Palaeogeography, Palaeoclimatology, Palaeoecology 309 (2011) 309–326

Contents lists available at ScienceDirect

Palaeogeography, Palaeoclimatology, Palaeoecology

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

Aliphatic and aromatic biomarkers from Carboniferous coal deposits at Dunbar (East Lothian, Scotland): Palaeobotanical and palaeoenvironmental significance

Maria-Fernanda Romero-Sarmiento [a,1], Armelle Riboulleau [a,*], Marco Vecoli [a], Fatima Laggoun-Défarge [b], Gerard J.M. Versteegh [c]

[a] Université Lille 1 & CNRS FRE 3298, bâtiment SN5, 59655 Villeneuve d'Ascq cedex, France
[b] Université d'Orléans, CNRS/INSU-Institut des Sciences de la Terre d'Orléans UMR 6113, Campus Géosciences-1A, rue de la Férollerie, 45071 Orleans cedex 2, France
[c] MARUM, Universität Bremen, Leobenerstraße, 28359 Bremen, Germany

ARTICLE INFO

Article history:
Received 15 December 2010
Received in revised form 9 June 2011
Accepted 13 June 2011
Available online 7 July 2011

Keywords:
Land plant biomarkers
Terrestrial terpenoids
Combustion derived- polycyclic aromatic hydrocarbons
Lower Carboniferous coals
Megaspores

ABSTRACT

Carboniferous (Viséan) coals from Dunbar, East Lothian, Scotland, contain well-preserved miospore and megaspore assemblages suggesting a lycopod-dominated forest ecosystem with some ferns, sphenopsids and pteridosperms. The low rank of the coals and the well defined microflora permit assessment of the palaeoenvironmental significance of lipid biomarkers during the Early Carboniferous. Rock-Eval, petrographic, and lipid analyses indicate a fully terrestrial depositional environment. Although we also present and discuss a wide diversity of other lipid biomarkers (alkanes, hopanoids, steroids), we focus on the terrestrial-derived biomarkers. Combustion-derived PAHs pyrene, fluoranthene, benzo[a]anthracene, chrysene and triphenylene indicate the occurrence of forest fires in the study areas during Early Carboniferous times. Alkyldibenzofurans are considered to derive from lichen-biomass. Retene, cadalene, simonellite, tetrahydroretene and kaurane are poorly specific and can derive from a variety of early Palaeozoic land plants. Abietane, phyllocladane, *ent*-beyerane and 4β(H)-eudesmane, as well as bisnorsimonellite, diaromatic totarane, diaromatic sempervirane and 2-methylretene, however, as yet had only been reported from conifers, which do not appear in the fossil record until the Late Carboniferous. Within the lower Carboniferous forest ecosystem, arborescent lycopsids and pteridosperms are proposed as alternative sources for these compounds.

1. Introduction

Biomarkers are molecular compounds which can be extracted from crude oils, coals and all kinds of sedimentary rocks (Tissot and Welte, 1984). Biomarkers have numerous biological origins, and their occurrence can be related to a specific source, giving information of the type of fauna/flora present in the environment, or to depositional conditions, such as salinity or temperature (Peters et al., 2005). For these reasons, biomarkers are regularly used in palaeoenvironmental studies (e.g. Olcott, 2007; Eglinton and Eglinton, 2008). Recent applications of biomarkers aim at tracing the evolution of life. In archean rocks, biomarkers give information on the timing and evolution of early forms of life (e.g. Brocks et al., 1999, 2003, 2005; Ventura et al., 2007; Eigenbrode et al., 2008; Waldbauer et al., 2009), while in more recent rocks and sediments, biomarkers help determining taxonomic relationships between taxa (e.g. Arouri et al., 2000; Talyzina et al., 2000). In the last decades, chemotaxonomic applications have been particularly developed for the study of flora associated with amber and coal deposits mostly of Mesozoic to recent age (e.g. Simoneit et al., 1986; Otto et al., 1997, 2002; Bechtel et al., 2005; Stefanova et al., 2005 among others). Chemotaxonomic studies of Palaeozoic land plant based on extractible biomarkers were developed in the 70s (Niklas, 1976a,b; Niklas and Chaloner, 1976; Niklas and Pratt, 1980) but have been relatively limited in more recent years (Schulze and Michaelis, 1990; Fleck et al., 2001; Auras et al., 2006), despite the interest of Palaeozoic plants regarding the evolution of terrestrial life.

The aim of this study is to identify and characterize aliphatic and aromatic biomarkers for Lower Carboniferous plants preserved in coals and to relate these biomarkers to specific plant taxa in order to apply chemotaxonomy to Palaeozoic land plants. Biomarker analyses were performed on four Lower Carboniferous (Viséan) coal samples from Dunbar, East Lothian, Scotland. Though megafossils are absent from these coals, their palynological content is rich and comprises abundant miospore and megaspore assemblages (Spinner, 1969; Spinner and Clayton, 1973). This gives us an opportunity to correlate the identified biomarkers with the occurrence of land plant palynomorphs and possibly to terrestrial plant groups or families.

* Corresponding author. Tel.: +33 3 20 43 41 10; fax: +33 3 20 43 49 10.
E-mail address: armelle.riboulleau@univ-lille1.fr (A. Riboulleau).
[1] Present address: IFP Energies nouvelles, Direction Géologie-Géochimie-Géophysique, 1 et 4 avenue de Bois-Préau, 92852 Rueil-Malmaison cedex, France.

0031-0182/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.palaeo.2011.06.015

2. Geological setting and previous studies

The Midland Valley of Scotland is a rift valley bounded by Highland Boundary and Southern Uplands Faults on the North and the South, respectively (Fig. 1; Murchison and Raymond, 1989; Underhill et al., 2008). This sedimentary basin evolved in response to crustal extension and especially contains Devonian to Carboniferous sediments and some igneous rocks (Murchison and Raymond, 1989; George, 1992; Underhill et al., 2008). The Carboniferous rocks in the Midland Valley of Scotland are only well exposed along coastlines (Murchison and Raymond, 1989). Coal samples were collected from two outcrop sections located at Dunbar, East Lothian, on the east coast of southern Scotland, some 40 km East of Edinburgh (Fig. 1). These sections show a group of alternating Lower Carboniferous (Viséan) limestones, shales, sandstones and coals (Fig. 2; Spinner, 1969; Spinner and Clayton, 1973).

SKT coal samples were collected around the bay near Skateraw Harbour, approximately 6.4 km south-east of Dunbar, whereas WS coals were taken from rock successions exposed in White Sand Bay (Fig. 1). Both localities are clearly exposed on a geological map permanently exhibited just above the shoreline. In stratigraphic order, the lower seam is located immediately above the Middle Longcraig Limestone: samples WS-2 and WS-3 (Fig. 2); the upper one (samples SKT-E and SKT-D) occurs stratigraphically below the Chapel Point Limestone (Fig. 2). WS samples are equivalent to the Longcraig coal seam described by Spinner (1969). In contrast, SKT coals are more comparable to the sample horizon SC2 detailed by Spinner and Clayton (1973). In order to investigate the possible vertical stratigraphic variations, two samples were obtained from each coal seam (Fig. 2). Accordingly, WS coals are separated by approximately 30 cm while SKT samples by 15 cm.

A fluvio-deltaic environment has been assigned to these Carboniferous coals, which contain mainly land-plant derived organic matter (George, 1992). After deposition, these shallow-water deltaic deposits were mainly influenced by burial history and extensive volcanic, sill and dyke activities (Murchison and Raymond, 1989).

The sampled outcrop successions were previously studied palynologically (Spinner, 1969; Spinner and Clayton, 1973). Additional palynological analyses were performed for each of the collected samples for the present study. The WS coal interval is characterized by abundant and well-preserved megaspores such as (Spinner, 1969): *Zonalesporites fusinatus* Spinner 1969, *Lagenicula subpilosa* (Ibrahim) forma *major* Dijkstra ex Chaloner 1954 and *Setosisporites* (Ibrahim) Potonié and Kremp 1954 emend. Spinner 1969. Miospores are less abundant in this lower interval and are dominated by the following taxa: *Lycospora pusilla* (Ibrahim) Somers 1972 with *Calamospora spp.* and *Densosporites* spp. (Spinner and Clayton, 1973). All megaspore specimens recognized in the WS horizon (e.g. *Lagenicula subpilosa*, *Setosisporites* and *Zonalesporites fusinatus*) range through the SKT coal interval but *Zonalesporites* is less abundant (Spinner and Clayton, 1973). This upper interval also shows a notable diversity of miospores represented by *Lycospora pusilla*, *Calamospora*, *Densosporites* and *Cingulizonates cf. capistratus* (Hoffmeister, Staplin and Mallow) Staplin and Jansonius *in* Smith and Butterworth, 1967 (Spinner and Clayton, 1973). Megafossils are not known from these sediments. A megaspore-based flora reconstruction suggests that the vegetation consisted of large arborescent lycopsids with long leaves together with some diminutive forms (Spinner, 1969).

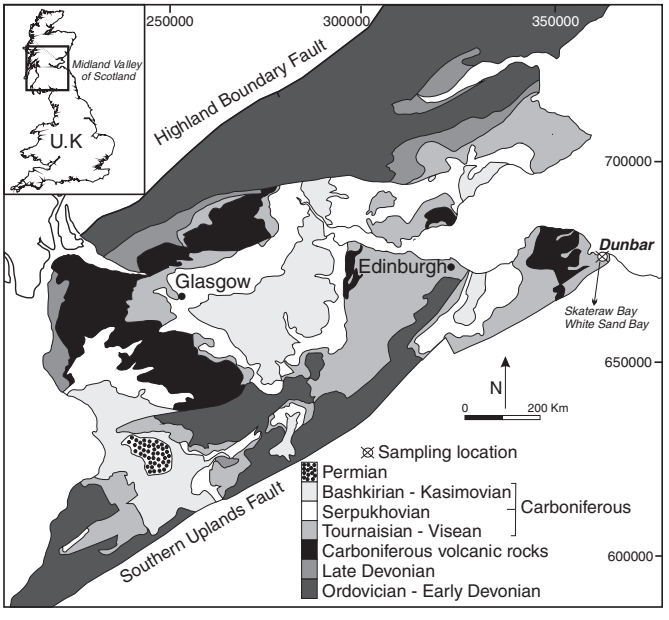

Fig. 1. Simplified geologic map showing the outcrop sample positions at Dunbar (White Sand and Skateraw Bays) in the Midland Valley of Scotland (modified from Spinner and Clayton, 1973; Underhill et al., 2008).

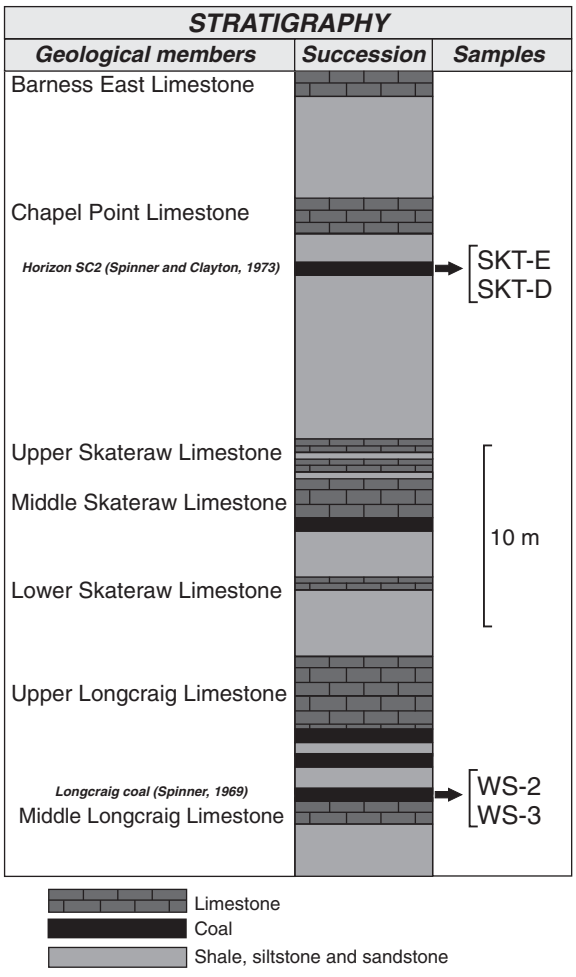

Fig. 2. The outcrop geological succession showing alternating Carboniferous limestones, shales, sandstones and coals (modified from Spinner and Clayton, 1973).

3. Analytical methods

3.1. Experimental procedures

The four coal samples (Fig. 2) were studied by Rock-Eval pyrolysis and biomarker analysis. Rock-Eval pyrolysis was performed on 100 mg of ground rock with an Oil Show Analyser device at the