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LOWER DEVONIAN COALY SHALES OF NORTHERN NEW BRUNSWICK, CANADA: PLANT ACCUMULATIONS IN THE EARLY STAGES OF TERRESTRIAL COLONIZATION

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ABSTRACT: **We describe two Early Devonian occurrences of coaly shale composed mainly of the compacted remains of early plants, such that they resemble coal. Among the earliest thick phytodebris accumulations known, the occurrences lie within Pragian strata of the Val d'Amour Formation and Emsian strata of the Campbellton Formation of northern New Brunswick, and were deposited in low-energy wetlands where they were rapidly buried. Although the coaly shales did not yield recognizable plant taxa, numerous taxa are present in adjacent beds. Petrographic analysis revealed an average of 80.7% vitrinite (predominantly telovitrinite) and 18.7% liptinite (predominantly sporinite) on a mineral-matter-free basis, with a higher vitrinite content than most Devonian coals. Low sulfur content and atomic C/N ratios that vary from 44.3 to 82.1 in organic-rich samples indicate terrestrial derivation. Vitrinite reflectance in organic-rich samples (21.4–35.6 wt % total organic carbon) ranges from 0.48 to 1.00, indicating a low degree of thermal alteration that is supported by cross-polarization spectra from studies of ^{13}C nuclear magnetic resonance; two carbon-poor samples were thermally altered to anthracitic rank adjacent to an intrusive body. Although plants at this time were still comparatively primitive, the presence at both sites of specimens with recognizable lignified cellular structures in vitrinite and particularly thick and resistant cuticle may represent an important step in peat development. In these Early Devonian formations, diverse assemblages of small vascular plants are present in a range of environments, and the plants were sufficiently abundant to form coal-like accumulations under suitable burial conditions, serving as a proxy for plant biomass and vegetation cover in the early stages of terrestrial colonization.**

INTRODUCTION

Over the course of the Devonian, vegetation underwent a critical transformation from communities of short herbaceous or shrubby plants to dense, multi-tiered communities comparable to modern forests. Changing vegetation types and patterns through geologic time are reflected in the character of coal (Collinson and Scott 1987; Cross and Phillips 1990). The formation of peat (coal precursor) from thick accumulations of phytodebris could not have taken place until terrestrial biomass production was prolific and plants had developed sufficient stature. Such conditions were in place during the Middle Devonian, when the earliest forests appeared on Earth (Stein et al. 2012).

A true coal is defined as a combustible rock resulting from the compaction of plant remains, containing over 50% by weight and over 70% by volume of carbonaceous material (Schopf 1956, 1966). Beds fitting this definition are found in Middle and Upper Devonian strata of North America, Europe, and China (Fig. 1), and the literature records a marked increase in coal and charcoal in Upper Devonian formations (Davies and Gibling 2010). This definition excludes purported coals of algal origin that occur as early as the Precambrian (Tyler et al. 1957; Maass et al. 1975), and implies that the lower age limit of coal formation is dependent on plant evolution and expansion.

It is less clear how commonly conditions suitable for the accumulation of peat existed prior to the Middle Devonian. The earliest true coal identified to date may be in the York River Formation of Gaspé, eastern Canada, of early Emsian age (Glasspool and Scott 2010, their Supplementary Data). Evaluating early vascular-plant and peat accumulation has significance for wetland ecosystems and organic soils (Greb et al. 2006), for deltas where peats influence compaction and channel-bank strength (Gouw 2008; van Asselen et al. 2008), for hydrocarbon potential, and for the composition of the atmosphere and ocean, which evolved as carbon was increasingly stored in sediments (Algeo and Scheckler 1998; Berner 2006). Estimates of atmospheric pCO_2 based on isotopic evidence suggest that CO_2 drawdown, widely attributed to vascular plants, did not take place until the Late Devonian (Berner 2006), and a considerable increase in plant cover may have taken place during the Late Devonian (Godderis and Joachimski 2004). However, recognizable plant accumulations may also serve as a partial but useful proxy for inferring vegetation abundance.

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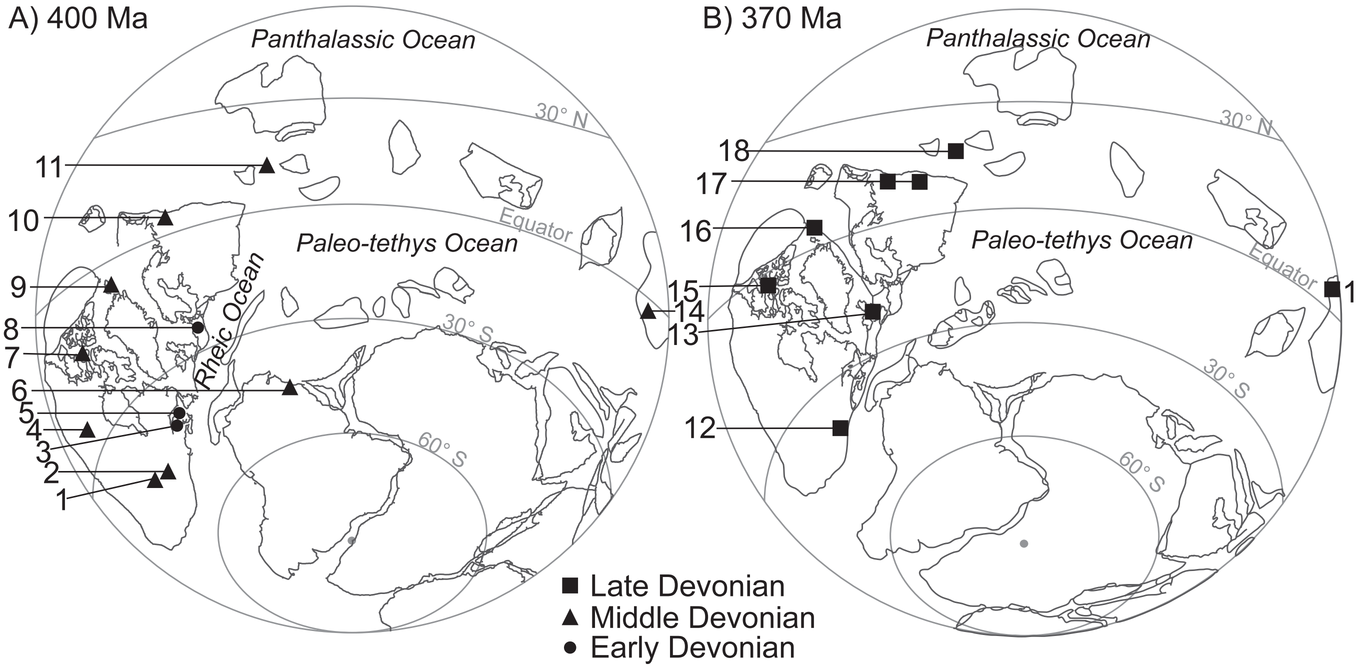


FIG. 1.—Occurrences of **A)** Early Devonian coaly shales and **B)** Middle–Late Devonian coals. Paleogeographical reconstructions from Torsvik and Cocks (2004). 1: Middle Devonian, Cedar Valley Limestone, Iowa, USA (Dow 1960; Sanders 1967); 2: Middle Devonian, Davenport Limestone Member, Wapsipinicon Limestone, Illinois, USA (Peppers and Damberger 1969); 3: Pragian–Emsian, Val d'Amour and Campbellton Formations, New Brunswick, Canada (this study); 4: Givetian, Watt Mountain Formation, Alberta, Canada (Duggan et al. 2001); 5: Emsian, York River Formation, Québec, Canada (Glasspool and Scott 2010; Lavoie et al. 2011); 6: Middle–earliest Late Devonian, Venezuela (Berry et al. 1993); 7: Givetian–Frasnian, Weatherall and Hecla Bay formations, Melville Island, Canada (Goodarzi and Goodbody 1990; Fowler et al. 1991); 8: Early Devonian, Haliseriten beds, Rhenish Massive, Germany (Stach et al. 1982); 9: Givetian–Frasnian, Mimer Valley Formation, Spitsbergen, Norway (Harland et al. 1976, 1997; Wollenweber et al. 2006); 10; Middle Devonian, Timan region of the Ural Mountains, Russia (Volkova 1994); 11: Givetian, Barzas Formation, Kuznetsk Basin, Russia, and Middle Devonian, Aidarly deposits and Ermentau coals, Kazakhstan (Volkova 1994); 12: Middle–late Famennian, Hampshire Formation, West Virginia, USA (Gillespie et al. 1981; Scheckler 1986); 13: Frasnian, Portscatho Formation, Cornwall, England (Cook et al. 1972); 14: Middle Devonian, Haikou Formation, Yunnan Province, and Givetian, Dongganling Formation in Guangdong Province, China (Han 1989; Dai et al. 2006); 15: early–middle Frasnian, Beverley Inlet Formation, Melville Island, Canada (Goodarzi and Goodbody 1990; Fowler et al. 1991); 16: late Famennian–Tournasian, Røedvika Formation, Bear Island, Norway (Harland et al. 1976; Harland 1997); 17: Late Devonian, Timan region of the Ural Mountains and central Russia (Volkova 1994); 18: Late Devonian, Kazakhstan and Russia (Volkova 1994); 19: Famennian, Wutung and Xikuangshan formations, Hubei, Hunan, Anhui, and Jiangsu provinces, China (Han 1989).

Here, we present stratigraphic, paleobotanical, and technical information about two suites of Early Devonian coaly shales from the Val d'Amour and Campbellton formations of northern New Brunswick, which predate nearly all true coal occurrences. The formations have also yielded world-class paleobotanical collections, and we link the available botanical information from the samples and the formations more broadly with the petrographic analysis provided from standard coal procedures. These occurrences approach coal as technically defined and are derived from accumulations of compressed and indurated plant remains, diluted by mineral matter. As such, they represent a substantial milestone in the evolutionary history of plants, wetlands, and peat development. We also draw together technical information from other Devonian coals worldwide, in order to provide a chronological context for the New Brunswick occurrences.

Devonian Vegetation and the Components of Early Coals

Pre-Devonian communities of vascular plant were composed of small, structurally simple floras, dominated by *Cooksonia* spp. and *Cooksonia*-like plants (Edwards and Feehan 1980; Edwards and Wellman 2001; Gensel 2008). By the Late Silurian and Early Devonian, plants had become increasingly complex with the evolution of rhyniaceans, lycophytes, and euphyllophytes (Bateman and DiMichele 1994; Kenrick et al. 2012). These Early Devonian tracheophytes were generally herbaceous, slender, and of fairly short stature, and had only shallowly penetrating root-bearing rhizomes; they would rarely have accumulated sufficient aerial biomass to form layers of peat (Greb et al. 2006). By the Middle Devonian, woody lycopsid trees had evolved, and new clades of euphyllophytes included progymnosperms and cladoxylaleans, some of which were trees (Mintz et al. 2010; Stein et al. 2012). Late Devonian communities included leafy, well-rooted, arborescent lycopods and archaeopterid progymnosperms; early sphenopsids (horsetails), zygopterid ferns, and gymnosperms (seed plants) made up the undergrowth (Algeo and Scheckler 1998; DiMichele and Philips 2002).

Because the architecture of these early plants changed radically through the Devonian, one might expect that maceral composition of Devonian coals and coaly shales would reflect the emergence of specific plant components such as woody tissue, spores, and seeds, as observed over space and time in the biomass composition of Carboniferous coal measures (e.g., Winston 1988, 1990). However, no similar analysis has been conducted for Devonian materials to date.

Macerals in a carbonaceous rock, akin to minerals in a crystalline rock, represent organic constituents and are divided into three groups: vitrinite, liptinite, and inertinite. The vitrinite maceral group arises from any tissue with significant cellulose and lignin, mainly in the secondary cell walls of primary and secondary xylem (wood), bark, leaves, and roots, and in parenchymal tissues (ICCP 1998). Many of these tissues were only rarely present in Early Devonian plants. However, lignin, which is likely the primary source of most vitrinite, is not unique to woody eutracheophytes and has been demonstrated in primary vascular tissues of herbaceous

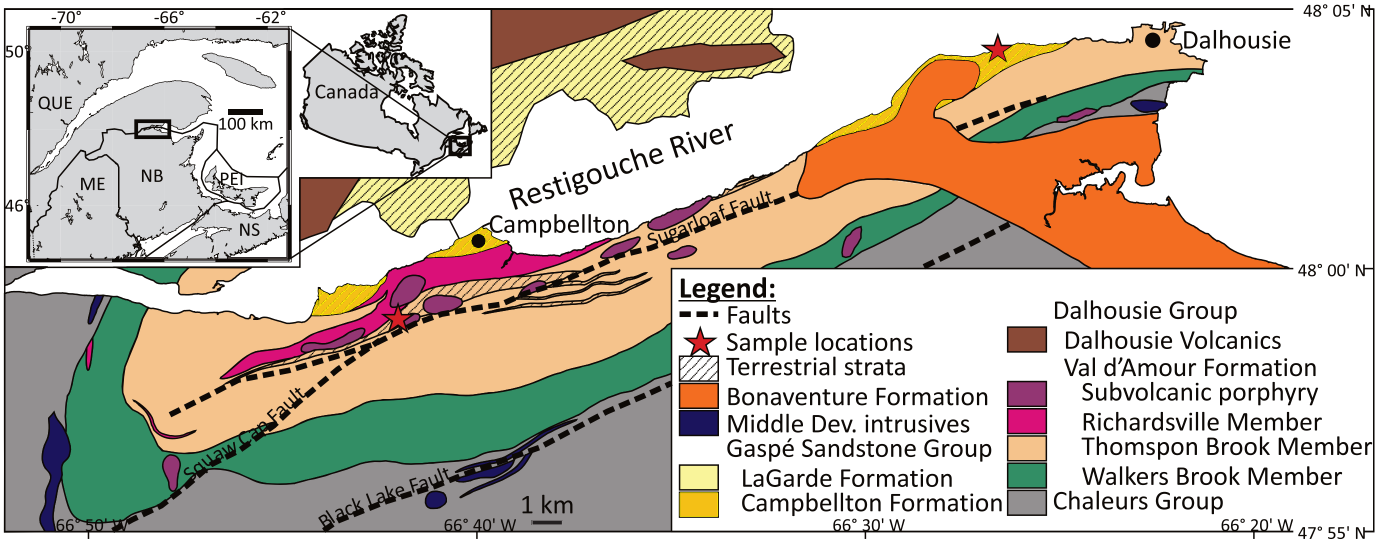


FIG. 2.—Regional geology of the study area in the Restigouche Syncline of eastern Canada. Sampling locations of coaly shales are indicated.

plants as well as extant liverworts, bryophytes, and some red algae (Espiñeira et al. 2011). Secondary xylem (wood) is first reported in minute amounts from the late Pragian to earliest Emsian of France and Canada, but until the Middle Devonian virtually all plants were herbaceous (Gerrienne et al. 2011). Large laminate leaves and roots were poorly developed until the Middle to Late Devonian, and rarely contribute significant biomass even in younger peats (Collinson and Scott 1987; Galtier 2010).

Liptinite-group macerals are attributed to algae and a variety of vascular-plant components or associated elements such as resin. Plant cuticles, from which some cutinite macerals are derived, are found in all early vascular plants, as well as in problematic organisms such as *Spongiophyton* and *Protosalvinia* (Mastalerz et al. 1998; Fletcher et al. 2004). The cuticles of arthropods can also form cutinite macerals (Scott 2002). Sporinite, from spores in the Devonian and later from pollen, may be expected to show changing characteristics over the course of the Devonian as the size range (through heterospory) and spore ornamentation increased with evolutionary diversity (Chaloner 1967; Knoll et al. 1984; Bateman and DiMichele 1994; Zhou 1994). Seeds, a major evolutionary development, first appear in the fossil record in the Famennian (Gillespie et al. 1981), accompanied by pre-pollen (still spore-like), but it is not clear what maceral type would represent seeds in petrographic samples (Scott 2002).

Inertinite-group macerals are the product of strong oxidative reactions such as combustion or intense microbial action. The occurrence of large amounts of fusinite or semifusinite macerals, derived from plant material, is commonly attributed to charcoal-producing wildfires (Glasspool and Scott 2010). Plant-derived charcoal can be found as early as the Pridolian (Glasspool et al. 2004), and fluctuates in abundance in response to changing oxygen levels through the Paleozoic (Scott and Glaspool 2006; Diessel 2010).

GEOLOGIC SETTING

The samples reported here came from two formations near the Restigouche River in northern New Brunswick, Canada: the Val d'Amour and Campbellton formations (Fig. 2). These formations were deposited during the late stages of Ordovician–Devonian basin filling at the eastern margin of Laurentia, today represented by a tract of outcrops from southern Maine to the Gaspé Peninsula, known as the Gaspé Belt. The filling of the Gaspé Belt basin records complex interactions between tectonic events and sea-level change (Bourque et al. 2000). In northern New Brunswick, a 5–6 Ma hiatus in the Wenlockian marks the cessation of subduction of the closing Tetagouche–Exploits back-arc basin, associated with the collision of Ganderia and Laurentia (Salinic Orogeny) (Wilson and Kamo 2012). Late Pridolian–early Lochkovian transgression was succeeded by Lochkovian–Pragian regression related to the impending collision of Avalonia with Laurentia (Acadian Orogeny); dextral oblique convergence of Avalonia with the irregular Laurentian margin created local transtensional zones within which terrestrial intraplate volcanism of the Val d'Amour Formation (Dalhousie Group) occurred (Wilson et al. 2004, 2005). The deformation front of the Acadian Orogeny is estimated to have arrived in the Restigouche region by the early Emsian, as evidenced by the angular unconformity between the Val d'Amour and Campbellton formations (Wilson et al. 2004, 2005), the paleontologically and isotopically constrained position of the deformational front in Maine (Hubacher and Lux 1987; Bradley and Tucker 2002). The Campbellton Formation (Gaspé Sandstones Group) contains terrestrial strata deposited in an intermontane basin associated with the Acadian Orogeny. The study area lies on the southern limb of the Restigouche Syncline, a subdivision of the Chaleur Bay Synclinorium.

Val d'Amour Formation

The Val d'Amour Formation, 5800 m thick, comprises the Walker Brook, Thompson Brook, and Richardsville members (Fig. 3), which were described in detail by Wilson et al. (2004, 2005). The Walker Brook Member rests conformably upon the latest Silurian–earliest Devonian Indian Point Formation (Chaleurs Group). Shallow-marine deposition is restricted to the eastern exposed limit of the formation at Dalhousie, where the Walker Brook Member comprises fossiliferous limestones, pillow basalts, and hyaloclastites. Elsewhere, a dominantly terrestrial environment is indicated by massive (non-pillowed) basaltic flows, mafic ash and lapilli tuffs, thick accumulations of andesitic lavas and pyroclastic rocks, and local intercalated, commonly red or greenish gray sedimentary rocks containing a diverse assemblage of terrestrial spores (Wilson et al. 2005). The Thompson Brook Member contains mainly andesitic to dacitic subaerial flows, tuffs, and volcaniclastics, and one interval of terrestrial siliciclastic strata with plant debris. Flow-layered rhyolites of the Richardsville Member complete a formation-scale

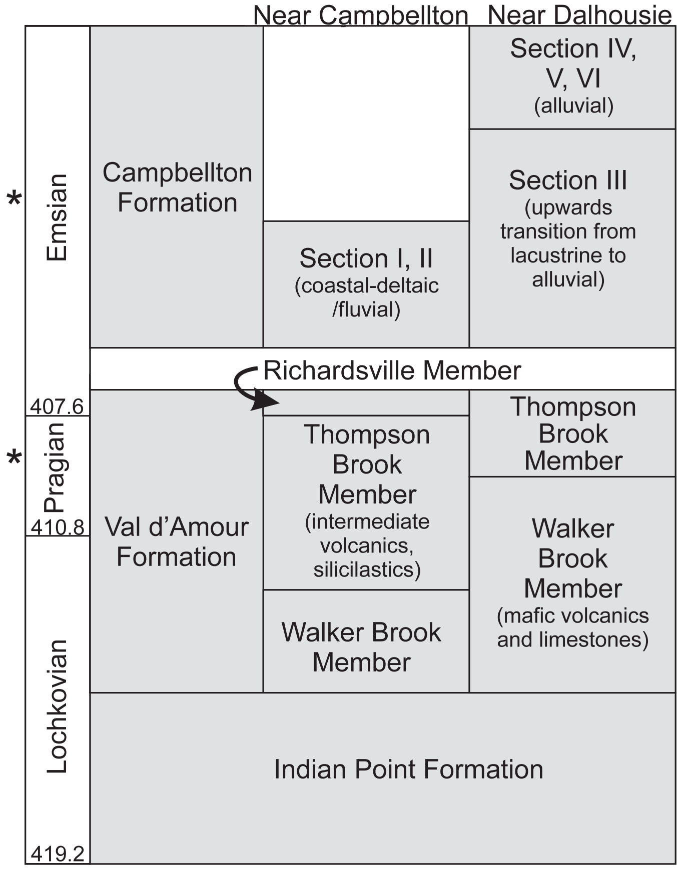


FIG. 3.—Lateral environmental variation and chronostratigraphic relationships between eastern (near Campbellton, New Brunswick), and western (near Dalhousie, New Brunswick) strata of the study area. Asterisks (*) indicate approximate age of samples analyzed and their position within the western part of the Thompson Brook Member (Val d'Amour Formation), and in the eastern Section III of the Campbellton Formation. Absolute ages of stage boundaries are from the International Chronostratigraphic Chart (ICS 2012). Data sources for stratigraphy are from Gensel and Andrews (1984), and Wilson et al. (2004, 2005).

transition upwards from mafic to felsic compositions. These rhyolites are isotopically dated to 407.4 ± 0.8 Ma and are unconformably overlain by the Campbellton Formation near the city of Campbellton (Wilson et al. 2004).

At and near Campbellton (Fig. 2), water-laid terrestrial strata of mainly medium- to coarse-grained volcaniclastic sandstone, cobble to boulder conglomerate, and mafic tuffs constitute an ENE–WSW-trending belt extending for about 12 km. This belt lies within the Thompson Brook Member, and is in contact with overlying rhyolites of the Richardsville Member. Near the center of the belt, a single outcrop of relatively fine-grained strata is present on the north side of Highway 11, about 200 m west of the intersection with Val d'Amour Road. It is only from this outcrop that coaly shales have been recovered (Ruitenberg et al. 1977; Wilson et al. 2004). The occurrence of coaly shales and related mudstones within this belt of generally coarse-grained volcaniclastic rocks implies that the former were deposited in the central part of an intermontane lowland characterized by wetlands and flanked by volcanic headlands. These strata are dated to the early (but not earliest) Pragian to early Emsian, on the basis of a palynological assemblage that corresponds to the *polygonalis–emsiensis* Assemblage Zone of Richardson and McGregor (1986; Wilson et al. 2004).

Campbellton Formation

The Campbellton Formation, approximately 940 m thick, was deposited in two subbasins, separated in the early Emsian by a paleotopographic high (Kennedy and Gibling 2011). The western subbasin (sections I and II) represents early stages of basin filling by coastal–deltaic and braided-river facies above an angular unconformity with the Richardsville Member of the Val d'Amour Formation (Kennedy and Gibling 2011). An exceptionally well-preserved assemblage of fish, eurypterids, small invertebrates, and plants can be found in mudstones (Kennedy et al. 2012a). The eastern subbasin contains an overall coarsening-upwards sequence of lower lacustrine (section III) facies that pass upward to wetland, fluvial, and proximal alluvial facies (sections III, IV, V, and VI). Tracheophytic plant material is common throughout all parts of the formation, the paleoecology of which is discussed in Kennedy et al. (2012a). The diverse assemblage includes lycopsids (*Drepanophycus* spp., *Leclercqia* spp.), trimerophytes (*Psilophyton* spp., *Pertica dalhousii*), zosterophyllopsids (*Sawdonia* spp., *Zosterophyllum divaricatum*, *Oricilla bilinearis*), rhyniaceans (*Taeniocrada* sp.), and other unstudied plants (Gensel and Andrews 1984; Gensel and Kasper 2005). *Spongiophyton minutissimum* and *Prototaxites*, as well as several small terrestrial arthropods, also occur amongst phytodebris (Gensel et al. 1991; Shear et al. 1996). This formation contains one of the earliest occurrences of wood and the earliest record of heterospory (Andrews et al. 1974; Gerrienne et al. 2011).

Beds particularly rich in carbonaceous material were first noted by Gesner (1843), who observed 5–10 cm "coal" seams that were rumored to have been mined out by early French settlers. Later surveyors deemed them uneconomic (Ells 1881), and they were not investigated further. The carbon-rich outcrop occurs about 170 m west of Pin Sec Point. The sample locality itself has not been dated, but the beds lie about 20 m stratigraphically above a plant locality at Pin Sec Point that contains a palynologic assemblage corresponding to the *sextantii* subzone of the *annulatus–lindlarensis* Assemblage Zone of Eastern Canada (McGregor and Camfield 1976), or the middle part of the *annulatus–sextantii* Assemblage Zone of Richardson and McGregor (1986). This attribution indicates a mid Emsian age (Gensel and Andrews 1984).

MATERIALS AND METHODS

Measured sections of the two outcrops containing carbonaceous strata were described on a bed-by-bed basis during field work in August 2009 and 2010. Samples were collected from beds within the outcrop or from nearby loose slabs, and eight were analyzed using the following range of techniques (Table 1).

Cuticles were macerated by bathing samples from coaly shale layers and adjacent shales in cold hydrochloric and hydrofluoric acid and, after washing, with a Schulze treatment. The residue of plant fragments was then collected and examined under transmitted light.

The identification of maceral constituents and the measurement of vitrinite reflectance as an indication of thermal maturity were performed on petrographic samples under reflected light. Samples for analysis were placed in phenolic ring-form molds (3.2, 3.8, and 5.1 mm diameter, depending on sample size), covered with epoxy resin, and allowed to cure. Once hardened they were ground using 400 and 600 grit papers, and polished using 1.0 and 0.3 μm alumina suspensions. Final polishes were obtained using 0.05 micron colloidal silica. Maceral analyses were performed on a Zeiss UEM microscope using both white and blue (UV) light for identification. Maceral percentages are based on 500 point counts/sample. Random vitrinite reflectance values ($R_{o\ \mathrm{random}}$) were obtained from 50 points/sample, after calibrating with a glass standard of known reflectance (0.52, 0.95, and 3.25, depending on the sample). Reflectance acquisition protocol followed ASTM International Test

TABLE 1.—*Maceral analysis, vitrinite reflectance values, proximate analysis, and elemental analysis of coaly shales.*

	VA1	VA2	VA3	VA4	CF1	CF2	CF3	CF4
Maceral Analysis (%)^{d,mmf}								
Telinite (%)	23.2	12.4	7.2	24.8	11.2	-	12.4	-
Collotelinite (%)	34.8	51.2	50.4	30.8	59.2	-	38.8	-
Collodetrinite (%)	12.4	4.0	0.0	14.8	0.0	-	0.0	-
Vitrodetrinite (%)	6.8	12.4	13.6	6.0	0.4	-	20.0	-
Corpogelinite (%)	0.0	0.0	0.0	0.0	0.0	-	0.0	-
Gelinite (%)	2.4	8.0	1.6	9.2	0.4	-	16.0	-
Sporinite (%)	14.8	10.0	13.2	8.8	1.6	-	12.4	-
Cutinite (%)	0.0	0.0	11.6	0.4	27.2	-	0.0	-
Resinite (%)	3.2	0.0	0.4	0.4	0.0	-	0.0	-
Exsudatinite (%)	0.0	0.0	0.0	0.0	0.0	-	0.0	-
Liptodetrinite (%)	1.6	1.6	2.0	2.8	0.0	-	0.4	-
Fusinite (%)	0.0	0.4	0.0	1.2	0.0	-	0.0	-
Semifusinite (%)	0.4	0.0	0.0	0.0	0.0	-	0.0	-
Macrinite (%)	0.0	0.0	0.0	0.4	0.0	-	0.0	-
Micrinite (%)	0.0	0.0	0.0	0.0	0.0	-	0.0	-
Secretinite (%)	0.0	0.0	0.0	0.0	0.0	-	0.0	-
Funginite (%)	0.0	0.0	0.0	0.0	0.0	-	0.0	-
Inertodetrinite (%)	0.4	0.0	0.0	0.4	0.0	-	0.0	-
Telovitrinite (TV)	58.0	63.6	57.6	55.6	70.4	-	51.2	-
Detrovitrinite + Gelovitrinite (DV + GV)	21.6	24.4	15.2	30.0	0.8	-	36.0	-
TV/(DV + GV)	2.7	2.6	3.8	1.9	88.0	-	1.4	-
Vitrinite Reflectance						-		-
$R_{o\ max}$	0.86	1	0.91	0.81	0.48	4.48	0.84	5.22
$R_{o\ random}$	0.8	0.94	0.85	0.76	0.45	4.21	0.79	4.9
Proximate Analysis								
Ash (%)^d	-	-	59.96	71.52	74.29	94.34	65.53	98.38
Fixed Carbon (%)^d	-	-	21.52	14.4	13.13	2.63	19.09	0
Moisture (%)	-	-	2.06	1.83	1.12	1.91	1.7	0.65
Volatile Matter (%)^d	-	-	18.52	14.08	12.58	3.03	15.38	1.79
Elemental Analysis								
TC (wt%)^d	27.02	28.44	32.74	22.62	21.37	5.4	28.89	2.27
TS (wt%)^d	0.24	0.22	0.39	0.20	0.54	0.05	0.79	0.20
TOC (%)^{ad}	32.39	22.89	32.39	22.89	35.63	4.93	29.51	1.52
TON (%)^{ad}	0.5	0.4	0.5	0.4	0.35	0.07	0.33	0.04
C/N	75.5	66.7	75.5	66.7	118.7	82.1	104.3	44.3
N/C	0.0132	0.015	0.0132	0.015	0.0084	0.0122	0.0096	0.0226

^{d} dry basis. ^{ad} as determined. ^{mmf} mineral matter free.

Method D2798-11a, Standard Test Method for Microscopical Determination of the Vitrinite Reflectance of Coal.

Proximate analysis for the basic rank parameters of ash yield, moisture, volatile matter, and fixed carbon was carried out by heating the samples in a stepwise manner and measuring changes in mass at each stage in accordance with ASTM International Test Method D 5142-09 using a Leco TGA 701 thermogravimetric analyzer.

Geochemical analysis included the measurement of total carbon and sulfur, as well as the elemental analysis of total organic carbon (TOC), hydrogen (TOH), and nitrogen (TON). Total carbon and sulfur were determined using a LECO SC-144 DR analyzer by combusting the samples under an oxygen atmosphere at 1350°C. A Perkin Elmer Elemental Analyzer 2400 was used to determine elements on samples ground to ~ 10 μm and treated with hydrochloric acid. Weighed samples ranging between 2 and 4 μg were incinerated in a pure O_2 atmosphere at 960°C, with resulting gases compared against an acetanilide standard. Values are reported as percentages.

Although vitrinite reflectance is a standard means of assessing maturation level, it was not clear at the start of the analysis what kerogen types would be present in the samples, in view of their Early Devonian age. Consequently, solid-state ^{13}C NMR (nuclear magnetic resonance) cross-polarization spectra of four samples, two from each formation, were obtained to provide an additional assessment of maturation level (Werner-Zwanziger et al. 2005). The technique used a Bruker Avance DSX NMR spectrometer with a 9.4 T magnet (400.24 MHz proton Larmor frequency, 100.65 MHz ^{13}C Larmor frequency). Samples were crushed into a fine powder, packed into 4-mm-diameter rotors, and spun between 6.0 and 14.0 kHz. Two experimental techniques were used: cross-polarization with magic angle spinning (CP/MAS) and direct excitation. The parameters for the ^{13}C CP/MAS experiments with TPPM (two-pulse phase modulation) proton decoupling were optimized on glycine, the carbonyl resonance of which also served as an external, secondary chemical shift standard at 176.06 ppm. ^{13}C CP/MAS spectra were measured with ramped proton powers accumulating 6400 scans with 1 s repetition times at a spinning rate of 13.5 kHz. CP contact times of 200 μs and 2600 μs were respectively chosen to give the best overall signal intensity and to enhance long range proton-carbon coupling. One sample (VA2) from the Val d'Amour Formation was additionally chosen for quantitative analysis using direct excitation. Its ^{13}C spin-lattice relaxation times, T_1, were measured with an inversion-recovery sequence initiated by cross-polarization, giving T_1 values of 8 s for the aromatic and 3 s for the

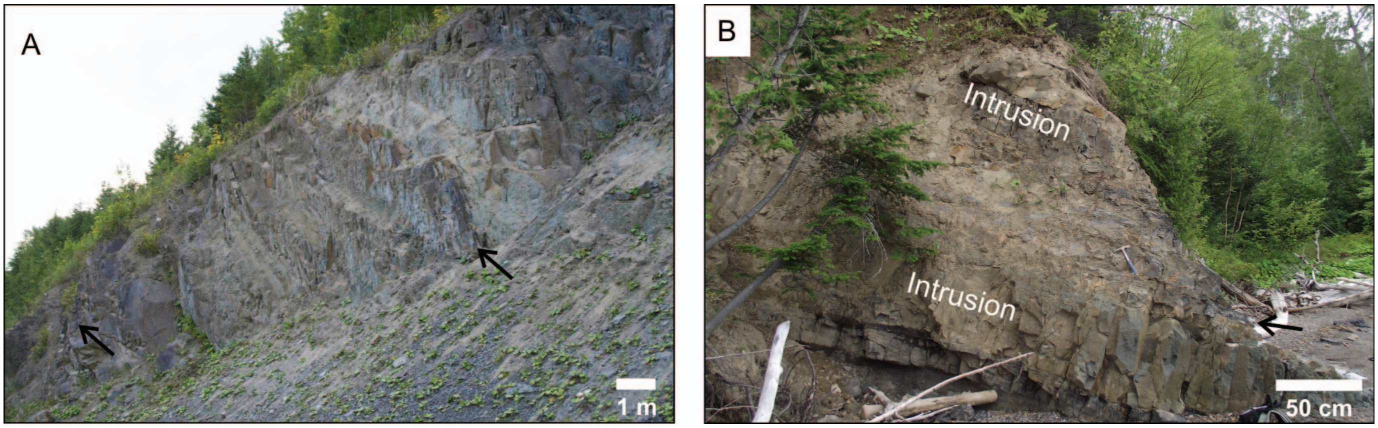


FIG. 4.—Outcrop photographs. Arrows indicate carbon-rich beds. **A)** Steeply dipping strata of the Highway 11 outcrop, Val d'Amour Formation, corresponding to approximately the 0–10m interval of Figure 5A. **B)** Campbellton Formation outcrop bearing carbon-rich layers immediately adjacent to igneous intrusions as depicted in Figure 5B.

aliphatic signals. The final ^{13}C NMR spectra were acquired using single pulse excitation (SPE), background suppression (Cory and Ritchie 1988), and proton decoupling at 8 kHz and 14 kHz spinning speeds accumulating 2000 scans pulsing every 40 s. Finally, to unambiguously identify the overlap of the signals with spinning sidebands, which are separated from the isotropic center peaks by multiples of the spinning frequency, ^{13}C SPE/MAS NMR spectra with total suppression of spinning sidebands (TOSS) (Dixon 1982) were acquired accumulating 4096 scans at 6 kHz spinning rate.

To compare to literature, we calculated the NMR aromaticity factor, f_a, which is defined as the fraction of the integrated aromatic region of the total signal intensity where aromatic signals occur between 90 and 165 ppm, aliphatic signals between 7 and 66 ppm, and other signals between 165 and 212 ppm. Additionally, spinning sidebands were summed to their corresponding center peaks. Intensities below 7 ppm were classified as spinning sidebands of the aromatic region. The TOSS spectrum shows that the intensity of the aliphatic groups below 7 ppm overlapping with the spinning sideband (at 14 kHz) is less than 2% of the aliphatic sites, an error that is below our precision (approximately 5%).

RESULTS

Stratigraphy

Val d'Amour Formation: Description and Interpretation.—The studied section crops out as almost 15 m of steeply dipping terrestrial strata, resting upon a volcaniclastic cobble conglomerate (Fig. 4A). Here, we have represented the outcrop in two measured sections (Fig. 5A), separated by a gully.

Conglomeratic facies include two pebble-conglomerate units and a mud-clast conglomerate. The pebble conglomerates, up to 1.2 m thick, are poorly sorted and supported by a sand matrix. Some weak stratification is present, as well as rare rip-up clasts of carbonaceous material from underlying units of carbon-rich sediment, 1–2 cm thick and several centimeters wide, in the topmost conglomerate. Mud-clast conglomerates are up to 0.25 m thick with angular mud clasts lying parallel to bedding, and are interbedded with siltstone and coarse granule-bearing sandstone up to 0.15 m thick, banded on a 3–5 cm scale.

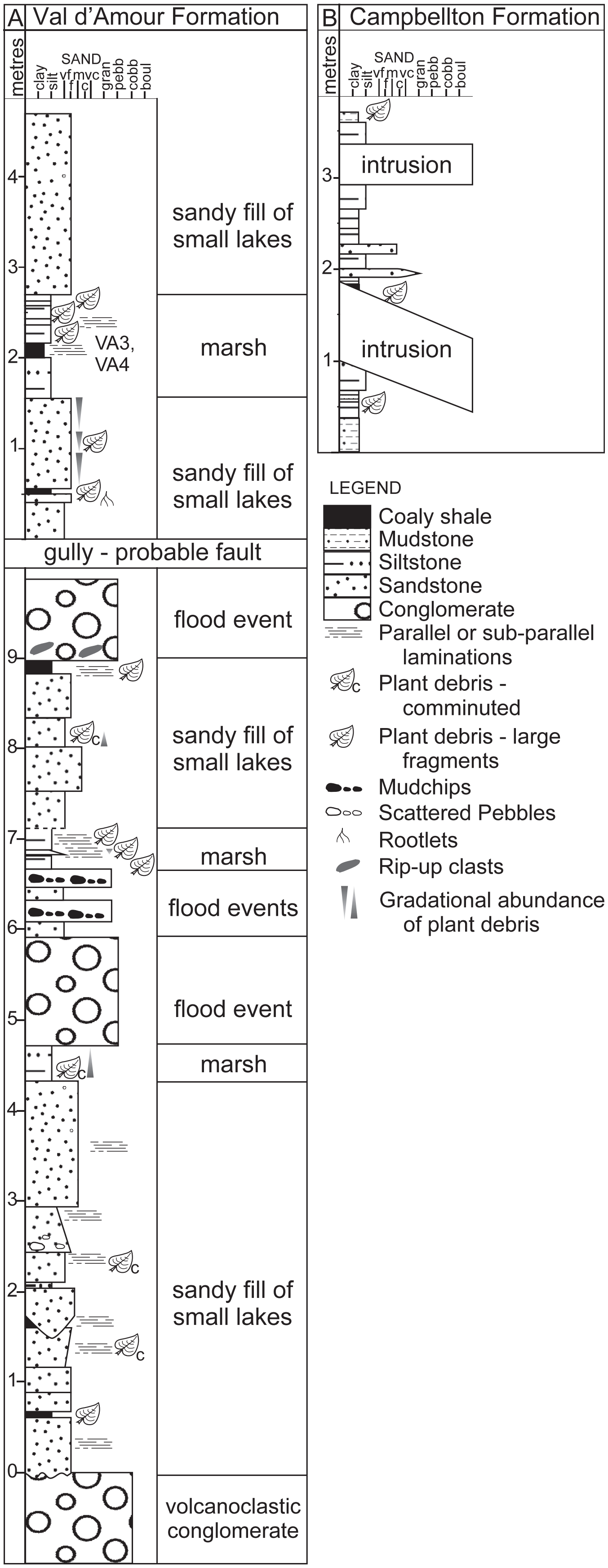
Sandstone-dominated facies occur at four levels, ranging from 1.5 m to 4.5 m in thickness. They are typically gray, fine- to medium-grained, parallel-laminated or subparallel-laminated lithic wackes with interbedded lenses or thin beds of organic-rich siltstone. Within a single bed, laminae commonly thin upwards and phytodebris commonly increases or decreases in abundance. Comminuted or fragmental phytodebris up to 10 cm long is present in many sandstone beds, and short rootlets penetrate 2–3 cm into one bed.

Plant-bearing siltstone and shale units range from 0.4 m to 1 m in thickness. Within these units, thinly laminated and lenticular siltstones are interbedded with beds or lenses of coaly shale.

The strata are interpreted as terrestrial wetland deposits, where deposition in small lakes and marshes was interrupted by major flood events that laid down gravel and sand (Fig. 5A). The overall abundance of phytodebris and the presence of one rooted level indicates a position in the littoral zone or fringing wetlands (cf. Bashforth et al. 2010), and the absence of acritarchs in palynological samples from this section supports a fresh-water setting (Wilson et al. 2004). Periods of high discharge that brought coarse clastics into the system are indicated by weakly stratified pebble conglomerate. Mud-clast conglomerates provide evidence for periods of intense erosion of intraformational mudstones with little subsequent transport. Parallel-laminated sandstone is inferred to represent filling of standing water bodies, which shallowed to marsh-like conditions as indicated by organic-rich lenses in the sandstone or organic-rich siltstone and shale (cf. Tibert and Gibling 1999; Hillier et al. 2007; Bashforth et al. 2010). The intercalation of coaly shales with thick conglomerate and sandstone beds implies rapid burial of the organic material, in a setting with abundant volcaniclastic detritus.

Campbellton Formation: Description and Interpretation.—The studied outcrop occurs at the 224–229 m level of section III of Kennedy and Gibling (2011). The outcrop (Figs. 4B, 5B) comprises only 3.6 m of strata, of which about 1.4 m are porphyritic igneous intrusions emplaced as two sills and heavily altered at a later date. The sedimentary strata include featureless dark gray to black siltstone and shale and two coarse sandstone beds, each about 10 cm thick.

Carbonaceous material was found in siltstone and shale in the lower 60 cm of the section. These beds are composed of alternate laminae, 0.05–0.1 mm thick, of carbonized plant remains and siltstone, with graded laminae of siltstone a few millimeters thick. There are no signs of soil horizons or rootlets (cf. Allen and Gastaldo 2006) in the outcrop. Other pieces of carbonaceous material, a few centimeters thick and significantly lower in density than those found in outcrop, were strewn upon the surrounding beach. These pieces did not correspond to any



layer still visible, but they could not have travelled far. Siltstone beds directly in contact with the sills appeared black due to contact metamorphism, rather than indicating a significant enrichment in carbon.

Interpretation of these strata is limited by the small size of the outcrop and obstruction by the two sills. Fine-grained sediments, the absence of current- or wave-induced structures, and preservation of organic-rich beds indicate a generally low-energy setting where oxygen depletion prevented oxidation of organic matter (DiMichele and Gastaldo 2008). We propose that this outcrop represents a shallow, stagnant pond, where plant material accumulated from the surrounding vegetated landscape. At this stratigraphic level, the landscape was in a period of predominantly subaerial deposition, with proximal alluvial deposits at Pin Sec Point stratigraphically below the outcrop and braided-river deposits and associated wetland material above (Kennedy and Gibling 2011). The outcrop belongs to facies association 1 of Kennedy and Gibling (2011), which includes floodplain pond deposits. Sandstone beds, although rather featureless, likely represent minor, higher-discharge events where coarser sediment was introduced during flooding.

Cuticle Macerations

Although maceration of coaly shales produced no identifiable plant remains at either locality, shales immediately adjacent to carbon-rich layers were more productive. Five types of stem were recognized: 1) a branched stem approximately 8 mm wide with branching comparable to a trimerophyte, 2) stems that either are highly folded or ridged, reminiscent of *Bitelaria*, 3) smooth stems approximately 3 mm wide, some with a dark central strand, similar to *Taeniocrada*, 4) smooth, circular, stems with zosterophyll-type lateral sporangia (round-reniform), arranged similarly to the genus *Zosterophyllum* (Fig. 6A, B), and 5) spiny stems similar to *Sawdonia* (Fig. 6C). A thick cuticle with raised bumps (Fig. 6D) is comparable to the thallus of *Spongiophyton*. Three-dimensional stems can be isolated where the cuticle encloses an amorphous black filling, possible representing detrital clay and degraded cellular tissue trapped within hollow stems. All plant material in the shale appears to be transported and is interspersed amongst layers of sediment.

Petrography

All the samples, except for the two thermally altered samples (CF2 and CF4), are high in vitrinite (average 80.7% on a mineral-matter-free basis; Fig. 7, Table 1). In all samples, telovitrinite, a vitrinite subgroup derived from well-preserved (although not always visible) cell walls, was the dominant maceral group, considerably more abundant than detrovitrinite and gelinite, which are derived from highly fragmented plant remains and colloidal gels from decaying cells, respectively (average TV/(DV + GV) ratio is 16.7:1). This suggests that 1) conditions in the paleomire were conducive to the overall preservation of organic matter (i.e., anoxic and acidic), resulting in high percentages of telovitrinite; or 2) the telovitrinite represents certain plant tissues that were highly resistant to decay.

Liptinite macerals are moderately abundant (average 18.7% on a mineral-matter-free basis), chiefly sporinite. In two samples oriented perpendicular to bedding (CF1 and VA3), cutinite was especially abundant (27% and 12% on a mineral-matter-free basis). In these two samples the cuticles, which are quite thick (crassicutinite of Stach et al. 1982), are usually separated by bands of telovitrinite (telinite and

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FIG. 5.—Measured stratigraphic sections of outcrops containing sampled carbonaceous material to illustrate sedimentary facies and interpreted depositional events in **A)** the Val d'Amour Formation, and **B)** the Campbellton Formation.

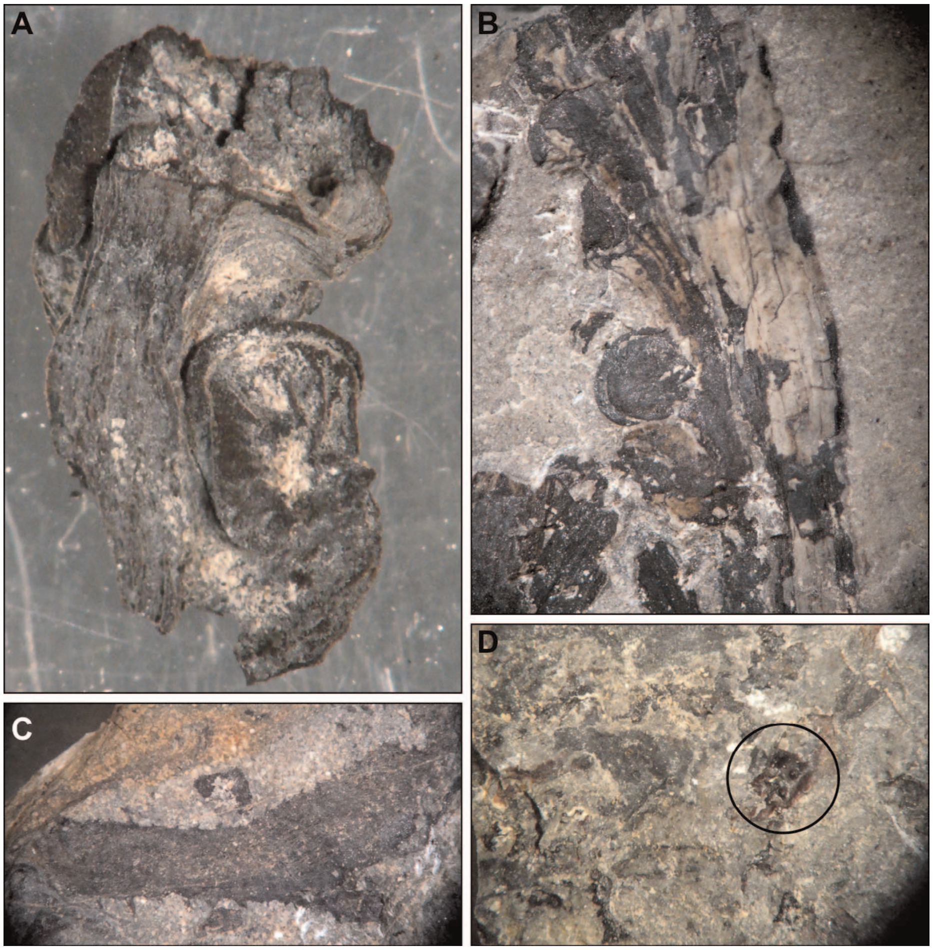

FIG. 6.—Selected plant fragments macerated from coaly shale layers and adjacent shales in the Val d'Amour Formation. **A, B)** Zosterophyll axes with lateral sporangia with some three-dimensional preservation visible. **C)** A spiny plant axis similar to *Sawdonia*. **D)** A fragment of a specimen with a thick cuticle with raised bumps, encircled, similar to the thallus of *Spongiophyton*.

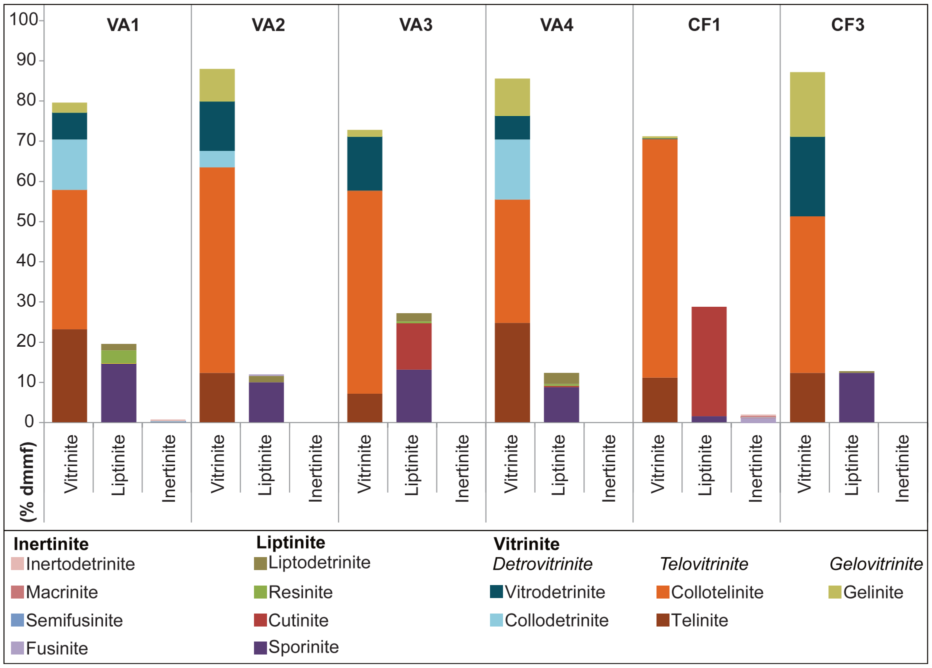

FIG. 7.—Relative frequency of maceral types, categorized by maceral group, from 500-point counts of Val d'Amour (VA-series) and Campbellton (CF-series) Formation samples. Precise values are supplied in Table 1.

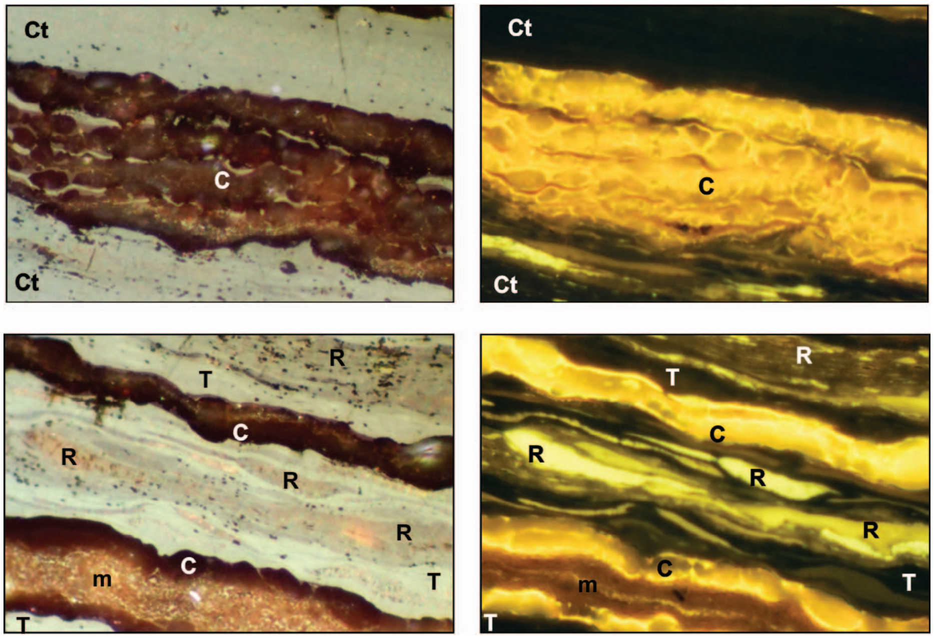

FIG. 8.—Photomicrographs of petrographic samples from the Campbellton Formation oriented perpendicular to bedding (left in reflected white light, right in UV fluorescent light). Couplets of thick-walled cutinite (C) surround an inorganic mineral filling (m), and alternate with bands of collotelinite (Ct) telinite (T) and resinite (R). Field of view is 200 µm.

collotelinite) arranged repetitively (Fig. 8). In addition, the cuticles typically occur as couplets (double-walled?) with a thickness of 5 µm to 90 µm, wall to wall, where each wall individually ranges from 1 µm to 25 µm in thickness. The central portion of each couplet, up to 50 µm thick, is commonly occupied by inorganic material (clay, with lesser amounts of quartz and pyrite), with spores and other degraded organic components interspersed in the inorganic matrix.

Inertinite macerals resulting from the intense oxidation of organic material form a small component of the coaly shales (average total inertinite 0.5%). This indicates either a paucity of wildfire during peat accumulation (e.g., Scott and Jones 1994) or is a further reflection of acidic, anoxic conditions in the paleomire that prohibited the formation of inertinite through degradational pathways (Hower et al. 2009). This low value accords with data from Glasspool and Scott (2010), who found a range of inertinite from zero to 2.3% in coals from nine Devonian formations worldwide, with a formational average of 0.63% inertinite based on 35 samples Glasspool and Scott (2010) used the inertinite data to estimate atmospheric pO_2 through geological time, and their results suggest that values were relatively low in the Early Devonian, although above the 13% level required for combustion (Scott and Glasspool 2006).

Vitrinite Reflectance

The assessment of rank is an important indicator of the degree of coalification in response to the heat, pressure, and duration of burial. Here, we determine rank primarily through vitrinite reflectance, which is a measurement of the percentage of light reflected from polished vitrinite macerals immersed in oil (R_o). Vitrinite reflectance ($R_{o\ max}$) of Val d'Amour Formation samples ranges from 0.81 to 1.00, indicating that the samples correspond to a coal rank of High-volatile Bituminous A (Table 1) (Stach et al. 1982). Samples in the younger Campbellton Formation show a greater range of values. Two samples, with $R_{o\ max}$ of 0.48 and 0.84, indicate ranks of Sub-bituminous B and High-volatile Bituminous A. Considering their Devonian age, this sample suite represents only a moderate degree of maturation. However, the remaining two samples ($R_{o\ max}$ of 5.22 and 4.48) are of anthracitic rank. At this rank, liptinite, vitrinite, and inertinite macerals have essentially the same reflectance level, and thus become optically indistinguishable. As such, these samples were omitted from quantitative petrographic analysis.

Ash Yields and Geochemistry

The eight samples contain up to 35.6% of total organic carbon (TOC), and are classified here as coaly (carbonaceous) shale rather than coal (Table 1). This classification is confirmed by ash yields (i.e., the inorganic material that remains after controlled combustion) on six samples, which reached a minimum of 59.96% on a dry basis. Thermally altered siliciclastic-rich samples from the Campbellton Formation (CF2, CF4) are low in TOC (2.27 and 5.40%), with comparably low TON values (0.04 and 0.07%), and high ash yields (94.34% and 98.38%). Atomic C/N ratios are 44 and 82. Sulfur values also are low at 0.05 and 0.20 wt%.

Organic-rich samples from the Val d'Amour and Campbellton formations are comparable with each other in geochemical character (other samples in Table 1). TOC values of the four samples from the Val d'Amour Formation range from 22.89 wt % to 32.39 wt %, with TON values within a small range from 0.40 to 0.50%. Atomic C/N ratios range from 67 to 76. Sulfur values also are low, between 0.20 wt % and 0.39 wt %. In comparison, the remaining two organic-rich samples from the Campbellton Formation have TOC values of 29.51 and 35.63%, TON values of 0.33 and 0.35%, and slightly higher sulfur values of 0.54 and 0.79 wt %. Atomic C/N ratios are high, with a maximum value of 119.

^{13}C NMR

All ^{13}C NMR spectra (Fig. 9) show two separated intensity ranges with well understood chemical origins. The resonances between about 2 and 60 ppm correspond to aliphatic sites that include methyl groups, more and less mobile methylene groups, highly branched aliphatics, and possibly some oxygenated groups. The intensities between about 90 and 165 ppm originate from aromatic carbons composed of aromatic ring carbons, bridge-head carbons, and oxygen-substituted aromatic carbons with maxima around 119–127 ppm, around 139 ppm, and around 153 ppm, respectively. Other carbons, for example carboxyl groups (160–190 ppm) and carbonyl groups (190–220 ppm), were detected at higher ppm values in the directly excited data of VA2 (Fig. 9C). Spectral editing techniques (Wu et al. 1994; Hu et al. 2001; Mao et al. 2010) can experimentally disentangle some resonances. Additional to the center resonances, spinning sidebands mainly from the aromatic groups were observed and are indicated by * in Figure 9.

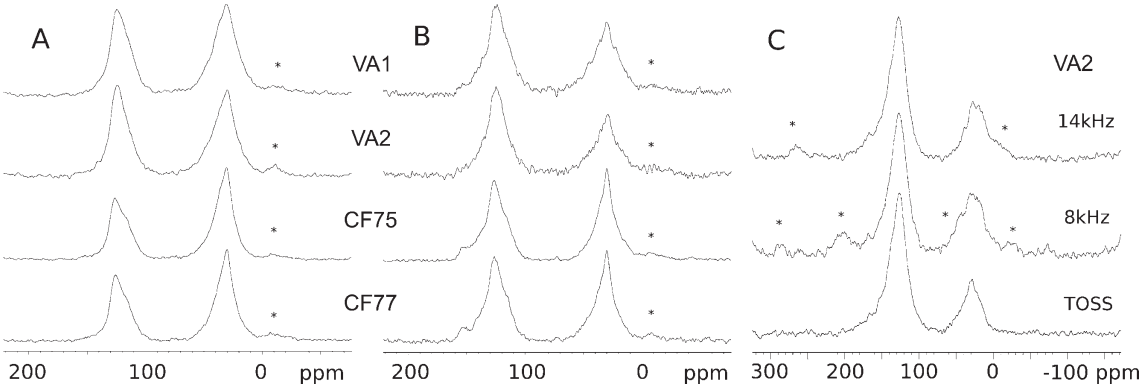

FIG. 9.—^{13}C NMR spectra. Peaks between 2 and 60 ppm correspond to aliphatic sites, and peaks between 90 and 165 ppm correspond to aromatic carbons. **A)** Cross-polarization spectra with 200 μs contact time. **B)** Cross-polarization spectra with 2600 μs contact time. **C)** Direct excitation spectra of VA2 with indicated spinning speeds (top and middle) and sideband suppression (bottom). (* indicate spinning sidebands).

Whereas cross-polarization allowed fast spectral acquisition, the technique edits the intensities of the signals depending on the distances to protons via the dipole–dipole coupling and related relaxation processes in well understood ways. The short CP contact time (200 μs, Fig. 9A) heavily emphasized the aliphatic region, whereas the long CP contact time (2600 μs, Fig. 9B) increased signal intensities of long-range proton-carbon couplings of the oxygenated and bridgehead aromatics around 139 ppm and 153 ppm, respectively. The direct excitation technique (Fig. 9C) revealed the true intensities of the aliphatic signals and also showed weak signals from carboxyl, and possibly carbonyl, groups up to 200 ppm, which were not excited by the CP technique.

Comparing the specimens, the ^{13}C CP/MAS spectra within the Val d'Amour Formation (VA1 and VA2) and the Campbellton Formation (CF77 and CF75) series were almost indistinguishable, showing that samples within the series have similar compositions. However, the aliphatic region of the CF series was stronger than in the VA-series indicating slightly lower maturity in the CF series. Compared to the maturity range of other kerogens observed through NMR (see for example fig. 5 of Werner-Zwanziger et al. 2005, acquired under identical conditions), the difference in maturation between the two locations was not large. The CF series showed a small but more pronounced peak from the mobile CH_2 chains (32 ppm), which typically is lost with increasing maturity during oil and gas production. Notably, the signal quality of the VA series was lower than the CF series, despite identical experimental conditions, which we attribute to a faster decay during the spin locking.

While the CP data are not quantitative, they can be compared with spectra taken under identical experimental conditions, such as the samples and curves studied by Werner-Zwanziger et al. (2005, their fig. 6). For the long contact time (2600 μs), we found aromaticities (the fraction of aromatic carbons over the total signal intensity), $f_a^{CP,2600\mu s}$, of 0.55 ± 5 for both CF samples, and 0.58 ± 5 and 0.63 ± 5 for the VA1 and VA2 samples, respectively. Based on the published correlation for measurements with identical CP conditions, these $f_a^{CP,2600\mu s}$ aromaticities predict vitrinite reflectance values, R_o [%] of 0.9 ± 0.1 for both CF samples and 1.0 ± 0.1 and 1.1 ± 0.1 for the VA1 and VA2 samples, respectively.

These predicted vitrinite reflectance values confirm that the Val d'Amour samples are slightly more mature than those from the Campbellton Formation. Notably, the vitrinite reflectance values predicted by ^{13}C NMR analysis of the whole sample are similar to the values directly determined through reflectance on vitrinite alone. A better evaluation using the aromaticity, f_a, of the quantitative spectra of sample VA2 (0.72 ± 0.5) predicts a vitrinite reflectance value of 0.9 ± 0.2 based on published curves, for example by Carr and Williamson (1989) and Suggate and Dickinson (2004).

DISCUSSION

Paleoenvironmental Setting

At the beginning of the Devonian, the Restigouche area was positioned at about 30° S, drifting south a further 5–10° by the Emsian (Fig. 1) (Mac Niocaill and Smethurst 1994; Cocks and Torsvik 2002). The Rheic ocean and Acadian seaway were situated east of the main zone of Acadian deformation, and water bodies in the Acadian foreland basin were nearby to the west (van Staal et al. 2009). Both formations yield evidence, including accumulations of phytodebris, for a generally or periodically humid climate, as well as evidence of high-discharge flooding events. Constant moisture and a high water table were particularly important for the primitive vegetation of the time, which had few specialized vegetative adaptations to withstand extended dry conditions (Bateman et al. 1998). The paleogeographic maps of Figure 1 indicate that most preserved Devonian plant accumulations were equatorial, between about 30° N and S, although some Early and Middle Devonian occurrences in North America represent more southerly climes.

The depositional environments of carbon-rich occurrences in the two formations share several similarities. Total sulfur content is low (< 0.79%, dry basis) in all samples, supporting nonmarine conditions (Williams and Keith 1963; Treworgy and Jacobson 1985; Chou 1997). This inference is supported by the absence of acritarchs in the Val d'Amour Formation outcrop and in the eastern belt of the Campbellton Formation, as well as by the abundance of dispersed phytodebris. The depositional sites were subjected to flooding events of varying intensity, resulting in the deposition of pebble conglomerates, mud-clast conglomerates, and sandstones in the Val d'Amour Formation outcrop and sandstone layers in the Campbellton Formation outcrop.

Terrestrial sediments of the Val d'Amour Formation were deposited amongst voluminous intermediate volcanic flows and volcaniclastic deposits. Between individual flow events, the landscape became at least locally vegetated along the fringes of depressions where the water table was high. Although identifiable plants are not well preserved and the assemblage is undescribed, over 50 species of spores have been identified from the Val d'Amour outcrop (Wilson et al. 2004), implying the presence of a diverse plant assemblage in the region. Broad and smooth branching axes are consistent with the form genus *Taeniocrada,* and remains of a zosterophyll and possible trimerophyte are also present.

The stratigraphic position of the Campbellton Formation coaly shale beds is near the base of a transition from predominantly lacustrine deposition to predominantly alluvial deposition. The steep-sided basin was fringed with proximal alluvium, and axial braided rivers with a marshy floodplain occupied the central regions (Kennedy and Gibling 2011). Plants grew on low-lying, periodically water-saturated marshy land

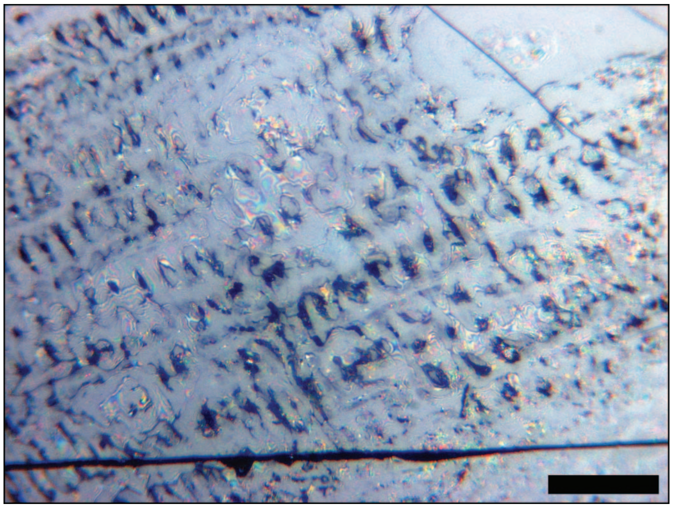

FIG. 10.—Photomicrograph in reflected light of stacked cells in telinite representing tracheids with secondary wall thickenings. Scale is 25 µm.

fringing large lakes and on floodplains, on the banks of high-energy fluvial systems, and bordering upland areas (Kennedy et al. 2012b). The relative abundance of plant material across a variety of terrestrial facies suggests that vascular plants had colonized much of the basin floor.

Thermal Maturation of Sediments

Indicators of regional thermal maturity for the upper parts of the Val d'Amour Formation lie within the oil window, as indicated by a thermal alteration index (TAI) of spores of less than 2.7 (Wilson et al. 2004). Vitrinite reflectance similarly corresponds to the light oil window of hydrocarbon generation (Heroux et al. 1979). The loss of some aliphatic compounds can be seen in the relatively low relief of the aliphatic peak in the ^{13}C NMR CP-MAS spectra of the Val d'Amour Formation samples compared to the Campbellton Formation samples. Zeolite-facies metamorphism seen in lower parts of the formation (Walker Brook Member) suggests that temperatures at that level of burial did not exceed 200°C (Mobsman and Bachinski 1972).

Less is known about the regional thermal maturity of the Campbellton Formation. The lower range of vitrinite-reflectance measurements corresponds to the wet-gas and light-oil window substages of hydrocarbon generation (Heroux et al. 1979). This is consistent with ^{13}C NMR spectra indicating that the Campbellton Formation samples are less mature than those of the Val d'Amour Formation. Two samples with low carbon content (CF2 and CF4) have high reflectance values ($R_{o\ max}$) of 4.48 and 5.22 that are inconsistent with the assessments of regional thermal maturity. These samples are inferred to have undergone contact catagenesis adjacent to igneous intrusions (cf. Melenevsky et al. 2008), resulting in thermal alteration and degradation of cellular structure in collotelinite.

In general, the organic-rich samples have undergone only a modest degree of burial maturation. Hence, observed petrographical characteristics can be used to provide reasonably reliable information about the structural components of the original plants.

Paleobotanical Links to Maceral Composition

Telovitrinite and detrovitrinite, together forming 74% on average of total maceral composition on a mineral-matter-free basis, are derived mainly from lignified tissues concentrated in the walls of xylem and parenchymal cells. Although vitrinite is traditionally attributed to woody tissue, there was a paucity of wood (secondary xylem) until the Middle Devonian (Bateman et al. 1998; Edwards 2003; Gerrienne et al. 2011). Parenchyma cells, however, were present in all parts of these early tracheophytes, concentrated in the cortex of stems, with outer layers often thickened (sterome), and primary xylem was composed of conducting cells that were probably cored by cellulose and impregnated with lignin as early as the Llandoverian (Early Silurian) (Niklas and Pratt 1980; Edwards et al. 1997; Edwards 2003). The presence of abundant telinite (15% mineral-matter-free, on average) with recognizable vertically stacked cell structure (Fig. 10) represents tracheids with tough, resistant, lignified tissue. Tracheids were far more common in the primary vascular strand of Early Devonian plants than in earlier plants, which may have been a contributing factor in forming coaly layers.

The cutinite macerals present in two samples are of particular note. In petrographic samples, the macerals are commonly double walled and occur adjacent to bands of telinite and collotelinite (Fig. 8). Cuticles surrounding clays, degraded cellular tissue, and spores, observed in both petrographic and macerated samples, may represent the collapse of hollow stems. The thickness of the cutinite macerals is comparable with cutinite in Middle Devonian coals from the Haikou Formation in China (Dai et al. 2006) derived from psilophytes and lycopsids, which falls into three thickness classes: 1–3 µm, 3–20 µm, and 20–50 µm. Cutinite in the Barzas coals of Russia, (80–240 µm thick) and composed largely of *Orestovia* is also somewhat comparable (Volkova 1994).

Several taxa known from one or both of the Val d'Amour and Campbellton formations may have contributed to cutinite occurrences. Zosterophylls, although common in both formations, typically have cuticles only a few microns thick, and would have created very thin cutinite macerals. *Bitelaria dubjanskii*, which forms paper shales in parts of the Campbellton Formation, has a cuticular epithelium that may reach thicknesses of 30–100 µm. The thallus of *Spongiophyton*, found in both formations, varies in thickness from about 30–50 µm on the lower surface and up to 250 µm on the upper exposed surface. Given that the maximum thickness of individual walls was observed to be about 25 µm, the closest candidate is something similar to *Bitelaria*.

Comparison with Other Early Coal Occurrences

Most reported Devonian coals are liptinite-rich, usually exhibiting high concentrations of sporinite or cutinite. Sporinite-rich cannel coals include those of the Givetian Mimer Valley Formation of Spitsbergen, Norway (Harland et al. 1976; Wollenweber et al. 2006) and some late Emsian to Frasnian coals of the Weatherall, Hecla Bay, and Beverley Inlet formations of Melville Island, Canada (Goodarzi and Goodbody 1990). Cutinite-rich coals include those of the late Givetian Barzas Formation, Russia (Ammosov 1964; Lapo and Drozdova 1989; Volkova 1994; Kashirtsev et al. 2010), and the Middle–Late Devonian of the Timan Region, along the Kama River, northern Urals (Volkova 1994). The Middle Devonian coals of the Haikou Formation, Yunnan Province, China, are also liptinite-rich, but include both sporinite and cutinite-rich varieties (Dai et al. 2006).

These studies indicate that relatively few Devonian coals are as rich in vitrinite as the New Brunswick coaly shales. Vitrinite is a common component of the humic coals of Melville Island, Arctic Canada, which consist of as much as 98.9% vitrinite, on a mineral-matter-free basis (Goodarzi and Goodbody 1990). Elsewhere, vitrinite makes up only 22% of Mimer Valley Formation coal macerals (Wollenweber et al. 2006), up to 58% of the Barzas coal macerals (Ammosov 1964), and up to 21% of Haikou Formation coal macerals (Dai et al. 2006).

Inertinite is only rarely a significant component in any Devonian coal (Diessel 2010). Fusinite occurs in the Barzas Formation coals, and some of the Weatherall and Hecla Bay formation coals have an inertinite content of up to 26.8% (mineral-matter-free) (Ammosov 1964; Goodarzi and Goodbody 1990; Fowler et al. 1991).

Geochemical Considerations

The origin of phytoclasts as an algal or land-plant contribution to an organic-rich rock can be assessed using atomic C/N ratios. Typically, algal debris exhibits C/N ratios between 4 and 10, whereas vascular land plants exhibit C/N ratios > 20 because of the presence of cell-wall cellulose in the latter (e.g., Meyers 1994). The highest C/N ratios are > 100 and are reported in woody plants (Raven et al. 2004). C/N ratios found in the present study range from 44 to 119, and are indicative of terrestrial photosynthesizing plants. These values are higher than expected given the paucity of woody vegetation in this part of the stratigraphic column (Bateman et al. 1998; Edwards 2003; Gerrienne et al. 2011). The samples appear to have been buried rapidly, and high C/N values do not appear to be a function of taphonomic alteration prior to burial.

Bacterial processes operating in some depositional environments are reported to alter the atomic C/N ratio of phytodebris (Grocke 1998). A decrease in C/N ratio occurs when bacterial and/or anaerobic conditions are operating during deposition and early diagenesis following burial, whereas aerobic conditions result in an increase (e.g., Benner et al. 1990). This diagenetic alteration appears to be associated with the sediment in which the plant material is buried: Grocke (1998) suggested that low C/N ratios (32) of Aptian woods are found in muddy depositional environments whereas significantly higher C/N ratios (85) occur in sandy sediments where bacterial activity and/or aerobic decomposition was limited. Although the high C/N ratios of both the Val d'Amour and Campbellton samples are from stratigraphic positions associated with sandstones, the preservational quality and diversity of plant parts negates an aerobic depositional setting for these deposits (see Gastaldo and Staub 1999). Hence, we infer that the observed high C/N ratios reflect the composition of these earliest vascular plants, rather than taphonomic effects.

Little published data exist on the elemental composition of Devonian macrofossil plants. Niklas (1976) and Niklas and Gensel (1976) reported on 15 biogeochemical characters of early non-vascular and land-plant taxa, and used N/C ratios of each as one parameter in their cluster analyses. A plot of N/C ratios for vascular plants was provided (Niklas and Gensel, their Fig. 7), omitting data tables, demonstrating that values for *Renalia*, *Sawdonia*, *Psilophyton*, *Pertica*, and *Chaleuria* range from 1.7×10^{-2} to 2.1×10^{-2} in a siliciclastic environment. These N/C values are higher than those for the VA and CF-series organic-rich samples, which range from 1.32×10^{-2} to 1.50×10^{-2} and 0.9×10^{-2}, respectively (Table 1). N/C values from the siliciclastic samples range from to 1.22×10^{-2} to 2.26×10^{-2}, and conform more closely with those reported by Niklas and Gensel (1976). As noted above, these differences may be a reflection of taphonomic factors on diagenesis in siliciclastic versus peat-accumulating environments.

CONCLUSIONS

Carbonaceous material from the Pragian and Emsian of the Val d'Amour and Campbellton formations in the northern New Brunswick region of Canada are among the first thick accumulations of phytodebris in the geological record. Although these occurrences contain less than 35.63 wt % TOC and more than 59.96% ash (dry basis) and thus cannot be considered true coals, they nonetheless contain significant amounts of well-preserved organic material derived from plants. Their appearance corresponds with a significant period of diversification of vascular-plant communities, as plants spread away from low-lying wet areas across alluvial plains and as vegetation on low-lying areas increased in abundance and diversity. These trends are indicated by the presence of vascular plants across a wide facies spectrum in the two formations. Rapid burial under volcaniclastic detritus and in proximal alluvial settings probably aided preservation of the organic accumulations.

The composition and character of the samples studied here was largely influenced by the comparatively primitive nature of the existing plant communities. In all samples, vitrinite was a major component despite a general paucity of plants with secondary xylem (woody tissue) at this time. Instead, vitrinite macerals were likely mainly derived from parenchymal tissues and tracheids in the primary xylem. Unusually thick cuticles form a significant component of some samples. C/N ratios vary from 67 to 118 in organic-rich samples, consistent with an origin from vascular land plants preserved in a setting with little decomposition.

Vitrinite reflectance ranges from 0.48 to 1.00, with most samples corresponding in rank to High-volatile Bituminous A coals, and these maturation levels are confirmed by NMR results. Two carbon-poor samples were contact-heated to anthracitic rank, and samples from the Val d'Amour Formation are generally more mature than those of the overlying Campbellton Formation. The relatively low maturation level of the samples lends support to the hypothesis that the original plant material underwent only modest geochemical modification during burial.

The Early Devonian coaly shales studied here are comparable to some true coals of the Middle and Late Devonian. Their presence indicates that, under suitable conditions of climate and burial, a considerable amount of material derived from relatively small vascular plants was capable of accumulating in wetlands prior to the development of forests with large plants. Hence, an important stage in the evolutionary history of plants, peat, and coal was reached at this time.

These early coal-like accumulations were precursors to the thick and widespread coals of the later Devonian and Carboniferous. Thus, they provide a proxy record for plant biomass and vegetation cover as plants expanded across Devonian terrestrial landscapes, supporting existing isotopic proxy records for changes in atmospheric composition. The coaly shales also mark an increase in the terrestrial storage of organic carbon, with the release of increased volumes of hydrocarbons during burial maturation, as inferred from the relatively evolved composition of the Val d'Amour Formation shales.

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