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Lepidodendron dawsonii: functional groups and pyrolysates of compression and fossilized-cuticle (Late Asturian, Canada)

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ABSTRACT

Lepidodendron dawsonii BELL 1938 is an endemic species of Late Asturian age in the Canadian Sydney Coalfield, with conspicuous elongate leaf cushions. The study specimen, 35 cm long and 10 cm wide, represents a dichotomous bough from the tree crown in which the inner part of one side is black and compression-preserved, whereas the one in contact with the entombing rock matrix is dark-amber in colour and fossilized-cuticle preserved. Only stomatal pits and cuticular details are preserved. Comparison of these preservation states, based on Fourier transform infrared (FTIR) spectrometry, and flash pyrolysis gas chromatography mass spectroscopy (Py-GC/MS), demonstrate sufficient differences in chemistry to be able to link the two preservation states with differing pathways of organic matter transformation (diagenesis). The aliphatic-hydrocarbon chains of the cuticles are comparatively shorter and more branched than the longer chains of the compressions. Py-GC/MS results support the presence of hydrocarbon markers of plant cuticles. The high abundances of C_1 and -C_2 alkylphenols and C_1 and -C_2 alkylbenzenes in pyrolysates are likely derived from maturing lignin or lignin-like biomacromolecules. We suggest comparison of *L. dawsonii*'s cuticles with *Lepidodendron* coal macerals in Chinese Permian Leping coal, and with suberinite.

Keywords: FTIR, flash pyrolysis, bark, compression-fossilized-cuticle, *Lepidodendron*

1. INTRODUCTION

Lepidodendron dawsonii BELL 1938 is a fairly common lepidophyte component in the Late Asturian of Sydney Coalfield, Canada (Fig. 1A & B), and ranges from the Emery Seam to the highest strata at Point Aconi (Fig. 1C). Its phytostratigraphic utility is limited, but BELL (1966, Pl. XXVII, Fig. 5) believed it was early Westphalian D in the Canadian Carboniferous Maritime Provinces. THOMAS (2009, Table 6) stated that it was not found outside the Sydney Basin in Variscan Euramerica, i.e., it was endemic. The specimen is significant (Pl. 1A) because of the dual preservation as 1) a coalified compression, typical of fossil plants in the Sydney Coalfield (Pls. 1B & C), and 2) as rare fossilized-cuticle (Pls. 2A & B), i.e., this is the only specimen known from the Sydney Coalfield. The co-occurrence of coal and cuticle in the specimen invites analogy with a coal-seam, particularly as lycophytes provided considerable biomass for coal-seam accumulation (e.g., ARNOLD, 1947, p. 94; DIMICHELE et al., 1985; CLEAL et al., 2010).

Here, the focus is on the two preservation states in one contiguous specimen of *L. dawsonii.* as each is capable of providing its own spectrochemical information as a consequence of its fossilization history, i.e., coalification and natural maceration (ZODROW & MASTALERZ, 2009). Though cuticular information is provided taxonomy is not an objective here and is not discussed further.

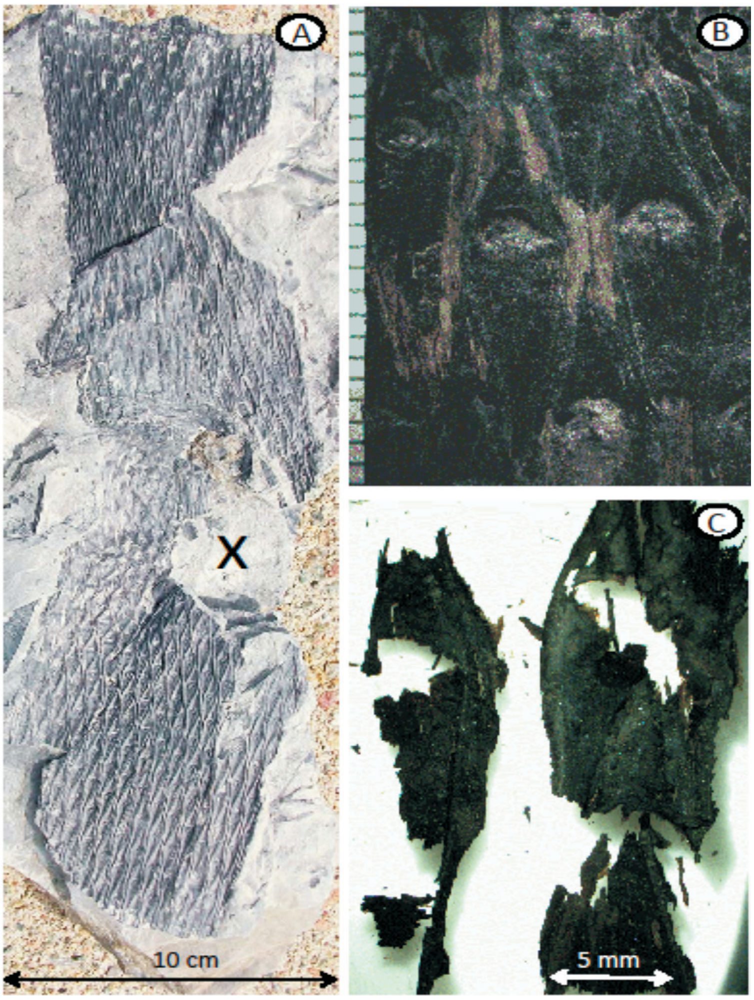

PLATE 1
Lepidodendron dawsonii

A Entire specimen, where X marks the base of the dichotomy and sample location? (this is what x is referred to in the text as representing).
B Compressed leaf cushions *in situ*.
C Lose compressed leaf-cushion material after 30-min HF treatment. Specimen 980-391-1 in the Palaeobotanical Collection of Cape Breton University.

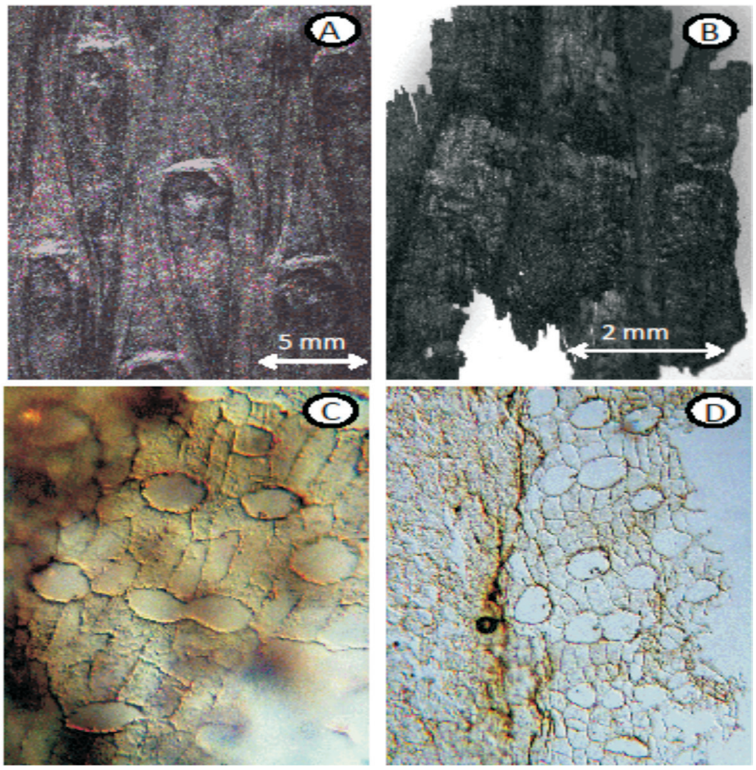

PLATE 2
Lepidodendron dawsonii

A Amber-coloured fossilized-leaf cushions *in situ*.
B Fossilized-leaf cushions after 20-min HF treatment.
C Cuticle of (B) is in focus above the lower surface. x125. Slide 980-391-1/2.
D Cuticle (right) and lower surface (left). x125. Slide 980-391-1/1. The round or oval holes are stomatal pits.

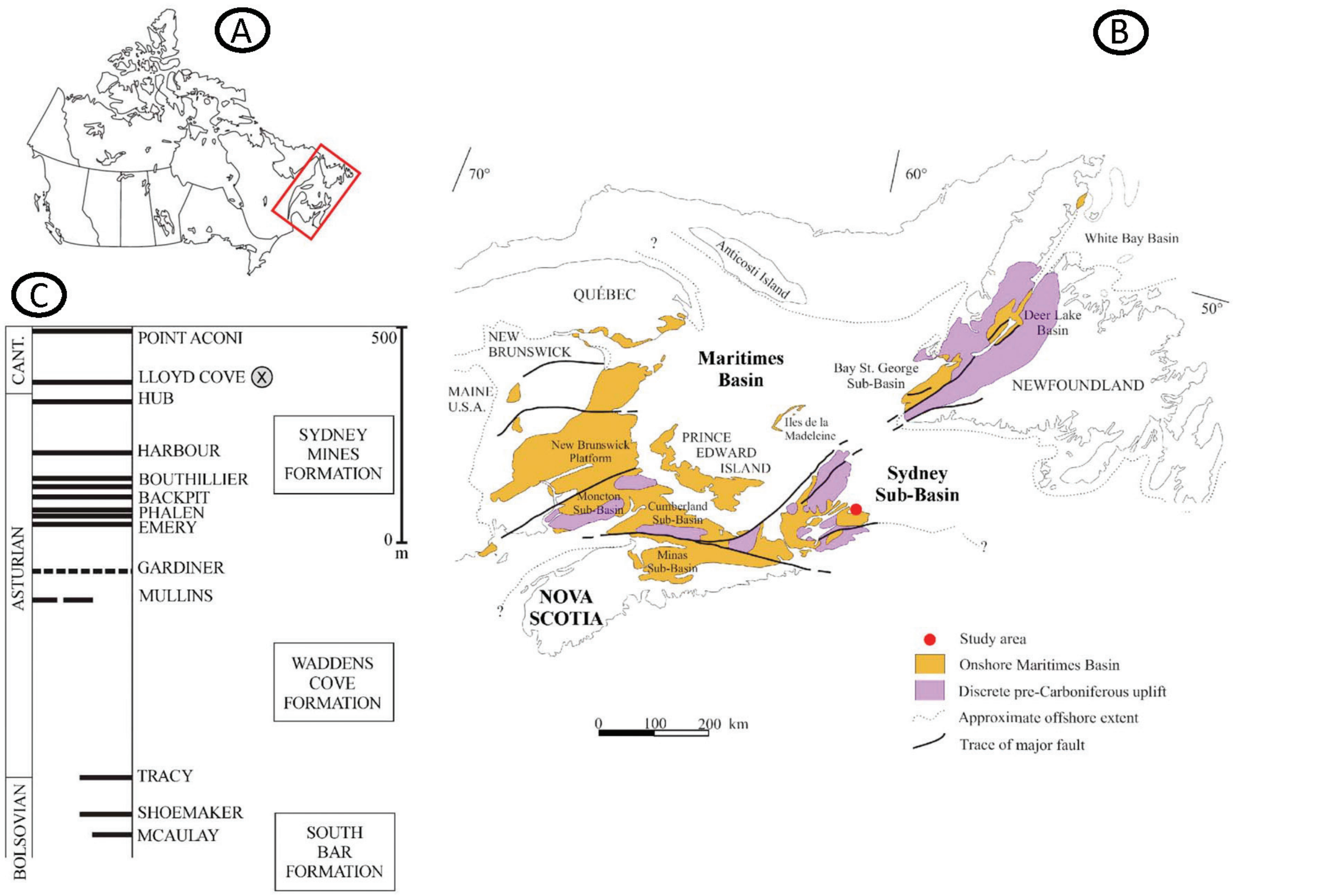

Figure 1: A) Canada. B) Canadian Maritimes Basin. C) Local coal-lithostratigraphy of the Sydney Coalfield, Nova Scotia, where X marks the Lloyd Cove Seam for the sample.

2. PRESERVATIONS AND CUTICULAR MORPHOLOGY

The specimen originated from a section 1 m above the Lloyd Cove Seam in the unaltered shaly roof rock, at the base of the Cantabrian Substage (Fig. 1C), that is known to be very fossil-rich and biodiverse (e.g., ZODROW, 2002). Its dichotomizing habit (Pl. 1A) is typical for the crown of *Lepidodendron* Sternberg (HIRMER, 1927, Figs. 200–202; THOMAS, 1966). The cortex of the inner surface of the branch that is pressed upon the prolongation is coalified with preserved cuticle, whereas the cortex facing the entombing rock matrix (Fig. 2) is fossilized as cuticle *sensu* ZODROW & MASTALERZ (2009).

Leaf cushions are slender ca. 20 mm long and 5 mm wide and separated by secondary growth enlargements (Pl. 1B, Pl. 2A and B); see also THOMAS (1966, Fig. 5b). The leaf scars are rhomboidal in shape, and BELL (1938) compared older stems of *L. dawsonii* with *L. rimosum*. The epidermis of both preservation states shows little morphological difference and is diaphanous and very thin. Details of stomatal apparatuses are not preserved, only stomatal pits (THOMAS, 1966, Fig. 3) that are oval to round in shape, sometimes touching or merging into one another, averaging

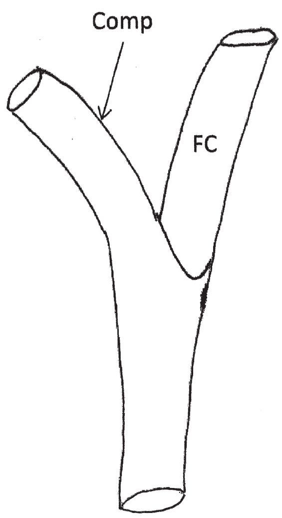

Figure 2: Study specimen showing sample locations for analyses (schematic), where FC stands for fossilized-cuticle and Comp for compression.

for the longer diameter 39 μm, ranging from 30 μm – 50 μm, n= 40. Two cell morphologies are evident, based not so much on their variability which is considerable (compare Pl. 2C

Table 1: Average cellular length/width ratios (µm).

Cushion part	n	Range		Average		Ratio length/ width
		length	width	length	width	
Above leaf scar	22	22–65	7–30	34.8	19.4	ca. 2
	18	45–114	5–19	74.8	12.4	ca. 6

and D), but on differences in average ratios of length/width (Tab. 1). The elongate cells probably represent the epidermis above the leaf scar (see THOMAS, 1966, p. 297; 1970). In either morphology anticlinal walls are straight.

3. MATERIAL AND METHODS

Samples were chipped from a location marked X on Pl. 1A, supplemented by fossilized-cuticles from the lower right-hand edge of the specimen. HF (48 %) was used to free all sample materials that were then washed and rinsed in distilled water for one week to eliminate as much acidic residue as possible. For a clearer view of the cuticular topography under a binocular microscope equipped with Nomarski capability, the fossilized-cuticles were lightly macerated (3 h), using SCHULZE'S well-known oxidative process (CLEAL & ZODROW, 1989; and others).

Compression and macerated fossilized-cuticle samples for IR (infrared) spectra were prepared by the pellet method, where 250 mg of KBr were finely ground with ca. 1.2 to 1.5 mg of the organic material, and pressed for 20 min (20,000 psi) into a 1-cm diameter pellet. IR analysis was performed on a Nicolet Thermo-Electron 6700 spectrometer, accumulating 256 scans at a resolution of 4 cm^{-1} wavenumber. Assignments of functional groups were according to PAINTER et al. (1981), WANG & GRIFFITHS (1985), and GOODARZI & MCFARLANE (1991).

The flash pyrolysis (Py) of 0.6 mg, and subsequent analysis of the pyrolysates were carried out using a Frontier Lab vertical micro-furnace at 600 °C which was interfaced to a HP GC/MS with a 30m x 0.25mm (0.25 um thickness) DB-1701 capillary column. All interface temperatures were at 260 °C. The GC oven program is 35 °C (initial) to 265 °C at 7 °/min temperature ramp. The identity of the peaks was verified using standards.

Elemental analyses for nitrogen, carbon, hydrogen, sulfur, and oxygen (by difference) were performed in duplicate (2–3 mg) on a Carlo Erba EA 1108 Elemental Analyzer, and the averages are presented in Table 2.

Table 2: Elemental analyses (weight %) of the fossilized cuticle, compression, and coal (vitrain) from the underlying Lloyd Cove Seam.

	N	C	H	S
Fossilized cuticle	1.71	67.85	4.70	5.35
Compression	1.68	65.50	4.48	4.82
Coal	1.36	75.92	5.22	nd

nd not determined (LYONS et al., 1995, Table 1).

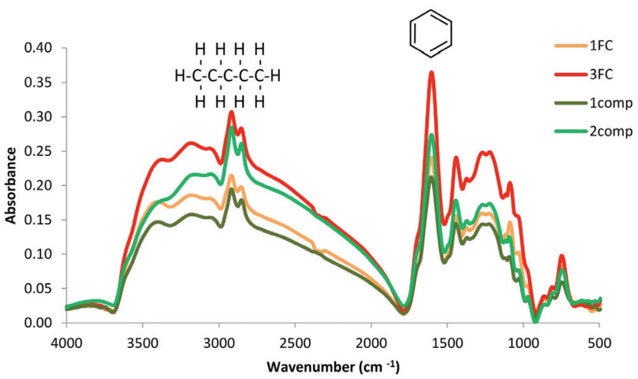

Figure 3: Composite presentation of the spectra, where FC is fossilized cuticle, and Comp the compression. The benzene ring (right) symbolizes the oxygenated aromatics and the chain the aliphatic hydrocarbon chain.

4. DISCUSSION OF RESULTS

The mid range IR spectrum used for interpreting organic analyses, 4000–400 cm^{-1} wavenumber, is subdivided into two peak-containing regions, separated by a broad interval of low or no absorbance. The lower-wavenumber region ranges from 1800 to 700 cm^{-1} and includes the 1800–1600 cm^{-1} region with oxygen-containing and aromatic moieties. Comparative wave-number changes/differences/shifts in this region reflect diagenetic influence, e.g. particularly oxidation (BERNER, 1980) through geological time. The second peak series is located in the 3000–2800 cm^{-1} region and relates to aliphatic side-chain characteristics as signals from the biopolymer-cuticle matrix (STARK & TIAN, 2006). From this region the CH_2/CH_3 ratios were calculated after deconvolution of bands, with the band width and band enhancement kept constant. But caution is necessary in the interpretation, as the ratio is sensitive to changes in maturity levels (VAN BERGEN et al., 2004).

Qualitative examination of FTIR spectra shows close similarity between the fossilized-cuticle and compression spectra (Fig. 3), i.e., all show distinct aliphatic bands in the 3000–2800 cm^{-1} aliphatic stretching region, and in the 1500–1300 cm^{-1} aliphatic bending region. The most prominent band at 1607 cm^{-1} is assigned to aromatic carbon on the basis of the position of the peak as well as its shape. Aromatic hydrogen bands in the 3100–3000 cm^{-1} region are very small but present in all spectra. In the 900–700 cm^{-1} aromatic out-of-plane region, only one band at ~750cm^{-1} is detected that indicates four adjacent C-H groups. A slight difference is

Table 3: Sample weights for FTIR spectra.

Spectrum	Weight	Spectrum	Weight
Comp1	1.1	2FC	1.1
Comp2	1.1	1FC	1.2
Comp3	1.1	3FC	1.3

Comp compression, FC fossilized cuticle.

Table 4: FTIR absorption region and ratios used.

Absorption regions (cm^{-1})	Assignment
3100–3000	Aromatic C-H groups in stretching mode
3000–2800	Aliphatic C-H groups in stretching mode
1800–1517	C=C plus oxygen-containing groups (carboxyl, carbonyl, ketones, etc)
1500–1300	Aliphatic C-H groups in bending mode
900–700	Aromatic out-of-plane C-H groups[a]
Ratios	**Interpretation**
CH_2/CH_3 in 3000–2800 region	Relates to aliphatic chain length and degree of branching; larger = longer and less branched chains
Al/Ox (3000–2800)/(1517–1800)	Estimates proportions of aliphatic C-H groups in relation to the sum of oxygen-containing groups and C=C
Ar1 (3100–3000)/(3000–2800)	Indicates aromaticity of organic matter based on aromatic stretching region; larger = more aromatic
Ar2 (900–700)/(3000–2800)	Indicates aromaticity of organic matter based on aromatic out-of-plane region; larger = more aromatic
CAR1 (3100–3000)/(1800–1517)	Estimates degree of condensation of aromatic ring structure based on aromatic stretching region; larger = higher degree of condensation
CAR2 (900–700)/(1800–1517)	Estimates degree of condensation of aromatic ring structure based on aromatic out-of-plane region; larger = higher degree of condensation

[a] If present, it is not taken into account in calculations.

noted in relative band absorbance; it is higher for 1FC (fossilized cuticle) and 3FC, correlating with increasing sample weight (Tab. 3) because the spectra are not weight-normalized. This observation conforms to the empirical Lambert-Beer Law that relates absorption of light to the amount of material through which the light travels.

Closer semi-quantitative evaluation and comparison of spectra can be achieved by means of integration of area under spectral bands, and calculation of their ratios (see ZODROW & MASTALERZ, 2007; D'ANGELO et al., 2011a). Table 4 lists the spectral regions and FTIR-derived ratios selected as being the most useful for the purpose of this study. In effect, the ratios have a semi-quantitative chemical meaning and have been utilized, for example, in palaeochemotaxonomic studies (LYONS et al., 1995; ZODROW & MASTALERZ, 2001; ZODROW et al., 2003), characterizing morphotypes (ZODROW et al., 2000), reconstructing kerogen (D'ANGELO et al., 2011a), or in documenting preservation variability (D'ANGELO et al., 2011b). Table 5 summarizes the semi-quantitative chemical data (FTIR-derived ratios) that in effect constitute the remaining organic material of the plant we call *L. dawsonii*, in these particular preservation states.

The analytical data (Tab. 5) clearly show that in respect to aromaticity some differences exist between the compressions and fossilized-cuticles, with the average aromaticity (AR1) and AR2) being slightly higher for fossilized cuticles, which corresponds to slightly higher elemental carbon (Tab. 2). However, the estimated degree of condensation of aromatic ring structure, benzene ring (CAR1 and CAR2) is higher for the coaly compression, as is expected. The most noted spectrochemical difference between these two preservation states is, however, for the CH_2/CH_3 ratios which are consistently smaller (mean 2.24) in fossilized-cuticle vs the

Table 5: Semi-quantitative FTIR data.

	CH_2/CH_3	Al/Ox	AR1	AR2	CAR1	CAR2
980-391-1FC	2.08	0.29	0.06	0.44	0.017	0.13
980-391-2FC	2.58	0.34	0.05	0.26	0.017	0.09
980-391-3FC	2.07	0.30	0.06	0.38	0.018	0.12
Average	2.24	0.31	0.06	0.36	0.017	0.11
980-391-2comp	2.66	0.37	0.05	0.23	0.018	0.09
980-391-3comp	2.52	0.41	0.05	0.36	0.019	0.11
980-391-4comp	2.63	0.32	0.06	0.50	0.019	0.16
Average	2.60	0.37	0.05	0.33	0.019	0.12

Note: FC– fossilized cuticle; comp – compression

compressions (2.60), implying comparatively shorter and more branched hydrocarbon chains in the biomacromolecule for the fossilized-cuticles. This is unexpected, as in our experience with Laurasian-Gondwanan compression-fossilized-cuticle of the medullosalean foliage of Carboniferous-Upper Triassic ages, the reverse is the case, and fossilized-cuticles normally show higher CH_2/CH_3 ratios (see ZODROW et al., 2011, Table 4; ZODROW & MASTALERZ, 2009, Fig. 5; ZODROW et al., 2009, Table 6; and D'ANGELO et al., 2011b, Table 4). We mention parenthetically that a similar relationship exists between medullosalean fossilized-cuticles and those that are treated by SCHULZE'S maceration process. In nearly each case, the Schulze's treated fossilized-cuticle revealed higher CH_2/CH_3 ratios from which comparatively longer and less-branching hydrocarbon chains are interpreted (ZODROW et al., 2010, Table 3). Equally, cuticles obtained by SCHULZE'S process

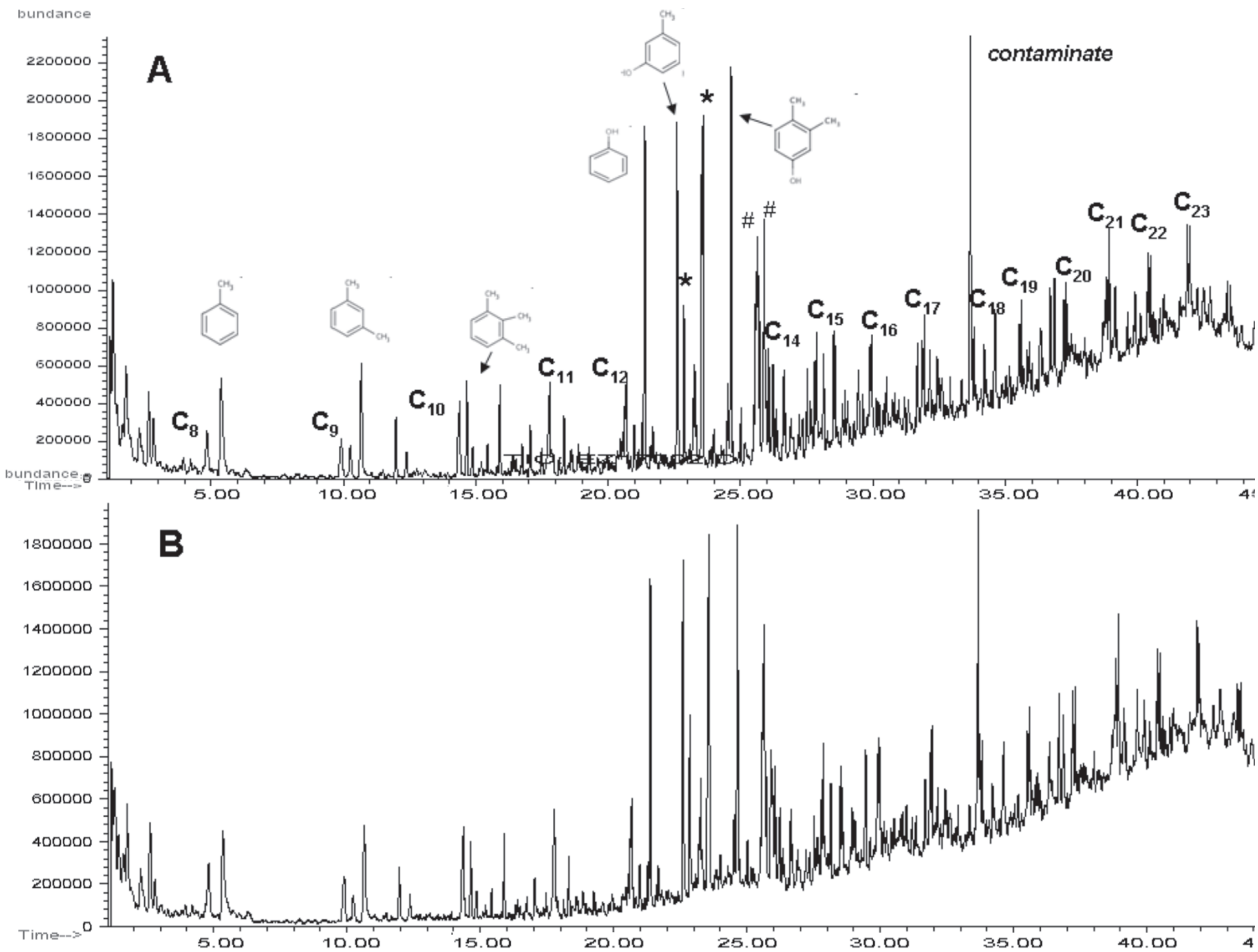

Figure 4: Flash Py- GC/MS chromatograms of *Lepidodendron dawsonii*. A) Fossilized-cuticle. B) Compression. Peaks are annotated with appropriate chemical structures. *n*-alkene/*n*-alkane doublets (note: early eluting pairs have extensive overlap) numbered according to the appropriate carbon chain length. The peaks denoted as * are other C_1-alkyphenols and as # are C_2-alkylphenols.

from medullosalean compression foliage have larger CH_2/CH_3 ratios (e.g. ZODROW & MASTALERZ, 2007, Figs. 8 and 9 compared with Fig. 7) which are presently being investigated (unpublished research notes, 2012).

Another small difference is seen in the Al/Ox ratios, Tab. 5, with fossilized-cuticles having smaller values (average 0.31) vs compressions (0.37), indicating a larger, relative to aliphatic hydrogen, contribution of carboxyl/carbonyl groups in the cuticle. A large element-oxygen content in the compression suggests significant portions of oxygen in compounds, other than carboxyl/carbonyl (for example in hydroxyl OH HO).

The major pyrolysates (and their relative abundances) are strikingly similar (Fig. 4). Both fossilized-cuticles and compressions show an *n*-alkene/n-alkane series up to C_{23}. The *n*-aliphatic hydrocarbon series is indicative of the presence of resistant cuticle hydrocarbon polymers that have been observed by EDWARDS et al. (1997), or COLLINSON et al. (1998). The abundant aromatic pyrolysates, those being C_0-C_3 alkylbenzenes and C_0-C_2 alkylphenols, are most probably markers of matured lignin components (see LOGAN & THOMAS, 1987). These pyrolytic chemical features were also observed by EDWARDS et al. (1997; and references there in) who performed analytical pyrolysis of the outer cortical tissue in Lower Devononian *Psilophyton dawsonii.*

Comparison of elemental percentages shows a slightly lower carbon and hydrogen content in the compression (Tab. 2), though sulfur is high and is regarded as being of dominantly pyritic origin, which is supported by observed submicron framboidal pyrite on some cushions. Disregarding the sulfur, oxygen by subtraction is ca. 25% for the fossilized-cuticle and 28% for the compression. In comparison with the bituminous coal from the same coal seam the roof rocks of which entombed *L. dawsonii*, we note that the coal-carbon content is significantly higher hydrogen is slightly higher, whereas the nitrogen content is lower.

In conclusion, it is suggested that the reversal of the CH_2/CH_3 ratios from the bark of *L. dawsonii* signals kinship with the bark of *Lepidodendron* (and *Psaronius*) that is a major maceral constituent in Chinese Permian coal (QUEROL et al., 2001). The argument is based on SUN'S (2005) work who described that bark, using transmitted-light FTIR microspectroscopy, as generally being highly aliphatic (long and straight hydrocarbon chains) and low (rare) in oxygenated components. Though a direct comparison with our FTIR data cannot be made because we use the KBr pellets, we note that the bark from *L. dawsonii* has shorter and more branched hydrocarbon chains. But its low content of oxygenated groups fits the description for the Chinese coal maceral. Py-GC/MS data support the FTIR evidence of aliphatic hydrocarbon chains and gives additional evidence that the oxygen-containing molecules (i.e., observed high abundance of phenolic markers) are likely associated with matured lignin marcomolecules. Overall, our results demonstrate that there are only subtle differences between the two preservation states of *L. dawsonii* which are, however, macroscopically manifest by the colour differences of the specimen. Preservation can therefore be remarkably variable over shorter specimen distances of these large plants, depending on compaction condition after burial and taphonomy.

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