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# Geochemistry, petrology, and palynology of the Princess No. 3 coal, Greenup County, Kentucky

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**Abstract** The high volatile C bituminous-rank, Bolsovian-age Princess No. 3 coal, a correlative of the heavily-mined Hazard No. 7 coal and the Peach Orchard and Coalburg Lower Split coals, was investigated three sites at a mine in Greenup County, Kentucky. The coal exhibits a "dulling upwards" trend, with decreasing vitrinite and a greater tendency towards dull clarain and bone lithotypes towards the top of the coal. The relatively vitrinite-rich basal lithotype is marked by a dominance of lycopod tree spores. The palynology transitions upwards to a middle parting co-dominated by tree fern and small lycopod spores and an upper bench dominated by tree ferns with contributions from small ferns, cordaites, and calamites. The lithotypes generally have a moderate- to high-S content with a variable ash yield. Sulfur, Fe<sub>2</sub>O<sub>3</sub>, and certain siderophile elements are highest near the top of the coal. As observed in other coals, uranium and Ge are enriched at the top and bottom margins of the coal. The rare earth chemistry at the top of the coal has a significantly lighter distribution (higher LREE/HREE) than at the base of the coal.

Keywords Maceral · Rare earth elements · Lanthanides · Coal lithology

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# 1 Introduction

The Bolsovian age (Westphalian C, Middle Pennsylvanian) Princess No. 3 coalbed in the Argillite 7.5' quadrangle in Greenup County, Kentucky (Fig. 1), is approximately correlative to the lower split of the Peach Orchard or Coalburg and the Hazard No. 7 coals (among other names), which have been mined extensively elsewhere in the eastern Kentucky and southern West Virginia coalfields (based on compilations of coal names by the Kentucky Geological Survey and the Center for Applied Energy Research in the 1980s). In northeastern Kentucky, the Princess No. 3 coal, with an estimated original resource estimate of approximately 200 Mt, occurs about 60-m below the Princess No. 7 coal bed.

The original investigation of the coal was part of a study of methods for the enhanced recovery of coal from abandoned surface mine highwalls. Highwall mining is a hybrid of surface and underground mining, mining coal from a surface exposure, such as a contour mining operation,

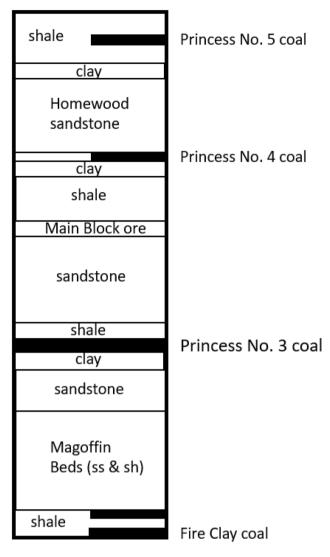


Fig. 1 Stratigraphic section after Sheppard and Ferm (1962). The interval thickness is approximately 55 m

utilizing a continuous miner cutting head. No mining personnel are required to go underground. In the case of the study, the remaining coal was to be mined using a highwall miner (ADDCAR 2019), with a circulating fluidized bed fly ash grout pumped into the horizontal mine slots, stabilizing the roof so that the pillars could be mined on a second pass. Because of logistics, including unsafe mining conditions due to the highwall lithology, the experiment was not conducted at this site and the test was conducted elsewhere in eastern Kentucky (Robl et al. 1998).

In this study, the geochemistry, with an emphasis on the Ge and Rare Earth Element concentrations; organic and inorganic petrology; and the palynology of the Princess No. 3 coal in a small area of Greenup County, Kentucky, are investigated. With the exceptions of a regional investigation of whole-channel samples from cores (Hower and Wild 1981) and the study of the Mudseam coal in Elliot

County, the correlative of the Princess No. 3 coal (Esterle et al. 1992), few detailed studies of northeastern Kentucky coals have been undertaken. As such, this investigation is an opportunity to further examine coals in a part of eastern Kentucky that is geologically more akin to the settings found in Ohio, northern West Virginia, and southwestern Pennsylvania than it is to the remainder of eastern Kentucky.

#### 2 Methods

The coal was collected in lithotype intervals from two cores and one mine face site at a single mine site (Figs. 2, 3a). The underlying Princess No. 3 leader coalbed was sampled a short distance from the mine face, at a point overlying a drainage pond (Fig. 3b).

Petrology was conducted at the University of Kentucky Center for Applied Energy Research (CAER) on epoxybound particulate pellets prepared to final 0.05- $\mu$ m alumina polish. Optical microscopy was conducted on a Leitz Orthoplan microscope with polarized reflected-light, oilimmersion optics at a final magnification of 500 ×. Vitrinite reflectance was done with the incoming light polarized at 45° and the reflected light passing through a 546-nm bandwidth filter on the path to the photomultiplier. The photomultiplier was standardized using glass standards of known reflectance. Maceral identification was based on nomenclature from the International Committee for Coal and Organic Petrology (1998, 2001) and Pickel et al. (2017).

For the basic coal analyses performed at the CAER, proximate analysis followed ASTM Standards D3173/ D3173M-17a (2017), D3175-18 (2018b), and D3174-12 (2018a); total sulfur and forms of sulfur analyses followed ASTM Standards D4239-18e1 (2018c) and D2492-02 (2012), respectively; and the ultimate analysis and heating value determinations were performed based on ASTM Standards D3176-15 (2015) and D5865/D5865M-19 (2019), respectively. Ash chemistry at the CAER was analyzed by X-ray fluorescence on a Phillips PW2404 X-ray spectrometer following procedures outlined by Hower and Bland (1989). Inductively coupled plasma mass spectrometry (X series II ICP-MS), in pulse counting mode (three points per peak), was used to determine trace elements in the coal samples (samples from 1155 to 117) at China University of Mining and Technology, Beijing (CUMTB). For ICP-MS analysis, samples were digested using an UltraClave Microwave High Pressure Reactor (Milestone) (after Dai et al. 2011). Arsenic and Se were determined by ICP-MS using collision cell technology (CCT) in order to avoid disturbance of polyatomic ions (Li et al. 2014). Multi-element standards (Inorganic Ventures:

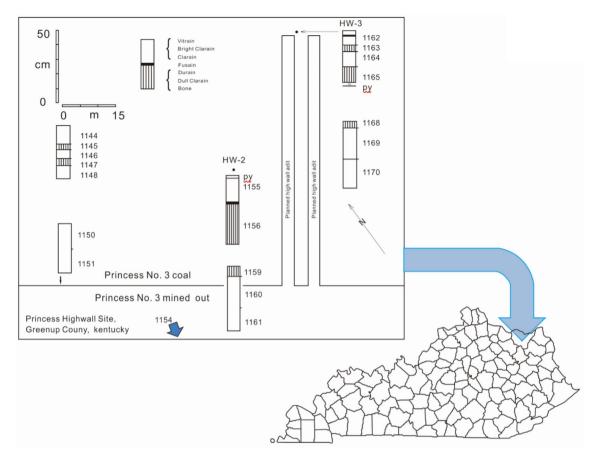


Fig. 2 Location of Greenup County (arrow), Kentucky, with inset of sampling locations. Simplified lithologic profiles of the three sampling sites are shown on the local-area map

CCS-1, CCS-4, CCS-5, and CCS-6; NIST 2685b and Chinese standard reference GBW 07114) were used for calibration of trace element concentrations. The method detection limit (MDL) for each of the trace elements is calculated as three times the standard deviation of the average from the blank samples (n = 10).

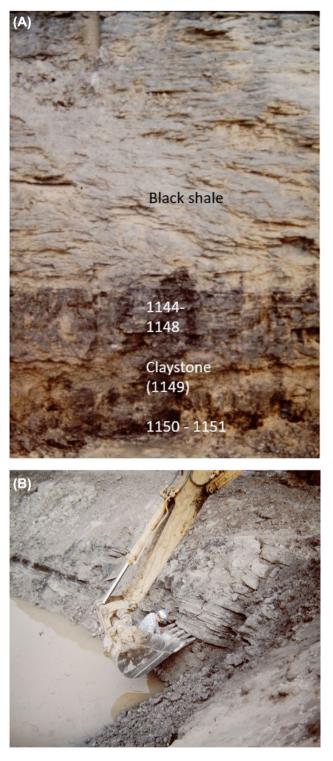
A field emission-SEM (FEI Quanta<sup>TM</sup> 650 FEG), in conjunction with an EDAX energy-dispersive X-ray spectrometer (Genesis Apex 4), at CUMTB was used to study the modes of occurrence of the minerals, and also to determine the occurrence of selected elements. Samples were carbon-coated using a Quorum Q150T ES sputtering coater, and were then mounted on standard aluminum SEM stubs using sticky conductive carbon tabs. The working distance of the FE-SEM–EDS was 10 mm, beam voltage 20.0 kV, aperture 6, and spot size 5.0. The images were captured via a retractable solid state back-scattered electron detector.

Palynology was investigated at the Kentucky Geological Survey. Palynomorphs were liberated by first oxidizing 2-3 g of -20 mesh coal with Schulze's Solution (concentrated nitric acid saturated with potassium chlorate). Following oxidation, samples were digested with 5%

potassium hydroxide, repeatedly washed with distilled water, and concentrated with zinc chloride (specific gravity 1.9). Amorphous organic matter (AOM) was removed from the residues using ethylene glycol monoethyl ether (2ethoxyethanol), ultrasonic vibration, and short centrifugation (Eble 2017). Samples were strew-mounted onto 25-mm square cover glasses with polyvinyl alcohol, and fixed to 75-  $\times$  25-mm microscope slides with acrylic resin. Spore and pollen abundances are based on a count of 250 palynomorphs for each sample. Palynomorph data are listed according to natural affinity for the following plant groups: lycopod trees, small lycopods, tree ferns, small ferns, seed ferns (pteridosperms), calamites and cordaites. Parent plant affinities of dispersed Carboniferous miospore taxa were derived from extensive summaries provided by Ravn (1986), Traverse (1988) and Balme (1995).

#### 3 Results and discussion

The Princess No. 3 at the study site and, in general, throughout the immediate vicinity of the mine (Sheppard and Ferm 1962; Ferm 1963) is overlain by a gray shale.



**Fig. 3 a** 1-m-thick section of coal and clay split (samples 1144–1151). **b** Sampling of the 13-cm-thick leader coalbed illustrating expedient, albeit not recommended, sampling procedure

Sheppard and Ferm (1962) and Dobrovolny et al. (1966) noted that the shale is locally channeled, but no such features were observed at the study site.

#### 3.1 Chemistry

Samples identified as coal have a wide range of ash yields, ranging from < 5% (sample 1164; dry basis) to a clarain with > 77% ash yield (sample 1148) and a bone with nearly 52% ash yield (sample 1168) (Table 1). Megascopically, bone is nominally a high-ash, dull lithotype. Sample 1163, also identified as bone, has 6.14% ash yield, illustrating that the translation between field descriptions and actual analyses of dull lithotypes (bone, dull clarain, durain) can be difficult because much of the lithotype description is driven by the texture; the fine grain size of dull lithologies conceals the details of the composition (Hower et al. 1990). The lithologies above and, in the case of sample 1168, below the 25- to 31-cm-thick parting have the highest ash yield.

Total sulfur content ranges from 0.63% (as-determined basis) in coal sample 1168, in which case the sulfides are diluted by the clay content, to 13.40% in sample 1165, a coal with a 2.2-cm pyrite layer between the dull clarain lithologies. In general, the total sulfur is high, above 2% (as-determined basis). With the exception of sample 1165, the highest pyritic sulfur in each seam section is found in the top lithotype, a reflection of possible marine influence associated with the deposition of the overlying black to gray shale. The highest concentrations of Fe<sub>2</sub>O<sub>3</sub> (expressed as a percent on the ash basis) (Table 1) and siderophile elements (such as Ni, Co, and As and, to a lesser extent, Se; ppm ash basis; Table 1)<sup>1</sup> are generally also found in the top lithotypes.

#### 3.2 Petrology

The maceral content of the samples is given on Table 2. Since the samples were from a small area, reflectance was only done on sample 1146, which has a  $R_{\text{max}} = 0.58\%$  and a  $R_{\text{random}} = 0.54\%$ , indicating a high volatile C bituminous rank.

The megascopic lithology, generalized as the seam sections on Fig. 2, is simple, with dull clarain and bone being the dull lithologies and clarain being the lone bright lithology. Both in the upwards shift from clarain to a dull clarain mix and in the upwards decrease in the amount of vitrinite, the coal shows the "dulling upwards" trend found in many Appalachian coals (Esterle and Ferm 1986; Esterle et al. 1989, 1992; Hubbard et al. 2002). The total vitrinite content is dominated by telovitrinite macerals and the total inertinite content is dominated by fusinite + semifusinite. The "dulling upwards" trend also seems to be related to the absence of any obvious TiO<sub>2</sub>-Zr enrichment in the basal

<sup>&</sup>lt;sup>1</sup> Not all samples analyzed by the CAER were available for analysis at the CUMTB.

Table 1	Thickness (cm).	proximate and u	ultimate analys	ses (%),	forms of sulfur,	and heat values	(MJ/kg) of the	investigated samples

No.	Bench	Thickness	$M_{ad}$	A <sub>d</sub>	$V_{daf}$	S <sub>t,d</sub>	S <sub>p,d</sub>	$S_{s,d}$	$S_{o,d}$	$C_{daf}$	$\boldsymbol{H}_{\text{daf}}$	$N_{daf} \\$	HV
1143	Roof		2.09	35.95	45.72	3.77	nd	nd	nd	78.92	5.66	1.74	nd
1144	1 of 7 (top)	12.95	2.58	11.21	40.95	7.83	5.70	0.12	2.01	79.70	5.27	1.46	29.61
1145	2 of 7	4.06	4.47	6.19	44.31	3.32	1.78	bdl	1.54	81.66	6.00	1.41	31.91
1146	3 of 7	6.1	6.98	8.35	41.51	5.96	3.49	0.03	2.43	81.04	5.90	1.52	30.58
1147	4 of 7	5.08	3.10	25.12	44.29	3.20	2.06	bdl	1.14	78.51	5.36	1.57	24.10
1148	5 of 7	8.89	1.19	77.42	64.99	5.49	4.60	bdl	0.88	60.65	4.84	2.78	nd
1149	Parting	30.99	1.83	76.91	62.64	0.44	nd	nd	nd	62.64	6.09	2.91	nd
1150	6 of 7	18.03	6.39	7.58	43.05	1.69	0.71	bdl	0.98	82.11	6.18	1.58	31.14
1151	7 of 7	16	3.74	9.51	42.67	2.49	1.66	bdl	0.83	80.19	5.63	1.61	30.13
1152	Floor		1.50	84.26		0.92	nd	nd	nd	43.81	6.32	3.94	nd
1153	Floor		0.83	92.87		1.31	nd	nd	nd	25.88	5.52	7.21	nd
1154	Leader	12.95	5.22	9.63		5.60	3.64	0.06	1.90	79.51	5.84	1.54	30.09
1155	1 of 5 (top)	19.61	4.69	6.41	41.60	4.25	2.20	0.02	2.02	81.57	6.05	1.57	31.46
1156	2 of 5	15.9	3.18	30.85	41.70	1.94	0.86	0.02	1.06	79.94	5.60	1.94	22.50
1157	Parting	11	3.33	82.34		0.35	0.23	bdl	0.12	51.96	7.50	5.33	nd
1158	Parting	16	1.63	88.54		0.16	0.16	bdl	bdl	28.13	8.34	7.72	nd
1159	3 of 5	6.5	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
1160	4 of 5	19.99	5.26	6.14	43.09	1.88	0.70	bdl	1.18	82.32	6.04	1.63	32.00
1161	5 of 5	17.81	3.62	8.09	41.53	3.67	1.56	bdl	2.12	79.95	5.66	1.66	30.86
1162	1 of 7 (top)	9.98	3.91	8.66	39.18	6.54	3.80	0.06	2.67	81.54	5.37	1.50	30.89
1163	2 of 7	4.5	3.96	6.14	39.87	3.68	1.93	bdl	1.75	83.28	5.56	1.64	32.29
1164	3 of 7	9.98	4.91	4.71	40.88	2.53	1.05	0.01	1.47	82.65	5.77	1.64	32.67
1165	4 of 7	13.79	3.01	36.00	42.47	13.82	10.16	0.31	3.35	72.13	5.09	2.00	19.95
1166	Parting	14.68	3.23	84.84		0.51	0.44	0.03	0.03	46.15	7.57	6.27	nd
1167	Parting	10.49	1.65	88.87		0.14	0.13	0.01	bdl	28.13	7.58	8.31	nd
1168	5 of 7	4.5	4.06	51.80	45.89	0.66	0.26	0.02	0.38	77.83	6.34	2.44	14.44
1169	6 of 7	21.69	5.71	11.48	41.21	1.52	0.56	0.01	0.94	81.36	6.40	1.71	29.73
1170	7 of 7	19.81	5.93	6.87	40.90	2.51	1.49	0.03	0.99	81.03	6.16	1.71	31.41

M moisture, A ash yield, V volatile matter, C carbon, H hydrogen, N nitrogen,  $S_t$  total sulfur, ad as-determined basis, d dry basis, daf dry and ashfree basis, HV gross heat value, on a air-dry basis

lithotype. The latter chemical association is often found in basal durains (Hower and Bland 1989; Hower et al. 1994a, b; Johnston et al. 2015), suggesting a greater detrital influx into the developing mire.

Among the minerals, clays are found dispersed within macerals, as thin layers, and as cell fillings within fusinite (Fig. 4). Clay/quartz layers contain  $TiO_2$  minerals. Pyrite and marcasite occur as euhedra, framboids, cell lumen fills, and multiple-generation overgrowths of euhedra and framboids (Figs. 5, 6). Complex two- and three-generation overgrowths of Fe-sulfides have been noted in other coals in eastern Kentucky (Hower and Pollock 1989; Ruppert et al. 2005; Diehl et al. 2012).

#### 3.3 Coal geochemistry

The percentages of major-element oxides and concentrations of trace elements in the samples investigated in this study are listed in Tables 3, 4 and 5. The highest concentrations of  $Fe_2O_3$  (expressed as a percent on the ash basis) (Table 3) and siderophile elements [such as Ni, Co, and As and, to a lesser extent, Se; ppm ash basis; Tables 4, 5 (see footnote 1)] are generally also found in the top lithotypes.

Compared to average values for world hard coals (Ketris and Yudovich 2009) and based on the enrichment classifications by Dai et al. (2015), elements Li, Be, Zn, Ge, Se, Ta and W in HW-2 series samples are slightly enriched (2 < CC < 5; Fig. 7); elements such as Cu, In, Sn, Ba, Hf, Tl, Bi, Th, and U HW-2 series samples are depleted (CC < 0.5). Selenium HW-2 series samples is enriched (5 < CC < 10) and As, Tl and Pb are slightly enriched

 Table 2
 Petrological compositions of samples investigated in this study (vol%, mineral-free basis)

Sample	tv	DV	GV	TV	F	SF	Mi	Ma	St	Fg	ID	TI	Sp	Cut	Res	Ag	LD	Sub	Ex	TL
1144	59.5	4.9	0.0	64.4	7.3	19.8	0.0	0.0	0.0	0.0	0.0	27.1	8.5	0.0	0.0	0.0	0.0	0.0	0.0	8.5
1145	57.4	5.2	0.0	62.5	11.2	16.7	0.0	0.4	0.4	0.4	0.0	29.1	8.4	0.0	0.0	0.0	0.0	0.0	0.0	8.4
1146	70.1	4.4	0.4	74.9	8.9	9.2	0.0	0.0	0.0	0.0	0.0	18.1	7.0	0.0	0.0	0.0	0.0	0.0	0.0	7.0
1147	63.3	4.4	0.0	67.7	4.4	17.9	0.0	0.8	0.4	0.0	0.0	23.5	8.8	0.0	0.0	0.0	0.0	0.0	0.0	8.8
1148	67.7	0.0	0.0	67.7	12.9	6.5	0.0	0.0	0.0	0.0	0.0	19.4	12.9	0.0	0.0	0.0	0.0	0.0	0.0	12.9
1150	64.8	5.1	0.5	70.4	12.0	7.4	0.0	0.0	0.0	0.5	0.5	20.4	9.3	0.0	0.0	0.0	0.0	0.0	0.0	9.3
1151	72.3	4.2	0.4	76.9	10.0	3.1	0.0	0.0	0.0	0.0	1.2	14.2	8.5	0.0	0.0	0.0	0.4	0.0	0.0	8.8
1154	79.2	4.4	0.0	83.6	7.2	5.2	0.0	0.0	0.0	0.0	0.4	12.8	3.6	0.0	0.0	0.0	0.0	0.0	0.0	3.6
1155	73.0	1.6	0.0	74.6	13.3	6.0	0.0	0.0	0.0	0.0	0.0	19.4	6.0	0.0	0.0	0.0	0.0	0.0	0.0	6.0
1156	56.1	3.0	0.0	59.1	9.3	24.1	0.0	0.0	0.0	0.0	0.4	33.8	7.2	0.0	0.0	0.0	0.0	0.0	0.0	7.2
1159	58.4	0.4	0.0	58.9	13.0	17.3	0.0	0.0	0.0	0.0	1.3	31.6	9.5	0.0	0.0	0.0	0.0	0.0	0.0	9.5
1160	67.3	1.6	0.4	69.3	13.2	9.3	0.0	0.0	0.0	0.0	0.0	22.6	8.2	0.0	0.0	0.0	0.0	0.0	0.0	8.2
1161	82.1	3.6	0.0	85.7	6.8	1.6	0.0	0.0	0.0	0.0	0.0	8.4	6.0	0.0	0.0	0.0	0.0	0.0	0.0	6.0
1162	64.5	2.4	0.0	66.9	14.7	6.4	0.0	0.0	0.0	0.0	0.0	21.1	12.0	0.0	0.0	0.0	0.0	0.0	0.0	12.0
1163	53.8	6.8	0.0	60.6	19.5	13.5	0.0	0.4	0.0	0.0	0.4	33.9	5.6	0.0	0.0	0.0	0.0	0.0	0.0	5.6
1164	57.1	10.7	0.0	67.9	11.1	11.1	0.0	0.4	0.0	0.0	0.8	23.4	8.7	0.0	0.0	0.0	0.0	0.0	0.0	8.7
1165	66.1	6.5	0.0	72.6	4.4	18.5	0.0	0.0	0.0	0.0	0.4	23.4	4.0	0.0	0.0	0.0	0.0	0.0	0.0	4.0
1168	53.2	7.2	0.0	60.4	6.8	25.6	0.0	0.0	0.0	0.0	0.4	32.8	6.8	0.0	0.0	0.0	0.0	0.0	0.0	6.8
1169	70.9	3.1	0.0	73.9	8.0	8.4	0.0	0.0	0.0	0.0	0.0	16.5	9.6	0.0	0.0	0.0	0.0	0.0	0.0	9.6
1170	78.1	4.4	0.0	82.5	6.4	2.4	0.0	0.0	0.0	0.0	0.0	8.8	8.8	0.0	0.0	0.0	0.0	0.0	0.0	8.8

tv telovitrinite, DV detrovitrinite, GV gelovitrinite, TV total vitrinite, F fusinite, SF semifusinite, Mi micrinite, Ma macrinite, St secretinite, Fg funginite, ID inertodetrinite, TI total inertinite, Sp sporinite, Cut cutinite, Res resinite, Ag alginate, LD liptodetrinite, Sub suberinite, Ex exsudatinite, TL total liptinite, M Parr mineral matter

(2 < CC < 5) relative to average values for world hard coals (Ketris and Yudovich 2009). The elements (with an exception of Tl) that are depleted in HW-2 series samples also have a lower concentration HW-2 series samples (CC < 0.5).

As has been widely observed in other coals (Hower et al. 2002; Yudovich Ya 2003b), the Ge content is highest in the top and bottom lithotypes of the two sections. Similarly, U is highest in the uppermost lithotype, with significant concentrations in basal lithotypes, as has been observed for U concentrations in many other coals (for example, studies by Berthoud 1875; Breger et al. 1955a, b; Breger and Schopf 1955; Zubovic 1966; Szalay and Szilágyi 1969; Eskenazy 1992; Yudovich Ya 2003a). In both cases, the enrichment can be attributed, at least in part, to infiltration of mineralized fluids from the surrounding sediments (Yudovich Ya 2003a, b).

In the HW-2 and HW-3 series samples, parting samples are characterized by higher REY (rare earth elements and Y) concentrations than the coal benches, and have light-REE enrichment type. However, REY in the coal benches were weakly fractionated (Fig. 8).

The ratio of light to heavy rare earth elements (LREE/ HREE) is lower at the top of the coalbed, coincident with the high-S/high-Fe<sub>2</sub>O<sub>3</sub> zone noted above (Table 6). The transition from LREE/HREE < 3.6 at the top of the coal to > 8 (and up to 10.58) in the lower parts of the coal is primarily a function of an increase in the LREE. For example, sample 1162, the top bench, has an LREE/HREE of 3.14 while sample 1168 has a ratio of 10.58; the HREE's are 29.6 and 28.9 ppm, respectively.

#### 3.4 Palynology

The palynology indicates that lycopod tree-derived spores dominate the basal bench of the two columns analyzed (Table 7; Fig. 9). The correlation between abundant lycopod tree spores, particularly *Lycospora micropapillata* and *L. granulata*, and high vitrinite, seen here in the basal lithotypes, has been noted elsewhere in the region (Eble et al. 1994; Hubbard et al. 2002). The thick parting in both sequences is co-dominated by small lycopod spores (mainly *Radiizonates difformis and R. rotatus*) and tree fern (mainly *Punctatisporites minutus*) spores in the lower section of the parting. The upper section of the parting is dominated by tree fern spores (*Punctatisporites minutus*); tree ferns continue to be important in the upper part of the coal with small ferns (various taxa, but no dominant

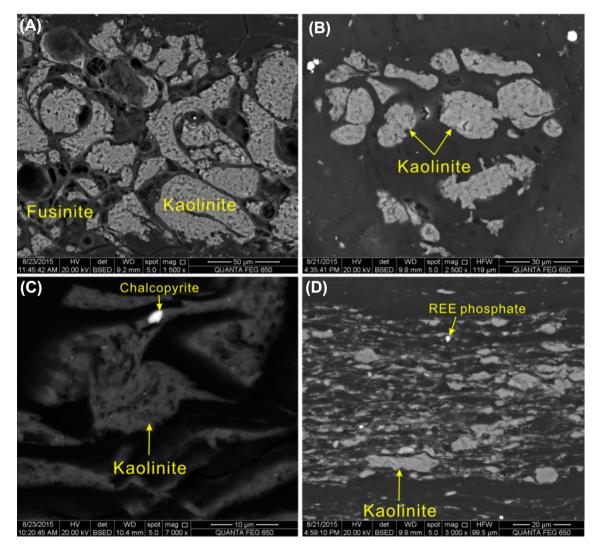


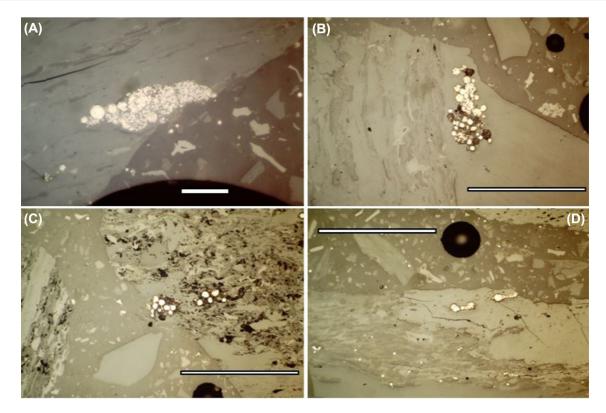
Fig. 4 Kaolinite in the samples investigated in this study. **a**, **b** kaolinite in fusinite lumens. **c** Kaolinite and chalcopyrite in fusinite lumens. **d** Detrital kaolinite and quartz and La–Ce–Nd-bearing phosphate mineral in collodetrinite. **a** Sample 1165; **b**, **d** sample 1155; **c** sample 1168

species), cordaites (*Florinites florini*), and calamites (primarily *Laevigatosporites minor*) present in significant amounts. Overall, the palynology of the coal lithotypes above the parting shows much greater floral diversity than is seen in the basal lithotypes.

Of all the Pennsylvanian plant types, the growth habits, reproductive biology and paleoecology of the arborescent lycopods is best known. Furthermore, much of what we know about lycopod trees has been derived from the study of coal balls, which represent permineralized peat, in the Illinois Basin (e.g., Phillips et al. 1974, 1985; DiMichele et al. 1985; DiMichele and Phillips 1994). All of the lycopod trees were heterosporous and dominated a majority of Early and Middle Pennsylvanian mire communities. Lycopod trees possessed vegetative and reproductive traits that allowed them to exploit low-nutrient swamp

environments more effectively than any other contemporaneous Pennsylvanian plant group (DiMichele and Phillips 1985).

In the Princess No. 3 coal, *Lycospora granulata* and *L. micropapillata* are the dominant arborescent lycopod spores. *Lycospora granulata* was produced by *Lepidophloios halli. Lepidophloios* was best adapted to very wet environments (like paleomires). The reproductive structure of *Lepidophloios* was *Lepidocarpon*, a boatshaped megasporanium/megasporophyll specifically adapted for water dispersal (Phillips 1979). Other vegetative features included root systems (*Stigmaria*) with abundant aerenchymatous tissue and outer cortex (bark) tissue that was water and rot resistant (DiMichele and Phillips 1985, 1994). Community paleoecology indicates that *Lepidophloios* was dominant in low-diversity ecotones. This relationship suggests high levels of abiotic stress that



**Fig. 5** SEM backscattered electron images of framboidal in coal samples. **a** Framboidal pyrite in vitrinite. Sample 1154. Image 301-25. Scale =  $50 \mu m$ ; air optics. **b** Framboidal pyrite in vitrinite. Sample 1154. Image 301-28. Scale =  $50 \mu m$ ; air optics. **c** Overgrown framboidal pyrite in macrinite. Sample 1148. Image 302-36. Scale =  $50 \mu m$ ; air optics. **d** Overgrown framboidal pyrite in macrinite. Sample 1145. Image 302-36. Scale =  $50 \mu m$ ; air optics. **d** Overgrown framboidal pyrite in macrinite. Sample 1145.

excluded other kinds of plants. It appears likely that a longstanding water regime was probably the major abiotic factor controlling the composition of *Lepidophloios*-dominant assemblages. Under such conditions, small, ground-cover and plants would have had difficulty becoming established.

Lycospora micropapillata was produced by Paralycopodites. Paralycopodites, may have been part of a pioneer type flora, based on the common occurrence of Lycospora micropapillata and L. orbicula in seat rocks (coal underclays) and basal coal layers. These palynotaxa are also prevalent within, or near, clastic layers in many coal beds. In coal ball assemblages, Paralycopodites-rich intervals are commonly associated with degraded peat and fusain, which suggest marginal conditions of peat preservation and frequent oxidation of the surficial peat through both biotic (microbial degradation) and abiotic (fire) pathways. In the Princess No. 3 coal, Lycospora micropapillata and L. orbicula are most abundant in the basal benches of both columns that were studied palynologically.

*Radiizonates difformis* and *R. rotatus* are the principle small lycopod spores in the Princess No. 3 coal bed and, biostratigraphically, serve to identify the coal as being equivalent with Bolsovian age strata of western Europe (Clayton et al. 1977), and Atokan age strata of the Eastern Interior (Illinois) Basin (Peppers 1985, 1996). Densosporites (and related crassicingulate genera, e.g. Cristatisporites) were produced by Omphalophloios, which was first described by David White (1897) from the Middle Pennsylvanian of Missouri. High percentages of Densosporites defined, in part, the "densospore" phase, which reflected the terminal part of a hydroseral series associated with peat accumulation in domed, ombrogenous mires (Smith 1957, 1962, 1964, 1968). Alternatively, high percentages of Densosporites in the terminal portions of the Lower Kittanning coal in the northern Appalachian Basin were thought to indicate a halophytic flora that developed in response to marine transgression and deposition of the overlying Columbiana Limestone (Habib 1966; Habib and Groth 1967).

Although these interpretations of *Omphalophloios* are highly disparate, both appear to have merit. Subsequent work by the current authors indicate that abundant *Densosporites* is commonly associated with (1) coal that is low in ash and sulfur, supporting formation in a domed, ombrogenous peat-forming environment, but also (2) coal with elevated amounts of ash and sulfur, which is

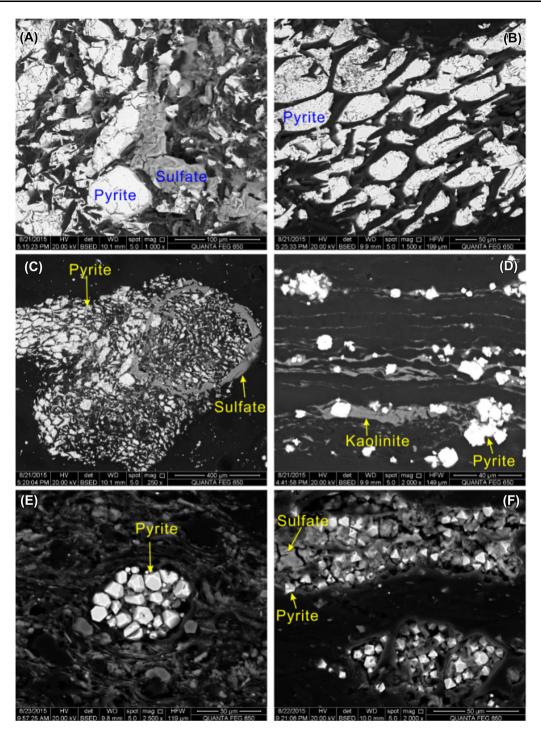


Fig. 6 SEM backscattered electron images of pyrite in coal samples. a Pyrite and sulfate minerals in fusinite matrix. SEM image 1155 025. b Pyrite in fusinite lumens. SEM image 1155 027. c Pyrite in fusinite lumens. SEM image 1155 026. d Pyrite in clay and vitrinite. SEM image 1155 020. e Pyrite framboid with euhedral crystals. SEM image 1143 058. f Euhedral pyrite in fusinite lumens. SEM image 1147 051

indicative of peat formation in a planar, topogenous mire. The common element in both cases is that high percentages of *Densosporites* are almost always associated with increased amounts of liptinite and inertinite macerals, and relatively low percentages of vitrinite. Based on this observation, *Omphalophloios* was apparently a lycopod that could develop in areas where peat preservation was poor, or even minimal. Although there is no direct paleobotanical evidence that *Omphalophloios* was a true halophyte, some species may very well have been saline tolerant to some degree, or at least were water-stress tolerant.

No.	Thick (cm)	Bench	$SiO_2$	TiO <sub>2</sub>	$Al_2O_3$	Fe <sub>2</sub> O <sub>3</sub>	MgO	CaO	Na <sub>2</sub> O	$K_2O$	$P_2O_5$	$SO_3$	LOI
1143		Roof	56.79	1.66	25.59	11.69	0.90	0.66	0.18	2.27	0.15	0.10	64.80
1144	12.95	1 of 7 (top)	17.19	0.34	7.82	71.26	0.70	1.34	0.45	0.45	0.07	0.39	89.10
1145	4.06	2 of 7	35.67	0.98	17.77	42.02	0.58	1.57	0.13	0.29	0.59	0.41	94.10
1146	6.1	3 of 7	23.80	0.30	12.60	60.24	0.58	1.38	0.29	0.42	0.11	0.29	92.20
1147	5.08	4 of 7	57.07	1.70	24.33	13.13	0.72	0.77	0.26	1.66	0.23	0.11	75.70
1148	8.89	5 of 7	59.27	1.11	22.03	11.61	1.35	0.66	0.00	3.44	0.25	0.30	23.50
1149	30.99	Parting	60.20	1.85	29.86	2.95	1.12	0.58	0.27	3.06	0.09	0.03	24.50
1150	18.03	6 of 7	47.27	0.92	31.31	15.54	0.90	1.62	0.24	1.39	0.50	0.30	92.90
1151	16	7 of 7	45.11	0.82	25.48	24.16	0.79	1.26	0.23	1.32	0.56	0.27	90.90
1152		Floor	57.31	1.31	30.97	4.30	1.15	0.56	0.39	3.89	0.09	0.03	17.00
1153		Floor	65.31	1.09	20.29	6.94	1.65	0.50	0.30	3.61	0.14	0.16	7.90
1154	12.95	Leader	26.40	0.52	12.16	57.10	0.66	1.53	0.23	0.72	0.23	0.47	90.90
1155	19.61	1 of 5 (top)	23.94	0.46	14.28	57.94	0.59	1.51	0.08	0.52	0.11	0.56	93.90
1156	15.9	2 of 5	58.80	1.78	28.19	7.01	0.98	0.48	0.14	2.38	0.19	0.06	70.10
1157	11	Parting	60.95	2.14	29.07	2.90	1.17	0.37	0.24	3.06	0.09	0.01	20.40
1158	16	Parting	59.73	1.76	30.63	2.82	1.11	0.37	0.20	3.27	0.07	0.02	12.90
1159	6.5	3 of 5											
1160	19.99	4 of 5	43.12	0.95	31.17	20.60	0.68	1.38	0.13	1.15	0.54	0.29	94.20
1161	17.81	5 of 5	31.30	0.58	22.19	42.46	0.61	1.24	0.16	0.64	0.44	0.39	92.20
1162	9.98	1 of 7 (top)	17.43	0.38	8.30	69.92	0.76	1.67	0.10	0.56	0.11	0.77	91.70
1163	4.5	2 of 7	32.00	0.79	15.64	47.54	0.73	1.63	0.10	0.73	0.09	0.73	94.10
1164	9.98	3 of 7	38.20	0.68	22.16	35.24	0.63	1.65	0.14	0.43	0.30	0.56	95.50
1165	13.79	4 of 7	35.59	1.13	15.69	45.09	0.54	0.34	0.09	1.35	0.08	0.11	65.10
1166	14.68	Parting	58.97	1.91	30.02	3.43	1.19	0.46	0.27	3.64	0.09	0.02	17.90
1167	10.49	Parting	59.74	1.83	29.96	3.06	1.20	0.39	0.23	3.49	0.08	0.01	12.60
1168	4.5	5 of 7	56.70	1.39	33.53	3.24	1.15	0.46	0.18	3.26	0.09	0.01	50.30
1169	21.69	6 of 7	51.45	1.26	33.64	8.51	1.05	0.85	0.20	2.44	0.40	0.21	89.20
1170	19.81	7 of 7	37.19	0.74	26.73	30.27	0.68	1.56	0.12	1.05	0.87	0.79	93.50

Table 3 Major-elements oxides (%, ash basis; normalized to 100%)

**Table 4** Concentrations of trace elements in samples 1143–1154, determined in at the CAER by the XRF (ppm; on whole coal basis, calculated from ash basis based on ash yield)

Sample	V	Cr	Mn	Со	Ni	Zn	Rb	Sr	Zr	Мо	Ba
1143	71	34	29	11	20	31	85	222	147	5	142
1144	7	bdl	bdl	14	2	bdl	bdl	19	bdl	3	14
1145	9	2	bdl	6	5	1	bdl	147	9	2	17
1146	13	2	bdl	10	9	12	bdl	21	1	3	12
1147	41	20	11	9	12	1	34	263	102	5	91
1148	103	26	277	26	57	73	193	187	239	11	371
1149	128	60	72	6	23	14	279	327	445	4	353
1150	21	8	6	5	19	33	7	226	22	4	31
1151	48	18	bdl	7	70	41	7	278	28	3	40
1152	139	39	bdl	8	40	72	385	481	448	10	432
1153	109	10	285	22	35	99	265	251	461	11	507
1154	26	11	9	12	46	40	bdl	42	2	2	25

 Table 5
 Concentrations of trace elements in samples 1155–1170 (ppm; on whole-coal basis)

Sample	Li	Be	Sc	V	Cr	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Rb	Sr	Zr
1155	4.67	3.23	1.40	9.04	13.7	2.41	8.73	8.45	36.1	4.85	8.07	32.8	4.52	BDL	36.5	4.42
1156	85.1	3.47	7.87	65.2	62.3	3.45	14.3	30.7	21.4	16.6	2.44	3.29	5.27	45.2	150	77.1
1160	16.3	2.80	2.79	20.1	25.4	7.42	24.4	7.88	151.4	6.84	2.03	4.66	8.23	2.89	110	9.89
1161	11.4	5.39	6.12	55.8	44.0	10.9	55.5	16.58	60.0	13.59	13.88	10.0	4.69	0.87	113	12.13
1163	5.04	3.29	0.63	7.29	30.5	1.80	6.27	11.07	10.2	2.20	0.62	7.27	3.30	0.47	31.9	6.16
1164	6.12	2.52	0.43	5.95	19.3	2.08	5.54	9.45	28.0	4.08	1.00	4.83	3.19	BDL	52.1	4.64
1165	60.4	2.22	6.81	52.7	78.1	11.8	45.0	33.9	16.0	12.6	2.47	103	16.6	26.6	52.2	53.9
1168	86.7	3.47	7.18	125	108	4.46	26.5	46.6	27.2	21.8	1.06	1.78	14.5	95.7	92.5	122
1169	31.3	2.83	4.56	37.1	36.8	5.32	16.0	15.0	20.7	9.29	1.94	2.51	8.47	15.3	156	21.6
1170	11.3	5.64	4.36	32.9	31.2	7.92	26.4	16.9	48.5	10.57	10.5	9.87	6.47	2.08	207	8.15
1162	3.82	3.15	2.31	8.36	19.3	1.62	6.03	8.19	15.8	7.02	14.2	25.3	5.96	0.33	43.0	3.77
1157	264	3.08	9.35	187	129	10.2	39.9	39.6	35.9	36.1	1.46	5.70	7.45	79.6	95.1	272
1158	213	2.85	9.48	148	119	9.21	35.3	28.1	53.9	34.6	1.54	2.45	5.40	95.3	83.0	255
1159	138	2.63	17.2	145	107	5.57	30.6	38.0	33.5	22.3	1.34	1.78	16.5	89.6	86.0	129
1166	215	2.92	18.1	157	129	11.7	43.4	36.1	39.6	40.4	1.49	5.42	8.92	140	144	239
1167	183	2.65	16.8	142	121	8.40	31.0	25.7	46.6	37.3	1.52	1.85	5.17	152	124	259
1168	86.7	3.47	7.18	93.4	62.6	3.48	16.4	1.49	28.3	21.8	1.06	1.78	14.53	187	258	244
1169	31.3	2.83	4.56	29.5	14.9	4.00	9.41	3.46	15.7	9.29	1.94	2.51	8.47	25.1	265	39.4
1170	11.3	5.64	4.36	28.2	10.9	6.98	19.6	3.75	51.7	10.6	10.54	9.87	6.47	2.45	271	15.1
Sample	Nb	Мо	Cd	In	Sn	Sb	Cs	Ва	Hf	Та	W	Tl	Pb	Bi	Th	U
1155	BDL	1.89	0.25	BDL	0.26	0.23	0.11	22.4	BDL	0.10	4.13	0.56	19.8	BDL	BDL	1.06
1156	9.50	1.35	0.17	0.04	1.65	0.30	4.26	150	2.28	1.29	3.67	0.22	11.6	0.16	4.13	1.89
1160	0.53	2.40	0.44	BDL	0.17	0.29	0.29	41.5	0.13	1.44	1.92	0.04	6.51	BDL	BDL	0.35
1161	0.05	2.32	0.13	BDL	0.07	2.75	0.22	33.6	0.09	BDL	0.74	0.46	27.0	BDL	BDL	0.59
1163	0.07	1.68	0.05	BDL	0.08	0.14	0.19	22.5	0.52	0.09	0.97	BDL	3.04	BDL	BDL	0.18
1164	BDL	1.33	0.19	BDL	0.10	BDL	0.06	15.9	0.10	0.02	1.08	BDL	2.75	BDL	BDL	0.09
	DDL	1100			0.10		0.00		0.10							1 20
1165	6.85	5.90	0.23	0.03	1.90	1.67	2.53	85.3	1.66	0.85	1.23	11.88	126	0.07	2.77	1.39
1165			0.23 0.22			1.67 0.11					1.23 1.36	11.88 0.59	126 38.8	0.07 0.28	2.77 6.65	2.55
1165 1168	6.85	5.90		0.03	1.90		2.53	85.3	1.66	0.85						
	6.85 13.1	5.90 0.42	0.22	0.03 0.09	1.90 3.86	0.11	2.53 6.99	85.3 217	1.66 3.66	0.85 1.46	1.36	0.59	38.8	0.28	6.65	2.55
1165 1168 1169	6.85 13.1 2.18	5.90 0.42 0.99	0.22 0.11	0.03 0.09 0.01	1.90 3.86 0.34	0.11 0.38	2.53 6.99 1.22	85.3 217 68.1	1.66 3.66 0.52	0.85 1.46 0.29	1.36 0.52	0.59 0.25	38.8 9.18	0.28 BDL	6.65 BDL	2.55 0.75
1165 1168 1169 1170	6.85 13.1 2.18 0.18	5.90 0.42 0.99 1.94	0.22 0.11 0.21	0.03 0.09 0.01 BDL	1.90 3.86 0.34 0.02	0.11 0.38 2.26	2.53 6.99 1.22 0.30	85.3 217 68.1 43.8	1.66 3.66 0.52 0.06	0.85 1.46 0.29 0.04	1.36 0.52 0.47	0.59 0.25 0.18	38.8 9.18 7.73	0.28 BDL BDL	6.65 BDL BDL	2.55 0.75 0.54 0.83
1165 1168 1169 1170 1162	6.85 13.1 2.18 0.18 BDL	5.90 0.42 0.99 1.94 3.47	0.22 0.11 0.21 0.08	0.03 0.09 0.01 BDL BDL	1.90 3.86 0.34 0.02 0.02	0.11 0.38 2.26 0.42	2.53 6.99 1.22 0.30 0.12	<ul> <li>85.3</li> <li>217</li> <li>68.1</li> <li>43.8</li> <li>28.7</li> </ul>	1.66 3.66 0.52 0.06 BDL	0.85 1.46 0.29 0.04 BDL	1.36 0.52 0.47 0.71	0.59 0.25 0.18 0.50	38.8 9.18 7.73 4.33	0.28 BDL BDL BDL	6.65 BDL BDL BDL	2.55 0.75 0.54
1165 1168 1169 1170 1162 1157	<ul> <li>6.85</li> <li>13.1</li> <li>2.18</li> <li>0.18</li> <li>BDL</li> <li>35.7</li> </ul>	5.90 0.42 0.99 1.94 3.47 3.38	0.22 0.11 0.21 0.08 0.46	0.03 0.09 0.01 BDL BDL 0.14	1.90 3.86 0.34 0.02 0.02 6.31	0.11 0.38 2.26 0.42 0.96	2.53 6.99 1.22 0.30 0.12 9.81	<ul> <li>85.3</li> <li>217</li> <li>68.1</li> <li>43.8</li> <li>28.7</li> <li>179</li> </ul>	1.66 3.66 0.52 0.06 BDL 8.77	0.85 1.46 0.29 0.04 BDL 4.39	1.36 0.52 0.47 0.71 4.22	0.59 0.25 0.18 0.50 0.92	<ul><li>38.8</li><li>9.18</li><li>7.73</li><li>4.33</li><li>30.2</li></ul>	0.28 BDL BDL BDL 0.77	6.65 BDL BDL BDL 8.61	2.55 0.75 0.54 0.83 3.05
1165 1168 1169 1170 1162 1157 1158	<ul> <li>6.85</li> <li>13.1</li> <li>2.18</li> <li>0.18</li> <li>BDL</li> <li>35.7</li> <li>32.9</li> </ul>	5.90 0.42 0.99 1.94 3.47 3.38 1.20	0.22 0.11 0.21 0.08 0.46 0.43	0.03 0.09 0.01 BDL BDL 0.14 0.12	1.90 3.86 0.34 0.02 0.02 6.31 5.41	0.11 0.38 2.26 0.42 0.96 0.69	2.53 6.99 1.22 0.30 0.12 9.81 10.5	<ul> <li>85.3</li> <li>217</li> <li>68.1</li> <li>43.8</li> <li>28.7</li> <li>179</li> <li>241</li> </ul>	1.66 3.66 0.52 0.06 BDL 8.77 8.25	0.85 1.46 0.29 0.04 BDL 4.39 3.85	1.36 0.52 0.47 0.71 4.22 3.57	0.59 0.25 0.18 0.50 0.92 0.82	<ul> <li>38.8</li> <li>9.18</li> <li>7.73</li> <li>4.33</li> <li>30.2</li> <li>21.6</li> </ul>	0.28 BDL BDL 0.77 0.46	6.65 BDL BDL 8.61 8.11	2.55 0.75 0.54 0.83 3.05 2.59
1165 1168 1169 1170 1162 1157 1158 1159 1166	<ul> <li>6.85</li> <li>13.1</li> <li>2.18</li> <li>0.18</li> <li>BDL</li> <li>35.7</li> <li>32.9</li> <li>16.1</li> </ul>	5.90 0.42 0.99 1.94 3.47 3.38 1.20 0.92	0.22 0.11 0.21 0.08 0.46 0.43 0.25	0.03 0.09 0.01 BDL 0.14 0.12 0.10	1.90 3.86 0.34 0.02 0.02 6.31 5.41 3.81	0.11 0.38 2.26 0.42 0.96 0.69 0.62	2.53 6.99 1.22 0.30 0.12 9.81 10.5 6.12	<ul> <li>85.3</li> <li>217</li> <li>68.1</li> <li>43.8</li> <li>28.7</li> <li>179</li> <li>241</li> <li>224</li> </ul>	1.66 3.66 0.52 0.06 BDL 8.77 8.25 4.12	0.85 1.46 0.29 0.04 BDL 4.39 3.85 1.96	1.36 0.52 0.47 0.71 4.22 3.57 1.93	0.59 0.25 0.18 0.50 0.92 0.82 0.67	<ul> <li>38.8</li> <li>9.18</li> <li>7.73</li> <li>4.33</li> <li>30.2</li> <li>21.6</li> <li>36.7</li> </ul>	0.28 BDL BDL 0.77 0.46 0.35	<ul> <li>6.65</li> <li>BDL</li> <li>BDL</li> <li>8.61</li> <li>8.11</li> <li>8.23</li> </ul>	2.55 0.75 0.54 0.83 3.05 2.59 2.45
1165 1168 1169 1170 1162 1157 1158 1159 1166 1167	6.85 13.1 2.18 0.18 BDL 35.7 32.9 16.1 31.4	5.90 0.42 0.99 1.94 3.47 3.38 1.20 0.92 2.77	0.22 0.11 0.21 0.08 0.46 0.43 0.25 0.39	0.03 0.09 0.01 BDL 0.14 0.12 0.10 0.15	1.90 3.86 0.34 0.02 0.02 6.31 5.41 3.81 6.42	0.11 0.38 2.26 0.42 0.96 0.69 0.62 0.97	2.53 6.99 1.22 0.30 0.12 9.81 10.5 6.12 11.7	<ul> <li>85.3</li> <li>217</li> <li>68.1</li> <li>43.8</li> <li>28.7</li> <li>179</li> <li>241</li> <li>224</li> <li>357</li> </ul>	1.66 3.66 0.52 0.06 BDL 8.77 8.25 4.12 7.50	0.85 1.46 0.29 0.04 BDL 4.39 3.85 1.96 3.56	1.36 0.52 0.47 0.71 4.22 3.57 1.93 3.63	0.59 0.25 0.18 0.50 0.92 0.82 0.67 1.25	<ul> <li>38.8</li> <li>9.18</li> <li>7.73</li> <li>4.33</li> <li>30.2</li> <li>21.6</li> <li>36.7</li> <li>36.2</li> </ul>	0.28 BDL BDL 0.77 0.46 0.35 0.66	<ul> <li>6.65</li> <li>BDL</li> <li>BDL</li> <li>8.61</li> <li>8.11</li> <li>8.23</li> <li>12.2</li> </ul>	2.55 0.75 0.54 0.83 3.05 2.59 2.45 2.89
1165 1168 1169 1170 1162 1157 1158 1159	<ul> <li>6.85</li> <li>13.1</li> <li>2.18</li> <li>0.18</li> <li>BDL</li> <li>35.7</li> <li>32.9</li> <li>16.1</li> <li>31.4</li> <li>33.8</li> </ul>	5.90 0.42 0.99 1.94 3.47 3.38 1.20 0.92 2.77 1.04	0.22 0.11 0.21 0.08 0.46 0.43 0.25 0.39 0.43	0.03 0.09 0.01 BDL 0.14 0.12 0.10 0.15 0.13	1.90 3.86 0.34 0.02 0.02 6.31 5.41 3.81 6.42 5.91	0.11 0.38 2.26 0.42 0.96 0.69 0.69 0.62 0.97 0.57	2.53 6.99 1.22 0.30 0.12 9.81 10.5 6.12 11.7 12.6	<ul> <li>85.3</li> <li>217</li> <li>68.1</li> <li>43.8</li> <li>28.7</li> <li>179</li> <li>241</li> <li>224</li> <li>357</li> <li>380</li> </ul>	1.66 3.66 0.52 0.06 BDL 8.77 8.25 4.12 7.50 8.31	0.85 1.46 0.29 0.04 BDL 4.39 3.85 1.96 3.56 3.71	1.36 0.52 0.47 0.71 4.22 3.57 1.93 3.63 3.61	0.59 0.25 0.18 0.50 0.92 0.82 0.67 1.25 0.83	38.8 9.18 7.73 4.33 30.2 21.6 36.7 36.2 21.6	0.28 BDL BDL 0.77 0.46 0.35 0.66 0.44	<ul> <li>6.65</li> <li>BDL</li> <li>BDL</li> <li>8.61</li> <li>8.11</li> <li>8.23</li> <li>12.2</li> <li>11.5</li> </ul>	2.55 0.75 0.54 0.83 3.05 2.59 2.45 2.89 2.88

Tree fern spores are both diverse and abundant in the Princess No. 3 coal. Tree ferns have their origins in the Early Pennsylvanian, rapidly expand in abundance in the late Middle Pennsylvanian (Desmoinesian, Asturian), and are a dominant element of mire floras in the Late Pennsylvanian (Stephanian). Tree ferns, and probably ferns in general, exhibited considerable ecological amplitude and adaptability. They had the least specialized method of reproduction of all the major coal-forming plant groups, exhibited a totally herbaceous growth habit, and possessed a massive root mantle for aeration and support. These features adapted them to a wide variety of swamp and swamp-like environments (Phillips and Peppers 1984).

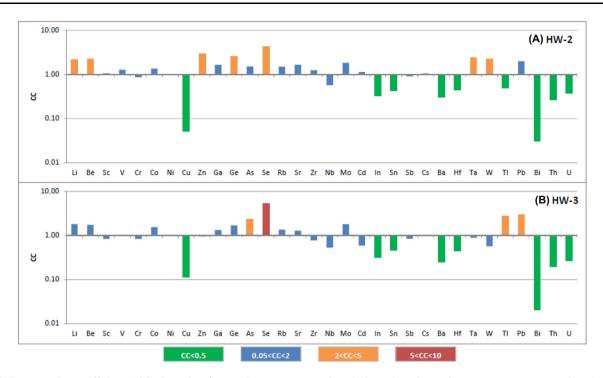


Fig. 7 Concentration coefficients (CC, the ratio of trace-element concentrations in investigated samples vs. average concentrations in world coals) for HW-2 and HW-3 series samples

Sphenopsid spores are a subdominant element of the Princess No. 3 coal palynoflora. Sphenopsid spores in the Pennsylvanian include Calamospora, large species of Laevigatosporites and, to a lesser extent, Vestispora, and Reticulatisporites. Sphenopsids are subdivided into two major evolutionary groups: arborescent calamites and the shrubby or vine-like Sphenophyllum (DiMichele et al. 1986). Both groups occurred in paleomires and were locally abundant in clastic substrate areas. Sphenophyllum was widespread throughout most of the Pennsylvanian, though a minor contributor to biomass because of its small size of (DiMichele et al. 1986). Calamites were also common constituents in Pennsylvanian swamps but, like Sphenophyllum, were also minor peat-biomass contributors (DiMichele et al. 1986). Although their abundance is generally associated with inorganic partings and high ash coal, exceptions exist. This type of general distribution supports the interpretation that calamites may have been centered outside of mires, with some forms persisting in both mire and clastic substrate environments (DiMichele et al. 1985).

Cordaite pollen in the Princess No. 3 coal occurs primarily as Florinites, with F. florini being the most common species. In general, Florinites is more common in the parting and coal benches that occur above the parting. Cordaites were a diverse group of plants with a broad ecological spectrum during the Pennsylvanian, ranging from dry, upland areas to waterlogged areas including mires (Raymond 1988). Coal ball studies recognize two principle stem genera, Mesoxylon and Pennsylvanioxylon (Cordaixylon). Mesoxylon was prominent in Early though mid-Middle Pennsylvanian (Langsettian—Bolsovian) mires (Phillips and Peppers 1984; Costanza 1985), and is inferred to have occupied areas of mires that were welldrained and periodically exposed. This interpretation is largely based on Mesoxylon roots lacking aerenchymatous tissues, and the poorly-preserved nature of Mesoxylon peats in coal balls. Mesoxylon produced Sullisaccites pollen, which is seldom reported in Pennsylvanian palynological literature. This is probably the result of misidentification with morphologically similar palynotaxa (e.g., Florinites, Wilsonites and Potonieisporites).

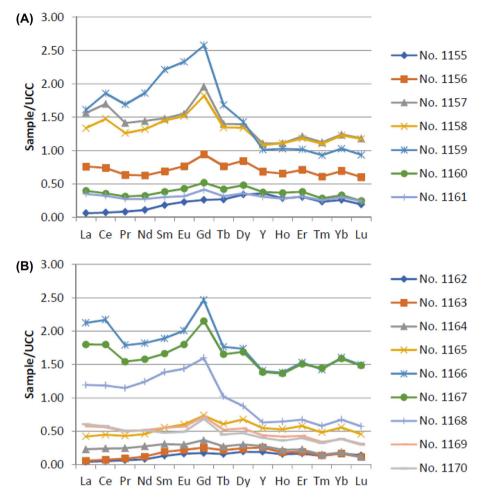


Fig. 8 REY distribution patterns of the HW-2 and HW-3 series samples (Normalized to Upper Continental Crust, UCC; Taylor and McLennan 1985)

Table 6 Concentrations of rare earth elements and Y in the samples (ppm, on whole-coal basis)

Sample	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Y	Но	Er	Tm	Yb	Lu
1155	1.92	4.67	0.60	2.88	0.83	0.20	0.99	0.17	1.20	7.90	0.23	0.71	0.08	0.58	0.06
1156	22.85	47.36	4.50	16.35	3.11	0.68	3.58	0.49	2.97	15.04	0.52	1.64	0.20	1.52	0.19
1157	46.91	108.75	10.04	37.51	6.67	1.37	7.45	0.90	4.88	24.37	0.89	2.80	0.37	2.73	0.38
1158	40.06	94.29	8.97	34.30	6.53	1.33	6.92	0.86	4.70	23.79	0.89	2.72	0.36	2.70	0.38
1159	48.31	118.87	12.00	48.44	9.96	2.05	9.78	1.08	5.01	22.29	0.82	2.34	0.31	2.26	0.30
1160	11.93	22.89	2.22	8.46	1.72	0.38	1.98	0.27	1.68	8.29	0.29	0.88	0.09	0.73	0.08
1161	10.48	20.66	1.95	7.15	1.36	0.28	1.57	0.20	1.26	6.74	0.22	0.72	0.08	0.66	0.08
1162	1.29	3.53	0.47	2.15	0.61	0.14	0.66	0.10	0.68	4.20	0.13	0.38	0.04	0.37	0.05
1163	1.78	4.86	0.66	3.18	0.88	0.20	0.96	0.14	0.86	5.64	0.15	0.45	0.05	0.37	0.04
1164	6.94	15.43	1.75	7.18	1.38	0.26	1.39	0.18	1.05	6.08	0.18	0.52	0.05	0.41	0.04
1165	12.65	28.63	3.06	11.93	2.49	0.53	2.79	0.39	2.37	12.02	0.42	1.33	0.16	1.22	0.15
1166	63.72	138.87	12.71	47.32	8.51	1.77	9.37	1.13	6.08	30.87	1.10	3.52	0.47	3.52	0.48
1167	54.05	115.12	10.96	41.00	7.48	1.59	8.19	1.06	5.91	30.54	1.09	3.46	0.48	3.49	0.47
1168	35.85	75.98	8.15	32.31	6.23	1.27	6.06	0.65	3.08	13.90	0.52	1.55	0.19	1.48	0.18
1169	17.30	35.76	3.50	13.53	2.49	0.50	2.73	0.33	1.90	9.62	0.33	0.99	0.11	0.84	0.10
1170	18.17	36.85	3.61	13.30	2.15	0.43	2.59	0.29	1.65	8.85	0.29	0.91	0.11	0.85	0.10

Sample ID	1155 (top)	1156	1157 (parting)	1158 (parting)	1159	1160	1161 (base)	1162 (top)	1163	1164	1165	1166 (parting)	1167 (parting)	1168	1169	1170 (base)
Lycospora pellucida	1.2	0.8		0.4		0.4	5.2	0.4	1.2				0.4		1.6	4.4
L. pusilla	1.2	2.4	0.4	2.0		2.0	2.4	1.2	3.6	0.4	3.6	0.4	1.6	0.8	0.4	3.2
L. granulata	6.0	2.8	2.8	1.6	0.4	30.0	10.4	2.4	15.2	6.4	2.0	2.0	2.0		8.0	7.2
L. orbicula						1.2	9.2	0.4	1.2			0.4			0.8	5.6
L. micropapillata	2.8	0.8	1.2	1.2		1.6	42.0	0.8	7.2	0.8	0.4	1.2	0.4		7.6	48.4
Granasporites medius	0.4	0.8	1.2	0.4	0.4	2.4	0.4	0.8	0.8	0.4	0.4	0.4				0.8
Crassispora kosankei													0.4			
Total Lycopsid Trees	11.6	7.6	5.6	5.6	0.8	37.6	9.69	6.0	29.2	8.0	6.4	4.4	4.8	0.8	18.4	69.69
Densosporites sphaerotriangularis	1.2	1.2		1.6	0.4			0.8	0.4	0.4			7.2	0.4	0.8	
D. annulatus		0.8								1.2						0.4
D. lobatus			0.4	5.2				1.2				1.2	12.4	1.6	0.8	
Radiizonates difformis- rotatus	20.4	7.6		28.4	63.6	10.8		42.8	1.2	34.0	7.2	4.8	17.2	56.0	34.4	
Cristatisporites indignabundus													2.0			
C. saturni						0.4			0.4							
Endosporites globiformis			0.4	0.4		0.8		0.4								
Anacanthotriletes spinosus															0.4	
Total small lycopsids	21.6	9.6	0.8	35.6	64.0	12.0	0.0	45.2	2.0	35.6	7.2	6.0	38.8	58.0	36.4	0.4
Punctatisporites minutus	34.8	36.0	56.8	23.2	10.0	21.6	13.2	24.8	29.2	23.2	31.2	43.6	27.2	13.6	4.8	8.8
Punctatosporites minutus	4.0	6.4	4.8	4.0	3.6	3.6	4.8	7.2	8.0	14.4	9.2	4.0	4.0	4.0	26.0	4.0
P. rotundus		3.2	1.2	0.8	1.2	2.0	0.8		1.6	0.4		1.2	2.0	0.8	0.8	1.2
Laevigatosporites globosus	1.2	4.0	2.0	2.4	3.6		0.4	1.6			13.2		2.4	3.6	2.0	
L. minimus	3.2	0.8	3.6	2.4	2.8	0.4			0.4	0.4	0.4	0.8	2.4	0.8	1.2	2.0
L. ovalis		0.4				0.4	0.4			0.4			0.4			
Cyclogranisporites minutus				0.4												
Total tree ferns	43.2	50.8	68.4	33.2	21.2	28.0	19.6	33.6	39.2	38.8	54.0	49.6	38.4	22.8	34.8	16.0
Granulatisporites piroformis								0.4	0.4		0.4	0.8				
G. parvus	0.8	0.8	2.8		2.0	0.8	0.8	2.0	1.2	2.0	0.8	2.8		0.8	2.8	0.4
G. adnatoides	0.4															0.4
G. minutus		1.2		0.4												
Lophotriletes microsaetosus	0.4	0.8	0.4	1.6	1.6	0.4			0.8					1.2		0.8
L. commissuralis	0.4	0.8	1.2	0.4	0.4	0.4	1.2				0.8	1.2				0.4

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Sample ID L insignitus																
L. insignitus	1155 (top)	1156	1157 (parting)	1158 (parting)	1159	1160	1161 (base)	1162 (top)	1163	1164	1165	1166 (parting)	1167 (parting)	1168	1169	1170 (base)
												0.8				
Letotriletes subadnatoides	0.4	0.8	0.4	1.2	0.4	0.4	0.4	0.4	0.8		1.6	0.8	0.4			0.8
L. adnatus									0.4							
L. levis		0.4	0.4	0.4					0.4			0.4	0.4			
Acanthotriletes aculeolatus			0.8	0.4	0.4					1.2	1.6			0.4		
A. triquetrus	0.4	1.2	0.4	2.4	2.4						1.2		0.4	5.2		
Punctatisporites punctatus			0.8	0.4												
P. aerarius														0.4		
Raistrickia saetosa		0.8	0.8				0.4				0.4	0.4				0.4
Dictyotriletes bireticulatus					0.4											
Reticulitriletes reticulocingulum	0.4															
Verrucosisporites donarii													0.4	0.4		
V. microtuberosus		0.4								0.4						
V. sifati											0.4					
V. verrucosus	1.2														0.4	
Camptotriletes bucculentus											0.4					
Microreticulatisporites sulcatus		0.8	1.2								0.8	1.2				
Total small ferns	4.4	8.0	9.2	7.2	7.6	2.0	2.8	2.8	4.0	3.6	8.4	8.8	1.6	8.4	3.2	3.2
Calamospora breviradiata		0.8	0.8	4.0	0.8	0.4	1.2	0.4	1.2			1.6	3.2	0.8		0.8
C. straminea									0.4					0.4		
C. pedata		0.4								0.4						
C. parva													0.4			
C. microrugosa	0.4	0.4				0.8							0.8			
Laevigatosporites minor	12.0	6.4	3.6	8.4	4.8	12.0	5.2	8.8	6.8	11.6	9.2	5.2	8.8	8.0	5.2	6.4
L. vulgaris	1.6	0.8	0.4		0.4	2.4		2.4	4.8			1.2		0.4	1.2	
Vestispora fenestrata									0.4							
Reticulatisporites reticulatus												0.4				
Total calamites	14.0	8.8	4.8	12.4	6.0	15.6	6.4	11.6	13.6	12.0	9.2	8.4	13.2	9.6	6.4	7.2
Florinites florini	4.8	13.2	7.2	3.2	0.4	2.8	1.2	0.4	11.6	1.6	12.0	15.6	2.8		0.8	3.2
F. mediapudens		0.4				2.0	0.4	0.4		0.4	2.0	1.2	0.4			
F. visendus		0.4														
Pityosporites westphalensis														0.4		
Total cordaites	4.8	14.0	7.2	3.2	0.4	4.8	1.6	0.8	11.6	2.0	14.0	16.8	3.2	0.4	0.8	3.2

 ${\begin{tabular}{ll} \underline{ {\begin{subarray}{c} \underline{ {\begin{subarray}{ {\begin{subarray}{ \underline{ {\begin{subarray}{ \underline{ {\begin{subarray}{ \underline{ {\begin{subarray}{ {\begin{subarray}{ {\begin{subarray}{ \underline{ {\begin{subarray}{ {\begin{subarray}{ {\begin{subarray}{ {\begin{subarray}{ {\begin{subarray}{ {\begin{subray}{ {\begin{subarray}{ {\begin{subarray}{ {\begin{subray}{ {\begin{subray}{ {\begin{subarray}{ {\begin{subarray}{ {\begin{subray}{ {\begin{subray}{ {\begin{subray}{ {\begin{subray}{ {\begin{subray}{ {\begin{subarray}{ {\begin{subarray}} { {\begin{subray}{ {\bent}} {\begin{subray$ 

Table 7 continued																
Sample ID	1155 1156 1157 (top) (partii	1156	1157 (parting)	1158 (parting)	1159	1159 1160 1161 (base)	1161 (base)	1162 1 (top)	1163	1164	1165	1163 1164 1165 1166 1167 (parting) (parting)	1167 (parting)	1168 1169 1170 (base)	1169	1170 (base)
T. bransonii				0.4												
T. sculptilis	0.4	1.2 4.0	4.0	2.0					0.4		0.8	5.2				0.4
Dictyotriletes castanaeformis												0.4				
Echinatisporis knoxiae				0.4												
Hymenospora paucigracilis												0.4				
Total unknown affinity	0.4 1.2 4.0	1.2	4.0	2.8	0.0	0.0 0.0 0.0		0.0		0.4 0.0 0.8 6.0	0.8	6.0	0.0	0.0	0.0 0.0 0.4	0.4

*Pennsylvanioxylon* was originally described as a small mangrove-like tree, with some species being saltwater tolerant (Raymond 1988). Others apparently developed in fresh water conditions. Unlike *Mesoxylon, Pennsylvanioxylon* roots were aerenchymatous, thus suggesting growth in water saturated, or even flooded, areas. As with *Mesoxylon, Pennsylvanioxylon* peats tend to be highly degraded and fusinized in coal balls. *Pennsylvanioxylon* produced *Florinites* pollen, which tends to be erratic in distribution. Samples with abundant *Florinites* are commonly high in ash, liptinite and inertinite, all of which are suggestive of peat accumulation under marginal conditions of preservation (DiMichele and Phillips 1994).

# 4 Summary

The high volatile C bituminous Princess No. 3 coal, correlative with the Hazard No. 7 and the lower splits of the Peach Orchard and Coalburg coals, was studied as lithotype intervals from three sites at a mine site in the Argillite 7.5' quadrangle, Greenup County, Kentucky.

In general, the coal exhibits a "dulling upwards" trend, with decreasing vitrinite and a greater tendency towards dull clarain and bone lithotypes towards the top of the coal. The basal lithotype is marked not only by relatively high concentrations of vitrinite, but also by a dominance of lycopod tree spores. The lower portion of the middle parting is co-dominated by tree fern and small lycopod spores. Tree ferns dominate the upper bench of the coal, with contributions from small ferns, cordaites, and calamites.

The lithotypes have a wide range of ash yield contents and are generally have a moderate- to high-S content. Sulfur, Fe<sub>2</sub>O<sub>3</sub>, and certain siderophile elements are highest near the top of the coal. Uranium and Ge are enriched at the top and bottom margins of the coal. The rare earth chemistry at the top of the coal has a significantly lighter distribution (higher LREE/HREE) than at the base of the coal. While REE in coal attracted attention in the 2010s, as with most, if not all, coal resources, the exploitation of the coal for its REE content is likely to be driven by the need for the coal, with the REE being a valuable by-product of the coal processing and combustion. At present, coal production in eastern Kentucky is significantly less than what it was 30 years ago, decreasing from 131 Mt in 1990 to about 17 Mt in 2018 (Kentucky Energy and Environment Cabinet 2017, 2019) with much of the current production centered in central eastern Kentucky, therefore, exploitation of the coal studied here is not likely to be a near-term prospect.

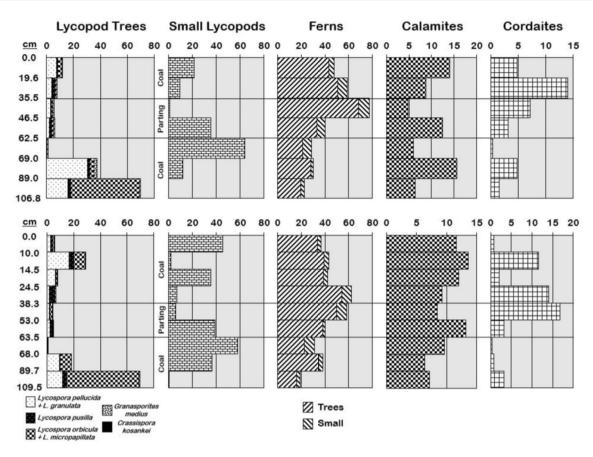


Fig. 9 Graphical representation of the palynology of the 1155 (top of coal) to 1161 (seat rock) section

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Authors' contribution MMH: petrology and SEM study at CAER; CFE: palynology; SD: ICP geochemistry and electron microbeam studies at CUMT-B; JCH: sampling and overall coordination of project; everyone participated in the writing and editing. As best as possible, all of the remaining samples are stored at the Kentucky Geological Survey.

#### **Compliance with ethical standards**

**Conflict of interest** The authors declare that they have no conflict of interest.

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#### References

- ADDCAR Highwall Mining System (2019). http://addcarsystems. com/technology/. Accessed 19 Nov 2019
- ASTM Standard D3176-15 (2015) Standard Practice for Ultimate Analysis of Coal and Coke. ASTM International, West Conshohocken, PA
- ASTM Standard D3174-12 (2018a) Annual book of ASTM standards. Test method for ash in the analysis sample of coal and coke. ASTM International, West Conshohocken, PA
- ASTM Standard D3175-18 (2018b) Test method for volatile matter in the analysis sample of coal and coke. ASTM International, West Conshohocken, PA
- ASTM Standard D4239-18e1 (2018c) Standard test method for sulfur in the analysis sample of coal and coke using high-temperature tube furnace combustion. ASTM International, West Conshohocken, PA
- ASTM Standard D2492-02 (2012) Standard test method for forms of sulfur in coal. ASTM International, West Conshohocken, PA
- ASTM Standard D3173/D3173M-17a (2017) Test method for moisture in the analysis sample of coal and coke. ASTM International, West Conshohocken, PA
- ASTM Standard D5865/D5865M-19 (2019) Standard test method for gross calorific value of coal and coke. ASTM International, West Conshohocken, PA
- Balme BE (1995) Fossil in situ spores and pollen grains: an annotated catalogue. Rev Palaeobot Palynol 87:81–323

- Berthoud EL (1875) On the occurrence of uranium, silver, iron, etc., in the tertiary formation of Colorado Territory. Acad Nat Sci Phila Proc 27:363–365
- Breger IA, Schopf JM (1955) Germanium and uranium in coalified wood from upper devonian black shale. Geochim Cosmochim Acta 7:287–293
- Breger IA, Deul M, Rubenstein S (1955a) Geochemistry and mineralogy of a uraniferous lignite (South Dakota). Econ Geol 50:206–226
- Breger IA, Deul M, Meyrowitz R (1955b) Geochemistry and mineralogy of a uraniferous subbituminous coal (Wyoming). Econ Geol 50:610–624
- Clayton G, Coquel R, Doubinger J, Gueinn KJ, Loboziak S, Owen B, Streel M (1977) Carboniferous miospores of western Europe: illustration and zonation. Meded Rijks Geol Dienst 29:1–71
- Costanza SH (1985) Pennsylvanioxylon of middle and upper Pennsylvanian coals from the Illinois Basin and its comparison with Mesoxylon. Palaeontographica B197:81-121
- Dai S, Wang X, Zhou Y, Hower JC, Li D, Chen W, Zhu X (2011) Chemical and mineralogical compositions of silicic, mafic, and alkali tonsteins in the late Permian coals from the Songzao Coalfield, Chongqing, Southwest China. Chem Geol 282:29–44
- Dai S, Seredin VV, Ward CR, Hower JC, Xing Y, Zhang W, Song W, Wang P (2015) Enrichment of U–Se–Mo–Re–V in coals preserved within marine carbonate successions: geochemical and mineralogical data from the Late Permian Guiding Coalfield, Guizhou, China. Miner Depos 50:159–186
- Diehl SF, Goldhaber MB, Koenig AE, Lowers HA, Ruppert LF (2012) Distribution of arsenic, selenium, and other trace elements in high pyrite Appalachian coals: evidence for multiple episodes of pyrite formation. Int J Coal Geol 94:238–249
- DiMichele WA, Phillips TL (1985) Arborescent lycopod reproduction and paleoecology in a coal-swamp environment of late middle Pennsylvanian age (Herrin Coal, Illinois, U.S.A.). Rev Palaeobot Palynol 44:1–26
- DiMichele WA, Phillips TL (1994) Paleobotanical and paleoecological constraints on models of peat formation in the Late Carboniferous of Euramerica. Palaeogeogr Palaeoclimatol Palaeoecol 106:39–90
- DiMichele WA, Phillips TL, Peppers RA (1985) The influence of climate and depositional environment on the distribution and evolution of Pennsylvanian coal-swamp plants. In: Tiffney BH (ed) Geological factors and the evolution of plants. Yale Univ. Press, New Haven, pp 223–256
- DiMichele WA, Phillips TL, Willard DA (1986) Morphology and paleoecology of Pennsylvanian age coal-swamp plants. In: Gastaldo RA (Organizer), Land plants: notes for a short course, vol 15. University of Tennessee, Department of Geological Sciences Studies in Geology, pp 97–114
- Dobrovolny E, Ferm JC, Eroskay SO (1966) Geologic map of parts of the Greenup and Ironton quadrangles, Greenup and Boyd counties, Kentucky. U.S. Geological Survey Map GQ-532, scale, vol 1, p 24,000
- Eble CF (2017) The use of glycol ethers to help reduce amorphous organic matter (AOM) in palynological preparations. Palynology 41:180–182
- Eble CF, Hower JC, Andrews WM Jr (1994) Paleoecology of the Fire Clay coal bed in a portion of the Eastern Kentucky coal field. Palaeogeogr Palaeoclimatol Palaeoecol 106:287–305
- Eskenazy G (1992) Geochemistry of thorium and uranium in bulgarian coals. Annuaire de L'Universite de Sofia "St. Kliment Ohridski" Faculte de Geologie et Geographie, Livre 1- Geologie, vol 83, pp 43–70
- Esterle JS, Ferm JC (1986) Relationship between petrographic and chemical properties and coal seam geometry, Hance seam,

Breathitt Formation, southeastern Kentucky. Int J Coal Geol 6:199-214

- Esterle JS, Ferm JC, Tie Y-L (1989) A test for the analogy of tropical domed peat deposits to ''dulling up'' sequences in coal beds—preliminary results. Organ Geochem 14:333–342
- Esterle JS, Gavett KL, Ferm JC (1992) Ancient and modern environments and associated controls on sulfur and ash in coal. In: Platt J et al (eds) One point two—new perspectives on Central Appalachian low-sulfur coal supplies. Coal decisions forum. TechBooks, Fairfax, pp 143–170
- Ferm JC (1963) Coal beds of the Princess Reserve District. In: Huddle JW, Lyons EJ, Smith HL, Ferm JC (eds) Coal reserves of Eastern Kentucky. United States Geological Survey Bulletin, vol 1120, pp 32–55
- Habib D (1966) Distribution of spore and pollen assemblages in the Lower Kittanning coal of western Pennsylvania. Paleontology 14:629–666
- Habib D, Groth PKH (1967) Paleoecology of migrating Carboniferous peat environments. Palaeogeogr Palaeoclimatol Palaeoecol 3:185–195
- Hower JC, Bland AE (1989) Geochemistry of the Pond Creek coal bed, Eastern Kentucky coalfield. Int J Coal Geol 11:205–226
- Hower JC, Pollock JD (1989) Petrology of the River Gem Coal Bed, Whitley County, Kentucky. Int J Coal Geol 11:227–245
- Hower JC, Wild GD (1981) Petrography of Kentucky coals in the Princess Reserve District. University of Kentucky Institute for Mining and Minerals Research, Resource Characterization Series, IMMR80/056, 21 pp
- Hower JC, Esterle JS, Wild GD, Pollock JD (1990) Perspectives on coal lithotype analysis. J Coal Qual 9:48–52
- Hower JC, Andrews WM Jr, Wild GD, Eble CF, Dulong FT, Salter TL (1994a) Coal quality trends for the Fire Clay coal bed, southeastern Kentucky. J Coal Qual 13:13–26
- Hower JC, Taulbee DN, Rimmer SM, Morrell LG (1994b) Petrographic and geochemical anatomy of lithotypes from the Blue Gem coal bed, southeastern Kentucky. Energy Fuels 8:719–728
- Hower JC, Ruppert LF, Williams DA (2002) Controls on boron and germanium distribution in the low-sulfur amos coal bed: Western Kentucky Coalfield, USA. Int J Coal Geol 53:27–42
- Hubbard TE, Miller TR, Hower JC, Ferm JC, Helfrich CF (2002) The Upper Hance coal bed in southeastern Kentucky: palynologic, geochemical, and petrographic evidence for environmental succession. Int J Coal Geol 49:177–194
- International Committee for Coal Petrology (ICCP) (1998) The new vitrinite classification (ICCP System 1994). Fuel 77:349–358
- International Committee for Coal Petrology (ICCP) (2001) The new inertinite classification (ICCP System 1994). Fuel 80:459–471
- Johnston MN, Hower JC, Dai S, Wang P, Xie P, Liu J (2015) Petrology and geochemistry of the Harlan, Kellioka, and Darby coals from the Louellen 7.5-minute quadrangle, Harlan County, Kentucky. Minerals 5:894–918
- Kentucky Energy and Environment Cabinet (2017) Kentucky coal facts, 17th edn. https://www.eec.ky.gov. Accessed 3 Jan 2020
- Kentucky Energy and Environment Cabinet (2019) Kentucky Quarterly Coal Report: January to March 2019. www.eec.ky.gov. Accessed 3 Jan 2020
- Ketris MP, Yudovich YaE (2009) Estimations of Clarkes for carbonaceous biolithes: world average for trace element contents in black shales and coals. Int J Coal Geol 78:135–148
- Li X, Dai S, Zhang W, Li T, Zheng X, Chen W (2014) Determination of As and Se in coal and coal combustion products using closed vessel microwave digestion and collision/reaction cell technology (CCT) of inductively coupled plasma mass spectrometry (ICP-MS). Int J Coal Geol 124:1–4
- Peppers RA (1985) Comparison of miospore assemblages in the Pennsylvanian system of the Illinois Basin with those in the

upper Carboniferous of western Europe. In: Sutherland PK, Manger WL (eds) Compte Rendu ninth international congress of carboniferous stratigraphy and geology, vol 2. Washington, D.C. and Champaign-Urbana, pp 483–502

- Peppers RA (1996) Palynological correlation of major Pennsylvanian (middle and upper Carboniferous) chronostratigraphic boundaries in the Illinois and other coal basins, vol 188. Geological Society of America Memoir 111 p 1 plate
- Phillips TL (1979) Reproduction of heterosperous arborescent lycopods in the Mississippian—Pennsylvanian of Euramerica. Rev Palaeobot Palynol 27:239–289
- Phillips TL, Peppers RA (1984) Changing patterns of Pennsylvanian coal-swamp vegetation and implications of climatic control on coal occurrence. Int J Coal Geol 3:205–255
- Phillips TL, Peppers RA, Avcin MJ, Laughnan PF (1974) Fossil plants and coal: patterns of change in Pennsylvanian coal swamps of the Illinois Basin. Science 154:1367–1369
- Phillips TL, Peppers RA, DiMichele WA (1985) Stratigraphic and interregional changes in Pennsylvanian coal-swamp vegetation: environmental inferences. Int J Coal Geol 5:43–109
- Pickel W, Kus J, Flores D, Kalaizidis S, Christanis K, Cardott BJ, Misz-Kennan M, Rodrigues S, Hentschel A, Hamor-Vido M, Crosdale P, Wagner N, ICCP (2017) Classification of liptinite: ICCP System 1994. Int J Coal Geol 169:40–61
- Ravn RL (1986) Palynostratigraphy of the Lower and Middle Pennsylvanian coals of Iowa. Iowa Geological Survey Technical Paper, vol 7, p 245
- Raymond A (1988) The paleoecology of a coal-ball deposit from the Middle Pennsylvanian of Iowa dominated by cordaitalean gymnosperms. Rev Palaeobot Palynol 53:233–250
- Robl TL, Rathbone RF, Graham U, Hower JC (1998) Field demonstration of mine grout made from fluidized bed combustion ash. In: Paşamehmeğlo AG, Özgenğlu, A, Environmental issues and waste management in energy and mineral production. Fifth international symposium on environmental issues and

waste management in energy and mineral production—SWEMP' 98, 18–20 May 1998, Ankara, Turkey, Rotterdam, A.A. Balkema Publishers, pp 525–530

- Ruppert LF, Hower JC, Eble CF (2005) Arsenic-bearing pyrite and marcasite in the Fire Clay coal bed, Middle Pennsylvanian Breathitt Formation, eastern Kentucky. Int J Coal Geol 63:27–35
- Sheppard RA, Ferm JG (1962) Geology of the Argillite quadrangle, Kentucky. U.S. Geological Survey Map GQ-175, scale 1:24,000
- Smith AHV (1957) The sequence of miospore assemblages associated with crassidurite in coal seams of Yorkshire. Geol Mag 94:345–363
- Smith AHV (1962) The palaeoecology of Carboniferous peats based on miospores and petrography of bituminous coals. Proc Yorks Geol Soc 33:423–446
- Smith AHV (1964) Palaeoecology of Carboniferous peats. In: Nairn AEM (ed) Problems in palaeoecology. Wiley, London, pp 57–66
- Smith AHV (1968) Seam profiles and seam characters. In: Murchison D, Westoll TS (ed) Coal and coal-bearing strata. Elsevier, New York, pp 31–40
- Szalay A, Szilágyi M (1969) Accumulation of microelements in peat humic acids and coal. In: Schenck PA, Havenaar I (ed) Advances in organic geochemistry 1968, Pergamon
- Taylor SR, McLennan SH (1985) The continental crust: its composition and evolution. Blackwell, Oxford, 312 pp
- Traverse A (1988) Paleopalynology. Unwin Hyman Ltd, London, p 600
- White D (1897) Omphalophloios, a new lepidodendroid type. Geol Soc Am Bull 9:329–342
- Yudovich Ya E (2003a) Coal inclusions in sedimentary rocks: a geochemical phenomenon. A review. Int J Coal Geol 56:203–222
- Yudovich Ya E (2003b) Notes on the marginal enrichment of Germanium in coal beds. Int J Coal Geol 56:223–232
- Zubovic P (1966) Physicochemical properties of certain minor elements as controlling factors in their distribution in coal. In: Given PH (ed) Coal science, vol 55, pp 221–231