

# Constraining the provenance of black shales using rare earth elements and neodymium isotopes, Midcontinent United States

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## ABSTRACT

We conducted research to determine neodymium model dates ( $T_{DM}$ ),  $\epsilon_{Nd}$  values, and the relative proportions of rare earth elements (REEs) of Paleozoic black shales from the Midcontinent United States to constrain their sediment sources. Twenty-one Cambrian to Pennsylvanian shale formations of the Illinois, Cherokee, Forest City, and Arkoma basins, the Ozark Dome, and the Ouachita Mountains were examined. Findings reveal that these midcontinental shales consist primarily of felsic detrital minerals that originated from the craton. The Cambrian Mt. Simon, Eau Claire, and Tunnel City shales of the northern Illinois Basin exhibit REE patterns and Nd isotopic signatures similar to those of the Ordovician Mazarn and Womble shales of the Ouachita Mountains, which indicates derivation from a similar sediment source. Sediment was likely derived from the Superior and/or Trans-Hudson cratonic provinces. The dominant sediment source shifted during deposition of the Middle Ordovician Womble Shale due to the uplift of the Appalachian Mountains during the Taconic orogeny, as suggested by the younger  $T_{DM}$  dates, less negative  $\epsilon_{Nd}$  values, and similar REE patterns compared to those of the older Cambrian and Early Ordovician shales. The Grenville province and Appalachian Basin remained the primary sediment source into the Pennsylvanian.

## INTRODUCTION

The presence of rare earth elements (REEs) within sedimentary rocks can serve as a tool for constraining sedimentary provenance and recycling processes (McLennan, 1989; Gleason et al., 1994).

This can be extended to black shales, if a sufficiently large dataset encompassing multiple shale units distributed across a broad region is available. This study provides a trace-element and isotopic survey of Paleozoic black shales from the Midcontinent United States (Fig. 1), with the aim of constraining the source, or multiple sources, of the sediments that comprise these shales and identifying potential patterns associated with metalliferous black shales using 14 REEs, plus yttrium (Y). Rare earth elements, particularly Nd isotopes, provide a tool for identifying how sediment is cycled from the craton in this analysis of 69 samples from 21 shale formations (Fig. 2). The samples include Cambrian to Pennsylvanian shales from the Ouachita Mountains, the Ozark Dome, and the Arkoma, Cherokee, Forest City, and Illinois basins. The black shales, which vary spatially and temporally, were selected for their proximity to various Mississippi Valley-type ore deposits in the Midcontinent United States or for having been described as organic-rich, metalliferous black shales (Coveney and Glascock, 1989; Coveney, 2003).

Shales can form in a variety of depositional environments in which energy is low enough to allow clay-sized sediment to settle out of the water column in sufficient quantities. These clay-sized particles may be minerals derived from a local or distal source and may carry with them geochemical signatures that are characteristic of their sources, such as a felsic igneous terrane from a passive continental margin. By analyzing the mineralogical compositions, Nd isotopic signatures, and REE patterns, it is possible to constrain the source—or sources—of sediments that contributed to the formation of these shales. Based on Nd isotopes, previous work by Gleason et al. (1994, 1995, 2002) showed that the Taconic orogeny is genetically linked to Middle to Late Ordovician shales in the Ouachita Mountains. Ouachita shales from the Early Ordovician have  $\epsilon_{Nd}$  values of approximately  $-15$  until the deposition of the

Womble Shale (Middle Ordovician), at which there is a shift to values near  $-8$  (Gleason et al., 2002). Gleason et al. (1994) presumed a northerly Cambrian–Early Ordovician sediment source(s). However, this source(s) is not well-constrained.  $\epsilon_{Nd}$  values of the cratonic provinces are generally more negative toward the Trans-Hudson and Superior provinces ( $\epsilon_{Nd} < -16$ ), while less negative values are present in the Grenville Appalachian Basin ( $\epsilon_{Nd} -7$  to  $-9$ ; Gleason et al., 2002; Fisher et al., 2010; Sattkoski et al., 2013; Lodge et al., 2015).

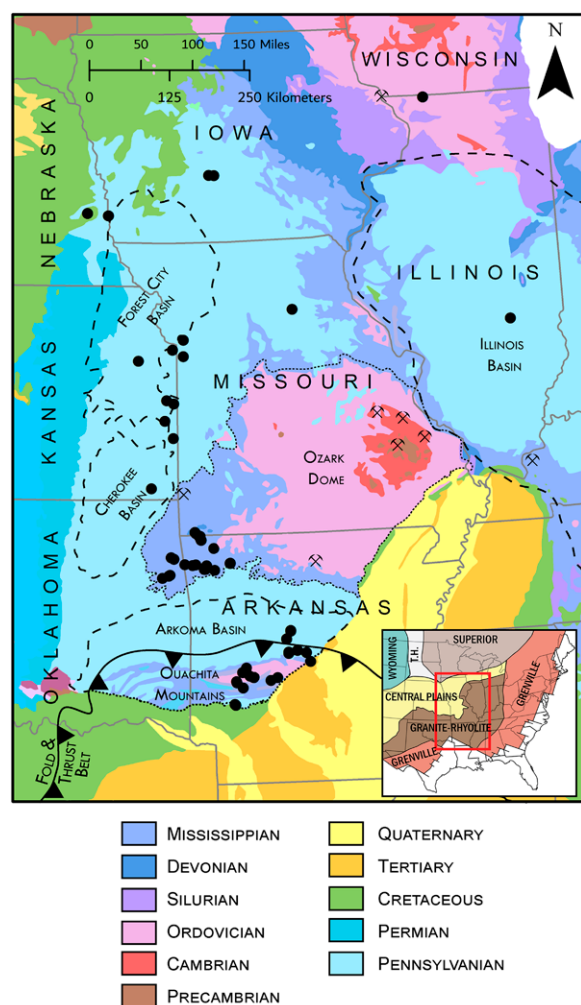
While interpretations of authigenic sediments based on REEs include depth of deposition (Grandjean et al., 1987), environmental effects on marine phosphates (McArthur and Walsh, 1984; Grandjean et al., 1988; Shields and Stille, 2001), environmental effects on REEs in marine sediments (Elderfield and Pagett, 1986), and paleoredox effects on REEs in marine sediments (German and Elderfield, 1990; Shields and Stille, 2001), the REE composition of detrital sediments generally represents the average composition of their provenance (McLennan, 1989). The use of REEs as a provenance indicator has been discussed and shows promising potential (Munksgaard et al., 2003). Specifically, neodymium isotopes ( $^{143}\text{Nd}/^{144}\text{Nd}$ ) have been used as an indicator of sediment provenance and recycling (Andersen and Samson, 1995; Patchett et al., 1999; Bayon et al., 2015).

## GEOLOGICAL SETTING

The Ozark Dome, situated in the central part of the study area, is an uplifted area of Precambrian ( $1.476 \pm 0.016$  Ga) granite and rhyolite, 1.38 Ga alkaline intrusions, and ca. 1.33 Ga mafic intrusions (Lowell and Young, 1999; Meert and Stuckey, 2002). These igneous rocks outcrop in the St. Francis Mountains of southeastern Missouri. Clastic and carbonate layers from the Cambrian to Carboniferous periods overlie these rocks as an asymmetrical structure, with Paleozoic layers tilting at less than a

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**Figure 1.** Sample localities (black dots) in the Midcontinent United States with basins (dashed lines), uplifts (dotted lines), the Ouachita fold-and-thrust belt, and regional mining districts (crossed picks). All samples are from outcrops, except for those from the central Illinois Basin (well cuttings) and northern Illinois border (cores). Generalized cratonic provinces are shown in inset map (modified from Fisher et al., 2010).

1° angle on its southwestern edge. The eastern margin terminates sharply along fault zones that include reverse faults, and the Reelfoot Rift, a late Proterozoic to Early Cambrian rift zone now buried under Cretaceous and Cenozoic sediments of the northern reaches of the Mississippi Embayment (Devera and Fraunfelder, 1988; Nelson and Zhang, 1991; Parrish and van Arsdale, 2004; Arsdale and Cupples, 2013), which separates the Ozark Dome from the Illinois Basin (Chinn and König, 1973; McBride and Nelson, 1999). These fault zones initiated during the early Middle Devonian and were preceded by the Reelfoot Rift. The southern Ozark Dome primarily features E-striking normal faults, along with a mix of NE-striking, strike-slip faults that formed during the Ouachita orogeny (Hudson, 2000). Two units were sampled in this region: the Chattanooga Shale (Devonian to Mississippian) and the Fayetteville Shale (Mississippian).

The Ouachita Mountains are situated along the Alleghanian–Ouachita–Marathon–Sonora fold-and-thrust belt, which extends from south-

western Texas, USA, and northern Mexico to the southern Appalachian Mountains. The Ouachita Mountains resulted from the transpressional orogeny of Laurentia and Gondwana during the early Carboniferous as the Laurentian plate subducted under the Gondwanan plate (Hatcher, 2002; Nance et al., 2010). The collision of Laurentia and Gondwana resulted in the Alleghanian orogeny, leading to a “zipper” effect as the sea closed from east to west and the orogeny continued along the Alleghanian–Ouachita–Marathon–Sonora fold-and-thrust belt (Hatcher, 2002). In response, some foreland basins developed along the northern periphery of the fold-and-thrust belt, such as the Arkoma and Black Warrior basins. These foreland basins were likely linked to the southern Appalachians and channeled sediment to the west along the southern margins of Laurentia (Gleason et al., 1994).

The Ouachita strata mainly comprise deep-water, turbiditic facies, which are dominated by sandstones and shales (Morris, 1971; Owen and Carozzi, 1986). Samples from the Ouachita

Mountains in this study include the Collier Shale (Upper Cambrian to Lower Ordovician), the Mazarn Shale (Lower Ordovician), the Womble Shale (Middle to Upper Ordovician), the Polk Creek Shale (Upper Ordovician), Stanley Shale (Meramecian to Chesterian Series, Mississippian), Jackfork Sandstone (Morrowan Series, Pennsylvanian), and Atoka Formation (Atokan Series, Pennsylvanian; Fig. 3). Samples of these units originated in Arkansas, with some formations studied less due to limited exposure, like the Collier Shale, which is the oldest unit exposed in Arkansas, USA (McFarland, 2004). The Jackfork Formation, which predates the Arkoma Basin’s formation, contains deep-water turbidites from the onset of the Ouachita orogeny, followed by the Atoka Formation, which comprises a significant portion of the basin’s sediment load (up to ~7620 m thick; Morris, 1971; Owen and Carozzi, 1986; McFarland, 2004).

The Illinois Basin originated from multiple tectonic events spanning Precambrian to Cambrian times and is notably associated with the Reelfoot Rift and the Rough Creek Graben following the breakup of a supercontinent (Klein and Hsui, 1987; Kolata and Nelson, 1990a, 1990b). The subsidence of this basin occurred during the Carboniferous and Permian due to compressional stresses from the Alleghanian and Ouachita orogenies (Klein and Hsui, 1987; Kolata and Nelson, 1990a, 1990b). The basin’s stratigraphic units generally dip southward toward the Reelfoot Rift and the Rough Creek Graben, with the Mt. Simon Sandstone typically overlaying the Precambrian basement rocks throughout much of the basin (Sargent, 1990). The Illinois Basin is thought to be likely linked to both the Appalachian foreland basin and the Arkoma Basin, with sediment being channeled to the west (Gleason et al., 1994). The Illinois Basin region includes several clastic and carbonate successions, including those we sampled: the Cambrian Mt. Simon Sandstone, Eau Claire Formation, and Tunnel City Group, as well as the Devonian to Mississippian New Albany Shale.

The Cherokee Basin and Forest City Basin, which span Oklahoma, Kansas, Missouri, Nebraska, and Iowa, USA, consist of clastic and carbonate formations. These basins, which are separated by the Bourbon Arch and primarily have been subsiding since the Cambrian era, experienced intensified subsidence during the Pennsylvanian due to intra-cratonic stresses triggered by the Alleghanian and Ouachita orogenies, mirroring the Illinois Basin (Anderson and Wells, 1968; Harris, 1985; Leighton and Kolata, 1990; Newell, 1995). The stratigraphic units sampled in these basins are Pennsylvanian.

|               |               | Illinois Basin       | Cherokee & Forest City Basins | Ozark Dome         | Ouachita Mountains |
|---------------|---------------|----------------------|-------------------------------|--------------------|--------------------|
| Carboniferous | Pennsylvanian |                      | Shawnee Group                 |                    |                    |
|               |               |                      | Heebner Shale                 |                    |                    |
|               |               |                      | Lansing Group                 |                    |                    |
|               |               |                      | Eudora Shale                  |                    |                    |
|               |               |                      | Vilas Shale                   |                    |                    |
|               |               |                      | Kansas City Group             |                    |                    |
|               |               |                      | Muncie Creek Sh               |                    |                    |
|               |               |                      | Stark Shale                   |                    |                    |
|               |               |                      | Hushpuckney Sh                |                    |                    |
|               |               |                      | Marmaton Group                |                    |                    |
| Mississippian |               |                      | Little Osage Sh.              |                    |                    |
|               |               |                      | Excello Shale                 |                    |                    |
|               |               |                      |                               | Fayetteville Shale | Stanley Shale      |
|               |               |                      |                               |                    |                    |
| Devonian      |               | New Albany Shale     |                               | Chattanooga Shale  |                    |
|               |               |                      |                               |                    |                    |
| Silurian      |               |                      |                               |                    |                    |
|               |               |                      |                               |                    |                    |
| Ordovician    |               |                      |                               |                    | Polk Creek Shale   |
|               |               |                      |                               |                    | Womble Shale       |
|               |               |                      |                               |                    | Mazarn Shale       |
|               |               |                      |                               |                    | Collier Shale      |
| Cambrian      |               | Tunnel City Group    |                               |                    |                    |
|               |               | Eau Claire Formation |                               |                    |                    |
|               |               | Mt. Simon Sandstone  |                               |                    |                    |
|               |               |                      |                               |                    |                    |

**Figure 2. Generalized stratigraphic columns of the relative ages of the shales (Sh) sampled in the Midcontinent United States.**

nian in age and vary in lithostratigraphic rank across the states, but they are generally referred to as a member within the states where they were sampled. These units include the Excello Shale; the Little Osage Shale Member of the Marmaton Group (Desmoinesian Series); the Hushpuckney, Stark, and Muncie Creek Shale Members of the Kansas City Group (Missourian Series); the Vilas and Eudora Shale of the Lansing Group (Missourian Series); and the Heebner Shale Member of the Shawnee Group (Virgilian Series).

## SAMPLING AND METHODOLOGY

### Sample Collection and Preparation

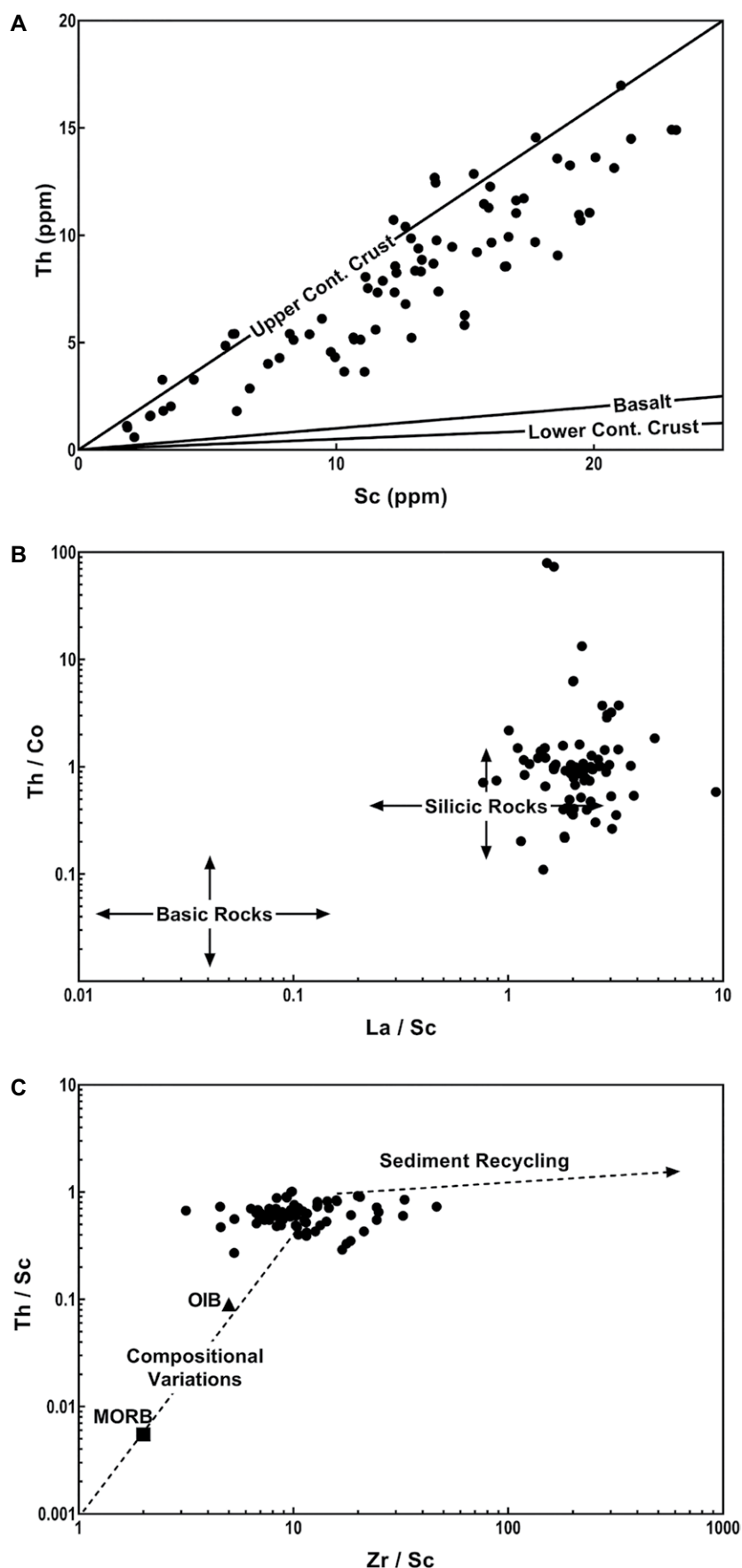
Our study analyzed a total of 69 shale samples from 21 shale formations located throughout the midcontinental region of the United States (Figs. 1 and 2). Samples were predominantly obtained from outcrops in Arkansas, Iowa, Kansas, Missouri, Nebraska, and Oklahoma

(see Table S1 in the Supplemental Material<sup>1</sup> for locations). Only fresh samples were collected, with preference given to samples extracted from behind the exposed surface of the outcrop to minimize weathering effects. Whenever possible, type sections or type localities were selected for sampling. The type localities of the following shales were sampled during August 2020: Stark Shale (Moore, 1932; Jewett, 1933), Hushpuckney Shale (Moore, 1932), Muncie Creek

Shale (Moore, 1932), and Fayetteville Shale (Simonds, 1891). The Excello Shale was sampled ~1.5 miles from the type section described in Searight (1955).

Four additional samples are from the Commonwealth Edison UPH-1 core in northern Illinois, USA (Wisconsin Geological and Natural History Survey [WGNHS] ID #33000331) and one additional sample is from the WGNHS Highway A Quarry 2 (H) core from southern Wisconsin, USA (WGNHS ID #25000529). The core samples were donated by the Wisconsin Geological and Natural History Survey to provide additional geochemical data for shales in the northern Mississippi River Valley. Samples from these cores include the Eau Claire (UPH-1 depth: 853 ft and 977 ft; H depth: 520 ft), Tunnel City (UPH-1 depth: 658 ft), and Mt. Simon (UPH-1 depth: 1363 ft) units and were included in a previous Pb isotopic study (Doe et al., 1983). One other sample, representing the New Albany Shale, originated from well cuttings at an unknown depth from the Morris

<sup>1</sup>Supplemental Material. Table S1: Locality information for each sample. Table S2: Detailed mineralogical compositions of each sample based on X-ray diffraction measurements. Table S3: Trace-element concentrations in each sample (in ppm). Table S4: Trace-element concentration uncertainty (1σ). Table S5: Calculated dissimilarity values of each sample relative to other samples. Lower values correspond with increasing similarity in rare earth element patterns. Please visit <https://doi.org/10.1130/GSAB.S.25086050> to access the supplemental material, and contact [editing@geosociety.org](mailto:editing@geosociety.org) with any questions.



**Figure 3.** (A) Th/Sc ratios indicating provenance of the shale mineral assemblages. Typical chemical compositions of the upper continental (cont.) crust (Th/Sc = 0.8), basalt (Th/Sc = 0.1), and lower continental crust (Th/Sc = 0.05; from Taylor and McLennan, 2003). (B) Th/Co versus La/Sc plot depicting the relative concentrations in basic and silicic rocks (from Taylor and McLennan, 2003). (C) Th/Sc versus Zr/Sc plot depicting the general evolutionary trends of igneous mid-oceanic-ridge basalt (MORB) and oceanic-island basalt (OIB) and their similarities to the shales (McLennan et al., 1993; MORB and OIB data are from Taylor and McLennan, 2003).

#1 well drilled by the Ceja Corporation in 2012 in Shelby County, Illinois (API #12-173-24362). Seven shale units sampled in this study have one sample each (Mt. Simon and Tunnel City [Cambrian]; Collier [Ordovician]; New Albany [Devonian]; and Muncie Creek, Stark, and Vilas [Pennsylvanian]). Samples were rinsed with deionized water, dried, and then crushed into fragments (<1 cm). The least-weathered fragments were powdered in an alumina-ceramic dish using a Spex SamplePrep Shatterbox that yielded various quantities of powdered samples. All further processing of the samples was conducted in a class 100 clean room at the University of Arkansas, Fayetteville, Arkansas, USA. All labware used for chemical processing of the samples was acid cleaned to minimize possible contamination. All acids used in the chemical processing were previously distilled in dedicated HNO<sub>3</sub> and HCl Savillex DST-1000 acid purification systems.

### X-Ray Diffraction

The mineralogical composition of 25 dry, untreated, powdered samples was analyzed using a Philips PW1830 double system diffractometer at the University of Arkansas Institute for Nanoscience and Engineering. Samples were placed in a fixed stage, and diffraction patterns were obtained using Cu K- $\alpha$ 1 wavelength at 15.40598 Å and Cu K- $\alpha$ 2 wavelength at 15.44426 Å, at 2 $\theta$  angles ranging from 10.02° to 69.98° with increments of 0.02° and a step time of ~50 s per degree. Diffraction data were interpreted with Profex version 5.0 software using Crystallography Open Database (COD) structure files. Semiquantitative compositional percentages were estimated using selected COD structure files for each mineral phase. To maintain consistency, the same structure files of each mineral phase were used for all samples. Clays and micas, which can be difficult

to distinguish quantitatively without treatments, were considered as phyllosilicates, and feldspar minerals were broadly grouped together as the feldspar group.

# Trace Elements

A total of 100 mg of powder from each sample was placed in a PFA (perfluoroalkoxy) liner of a Parr acid digestion vessel (model #4749). A volume of 2 mL of reverse aqua regia (3 distilled HNO<sub>3</sub>:1 distilled HCl) was added to each sample in a laminar flow fume hood. Two mL of concentrated hydrofluoric acid was also added to each sample, and they were then left uncovered for 10 min to vent volatile gases. The samples in the Parr liners were inserted into the Parr acid digestion vessels and tightened. The vessels were placed in a Lindberg Blue M 828 oven and heated to 200 °C for eight hours. The vessels were allowed to cool for 24 h, and the liners were extracted and placed in a laminar flow fume hood in the clean room. The solution in each liner was pipetted into a clean 30 mL PFA vial and dried at 90 °C. Each sample had 4 mL of distilled HNO<sub>3</sub> added, which was heated to 150 °C for eight hours while tightly capped, and subsequently dried at 90 °C. Four mL of distilled HCl was then added and heated to 150 °C for eight hours while capped, and dried at 90 °C. This process of

adding HNO<sub>3</sub> and HCl was repeated once more. After each addition of heat, the samples cooled to room temperature, and after each addition of acid, the samples were allowed to remain uncovered for 10 minutes to remove any volatile gases.

Elemental concentration data were acquired by redissolving the dried, digested samples in 2 mL 2% HNO<sub>3</sub> at 150 °C for 1 h. Then, a volume of 0.1 mL of each sample solution was transferred to clean 5 mL centrifuge tubes and diluted with 2.9 mL 2% HNO<sub>3</sub>. The samples were analyzed on a Thermo Scientific iCAP Q inductively coupled plasma-mass spectrometer (ICP-MS) at the University of Arkansas Trace Element and Radiogenic Isotope Lab. The samples were analyzed for REEs and elements associated with sediment provenance and cycling (Co, Sc, Zr, and Th). In addition, two sets of ICP-MS multielement solution standards were made using 10 ppm Inorganic Ventures IV-ICPMS-71B and 10 ppm High Purity Standards ICP-MS-68A-A-100 diluted to multiple concentrations (500 ppb, 100 ppb, 50 ppb, 10 ppb, 5 ppb, and 1 ppb, and 10 ppt). Seven duplicate samples and five replicate samples were also analyzed; these samples were chosen based on age, number of samples for each shale, and total mass of each sample available.

Extraction of Nd followed the column chemistry protocol outlined in Pin et al. (2014). Upon

extraction of Nd, the samples were dried down at 80 °C. Prior to multicollector (MC)-ICP-MS analysis, they were capped and redissolved in 2 mL 2% HNO<sub>3</sub> at room temperature, then diluted with 2% HNO<sub>3</sub>. The samples were run on a Nu Plasma MC-ICP-MS at the Trace Element and Radiogenic Isotope Laboratory at the University of Arkansas. For each sample, 60 Nd isotopic ratio readings were recorded and averaged. Raw isotopic data were corrected using sample-standard bracketing along with using the JNdi Nd standard (<sup>143</sup>Nd/<sup>144</sup>Nd = 0.512115). Neodymium isotopes were age corrected to the approximate time of deposition (Tables 1 and 2) and normalized to the chondritic uniform reservoir (CHUR), which is signified as ε<sub>Nd</sub>, using the formula from Dickin (2005), the CHUR constants for <sup>143</sup>Nd/<sup>144</sup>Nd<sub>0</sub> (0.512638) and <sup>147</sup>Sm/<sup>144</sup>Nd<sub>0</sub> (0.1967), and the decay constant of <sup>147</sup>Sm (6.54 × 10<sup>-12</sup>). The depleted mantle model dates (T<sub>DM</sub>) of the shales were calculated for each sample to derive an estimated average date of the minerals in the whole rock. This was done using an abundance of 15% for <sup>147</sup>Sm, 23.8% for <sup>144</sup>Nd, and the T<sub>DM</sub> formula from DePaolo (1981). Values for the decay constant of <sup>147</sup>Sm (6.54 × 10<sup>-12</sup>) and the depleted mantle ratios of <sup>143</sup>Nd/<sup>144</sup>Nd (0.5132) and <sup>147</sup>Sm/<sup>144</sup>Nd (0.2148) are from Reiners et al. (2018).

TABLE 1. NEODYMIUM AND SAMARIUM DATA OF CAMBRIAN TO DEVONIAN SAMPLES

| Shale unit  | Sample ID       | Approximate age (Ma) | Nd (ppm) | Sm (ppm) | <sup>143</sup> Nd/ <sup>144</sup> Nd measured | <sup>143</sup> Nd/ <sup>144</sup> Nd age-corrected | ε <sub>Nd</sub> | <sup>147</sup> Sm/ <sup>144</sup> Nd present-day | T <sub>DM</sub> (Ga) |
|-------------|-----------------|----------------------|----------|----------|-----------------------------------------------|----------------------------------------------------|-----------------|--------------------------------------------------|----------------------|
| Chattanooga | CS1             | 360                  | 27.07    | 5.31     | 0.51198 ± 4.56 × 10 <sup>-6</sup>             | 0.51170                                            | -9.231          | 0.12285                                          | 1.94                 |
| Chattanooga | CS2             | 360                  | 32.20    | 6.28     | 0.51198 ± 4.78 × 10 <sup>-6</sup>             | 0.51170                                            | -9.171          | 0.12327                                          | 1.95                 |
| Chattanooga | CS3             | 360                  | 35.83    | 7.01     | 0.51194 ± 4.81 × 10 <sup>-6</sup>             | 0.51167                                            | -9.878          | 0.11937                                          | 1.94                 |
| Chattanooga | CS4             | 360                  | 26.73    | 5.06     | 0.51193 ± 1.59 × 10 <sup>-5</sup>             | 0.51166                                            | -10.139         | 0.12219                                          | 2.01                 |
| Chattanooga | CS5             | 360                  | 34.51    | 6.69     | 0.51194 ± 3.49 × 10 <sup>-6</sup>             | 0.51168                                            | -9.657          | 0.11701                                          | 1.88                 |
| Chattanooga | CS6             | 360                  | 33.83    | 6.28     | 0.51200 ± 2.89 × 10 <sup>-5</sup>             | 0.51170                                            | -9.239          | 0.13370                                          | 2.16                 |
| Chattanooga | CS7             | 360                  | 47.74    | 10.13    | 0.51196 ± 4.86 × 10 <sup>-6</sup>             | 0.51169                                            | -9.390          | 0.11937                                          | 1.90                 |
| Chattanooga | CS8             | 360                  | 30.11    | 5.70     | 0.51195 ± 1.92 × 10 <sup>-5</sup>             | 0.51168                                            | -9.617          | 0.11786                                          | 1.89                 |
| Chattanooga | CS9             | 360                  | 31.06    | 5.88     | 0.51198 ± 3.14 × 10 <sup>-6</sup>             | 0.51172                                            | -8.847          | 0.11279                                          | 1.76                 |
| Chattanooga | CS10B           | 360                  | 33.47    | 6.26     | 0.51191 ± 6.45 × 10 <sup>-6</sup>             | 0.51169                                            | -9.484          | 0.09928                                          | 1.63                 |
| Chattanooga | CS11            | 360                  | 35.74    | 6.40     | 0.51199 ± 3.29 × 10 <sup>-5</sup>             | 0.51173                                            | -8.737          | 0.11516                                          | 1.78                 |
| Chattanooga | CS12            | 360                  | 30.98    | 4.88     | 0.51197 ± 3.85 × 10 <sup>-6</sup>             | 0.51170                                            | -9.181          | 0.11730                                          | 1.85                 |
| Chattanooga | CS13            | 360                  | 37.88    | 6.92     | 0.51192 ± 4.56 × 10 <sup>-6</sup>             | 0.51165                                            | -10.217         | 0.11775                                          | 1.94                 |
| New Albany  | Ceja Morris #1  | 360                  | 37.84    | 7.04     | 0.51206 ± 1.70 × 10 <sup>-5</sup>             | 0.51178                                            | -7.668          | 0.12328                                          | 1.82                 |
| Polk Creek  | PC1             | 445                  | 36.13    | 6.75     | 0.51220 ± 1.85 × 10 <sup>-5</sup>             | 0.51187                                            | -3.881          | 0.11899                                          | 1.52                 |
| Polk Creek  | Polk Creek 1    | 445                  | 19.85    | 3.88     | 0.51202 ± 3.04 × 10 <sup>-5</sup>             | 0.51167                                            | -7.750          | 0.12692                                          | 1.96                 |
| Polk Creek  | Polk Creek 1-D* | 445                  | 19.00    | 3.72     | 0.51205 ± 3.44 × 10 <sup>-5</sup>             | 0.51169                                            | -7.371          | 0.12966                                          | 1.97                 |
| Womble      | Womble 1        | 460                  | 5.44     | 1.10     | 0.51140 ± 1.63 × 10 <sup>-5</sup>             | 0.51112                                            | -18.271         | 0.09882                                          | 2.23                 |
| Womble      | Womble 2        | 460                  | 5.55     | 1.14     | 0.51199 ± 3.14 × 10 <sup>-5</sup>             | 0.51170                                            | -6.952          | 0.10159                                          | 1.57                 |
| Womble      | Womble 3        | 460                  | 5.13     | 0.97     | 0.51195 ± 1.80 × 10 <sup>-5</sup>             | 0.51167                                            | -7.668          | 0.10108                                          | 1.61                 |
| Womble      | Womble 3-D*     | 460                  | 5.23     | 0.96     | 0.51157 ± 7.48 × 10 <sup>-6</sup>             | 0.51120                                            | -16.699         | 0.12912                                          | 2.81                 |
| Mazarn      | Mazarn 1        | 475                  | 24.47    | 3.84     | 0.51172 ± 4.22 × 10 <sup>-5</sup>             | 0.51138                                            | -13.334         | 0.12067                                          | 2.32                 |
| Mazarn      | Mazarn 2        | 475                  | 5.03     | 0.81     | 0.51163 ± 2.90 × 10 <sup>-5</sup>             | 0.51129                                            | -14.939         | 0.11896                                          | 2.42                 |
| Mazarn      | Mazarn 3        | 475                  | 5.20     | 0.83     | 0.51131 ± 3.85 × 10 <sup>-5</sup>             | 0.51098                                            | -21.046         | 0.11566                                          | 2.83                 |
| Mazarn      | Mazarn 4        | 475                  | 27.84    | 5.70     | 0.51165 ± 2.50 × 10 <sup>-5</sup>             | 0.51131                                            | -14.641         | 0.12066                                          | 2.43                 |
| Collier     | Collier CS1     | 485                  | 5.12     | 0.98     | 0.51185 ± 1.77 × 10 <sup>-5</sup>             | 0.51149                                            | -10.265         | 0.11854                                          | 2.06                 |
| Tunnel City | UPH-658         | 510                  | 7.26     | 1.37     | 0.51134 ± 1.48 × 10 <sup>-5</sup>             | 0.51118                                            | -18.821         | 0.10182                                          | 2.43                 |
| Eau Claire  | Hwy A2 520      | 510                  | 3.84     | 0.70     | 0.51133 ± 1.22 × 10 <sup>-5</sup>             | 0.51115                                            | -19.637         | 0.11010                                          | 2.65                 |
| Eau Claire  | UPH-853         | 510                  | 11.56    | 2.21     | 0.51141 ± 1.27 × 10 <sup>-5</sup>             | 0.51127                                            | -16.614         | 0.08620                                          | 2.07                 |
| Eau Claire  | UPH-977         | 510                  | 7.73     | 1.45     | 0.51131 ± 2.11 × 10 <sup>-5</sup>             | 0.51118                                            | -18.529         | 0.08803                                          | 2.21                 |
| Mt. Simon   | UPH-1363        | 515                  | 7.72     | 1.45     | 0.51112 ± 9.90 × 10 <sup>-6</sup>             | 0.51097                                            | -22.876         | 0.09854                                          | 2.65                 |

\*Duplicate sample.

TABLE 2. NEODYMIUM AND SAMARIUM DATA OF CARBONIFEROUS SHALE SAMPLES

| Shale unit   | Sample ID         | Approximate age (Ma) | Nd (ppm) | Sm (ppm) | <sup>143</sup> Nd/ <sup>144</sup> Nd measured | <sup>143</sup> Nd/ <sup>144</sup> Nd age-corrected | ε <sub>Nd</sub> | <sup>147</sup> Sm/ <sup>144</sup> Nd present-day | T <sub>DM</sub> (Ga) |
|--------------|-------------------|----------------------|----------|----------|-----------------------------------------------|----------------------------------------------------|-----------------|--------------------------------------------------|----------------------|
| Heebner      | 9 Heebner         | 300                  | 10.78    | 1.93     | 0.51194 ± 7.17 × 10 <sup>-6</sup>             | 0.51172                                            | -10.293         | 0.11285                                          | 1.82                 |
| Heebner      | 13 Heebner        | 300                  | 24.85    | 4.81     | 0.51195 ± 9.73 × 10 <sup>-6</sup>             | 0.51172                                            | -10.374         | 0.12199                                          | 1.97                 |
| Eudora       | 15 Eudora         | 305                  | 27.77    | 5.46     | 0.51203 ± 2.01 × 10 <sup>-5</sup>             | 0.51179                                            | -8.866          | 0.12271                                          | 1.86                 |
| Eudora       | 21 Eudora         | 305                  | 34.70    | 6.76     | 0.51195 ± 3.58 × 10 <sup>-6</sup>             | 0.51174                                            | -9.839          | 0.10796                                          | 1.72                 |
| Vilas        | 15 Vilas          | 305                  | 10.91    | 1.87     | 0.51204 ± 5.23 × 10 <sup>-6</sup>             | 0.51181                                            | -8.422          | 0.11867                                          | 1.76                 |
| Muncie Creek | 11-1 Muncie Creek | 305                  | 24.80    | 4.67     | 0.51202 ± 1.87 × 10 <sup>-5</sup>             | 0.51178                                            | -9.064          | 0.12280                                          | 1.87                 |
| Muncie Creek | 11-2 Muncie Creek | 305                  | 16.10    | 3.14     | 0.51199 ± 1.60 × 10 <sup>-5</sup>             | 0.51176                                            | -9.535          | 0.12076                                          | 1.89                 |
| Stark        | 2 Stark           | 305                  | 11.26    | 2.16     | 0.51215 ± 6.23 × 10 <sup>-6</sup>             | 0.51192                                            | -6.394          | 0.12280                                          | 1.66                 |
| Hushpuckney  | 5 Hushpuckney     | 305                  | 76.12    | 14.53    | 0.51197 ± 1.03 × 10 <sup>-5</sup>             | 0.51174                                            | -9.779          | 0.11787                                          | 1.86                 |
| Hushpuckney  | 6 Hushpuckney     | 305                  | 19.21    | 3.59     | 0.51209 ± 7.26 × 10 <sup>-6</sup>             | 0.51185                                            | -7.798          | 0.12602                                          | 1.83                 |
| Hushpuckney  | 8 Hushpuckney     | 305                  | 49.77    | 9.95     | 0.51190 ± 1.22 × 10 <sup>-4</sup>             | 0.51169                                            | -10.813         | 0.11051                                          | 1.82                 |
| Hushpuckney  | 8-D Hushpuckney*  | 305                  | 5.51     | 0.97     | 0.51206 ± 5.24 × 10 <sup>-5</sup>             | 0.51184                                            | -7.886          | 0.11263                                          | 1.63                 |
| Hushpuckney  | 20 Hushpuckney    | 305                  | 20.52    | 3.91     | 0.51204 ± 1.43 × 10 <sup>-5</sup>             | 0.51181                                            | -8.530          | 0.12000                                          | 1.79                 |
| Little Osage | 3 Little Osage    | 310                  | 7.03     | 1.26     | 0.51208 ± 3.21 × 10 <sup>-5</sup>             | 0.51186                                            | -7.362          | 0.11475                                          | 1.63                 |
| Little Osage | 16A Little Osage  | 310                  | 10.69    | 1.95     | 0.51195 ± 1.06 × 10 <sup>-5</sup>             | 0.51173                                            | -9.954          | 0.11154                                          | 1.78                 |
| Excello      | 1 Excello         | 310                  | 15.17    | 2.69     | 0.51235 ± 4.48 × 10 <sup>-5</sup>             | 0.51217                                            | -1.386          | 0.09403                                          | 1.01                 |
| Excello      | 17 Excello        | 310                  | 7.40     | 1.10     | 0.51193 ± 2.61 × 10 <sup>-5</sup>             | 0.51172                                            | -10.032         | 0.10431                                          | 1.69                 |
| Excello      | 19 Excello        | 310                  | 10.01    | 1.66     | 0.51200 ± 2.42 × 10 <sup>-5</sup>             | 0.51180                                            | -8.618          | 0.10564                                          | 1.60                 |
| Atoka        | Atoka 2           | 315                  | 7.35     | 1.23     | 0.51196 ± 1.52 × 10 <sup>-5</sup>             | 0.51171                                            | -9.978          | 0.12190                                          | 1.96                 |
| Atoka        | LA1Sh             | 315                  | 24.25    | 4.59     | 0.51198 ± 9.75 × 10 <sup>-6</sup>             | 0.51173                                            | -9.601          | 0.12423                                          | 1.97                 |
| Atoka        | LA2Sh             | 315                  | 20.38    | 4.02     | 0.51197 ± 8.85 × 10 <sup>-6</sup>             | 0.51171                                            | -9.969          | 0.12611                                          | 2.04                 |
| Atoka        | LA2Sh-D*          | 315                  | 28.93    | 5.79     | 0.51198 ± 8.86 × 10 <sup>-6</sup>             | 0.51173                                            | -9.633          | 0.12453                                          | 1.98                 |
| Atoka        | UA1Sh             | 315                  | 29.59    | 5.85     | 0.51196 ± 1.27 × 10 <sup>-5</sup>             | 0.51172                                            | -9.818          | 0.11935                                          | 1.90                 |
| Jackfork     | LJ1               | 315                  | 25.52    | 4.94     | 0.51206 ± 2.77 × 10 <sup>-5</sup>             | 0.51180                                            | -8.271          | 0.13153                                          | 1.99                 |
| Jackfork     | MJ1               | 315                  | 31.81    | 6.15     | 0.51197 ± 1.46 × 10 <sup>-5</sup>             | 0.51173                                            | -9.518          | 0.11917                                          | 1.87                 |
| Jackfork     | MJ2               | 315                  | 28.11    | 5.63     | 0.51200 ± 1.09 × 10 <sup>-5</sup>             | 0.51174                                            | -9.271          | 0.12427                                          | 1.94                 |
| Jackfork     | UJ1Sh             | 315                  | 38.33    | 7.25     | 0.51198 ± 1.27 × 10 <sup>-5</sup>             | 0.51173                                            | -9.528          | 0.12188                                          | 1.92                 |
| Jackfork     | UJ2Sh             | 315                  | 28.24    | 5.57     | 0.51197 ± 1.32 × 10 <sup>-5</sup>             | 0.51171                                            | -9.899          | 0.12632                                          | 2.03                 |
| Fayetteville | FS1L              | 325                  | 13.88    | 2.90     | 0.51200 ± 3.91 × 10 <sup>-6</sup>             | 0.51174                                            | -9.426          | 0.12868                                          | 2.04                 |
| Fayetteville | FS2U              | 325                  | 48.10    | 9.82     | 0.51184 ± 1.86 × 10 <sup>-5</sup>             | 0.51163                                            | -11.579         | 0.10568                                          | 1.83                 |
| Fayetteville | FS3               | 325                  | 31.65    | 5.31     | 0.51192 ± 1.26 × 10 <sup>-5</sup>             | 0.51167                                            | -10.809         | 0.12319                                          | 1.05                 |
| Fayetteville | FS4               | 325                  | 38.02    | 7.43     | 0.51184 ± 3.97 × 10 <sup>-6</sup>             | 0.51167                                            | -10.744         | 0.10444                                          | 1.81                 |
| Fayetteville | FS6L              | 325                  | 25.71    | 4.26     | 0.51197 ± 2.47 × 10 <sup>-5</sup>             | 0.51166                                            | -10.933         | 0.12498                                          | 2.01                 |
| Fayetteville | FS7L              | 325                  | 34.20    | 6.78     | 0.51191 ± 3.79 × 10 <sup>-6</sup>             | 0.51177                                            | -8.849          | 0.09499                                          | 1.58                 |
| Fayetteville | FS8UU             | 325                  | 39.18    | 5.90     | 0.51197 ± 5.87 × 10 <sup>-6</sup>             | 0.51185                                            | -7.200          | 0.14665                                          | 2.64                 |
| Fayetteville | FS9LU             | 325                  | 20.30    | 4.72     | 0.51194 ± 4.05 × 10 <sup>-6</sup>             | 0.51170                                            | -10.142         | 0.13664                                          | 2.36                 |
| Fayetteville | FS10L             | 325                  | 28.05    | 6.08     | 0.51200 ± 3.74 × 10 <sup>-6</sup>             | 0.51180                                            | -8.189          | 0.11413                                          | 1.74                 |
| Fayetteville | FS11              | 325                  | 44.53    | 8.06     | 0.51212 ± 3.95 × 10 <sup>-6</sup>             | 0.51190                                            | -6.237          | 0.13358                                          | 1.93                 |
| Stanley      | Stanley 1         | 330                  | 61.53    | 13.04    | 0.51210 ± 1.56 × 10 <sup>-5</sup>             | 0.51184                                            | -7.398          | 0.12726                                          | 1.83                 |
| Stanley      | Stanley 2         | 330                  | 26.19    | 5.29     | 0.51202 ± 1.69 × 10 <sup>-5</sup>             | 0.51178                                            | -8.669          | 0.12070                                          | 1.83                 |
| Stanley      | Stanley 3         | 330                  | 20.20    | 3.87     | 0.51188 ± 2.31 × 10 <sup>-5</sup>             | 0.51165                                            | -11.083         | 0.11304                                          | 1.90                 |
| Stanley      | Stanley 4         | 330                  | 16.69    | 2.99     | 0.51198 ± 9.12 × 10 <sup>-6</sup>             | 0.51173                                            | -9.500          | 0.12024                                          | 1.89                 |
| Stanley      | Stanley 4-D*      | 330                  | 46.70    | 8.91     | 0.51201 ± 8.31 × 10 <sup>-6</sup>             | 0.51176                                            | -8.937          | 0.12352                                          | 1.90                 |

\*Duplicate sample.

## REE Pattern Analysis

To assess the possibility of genetic relationships in the sediment that could be used as an indicator of sediment source, the Post-Archean Australian Shale (PAAS)-normalized REE pattern of each sample was compared with those of all analyzed samples using the following equation:

$$\text{Dissimilarity} = \frac{\left| \frac{\text{La}_A}{\sum \text{REE}_A} - \frac{\text{La}_B}{\sum \text{REE}_B} \right| + \left| \frac{\text{Ce}_A}{\sum \text{REE}_A} - \frac{\text{Ce}_B}{\sum \text{REE}_B} \right| + \dots + \left| \frac{\text{Lu}_A}{\sum \text{REE}_A} - \frac{\text{Lu}_B}{\sum \text{REE}_B} \right|}{\text{total number of elements}} \quad (1),$$

where A and B represent two samples being compared with one another, and La<sub>A</sub>, La<sub>B</sub>, Ce<sub>A</sub>, Ce<sub>B</sub>, etc., represent the concentration of specific REEs in sample A and sample B. In this study, a total of 15 elements (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Y) were analyzed. This equation provides a simple approach for discerning the average difference between the proportions of REEs within two REE + Y patterns as an alternative to statistical correlation methods (e.g., multivariate comparisons, such as a principal component analysis), as well as a novel method for REE analysis of shales.

## RESULTS

The X-ray diffraction (XRD) results show that quartz, feldspars, and phyllosilicates are the major constituents of nearly all samples, and most samples have relatively similar percent-

ages (Table S2 provides detailed percentages); quartz averages 30.0% (and ranges from 0.0% to 89.8%), feldspars average 17.6% (and range from 3.2% to 50.4%), and phyllosilicates average 41.8% (and range from 5.9% to 57.5%). Other minerals are present in trace amounts, although the Stark Shale has 19.9% fluorapatite, which concentrates the REEs.

The Th/Sc ratios of the shale samples analyzed range from 0.27 to 1.01 (average 0.63) and more closely relate to the upper continental crust. Those with the lowest Th/Sc ratios are the shales from the Atoka Formation (0.33–0.43), the Eau Claire Formation (0.29–0.55), and the Mt. Simon Sandstone (0.35). These samples might have had a limited amount of mafic/orogenic input, but this cannot be assessed from the Th/Sc proxy. Additionally, the Mazarn Shale has both the lowest and highest Th/Sc ratios (0.27 and 1.01, respectively) of the

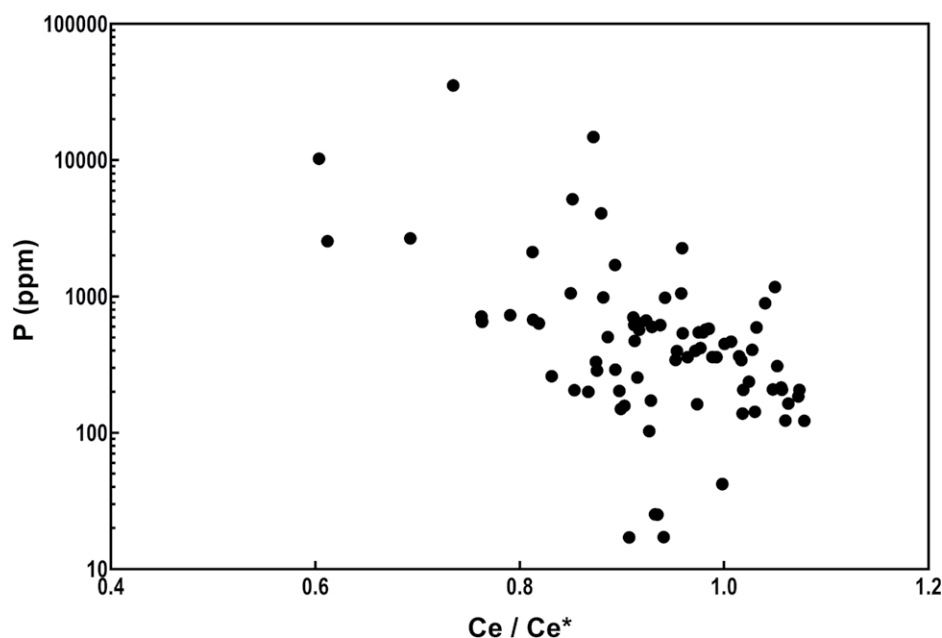


Figure 4. These samples exhibit a negative relationship between P concentrations and Ce anomalies (Ce/Ce\* data are from Chen et al., 2003).

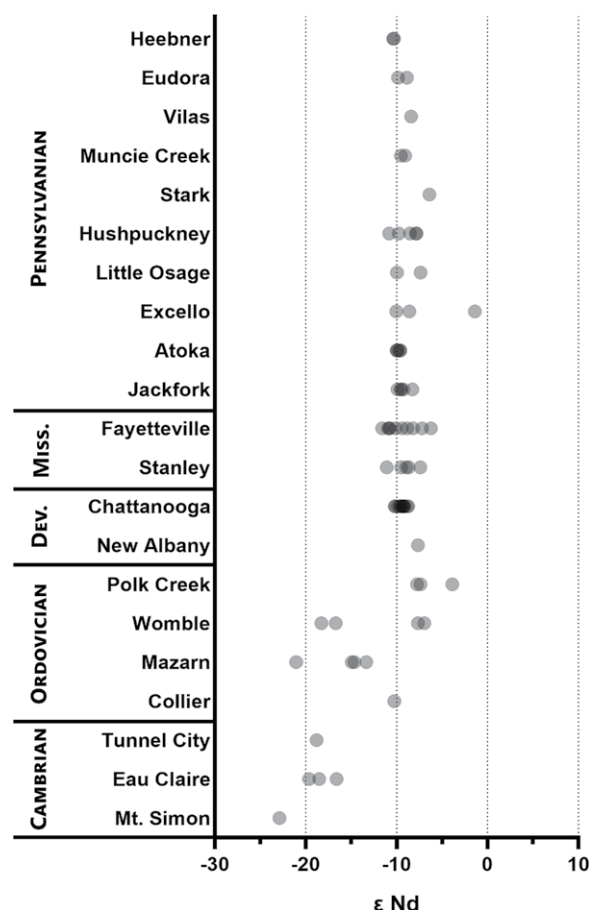
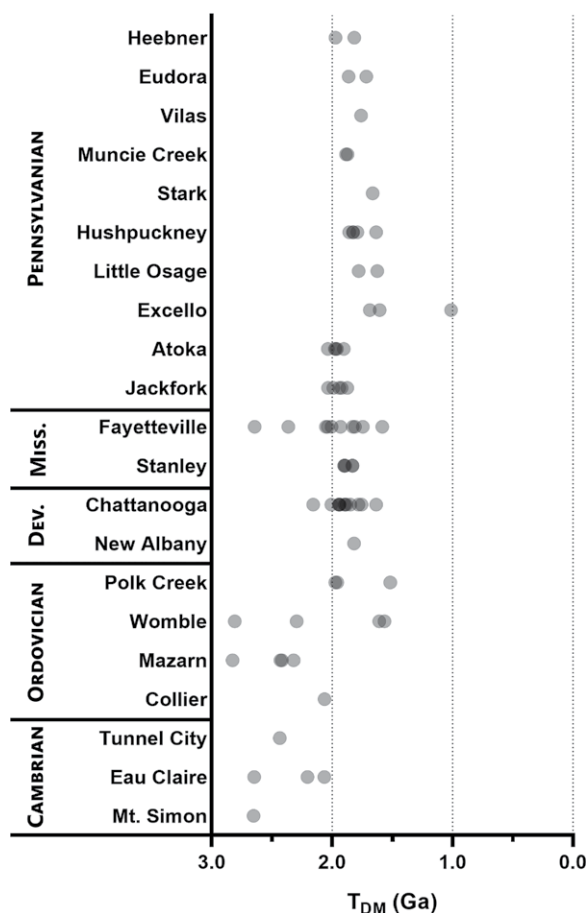


Figure 5.  $\epsilon_{Nd}$  values for each of the shale samples (gray dots). Darker shades of gray indicate overlapping samples of similar values. Dotted line indicates the chondritic uniform reservoir (CHUR). Dev.—Devonian; Miss.—Mississippian.

samples studied, averaging 0.64. It is unclear whether the inverse relationship between P concentrations and Ce anomalies (Ce/Ce\* from Chen et al., 2003; Fig. 4) is related to sediment source. An increase in P may be related to an increase in REE concentrations; however, the Ce anomalies appear to be more muted with increasing P content.

The Nd isotopes provide constraints on the sediment source. Positive  $\epsilon_{Nd}$  values suggest a relatively juvenile source(s), while negative  $\epsilon_{Nd}$  values indicate one or more isotopically evolved sources (Fig. 5; Tables 1 and 2; Faure, 1977). The Cambrian Mt. Simon, Eau Claire, and Tunnel City shales have more negative  $\epsilon_{Nd}$  values (−16.6 to −22.9), and the Ordovician Collier and Mazarn shales have overall slightly higher  $\epsilon_{Nd}$  values (−10.3 to −21.1). However, a distinct change is observed in the Middle to Late Ordovician Womble Shale, which has substantially higher  $\epsilon_{Nd}$  values (−18.3 to −7.0). For all younger shales analyzed in this study, the  $\epsilon_{Nd}$  values are similarly less negative (approximately −4 to −11). The  $T_{DM}$  dates follow a pattern similar to that of the  $\epsilon_{Nd}$ , where the Cambrian shales of the northern midcontinent range from 2.65 Ga to 2.07 Ga, the Collier and Mazarn range from 2.50 Ga to 2.06 Ga, and the Womble Shale ranges from 2.81 Ga to 1.57 Ga (Fig. 6; Table 1). Most of the post-Taconic orogeny shales have  $T_{DM}$  dates after 2.0 Ga (Fig. 6; Tables 1 and 2).

The PAAS-normalized REE + Y concentrations in the shales are generally similar to those of the PAAS (Fig. 7). However, their general patterns and proportions vary from one formation to another (e.g., flat, middle REE-depleted, light REE-depleted/heavy REE-enriched, light REE-enriched/heavy REE-depleted, etc.). When comparing the REE + Y patterns of the samples analyzed in this study with one another, a correlation matrix may be generated to rank the similarity and dissimilarity among samples; this is done by comparing the REE + Y pattern of each sample with those of all other samples to find the samples with the most similar REE + Y patterns (Fig. 8; Table S5). The similarity in the REE + Y patterns increases as the average dissimilarity values approach zero. The mean dissimilarity value among all samples relative to one another is 1.24%. As a baseline, five pairs of replicate samples analyzed in this study have dissimilarity values of between 0.06% and 0.09%, which indicates that dissimilarity values of <0.10% are essentially equal. To determine an approximate average dissimilarity for a single shale formation, the formation with the most samples analyzed is considered to be the most representative one. In the current study, this is represented by the Chattanooga Shale, with 13 samples, and an average dissimilarity



**Figure 6.** Depleted model dates ( $T_{DM}$ ) for each of the shale samples (gray dots) based on the Nd isotopes calculated from DePaolo (1981). Darker shades of gray indicate overlapping samples of similar values. Dev.—Devonian; Miss.—Mississippian.

among all samples of 0.45%. For the purposes of this study, the samples with values  $>1.0\%$  are arbitrarily considered to have no relationships in their REE + Y patterns. Based on the average of the Chattanooga samples, dissimilarity values of  $<0.50\%$  are arbitrarily considered to be likely related, and those between 0.50% and 1.00% are considered weakly related. The Polk Creek and Excello Shale samples, and one sample of the Fayetteville Shale (FS11), exhibit differences of  $>3\%$  when compared with other samples (including samples of other formations). Conversely, the Pennsylvanian shales tend to display the lowest dissimilarities when compared with one another, with differences of  $<0.20\%$ . The two samples that exhibit the most similar REE + Y patterns—one of the Fayetteville Shale (FS10L) and one of the Chattanooga Shale (CS11)—have a difference of 0.13%.

## DISCUSSION

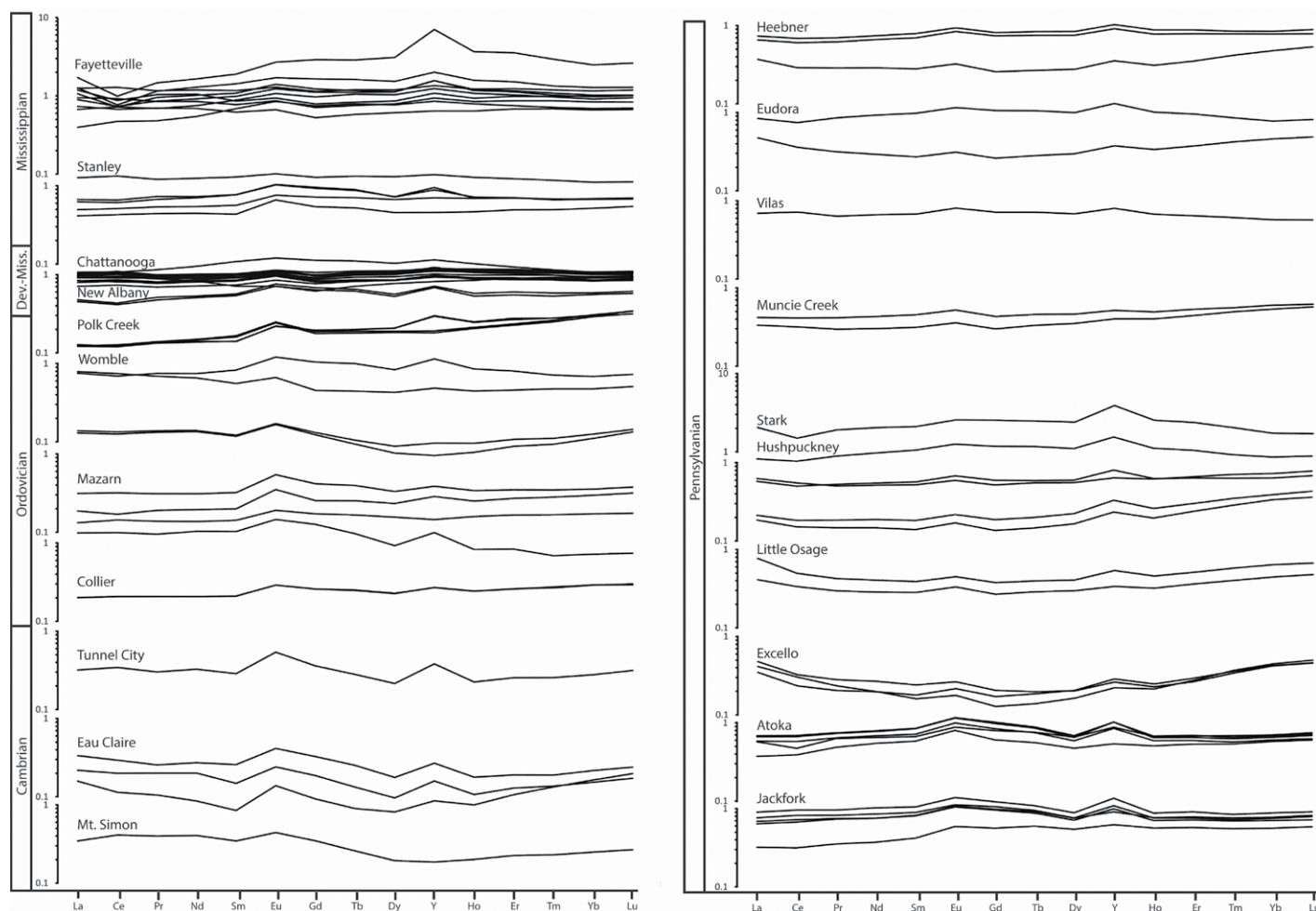
The results of this study indicate that the black shales of the Midcontinent United States have Nd isotopic and REE + Y signatures that are comparable to those of two major regions: the Superior/Trans-Hudson provinces of central

Laurentia and the Grenville province of southern Laurentia (Fig. 1).

Mineralogic analyses reveal that the shales we studied are predominately composed of detrital minerals, with high abundances of quartz, feldspars, and phyllosilicates (Table S2). Diagenetic minerals, such as pyrite and phosphate (fluorapatite), are generally present in sufficiently low quantities to avoid overprinting the REE and Nd signatures of most shales. Trace elements (Tables S3 and S4) suggest that much of the mineral assemblage in the shales analyzed was primarily derived from continental sources. These detrital minerals point to a predominantly felsic cratonic source, as indicated by the Th/Sc, Th/Co, and La/Sc ratios (Fig. 3; Bhatia, 1981; McLennan et al., 1993; Taylor and McLennan, 2003). Therefore, the concentrations and signatures of the REEs in these shales represent the bulk mineral assemblages of the shales except for select samples that have high phosphate concentrations. Samples with high phosphate abundances may have formed under specific environmental conditions and accumulated high REE concentrations that overprinted the authigenic REE signature (Ilyin, 1998; Cruse et al., 2000).

Interestingly, the Cambrian shales from the northern midcontinent (Mt. Simon, Eau Claire, and Tunnel City) exhibit REE + Y signatures that show similarities to those of the Ordovician Mazarn and Womble Shales from the Ouachita Mountains, while displaying characteristics that are distinct from those of the other shales analyzed. The Mt. Simon, Eau Claire, Tunnel City, Mazarn, and Womble Shales have samples with  $T_{DM}$  ranging from 2.8 Ga to 2.0 Ga, and  $\epsilon_{Nd}$  values that vary between  $-13$  and  $-23$  (Figs. 5 and 6; Tables 1 and 2). The negative  $\epsilon_{Nd}$  values in these and all other shales analyzed suggest that an enriched source or an evolved reservoir of REEs, such as the continental crust, was the dominant supplier of sediment to the shales. The  $T_{DM}$  dates resemble those of the Superior and Trans-Hudson provinces, which have dates ranging from before 2.7 Ga to 1.8 Ga (Fisher et al., 2010). The dissimilarity in REE + Y patterns among the Mt. Simon, Eau Claire, and Tunnel City shales ranges from 0.6% to 2.4%, with an average of 1.2%, which suggests a weak to nonexistent relationship for most samples. However, the highest similarity indicates that the Tunnel City Shale and one sample of the Eau Claire Shale (Hwy A-2-520) potentially share a sediment source. On the other hand, the Early Ordovician Mazarn Shale exhibits REE + Y patterns that are more similar to those of the Cambrian–Ordovician Collier Shale, with dissimilarity as low as 0.4%, while the Middle Ordovician Womble Shale shows greater similarity with the northern midcontinental Cambrian shales, with dissimilarity as low as 0.5%. Notably, the Collier Shale, which was analyzed from a single sample, stands out as distinct from the other shales. This sample displays a  $T_{DM}$  date of 2.06 Ga, an  $\epsilon_{Nd}$  value of  $-10$ , and weak to nonexistent similarity with the REE + Y patterns of the Mt. Simon, Eau Claire, Tunnel City, and Womble shales (dissimilarity  $>0.8\%$ ; Figs. 7 and 8; Table S5).

The data suggest that the Mt. Simon, Eau Claire, Tunnel City, Mazarn, and Womble shales may share a common sediment source, which is possibly located in the Superior/Trans-Hudson region, as the basement rocks in these regions exhibit comparable  $T_{DM}$  (commonly before 2.14 Ga) and  $\epsilon_{Nd}$  values (commonly  $<-16$ ; Hemming et al., 1995; Van Schmus et al., 2007; Fisher et al., 2010; Satkoski et al., 2013; Bayon et al., 2015; Lodge et al., 2015). However, the single sample analyzed from the Collier Shale indicates that this shale may have originated from or mixed with a different source, possibly from the Ozark Uplift or another local area, which was subsequently overlain by sediment derived from the northern midcontinent and transported around the Ozark Dome via the



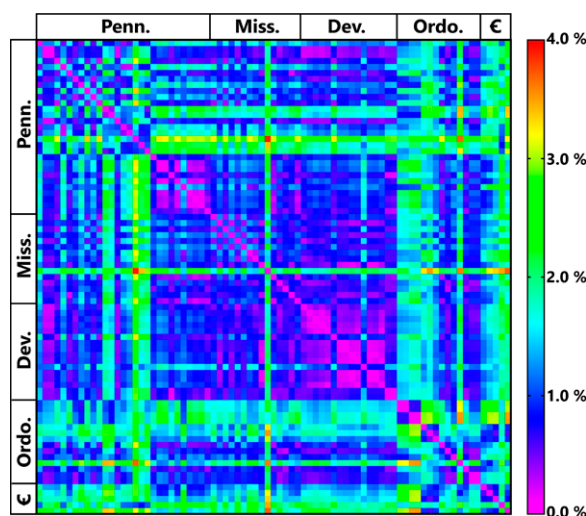
**Figure 7.** Rare earth element plus yttrium (REE + Y) concentrations normalized to Post-Archean Australian Shale (PAAS) for each sample in each formation arranged by stratigraphic age. Each formation is displayed on a logarithmic scale. Dev.—Devonian; Miss.—Mississippian.

Midcontinent Rift or Reelfoot Rift. However, no inferences can be made without additional samples of the Collier Shale.

A distinct shift in signatures is observed in the Middle Ordovician Womble Shale, which likely resulted from the Grenville province (Taconic orogeny) becoming the dominant sediment source during the Middle to Late Ordovician (ca. 460–450 Ma; Gleason et al., 1994, 1995, 2002). This is marked by a distinct shift to younger  $T_{DM}$  dates (2.0–1.5 Ga; Fig. 6) and less negative  $\epsilon_{Nd}$  values (–7 to –10; Fig. 5). These less negative  $\epsilon_{Nd}$  values and younger  $T_{DM}$  dates persist into the Pennsylvanian and are similar to those of the “Appalachian type” signature ( $\epsilon_{Nd}$  values of between –7 and –9) of Gleason et al. (1994, 1995, 2002). The Nd isotopes suggest that the Grenville province was a primary sediment source for the shales in the study area and remained so throughout much of the Paleozoic (Gleason et al., 1994, 1995). The REE + Y patterns in the Womble Shale also indicate a pos-

sible change in sediment source, with samples shifting from 0.9% to 1.0% dissimilarity to up to 1.8% dissimilarity (Figs. 7 and 8; Table S5).

It is important to note that using REE + Y dissimilarity values to constrain sediment sources has limitations and requires cautious



**Figure 8.** Heat map of the dissimilarity of each sample in comparison to others arranged by stratigraphic age (values are provided in Table S5 [see text footnote 1]). Samples with the lowest dissimilarity (pink) tend to be within the same formation, and some of those with the greatest dissimilarity (red) have relatively high P concentrations. Ordo.—Ordovician; Dev.—Devonian; Miss.—Mississippian; Penn.—Pennsylvanian.

interpretation, as various environmental factors, such as diagenesis and phosphate accumulation, can modify the REE concentrations in sediment (Elderfield et al., 1990; Murray et al., 1990, 1992; Grandjean-Lécuyer et al., 1993; Murray and Leinen, 1993; Cruse et al., 2000). The Late Ordovician Polk Creek Shale exhibits distinct geochemical signatures that suggest either changes in the sediment source or changes in the depositional environment. The REE + Y pattern of the Polk Creek Shale shows very little similarity to the older shales in this study (dissimilarity >1%). However, the  $\epsilon_{\text{Nd}}$  values (−4 to −8) and  $T_{\text{DM}}$  dates (2.0 Ga to 1.5 Ga) are similar to those of the Middle Ordovician Womble Shale.

One sample of the late Mississippian Fayetteville Shale (FS11) in the Ozark Dome shows no correlation with the REE + Y pattern of any other sample analyzed (dissimilarity >1%); however, this sample has one of the highest P concentrations among the shales analyzed. The organic-rich Pennsylvanian shales indicate that organic matter and/or environmental factors may influence the preservation of detrital REEs.

Anomalously low  $T_{\text{DM}}$  dates (1.01 Ga) were observed in one sample of the early Pennsylvanian Excelsio Shale (Cherokee and Forest City basins) relative to the other Excelsio samples (1.60 Ga and 1.68 Ga) and other Pennsylvanian shales (Fig. 6); this date is similar to those of the tuff beds in the late Mississippian Stanley Shale (1.18–1.04 Ga) in the Ouachita Mountains (Gleason et al., 1995). Totten et al. (2000) identified three potential sediment sources for the Stanley Shale based on trace-element ratios: a continental source, a felsic source enriched in incompatible elements, and a mafic, oceanic source (possibly an ophiolite). Whether volcanic detritus is responsible for the younger age observed in the Excelsio Shale is unclear.

The REE + Y patterns indicate potential genetic relationships among various other shales, including the late Mississippian Stanley Shale and the Devonian–Mississippian Chattanooga Shale (Ozark Dome; dissimilarity as low as 0.3%), the late Mississippian Fayetteville Shale (Ozark Dome), and the Chattanooga Shale (dissimilarity as low as 0.1%), and the Early Pennsylvanian Atoka and Jackfork shales in the Ouachita Mountains (dissimilarity as low as 0.2%; Figs. 7 and 8; Table S5). Cruse et al. (2000) identified three REE + Y patterns in the Pennsylvanian midcontinental shales: a flat pattern, an MREE-enriched pattern, and an MREE-depleted pattern. This study observed an additional positive linear pattern in Pennsylvanian shales (Cherokee and Forest City basins) and a negative linear pattern in the Late Ordo-

vician Polk Creek Shale (Ouachita Mountains; Fig. 7). However, the causes of these patterns remain uncertain. Early diagenetic uptake of MREE into phosphate nodules has been proposed as a cause of MREE-depleted patterns (Cruse et al., 2000); however, the early Pennsylvanian Excelsio and Little Osage shale samples with MREE-depleted patterns lack significant P concentrations (202–728 ppm, respectively; Table S3).

This study shows that REE + Y patterns of shales can be used to constrain sediment sources; however, further assessment of the utility of the REE pattern dissimilarity as an indicator of sediment source is needed. Additional sampling of Cambrian and Ordovician shales is also desired to understand the source of sediments of these ages and their relationships with one another. The scarcity of comprehensive REE data in the existing literature necessitates larger REE datasets that incorporate samples from additional North American shale formations to identify further relationships in shales.

## CONCLUSIONS

Geochemical and XRD analyses of midcontinental shales indicate that they are comprised primarily of older detrital minerals that eroded from the Superior/Trans-Hudson and Grenville provinces. The Nd isotopic signatures of the Cambrian shales in the northern midcontinent region (Mt. Simon, Eau Claire, and Tunnel City) suggest that they consist of minerals that eroded from older igneous rocks originating from the Superior province. Furthermore, the Th/Sc ratios of these shales are lower than those of younger midcontinental shales that consist of reworked sediments, which indicates that these sediments may have undergone less reworking or could have originated from other sources. The Late Cambrian to Early Ordovician Collier Shale and part of the Early Ordovician Mazam Shale of the Ouachita Mountains have REE + Y signatures that suggest derivation from a different sediment source. However, Nd isotopes suggest that the Mazam Shale and the Womble Shale (Middle–Late Ordovician) consist of sediment that may have been derived from the Superior province. Cessation of deposition of the Womble Shale caused the dominant sediment source to change again, likely due to the Taconic orogeny and uplift of the Appalachian Mountains, which became the dominant sediment source for the midcontinent into and throughout the Pennsylvanian. Of all of the shales studied, the Pennsylvanian Atoka and Jackfork formations show the most similar REE + Y patterns and Nd isotopic values, which indicates derivation from the same source.

## ACKNOWLEDGMENTS

Core samples were provided by the Wisconsin Geological and Natural History Survey. Thanks go to Erik Pollock, Barry Shaulis, and Andrian Kuchuk for their assistance with lab analyses using the Thermo Scientific iCAP Q ICP-MS, Nu Plasma MC-ICP-MS, and Philips PW1830 double system diffractometer. Thanks are also extended to Will Hadley, Jackson Copeland, and Alex Goodsuhm for field and lab support, as well as to Bryan Bottoms and Christophe Simbo for sample collection. This work was supported by the National Science Foundation (grant no. 1952088).

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SCIENCE EDITOR: MIHAI DUCEA  
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MANUSCRIPT RECEIVED 27 JULY 2023  
REVISED MANUSCRIPT RECEIVED 31 DECEMBER 2023  
MANUSCRIPT ACCEPTED 25 JANUARY 2024