

STERILE FOLIAGE OF FERTILE *SYDNEIA MANLEYI* AND SYNANGIAL CHEMISTRY (EUSPORANGIATE FERN, LATE ASTURIAN, CANADA): A NEW SUBFAMILY SYDNEIDEAE

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Abstract: *Typification of *Sydneia manleyi* Pšenička et al. 2003 is based entirely on fertile foliage. Of late, attached sterile-fertile segments have been found which are illustrated and described, together with cuticular preparations. A new subfamily, Sydneideae subfam. nov. is erected for the monotypic species. The synangial chemistry is compared with marattialean synangia/sporangia from the Czech Republic and from Canada.*

Key words: Sterile foliage, type, *Sydneia manleyi*, cuticles, Sydneideae subfam. nov., sporangial chemistry

INTRODUCTION

Marattialean ferns of Carboniferous age have been discussed in many papers during the history of palaeobotany. Most of them dealt with frond architecture, morphology of pinna/pinnule (e.g. Corsin, 1951; Wagner, 1958; Zodrow, 1990, and others), anatomy in petrified specimens (e.g. Millay, 1979, 1997; and others), or reproductive organs (e.g. Brousmiche, 1983; Pšenička et al., 2009, and others), including the *in situ* spores (e.g. Laveine, 1969, 1970, and others). Though cuticular studies of marattialean-fern pinnules were found by many palaeobotanists as inessential, cuticles are very thin and difficult to recover which accounts mostly for their unavailability in the study of these species. Nevertheless, Pšenička (2005) showed that cuticles could play a significant role for classification of several fossil marattialean species: *Lobatopteris aspidioides* (Sternberg) Wagner, *L. poly-podioides* (Sternberg) Pšenička, *L. miltonii* (Artis) Wagner, *Pecopteris* cf. *micromiltonii*, *P. alpina* Presl in Sternberg, *P. arborescens* (Schlotheim) Sternberg, *P. cyathea* (Schlotheim) Stur, *Acitheca polymorpha* (Brongniart) Schimper, and *A. alii* Zodrow et al. Comprehensive studies that deal with marattialean ferns, including morphology, sporangial structures with *in situ* spores and cuti-

cles, are published sporadically (e.g. Zodrow et al. 2006). Lately, when cuticles of some fossil marattialean ferns became available, chemotaxonomic investigations were published (e.g. Zodrow and Mastalerz, 2001; Pšenička et al., 2005).

A new fern species, *Sydneia manleyi* Pšenička et al. 2003, was described from the Upper Moscovian (Desmoinesian, upper Asturian) strata of Sydney Coalfield, Canada (Figure 1). The type specimen is fairly large (450 mm by 300 mm), entirely fertile, with a 10 mm thick penultimate rachis. The species concept is based on pendant synangial/sporangial pinna-pinnule morphology, and reproductive structures, together with information about the stomatal apparatus, which is preserved only on the abaxial pinnule (Pšenička et al., 2003, figs. 2-4, text p. 202, fig. 10, respectively). Marginally this paper alluded to cuticles.

Seventeen years after the collection of the type 989GF-275-276, 2 additional 90-120 mm long entirely fertile structures, not illustrated, were found in the *locus typicus* of the Prince Mine (accession numbers 07-4/25-5 and 07-9/14-1a,b).

The purpose of this paper is to present new information that supports the general view of *S. manleyi* as a fossil plant, which consists of here-

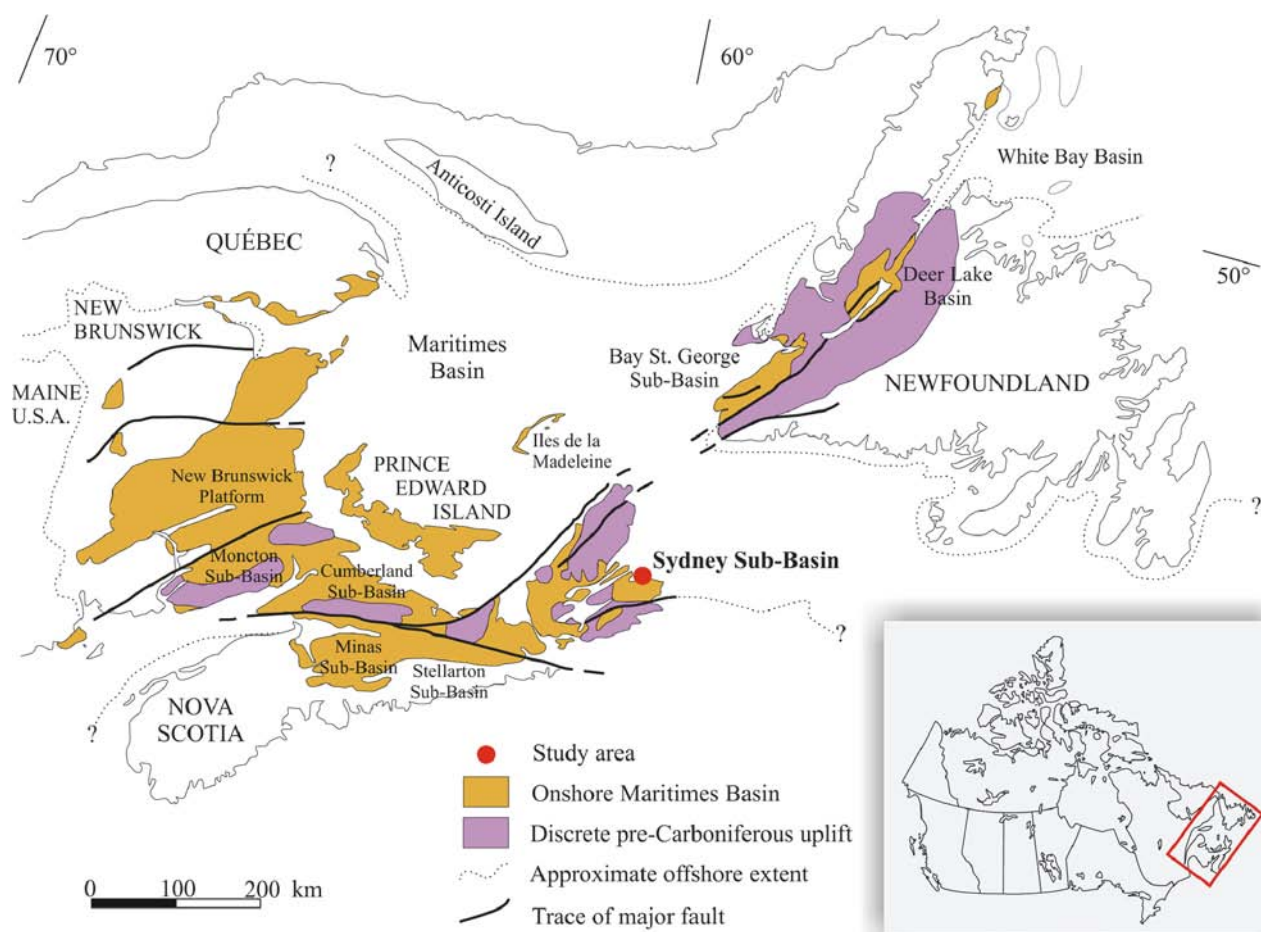


Figure 1. Study location. Maritimes Basin with Sydney Coalfield (Sub-Basin), Nova Scotia, Canada.

to-fore missing sterile/fertile pinnate structures in the typification of the species. In addition, synangial chemistry is presented by methods of solid-state Fourier transform infrared (FTIR) spectrometry. Moreover, based on the new foliar information, we propose a new Subfamily for this type of marattialean fern with mm-sized, sterile/fertile „sphenopteroid” foliage that does not fit the true pectopteroid modality, but significantly possesses spore and pendant synangial/sporangial morphologies that point to marattialean affinity.

SAMPLE PROVENANCE, PRESERVATION, AND METHODS

Exact stratigraphic documentation is unavailable, but the fossil material is entombed in a gray-mudstone lithology that compares with the *stratum*

typicum from which the type was collected in the Prince Mine coal mine, Sydney Coalfield, Canada (Pšenička et al., 2003) (Figure 1), to presume common provenance. Moreover, the study specimens 4-CF-1 to 6 presumably originated from one frond as they were split and cut from one rock specimen, roughly 130 mm by 70 mm in size. Of these, the main study and illustrated specimens are 4-CF-6a and 4-CF-1, where the latter is sterile/fertile. The prefix „4” refers to the year 2004 in which Ms. Cavelle Fraser (CF) donated the specimen, amongst others, to the Palaeobotanical Collection of Cape Breton University. The material is compression-preserved, but in the early stage of natural maceration, as is often the case for the Sydney Coalfield with medium-maturity level in the sample section (vitrinite reflectance is ca. $R_o\% = 0.65-0.70\%$, i.e., range within the oil window).

Table 1. Assignments of FTIR bands; ^a According to Wang and Griffiths (1985), Ganz and Kalkreuth (1987); Colthup et al. (1990), Petersen and Nytoft (2006); Petersen et al. (2008). ^b It should be noted that peak at 2925 cm⁻¹ (obtained after deconvolution of aliphatic C-H stretching region, not shown) represents the contribution from CH₃ and CH₂ groups attached directly to aromatic rings (see Petersen and Nytoft 2006).

Range (cm ⁻¹)	Group and class of compound	Assignment and remarks
3450 – 3250	-OH in alcohols and phenols	O-H stretch
2936 – 2913	CH ₃ -, CH ₂ - in aliphatic compounds ^b	CH ₃ -, CH ₂ - antisymmetric stretch
2864 – 2843	CH ₃ -, CH ₂ - in aliphatic compounds	CH ₃ -, CH ₂ - symmetric stretch
1724 – 1700	C=O in carboxylic acids, ketones	C=O stretch
1654 – 1630	C=O in highly conjugated ketonic structures, H-O in phenolic compounds	C=O stretch, H-O stretch
1458 – 1434	CH ₃ -, CH ₂ - in aliphatic compounds	CH ₃ -, CH ₂ - antisymmetric deformation or CH ₂ scissor deformation
1279 - 1260	C-O in aromatic ethers	C-O stretch
1100 – 1030	C-O-C in aliphatic ethers, Si-O in silicates	C-O-C antisymmetric stretch, Si-O stretch

HF-freed fertile specimens were macerated for 22 hours, and sterile foliage for 4-4.5 hours, using Schulze's process, i.e. 4-6 g of potassium chlorate dissolved in 150 ml of 78% nitric acid, followed by neutralizing ammonium hydroxide (4.5% volume/volume) treatment for 10 minutes. The resulting material was gently rinsed and washed for one day, and 7 representative samples were mounted on glass-covered slides for Nomarski phase-contrast microscopy. Also mounted were some HF-freed (non-macerated) sterile compressions for more acute observations than are otherwise possible when still *in situ*. Then, the synangial material was air-dried, and the resulting 0.7 mg sample amount ground together with 250 mg KBr into a pellet, and FTIR-analyzed. Only one reliable IR (infrared) spectrum could be produced from the sample amount. Spectrometric resolution is 4 cm⁻¹ wavenumber, and 256 scans were co-added to produce one spectrum. For further analytical details, the reader is referred to Pšenička et al. (2005). Table 1 lists the assignments of IR bands (range of wavenumbers cm⁻¹ in which the group and class of compounds absorb infrared radiation energy), and Table 2 defines the calculated ratios from the IR spectra (Figure 5), which represent semi-quantitative values. Refer to D'Angelo and Zodrow (2011) for details on the mathematical treatments applied to digitized IR spectra for refining and improving the semi-quantitative IR information. The new material, slides, and the KBr pellets are curated by ELZ, emeritus curator.

DESCRIPTIVE PART

Foliage in situ

The penultimate pinna, Plate I, Fig.1, shows distal foliage that is entirely sterile, and proximal foliage that is fertile, Plate I, Fig. 2, where pendant sporangia/synangia replace sterile pinnules. The penultimate rachis is ca. 2.1 mm wide, robust and longitudinally striate, with suboppositely inserted ultimate pinnae that in the upper part of the penultimate pinna gently taper to an obtuse apex. The ultimate rachis is ca.1.3 mm wide, straight, and longitudinally striate (Plate I, Fig. 2).

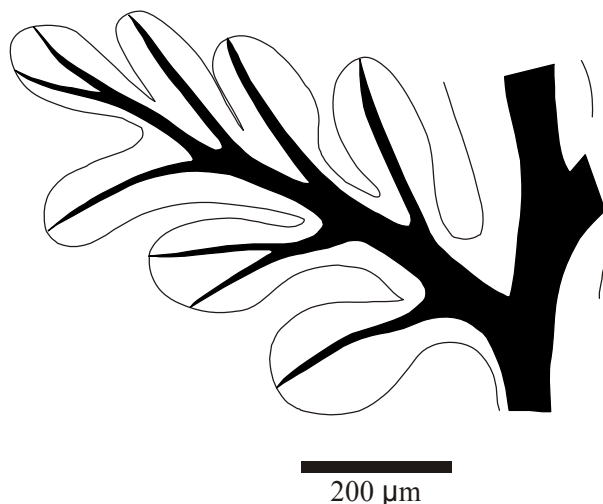


Figure 2. Reconstruction of a pinnule with venation.

The morphology of sterile pinnules (Figure 2) is best illustrated from selected pinnules of specimen 4-CF-1 (Plate II, Figs. 1, 2; Plate III, Figs. 1-3) whose exact orientation vis-a-vis Plate I, Fig. 1 is not known, though is comparable in every respect to the sterile apex of Plate I, Fig. 1. The pinnules are short, 4 mm to 5 mm long, deeply dissected into segments of claviform shape, with one or two terminal pinnules (Plate II, Fig. 2). Distal pinnules have 1 - 2, and proximal pinnules 5 - 7 claviform-shape lobes (Plate II, Fig. 2; Plate III, Fig. 1). The claviform-shape lobes are small 1-2 mm long, straight, with fully round apex (Plate III, Fig. 1 arrow). One lateral vein enters the base and follows an undivided or once divided (Plate II, Fig. 2 arrow), slightly flexuous course to the apex of a lobe (Figure 2). The pinnule lamina is very narrow (Plate III, Fig. 2).

Preservation assessment

For a preliminary assessment of the degree of coalification of such delicate sterile/fertile foliage prior to maceration, a number of HF-freed ultimate pinnae were examined under Nomarski phase-contrast microscopy. Clearly shown by claviform lobes is a degree of transparency (Plate IV, Fig. 1) which is incompatible with the optical property of opacity for coal (compressions). Higher magnification reveals a scaly surface (Plate IV, Fig. 2), and a detailed view of light-colored areas whose true color is darkish amber, which in turn is correlated to the variable degree of natural maceration/co-alification (chemical composition variability; see D'Angelo et al., 2012; Zodrow and D'Angelo, 2013, fig 2). This is interpreted as typical effects as a result of incipient natural maceration, and is regarded as an early-stage fossilized-cuticle (Zodrow and Mastalerz, 2009); hence the much shorter maceration time for the sterile foliage.

Sterile pinnules: Cuticles

The problem of obtaining fern cuticles from Carboniferous compressions for taxonomic studies has been known since Barthel (1962). However, this handicap was successfully overcome when Pšenička et al. (2003), Pšenička (2005) and Pšenička et al. (2005) routinely retrieved fern cuticles. Applying his maceration technique to the present material proved successful with the fertile material that yielded well-preserved synangia/sporangia with *in situ* *Punctatosporites*-type spores (summary: Pšenička et al. 2003, figs 8, 9, 11, 12). In contrast,

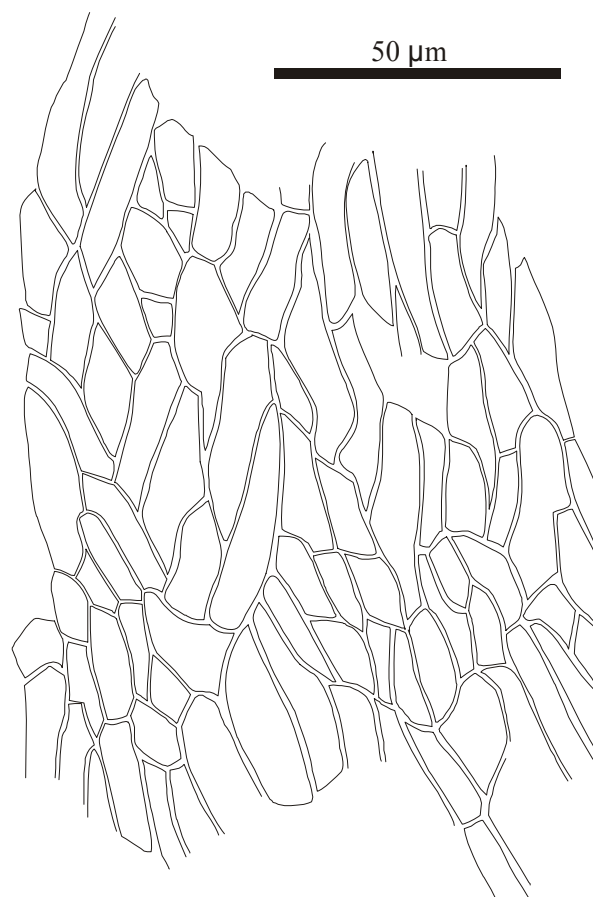


Figure 3. *Epidermal cells of a sterile pinnule. Surface orientation is indeterminate. Slide 4-CF-1/5.*

the sterile pinnules disintegrated during 3 maceration trials, and only small and thin fragments could be secured. Some of these showed a consistent cellular pattern (e.g. Plate III, Fig. 3; Figure 3). We were, however, unable to determine if the former is an abaxial or adaxial surface, though the absence of trichomes and stomata would point to an adaxial surface, but not necessarily. Two cellular patterns are apparent: (i) elongate 22-43 μm by 6-7 μm , costal field? (ii) ca. 11 μm by 4 μm , elongate, oval-shaped; intercostal field? The cells of both fields appear to be occasionally „furcated“. Anticlinal walls are comparatively thick, more or less straight sometimes very slightly undulating. Some other fragments showed no cellular morphology only a granular surface (Plate IV, Fig. 3), or a nondescript surface and questionable stomatal structures (Plate IV, Fig. 4). The topographic pattern in either case is unusual, but we have 4 additional fragments for confirmation.

Plate I.

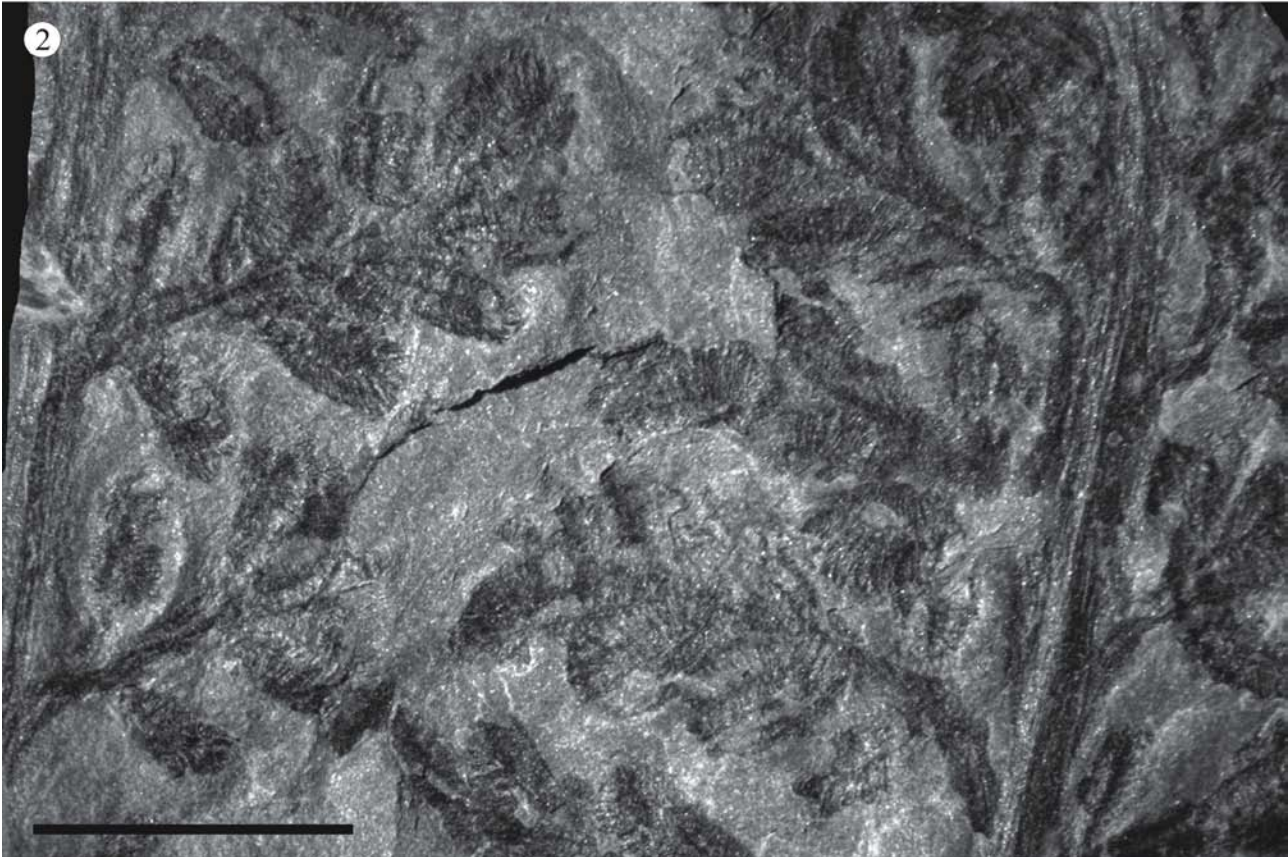
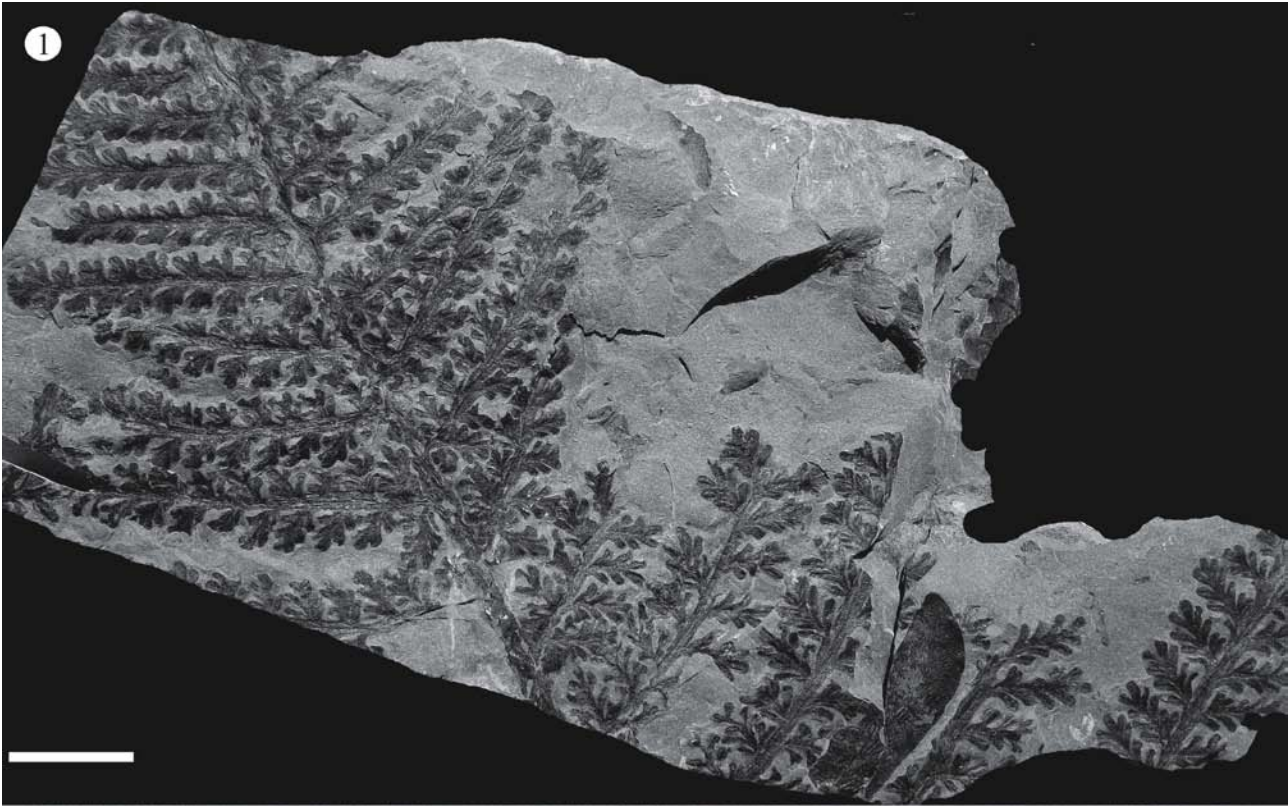


Plate II.

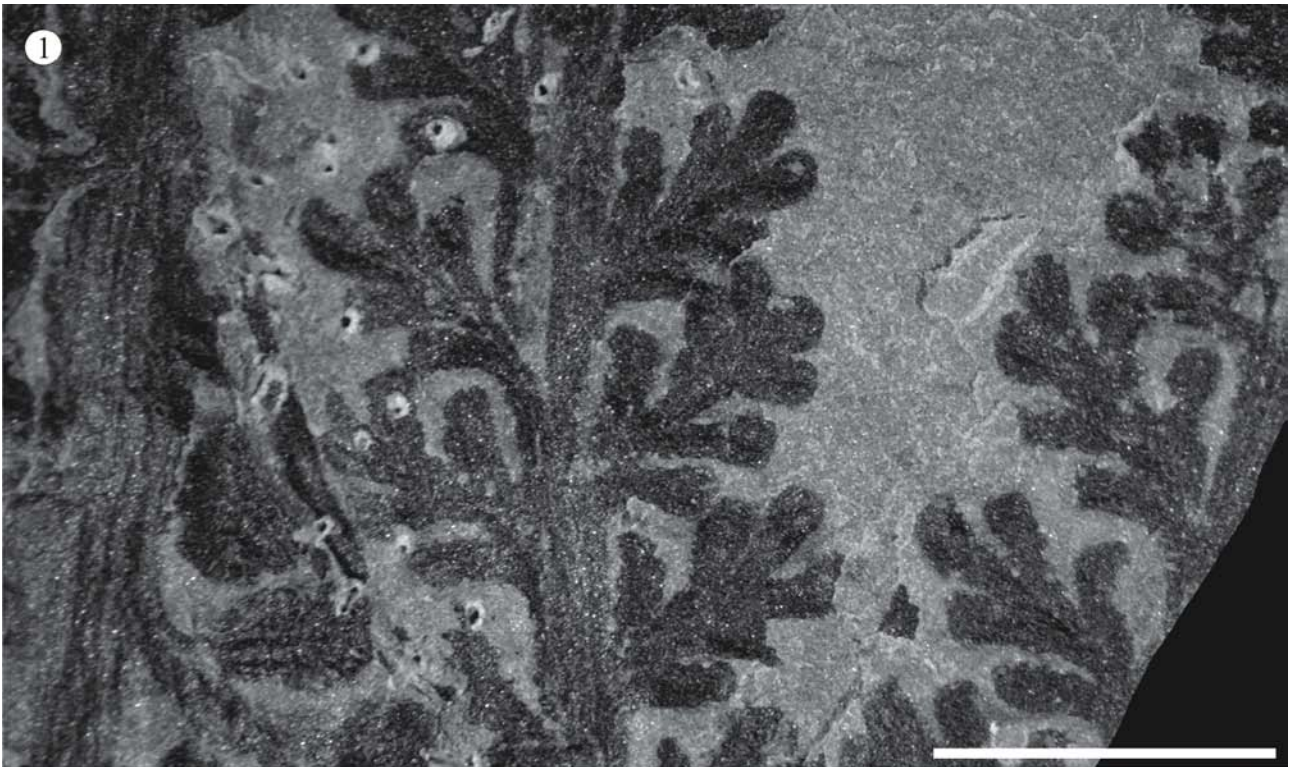


Plate III.

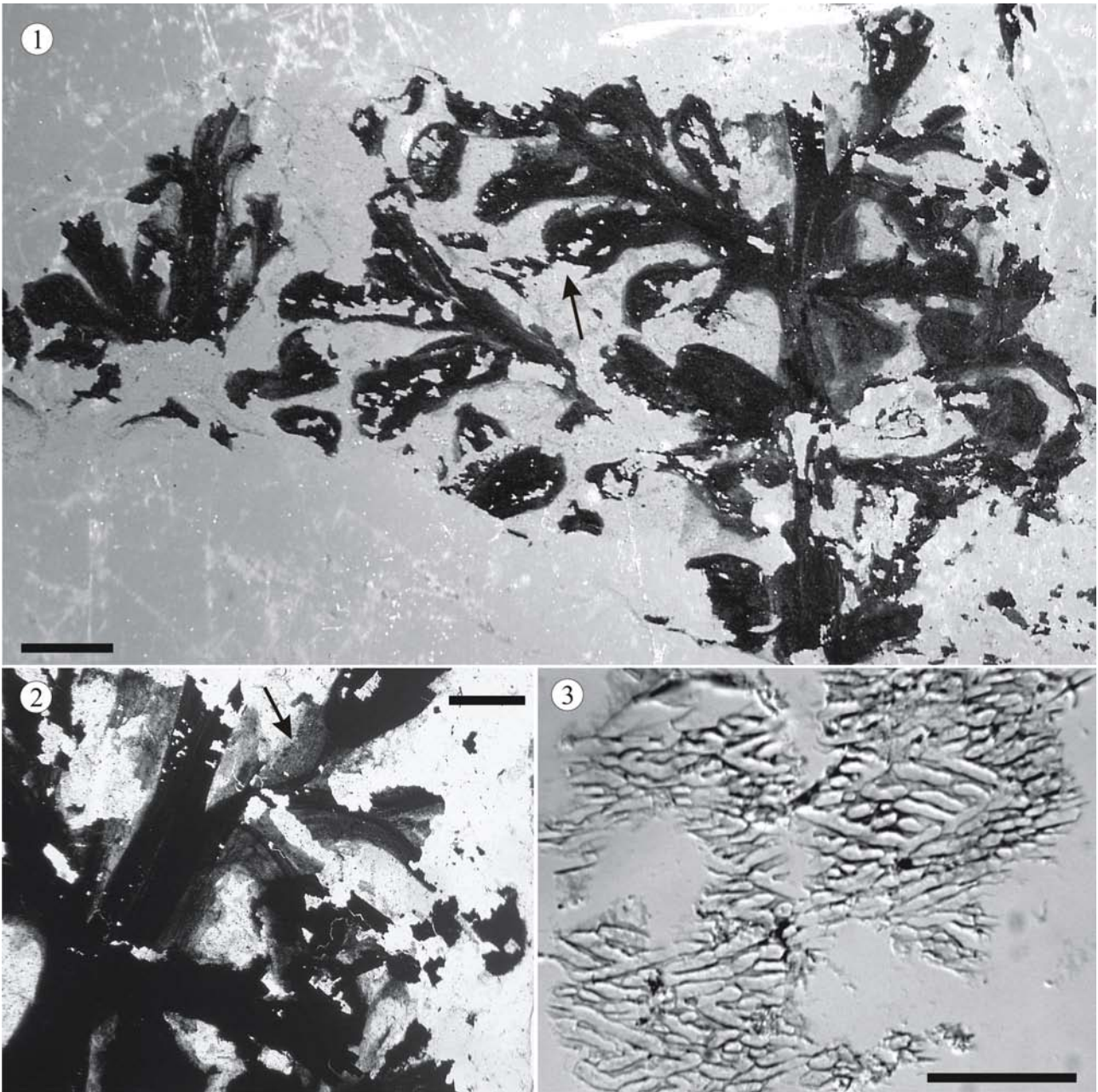
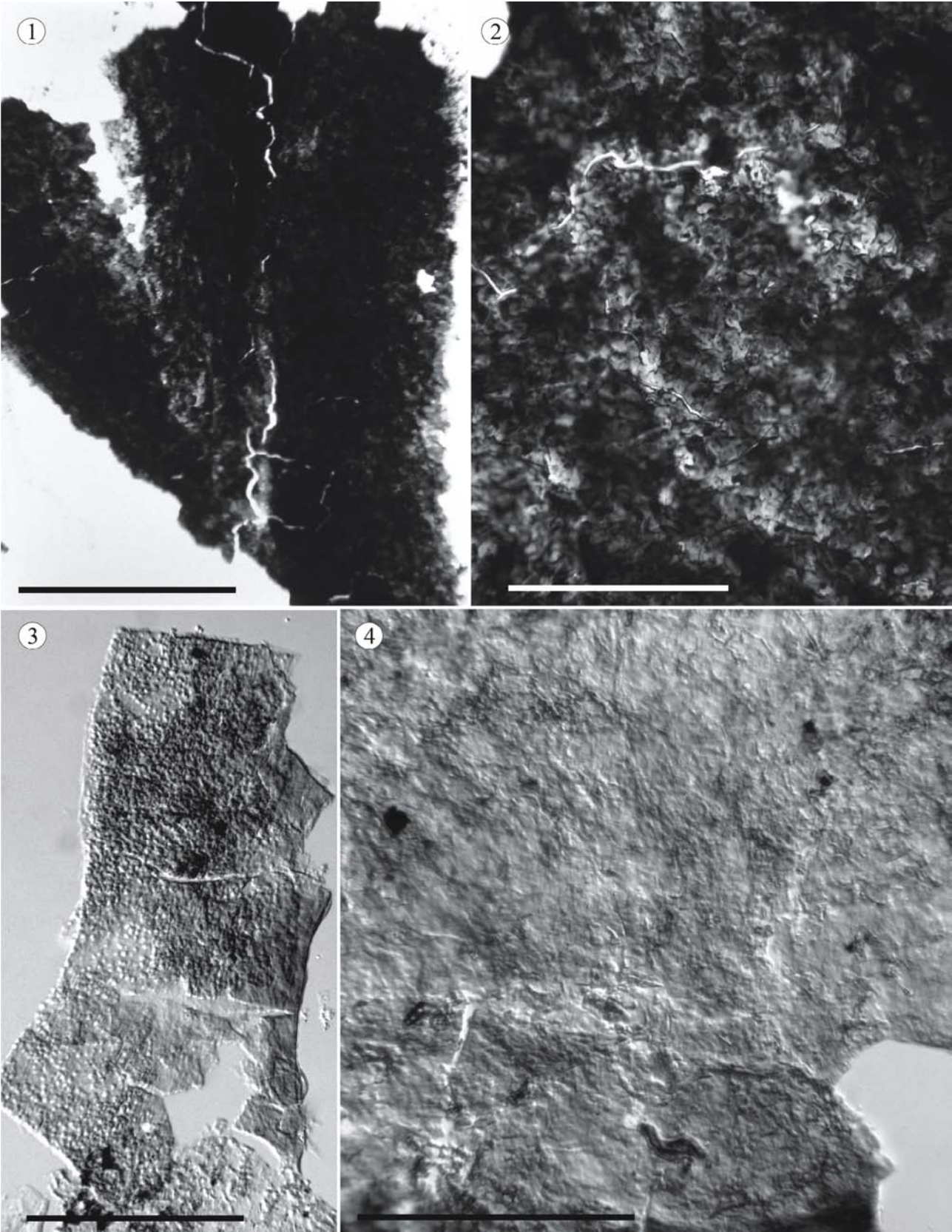


Plate III. *Sydneia manleyi*, 1) specimen 4-CF-1a; fragment of an ultimate pinna with well preserved sterile pinnules and round apex (arrowed), HF-treated only and fixed by collodion; scale bar 200 μm ; 2) specimen 4-CF-1a; detail of a pinnule with well-visible pinnule lamina (arrow; scale bar 1 mm; 3) slide 4-CF-1/5; sterile pinnule, cuticular morphology; scale bar 50 μm .

Plate I. *Sydneia manleyi*, specimen 4-CF-6a. 1) entire penultimate pinna; scale bar 10 mm; 2) detail of 1): fertile pinnules with synangia situated on lower part of pinnule lobes; scale bar 5 mm.

Plate II. *Sydneia manleyi*, specimen 4-CF-1. 1) sterile pinnules attached to an ultimate rachis; scale bar 5 mm; 2) detail of sterile pinnules with claviform-shape pinnule-margin lobes; scale bar 3 mm; arrow shows once divide lateral vein.

Plate IV.



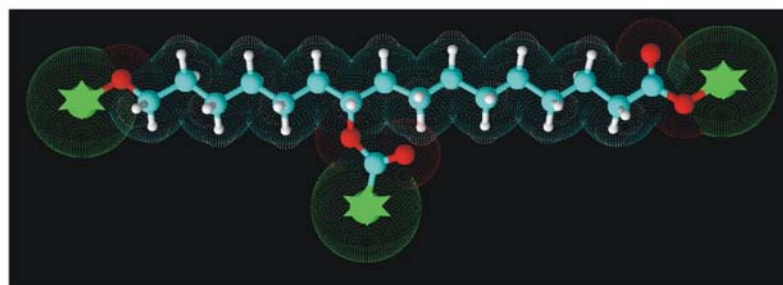
ANALYTICAL PART: SEMI-QUANTITATIVE CHEMISTRY

Sydneia manleyi synangium/ sporagium

For a short explanation, IR spectral interpretation is based on two peak series in the 4000-400 cm^{-1} wavenumber range which are separated by a broad valley in which little or no IR absorbance occurred, i.e., chemical groups do not absorb in the range 2800-1800 cm^{-1} (cf. Chen et al. 2012, Fig. 2; Fig. 1). The first series, in the 1800-1600 cm^{-1} band, relates mainly to oxygen-bearing and aromatic (ring-structured) compounds influenced during diagenesis. The second series, 3000-2800 cm^{-1} band, relates to methylenic hydrocarbon side-chain characteristics ('backbone' of the cutin structure, Figure 4) which are associated with the signal from the cutin, cutan, or alkyl structures. Increasing temperature, generated by metamorphism, igneous intrusion, or by burial load of sediments, modifies side-chain characteristics with a concomitant increase of aromaticity and condensation of aromatic carbon nuclei in the first series.

The *Sydneia* spectrum shows a dominant alkyl character as is indicated by the peaks at 2927, 2852 and 1435 cm^{-1} (Figure 5A; Table 1). Hydroxyl (H-O) groups (in the range 3450 – 3250 cm^{-1}) likely represent phenols or alcohols. Distinct carbonyl (C=O) groups are present as shown by peaks at 1718 cm^{-1} (representing C=O of carboxylic acids and ketones), and 1639 cm^{-1} assigned to highly conjugated ketonic structures (H-O in phenolic compounds may contribute as well). A small peak at 1277 cm^{-1} , corresponding to the C-O stretch in aromatic ethers, is characteristic of the structural geomacropolymer (see also Figure 5B, C). Sharp peaks below 1100 cm^{-1} are likely the contribution of mineral substances (impurities?), though aliphatic ether contribution cannot be ruled out.

Some comparisons with cuticles and cutin specimens of vegetative and reproductive structures



References

● Oxygen ● Carbon ● Hydrogen ★ R groups

Figure 4. Cutin-like 3-D monomer structure (redrawn from van Bergen et al., 2004) showing long-chain polymethylenic hydrocarbons $(\text{CH}_2)_n$, and carboxyl groups. The green star R represents *p*-coumaric acid or other monomer as the one represented.

from Sydney Coalfield are possible, based on the IR data base of over 100 spectra. Relatively low values of C=C cont and intermediate values of $\text{CH}_{\text{al}}/\text{C}=\text{C}$, 'A' factor, and 'C' factor (Tables 2 and 3) clearly indicate the important alkyl character of *S. manleyi* synangium. In agreement with other cuticle and cutin samples, comparatively low values of $\text{CH}_{\text{al}}/\text{C}=\text{O}$ (2.7, Table 3) indicate both a relatively higher C=O content and a higher cross-linking in the polymeric structure. This is supported by the ratios C=O/C=C, C=O cont, showing a relatively high carbonyl content.

IR comparison *Sydneia manleyi*- *Cyathotrachus altissemus*-*Pecopteris* (*Asterothea*) *nyranensis*

In general, the *S. manleyi* spectrum (Fig. 2A) shows the presence of more functional groups than those of *C. altissemus* (Fig. 2B) (Zodrow and Mastalerz, 2001, Table 3), and fertile *P. nyranensis* (Fig. 2C) (Pšenička et al. 2005, Fig. 10). Moreover, *S. manleyi* seems to have a more aliphatic structure than *C. altissemus* (compare peak intensities at 2927-2852 cm^{-1} and $\text{CH}_{\text{al}}/\text{Ox}$ ratio, Table 3 for both taxa). *P. nyranensis* has the lowest value of the $\text{CH}_{\text{al}}/\text{Ox}$ ratio. Despite the highest aliphatic character of *S. manleyi*, the CH_2/CH_3 value for this taxon is lower than that of *C. altissemus* (CH_2/CH_3 values are 4.5 and 5.2, respectively). This indicates the presence of relatively shorter and more

Plate IV. *Sydneia manleyi*, 1) slide 4-CF-6a/2; compression in the early stage of natural maceration, i.e., fossilized-cuticle; scale bar 500 μm ; 2) slide 4-CF-6a/2; detail of 1) showing a scaly surface. In natural color, the surfaces are black-darkish amber; scale bar 100 μm ; 3) slide 4-CF-6a/4; indeterminate, granulose cuticular surface; scale bar 500 μm ; 4) slide 4-CF-6a/4; indeterminate cuticular surface; scale bar 100 μm .

branched hydrocarbon side chains linked to the macromolecular structure in *S. manleyi*.

P. nyranensis has the lowest CH_2/CH_3 value.

Carboxylic acids and ketones, represented by peaks in the range $1718\text{-}1710\text{ cm}^{-1}$ are of low intensity in both *C. altissemus* and *P. nyranensis* spectra.

The three taxa show the contribution of $\text{C}=\text{O}$ in highly conjugated ketonic structures, and likely $\text{H}-\text{O}$ in phenolic compounds ($1654\text{--}1630\text{ cm}^{-1}$ interval). *C. altissemus* and *P. nyranensis* show very small peaks at $874\text{-}5\text{ cm}^{-1}$ (aromatic $\text{C}-\text{H}$ out-of-plane bending vibrations), which are absent in *S. manleyi*.

Table 2. Definition of semi-quantitative area ratios derived from FTIR spectra.

#	Ratio	Band-region (cm^{-1}) Band-region ratios	Interpretation and remarks
1	CH_2/CH_3	3000-2800	Methylene / methyl ratio. It relates to aliphatic chain length and degree of branching of aliphatic side groups (side chains attached to macromolecular structure; Lin and Ritz 1993a, b). Higher value implies comparatively longer and straight chains, a lower value shorter and more branched chains. Caution is advised using the ratio, as it may be misleading due to the contribution from CH_2 and CH_3 groups attached directly to aromatic rings (Petersen and Nytoft 2006).
2	$\text{CH}_{\text{al}}/\text{Ox}$	$(3000\text{-}2800) / (1800\text{-}1600)$	Aliphatic / Oxygen-containing compounds ratio. Relative contribution of aliphatic $\text{C}-\text{H}$ stretching bands (CH_{al}) to the combined contribution of oxygen-containing groups and aromatic carbon (Ox). From higher values decreasing oxygen-containing groups can be inferred, or the lower the $\text{CH}_{\text{al}}/\text{Ox}$ ratio, the higher the Ox term. This ratio could provide some information about oxidation in organic matter (e.g., Mastalerz and Bustin 1997; Zodrow and Mastalerz 2001).
3	$\text{C}=\text{O}/\text{C}=\text{C}$	$(1700\text{-}1600) / (1600\text{-}1500)$	Carbonyl / aromatic carbon groups ratio. Relative contribution of $\text{C}=\text{O}$ to aromatic carbon groups. Higher values indicate increasing carbonyl/carboxyl groups to aromatic carbon groups (D'Angelo, 2006).
4	$\text{C}=\text{O}$ cont	$(\sim 1714) / (1800\text{-}1600)$	Carbonyl contribution. Relative contribution of carbonyl/carboxyl groups ($\text{C}=\text{O}$; peak centered near 1714 cm^{-1}) to combined contribution of oxygen-containing groups and aromatic carbon ($\text{C}=\text{C}$) structures.
5	$\text{C}=\text{C}$ cont	$(\sim 1600) / (1800\text{-}1600)$	Aromatic carbon contribution. Relative contribution of aromatic carbon groups ($\text{C}=\text{C}$; peak in $1650\text{ to }1520\text{ cm}^{-1}$ region, centered near 1600 cm^{-1}) to combined contribution of oxygen-containing groups and aromatic carbon ($\text{C}=\text{C}$) structures.
6	$\text{CH}_{\text{al}}/\text{C}=\text{C}$	$(3000\text{-}2800) / (1600\text{-}1500)$	Aliphatic / aromatic carbon groups ratio. Relative contribution of aliphatic $\text{C}-\text{H}$ stretching bands to aromatic carbon groups ($\text{C}=\text{C}$). Higher values indicate increasing aliphatic groups to aromatic carbon groups. This ratio is equivalent to the I1 index of Guo and Bustin (1998).
7	'A' factor = $\text{CH}_{\text{al}}/(\text{CH}_{\text{al}}+\text{C}=\text{C})$	$(3000\text{-}2800) /$ $[(3000\text{-}2800)$ $+ (1650\text{-}1520)]$	Relative contribution of aliphatic $\text{C}-\text{H}$ stretching bands to sum of aliphatic $\text{C}-\text{H}$ stretching and aromatic carbon structures. According to Ganz and Kalkreuth (1987) it represents change in relative intensity of aliphatic groups.
8	'C' factor = $\text{Ox} / (\text{Ox}+\text{C}=\text{C})$	$(1800\text{-}1600) /$ $[(1800\text{-}1600)$ $+ (1650\text{-}1520)]$	Relative contribution of oxygen-containing compounds to sum of oxygen-containing structures and aromatic carbon bands. According to Ganz and Kalkreuth (1987) it represents change in carbonyl/carboxyl groups.
9	$\text{CH}_{\text{al}}/\text{C}=\text{O}$	$(3000\text{-}2800) / (1800\text{-}1700)$	Aliphatic / carbonyl groups ratio. Relative contribution of aliphatic $\text{C}-\text{H}$ stretching bands to carbonyl/carboxyl groups ($\text{C}=\text{O}$). Indicator for cross-linking degree of a polymeric structure. Lower values indicate higher $\text{C}=\text{O}$ content and higher cross-linking (Benítez et al. 2004).

Table 3. IR-derived data for macerated specimens of *Sydneia manleyi*, *Cyathotrachus altissemus* and *Pecopteris (Asterotheca) nyranensis*; ^a Taken from: Zodrow and Mastalerz (2001). ^b Taken from: Pšenička et al. (2005).

Taxon	CH ₂ /CH ₃	CH _{al} /Ox	C=O/C=C	C=O cont	C=C cont	CH _{al} /C=C	'A' factor	'C' factor	CH _{al} /C=O
<i>Sydneia manleyi</i>	4.5	0.42	1.6	0.2	0.10	4.21	0.81	0.61	2.7
<i>Cyathotrachus altissemus</i>	5.2 ^a	0.15 ^a	0.17	0.07	0.41	1.34	0.57	0.15	7.9
<i>Pecopteris (Asterotheca) nyranensis</i>	3.7 ^b	0.09 ^b	0.30	0.073 ^b	0.24	0.76	0.43	0.23	2.5

SYSTEMATIC PART

Order **Marattiales** Engler and Prantl, 1902

Family **Asterothecaceae** Engler and Gilg, 1919

Subfamily **Sydneideae** subfam. nov.

Diagnosis Fertile frond segmented with deeply incised ultimate pinnules. Pinnules with large synangia on abaxial surface. Synangia consist of connate sporangia with central cavity. Sporangia are elongated and exannulate.

Type species ***Sydneia manleyi*** Pšenička et al. 2003

List of species with affinity to this family:

Sydneia manleyi Pšenička et al. 2003

Radstockia kidstonii Taylor 1967

Germera mendescoreae (Teixeira 1939) Brous-miche 1983

CONCLUDING REMARKS

Amateur collecting played a decisive role in producing missing evidence for *S. manleyi* as a fossil plant, namely the sterile/fertile foliage, presumably from the *stratum typicum* in the Canadian Sydney Coalfield. A number of possibilities exist for comparing the sterile-pinnule morphology, but the most appropriate, given the constraints of the known reproductive

structure, is with *Urnatopteris* Kidston 1884, or *Zeilleria* Kidston 1884, as already noted by Pšenička et al. (2003). Despite the added knowledge of the sterile foliage, the actual frond architecture remains unresolved, though judging from the sturdy 10-mm thick penultimate rachis of the type specimen, speculating on a larger frond is probably not too far off. Of practical insight is that in the early stage of being naturally macerated, compressions

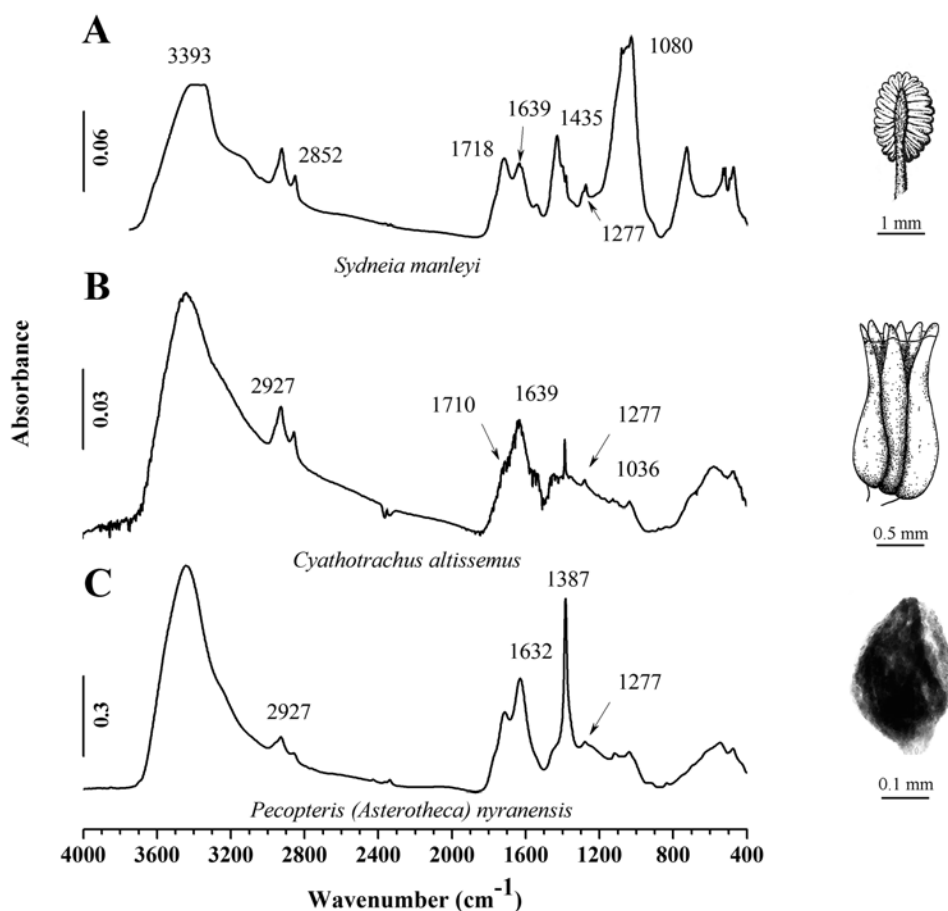


Figure 5. IR spectra. A) *Sydneia manleyi*, synangia. Arrow points to the ketonic structure; B) *Cyathotrachus altissemus*, synangia. Arrow points to ketonic structures. C) *Pecopteris (Asterotheca) nyranensis*, sporangium. Arrow points to aromatic ethers.

in general require shorter maceration times in Schulze's process.

The dominant alkyl character and other chemical groups (e.g., carbonyls) of macerated *S. manleyi* synangium is linked to, and could be derived from a very resistant structure (now a geomacropolymer) such as cutin, cutan or a mixture of them. The reproductive organs *S. manleyi*, *P. nyransensis* and the synangium of *C. altissemus* have in common a chemical composition which is related to polyether (and probably polyester) structures. Such a resistant composition on the one hand promoted preservation, and on the other hand could prove useful for chemotaxonomic studies.

A new subfamily of marattialean ferns is erected, which is based on several detailed features, and previously studied specimens (Pšenička et al., 2003). Assignment of *S. manleyi* among marattialean ferns is primarily based on the type of reproductive organ and type of spores, where synangia with partly laterally fused sporangia are arranged in an oval configuration. Although this configuration shows some similarities with *Marattia*-type of synangia (Taylor, 1967), some medullosaleans (e.g. *Whittleseya*-pollen organs) have a similar type or organization of reproductive organs. Nevertheless, the ultrastructure of the spores of *S. manleyi* is pteridophytic (Pšenička et al., 2003). All of the observations point to an affiliation with marattialean plants, and do not correspond with any known marattialean ferns, which justifies the erection of the Sydneideae subfam. nov.

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REFERENCES

- D'Angelo, J.A. 2006. Analysis by Fourier transform infrared spectroscopy of *Johnstonia* (Corytospermales, Corytospermaceae) cuticles and compressions from the Triassic of Cacheuta, Mendoza, Argentina. *Ameghiniana* 43, 669–685.
- D'Angelo, J.A., Zodrow, E.L. 2011. Chemometric study of functional groups in different layers of *Trigonocarpus grandis* (Pennsylvanian seed fern, Canada). *Organic Geochemistry* 42, 1039–1054.
- D'Angelo, J. A., Zodrow, E. L., Mastalerz, M. 2012. Compression map, functional groups and fossilization: A chemometric approach (Pennsylvanian neuropteroid foliage, Canada). *International Journal of Coal Geology* 90-91, 149-155.
- Barthel, M. 1962. Epidermisuntersuchungen an einigen inkohlten Pteridospermenblättern des Oberkarbons und Perms. *Beiheft, Geologie* 33, 1-140.
- Benítez, J., Matas, A.J., Heredia, A. 2004. Molecular characterization of the plant biopolymer cutin by AFM and spectroscopic techniques. *Journal of Structural Biology*, 147, 179-184.
- Brousriche, C. 1983. Les Fougères sphénoptéridiennes du Bassin Houiller Sarro-Lorrain. *Société Géologique Du Nord*, 10, 480 pp.
- Colthup, N.B., Daly, L.H., Wiberley, S.E. 1990. *Introduction to Infrared and Raman Spectroscopy*. 547 pp. Academic Press, New York.
- Corsin, P. 1951. *Bassin houiller de la Sarre et de la Lorraine, I. Flore Fossile 4me Fascicule Pécoptéridiées*. 370 pp. Études des Gîtes Minéraux de la France. Lille.
- Chen, Y., Mastalerz, M., Schimmelmann, A. 2012. Characterization of chemical functional groups in macerals across different coal ranks via micro-FTIR spectroscopy. *International Journal of Coal Geology* 104, 22-33.
- Engler, A., Gilg, E., 1919. *Syllabus der Pflanzenfamilien*. Borntraeger, Berlin.
- Engler, A., Prantl, K. 1902. *Die natürlichen Pflanzenfamilien. I Teil, Abteilung 4*.
- W. Engelmann, Leipzig.
- Ganz, H., Kalkreuth, W. 1987. Application of infrared spectroscopy to the classification of kerogen types and the evolution of source rock and oil-shale potentials. *Fuel* 66, 708-711.
- Guo, Y., Bustin R. M. 1998. Micro-FTIR spectroscopy of liptinite macerals in coal. *International Journal of Coal Geology* 36, 259-275.

- Kidston, R. 1884. On the fructification of *Zeilleria* (*Sphenopteris*) *delicatula*, Sternberg, sp., with remarks on *Urnatopteris* (*Sphenopteris*) *tenella* Brongt. and *Hymenophyllites* (*Sphenopteris*) *quadridactylites*, Gutbier, sp. *Quarterly Journal of the Geological Society, London*, 40, 590-598.
- Laveine, J.-P. 1969. Quelques Pécoptéridiées houillères a la lumière de la palynologie. *Pollen et Spores* 11, 619-668.
- Laveine, J.-P. 1970. Quelques Pécoptéridiées houillères a la lumière de la palynologie (II). Implications paléobotaniques et stratigraphiques. *Pollen et Spores* 12, 235-297.
- Lin, R., Ritz, G.P. 1993a. Reflectance FT-IR microspectroscopy of fossil algae contained in organic-rich shale. *Applied Spectroscopy* 47, 265-271.
- Lin, R., Ritz, G.P. 1993b. Studying individual macerals using i.r. microspectroscopy, and implications on oil versus gas/condensate proneness and „low-rank” generation. *Organic Geochemistry* 20, 695-706.
- Mastalerz, M., Bustin, R.M. 1997. Variation in chemistry of macerals in coals of the Mist Mountain Formation, Elk Valley coalfield, British Columbia, Canada. *International Journal of Coal Geology* 33, 43-59.
- Millay, M.A. 1979. Studies of Paleozoic marattialeans: A monograph of the American species of *Scolecopteris*. *Palaeontographica B* 169, 1-69.
- Millay, M.A. 1997. A review of permineralized Euramerican Carboniferous tree ferns. *Review of Palaeobotany and Palynology* 95, 191-209.
- Petersen, H. I., Nytoft, H. P. 2006. Oil generation capacity of coals as a function of coal age and aliphatic structure. *Organic Geochemistry* 37, 558-583.
- Petersen, H. I., Rosenberg, P., Nytoft, H. P. 2008. Oxygen groups in coals and alginite-rich kerogen revisited. *International Journal of Coal Geology* 74, 93-113.
- Pšenička, J. 2005. *Taxonomy of Pennsylvanian-Permian ferns from coal basins in the Czech Republic and Canada*. 185 pp. PhD Thesis, Charles University, Prague.
- Pšenička, J., Bek, J., Cleal, C.J., Wittry, J., Zodrow, E.L. 2009. Description of synangia and spores of the holotype of the Carboniferous fern *Lobatopteris miltoni*, with taxonomic comments. *Review of Palaeobotany and Palynology* 155, 133-144.
- Pšenička, J., Bek, J., Zodrow, E.L., Cleal, C.J., Hemsley, A.R. 2003. A new late Westphalian fossil marattialean fern from Nova Scotia. *Botanical Journal of the Linnean Society* 142, 199-212.
- Pšenička, J., Zodrow, E.L., Mastalerz, M., Bek, J. 2005. Functional groups of fossil marattialeans: chemotaxonomic implications for Pennsylvanian tree ferns and pteridophylls. *International Journal of Coal Geology* 61, 259-280.
- Taylor, T.N. 1967. On the structure and phylogenetic relationship of the fern *Radstockia Kidston*. *Palaeontology* 10, 43-46.
- Teixeira, C. 1939. Contribuição para o estudo do Estefaniano dos arredores do Pôrto. *Publicações do Museu e Laboratório Mineralógico e Geológico, Faculdade de Ciências*, 11, 5-24.
- Wagner, R. H. 1958. *Pecopteris pseudo-bucklandi* Andrae and its generical affinities. *Mededelingen van de Geologische Stichting, New Series* 12, 25-30.
- Wang, S.H., Griffiths, P.R. 1985. Resolution enhancement of diffuse reflectance i.r. spectra of coals by Fourier self-deconvolution. 1. C-H stretching and bending modes. *Fuel* 64, 229-236.
- Zodrow, E.L. 1990. Revision and emendation of *Pecopteris arborescens* group, Permo-Carboniferous. *Palaeontographica B* 217, 1-49.
- Zodrow, E.L., D'Angelo, J.A. 2013. Digital compression maps: an improved method for studying Carboniferous foliage. *Atlantic Geology* 49, 126-130.
- Zodrow, E.L., Mastalerz, M. 2001. Chemotaxonomy for naturally macerated tree-fern cuticles (Medullosales and Marattiales), Carboniferous Sydney and Mabou Sub-Basins, Nova Scotia, Canada. *International Journal of Coal Geology* 47, 255-275.
- Zodrow, E.L., Mastalerz, M. 2009. A proposed origin for fossilized Pennsylvanian plant cuticles by pyrite oxidation (Sydney Coalfield, Nova Scotia, Canada). *Bulletin of Geosciences* 84, 227-240.
- Zodrow, E.L., Šimůnek, Z., Cleal C. J., Bek, J., Pšenička, J. 2006. Taxonomic revision of the Palaeozoic marattialean fern *Acitheca* Schimper. *Review of Palaeobotany and Palynology* 138, 239-280.
- Zodrow, E.L., D'Angelo, J.A., Mastalerz, M., Cleal, C.J., Keefe, D. 2010. Phytochemistry of the fossilized-cuticle frond *Macronenuropteris macrophylla* (Pennsylvanian seed fern, Canada). *International Journal of Coal Geology* 84, 71-82.