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Fossil cutin of *Macroneuropteris scheuchzeri* (Late Pennsylvanian seed fern, Canada)

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ABSTRACT

Cutin polymer from compression-preserved specimens of *Macroneuropteris scheuchzeri* (seed fern, Medullosales) is recorded for the first time. Specimens of basal Cantabrian strata, Sydney Coalfield, Canada, exhibit excellent preservation. The cutin was concentrated by Schulze's process by time-controlled oxidation reaction. Reported are functional-group changes monitored via semi-quantitative Fourier transform infrared (FTIR) spectrometry as a function of cutin concentration in Schulze's solution. Distinct features of the cutin spectrum include intense peaks of ester C═O groups, centered at 1730–1715 cm^{-1}, and aromatic C═C absorption bands at 1640–1645 cm^{-1}. Cutin is characterized and differentiated from the corresponding *M. scheuchzeri* cuticle mainly by the comparatively higher values of CH_2/CH_3, C═O/C═C, and the very low values of CH_{al}/C═O and C═C contribution. Cutin data compare with available semi-quantitative FTIR data from modern *L. esculentum* cutin, particularly emphasized by CH_{al}/C═O ratios whose low value of ca. 0.9 indicates a similar cross-linking degree of the polymeric structure for the fossil and extant taxa.

1. Introduction

Chemical and petrographic studies of cutinite coal maceral date back to the 1920s (summary: Lyons et al., 1995) when in parallel taxonomic advances of Carboniferous seed ferns were based on cuticular analyses. In particular, the cuticular topography (hair, trichomes, files, papillae, cells and cell walls, stomata) of the Carboniferous compression seed-fern *Macroneuropteris scheuchzeri* was investigated by Gothan (1916), and later by Barthel (1961), Cleal and Zodrow (1989), and Zodrow et al. (under review). However, Lyons et al. (1992, 1995) produced first-time chemical data in the context of coalification characteristics and chemotaxonomy for *M. scheuchzeri* using ^{13}C nuclear magnetic resonance (^{13}C NMR) spectrometry, Fourier transform infrared (FTIR) spectrometry, fluorescence spectrometry, and gas chromatography. Moreover, a van Krevelen plot of atomic O/C vs. H/C revealed that the O/C ratio of the cuticle of *M. scheuchzeri* is virtually identical with pure cutin of modern plants. H/C values of the fossil cuticle were lower, implying molecular evolution of the cutin since the Carboniferous Period 300 Ma ago.

This communication summarizes functional-group changes (via FTIR analysis) as a function of cutin concentration of *M. scheuchzeri* in Schulze's solution (4–6 g $KClO_3$ dissolved in 150 mL 78% nitric acid). Results are compared with available FTIR data of modern cutin.

2. Materials and methods

M. scheuchzeri specimens originated from the roof shale of the Lloyd Cove Seam, basal Cantabrian (Fig. 1A–C). Preservation of this seam is excellent due to lower vitrinite reflectance (Ro% = 0.65) and higher volatile matter (36%: high volatile B bituminous rank).

Schulze's (1855) oxidation process was applied to *M. scheuchzeri* compressions to obtain its cuticle and finally the cutin. Details of the process and reasons for the use of the alkaline solution in our analytical approach can be found in Zodrow et al. (2009).

Samples for the solid-state FTIR spectra were prepared by the KBr-pellet method, and analyzed on a Nicolet Thermo-Electron 6700 spectrometer, accumulating 256 scans at a resolution of 4 cm^{-1} wavenumber (for further details see Zodrow et al., 2009). Semi-quantitative FTIR analyses include the application of different techniques to the digitized spectra (i.e., Fourier self-deconvolution, area integration methods, and calculation of area ratios) in accord with published procedures (D'Angelo et al., 2010; Zodrow et al., 2009).

3. Results—tracking oxidation effects by FTIR

Schulze's oxidation process applied to the *M. scheuchzeri* compression (Fig. 2A) solubilized the vitrain after 6 h. Sample neutralization with 4.5% v/v ammonium hydroxide retrieved a brownish cuticle

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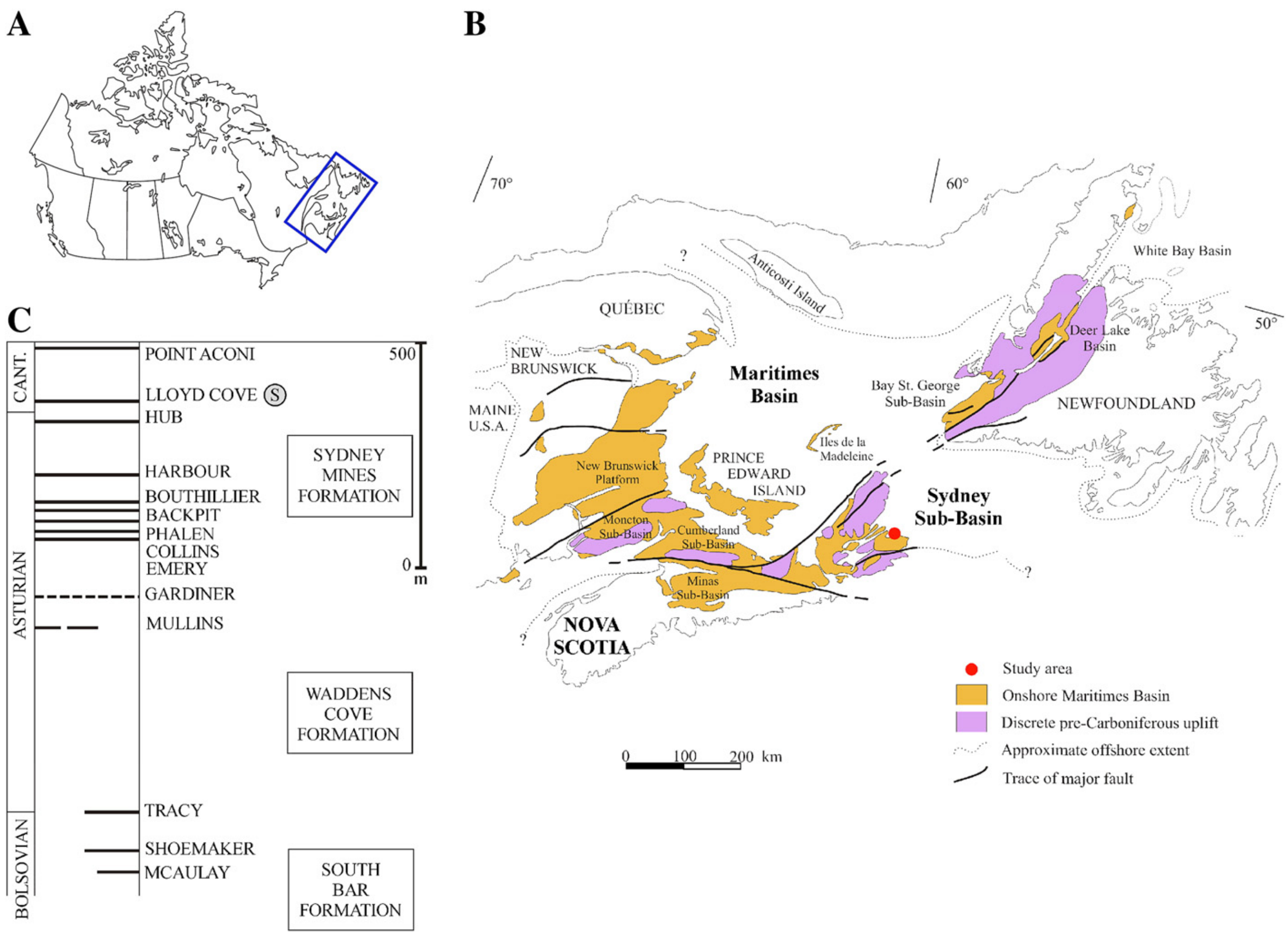

Fig. 1. Study location. (A) Canada. (B) Maritimes Basin with Sydney Coalfield (Sub-Basin), Nova Scotia. (C) Coal stratigraphy of the Coalfield, and names of coal seams. Sampled coal seam is marked S. Cant. = Cantabrian (Zodrow and Cleal, 1985).

shown in Fig. 2B. A net mass loss of ca. 85% was recorded after maceration and neutralization. After an additional 10 days oxidation of the non-neutralized sample portion, a whitish, glittering mass was formed (8% mass loss of the cuticle, Fig. 2C), for a total mass loss of 93% (from the initial compression sample to the final cutin material). Salient changes resulting from this process are summarized as follows (see Table 1 for details):

(1) Characteristic of the compression (Fig. 2A1) is (i) a prominent band centered at 1603 cm^{-1}, and (ii) distinct aromatic C–H out-of-plane peaks at ≈815 and 751 cm^{-1}. As these regions likely represent the contribution of vitrinitic matter (Lyons et al., 1992, 1995; Pšenička et al., 2005; Zodrow and Mastalerz, 2002), they are largely eliminated by oxidation or have very low intensity in the cuticle and cutin spectra.
(2) Characteristic of the cuticle (Fig. 2B1) and the cutin (Fig. 2C1) are intense peaks of ester C═O groups, centered at 1730–1715 cm^{-1}. Absorptions at 1640–1645 cm^{-1} are assigned to the stretching of C═C bonds.
(3) Characteristic of the cutin spectrum (Fig. 2C1) are also several peaks of medium to weak intensity (1095–1025 cm^{-1} region) assigned to C–OH in alcohols and C–O–C in aliphatic ethers. The latter are important structural groups in cutin of extant plants (e.g., Benítez et al., 2004; Villena et al., 2000).
(4) Cutin is characterized, and differentiated from the *M. scheuchzeri*-cuticle mainly by the comparatively higher values of CH_2/CH_3, C═O/C═C, and the very low values of CH_{al}/C═O and C═C contribution (Table 2).

4. Concluding observations

Paucity of published semi-quantitative IR data for extant cuticles and cutin-like materials prevented us from performing a more comprehensive comparison between fossil and extant cutin (van Bergen et al., 2004). However, Benítez et al. (2004) provided IR data on aliphatic/carbonyl group ratios CH_{al}/C═O for cutin isolated from ripe and younger *Lycopersicon esculentum* fruits. From this ratio, the degree of cross-linking of a polymeric structure can be inferred, where a higher C═O content (i.e., lower CH_{al}/C═O values) implies higher cross-linking (i.e., more ester bonds). The 0.9 value (Table 1) for *M. scheuchzeri* cutin compares with *L. esculentum* cutin (younger fruits: 0.92, and ripe fruits: 0.72). Furthermore, IR spectra of *M. scheuchzeri* and extant *Clivia miniata* and *L. esculentum* clearly show prominent aliphatic structures in the 3000–2800 cm^{-1} region, which is the most repeated structural unit in the cutin biopolyester (e.g., Benítez et al., 2004; Koch and Ensikat, 2008; Villena et al., 2000; and others). The ester bond is an important structural group since it is the link between different hydroxy fatty acids that forms the cross-linking of cutin biopolymer (Benítez et al., 2004). Several weak to medium intensity peaks located at about 1167, 1113, 1073, 1044, and 964 cm^{-1} and assigned to different C–O and O–H deformations