown	
10	53.13	380	172,145,157,380	C ₂₈ H ₄₄	Unknown	
11	54.16	376	145,172,156,189,204,361,376	C ₂₈ H ₄₀	dinor-oleana(ursa)-1,3,5(10),12-tetraene	G (27, 28 or 31), H (38,34,35,31), I (7c), J (18)
12	54.43	376	170,155,209,285,225,361,376	C ₂₈ H ₄₀	dinor-oleana(ursa)-1,3,5(10),13(18)-tetraene	G (29)
13	55.3	376	158,145,143,204,361,376	C ₂₈ H ₄₀	dinor-oleana(ursa)-1,3,5(10),12-tetraene	G (31), H(38,34,35,31), I (7b), J(20)
14	55.44	376	195,207,361,376,181,249,221,235	C ₂₈ H ₄₀	lanosta(eupha)pentaene	
15	55.55	378	145,157,172,378	C ₂₈ H ₄₂	dinor-oleana(ursa)-1,3,5(10)-triene	G (32), H(43), N (F)
16	55.84	340	255,188,325,340	C ₂₆ H ₂₈	tetranor-oleana(ursa)-1,3,5(10),6,8,11,13-octaene	G (46)
17	56.05	360	207,181,345,360,221,193	C ₂₇ H ₃₆	nor-lanosta(eupha)hexaene	
18	56.3	376	195,361,376,181,207,249,235,221	C ₂₈ H ₄₀	lanosta(eupha)pentaene	
19	56.42	340	255,270,340,239,283,325	C ₂₆ H ₃₀	tetranor-oleana(ursa)-1,3,5(10),6,8,11,13-octaene	G (46), K (D')
20	57.56	342	342,218,231,243,257,327,271,285,314	C ₂₆ H ₃₀	tetranor-oleana(ursa)-1,3,5(10),6,8,11,13-heptaene	G (39), H (39), J (22), K(F',H'), L(XI, XII) , M(19)
21	57.77	374	195,207,256,374,359	C ₂₈ H ₃₈	lanosta(eupha)hexaene	
22	57.84	378	145,157,172	C ₂₈ H ₄₂	dinor-lupa-1,3,5(10)-triene	I (7a), J(21), N(F)
23	57.88	342	257,342,242,228,218,281	C ₂₆ H ₃₀	tetranor-oleana(ursa)-1,3,5(10),6,8,11,13-heptaene	G (42), H(40), M(20), J(23)
24	58.12	342	342,257,243,299,228,205,271,327	C ₂₆ H ₃₀	tetranor-lupa-1,3,5(10),6,8,11,13-heptaene	G (43), H (47), L(XII), M(21)
25	58.54	374	195,207,374,221	C ₂₈ H ₃₈	lanosta(eupha)hexaene	H (42)
26	58.63	374	145,157,172,325,340	C ₂₈ H ₃₈	dinor-oleana(ursa)-1,3,5(10),12,14-pentaene	G (38)
27	58.69	374	195,207,374,221,359,	C ₂₈ H ₃₈	lanosta(eupha)hexaene	G (41), H(42)

References: A: Logan and Eglinton, 1994; B: Corbet, 1980; C: Philp, 1985; D: Trendel et al., 1989; E: Woolhouse et al., 1992; F: Jaffe and Hausmann, 1995; G: Stout, 1992; H: Hazai et al. 1986; I: Wolff et al., 1989; J: ten Haven et al., 1992; K: Chaffee et al., 1984; L: Chaffee and Fookes, 1988; M: Wakeham et al., 1980; N: Loureiro and Cardoso, 1990. Numbers into brackets correspond to peak number in the reference.

Table 1

Figure 1

a-



b-

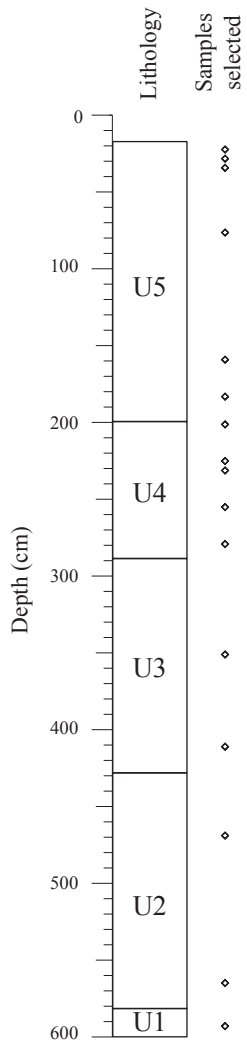
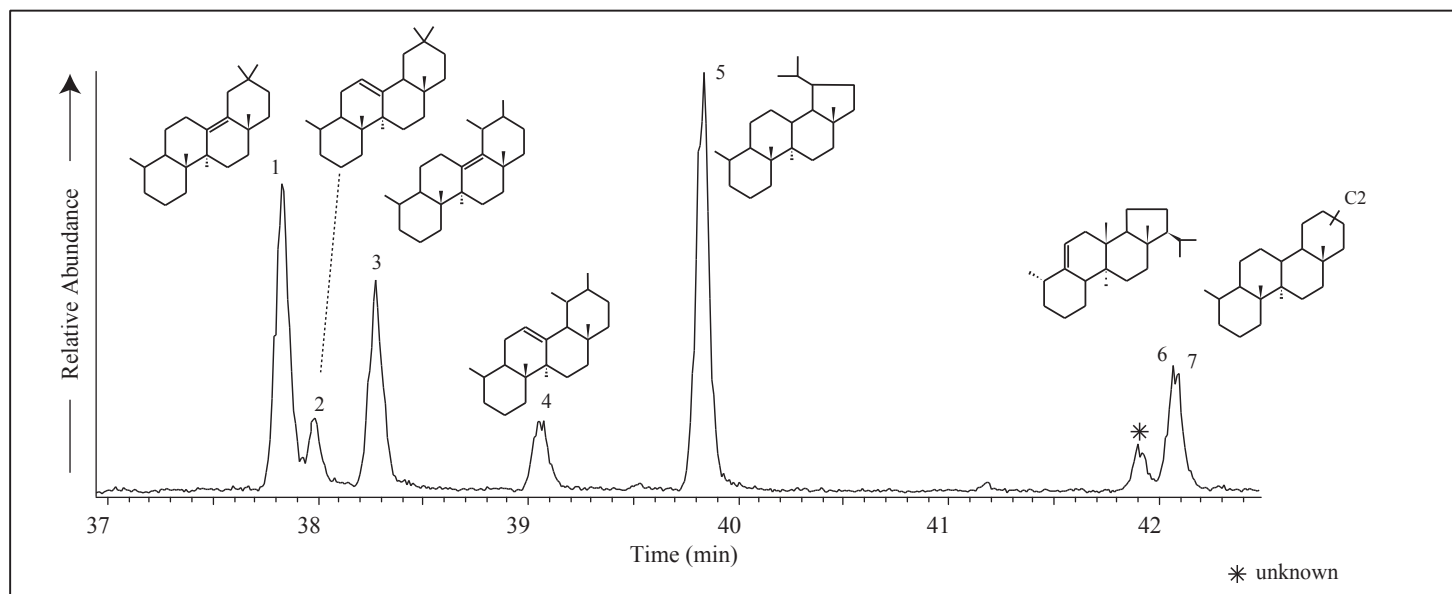


Figure 2



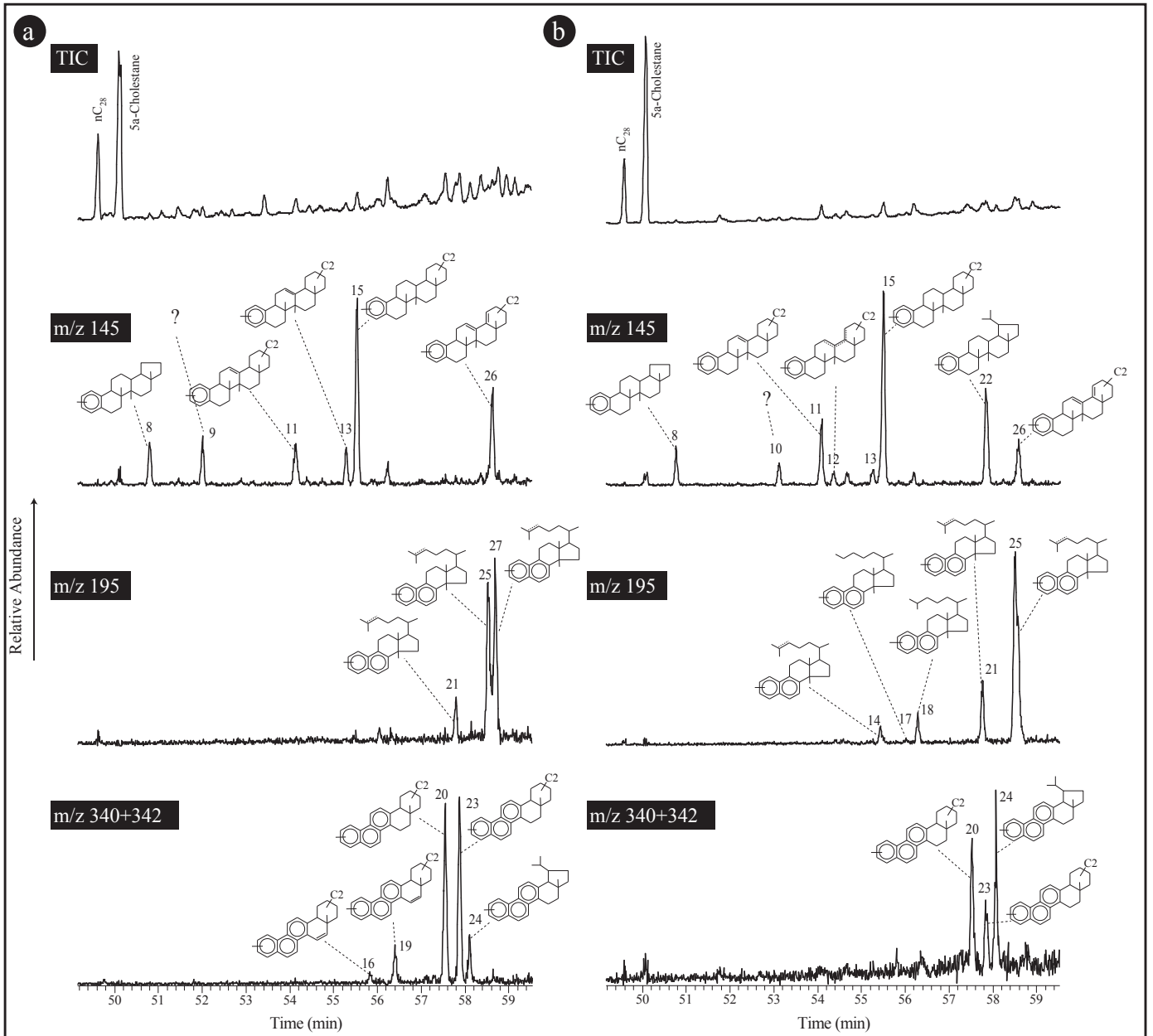


Figure 3

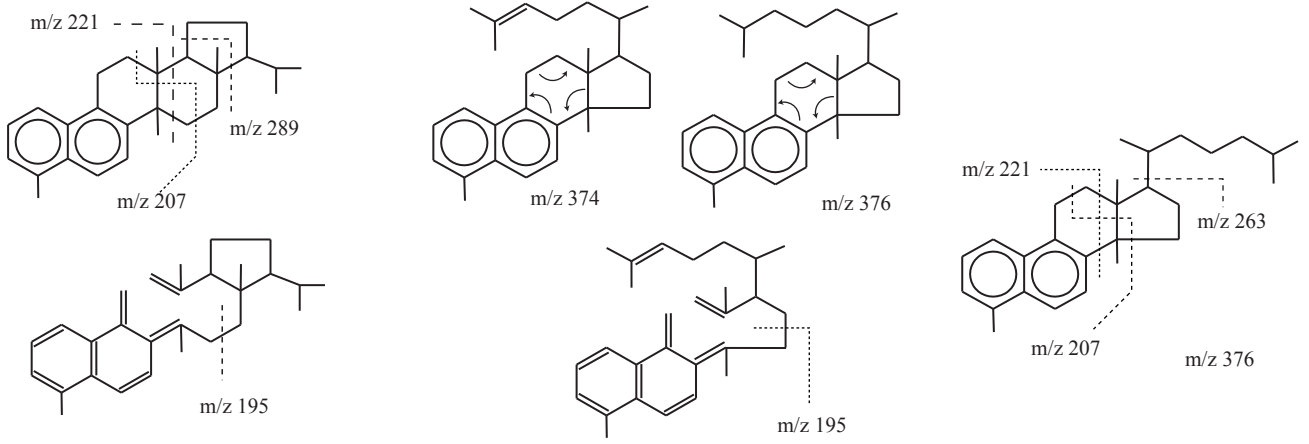


Figure 4

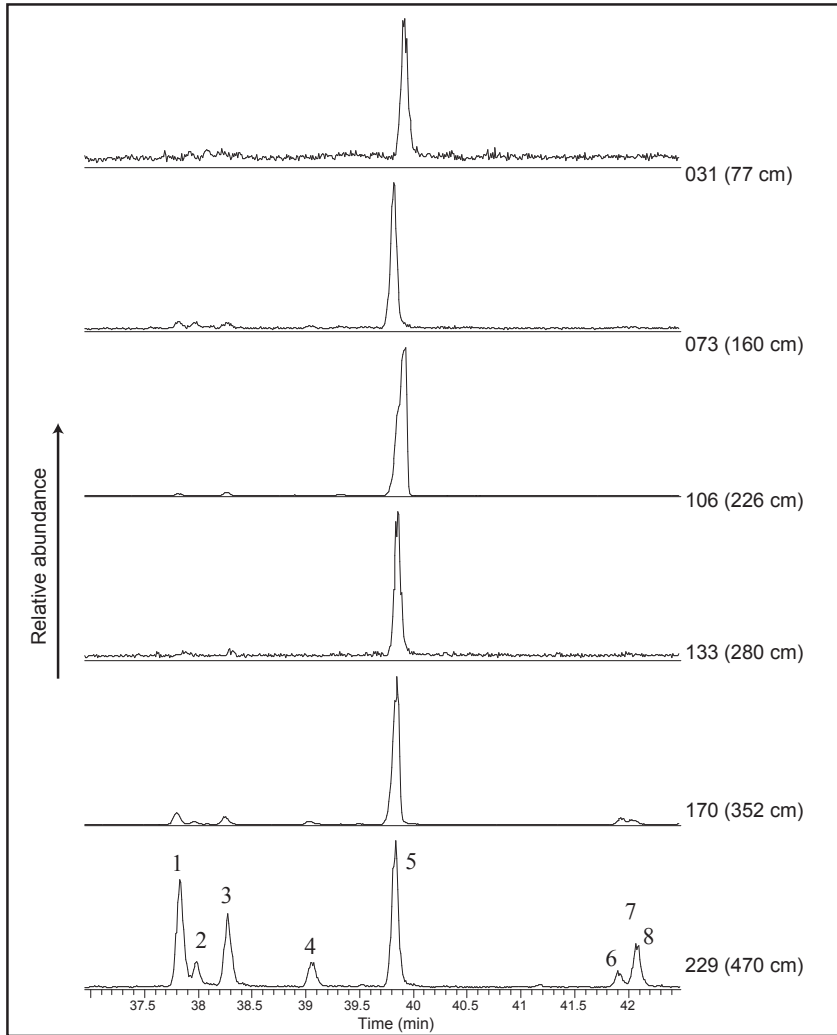


Figure 5

Figure 6

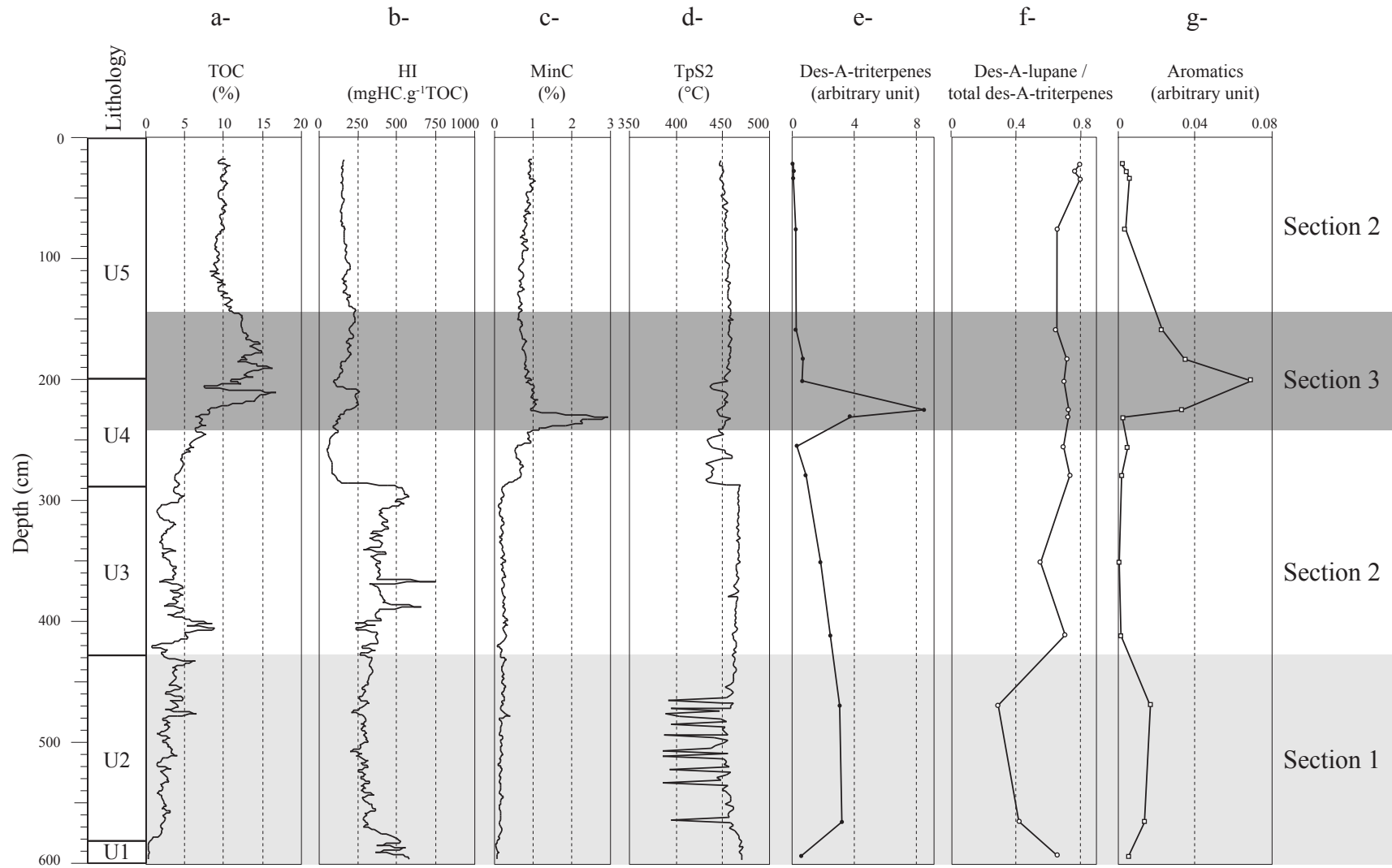


Figure 7

