

Organic-matter-rich Pennsylvanian Black Shales as a Source of Critical Minerals

Maria Mastalerz¹, Agnieszka Drobnik^{1,2}, and Philip Ames¹

¹ Indiana Geological and Water Survey, Indiana University, Bloomington, Indiana, USA

² Centre for Biomass Energy Research and Education, University of Silesia, Katowice, Poland

E-mail: mmastale@indiana.edu

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ABSTRACT

This study examines Pennsylvanian shales in Indiana as a potential source of selected critical elements: rare earth elements (REE), vanadium (V), zinc (Zn), arsenic (As), and cadmium (Cd). Widespread, organic-matter-rich marine Desmoinesian black shales are the main target, but other discontinuous shale horizons were also sampled in 11 locations. In total, 39 shale samples were analyzed in this study. The shales are early mature and represent the early oil generation window. The average concentrations of REE in the marine shales studied vary from 164.9 ppm in the Excello Shale to 338.7 ppm in the Carrier Mills Shale. REE distribution patterns show that most shales have REE values roughly representative of the upper continental crust (UCC). Only one sample of the Carrier Mills Shale was enriched compared to the upper continental crust (REE concentration/UCC > 5). The shales are characterized by high uranium (U) content, with averages for marine shales from 70.8 ppm in the Excello Shale to 133.8 ppm in the Veale Shale. In contrast, non-marine shales grouped under “other shales” category had the lowest U concentration of 3.3 ppm. Molybdenum (Mo) concentrations in the marine shales are very high at places exceeding 1000 ppm. Among the shales studied, the Mecca Quarry Shale is the most enriched in Mo (average 1103.8 ppm), followed by the Veale Shale (876.7 ppm). The “other shales” category has the lowest Mo content (2.5 ppm) due to deposition under oxygenated conditions. The marine shales are highly enriched in Zn, As, and Cd. Specifically, the Mecca Quarry Shale is the most enriched in Zn, with some samples having content as high as 5480 ppm. Furthermore, the Excello Shale and the Veale Shale have Zn concentrations more than ten times higher than the UCC (~70 ppm). The As content is the highest in the Veal Shale, averaging 61.7 ppm, and some samples reach more than 200 ppm — highly enriched compared to 1.8 ppm in UCC. The Excello Shale, Mecca Quarry Shale, and Veale Shale are all strongly enriched in Cd (76.1, 74.2, and 49.2 ppm on average, respectively), and the Carrier Mills Shale has the lowest average value of 8.5 ppm. These data demonstrate that Pennsylvanian marine black shales are a potential resource of V, Zn, As, and Cd, whereas in non-marine shales, the concentrations of these elements are much lower. In turn, the REE potential needs further investigation; more data are needed to better understand REE concentrations and their associations.

INTRODUCTION

Organic-matter-rich black shales of midcontinent North America are part of Pennsylvanian cyclothems (repeated sequences of transgressive marine limestone, marine black shales, regressive marine limestone, nearshore to terrestrial shale, and paleosols and coals) formed in response to sea level changes related to glacial events (e.g., Cecil et al., 2014). Within the cyclothems, marine black shales represent the maximum flooding surface and the high stand of sea level (e.g., Heckel, 1991). Heckel (1991) further suggested that these shales were deposited beneath pycnoclines established during interglacial high stands of sea level when the water at the surface was warm enough and water depth was large enough to maintain a thermocline for an extended period of time.

Organic matter content in Pennsylvanian black shales typically ranges from 4 to 40 % (Evans, 1967; Hatch and Leventhal, 1985; Wenger and Baker, 1986; Coveney and Glascock, 1989). These black shales have long been known to be enriched in various metals, such as Zn, Mo, or U (Runnels et al., 1953; Ostrom et al., 1955; Swanson, 1961; Zangler and Richardson, 1963; Coveney, 1979; Coveney and Glascock, 1989). Many studies suggest that the mineralization took place during sedimentation and early diagenesis by direct precipitation of sulfide minerals or by interaction between metals dissolved in the sea water and organic matter (Zangerl and Richardson, 1963; Coveney and Martin, 1983), although others suggested the possibility of additional diagenetic enrichment from metal-rich fluids (e.g., Coveney et al., 1987).

Data compiled by Embso et al. (2015) suggest that phosphatic Pennsylvanian black shales can be significantly enriched in rare earth elements (REE) at concentrations several times higher than those documented from some of the world's current REE sources. Although Pennsylvanian black shales have been of geologic interest over a century, only a handful of localized studies provide data on the REE potential of these shale units (e.g., Coveney et al., 1987; Kidder and Eddy-Dilek, 1994; Cruse et al., 2000; Kidder et al., 2003; Yang et al., 2017). Similar situations exist for other critical elements, such as V and U. Consequently, due to a lack of robust data, it is not possible to precisely quantify the economic potential of these resources (Breit et al., 1989; Hatch and Leventhal, 1992; Cruse and Lyons, 2004).

This study concentrates on properties of Pennsylvanian marine shales from eastern part of the Illinois Basin (Indiana). Some organic petrological and chemical aspects of some of these black shales were discussed recently by Teng et al. (2021), and their application in the correlation of coal-bearing strata was investigated

by Mastalerz et al. (2019). Mastalerz et al. (2020) discussed REE content in four marine black shale horizons (Excello Shale Member of the Carbondale Formation, Mecca Quarry Shale Member of the Linton Formation, and Carrier Mills Shale Member and Veale Shale Member of the Staunton Formation) from several locations in Indiana. This study is an extension of those previous studies and includes additional shale horizons and locations. The purpose of this study is to expand a geochemical database of Pennsylvanian black shales and to get a better understanding of their potential as a source of critical elements, especially for REE, V, Zn, As, and Cd.

METHODOLOGY

Samples

Eleven locations in southwestern Indiana were selected for this study (Fig. 1). Several dark-grey and black shale horizons in the Desmoinesian part of the Pennsylvanian section were sampled, with emphasis on six transgressive marine shales horizons (listed from the youngest to the oldest, Fig. 2): Anna Shale Member (two samples) and Turner Mine Shale Member (two samples) of the Dugger Formation, Excello Shale (six samples), Mecca Quarry Shale (seven samples), Carrier Mills Shale (five samples) and Veale Shale (six samples). These horizons have basinwide distribution (e.g., Algeo and Heckel, 2008) and are easily recognized on geophysical logs because of their high gamma-ray values (e.g., Mastalerz et al., 2019). In addition, other shales, often associated with coals, were sampled and analyzed (Fig. 2). These other shales were deposited under freshwater or brackish conditions, are discontinuous, and often of local extent. Eleven samples of such shales are grouped together under “other shales” category.

All shale core samples were split, with one half sent to the U.S. Geological Survey for REE and associated analyses, and the other half used for in-house analysis at the Indiana Geological and Water Survey, including portable X-ray fluorescence (pXRF), total carbon (TC) and total sulfur (S). Coal samples associated with these shales were measured for vitrinite reflectance (VR_o) to determine thermal maturity of the studied intervals.

Techniques

REE, trace elements, and major elements

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, and major

elements were determined by the wavelength dispersive X-ray fluorescence (WDXRF) technique. Throughout this paper, under the REE designation, we include true rare earth elements (lanthanum [La], cerium [Ce], praseodymium [Pr], neodymium [Nd], promethium [Pm], samarium [Sm], europium [Eu], gadolinium [Gd], terbium [Tb], dysprosium [Dy], holmium [Ho], erbium [Er], thulium [Tm], ytterbium [Yb], and lutetium [Lu] plus yttrium (Y).

Portable X-ray fluorescence (pXRF)

A pXRF analyzer (Thermo Niton XL3t GOLDD+) was used to analyze the major element contents of the studied samples. It was run in “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.

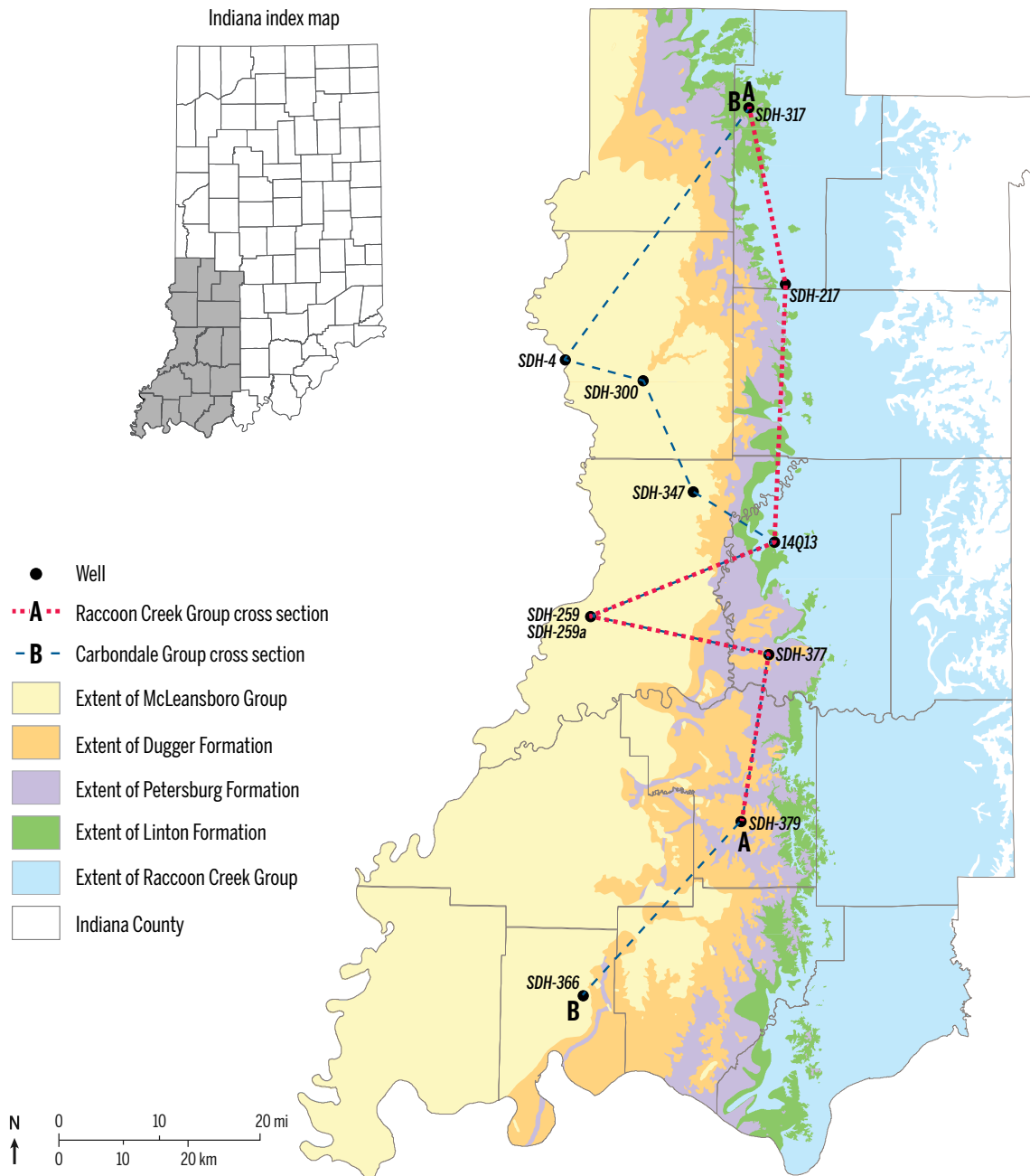


Figure 1. Map of southwestern Indiana showing locations of the boreholes analyzed in this study. Cross sections A and B can be found in Mastalerz et al., 2022.

INDIANA		MEMBER		
McLeansboro Group	Mattoon Fm.	Cohn Coal	Missourian	Stephanian
	Bond Fm.	Fairbanks Coal		
	Patoka Fm.	Parker Coal Raben Branch Coal Hazelton Bridge Coal Ditney Coal		
	Shelburn Fm.	Pirtle Coal		
Carbondale Group	Dugger Fm.	Danville Coal ★ Hymera Coal ★ Anna Shale / Energy Shale ★ Herrin Coal Bucktown Coal Turner Mine / Dykersburg Shale	Desmoinesian	Asturian
	Petersburg Fm.	Springfield Coal Stendal Limestone Excello Shale Houchin Creek Coal		
	Linton Fm.	Survant Coal Velpen Limestone Mecca Quarry Shale Colchester Coal Coxville Sandstone Upper Seelyville Coal ★ Lower Seelyville Coal ★		
Raccoon Creek Group	Staunton Fm.	Carrier Mills Shale Silverwood Limestone Veale Shale Wise Ridge Coal Holland Limestone Viking B Coal Unnamed Staunton Coals Perth Limestone	Atokan	Bolsolvian
	Brazil Fm.	Minshall / Buffaloville Coal ★ Upper Block Coal ★ Lower Block Coal ★		
	Mansfield Fm.	Shady Lane Coal Mariah Hill Coal Blue Creek Coal Pinnick Coal St. Meinrad Coal French Lick Coal	Morrowan	Langsettian

■ marine organic rich shales ★ other shales

Total carbon (TC) and total sulfur (TS)

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

Vitrinite reflectance

Coal samples associated with shales 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, 2015). A Zeiss Photoscope III reflected light microscope linked to a TIDAS PMT IV photometric system was used to measure the reflectance of vitrinite (VR_o), with more than 50 measurements collected on each sample.

RESULTS

General overview of black shales

Six Desmoinesian organic-rich marine black shales members — Anna Shale, Turner Mine Shale, Excello Shale, Mecca Quarry Shale, Carrier Mills Shale and Veale Shale — were the main targets of this study (Fig. 2). They each produce a high response on gamma-ray logs, have high organic matter content, and have large concentrations of U and Mo (Mastalerz et al., 2019). Below they are briefly defined and characterized from the youngest to oldest.

The Anna Shale Member occurs above the Herrin Coal Member of the Dugger Formation (Fig. 2) and it forms a discontinuous horizon (e.g., Eble and Greb, 2018). At places in Indiana, the Anna Shale is separated from the Herrin Coal by the Energy Shale interpreted to be non-marine in origin (Burk et al., 1987). In the locations studied, the Anna Shale was a black fissile shale, and its thickness did not exceed 2 ft.

The Turner Mine shale occurs directly above the Springfield Coal of the Petersburg Formation in Indiana (Fig. 2), except in places where it is separated from the Springfield by the non-marine Dykersburg Shale (e.g., Nelson et al., 2020). Because the top of the Springfield

Figure 2. Chart of Pennsylvanian stratigraphy in Indiana showing the position of marine shale horizons (highlighted in green) and other shales (red stars) 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).

Coal marks the upper boundary of the Petersburg Formation, the Turner Mine Shale forms the lowermost part of the Dugger Formation. This shale is not formally named in Indiana or Kentucky (Eble and Greb, 2018) but it is formalized as the Turner Mine Shale in Illinois (Nelson, 1983). It is a black, massive to fissile mudstone, containing some plant fossils, especially close to the contact with the underlying coal. In the location studied, its thickness is approximately 2 ft.

The Excello Shale Member occurs under the Stendal Limestone Member of the Petersburg Formation and directly overlies the Houchin Creek Coal Member of the Petersburg Formation (Fig. 2). In the locations studied, the Excello Shale ranged in thickness from ~1 to 5 ft, similar to the previously reported thickness range of this horizon (Hasenmueller and Ault, 1991; Mastalerz et al., 2019). Megascopically, it is a black fissile shale with thin vitrain bands and rare small pyrite nodules.

The Mecca Quarry Shale Member of the Linton Formation occurs above the Colchester Coal Member and underneath the Velpen Limestone Member (Fig. 2) (Zangerl and Richardson, 1963). It is grey to black carbonaceous shale ranging in thickness in the locations studied from 1 to 6 ft. At places it contains calcareous concretions and fragments of brachiopods and other fossils.

The Carrier Mills Shale is a hard black fissile shale occurring below the Seelyville Coal Member, in the upper part of the Staunton Formation (Fig. 2). This shale horizon has not been formally named in Indiana, but it is a formal unit in Illinois (Nelson et al., 1991). The name "Logan Quarry shale" previously was used for this shale in Indiana (Zangerl and Richardson Jr., 1963), but the name was not formally adopted. In the locations studied, its thickness ranged from less than 1 ft to ~2 ft, and at places contained small limestone concretions.

The Veale Shale is a fissile black shale that overlies the Wise Ridge Coal Member (Staunton Formation) and is overlain by the Silverwood Limestone Member in Indiana (Fig. 2). This shale has not been formally named in Indiana. Nelson (2016) suggested naming this unit the Veale Shale Member of the Staunton

Formation, after Veale Township in Daviess County, Indiana, and proposed a core from Indiana Geological and Water Survey borehole SDH-187 as the type section (Mastalerz et al., 2019). In the locations studied, its thickness ranges from 1 to 2 ft.

Other shales sampled in this study were usually associated with coal beds. They included both grey and black shales varying in thickness, and in this paper, they are grouped as "other shales." As mentioned above, these are dominantly non-marine, and include the Energy Shale, Dykersburg Shale, and other unnamed shales. Stratigraphically, they spread from the Brazil Formation of the Raccoon Creek Group to the Dugger Formation of the Carbondale Group (Fig. 2).

The vitrinite reflectance values of the coals (29 samples measured) associated with the shales studied show a narrow range of VR_o from 0.52 to 0.57 %, placing the coals within high volatile C bituminous coal rank, in agreement with previous maturity estimates of coal in Indiana (e.g., Mastalerz et al., 2009). Consequently, the shales are early mature and represent the early oil generation window, in agreement with their earlier maturity evaluations based on VR_o values (0.52-0.63 % in Mastalerz et al., 2019) This agreement between VR_o in shales and the associated coals counters the argument that there is suppression of vitrinite reflectance in these shales, such as suggested by Eble and Greb (2018) in the Anna and Turner Mine Shales of Kentucky.

The shales are characterized by high organic matter content, reflected by high values of total carbon (averages for individual shales ranging from 5.8 to 20.4 wt %, Fig. 3A). Although values in Fig. 3A represent the total carbon content, the carbonate contents in these shales are low (in the majority of cases calcium concentration is much below 1 %), and thus the majority of carbon (C) comes from organic matter. In addition, the C values in these shales are comparable to TOC values previously observed from some of these shale horizons (Mastalerz et al., 2019), further supporting that the total C content measured in this study comes dominantly from organic matter. Sulfur (S) content is relatively high, averaging 1.3 to 3.3 wt % (Fig. 3B). The lowest S content (1.3 %) in the "other shales" is a consequence of their dominantly non-marine origin.



Figure 3. Table data and graphs showing the total carbon and total sulfur content (ranges and average values, uncertainty ± 0.02 for C and ± 0.04 for S) in the shales studied.

Rare earth elements (REE)

The average concentrations of REE in the shales studied vary (Fig. 4A) from 164.9 ppm in the Excello Shale to 338.7 ppm in the Carrier Mills Shale, and this significant range is noted within each horizon, as indicated by the difference between maximal and minimal values. For example, in Carrier Mills Shale, REE content ranged from 217.5 to 701.8 ppm between the samples. These are similar ranges to those obtained for some of these shales in our previous study (Mastalerz et al., 2020). Specifically, in the Excello Shale, REE content ranged from 156 to 489 ppm, and in the Mecca Quarry Shale from 107 to 563 ppm. The highest values were previously recorded in the Veale Shale (833 ppm) and in the Carrier Mills Shale (675 ppm). Average content of heavy REE (Gd+Tb+Dy+Ho+Er+Tm+Yb+Lu+Y) of the

shale studied does not exceed 100 ppm, and the content of light REE (La+Ce+Pr+Nd+Pm+Sm+Eu) ranges from 126.8 to 242.9 ppm (Fig. 4 B, C). The largest variation of heavy REE (30.6 to 280.4 ppm) occurs in the Carrier Mills Shale (Fig. 4C).

Patterns of REE in the studied marine shales show some variations between and within the shales (Fig. 5). Some samples show very little fractionation, but some show positive anomalies for Gd (e.g., Figs. 5, 6), and one sample of the Mecca Quarry Shale has a positive Eu anomaly (Fig. 6D). The REE distribution patterns show that the majority of shales have REE values that are roughly representative of the upper continental crust (UCC). Some samples are slightly enriched in some elements (C/UCC values of 2 to 5) and only one sample of the Carrier Mills Shale is considered

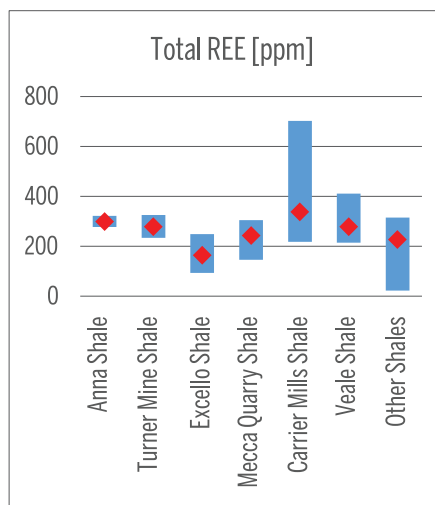
enriched compared to the upper continental crust ($C/UCC > 5$, Fig. 5A). Published data generated from coal combustion waste suggested that a combined REE oxides content above 1000 ppm (on ash basis) could be considered the threshold for beneficial recovery of the metals (Seredin, 2004; Seredin and Dai, 2012). Considering similar criteria for these shales, the samples would place below this threshold.

To identify possible proxies for higher REE concentrations, we investigated whether there were any relationships between selected routinely determined elements and REE that could be used to better predict zones of higher REE concentrations in these shales. Several elements were included for this purpose: P, Al, Zn, C, Ca, Fe, and S. We selected these elements guided by the available data on REE in sedimentary rocks; those data suggest that increased concentrations of REE might occur in phosphorites (Jarvis et al., 1994; Emsbo et al., 2015), could be hosted by clay minerals (e.g., Lefticariu et al., 2020), or occur in association with hydrothermal mineralization (Seredin and Dai, 2012). The comparison between REE and elemental

concentrations provided the following observations: a) there is no relationship with P; at best, there is a weak tendency of increasing REE content with increasing P content (Fig. 7A); b) there is a very weak tendency of REE to increase with increasing Al content (Fig. 7B); c) no correlation exists between REE and Zn ($R^2 = 0.0002$); d) there are no correlations between REE and Fe ($R^2 = 0.072$) or S ($R^2 = 0.0021$); and e) there is a weak tendency of decreasing REE content with increasing C content (Fig. 6C), which suggests that organic matter is not a host to REE. These observations support our previous observations on shales (Mastalerz et al., 2020) and suggest that REE associations in the studied shales are complex, but likely include clay minerals and phosphorites. More data on REE concentration and distribution controls in these organic-matter-rich marine black shales are needed. If indeed REE are hosted by multiple fractions, their pre-concentration and separation would be very difficult. This, together with relatively low total REE concentrations (below 400 ppm, Fig. 4A), suggests that significant efforts and resources would be needed to make such shales a viable REE resource.

A

	Total REE [ppm]		
	min	max	average
Anna Shale	277.5	322.5	300.0
Turner Mine Shale	233.7	325.6	279.6
Excello Shale	93.4	249.1	164.9
Mecca Quarry Shale	146.5	304.5	243.7
Carrier Mills Shale	217.5	701.8	338.7
Veale Shale	214.2	410.8	279.6
Other Shales	23.1	315.4	227.3



B

	Light REE [ppm]		
	min	max	average
Anna Shale	183.7	231.8	207.7
Turner Mine Shale	187.3	244.0	215.6
Excello Shale	80.0	175.0	126.8
Mecca Quarry Shale	105.8	242.3	178.3
Carrier Mills Shale	169.9	421.4	242.9
Veale Shale	174.4	254.2	204.3
Other Shales	16.6	266.9	185.5

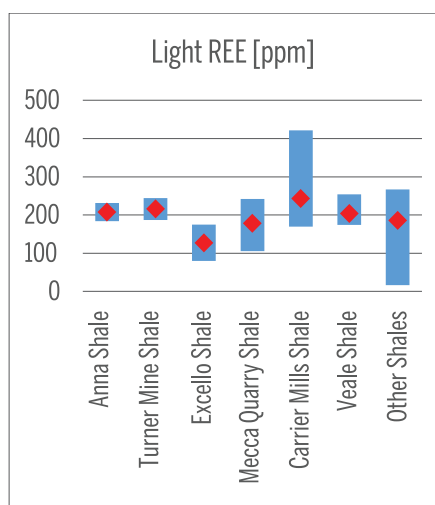


Figure 4. Table data and graphs showing REE (total, light, and heavy) concentrations in the shales studied. (Continued on next page.)

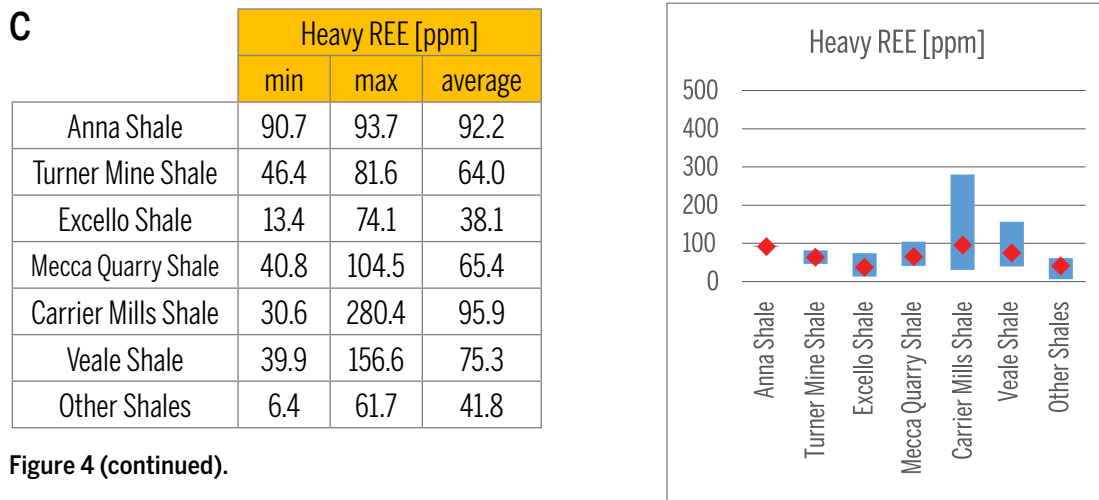


Figure 4 (continued).

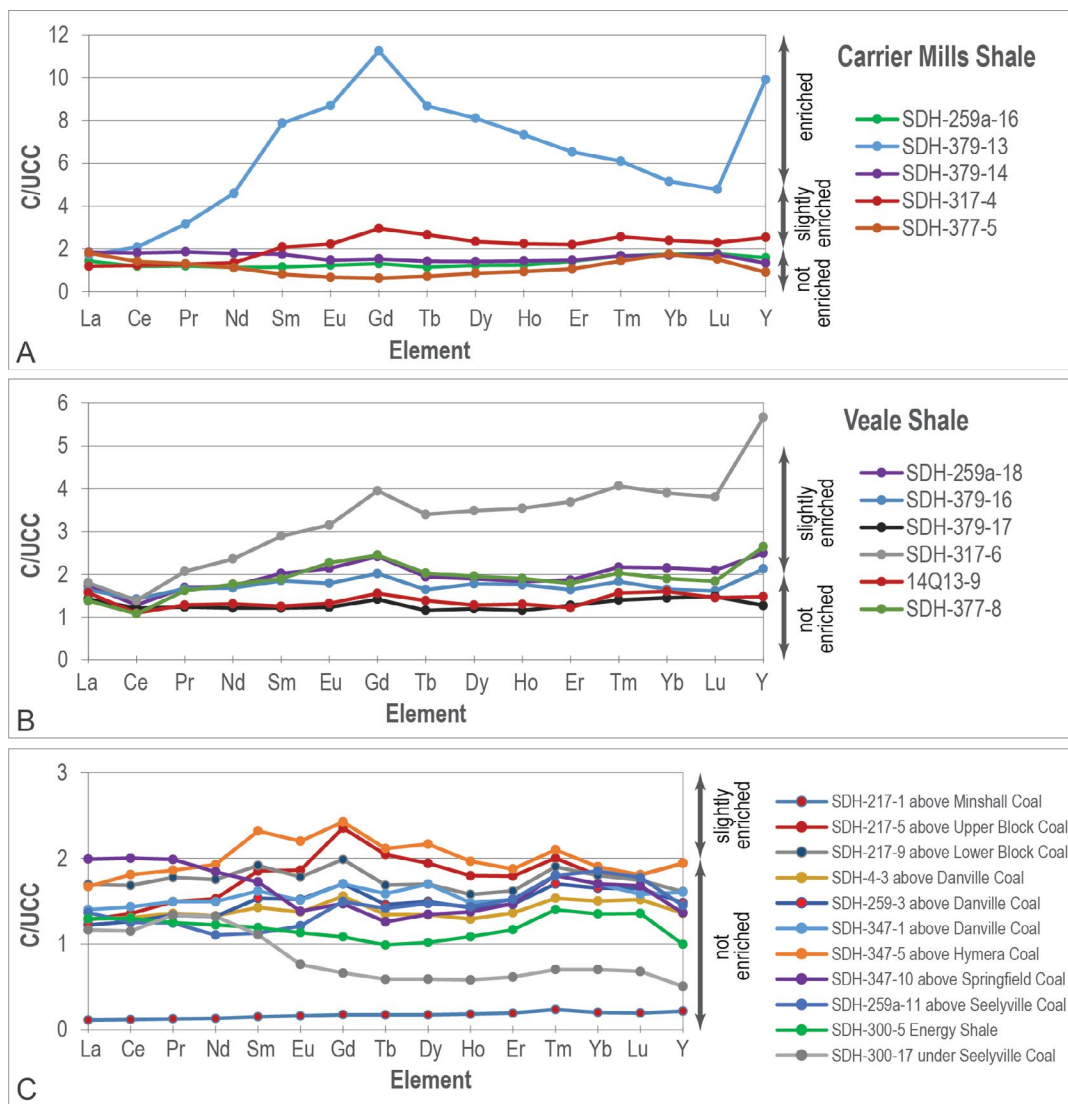


Figure 5. Line graphs of REE distribution patterns for the studied shales. C – element concentration in ppm, UCC – concentration in the upper continental crust. Element concentration values in the upper continental crust are from Rudnick and Gao, 2003.

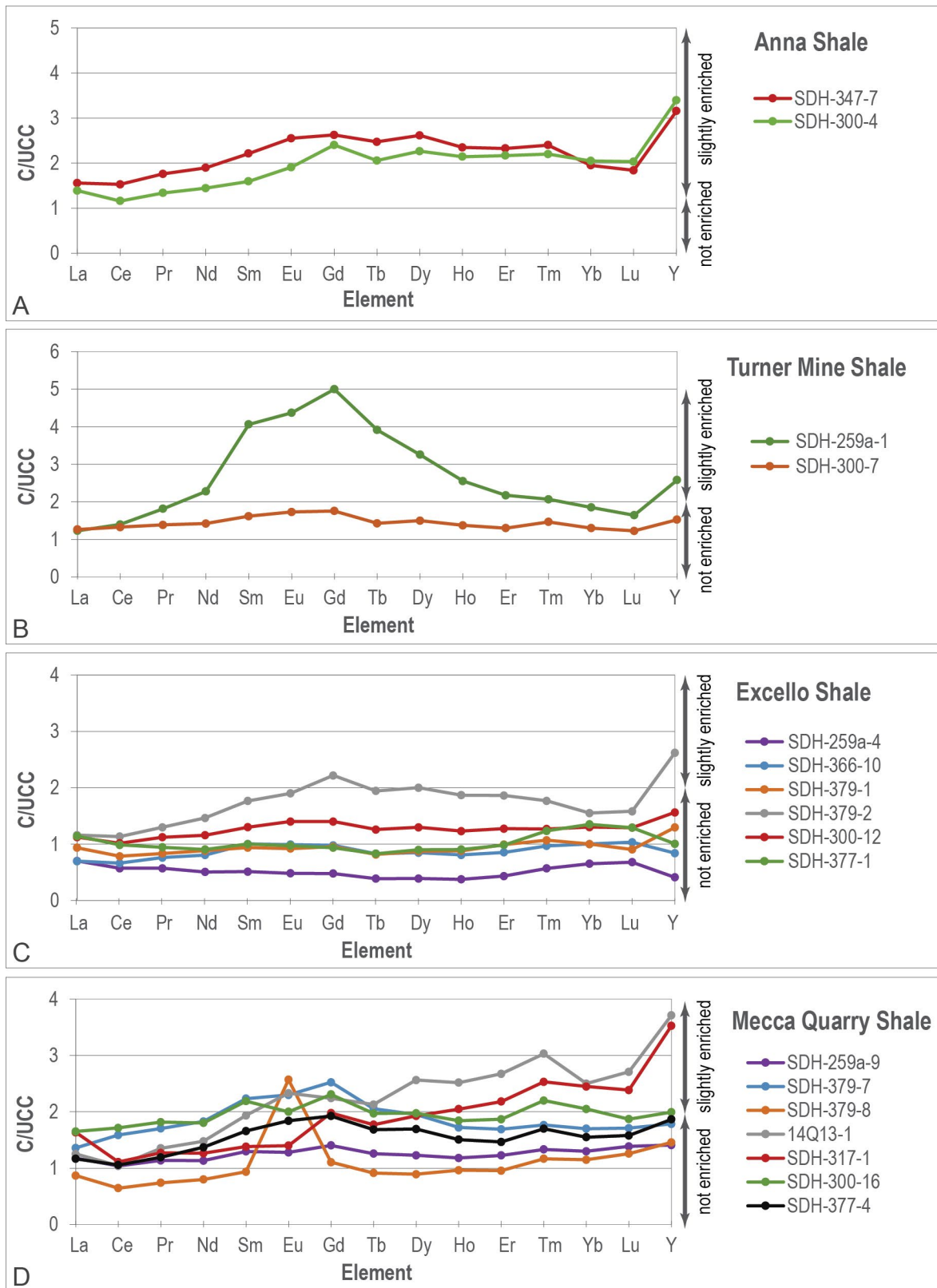


Figure 6. Line graphs of REE distribution patterns for selected samples of the studied shales. C – element concentration in ppm, UCC – concentration in the upper continental crust. Element concentration values in the upper continental crust are from Rudnick and Gao, 2003.

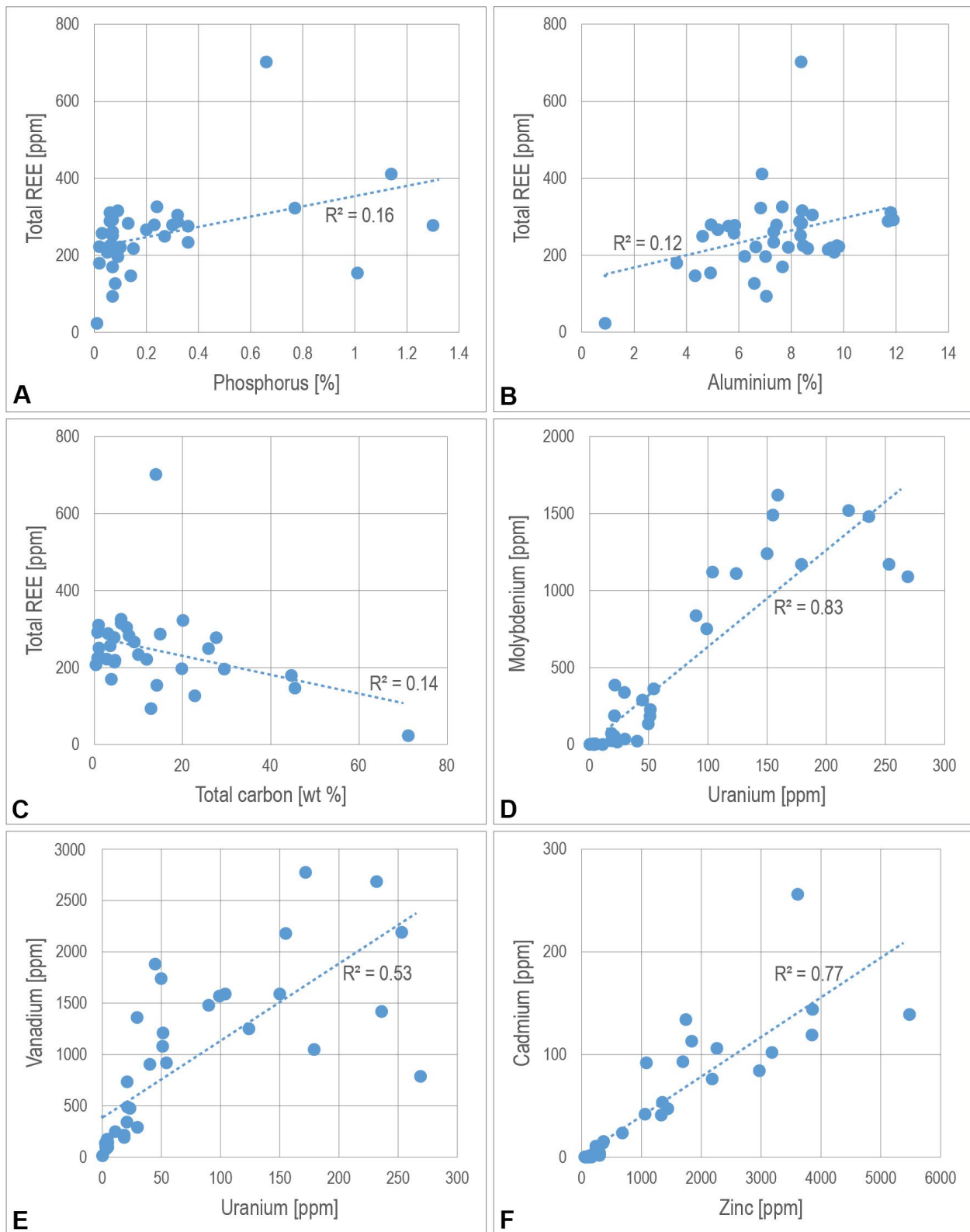


Figure 7. Scatter plots and regressions showing relationships between REE and other selected parameters.

Uranium (U)

The shales studied are characterized by high U content, averaging for marine shales from 70.8 ppm for the Excello Shale to 133.8 ppm for the Veale Shale. The “other shales” had the lowest U content at 3.3 ppm (Fig. 8A). The U content ranging from 25 ppm to more than 400 ppm was recorded for some of these shales in the previous study using the pXRF technique (Mastalerz et al., 2019). All these values are highly enriched compared to 2.7 ppm in UCC. Uranium in marine black shales is typically associated with organic matter but also can be incorporated into sedimentary phosphate (Swanson, 1961). The shales studied are rich in organic matter, and U is likely hosted by organic fractions of the shale intervals. Liu et al. (2020), in their study of Devonian New Albany Shale, discovered that amorphous organic matter was the main host of U, whereas other macerals such as alginite or vitrinite contribute very little to the total U amount. Liu et al. (2020) further suggested that, because primary organisms in the oceans do not have high U contents, U was likely incorporated into amorphous organic matter during early diagenesis when pore-water redox conditions and pH promoted reduction of U (VI) and subsequent incorporation into amorphous organic matter. Amorphous organic matter is the main component of the marine shales studied (Mastalerz et al., 2019), and this organic component is expected to be the most likely contributor of U in these shales.

Molybdenum (Mo)

Molybdenum is another element found to be very enriched in the studied shales (Fig. 8B). This element typically forms in anoxic conditions. Sediments in present-day marine euxinic environments show very strong Mo enrichment relative to the average upper continental crust (1.5 ppm) value (Dahl et al., 2013). Scott and Lyons (2012) suggested that Mo concentrations above 25 ppm indicated deposition under a euxinic water column in modern oceans. Mo is a valuable environmental indicator because its concentration does not change during diagenesis, unless there is enrichment from hydrothermal fluids (Dahl et al., 2013; Wirth et al., 2013). In the boreholes studied here, Mo concentration is very high (Fig. 8B), at places exceeding 1000 ppm. Among the shales studied, Mecca Quarry Shale is the most enriched in Mo (average 1103.8 ppm), followed by the Veale Shale (876.7 ppm). Such a high Mo content in these marine shales is likely a result of the combination of favorable anoxic depositional conditions and additional enrichment by Mo-bearing fluids of the Mississippi Valley-type that invaded the Illinois Basin in the Paleozoic or later (Hatch et al., 1976; Coveney et al., 1987). The significance of depositional factors

is supported by a strong positive correlation between Mo and U (Fig. 7D). The “other shales” category has the lowest Mo content (2.5 ppm), clearly an influence of non-marine horizons deposited in more oxygenated conditions.

Vanadium (V)

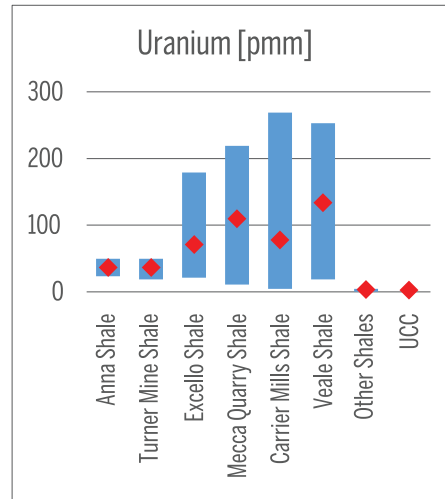
The content of vanadium is also highly enriched, with average values ranging from 111.7 ppm (in the “other shales”) to 1605.6 ppm in the Mecca Quarry Shale, compared to 135 ppm in UCC (Fig. 8C). Previous XRD, SEM, and TEM studies of the Mecca Quarry Shale showed that the majority of V (~65 %) is hosted by illite, and the remaining portion is associated with organic matter (Peacor et al., 2000). The authors further suggested that the Mississippi Valley-type brines were likely agents for diagenetic reactions that formed V-rich illite, and that prior to illitization, the majority of V might have been hosted by organic matter. This relationship to organic matter is also suggested by a relatively strong correlation between V and U (Fig. 7E).

Zinc (Zn), arsenic (As), and cadmium (Cd)

The shales studied are highly enriched in the content of Zn, As, and Cd (Fig. 9). The Mecca Quarry Shale is the most enriched in Zn, with some samples having contents as high as 5480 ppm (Fig. 9A). Considering 70 ppm as the value for UCC, the Excello Shale and the Veale Shale also have concentrations more than ten times higher. The As content is the highest in the Veale Shale, averaging 61.7 ppm, with some samples reaching more than 200 ppm (Fig. 9B)—again, highly enriched compared to 1.8 ppm in the UCC. Excello Shale, Mecca Quarry Shale, and Veale Shale are very enriched in Cd (76.1, 74.2, and 49.2 ppm on average, respectively), and the Carrier Mills Shale has the lowest average value of 8.5 ppm, still significantly enriched compared to 0.2 ppm in UCC (Fig. 9C). Mastalerz and Drobnik (2006) studied As, Cd, and Zn content in Pennsylvanian coals (the Danville and Springfield Coal Member) in Indiana and documented the following ranges for these elements on the whole coal basis: Zn – 10–292 ppm, As – 0.01–21 ppm, and Cd – 0.04 to less than 3 ppm. Clearly, these shales are much more enriched in these elements compared to the associated coals. Mastalerz and Drobnik (2006) suggested that Zn and Cd in coals were associated with sphalerite, whereas As was mainly associated with pyrite. A strong relationship between Zn and Cd for the shales studied (Fig. 7F) indeed suggests a close association between these two elements. Zn and Cd are chalcophile elements and their high concentration is considered an indicator of epigenetic mineralization (e.g., Gluskoter and Lindahl, 1973; Hatch et al., 1976), whereas As commonly occurs as a

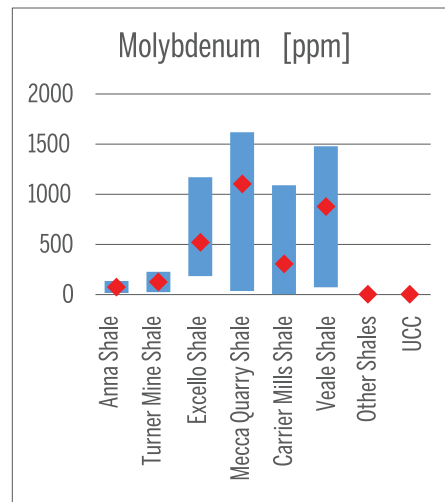
A

	Uranium [ppm]		
	min	max	average
Anna Shale	23.4	49.7	36.6
Turner Mine Shale	18.5	49.7	36.6
Excello Shale	21.3	179.0	70.8
Mecca Quarry Shale	11.0	219.0	109.7
Carrier Mills Shale	4.3	269.0	77.7
Veale Shale	18.5	253.0	133.8
Other Shales	0.3	4.7	3.3
UCC			2.7



B

	Molybdenum [ppm]		
	min	max	average
Anna Shale	16.0	135.0	75.5
Turner Mine Shale	25.0	228.0	126.5
Excello Shale	185.0	1170.0	520.2
Mecca Quarry Shale	36.0	1620.0	1103.8
Carrier Mills Shale	3.0	1090.0	306.6
Veale Shale	73.0	1480.0	876.7
Other Shales	2.0	5.0	2.5
UCC			1.5



C

	Vanadium [ppm]		
	min	max	average
Anna Shale	476.0	1740.0	1108.0
Turner Mine Shale	191.0	1210.0	700.5
Excello Shale	488.0	1880.0	1238.0
Mecca Quarry Shale	249.0	2770.0	1605.6
Carrier Mills Shale	174.0	919.0	625.4
Veale Shale	215.0	2190.0	1233.2
Other Shales	14.0	174.0	111.7
UCC			135.0

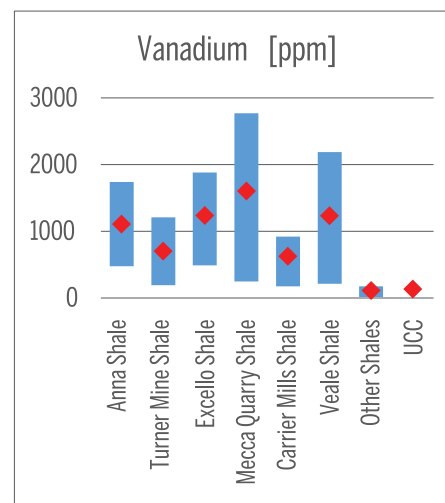
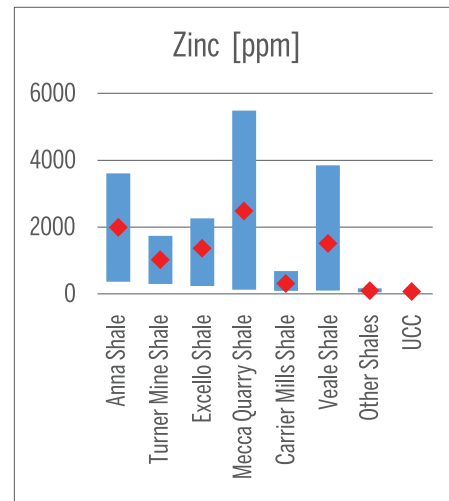


Figure 8. Table data and graphs of select elemental content (ranges and averages) in the shales studied. UCC –the upper continental crust.

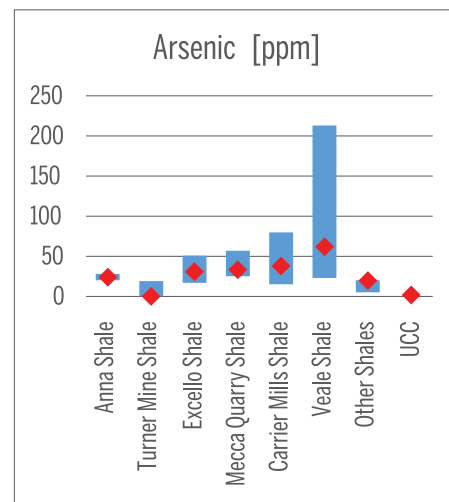
D

	Zinc [ppm]		
	min	Max	average
Anna Shale	365.0	3610.0	1987.5
Turner Mine Shale	296.0	1740.0	1018.0
Excello Shale	235.0	2260.0	1360.8
Mecca Quarry Shale	124.0	5480.0	2478.9
Carrier Mills Shale	89.0	681.0	309.8
Veale Shale	94.0	3850.0	1505.2
Other Shales	51.0	165.0	94.6
UCC			70.0



E

	Arsenium [ppm]		
	min	Max	average
Anna Shale	20.0	28.0	24.0
Turner Mine Shale	19.0	5.7	0.0
Excello Shale	17.0	51.0	30.8
Mecca Quarry Shale	25.0	57.0	33.1
Carrier Mills Shale	15.0	80.0	37.8
Veale Shale	23.0	213.0	61.7
Other Shales	5.0	20.0	19.5
UCC			1.8



F

	Cadmium [ppm]		
	min	Max	average
Anna Shale	15.4	256.0	135.7
Turner Mine Shale	1.9	170.1	68.0
Excello Shale	10.8	113.0	76.1
Mecca Quarry Shale	1.2	144.0	74.2
Carrier Mills Shale	0.2	23.6	8.5
Veale Shale	0.3	119.0	49.2
Other Shales	0.2	134.0	68.0
UCC			0.2

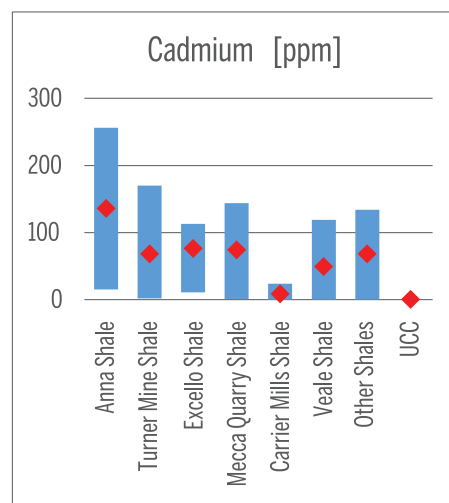


Figure 9. Table data and graphs of select elemental content (ranges and averages) in the shales studied. UCC –the upper continental crust.

solid phase in pyrite, and could be syngenetic or epigenetic in origin (e.g., Finkelman, 1982). For the shales studied, Zn and Cd could have been related to basinal brines, but it is also possible that later the shales functioned as sink beds for metals from Mississippi Valley-type brines (Coveney and Glascock, 1989). Similar to coal, pyrite is a possible host of As in the shales. We note that most of these shales are rich in framboidal pyrite (Mastalerz et al., 2019).

Comparison of pXRF to WDXRF data

As mentioned in the methods section, splits of all shale samples were analyzed for elemental composition using pXRF. Considering that pXRF is a fast and inexpensive technique that does not require complicated sample preparation, we wanted to assess its applicability for studying these shales. We emphasize that most of these shales were organic-matter-rich, and

large error was expected for most, especially minor, elements. Comparing elemental compositions obtained by pXRF to those using the WDXRF technique, a strong correlation was obtained for Al ($R^2=0.72$) and Si ($R^2=0.65$) (Fig. 10A, B). Results for Mg and Ca (Fig. 10C, D) were much less satisfactory; the relationships were much weaker than for the associated organic-matter-lean paleosols (Mastalerz et al., 2022). These observations indicate that pXRF can be successfully used to quickly obtain concentrations of Al and Si for organic-matter-rich shales, but for less abundant elements such as Mg (<2 %, Fig. 10) or Ca (<6 % for these shales, Fig. 10), pXRF results would have much lower confidence. One has to also remember that pXRF is a spot technique (8 mm diameter), and the more locations that are analyzed on a sample, the better the agreement that should be expected in comparison to the bulk sample analysis.

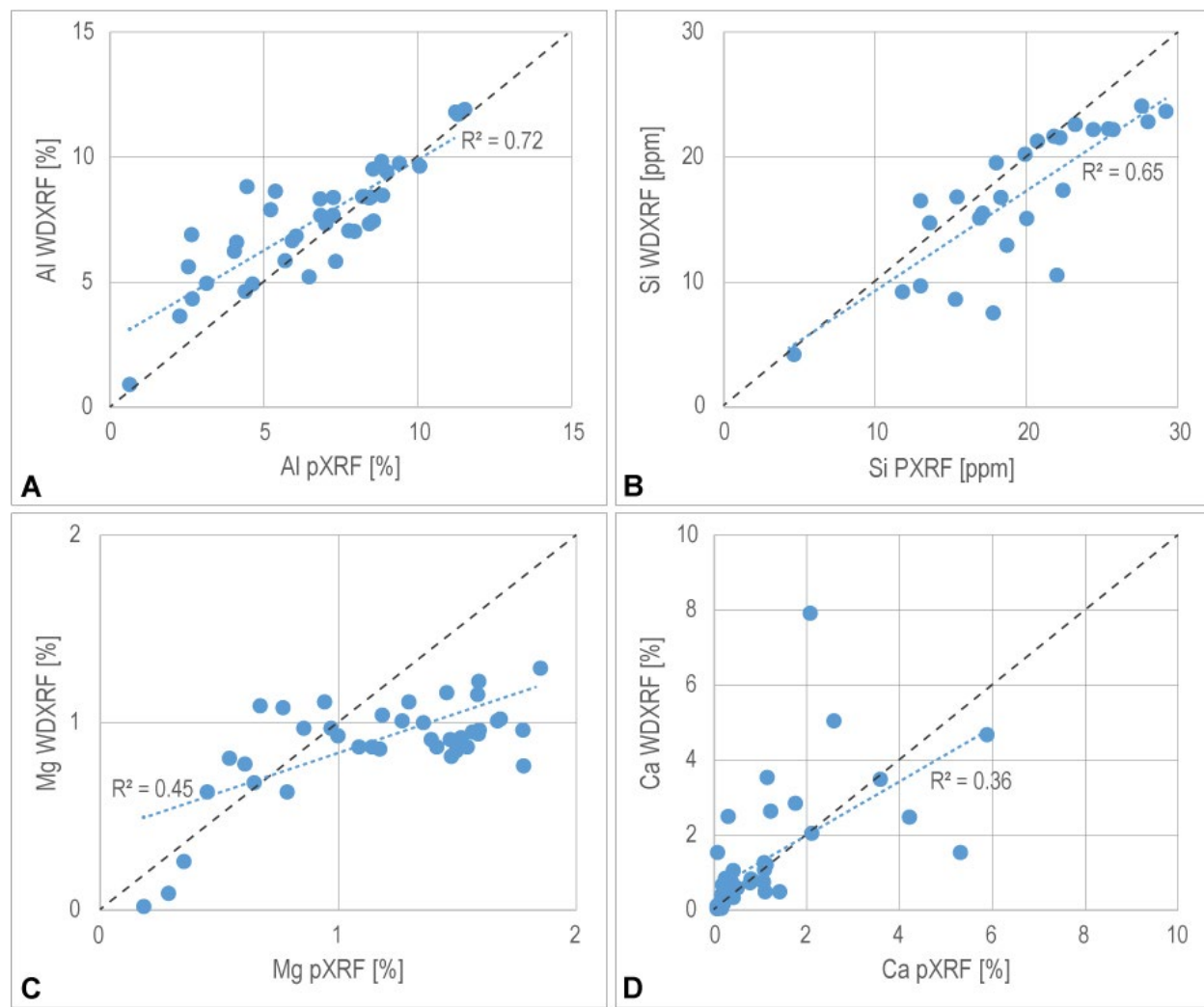


Figure 10. Scatter plots and regressions comparing pXRF and WDXRF elemental data. Black line shows 1:1 concentration.

CONCLUSIONS

This study provides new data on concentrations of selected critical elements (REE, U, Mo, V, Zn, As, and Cd) in Pennsylvanian black shales in Indiana. Based on data collected in 11 locations, the following conclusions are reached:

In marine shales, Mo and V concentrations are very high, at places exceeding 1000 ppm for Mo and 1600 for V. Among the six marine shales studied, the Mecca Quarry Shale is the richest in Mo (average 1103.8 ppm) and V (1605 ppm), followed by the Veale Shale and the Excello Shale, making them all valuable sources for these elements. Such high Mo and V contents in these marine shales likely resulted from the combination of favorable depositional conditions and additional enrichment by Mo-bearing fluids of the Mississippi Valley-type that invaded the Illinois Basin in the Paleozoic. In the non-marine shales, the concentration of Mo and V are low, only slightly above the values in the UCC.

The marine shales studied are highly enriched in concentrations of Zn, As, and Cd. The Mecca Quarry Shale is the most enriched in Zn, with some samples having more than 5000 ppm. Considering 70 ppm as the value for the UCC, the Excello Shale and the Veale Shale also have Zn concentrations more than ten times higher. The Excello Shale, Mecca Quarry Shale, and Veale Shale are all very enriched in Cd (76.1, 74.2, and 49.2 ppm on average, respectively), and the Carrier Mills Shale has the lowest average value of 8.5 ppm—still significantly enriched compared to 0.2 ppm in the UCC. Arsenic content is the highest in the Veal Shale, averaging 61.7 ppm, with some samples reaching more than 200 ppm, which is also highly enriched compared to 1.8 ppm in UCC. As already suggested in earlier studies, Zn and Cd concentrations were likely related to metals derived from basinal brines, but also later they might have functioned as sink beds for metals from Mississippi Valley-type brines. In turn, As is likely hosted by syngenetic pyrite abundant in these shales.

Concentrations of REE in the shales ranged from 231 to 701.8 ppm. Together with the previous data on Pennsylvanian shales showing a similar range, these values place below the 1000 ppm threshold to be considered a viable resource for REE. Although more research must be done on the associations and distribution controls in these organic-matter-rich marine black shales, our data suggest that REE are hosted by multiple fractions. This, in turn, suggests that significant efforts and resources would be needed to preconcentrate REE and ultimately make such shales a viable REE resource.

Comparison of elemental compositions obtained by pXRF to those using the WDXRF technique shows that

pXRF can be successfully used to measure concentrations of major elements such as Al and Si for organic-matter-rich shales, but less so for pXRF data from less abundant elements such as Mg or Ca.

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