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Characterization of Pennsylvanian Paleosols in Indiana with a Special Reference to Rare Earths (REE) and Lithium

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SUMMARY

This study characterizes Pennsylvanian paleosols from coal-bearing strata in Indiana, with the main emphasis on the abundance and distribution of rare earth elements (REE) and lithium (Li). Eleven locations in southwest Indiana were selected for this study, targeting paleosols of both the Carbondale Group and Raccoon Creek Group. Most paleosols were directly underlying coal beds. Lithologically, the paleosols range from grey mudstones to greenish-grey claystones and occasional siltstones. In the Carbondale Group, the thickest paleosol horizons occur under the Danville and the Houchin Creek Coal Members, with their thickness reaching close to 10 ft. In the Raccoon Creek Group, the paleosol under the Wise Ridge Coal appears to be thickest (4.6 to 11.4 ft) and best developed.

Total REE content in paleosol samples ranges from 138.8 ppm to 728.55 ppm, with an average range of 208.3 ppm (Colchester Coal paleosol) to 342.9 ppm in the paleosol under the Upper Block Coal. Light REE dominate over heavy REE, and the variation in the light REE is responsible for the largest variations of the total REE. The largest amount of the heavy REE (61 ppm) occurs in the paleosol under the Lower Block Coal. In contrast, the paleosol under the Upper Block Coal has the largest variation in heavy REE content (49-148 ppm). REE patterns for paleosol samples show very weak to no fractionation among light, medium, and heavy REE, with no major anomalies present. The majority of paleosols have REE values roughly representative of the upper continental crust. Only some paleosols are slightly enriched, and these are paleosol samples under the Danville Coal and the Upper Block Coal. Lithium content in the paleosol samples shows a variation from 21 ppm to 530 ppm. On average, the Wise Ridge Coal is the richest in Li (249.3 ppm), followed by Viking B Coal (190.8 ppm). The coals of the Brazil and Staunton Formations have higher Li content than the younger coals. Although this study has not uncovered large concentrations of REE or lithium, the wide range of concentrations and potential ease of their extraction from these clay-rich rocks imply that paleosols deserve further examination, and the current study can be used as a screening guide for a more focused investigation.

1. INTRODUCTION

Paleosols are ancient soils preserved in the rock record. Because they form in response to interactions among lithosphere, biosphere, hydrosphere, and atmosphere, paleosols are important for environmental and climatic reconstructions of the past (Cecil, 2013; Tabor and Myers, 2015 and references therein). In the rock record, they are common in coal-bearing sedimentary basins where they underly coal seams and represent periods of aerial exposure before the establishment of more humid conditions and development of peat mires.

In the Illinois Basin, paleosols (also known as underclays) commonly underlie coal beds in Pennsylvanian cyclothems and constitute a significant stratigraphic

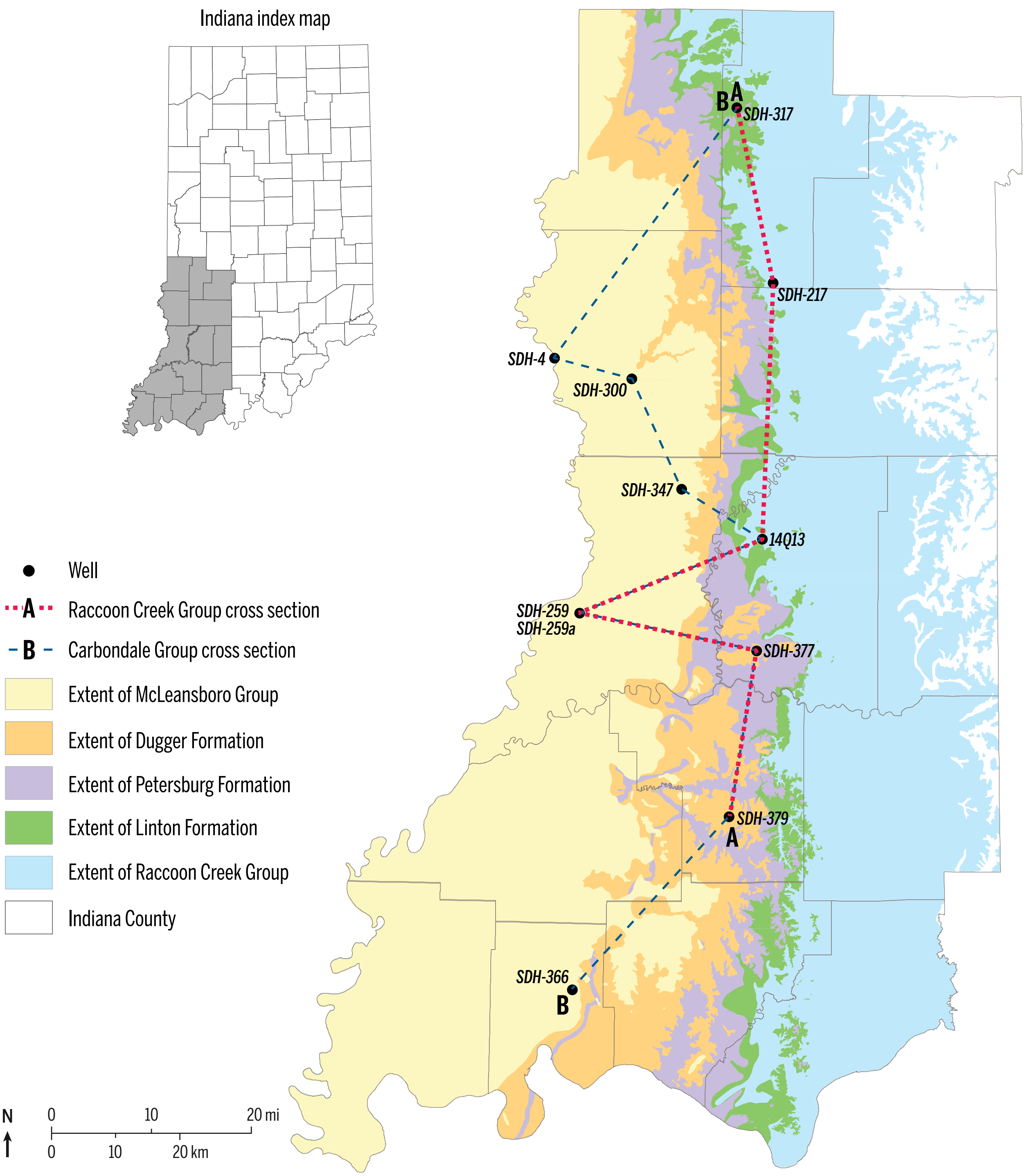

Figure 1. Map of southwestern Indiana showing locations of the boreholes analyzed in this study.

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component of the Pennsylvanian strata. Over decades, various interpretations regarding the origin of these paleosols have been developed (Potonie, 1910; Grim, 1935; Grim and Allen, 1938; Schultz, 1958; Baker, 1962; Duff and Walton, 1962; Parham, 1966 and references therein). Despite different interpretations, there is a general consensus that these strata are fossil soils that developed on paleolandscapes during periods of relative environmental stability. Based on the morphology and petrology of paleosols in the Illinois Basin, some researchers discussed variations in paleoenvironmental conditions (e.g., Weller, 1930; Archer and Greb, 1995; de Wet et al., 1997; Cecil et al., 2003; DiMichele et al., 2010; Falcon-Lang and DiMichele, 2010). Relatively detailed morphological and mineralogical characteristics of paleosol profiles preserved in Pennsylvanian (Atokan–Virgilian; Westphalian–Stephanian) strata of the Illinois Basin are provided in Rosenau et al. (2013a,b). These authors also discussed spatial variability and the pedogenic history of paleosols. In Rosenau et al. (2013a,b) study, four locations from Indiana (Pike, Gibson, Warrick, and Daviess counties) were included.

Paleosols have recently received attention in relation to the search for new sources of critical minerals, and rare earth elements (REE; in this paper yttrium [Y] is also included under the REE term) and lithium (Li) in particular. Lithium is used in rechargeable batteries and aluminum-lithium alloys for aerospace, and Australia and Chile are the world's largest producers and suppliers. Decades ago, paleosols and other clay-rich Pennsylvanian rocks were shown to contain relatively high, though variable, concentrations of lithium (Tourtelot and Brenner-Tourtelot, 1977). The authors state that "Flint clays and related rocks of Pennsylvanian age in Alabama, Ohio, Pennsylvania, Kentucky, and Missouri very commonly contain several hundred parts per million of lithium, with maximum values as large as 4,000 to 5,100 ppm in the Missouri samples." They further suggested that these clay-rich rocks were "an unevaluated potential resource for lithium." Studies of modern soils provide valuable information about controls on lithium distribution. For example, Tsai et al. (2014), based on a study of loess soil in China, suggested that Li in the detritus and carbonate fractions is derived from silicate weathering, and that detrital fractions are Li-enriched compared to the carbonate fractions.

Paleosols are attractive targets for REE mostly because of the relative ease of their potential recovery. As clay-rich sediments, paleosols have the potential to release REE using leaching technologies (Moldoveanu and Papangelakis, 2016; Montross et al., 2017; Yang et al., 2020). For example, Rozelle et al. (2016) demonstrated that in some cases, more than 90% of REE could be recovered from paleosols and shales associated with

Figure 2. Chart of Pennsylvanian stratigraphy in Indiana showing the position of the paleosol horizons (in red) analyzed in this study. Modified from the TriState Committee on Correlation of the Pennsylvanian System in the Illinois Basin (2001) and Mastalerz et al. (2018).

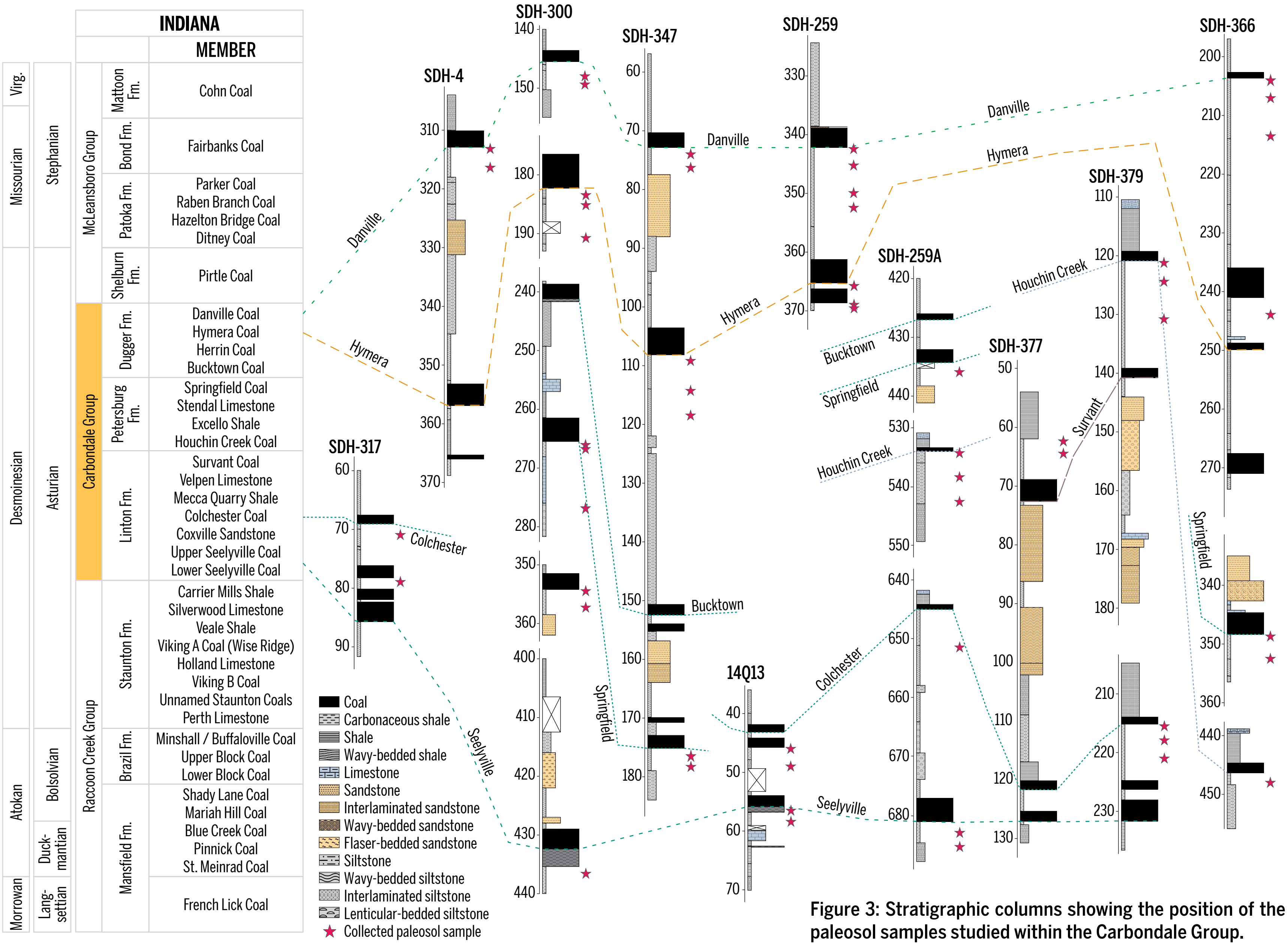

Figure 3: Stratigraphic columns showing the position of the paleosol samples studied within the Carbondale Group.

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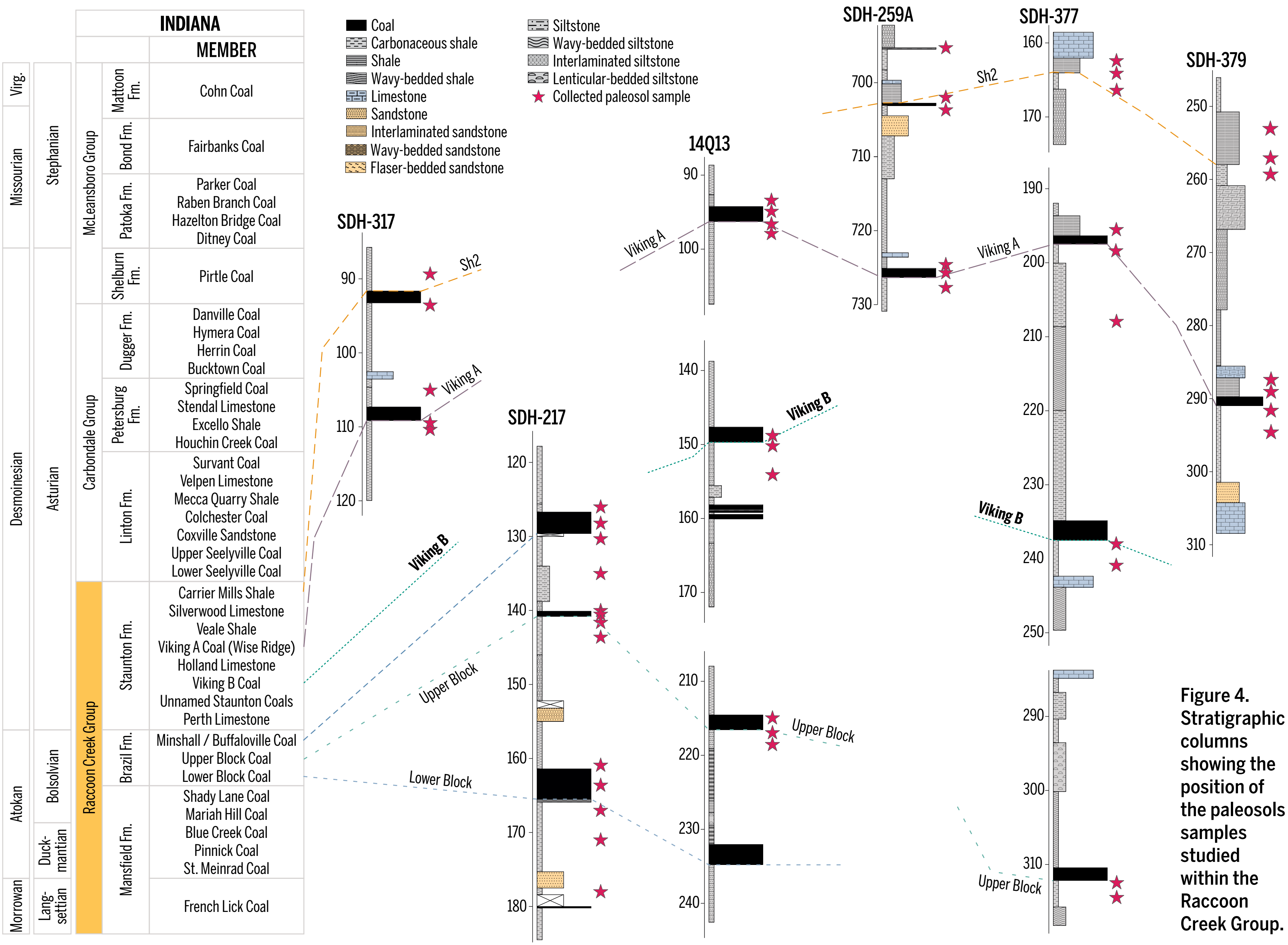

Figure 4. Stratigraphic columns showing the position of the paleosols samples studied within the Raccoon Creek Group.

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coals using $(NH4)_2SO_4$ as an ion exchange lixiviant. Ion-adsorption clays contain 0.05 to 0.3 % REE, with more than 60 % REE occurring in a physically adsorbed state recoverable by simple ion-exchange leaching (e.g., Chi and Tian, 2008; Luo et al., 2014. Available data suggest that the concentrations of REE in paleosols vary depending on many factors such as mineralogical composition or the extent of pedogenic processes (e.g., Aide and Aide, 2012; Menendez et al., 2019). Limited data on Pennsylvanian paleosols from Indiana show the range of REE from 254 to 356 ppm, comparable to those in the associated coals (Mastalerz et al., 2020)

The purpose of this study is to characterize Pennsylvanian paleosols from coal-bearing strata in Indiana, with the main emphasis on the abundance and distribution of REE and lithium.

2. METHODOLOGY

2.1 Samples

Eleven locations in southwest Indiana were selected for this study (Figs. 1, 2). The selection was guided by the availability of core material and the presence of paleosols at various stratigraphic horizons. Paleosols of both the Carbondale Group (middle and upper Desmoinesian), which contains major coal beds (Fig. 2), and the Raccoon Creek Group (upper Atokan and lower Desmoinesian), which contains thinner and discontinuous coal beds, were targeted (Fig. 3). Most paleosols were associated with the overlying coal beds, but a few isolated paleosols not associated with coals also were sampled (for example, the informally named "Maria Creek paleosol" occurring between the lower and middle benches of the West Franklin Limestone Member).

Core fragments containing paleosols were megoscopically described and photographed. Depending on paleosol thickness, one to three samples were collected from each paleosol horizon. In total, 86 samples were collected. Additionally, 29 coal and 39 shale samples associated with paleosols were collected, but they are not discussed in this paper. All samples were split into two portions; one was sent to the United States Geological Survey (USGS) for REE and associated analyses, whereas the other was kept at the Indiana Geological and Water Survey for the in-house analysis, including pXRF and carbon and sulfur content.

2.2 Techniques

REE, trace elements, and major elements

Reports on REE, trace elements, and major elements in all samples were provided to us by the USGS as part of the Earth Mapping Resources Initiative (Earth MRI). Trace elements and REE were analyzed by the inductively coupled plasma – optical emission spectrometry – mass spectroscopy (ICP-OES-MS) method, whereas major elements were determined by the wavelength dispersive X-ray fluorescence (WDXRF) technique.

Portable X-ray fluorescence (pXRF)

The pXRF analyzer (Thermo Niton XL3t GOLDD+) was used to analyze the major element contents of the studied samples. The pXRF analyzer was set to the "Test All Geo" mode for 75 seconds. Three USGS certified reference materials, one carbonatite (COQ-1) and two shales (SDO-1 and SBC-1), were analyzed at the beginning and end of each analytical session to examine the accuracy and precision of the analyses following McLaughlin et al. (2016).

Total carbon (TC) and total sulfur (TS)

A LECO elemental analyzer (SC832DR) was used to determine the total carbon (TC) and total sulfur (TS) contents of the samples. Dried and powdered samples of 0.5 g in weight were used in the analysis. Two splits were run on each sample, and the average value was used for interpretation.

Vitrinite reflectance

Vitrinite reflectance was measured on the associated coal samples to document sample maturity. The samples were crushed into rock chips finer than 0.85 mm (passing through a 20-mesh sieve) and made into whole-rock pellets following standard coal petrography procedures (ASTM, 2014). A Zeiss Photoscope III reflected light microscope linked to a TIDAS PMT IV photometric system was used to measure the reflectance of vitrinite, with more than 50 measurements made on each sample. The vitrinite reflectance values of the coals show a narrow range from 0.52 to 0.57 %, all placing within high volatile C bituminous coal rank, in agreement with previous maturity estimates of coal in Indiana (e.g., Mastalerz et al., 2009).

3. RESULTS

3.1 Megascopic characteristics

The thickness and general megascopic characteristics of the paleosols associated with major coal seams of the Carbondale Group and the Raccoon Creek Group in Indiana are summarized in Tables 1 and 2, respectively. Additional paleosol horizons at locations not associated with coals also were sampled (Figs. 3 and 4). These characteristics are based on the description of the paleosol samples collected for this study. Because the purpose of the sampling was to collect representative paleosol samples for the determination of REE concentrations, no detailed paleosol description, paleosol classification, or description of paleosol sections were done as part of this study.

In the Carbondale Group (mid-Desmoinesian age), the thickest paleosol horizons occur under the Danville and the Houchin Creek coal members; their thickness can reach close to 10 ft (Table 1). The greatest thickness of the paleosol under the Danville (13.5 ft) was noted at SDH-259 in Knox County, whereas the thickest paleosol under the Houchin Creek (9.1 ft) occurred at SDH-379 in Pike County. Lithologically, the Carbondale Group paleosols are dominantly represented by light grey, greenish-grey to dark grey claystones and mudstones, mostly massive, rarely showing faint laminations. Claystones often show pedogenic mottling and contain slickenside surfaces. The intensity of rooting varies from sporadic to abundant. There are also small plant fragments along bedding surfaces, and the occurrence of these plant fragments is especially common in the Danville Coal paleosol. Paleosols under the Springfield Coal in Vanderburgh County graded from mudstone to siltstone and fine-grained sandstone, the latter with detected cross-bedded lamination. The Springfield Coal paleosol also contained brownish siderite veins and nodules.

Paleosols of the Raccoon Creek Group are grey mudstones to greenish-grey claystones, and occasionally siltstones (Table 2). Paleosols of the Brazil Formation (under Minshall/Buffaloville/Upper Block, and Lower Block coals) are characterized by more intense rooting and more frequent plant fragments compared to those overlying the Staunton Formation (under Wise Ridge and Viking B coals). Based on the locations studied, the paleosol under the Wise Ridge Coal is the thickest (4.6 to 11.4 ft) and best developed among the paleosols of the Raccoon Creek Group.

Table 1. General characteristics of the paleosols under major coal beds of the Carbondale Group.

Stratigraphic position	Location	County	Sample depth (feet)	Thickness (feet)	Megascopic characteristics
Danville Coal	SDH-4	Sullivan	313 317.5	5.1	Gray mudstone to claystone, rooting very rare, plant fragments along bedding, slickensides
	SDH-300	Sullivan	148 149.8	4.8	Light to dark gray massive mudstone, rooting sporadic
	SDH-347	Knox	74 76.2	4.8	Massive light gray mudstone to claystone, rooting sporadic, siderite film
	SDH-259	Knox	342.5 345.2 350 352.5	13.5	Greenish-gray claystone, rooting sporadic, slickensides common
	SDH-366	Vanderburgh	204 207 213.5	10.3	Greenish-gray claystone to mudstone, rooting rare, some plant fragments, slickensides in some parts
Hymera Coal	SDH-259	Knox	366	3.3	Gray mudstone, rooting common, vitrain fragments present.
	SDH-366	Vanderburgh	244	4.1	Gray mudstone, abundant root fragments on bedding.
Herrin Coal	SDH-347	Knox	114.7 118.6	8.0	Light gray claystone to mudstone to siltstone, roots rare to very common, siderite nodules
	SDH-259	Knox	369.2 371.2	3.3	Gray claystone to mudstone, rooting rare, slickensides, plant fragments abundant
	SDH-300	Sullivan	190.8	3.0	Gray massive mudstone, plant fragments present

Springfield Coal	SDH-300	Sullivan	262 267.3 273.3	12.5	Gray massive mudstone, rooting rare, plant fragments and slickensides in some parts
	SDH-347	Knox	176.4 178.2	3.8	Light gray massive claystone to mudstone, rooting rare, plan fragments and slickensides present
	SDH-259A	Knox	436	3.0	Gray mudstone with siderite concretions, rooting rare
	SDH-366	Vanderburgh	348.6 352.6	4.0	Gray mudstone to siltstone to sandstone, rooting sporadic, irregular siderite veins
Houchin Creek Coal	SDH-300	Sullivan	354.8 357.5	4.3	Gray massive claystone to mudstone, rooting sporadic, slickensides
	SDH-259A	Knox	534.5 538.7 542.7	9.0	Gray massive mudstone to light grey massive siltstone, rooting sporadic, plant fragments on bedding surfaces
	SDH-377	Daviess	62.3 64.5	7.1	Light gray to greenish mudstone, brecciated
	SDH-379	Pike	121.2 124.4 130.9	9.1	Light gray claystone to gray massive mudstone, rooting sporadic, rare slickensides
	SDH-366	Vanderburgh	448	2.0	Gray massive mudstone, rooting sporadic
Colchester Coal	SDH-317	Clay	71	3.0	Light gray claystone, plant fragments abundant
	SDH-259A	Knox	651.5	6.2	Massive light gray siltstone, rooting sporadic
	SDH-379	Pike	215.8 218.1 221.2	10.0	Brownish-gray massive claystone, rooting and plant fragments abundant, some slickensides
Seelyville Coal	SDH-317	Clay	79 (U)	1.7	Light gray claystone, plant fragments, and rooting abundant
	SDH-300	Sullivan	436.2	3.6	Black massive to horizontally laminated shale, no rooting
	14Q13	Daviess	46 (U) 49 (U) 57.5 (L) 58.5 (L)	2.1 (U) 2.1 (L)	(U) Gray friable claystone, plant fragments present (L) Light gray to yellowish claystone, plant fragments abundant
	SDH-259A	Knox	683.2 (U) 685.4 (U) 696.5 (L)	3.6 (U) 2.8 (L)	(U) Gray mudstone to siltstone, rooting rare to common (L) Light gray claystone, slickensides, rooting rare

Table 2. General characteristics of the paleosols under major coal beds of the Raccoon Creek Group

Stratigraphic position	Location	County	Sample Depth (feet)	Thick-ness (feet)	Megascopic characteristics
Wise Ridge Coal	SDH-317	Clay	109.2 111	6.8	Gray mudstone, rare plant fragment, rooting sporadic
	14Q13	Daviess	96.5 97.8	8.5	Greenish-gray massive claystone, rooting rare
	SDH-259A	Knox	727.3	4.6	Gray massive mudstone, rooting sporadic
	SDH-377	Daviess	198.2 208.2	11.4	Gray mudstone to siltstone, common plant fragments
Viking B Coal	14Q13	Daviess	150.6 154	5.9	Gray massive claystone, rooting rare
	SDH-377	Daviess	238 240.8	4.9	Light gray to yellow-gray mudstone, crumbled with brown concretions. Rare plant debris
Minshall/ Buffaloville Coal	SDH-217	Clay	130.5 135	4.5	Massive gray siltstone with intense rooting
Upper Block	SDH-217	Clay	141.3 143.5	5.2	Greenish-gray claystone to grey mudstone, intense rooting and slickensides
	14Q13	Daviess	216.5 218.5	2.9	Gray mudstone, plant fragments rare, rooting sporadic
	SDH-377	Daviess	312.5 314.7	3.6	Gray mudstone with a lot of plant fragments
Lower Block Coal	SDH-217	Clay	167 171 173	9.8	Massive mudstone, rooting rare, plant fragments parallel and oblique to bedding
	14Q13	Daviess		7.8	Not sampled

3.2 Chemistry of paleosols

Carbon and sulfur

Carbon content of paleosols is low, below 1 wt % for the majority of samples (Table 3, Fig. 5). The carbon content measured in this study is total carbon, and the low values indicate low combined carbonate and organic carbon content. Occasional TC >3 % is related to the presence of thin coal layers or abundant plant fragments on bedding surfaces, thus indicating an increased contribution from organic carbon. Sulfur content is >1 % for the paleosols under the Danville and shows more variation in paleosols under the Houchin Creek, Springfield, and Wise Ridge Coals.

Table 3. Total carbon (TC) and total sulfur (TS) in weight % of all collected paleosols.SD – standard deviation

Paleosol under	N	TC Min	TC Max	TC Average	TC SD	TS Min	TS Max	TS Average	TS SD
Colchester	5	0.21	1.18	0.60	0.43	0.24	3.35	2.09	1.31
Danville	13	0.21	10.05	1.57	2.79	0.02	0.71	0.29	0.26
Herrin	5	0.47	6.53	2.36	2.60	0.18	1.74	0.79	0.66
Houchin Creek	11	0.38	2.44	1.06	0.89	0.18	6.15	1.35	1.76
Hymera	2	0.71	2.54	1.63	1.29	0.04	3.28	1.66	2.29
Lower Block	3	0.21	2.67	1.21	1.29	0.02	0.04	0.03	0.01
Maria Creek	4	0.22	2.70	1.00	1.16	0.01	0.16	0.06	0.09
Minshall	2	0.23	0.56	0.40	0.23			0.10	
Springfield	8	0.30	9.06	2.33	2.89	0.40	2.79	1.37	1.00
Upper Block	6	0.43	2.27	1.03	0.76	0.02	1.49	0.35	0.63
Seelyville	9	0.14	1.75	0.68	0.52	0.08	5.86	2.07	1.96
Viking B	4	0.33	2.44	1.46	1.09	0.29	1.05	0.63	0.38
Wise Ridge	7	0.14	2.44	1.13	1.04	0.11	1.26	0.48	0.43

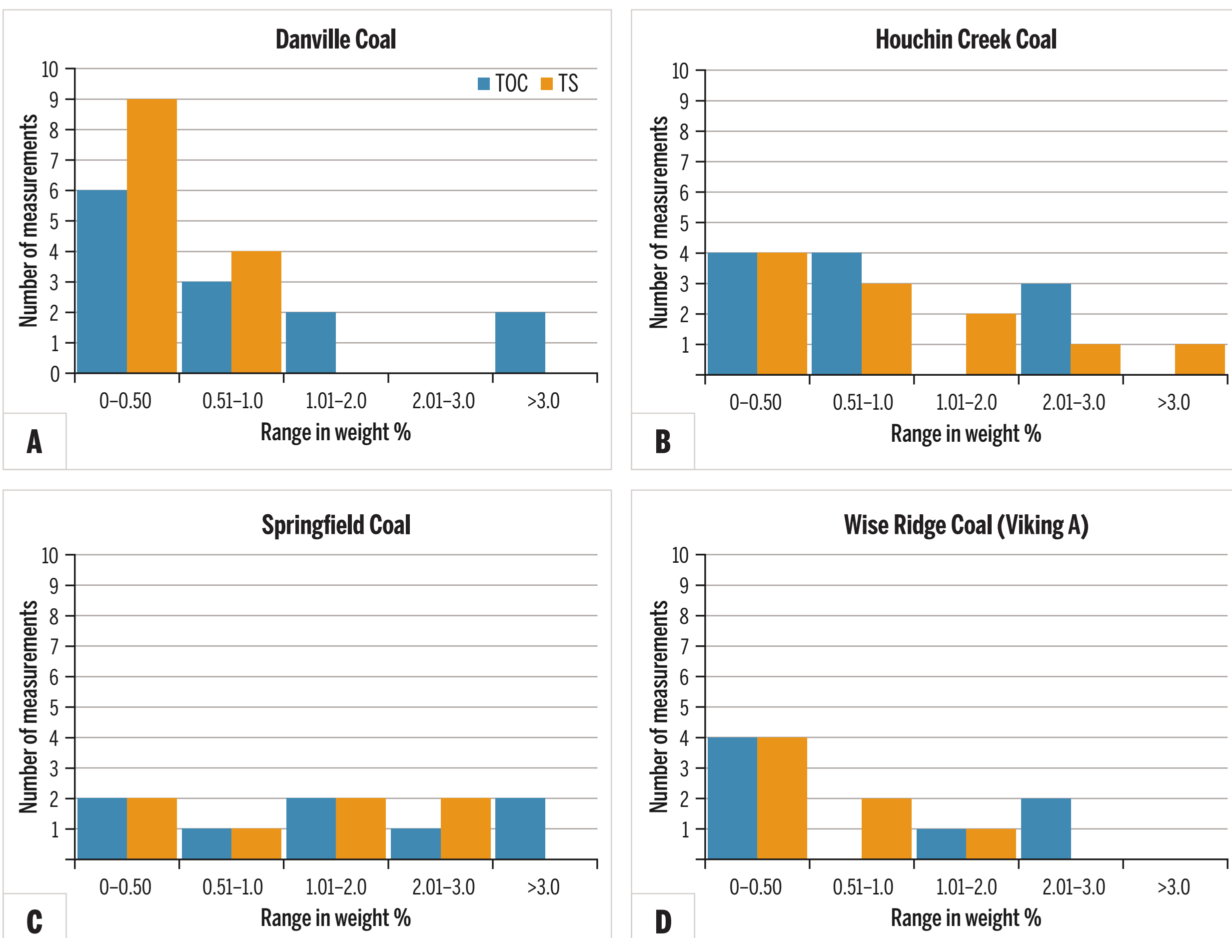

Figure 5. Bar graphs showing the total carbon (TC) and total sulfur (TS) of selected paleosols.

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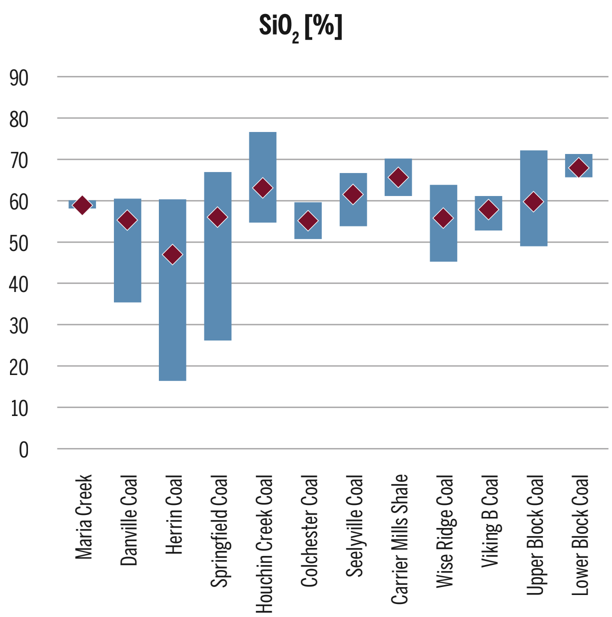
Major oxides

SiO_2 and Al_2O_3 are the principal oxides of paleosols. The average content of SiO_2 in individual paleosols varies from 55.2 to 67.9 weight % (Fig. 6), but in individual samples can be as low as 26.2 or as high as 76.6 wt %. There are notable variations within each paleosol; the largest variation in SiO_2 was recorded in the paleosol under the Herrin and the Springfield coals. Al_2O_3 content in individual paleosol samples ranged from 6.36 to 34.1 wt %, and on average, Wise Ridge Coal had the largest content (27.5 wt %), followed by Viking B Coal (24.6 wt %) and Upper Block Coal (22.0 wt %) (Fig. 6). The lowest average Al_2O_3 content was recorded under the Springfield and Herrin coals. Paleosols under these two coals also had the largest variations in Al_2O_3 content.

	SiO_2 [%]		
	min	max	average
Maria Creek	58.10	60.10	58.90
Danville Coal	35.40	60.50	55.32
Herrin Coal	16.40	60.30	46.92
Springfield Coal	26.20	66.90	55.98
Houchin Creek Coal	54.70	76.60	63.10
Colchester Coal	50.70	59.60	55.15
Seelyville Coal	53.80	66.70	61.52
Carrier Mills Shale	61.10	70.20	65.65
Wise Ridge Coal	45.20	63.80	55.77
Viking B Coal	52.80	61.10	57.80
Upper Block Coal	49.00	72.20	59.75
Lower Block Coal	65.70	71.30	67.90



	Al_2O_3 [%]		
	min	max	average
Maria Creek	12.40	22.30	19.45
Danville Coal	14.30	24.90	21.46
Herrin Coal	6.36	21.80	16.23
Springfield Coal	7.59	22.10	15.28
Houchin Creek Coal	10.40	22.00	16.84
Colchester Coal	17.80	21.40	19.60
Seelyville Coal	15.60	24.50	19.08
Carrier Mills Shale	14.60	22.80	18.70
Wise Ridge Coal	23.50	34.10	27.54
Viking B Coal	24.30	25.00	24.58
Upper Block Coal	14.70	29.20	22.02
Lower Block Coal	10.90	20.70	16.30

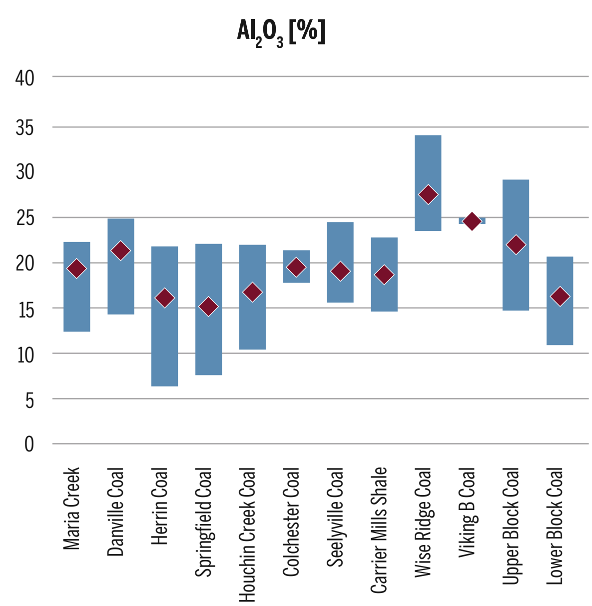


Figure 6. Table data and graphs illustrating the concentration of major oxides of selected paleosols.

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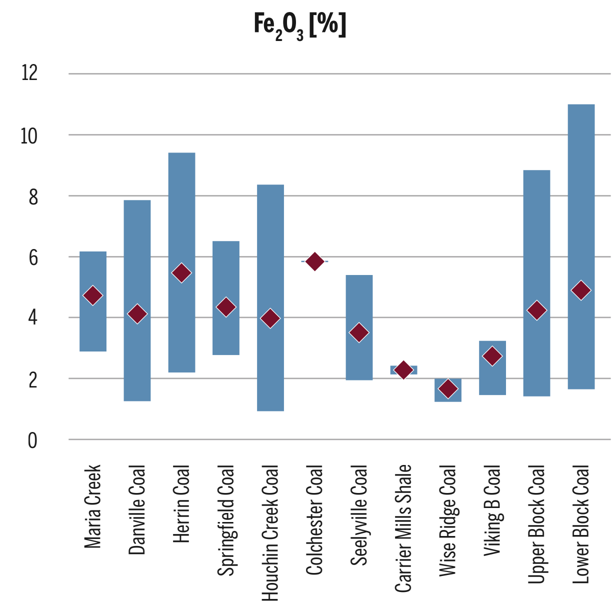
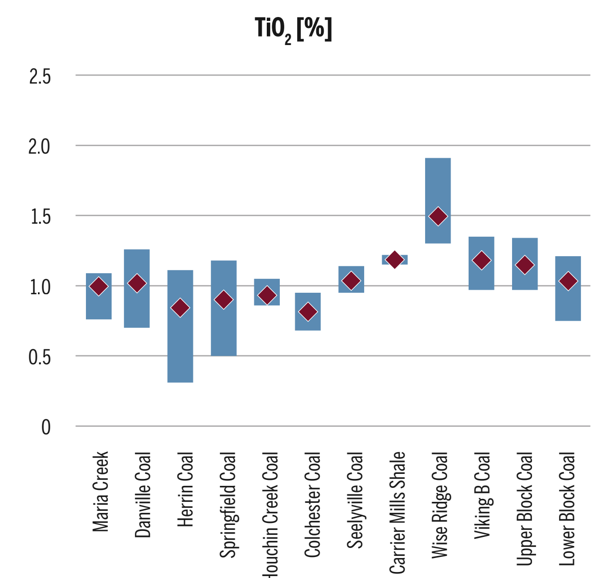
	Fe_2O_3 [%]		
	min	max	average
Maria Creek	2.89	6.17	4.72
Danville Coal	1.25	7.86	4.12
Herrin Coal	2.20	9.41	5.46
Springfield Coal	2.77	6.51	4.34
Houchin Creek Coal	0.92	8.36	3.98
Colchester Coal	5.82	5.86	5.84
Seelyville Coal	1.94	5.40	3.50
Carrier Mills Shale	2.13	2.42	2.28
Wise Ridge Coal	1.23	2.00	1.66
Viking B Coal	1.46	3.24	2.74
Upper Block Coal	1.41	8.84	4.24
Lower Block Coal	1.65	11.00	4.89

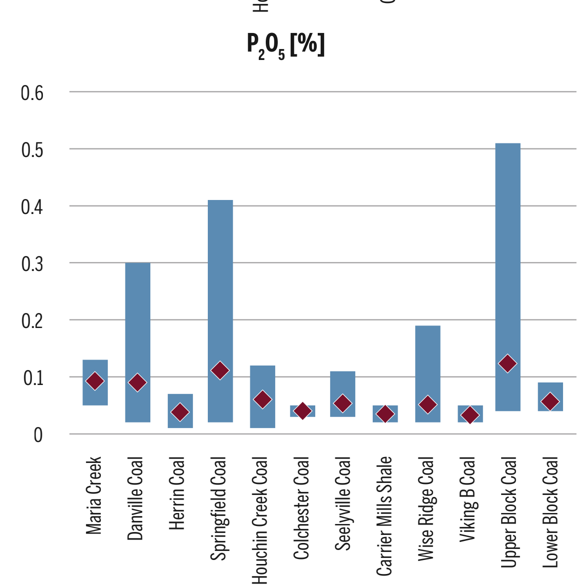
	TiO_2 [%]		
	min	max	average
Maria Creek	0.76	1.09	1.00
Danville Coal	0.70	1.26	1.02
Herrin Coal	0.31	1.11	0.84
Springfield Coal	0.50	1.18	0.90
Houchin Creek Coal	0.86	1.05	0.93
Colchester Coal	0.68	0.95	0.82
Seelyville Coal	0.95	1.14	1.03
Carrier Mills Shale	1.15	1.22	1.19
Wise Ridge Coal	1.30	1.91	1.49
Viking B Coal	0.97	1.35	1.18
Upper Block Coal	0.97	1.34	1.15
Lower Block Coal	0.75	1.21	1.03

	P_2O_5 [%]		
	min	max	average
Maria Creek	0.05	0.13	0.09
Danville Coal	0.02	0.30	0.09
Herrin Coal	0.01	0.07	0.04
Springfield Coal	0.02	0.41	0.11
Houchin Creek Coal	0.01	0.12	0.06
Colchester Coal	0.03	0.05	0.04
Seelyville Coal	0.03	0.11	0.05
Carrier Mills Shale	0.02	0.05	0.04
Wise Ridge Coal	0.02	0.19	0.05
Viking B Coal	0.02	0.05	0.03
Upper Block Coal	0.04	0.51	0.12
Lower Block Coal	0.04	0.09	0.06

Figure 6 (continued). Table data and graphs illustrating the concentration of major oxides of selected paleosols.







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Fe_2O_3 ranges from less than 1 to 11.0 wt % between individual paleosol samples, and average values for the paleosol horizons span between less than 2 wt % in the Wise Ridge Coal to 5.84 wt % in the Colchester Coal (Fig. 6). Internally most paleosols have a large spread of Fe_2O_3 content.

The average TiO_2 ranges narrowly from 0.84 wt % in the paleosol under the Herrin Coal to 1.49 wt % under the Wise Ridge Coal. Paleosols under the Herrin and Wise Ridge coals are the most variable with regard to TiO_2 content Fig. 6).

The average content of P_2O_5 ranges from 0.01 wt % in the Houchin Creek Coal to 0.41 wt % in the Springfield Coal, and the difference in P_2O_5 between different paleosol horizons are of similar magnitude as between the samples within individual paleosols (Fig. 6).

Rare earth elements and lithium of paleosols

Total REE content in paleosol samples ranges from 138.8 ppm to 728.6 ppm, with an average range of 208.3 ppm (Colchester Coal paleosol) to 342.9 ppm in the paleosol under the Upper Block Coal (Fig. 7). The largest variation in the total REE occurs under the Upper Block, Wise Ridge, and Danville Coals. As expected, light REE dominate over heavy REE (Fig. 7), and the variation in the light REE accounts for the most prominent variations of the total REE. The paleosol under the Upper Block Coal has the largest variation in heavy REE content (49-148 ppm).

REE patterns for paleosol samples are relatively uniform regardless of their stratigraphic position, even though each paleosol is associated with a different coal seam (Fig. 8 A-C). This pattern (normal N-type) represents very weak to no fractionation among light, medium, and heavy REE. No major anomalies have been revealed. As suggested in the previous study (Mastalerz and al., 2020), the majority of paleosols have REE values that are roughly representative of the upper continental crust. Only some paleosols are slightly enriched (C/UCC values of 2 to 5 or enriched (C/UCC >5), and these are paleosol samples occurring under Danville Coal (Fig. 8A) and the Upper Block Coal (Fig. 8B).

It has been previously suggested that paleosols could have increased concentrations of lithium. For the paleosol samples studied, the Li content shows a large variation, from 21 ppm to 530 ppm (Fig. 9). On average, the Wise Ridge Coal is most enriched in Li (249.3 ppm), followed by Viking B Coal (180.8 ppm). In general, the coals of the Brazil and Staunton Formations have higher Li content than the younger coals that often have Li content below 100 ppm.

	Total REE [ppm]		
	min	max	average
Maria Creek	224.3	384.8	275.6
Danville Coal	155.9	728.6	329.7
Herrin Coal	141.4	344.4	244.2
Springfield Coal	175.8	308.8	230.1
Houchin Creek Coal	129.5	318.7	243.4
Colchester Coal	138.8	286.5	208.3
Seelyville Coal	188.3	294.2	247.7
Carrier Mills Shale	230.3	404.5	328.0
Wise Ridge Coal	165.5	606.5	284.8
Viking B Coal	187.6	371.0	257.9
Upper Block Coal	264.0	635.0	342.9
Lower Block Coal	214.3	316.2	282.0

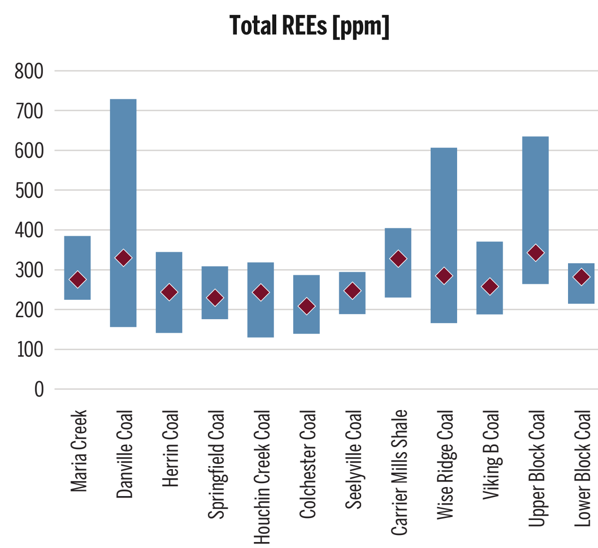
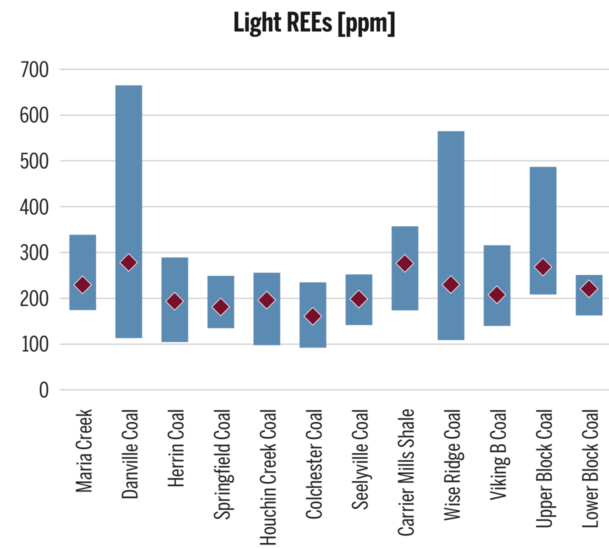


Figure 7. Table data and graphs of REE concentrations (total, light, and heavy) in the paleosols studied (continued on next page).

	Light REE [ppm]		
	min	max	average
Maria Creek	174.3	338.6	229.4
Danville Coal	113.2	665.0	278.7
Herrin Coal	104.5	289.2	193.5
Springfield Coal	134.7	249.0	181.6
Houchin Creek Coal	97.4	255.7	196.4
Colchester Coal	92.0	235.0	161.1
Seelyville Coal	141.6	252.2	198.9
Carrier Mills Shale	173.3	357.3	276.4
Wise Ridge Coal	108.5	565.0	230.2
Viking B Coal	139.7	315.5	207.8
Upper Block Coal	208.0	487.0	268.4
Lower Block Coal	162.6	251.0	221.1



	Heavy REE [ppm]		
	min	max	average
Maria Creek	40.2	50.1	46.2
Danville Coal	37.2	65.4	51.1
Herrin Coal	36.9	80.0	50.7
Springfield Coal	41.1	59.8	48.4
Houchin Creek Coal	32.1	63.1	47.0
Colchester Coal	33.5	67.1	47.2
Seelyville Coal	39.7	59.6	48.8
Carrier Mills Shale	47.2	57.0	51.6
Wise Ridge Coal	41.5	67.9	54.6
Viking B Coal	43.4	55.5	50.1
Upper Block Coal	49.0	148.0	74.5
Lower Block Coal	51.6	66.0	61.0

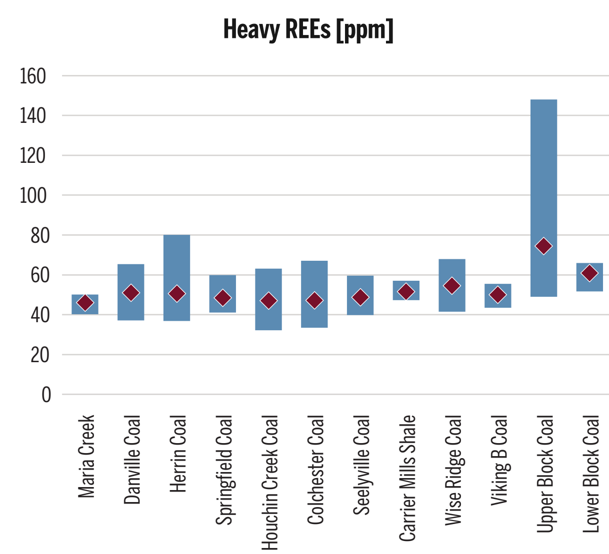


Figure 7 (continued). Table data and graphs of REE concentrations (total, light, and heavy) in the paleosols studied.

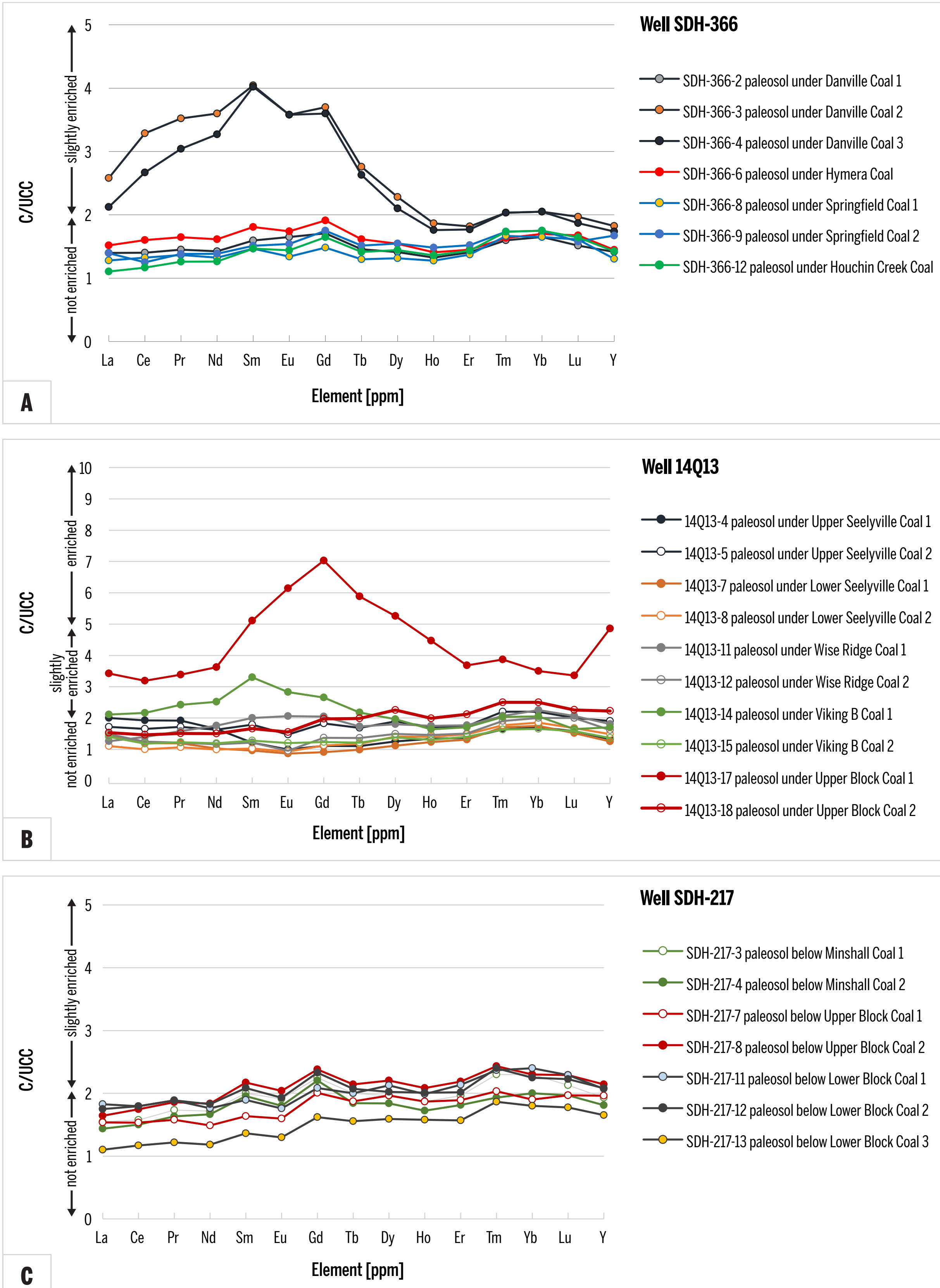


Figure 8. Line graphs of REE distribution patterns for the studied paleosols from wells SDH-366, 14Q13, and SDH-217. C – element concentration in ppm, UCC – concentration in the upper continental crust.

	Lithium [ppm]		
	min	max	average
Maria Creek	40.0	67.0	50.8
Danville Coal	45.0	258.0	115.6
Herrin Coal	25.0	129.0	76.0
Springfield Coal	29.0	118.0	51.1
Houchin Creek Coal	21.0	205.0	83.7
Colchester Coal	56.0	118.0	84.0
Seelyville Coal	39.0	205.0	85.8
Carrier Mills Shale	50.0	141.0	92.3
Wise Ridge Coal	89.0	530.0	249.3
Viking B Coal	58.0	328.0	180.8
Upper Block Coal	52.0	222.0	141.8
Lower Block Coal	34.0	204.0	129.7

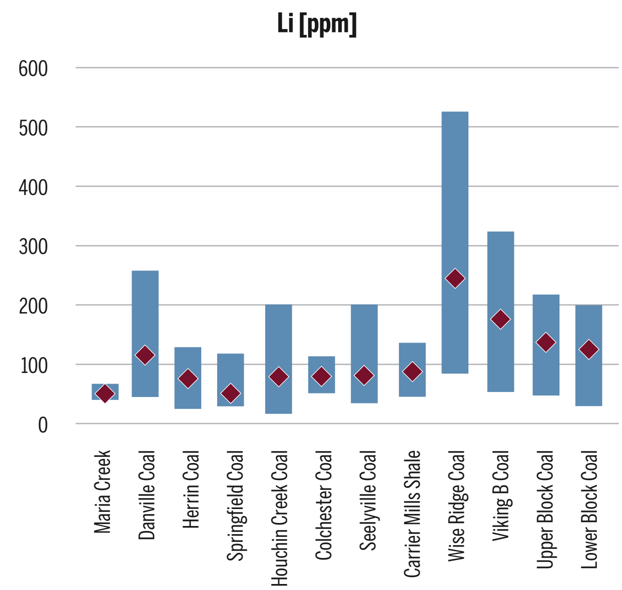


Figure 9. Table data and graph of the concentration of lithium in the paleosols studied.

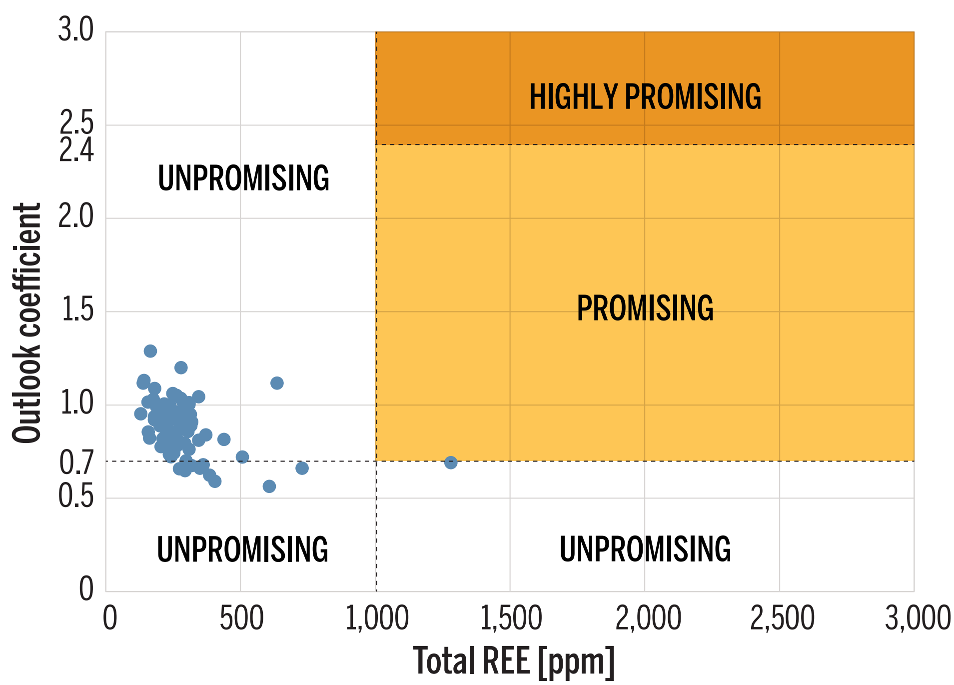


Figure 10. Scatter plot evaluating REE in collected paleosols, taking into account outlook coefficient and total REE content (after Xie et al, 2022).

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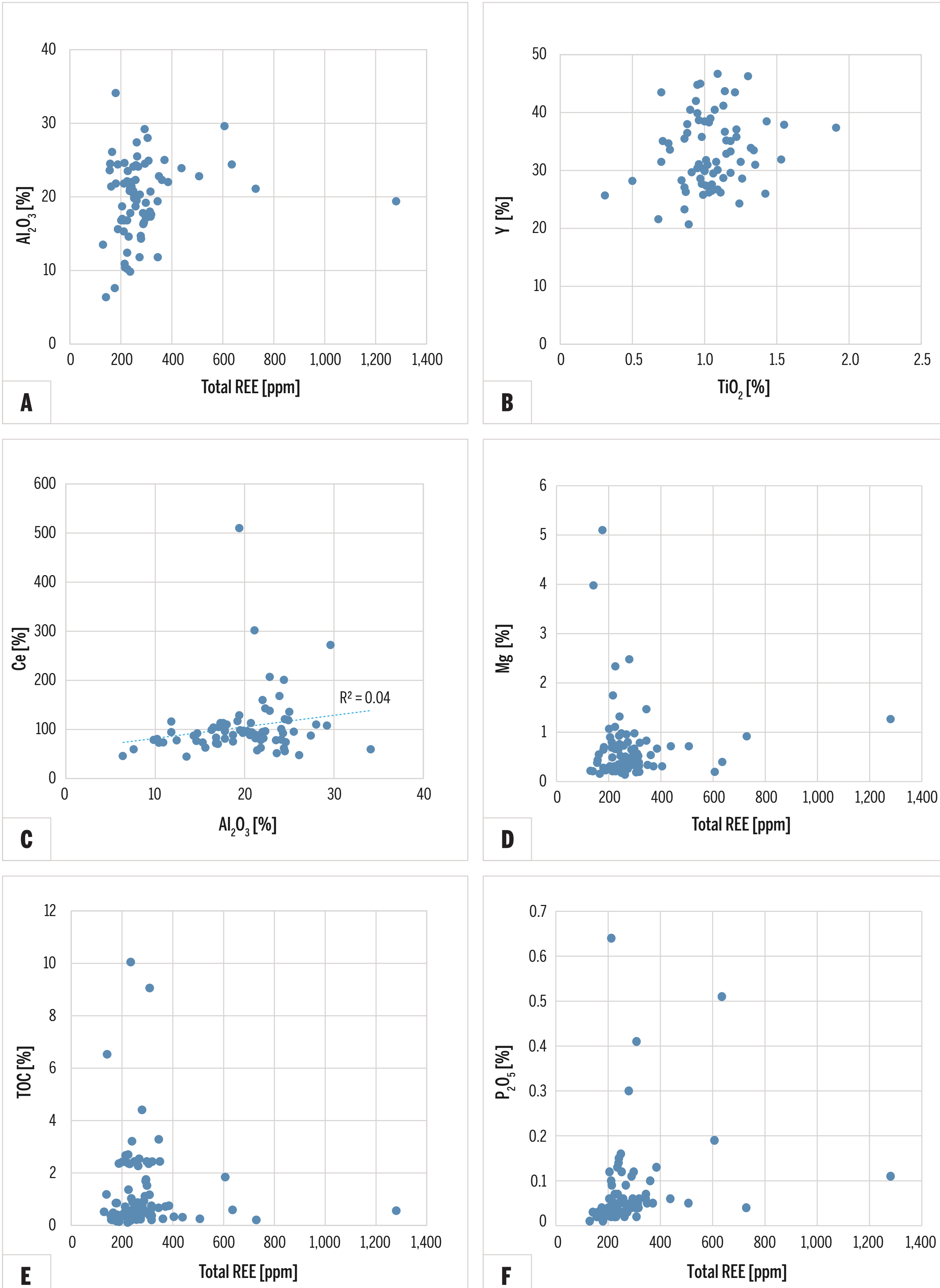

Figure 11. Scatter plots showing relationships between REE and other selected parameters.

4. DISCUSSION

4.1 Paleosols as a source for REE and lithium

Several factors must be considered when evaluating deposits as a potential source of REE. The total REE concentration is a good parameter for an initial screening. Data generated on coal combustion waste suggested that a combined REE oxides content above 1000 ppm (on ash basis) could be considered the threshold for beneficial recovery of the metals (Seredin, 2004). Seredin and Dai (2012) further suggested that this cut-off value could be lowered to 800–900 ppm, especially if the layers in consideration are thick. Considering similar criteria for paleosols, only one sample would satisfy the 700 ppm cut-off (Fig. 7). Compared to the upper continental crust concentrations, most paleosols are either not enriched or only slightly enriched (Fig. 8).

Another approach to evaluating REE potential takes into account the contribution of critical REE in relation to excessive elements: the best quality source should have as many critical elements and as few excessive elements as possible (Seredin, 2010). This approach uses a parameter known as the "outlook coefficient" (C_{outl}) that is calculated as:

C_{outl} = (Nd+Eu+Tb+Dy+ER+Y/SumREY) / (Ce+Ho+TM+Yb+Lu/Sum REY).

The higher the C_{outl} value, the more promising the ore with respect to potential industrial value. For the

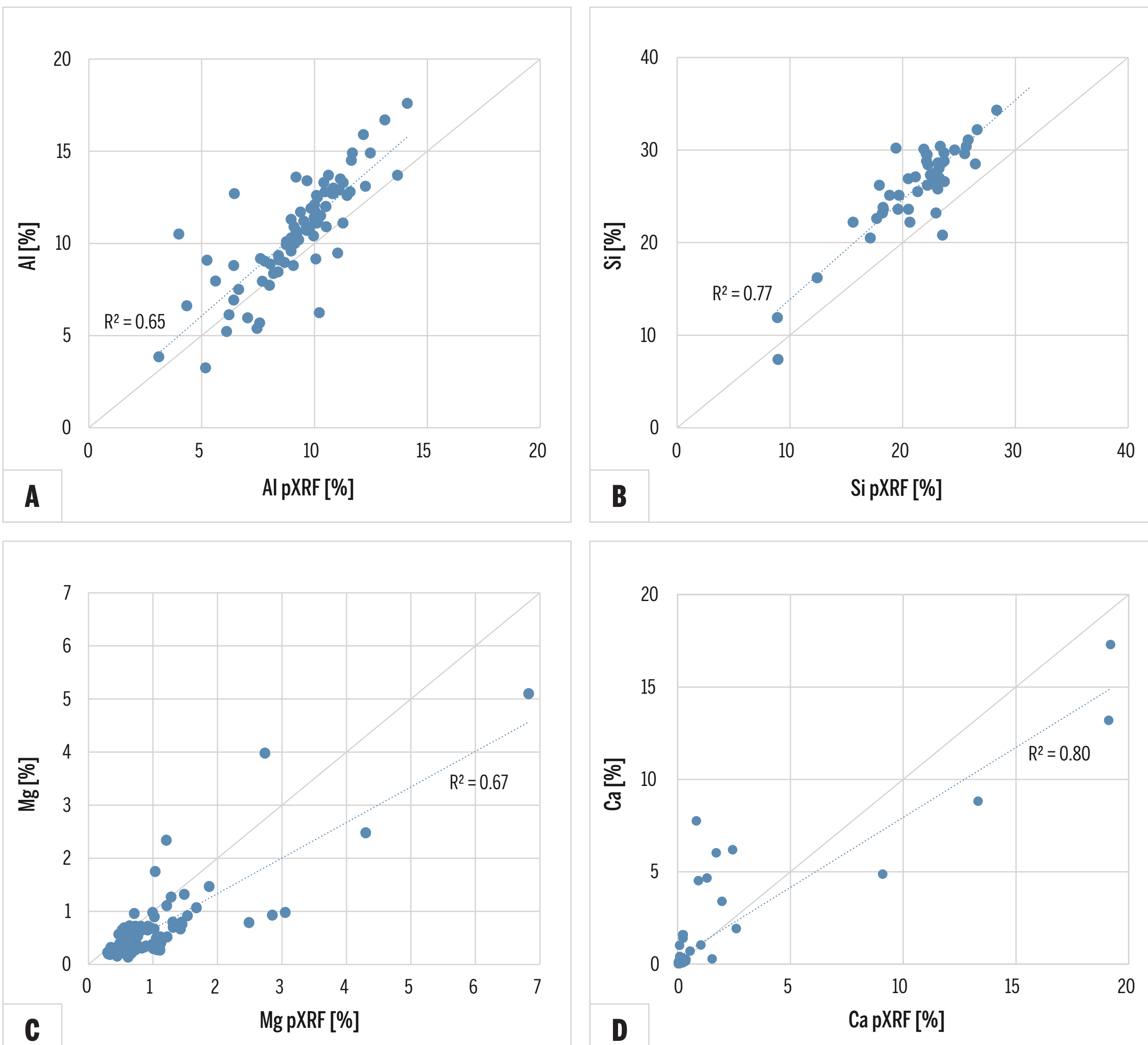

Figure 12. Scatter plots and linear regressions comparing pXRF and USGS (WDXRF) elemental data. Black line shows 1:1 concentration.

paleosols studied, the combination of REE concentrations and C_{outl} is shown in Figure 10. On this diagram, all samples place in the unpromising areas.

When evaluating REE potential, predicting REE high concentrations, and their beneficiation behavior, it is important to understand REE associations in the rock. Available data suggest that the concentrations of REE in paleosols depend on many factors, such as the mineralogical composition of the source material or the extent of pedogenic processes (e.g., Aide and Aide, 2012; Menendez et al., 2019). Considering that paleosols are dominantly claystones and clay-rich mudstones where Al_2O_3 and SiO_2 are the main components of the paleosols studied, identifying relationships between REE and major components can provide insights into their associations. To identify those associations and, consequently, possible proxies for higher REE concentrations, we compared REE concentrations to common oxides and numerous elements. In most cases, no trends were identified, and the best examples are shown in Figure 11. Although no distinct trends were revealed, the following observations may be helpful in screening for zones of increased REE concentrations: 1) low Al_2O_3 content (< 20 %) is associated with lower REY content (Fig. 11A); 2) there is no relationship between TiO2 and Y (Fig. 11B); 3) excluding several samples, there is a trend of increased Ce with an increase in Al_2O_3 (Fig. 11C); 4) there is no relationship between total carbon (TC) and Mg with REE, but higher values of REE are associated with low Mg and TC (Fig. 11D-E); and 5) there is no relationship between REE and P_2O_5 (Fig. 11F). These observations suggest that REE associations

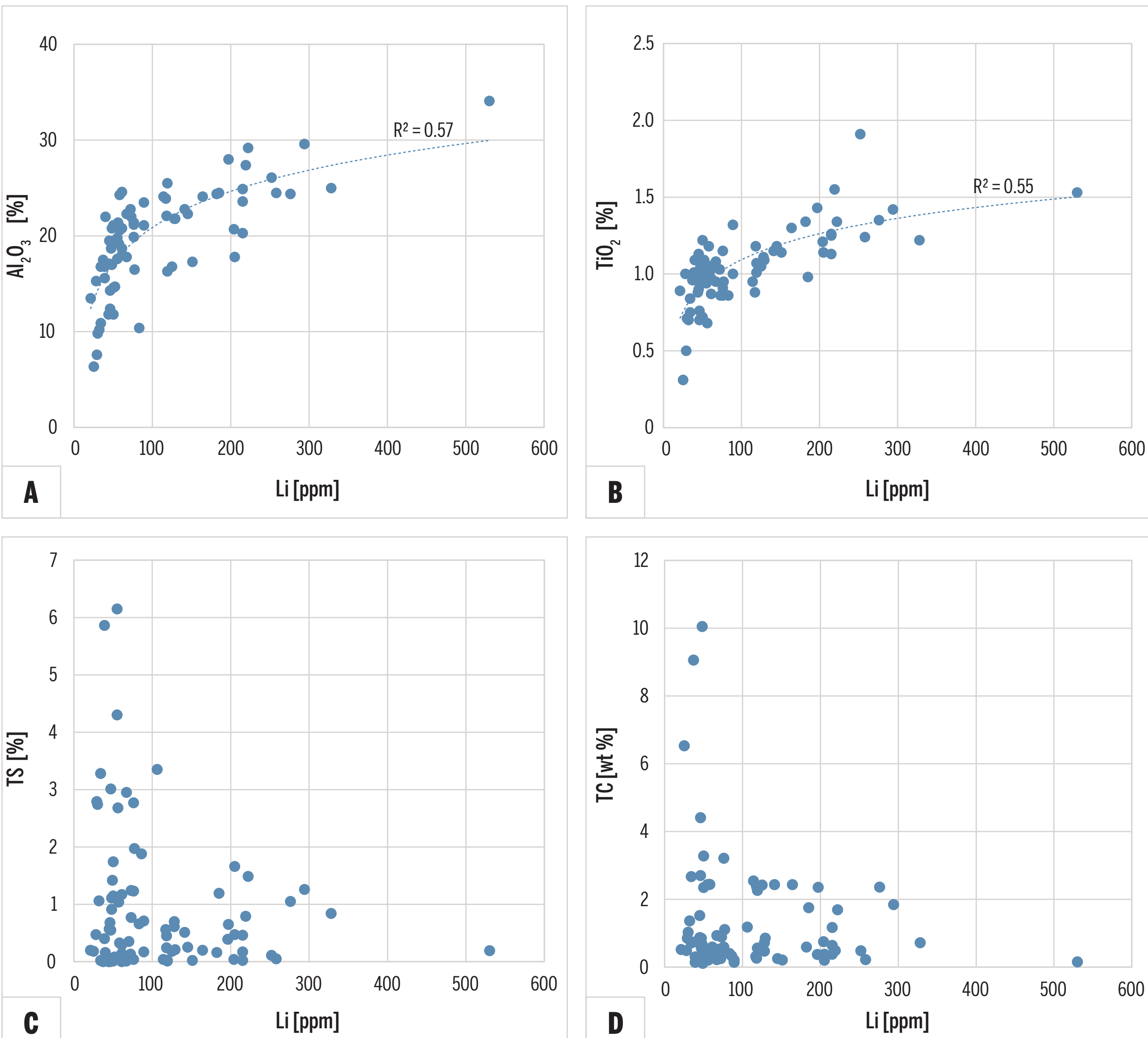

Figure 13. Scatter plots and fitted regressions showing the relationships between lithium and other selected parameters.

in the studied shales are complex, but mainly include clay minerals.

As mentioned in the methods section, splits of all paleosol samples were analyzed for elemental composition using pXRF. The pXRF is a fast and inexpensive technique, and its application for studying paleosols was evaluated. Comparing elemental composition obtained by pXRF to that using wavelength dispersive X-ray fluorescence (WDXRF), a good relationship was obtained for Al, Si, Mg, and Ca (Fig. 12), indicating that pXRF can be successfully used to quickly obtain concentrations of these elements. For Al and Si, the pXRF values were generally slightly lower than those obtained by WDXRF for the majority of samples.

With regard to lithium, the paleosols under the Brazil Formation (Lower and Upper Block coals) and Staunton Formation (Wise Ridge and Viking B coals) contain the highest lithium concentrations, with some samples having more than 300 ppm. The Wise Ridge Coal paleosol includes samples that have more than 500 ppm. Due to the wide range of Li content within these paleosols, further examination will be needed to identify zones containing the highest concentrations. In the paleosols of the younger coals, the average Li concentration is below 100, except for the Danville Coal, which contains 115.6 ppm of Li. Comparing Li concentrations to common oxides, sulfur, and TC (Fig. 13), a moderately strong positive correlation was obtained between Li and Al_2O_3 (Fig. 13A). This relationship, in addition to the negative trend with sulfur and TC, suggests that Li is associated with clay fraction and indicates that Al can be used for an initial screening of the paleosols in search for high Li concentrations.

5. CONCLUSIONS

This study provides general characteristics of the Pennsylvanian paleosols, with a special emphasis on REE and lithium. The selection of the boreholes was based upon a) stratigraphic variation within the Raccoon Creek and Carbondale Groups; and b) geographic location from Clay County in the north to Vanderburgh County in the south to provide a good overview of variability of REE and lithium that can be expected in Pennsylvanian paleosols in Indiana and likely in paleosols located elsewhere. As such, this study can serve as a screening guide for more detailed future geochemical studies of Pennsylvanian paleosols in Indiana.

Although the paleosols studied do not have high concentrations of REE, we need to consider that the liberation of REE by acid leaching clay-type deposits, like the paleosols studied, is relatively easy. Therefore, their potential as an REE source should be further studied, and special attention should be directed toward those that show the largest REE concentrations, such as the paleosols underlying the Danville Coal and the Brazil Formation coals.

Among the paleosols studied, those under the Brazil Formation (Lower and Upper Block Coals) and Staunton Formation (Wise Ridge and Viking B Coals) would be the best sources of lithium. The presence of samples with lithium concentrations exceeding 300 or 500 ppm makes the paleosols under these coals a primary target for further investigation. Our results suggest that Li is likely associated with clay fraction and that Al_2O_3 (or Al) can be used for an initial screening of the paleosols in search of high Li concentrations.

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REFERENCES

Aide, M. T., and Aide, C., 2012, Rare earth elements: Their importance in understanding soil genesis. International Scholarly Research Network ISRN Soil Science 2012, 783876.doi: 10.5402/2012/783876

Archer, A. W., and Greb, S. F., 1995, An Amazon-scale drainage system in the Early Pennsylvanian of North America: Journal of Geology 103, 611–628, <https://www.jstor.org/stable/30079761>.

ASTM, 2014, ASTM, 2014, ASTM D7708-14, Standard test method for microscopical determination of the reflectance of vitrinite dispersed in sedimentary rocks: West Conshohocken, PA, ASTM International. doi: 10.1520/D7708-14

Baker, D. R., 1962, Organic geochemistry of Cherokee Group in southeastern Kansas and northeastern Oklahoma: American Association of Petroleum Geologists, Bulletin 46, 1621–1642. <https://www.kgs.ku.edu/Publications/Bulletins/Sub11/sub11_cherokee.pdf>.

Cecil, C. B., 2013, An overview and interpretation of autocyclic and allocyclic processes and the accumulation of strata during Pennsylvanian-Permian transition in the central Appalachian Basin, USA: International Journal of Coal Geology 119, 21–31. doi: 10.1016/j.coal.2013.07.012

Cecil, C. B., Dulong, F. T., West, R. R., Stamm, R., Wardlaw, B., and Edgar, N. T., 2003, Climate controls on the stratigraphy of a middle Pennsylvanian cyclothem in North America, *in* Cecil, C.B., and Edgar, N.T., eds., Climate Controls on Stratigraphy: SEPM, Special Publication 77, 151–180.

Chi, R., and Tian, J., 2008, Weathered crust elution deposited rare earth ores: Nova Science Publishers, New York, USA, <https://www.amazon.com/Weathered-Crust-Elution-Deposited-Earth/dp/1604563877>.

De Wet, C.B., Moshier, S.O., Hower, J.C., De Wet, A., Brennan, S.T., Heifrich, C.T., and Raymond, A.L., 1997, Disrupted coal and carbonate facies within two Pennsylvanian cyclothems, southern Illinois basin, United States: Geological Society of America, Bulletin 109, 1231–1248. doi: 10.1130/0016-7606(1997)109<1231:DCACFW>2.3.CO;2

DiMichele, W.D., Cecil, B., Montanez, I.P., and Falcon-Lang, H.J., 2010, Cyclic changes in Pennsylvanian paleoclimate and effects on floristic dynamics in tropical Pangea: International Journal of Coal Geology 83, 329–344. doi: 10.1016/j.coal.2010.01.007

Duff, P.M., and Walton, E.K., 1962, Statistical basis for cyclothems: A quantitative study of the sedimentary succession in the east Pennine Coalfield: Sedimentology 1, 235–255. doi: 10.1111/j.1365-3091.1962.tb01149.x.

Falcon-Lang, H.J., and DiMichele, W.A., 2010, What happened to the coal forests during Pennsylvanian glacial phases?: Palaios 25, 611–617. <https://www.jstor.org/stable/40865494>

Grim, R.E., 1935, Petrology of the Pennsylvanian shales and noncalcareous underclays associated with Illinois coals: American Ceramic Society Bulletin 14, 113–119.

Grim, R.E., and Allen, V.T., 1938, Petrology of Pennsylvanian underclays of Illinois: Geological Society of America Bulletin 49, 1485–1514. <https://www.ideals.illinois.edu/bitstream/handle/2142/43206/petrologyofpenns52grim.pdf?sequence=2>.

Luo, X., Ma, P., Luo, C., Chen, X., Feng, B., and Yan, Q., 2014, The effect of LPF on the leaching process of a weathered crust elution-deposited rare earth ore, *in* Proceedings of the 53rd Conference of Metallurgists (COM 2014), Metallurgical Society of the Canadian Institute of Mining, Metallurgy and Petroleum (MetSoc-CIM), Vancouver, Canada.

Mastalerz, M., Eble, C., Ames, P., and Drobniak, A., 2018, Application of palynology and coals in the eastern part of the Illinois Basin: International Journal of Coal Geology 190, 191–204. doi: 10.1016/j.coal.2017.04.012

Mastalerz, M., Drobniak, A., Eble, C., Ames, P., and McLaughlin, P., 2020, Rare earth elements and yttrium in Pennsylvanian coals and shales in the eastern part of the Illinois basin: International Journal of Coal Geology 231, 103620. doi: 10.1016/j.coal.2020.103620

Mastalerz, M., A. Drobniak, and Hower, J.C., 2021, Controls on reservoir properties in organic-matter-rich shales–insights from MICP analysis: Journal of Petroleum Science and Engineering, v. 196, 107775. doi: 10.1016/j.petrol.2020.107775

Mastalerz, M., Drobniak, A., Rupp, J., and Shaffer, N., 2009, Characterization of Indiana's coal resource–availability of the reserves, physical and chemical properties of the coal, and present and potential uses: Indiana Geological Survey Special Report 66, 227 p., 104 figs. doi: 10.5967/ybrw-8y56

McLaughlin, P.I., Emsbo, P., Desrochers, A., Bancroft, A., Brett, C.E., Riva, J.F., Premo, W., Neymark, L., Achab, A., Asselin, E., and Emmons, M. M., 2016, Refining 2 km of Ordovician chronostratigraphy beneath Anticosti Island utilizing integrated chemostratigraphy: Canadian Journal of Earth Sciences, v. 53, 865−874. doi: 10.1139/cjes-2015-0242

Menendez, I., Campeny, M., Quevedo-Gonzales, L., Mangas, J., Llovet, X., Tauler, E., Barron, V., Torrent, J., and Mendez-Ramos, J., 2019, Distribution of REE-bearing minerals in felsic magmatic rocks and paleosols from Gran Canaria, Spain–intraplate of oceanic islands as a new example of potential, non-conventional sources of rare-earth elements: Journal of Geochemical Exploration 204, 270–288. doi: 10.1016/j.gexplo.2019.06.007

Moldoveanu, G.A., and Papengelakis, V.G., 2016, An overview of rare-earth recovery by ion-exchange leaching from ion-adsorption clays of various origins: Mineralogical Magazine 80, 63–76. doi: 10.1180/minmag.2016.080.051

Montross, S.N., Verba, C.A., Falcon, A., Poston, J., and McKoy, M., 2017, Characterization of rare earth elements in clay deposits associated with Central Appalachian coal seams: Poster of Research and Innovation Center, NETL, B13C-1786.

Parham, W.E., 1966, Lateral variations of clay mineral assemblages in modern and ancient sediments: International Clay Conference, Proceedings, v. 1, 135–145.

Potonie, H., 1910, Die Entstehung der Steinkohle und der Kaustobiolithe Oberhaupt, Fifth Edition: Berlin, Gebru¨der Borntraeger, 225 p.

Rosenau, N.A., Tabor, N.J., Elrick, S.D., and Nelson, W.J., 2013a, Polygenetic history of paleosols in Middle-Upper Pennsylvanian cyclothems of the Illinois basin, U.S.A. –part I, integrating geomorphology, climate, and glacioeustasy: Journal of Sedimentary Research 83, 637–668. <https://www.jstor.org/stable/48572603>.

Rosenau, N.A., Tabor, N.J., Elrick, S.D., and Nelson, W.J., 2013b, Polygenetic history of paleosols in Middle-Upper Pennsylvanian cyclothems of the Illinois basin, U.S.A.–part II, characterization of paleosol types and interpretation of pedogenic processes: Journal of Sedimentary Research 83, 606–636. doi: 10.2110/jsr.2013.50

Rozelle, P.L., Khadilkar, A.B., Pulati, N., Soundarrajan, N., Klima, M.S., Mosser, M.M., Miller, C.E., and Pisupati, S.V., 2016, A study of removal of rare earth elements from U.S. coal byproducts by ion exchange: Matallurgical and Materials Transactions 3E. doi: 10.1007/s40553-015-0064-7

Seredin, V.V., 2004, Metalliferous coals: formation conditions and outlooks for development *in* Coal Resources of Russia, v. VI. Geoinformmark, Moscow, pp. 452–519 (in Russian).

Seredin, V.V., 2010, A new method for primary evaluation of the outlook for rare earth element ores: Geology of Ore Deposits 52, 428–433.

Seredin, V.V., and Dai, S., 2012, Coal deposits as potential alternative sources for lantanides and yttrium: International Journal of Coal Geology 94, 67-93.

Schultz, L.G., 1958, Petrology of underclays: Geological Society of America Bulletin 69, 363–402. doi: 10.1130/0016-7606(1958)69[363:POU]2.0.CO;2

Tabor, N.J., and Myers, T.S., 2015, Paleosols as indicators of paleoenvironment and paleoclimate: Annual Review of Earth and Planetary Sciences 43, 333–361. doi: 10.1146/annurev-earth-060614-105355

Tourtelot, H.A., and Brenner-Tourtelot, E.F., 1977, Lithium in flint clay, bauxite, related high-alumina materials and associated sedimentary rocks in the United States – a preliminary survey: USGS Open-File Report 77-786. doi: 10.3133/ofr77786

The TriState Committee on Correlation of the Pennsylvanian System in the Illinois Basin, 2001, Toward a more uniform stratigraphic nomenclature for rock units (Formations and Groups) of the Pennsylvanian System in the Illinois Basin: Illinois Basin Consortium Study 5, joint publication of the Illinois State Geological Survey, Indiana Geological Survey, and Kentucky Geological Survey, 26 p.

Tsai, P-H, You, C-F., Huang, K-F, Chung, C-H., and Sun, Y-B., 2014, Lithium distribution and isotopic fractionation during chemical weathering and soil formation in loess profile: Journal of Asian Earth Sciences 87, 1–10. doi: 10.1016/j.jseaes.2014.02.001

Weller, J.M., 1930, Cyclical sedimentation of the Pennsylvanian Period and its significance: Journal of Geology 38, 97–135. <https://www.jstor.org/stable/30058933>.

Xie, P., Liu, J., Fu, B., Newmaster, T., and Hower, J.C., 2022, Resources from coal beneficiation waste– chemistry and petrology of the Ayrshire coal tailings ponds, Chandler, Indiana: Fuel 313, 123054. doi: 10.1016/j.fuel.2021.123054

Yang, J., Montross, S., Britton, J., Stuckman, M., Lopano, C., and Verba, C., 2020, Microanalytical approaches to characterizing REE in Appalachian Basin underclays: Minerals 10 (6), 546. doi: 10.3390/min10060546