International Journal of Coal Geology 138 (2015) 42–54

Contents lists available at ScienceDirect

International Journal of Coal Geology

journal homepage: www.elsevier.com/locate/ijcoalgeo

# Chemometric study of structural groups in medullosalean foliage (Carboniferous, fossil Lagerstätte, Canada): Chemotaxonomic implications

José A. D'Angelo [a,b,*], Erwin L. Zodrow [b]

[a] IANIGLA-CCT-CONICET-MENDOZA and Área de Química, FCEN, Universidad Nacional de Cuyo, M5502JMA Mendoza, Argentina
[b] Palaeobotanical Laboratory, Cape Breton University, Sydney, Nova Scotia B1P 6L2, Canada

ARTICLE INFO

*Article history:*
Received 16 October 2014
Received in revised form 3 December 2014
Accepted 4 December 2014
Available online 11 December 2014

*Keywords:*
Medullosales
Pennsylvanian
FTIR
Chemometrics
Chemotaxonomy

ABSTRACT

A larger chemometric study (data derived from Fourier transform infrared spectroscopy-FTIR interpreted by principal component analysis) is undertaken involving species (numbers bracketed) from the four medullosalean families Neurodontopteridaceae (7), Potonieaceae (1), Cyclopteridaceae (1), and Alethopteridaceae (1). Samples originated from the fossil Lagerstätte ("medullosalean forest") in the Late Pennsylvanian of Sydney Coalfield, Nova Scotia, Canada, where they are preserved as compressions or fossilized-cuticles. The study aims at demonstrating how the level of objectivity for medullosalean fossil-plant determinations can be raised through inquiring (i) if the chemistry of isolated foliage supports the specific classification based on morphologies alone, (ii) if chemistry of different preservation states hampers the application of chemometrics, and (iii) if taxonomic assignation of poorly preserved specimens can be assisted by chemometrics. Given the similar thermal history, direct chemical comparisons amongst taxa having the same preservation state were possible. The chemometric approach resulted into a two principal-component model (80% cumulative-explained variance) that provided information on the relative contributions of aromatic structures, oxygen-containing, and aliphatic groups. These functional groups enabled statistical distinction amongst most of the morphology-defined species, and families, irrespective of the two preservation states. We concluded that results, overall, support the aims of the study, with implications to solve some palaeobotanical difficulties related to biostratigraphy and palaeobiogeography.


## 1. Introduction

Fragmentary fern-like foliage represents one of the most common and widespread types of plant fossils preserved in early–middle Carboniferous times. Recognition by Oliver and Scott (1904) that some fern-like foliage represents seed-bearing plants (gymnosperms: order Medullosales, now extinct), thus establishing a whole new plant group, represents a major revolution in palaeobotany (Mosbrugger, 1989; Taylor et al., 2009). Medullosalean foliage corresponds to a grouping of many genera belonging to various families (e.g., Cleal and Shute, 2012; Laveine, 1997). Foliar species are distinguished based on character sets that include frond architecture, pinnule, and cuticular morphologies (e.g., summaries: Cleal and Zodrow, 1989; Zodrow and Cleal, 1988, 1998). These sets are not equally known for each which makes taxial identification difficult and, sometimes, ambiguous. This situation may lead to confusing medullosalean taxonomy or duplications of names, and besides these character sets, though contributory, are by themselves insufficient for approaching the concept of a more natural species (e.g., Zodrow and Cleal, 1998). Suggested is the addition of parameters to the character set derivable from the fossil-plant chemistry, and involvement of chemotaxonomic hypotheses for determining chemical similarities/differences amongst morphologically-based taxa (e.g., Lockheart et al., 2000; Nguyen Tu et al., 2007). However, chemotaxonomic hypotheses are very much circumscribed by diagenetic intervention and the limitations it imposes, i.e., what is actually preserved vs. original plant composition (Niklas, 1976; Niklas and Gensel, 1977)?

Because of "mild fossilization conditions", well-preserved medullosalean type of foliage from a Late Pennsylvanian fossil Lagerstätte of the Sydney Coalfield (Canada), have yielded useful chemical data, i.e., related to lipid-derived compounds such as n-alkanes, n-alkanols, and fatty acids. During the last 20 years, many Canadian seed-fern taxa have been chemically characterized (e.g., D'Angelo et al., 2010, 2012, 2013; Lyons et al., 1995; Stoyko et al., 2013; Zodrow and Mastalerz, 2001, 2002, 2007, 2009; Zodrow et al., 2007, 2009, 2010, 2012, 2013, 2014).

We present results of a larger chemometric study that involves ten foliar taxa from the four families of the order Medullosales. This

* Corresponding author at: IANIGLA-CCT-CONICET-MENDOZA and Área de Química, FCEN, Universidad Nacional de Cuyo, M5502JMA Mendoza, Argentina. Fax: +54 261 5244201.
*E-mail address:* joseadangelo@yahoo.com (J.A. D'Angelo).

http://dx.doi.org/10.1016/j.coal.2014.12.003
0166-5162/

**Table 1**
Sample forms used.

| Form | Description |
|---|---|
| Compression | Conceptualized by an analogue model of the anatomy of an extant leaf: vitrinite (mesophyll) + cuticle (biomacropolymer) = compression (Zodrow et al., 2009). |
| Fossilized-cuticle | Cuticle, where coalified layer (vitrinite) is no longer preserved, only the cuticle itself (summary Zodrow and Mastalerz, 2009). |
| Vitrain | Bright and shiny banded bituminous coal. |

approach essentially identifies taxon-specific functional-group ratios, which when combined with morphological data is bound to achieve a more objective level of taxonomic determinations than otherwise would be possible with morphological data alone. Thus, IR (infrared) data as additional taxonomic parameters find application with solving "problematic" groups, not necessarily confined to medullosaleans, and with several interrelated areas such as biostratigraphy, palaeobiogeography, and evolution.

## 2. Definitions

### 2.1. Functional groups and molecular structure

As it is well-established, Fourier transform infrared (FTIR) spectroscopy allows for both qualitative and semi-quantitative analyses of specific groups of atoms or bonds i.e., functional groups within molecules (e.g., Colthup et al., 1990; Shurvell, 2002). FTIR-derived information helps, but does not in itself determine complex molecular structures of organic compounds (or mixture of them) making up the sample under study. Semi-quantitative FTIR analysis is based on the peak-area integration used to calculate areal ratios, which do not represent absolute contents of functional groups. The rationale for using area ratios, and not individual peak areas, is for normalization and elimination of the spectral background. The reader is referred to Table 1 (Appendix A, supplementary data) for a list of the most important functional groups present in generalized molecular fragments and the meaning of semi quantitative area ratios derived from FTIR spectra. See Section 4.2 for further details.

### 2.2. Chemometrics

Chemometrics is a well-established discipline, where multivariate-statistical methods are applied to complex chemical-data sets to generate new insights for interpretation (e.g., Kvalheim et al., 1985; Lockheart et al., 2000). We use the statistical methods of PCA (principal component analysis) in two interrelated ways. First, as a complexity-reducing tool of the set of IR-derived data (functional groups or chemical structures) when subjectively accepting the number of components that cumulatively account for ca. 80% variance (Izenman, 2008; Johnson and Wichern, 2008; Jolliffe, 2002; Kaiser, 1960; Kendall, 1965). Secondly, as a method of evolving a set of data groupings which is facilitated by calculated component scores thereby revealing hidden patterns or trends that emphasize natural groupings. This identifies which variables most strongly influence those patterns. PCA was performed using STATISTICA® (StatSoft, 2012) on raw data (correlation matrices) consisting of the four variables, with 98 determinations each. See Section 5.2 for further details.

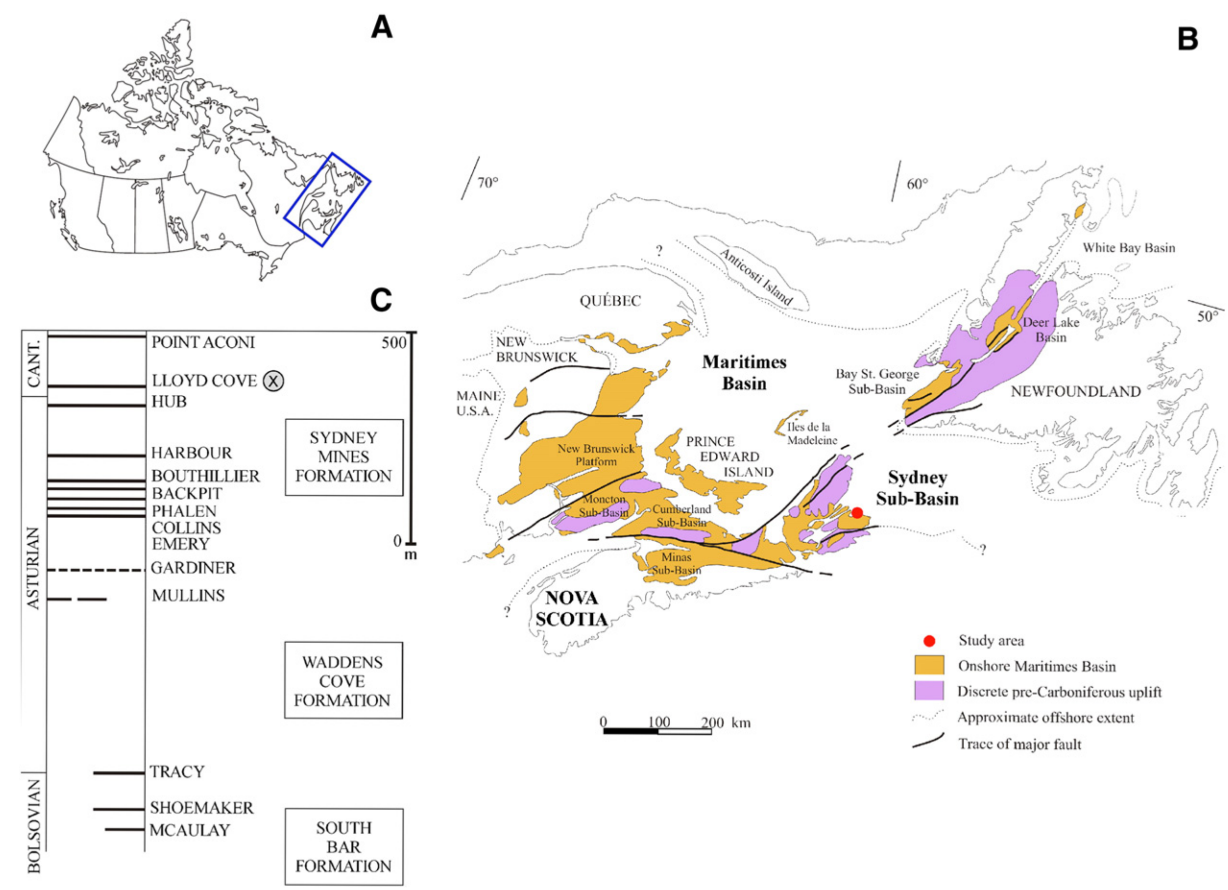


**Fig. 1.** Study location. (A) Canada. (B) Maritimes Basin with Sydney Coalfield (sub-basin), Nova Scotia. (C) Local coal stratigraphy. Sampled coal seam is marked (X), and the medullosalean forest occurs in the roof rocks of the Lloyd Cove Seam, basal Cantabrian (=CANT., Zodrow and Cleal, 1985).