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3D chemical map and a theoretical life model for *Neuropteris ovata* var. *simonii* (index fossil, Asturian, Late Pennsylvanian, Canada)

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ABSTRACT

The largest known 65-cm frond segment of *Neuropteris ovata* var. *simonii* (Order: Medullosales) from the Late Pennsylvanian of Sydney Coalfield, Canada, is preserved as compression and naturally macerated cuticle and comprises the study sample. The study objectives included (i) analyzing the chemical variability throughout the frond, (ii) interpreting chemical differences in the lower from the upper part of the frond (impossible to do from fragmented specimens), (iii) inferring the likely biopolymeric make-up of the tissues of the once-living plant, (iv) estimating the likely metabolic cost of plant tissue production, and (v) suggesting autecological aspects.

The chemical variables (functional groups), obtained by Fourier transform infrared (FTIR) spectroscopy, are interpreted by principal component analysis (PCA) where three PCs explain 89.9% cumulative variance. In effect, this chemometric analysis of functional groups, which is named the 3D chemical map, constitutes a first-time study of a three-dimensional component space in medullosalean frond architecture.

The 3D chemical map revealed new insights into relative contributions and distributions of aliphatic, aromatic, and oxygen-containing functional groups from which minimal diagenetic alteration was inferred. The proposed life model for the Sydney *ovata* plant is summarized as follows: (i) continuous variations of functional-group ratios from lower to upper frond parts are reflective of the continuous variation of foliar morphology (including the corresponding plant tissues), and thus frond architecture (ii) compounds likely related to tannins, lignins, and resins are proposed as the tissue biopolymers of the once-living frond, and (iii) comparison of average bond energy data of the functional groups allowed insights into the metabolic cost of tissue production, where the robust and stiffer lower part of the frond was metabolically more expensive than the slender and more flexible upper part. Inferred is that tannins, and resins were also factors in the chemical defenses against herbivory, and that the *ovata* plant was an opportunistic colonizer of flood-disturbed sites likely characterized by nitrogen-deficient soils and full-sun conditions.

Generalization extending to the *ovata* species (population) is hypothesized.

The use and results of the 3D chemical map introduced a paradigmatic shift into Carboniferous plant studies with profound implications for circumscribing more realistically species and their reconstructions of whole-plants as well as their autecology and synecology.

1. Introduction

Coalified foliage (compression, less so the fossilized-cuticle) has been, and continues to be a major source of information for studying pinnule morphology (including cuticular features) as well as frond architecture of medullosalean seed-ferns. However, during the last twenty years the chemical composition of these remains has been used as a complementary source of information (e.g., D'Angelo et al., 2012, 2013; D'Angelo and Zodrow, 2015; Lyons et al., 1995; Zodrow and Mastalerz, 2001, 2002, 2007, 2009; Zodrow et al., 2009, 2010, 2012, 2013, 2014). Such chemical studies have been based mainly on a limited number of pinnules from relatively smaller pinnate fragments. At the same time, only a few samples of axes (rachides) have been analyzed (e.g., Zodrow and Mastalerz, 2001).

In this paper, we expand the methodological approach of medullosalean chemometrics and apply it to the 65-cm frond segment of *Neuropteris ovata* Hoffmann (in Keferstein, 1826, Zodrow and Cleal, 1988), Sydney Coalfield, Canada (Fig. 1A–C). (Later, Cleal and Zodrow (1989) renamed this specimen *N. ovata* (Hoffmann, 1826) var. *simonii* (Bertrand, 1930) emend.) The present study introduces the three-dimensional model of principal component analysis (PCA, 3D chemical map) involving pinnules and all order rachides of this frond which

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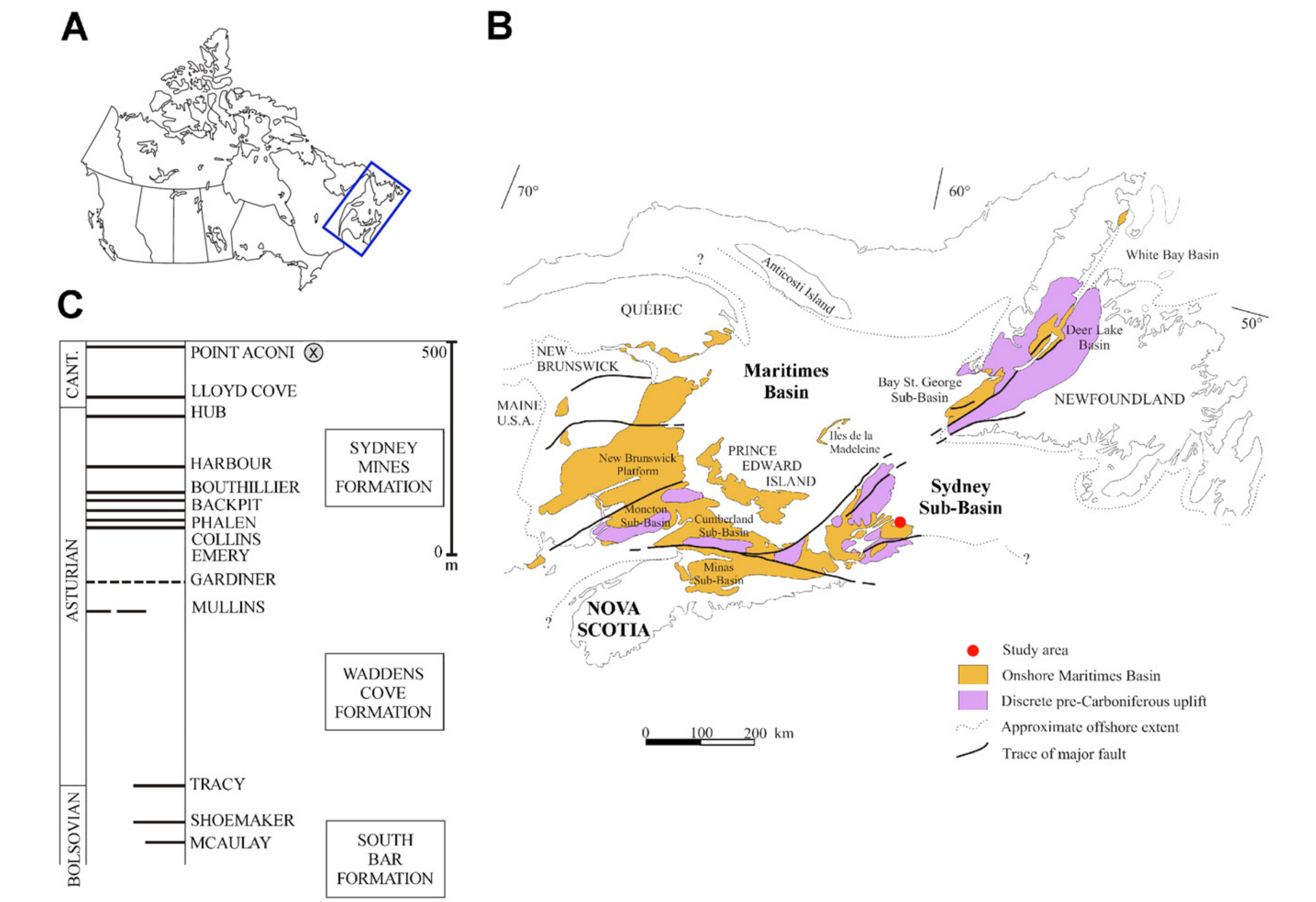

Fig. 1. Study location. (A) Canada. (B) Maritimes Basin with Sydney Coalfield (Sub-basin), Nova Scotia. (C) Local coal stratigraphy. Sampled crevasse-splay (X) above the Point Aconi Seam (basal Cantabrian = CANT., see Zodrow and Cleal, 1985, Fig. 5; Zodrow and Cleal, 1988, text—Figs. 1 to 4).

were analyzed via Fourier transform infrared spectroscopy (FTIR). The 3D PC model used, differentiating it from our previous two-dimensional principal component model of a neuropteroid specimen (e.g., D'Angelo et al., 2012), helps to better understand the hitherto poorly-known relationship between foliar architecture and its chemical (molecular) structure. Considering the relationships amongst chemical, morphological, architectural, and anatomical features, inferences are discussed regarding the likely biopolymers constituting the plant tissues of the living frond. Accordingly, we propose a theoretical life model for the *ovata* plant including aspects of the biomechanics and autecology.

Future research will analyze the implications of these results to deal with some paleobotanical problems, e.g., frond reconstructions of different taxa of medullosalean pteridosperms, including associated fossil-plant parts.

2. Frond nomenclature used

The frond (leafy branch) of seed ferns actually is a compound leaf, or megaphyll, because of its Aufbau (i.e., construction) by a number of hierarchical categories of axes (rachides). Specifically, Fig. 2A shows the rachial architecture of the 65-cm *N. ovata* frond segment, i.e., referred to as *ovata* frond following. The last (ultimate) division of the specimen is the pinnule (Pi), which is attached to the ultimate rachis (Ur). Pi's and Ur compose an ultimate pinna. The Ur is attached to still larger rachis called penultimate rachis (PUr), and the PUr to even a larger one named antepenultimate rachis (APUr), see Zodrow and Cleal (1988, text—Fig. 2). However, the *ovata* frond also shows intercalary (sandwiched-in) pinnate structures, directly attached to APUr (see arrow in Fig. 2B). Pinnules (Pin) of this structure are therefore architecturally not the same as the last frond division, but both Pi and Pin are commonly referred to as the *ovata* foliage. The frond structure proposed by Zodrow and Cleal (1988, text—Fig. 10) includes a lower bifurcation, where each fork represents an APUr from a petiole ("little foot"), and the latter is presumably connected with the trunk.

3. Material and methods

3.1. Provenance and sample forms

The *ovata* frond originated from the fine-grained sandstone of the crevasse-splay deposit 3.5 m above the Point Aconi Seam (Asturian Age, Late Pennsylvanian; Fig. 1C), and bears a collective accession number 985-248 in the Palaeobotanical Collection of Cape Breton University (Fig. 2A). Measured vitrinite reflectance Ro% $= 0.79 \pm 0.028$ ($n = 20$), or Bituminous, High Volatile A (Traverse, 2008), of the Point Aconi Seam is indicative of lower-rank coalification conditions ("milder fossilization"). The frond-preservation characteristics are such that two sample forms are involved in this study: compression (adpression of Shute and Cleal, 1987), and fossilized-cuticle, being a state of naturally-macerated compression (see Zodrow et al., 2009). Pi, Ur, PUr, and APUr were freed from the rock matrix for analysis using HF (48%) (Fig. 2B). An additional sample form is coal (vitrain samples) chemically not treated, from the associate Point Aconi Seam for chemical comparisons.