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GEOCHEMICAL INSIGHTS INTO PROVENANCE OF THE MIDDLE DEVONIAN HAMILTON GROUP OF THE CENTRAL APPALACHIAN BASIN, U.S.A.

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ABSTRACT: **In order to better understand the relationship of clastic influx and organic-matter accumulation and preservation in the Middle Devonian Acadian foreland basin, we conducted a high-resolution provenance analysis of a composite section of the Hamilton Group. The Hamilton Group includes the organic-rich Marcellus Shale, one of the most lucrative unconventional shale gas plays in the world, and the overlying Mahantango Formation. Geochemical analysis of 121 samples from two nearby wells in Monongalia County, West Virginia, reveals subtle changes in clay provenance throughout deposition of the Marcellus Shale and the Mahantango Formation. Major-element and trace-element geochemistry suggest derivation from a felsic igneous, granodioritic, upper-continental crustal source with additional influx from a recycled quartzose sedimentary source. All weathering indices indicate increasing chemical weathering intensities throughout deposition of the Marcellus Shale, followed by consistently moderate chemical weathering associated with accumulation of the Mahantango Formation. Sm-Nd isotopic analysis of ten samples throughout the Hamilton Group yield ε_{Nd} values ranging from –7.06 to –11.75, and Nd depleted-mantle model ages (τ_{DM}) ranging from 1.63 to 1.85 Ga, with ages becoming younger upsection. Our results suggest that the extrabasinal detritus of the Hamilton Group originated from a mixed sediment source, with clay influx from both rocks associated with the Superior Craton to the north and northwest ($\tau_{DM} > 2.7$ Ga) and Grenville-sourced sediments derived from the adjacent Acadian fold–thrust belt to the east ($\tau_{DM} \sim 1.4$–1.6 Ga). Older Sm-Nd model ages, felsic composition, and evidence of sediment recycling suggest little to no contribution from the Acadian volcanic arc, indicating that volcanic tuff of the Tioga ash beds represent isolated episodes of volcanic input into the basin. Model ages, ε_{Nd} values, and trace-element geochemistry indicate increased sediment influx from the Acadian fold–thrust belt throughout deposition of the Hamilton Group, with the highest sediment influx having occurred during Mahantango Formation deposition. Increased clay influx from sediment shed off from the Acadian fold–thrust belt associated with marginal marine regression increased delivery of clastic detritus, diluting the flux of organic matter and likely disrupting basin water stratification that aided in preservation of organic matter in the lower Marcellus Shale. The Middle Devonian Acadian Basin serves as an example of the influence of detrital influx on organic-matter accumulation and preservation in mud-dominated depositional systems.**

INTRODUCTION

Mudrocks make up most of the sedimentary rock record, yet they are the least understood and arguably among the most difficult to study, their fine-grained nature requiring micro-scale to nano-scale analysis. Evaluating provenance in mudrocks comes with its own set of challenges, particularly related to the lack of detrital framework silicate minerals and grains (e.g., zircon), necessitating their analysis by bulk geochemical techniques (e.g., Sageman and Lyons 2003). In recent decades, mudrocks have become central to petroleum-industry research due to their prevalence as unconventional hydrocarbon reservoirs. One of the most notable shale gas plays is the Middle Devonian Marcellus Shale of the Appalachian Basin (Coleman et al. 2011). The Marcellus Shale and the overlying, organic-poor Mahantango Formation constitute the Hamilton Group of the central Appalachian Basin (Fig. 1; Woodrow et al. 1988). Organic matter in the Marcellus Shale has been studied extensively due to its relevance to hydrocarbon production (e.g., Harper and Piotrowski 1978; Wang and Carr 2013; Enomoto et al. 2014; Yu 2015). However, less work has been done to understand the detrital sediments in the Marcellus Shale and associated mudrock formations. Constraining the provenance evolution of these mudrocks has implications for understanding the heterogeneous spatial and temporal distribution of organic-matter accumulation in clay-rich depositional environments and could aid in understanding organic-matter distribution in other unconventional mudrock reservoirs.

A comparison of high-resolution geochemical records from the organic-rich Marcellus Shale and the organic-poor Mahantango Formation provides an excellent opportunity to explore the influence of clastic influx on organic-matter accumulation and preservation in mudrock-dominated strata. Organic-matter deposition is heavily influenced by both climate and nutrient influx to the basin (Pedersen and Calvert 1990; Sageman et al. 2003; Arthur and Sageman 2005). Warmer, humid climates lead to

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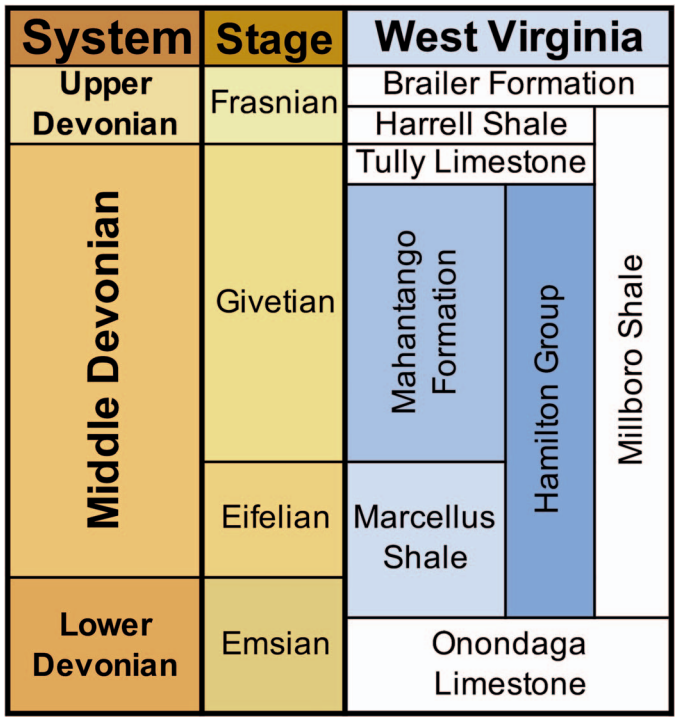

FIG. 1.—Stratigraphy of the Appalachian Basin Middle Devonian system in north-central West Virginia. The Marcellus Shale was deposited from the late Emsian to the late Eifelian (394–389 Ma), followed by deposition of the Mahantango Formation until the end of the Givetian (389–383 Ma; Harris et al. 1994; Repetski et al. 2013; Parrish 2013). Adapted from Milici and Swezey (2014).

increased terrestrial run-off and delivery of nutrients to the basin, thereby favoring increased primary biologic production of organic matter (Murphy et al. 2000). However, enhanced run-off can also increase influx of detrital clay minerals produced principally through hydrolysis of feldspars (Chamley 1989; Zhou and Keeling 2013), which may dilute organic-matter concentrations, thereby limiting hydrocarbon potential of mudrock deposits. Similarly, provenance changes, including variation in source lithology due to uplift, unroofing, or drainage capture, can alter volumes of clastic-sediment flux. We present a detailed provenance record of clastic detritus in the Middle Devonian Hamilton Group of the central Appalachian Basin to test the association between the origin of detrital clastic influx and organic-matter deposition and preservation.

Geologic Background

The Hamilton Group is part of an eastward–southeastward-thickening clastic wedge deposited in the retroarc foreland basin formed in association with the Acadian Orogeny (Ettensohn 1985; Ver Straeten 2010). Convergence of the Avalonia micro-continent with the eastern margin of Laurentia from the Late Ordovician to Early Mississippian time produced an orogenic belt that extended from southeastern Canada to Tennessee, perhaps as far south as Alabama (Ver Straeten 1995; Hibbard et al. 2010; Lash and Engelder 2011). Thrust-loading-induced subsidence and uplift related to the Acadian Orogeny produced a foreland basin in which Hamilton Group sediment accumulated (Ettensohn and Lierman 2013).

The Hamilton Group of the study area in north-central West Virginia includes the Marcellus Shale (~ 30.5 m; ~ 100 ft.) and the Mahantango Formation (~ 51.8 m; ~ 170 ft.), spanning approximately 11 million years (Fig. 1). The Marcellus Shale is a gray to black, thinly laminated, organic-rich mudrock that is gradationally overlain by the Mahantango Formation, a unit dominated by gray, thickly interlaminated silty mudstones and siltstones (Dennison and Hasson 1976; Soeder et al. 2014). The Tioga ash beds, also referred to as the Tioga bentonites, are found as thin layers in the basal part of the Marcellus (Roen and Hosterman 1982; Dennison and Textoris 1988; Ver Straeten 2004). The Marcellus–Mahantango contact is difficult to identify in core and is placed on well logs at an obvious reduction in gamma-ray signature from the Marcellus Shale to the Mahantango Formation (Soeder et al. 2014).

Provenance Terranes of the Middle Devonian Acadian Basin

The epeiric Kaskaskia Sea, which occupied regions west of the Acadian Basin, was dominated by carbonate deposition (Johnson 1974; Woodrow et al. 1988) and likely supplied minimal input of detrital clay to the Acadian Basin. Detrital clay of the Hamilton Group could have been derived from three northern and eastern sources, or provenance terranes adjacent to the Acadian Basin including 1) the Acadian arc, 2) the Acadian fold–thrust belt, and 3) the Superior Craton (Fig. 2). These potential source terranes vary in lithology, age, and geochemical compositions and served as the principal components in developing a provenance model of the Hamilton Group (Table 1).

Acadian Arc.—The Acadian arc was located to the east (in modern coordinates) of the Acadian Basin during the Middle Devonian. The Tioga ash beds reflect air-fall volcanic input from periodic eruptive events during the late Emsian (~ 394 Ma) to the late Eifelian (~ 389 Ma) based on U-Pb zircon ages (Tucker et al. 1998; Roden et al. 1990; Ver Straeten 2004; Parrish 2013). In addition to ash beds, subduction-driven Acadian arc magmatism also generated felsic to intermediate synorogenic (420–400 Ma) granitoid rocks (Sinha et al. 2010; van Staal et al. 2011; Parrish 2013). Acadian synorogenic volcanic rocks in northern Maine yield Sm-Nd depleted-mantle model ages (τ_{DM}) ranging from ~ 403 to 417 Ma (Schoonmaker et al. 2011).

Acadian Fold–Thrust Belt.—The Acadian fold–thrust belt was located to the east-northeast of the basin, extending from New Brunswick to Tennessee (Milici and Swezey 2014) and perhaps as far as Alabama (Rast and Skehan 1993). Grenville-age (~ 1250 Ma) through Early Devonian (~ 400 Ma) rocks were thrust westward during the Acadian Orogeny; however, much of the lower Paleozoic strata involved in these thrust sheets are carbonate rocks that contain some clays but probably would not have supplied a significant influx of clay minerals to the Acadian foreland. Acadian displacement also uplifted Ordovician to Early Devonian Taconic foreland-basin strata, a large proportion of which is mainly quartzolithic in composition. Detrital-zircon analysis from Taconic flysch reflect abundant ~ 1.0–1.3 Ga zircons, consistent with sediment input from the erosion of Grenville-terrane rocks (Scott et al. 2016), although a few 553 Ma zircon grains in the Silurian Tuscarora Sandstone suggest a contribution from a younger Neoproterozoic source of peri-Gondwanan origin (Thomas et al. 2014). Sm-Nd isotopic analysis of Grenville-terrane rocks that formed the eastern margin of Laurentia yield average τ_{DM} ages of 1.4–1.6 Ga (Dickin and Higgins 1992; Rainbird et al. 1997). Sediment derived from the Acadian fold–thrust belt would have displayed both a felsic igneous and a recycled orogenic source provenance signatures (Dickinson et al. 1983), the later characterized by highly evolved major-element abundances and enrichment abundances of elements associated with refractory heavy minerals (e.g., Zr and Ti; McLennan et al. 1993).

Superior Craton.—The Superior Craton, bordering the Acadian Basin to the north and apparently tectonically stable since the Precambrian (Canil 2008), was a locus of Acadian synorogenic sediments (Bradley 1983; Faill 1985). It is noteworthy, however, that the Illinois Basin pre-Mississippian clastic sediment was shed from eastern cratonic sources (Potter and Pryor

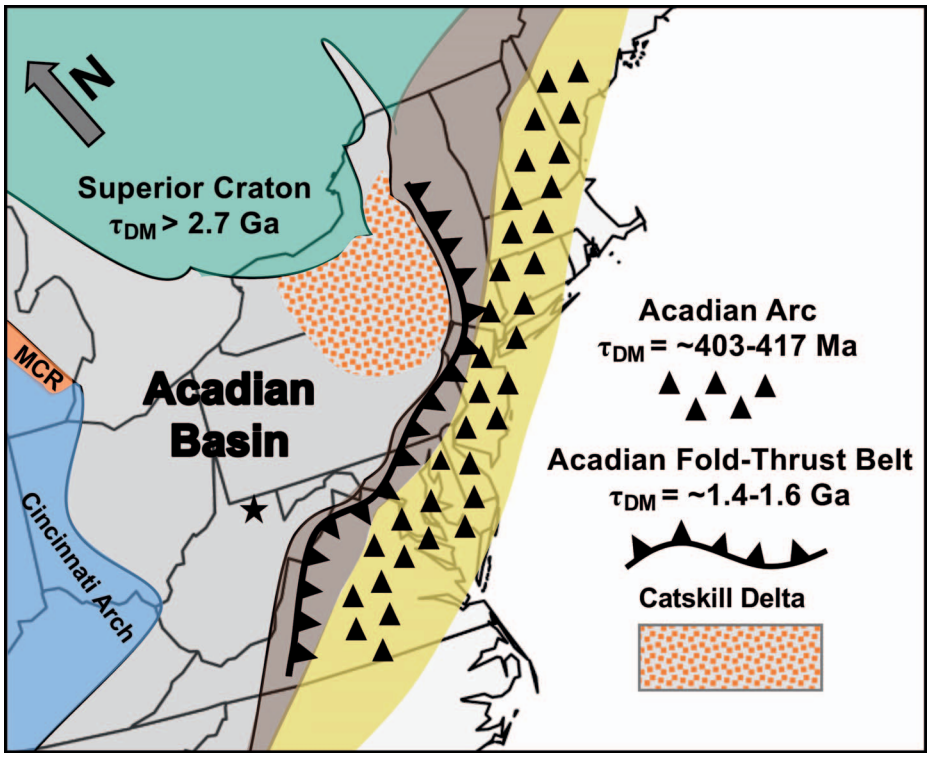

FIG. 2.—Map of potential provenance sources to the Appalachian Basin. The star denotes the approximate location of the study area, and the arrow indicates the direction of north in accordance to Devonian paleogeography. Adapted from Ettensohn (1985), Blakey (2009), Lash and Engelder (2011), and Fisher et al. (2010).

1961) indicating that part of the craton was subaerially exposed during Devonian time. Sm-Nd isotopic analysis of the cratonic rocks has yielded τ_{DM} ages of 2.7 to 3.1 Ga, with an average of ~ 2.8 Ga (Percival et al. 2006; Fisher et al. 2010; Percival et al. 2012). The Superior Craton serves as an old upper-continental-crust source, which would have yielded detritus exhibiting highly evolved major-element abundances reflecting both its dominantly granodioritic composition and intense chemical weathering. Overall, these rocks tend to display signatures of felsic-granitic composition affected by some degree of sediment recycling and old τ_{DM} ages of > 2.7 Ga (Percival et al. 2006, 2012; Fisher et al. 2010).

Previous Provenance Analysis of Acadian Synorogenic Sediments

Few studies have investigated provenance of the Hamilton Group in the central Appalachian Basin region, and many of these studies have focused on a few samples from the organic-rich Marcellus Shale (Gardiner et al. 2012; Hayward 2012; Parrish 2013; Chen 2016; Chen and Sharma 2017; Phan et al. 2018). Gardiner et al. (2012) and Phan et al. (2018) conducted Sm-Nd isotopic analysis of Marcellus Shale mudstone and zircon U-Pb analysis of Tioga ash beds recovered from a core in Green County, southwestern Pennsylvania. Their results yielded τ_{DM} ages of 1.38–1.61 Ga that they attributed to derivation from a source composed of Grenville-derived sedimentary rocks exposed in the Acadian highlands (Gardiner et al. 2012). Trace-element and rare-earth-element chemistry of mudstone samples from the Green County core by Chen (2016) and Chen and Sharma (2017) revealed that the lower Marcellus Shale geochemical signatures mimic bulk continental crust, with relatively low concentrations of Th, Rb, Cs, and Ta, whereas geochemical signatures of the organic-poor upper Marcellus Shale resembled upper-continental-crust (UCC) compositions characterized by enrichments in light rare earth elements (LREE), and major-element and trace-element chemistry consistent with UCC. Chen and Sharma (2017) attributed these signatures to tectonic evolution during the Acadian Orogeny, with the deposition of the organic-rich lower Marcellus Shale occurring during a period of increased mountain building and magmatic inactivity, and later deposition of organic-poor upper Marcellus Shale occurring during intrusion of granodioritic rocks during a magmatically active period.

To the north in New York, provenance investigations of the well-exposed Hamilton Group shale have documented fluctuations of Y, La, Zr, Sc, Cr, Co, and Ti consistent with derivation from rocks in the Acadian orogen fold–thrust belt (Ver Straeten and Sageman 1999a, 1999b). Sm-Nd isotopic analysis of these rocks yield τ_{DM} ages of ~ 946–1689 Ma, which have been attributed to the mixing of sediment influx from the Archean Canadian Shield and the eastern Acadian highlands (Caesar et al. 2010a; Caesar et al. 2010b; Mosher et al. 2010; Phan et al. 2018). Enrichment of Rb, U, V, and REEs further supported the interpretation of highly weathered source rocks of a well-mixed provenance (Caesar et al. 2010a). Detrital zircons sampled from the Marcellus Shale of New York were found to belong dominantly to two populations, either of 950–1350 Ma (Grenville Orogeny) or 400–450 Ma (Taconic and early Acadian), suggesting that sediment of the Marcellus Shale was derived from strata exposed in the Acadian fold–thrust belt (Selleck et al. 2014, 2016). In comparison, the younger Givetian clastics of the Manorkill Formation in the Catskill region, which are temporally correlative to the upper Mahantango Formation, are also dominated by Grenville detrital-zircon

TABLE 1.—*Reported depleted-mantle model ages (τ_{DM}) for Middle Devonian Acadian Basin potential source terranes.*

Source Terrane	τ_{DM}	Reference
Superior Craton	2.7–3.1 Ga	Percival et al. 2006, 2012; Fisher et al. 2010
Acadian Fold–Thrust Belt	1.4–1.6 Ga	Dickin and Higgins 1992; Rainbird et al. 1997
Acadian Arc	403–417 Ma	Schoonmaker et al. 2011

ages, but include a larger population of synorogenic zircon sourced in the Acadian orogen (470–420 Ma; Selleck et al. 2016).

METHODS

Sampling

In order to establish a continuous chemostratigraphic record of the Hamilton Group, 121 samples were collected from two wells drilled in Monongalia Co., West Virginia. These wells will be referred to as the MIP-3H well (API # 47061017050000; 39.601783 N, 79.976123 W) and WV-6 well (API #: 47061003700000; 39.667813 N, –79.973879 W). The MIP-3H well was sampled continuously through the Marcellus Shale into the lower Mahantango Formation. Sixty-two side-wall plugs were collected from the MIP-3H well as part of the Marcellus Shale Energy and Environmental Laboratory (MSEEL) drilling project. Side-wall plugs range in weight from ~ 10 to 50 g and were collected at variable intervals, ranging from every 0.2–2.6 m (0.5–8.5 ft.; average sampling interval = 0.52 m; 1.7 ft.) over the entire 32.9 m (108 ft.) of sampled section. Of the 62 samples, six were collected from the bottom of the Mahantango Formation, the remainder being recovered from the Marcellus Shale. Aliquots of all 62 samples were analyzed by XRF for major-element and trace-element composition, and six were analyzed for Sm-Nd whole-rock isotopic analysis.

A suite of 59 Mahantango Formation samples was obtained from the WV-6 well, approximately four miles northeast of the MIP-3H well. Samples range from ~ 30 to 100 g and were collected at approximately 0.91 m (3 ft.) intervals through the Mahantango Formation (58 samples); one sample was recovered from the uppermost Marcellus Shale. All 59 samples were analyzed via X-ray fluorescence for major-element and trace-element geochemistry, and four were analyzed for Sm-Nd whole-rock isotopic dating. In both cores, the Marcellus–Mahantango contact was identified by a distinct shift in gamma ray.

ANALYTICAL METHODS

X-Ray Fluorescence Analysis

X-ray fluorescence (XRF) analysis was performed on all 121 samples to establish the abundance of both major-elements and trace-elements. Samples were analyzed using a Thermo ARL Perform'X X-ray Fluorescence Spectrometer located at the Hamilton College Analytical Laboratory. MIP-3H samples were ground at West Virginia University for approximately 4 to 6 minutes using an A Spex shatterbox with steel grinding containers until powdered. Samples from the WV-6 well were ground in aluminum ceramic grinding containers at the Hamilton College Analytical Laboratory in preparation for XRF analysis. All powders were subjected to serial loss on ignition (LOI) at temperatures of 600°C and 900°C in order to remove and quantify organic matter and carbonate from the sample. Powders were fused into glass beads before XRF analysis. Standards including USGS AGV-2, BCR-2, BHVO-1, G-2, W-2, SCo-1, SDO-1, and STM-1 were used to monitor accuracy and precision (Hupp and Donovan 2018).

Various weathering indices were calculated from XRF data in order to provide insight into weathering intensity of the source region and source-rock composition. Oxide abundances calculated from XRF values were converted to moles in order to calculate chemical index of alteration (CIA; Eq. 1) and chemical index of weathering (CIW; Eq. 2), enabling assessment of weathering trends independent of potential K-metasomatism (Nesbitt and Young 1984; Harnois 1988; Fedo et al. 1995). The index of compositional variability (ICV; Eq. 3) was calculated using the oxide weight percentages to provide insight into provenance by heavy-mineral enrichment and aiding in the identification of oxide weathering trends influenced by non-clay silicate minerals (Cox et al. 1995).

$$\mathrm{CIA} = [\mathrm{Al_2O_3}/(\mathrm{Al_2O_3} + \mathrm{CaO^*} + \mathrm{K_2O} + \mathrm{Na_2O})] \times 100 \quad (1)$$

$$\mathrm{CIW} = [\mathrm{Al_2O_3}/(\mathrm{Al_2O_3} + \mathrm{CaO^*} + \mathrm{Na_2O})] \times 100 \quad (2)$$

$$\mathrm{CaO^*} = \text{mol CaO} - \text{mol } \mathrm{CO_{2cc}} - (0.5 \times \text{mol } \mathrm{CO_2})_{\mathrm{dol}} - [(10/3) \times \text{mol } \mathrm{P_2O_5}]_{\mathrm{ap}}$$

cc = calcite; dol = dolomite; ap = apatite

$$\mathrm{ICV} = (\mathrm{CaO} + \mathrm{K_2O} + \mathrm{Na_2O} + \mathrm{Fe_2O_{3total}} + \mathrm{MgO} + \mathrm{MnO} + \mathrm{TiO_2})/\mathrm{A1_2O_3} \quad (3)$$

Major-elements and trace-elements were compared with previously published shale composites and used as proxies for clastic influx and other environmental proxies (e.g., Al_2O_3, TiO_2, Zr, P_2O_5, etc.). Ternary diagrams, Al_2O_3 – (CaO + Na_2O) – K_2O and Al_2O_3 – (CaO + Na_2O + K_2O) – (FeO_{total} + MgO) were used to identify weathering trends indicative of primary source composition (Nesbitt and Young 1984, 1989; McLennan et al. 1990, 1993). Discriminant functions put forth by Roser and Korsch (1988) were used to further differentiate source-rock composition. Functions D3 (Eq. 4) and D4 (Eq. 5) were found to be most appropriate for evaluation of the Hamilton Group, as they account for influence from biogenic sedimentation. Previous petrographic evaluation of samples examined in this study indicated the presence of various fossils (e.g., radiolarians, styliolinids), supporting the use of the D3 and D4 discriminant functions as opposed to D1 and D2 (Hupp and Donovan 2018). Major-element and trace-element chemistry from both wells are reported in Supplemental Appendices 1 (MIP-3H) and 2 (WV-6).

$$\mathrm{DF3} = [30.638\ \mathrm{TiO_2} - 12.541\ \mathrm{Fe_2O_3(t)} + 7.32\ \mathrm{MgO} + 12.031\ \mathrm{Na_2O} + 35.402\ \mathrm{K_2O}]/\mathrm{Al_2O_3} - 6.382 \quad (4)$$

$$\mathrm{DF4} = [56.50\ \mathrm{TiO_2} - 10.879\ \mathrm{Fe_2O_3(t)} + 30.875\ \mathrm{MgO} - 5.404\ \mathrm{Na_2O} + 11.112\ \mathrm{K_2O}]/\mathrm{Al_2O_3} - 3.89 \quad (5)$$

Samarium–Neodymium (Sm-Nd) Isotopic Analysis

Sm-Nd isotopes were measured for 10 whole-rock samples (five from each formation) by ultra-high precision (< 20 ppm) thermal ionization mass spectrometry (TIMS) at Geochronex Analytical Services Ltd. Four samples (Table 2; Aliquot 1) were sent to Geochronex Analytical Services as 5 g rock chips. The chips were powdered, dissolved in a mixture of HF, HNO_3, and $HClO_4$, and spiked with a ^{149}Sm–^{150}Nd solution. Rare earth elements were separated via conventional cation-exchange techniques, with Sm and Nd further separated by extraction chromatography on HDEHP covered Teflon powder. A second set of samples (Table 2; Aliquot 2) consisting of 10 g was later sent to Geochronex Analytical Services Ltd. Samples were powdered in a jasper mortar, after which they were spiked with a ^{149}Sm–^{150}Nd trace solution. The mixture was decomposed in a Hf + HNO_3 (3:1) solution at 140°C for two days, followed by baking in HNO_3 at 250°C for two hours in a Milestone Ultra Clave high-pressure microwave oven. Separation of Sm and Nd was conducted via two-stage ion exchange and extraction chromatography (Richard et al. 1976; Pin and Zalduegui 1997). Measurements of isotope abundances were made on a Thermo-Fisher Triton TI mass spectrometer. Depleted-mantle (τ_{DM}) model ages and $\varepsilon_{Nd(0)}$ were calculated from results of Sm-Nd isotopic analysis (DePaolo and Wasserburg 1976; DePaolo 1988; Dickin 1995). $\varepsilon_{Nd(0)}$ is a useful notation that compares deviation of initial $^{143}Nd/^{144}Nd$ isotope ratios of the sample to a chondritic uniform reservoir (CHUR), where $^{143}Nd/^{144}Nd_{CHUR}$ is equal to 0.512638 (Eq. 6; DePaolo and Wasserburg 1976).

TABLE 2.—*Sm-Nd isotopic data from ten samples throughout the Hamilton Group including the well they were collected from, sample depth relative to the Marcellus Sh.–Mahantango Fm. contact, aliquot, ε_{Nd} values, and τ_{DM} ages.*

Well	Depth from Contact (m)	Aliquot	ε_{Nd}	τ_{DM} (Ga)
WV-6	51.9	2	–11.65	1.65
WV-6	38.2	2	–11.47	1.67
WV-6	24.6	2	–11.74	1.64
WV-6	10.7	2	–10.38	1.74
MIP-3H	1.7	1	–10.34	1.85
MIP-3H	–1.9	1	–10.51	1.79
MIP-3H	–10.7	2	–10.55	1.63
MIP-3H	–15.8	1	–10.18	1.81
MIP-3H	–25.6	2	–9.85	1.78
MIP-3H	–27.7	1	–7.06	–

$$\varepsilon_{Nd(0)} = \left[\frac{(^{143}Nd/^{144}Nd)_{sample}(T)}{(^{143}Nd/^{144}Nd)_{CHUR}(T)} - 1\right]10^4 \quad (6)$$

Proxies for Organic-Matter Content

Gamma-ray logs were used to evaluate approximate concentrations of organic matter throughout the Hamilton Group for both wells. However, as part of the MSEEL project, total organic content (TOC) was directly measured throughout the Marcellus Shale in the MIP-3H core using a source-rock analyzer (SRA) at the National Energy and Technology Laboratory (NETL), Morgantown, West Virginia. TOC measurements were then calibrated to the gamma ray in order to calculate a continuous uranium-predicted TOC log (Paronish 2018). Geochemical comparisons to TOC in this study for MIP-3H samples are compared to the continuous uranium-predicted TOC log, as direct TOC measurements of the MIP-3H core were made at intervals differing from the sample intervals of the present study. Sampling from only the MIP-3H well was used to investigate elemental relationships with TOC due to the wider range of TOC values ($\sim$ 3–14%) exhibited in the Marcellus Shale samples as well as the availability of an SRA-calibrated uranium-predicted TOC log.

RESULTS

X-Ray Fluorescence Elemental Abundances

Elemental abundances of the studied samples were compared with the North American Shale Composite (NASC; Gromet et al. 1984) to evaluate major-element chemistry. Marcellus Shale samples on average are depleted in Si, Al, Mn, and Mg relative to the NASC. Trace-element geochemistry of the Marcellus Shale in comparison to NASC also indicated enrichments of Ni, Ba, Rb, and U, and depletions in Zr. The Mahantango Formation samples are also depleted in Si, Mn, and Mg, but display enriched levels of Al relative to the NASC, whereas Ni, Rb, Ba are enriched in comparison with the NASC.

Weight % Al_2O_3 was examined as a proxy for clay influx throughout the Hamilton Group. In the Marcellus Shale, the wt. % Al_2O_3 showed a distinct increase upsection from $\sim$ 6% to $\sim$ 18% (Fig. 3). Geochemical trends show greater internal consistency in the Mahantango Formation. Concentrations of Al_2O_3 average approximately 16.5% in the lower 15 m of the formation, while the upper 37 m average $\sim$ 18.3%. Al_2O_3 concentrations from the Marcellus Shale were compared with TOC estimated from wireline log data in order to further evaluate the relationship between organic-matter content and clay influx to the basin. A cross-plot of TOC versus Al_2O_3 shows a moderate negative correlation (R^2 = –0.5356; Fig. 4A), suggesting that increased clay sedimentation to the basin is correlated to lower values of total organic content.

Cross-plots of other major and trace elements were compared to TOC in an attempt to identify potential relationships of clastic influx, nutrient availability, and organic-matter content. TOC was compared to both P_2O_5 and FeO to evaluate the effects of limiting nutrient input on primary production as reflected by organic-matter content. No correlation was exhibited in either of these cross-plots (P_2O_5, R^2 = 0.0055; FeO, R^2 = 0.0505), suggesting that nutrient flux may not have been the limiting factor in controlling primary productivity and thus, organic content, but that preservation played a more important role. However, recycling of phosphorus, common under reducing conditions, may have distorted any direct correlation between P_2O_5 and TOC. Zr and Ti can be used as elemental indicators of sediment influx from recycled sedimentary sources. A cross-plot of TOC versus Zr shows a moderate negative correlation (R^2 = –0.5363; Fig. 4B), suggesting that increases in influx of recycled sediment correlates with decreasing organic-matter content. Similarly, TiO_2 versus TOC yielded a moderate negative correlation (R^2= –0.6771; Fig. 4C), further supporting the association of higher clastic influx from recycled sedimentary sources and lower total-organic-carbon concentrations (Murphy et al. 2000). Strong positive covariations were found among TiO_2 in comparison to Al_2O_3 (R^2= 0.7918) and Zr (R_2= 0.8034) when examining all Hamilton Group samples.

Weathering indices were determined for all samples (Fig. 3) except those containing > 10% CaO, which were classified as calcareous mudrocks for purposes of this study, whose CaO content would yield biased index results not representative of the siliciclastic faction. Marcellus Shale CIA values range from 38.3 to 74.1 (n = 51), averaging 60.6 ± 11.3. Mahantango Formation samples (n = 62) display CIA values ranging from 42.8 to 75.0, averaging 69.5 ± 6.5. CIW values for the Marcellus Shale range from 43.0 to 91.6 (average = 73.0 ± 15.5) while CIW values for the Mahantango Formation range from 48.2 to 92.1 (average = 84.4 ± 9.1). Both the CIA and CIW increase upsection through the Marcellus Shale, whereas ICV diminishes upsection (Fig. 3). ICV values of the Mahantango Formation average 1.1 ± 1.9 and range from 0.69 to 1.62. Weathering indices are fairly constant throughout the Mahantango Formation (Fig. 3).

Geochemistry of the Hamilton Group suggested similar yet slight differences in source composition amongst the two units. Al_2O_3 – (CaO + Na_2O) – K_2O and Al_2O_3 – (CaO + Na_2O + K_2O) – (FeO_{total} + MgO) ternary diagrams reveal that the Marcellus Shale and Mahantango Formation samples tend to follow the typical trend of a weathered granodiorite (Nesbitt and Young 1984, 1989; McLennan et al. 1993) (Fig. 5). Discriminant functions calculated from data on major-element composition established by Roser and Korsch (1988) help to further elucidate source type by differentiating among quartzose sedimentary, felsic igneous, intermediate igneous, and mafic igneous sources. The Marcellus Shale appears to have been derived from a source composed of felsic igneous rocks and lesser quartzose sedimentary rocks, whereas the Mahantango Formation mainly reflected dominance of a felsic igneous source (Fig. 6). A cross-plot of Zr/Sc vs. Th/Sc can be used to identify signs of sediment recycling (McLennan et al. 1993) (Fig. 7). The Marcellus Shale displays some influence of sediment recycling, whereas the Mahantango Formation showed no signs of influence of a recycled sedimentary source. Mahantango and Marcellus samples plot nearest to an upper-crust source field of the La-Th-Sc ternary diagram, though the latter displays greater compositional variation (Fig. 8). Overall, the transition of the Marcellus Shale to the Mahantango Formation appears to have been accompanied by increasing contribution of sediment derived from felsic sources.

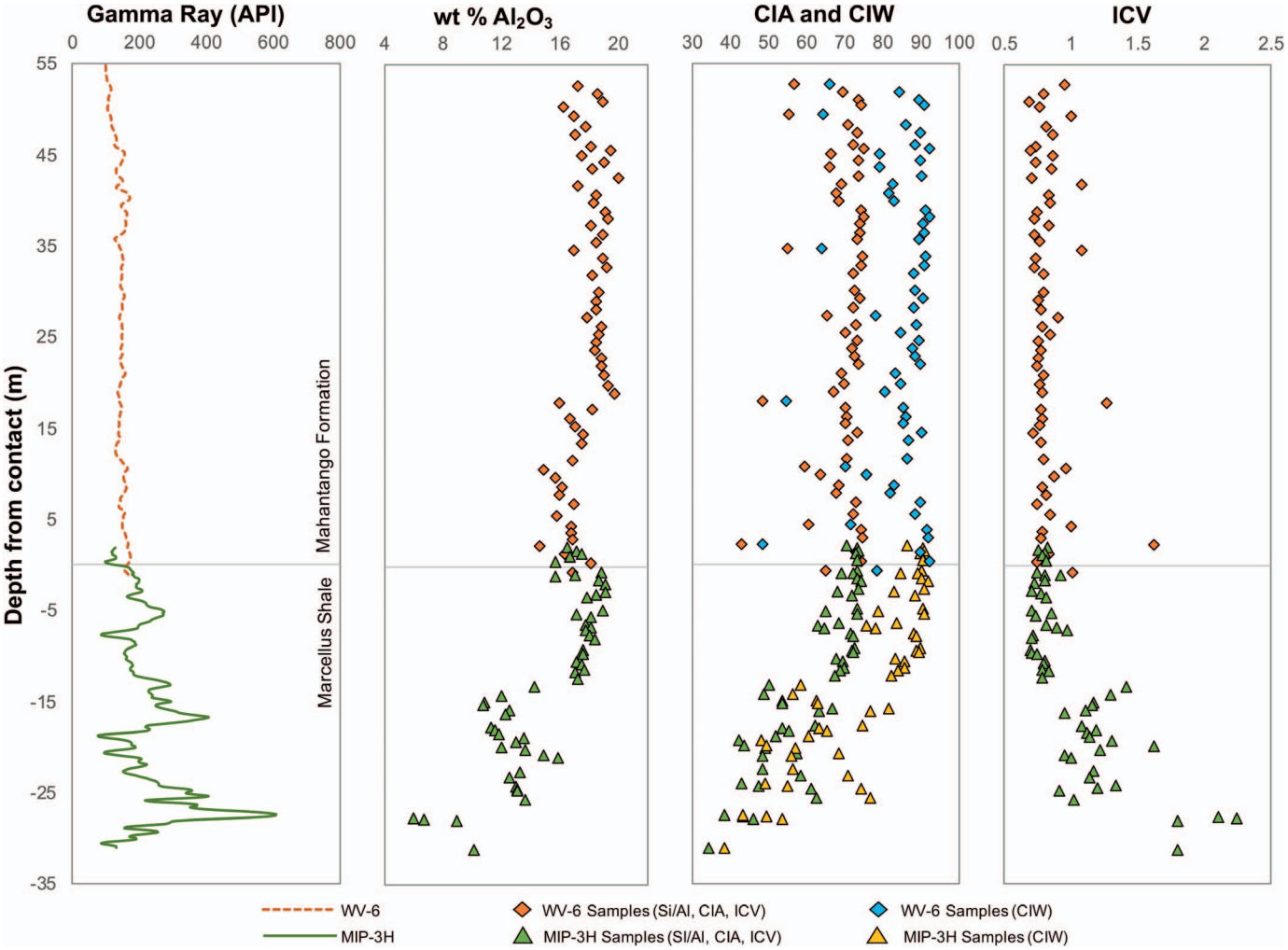

FIG. 3.—Stratigraphic trends of gamma-ray values, % Al_2O_3, chemical index of alteration (CIA), chemical index of weathering (CIW), and index of compositional variability (ICV). Stratigraphic elevations are relative to the Marcellus–Mahantango contact.

Sm-Nd Isotopic Results

Nine of the ten samples that were analyzed for Sm-Nd radiogenic isotopes yielded valid results. The anomalous sample, which was collected from the Marcellus Shale (–27.7 m; –90.85 ft.; Fig. 3), was enriched in ^{147}Sm relative to ^{144}Nd and characterized by high ε_{Nd} (–7.06) and anomalous τ_{DM} (5.33 Ga). Studies of other Paleozoic shale deposits have produced anomalous Sm-Nd results and consequent erroneous model ages that have been attributed to many possible distorting mechanisms (McLennan et al. 1990; Bock et al. 1994). Aberrant results may reflect authigenic precipitation of REE-bearing phosphate minerals or apatite from volcanic debris; however, phosphate-bearing minerals are not present in any samples analyzed by X-ray diffraction (XRD; Hupp and Donovan 2018). It is plausible that upper-crust-sourced sediments mixed with LREE-depleted volcanic ashes intermittently supplied to the basin. The fact that ash beds were not recognized proximal to the anomalous sample suggests that the flux of volcanic material was such that it was strongly diluted by terrigenous debris. It is worth considering that Sm-Nd abundances of the anomalous sample was affected by amorphous Mn or Fe oxides that host REEs (Caetano et al. 2009). Although this sample contained normal Mn abundances relative to the total sample suite, its Fe abundance (8.4 wt %) is the highest of the Marcellus Shale sample suite (average = 5.5 ±1.4 wt %) and could explain the aberration in Sm concentration observed in this sample.

The calculation of ε_{Nd} values and depleted-mantle model ages (τ_{DM}) resulted in ε_{Nd} values from –7.06 to –11.74 and model ages ranging from 1.85 to 1.64 Ga for the Hamilton Group (Table 2). Overall the Marcellus Shale and lowest Mahantango Formation samples show ε_{Nd} values of –7 to –10, whereas ε_{Nd} values of –11 are observed for the younger Mahantango Formation samples. The τ_{DM} ages are overall older for Marcellus Shale samples, with four of five samples yielding τ_{DM} ages of ~ 1.8 Ga (Fig. 9). In contrast, samples of the Mahantango Formation show younger, with τ_{DM} ages of 1.64–1.74 Ga. Cross-plots of Th/Sc vs. ε_{Nd} values further indicate an upper-crust composition of the source rock (McClennan et al. 1990, 1993) (Fig. 10).

DISCUSSION

Source-Rock Lithology and Age

Major-element and trace-element geochemistry suggest that deposits of the Hamilton Group were derived principally from upper-crust, granodioritic source rocks (Figs. 5, 7, 9). Specifically, the major-element and trace-element composition of the analyzed Marcellus samples indicate a dominantly felsic igneous source and quartzose sedimentary sources,

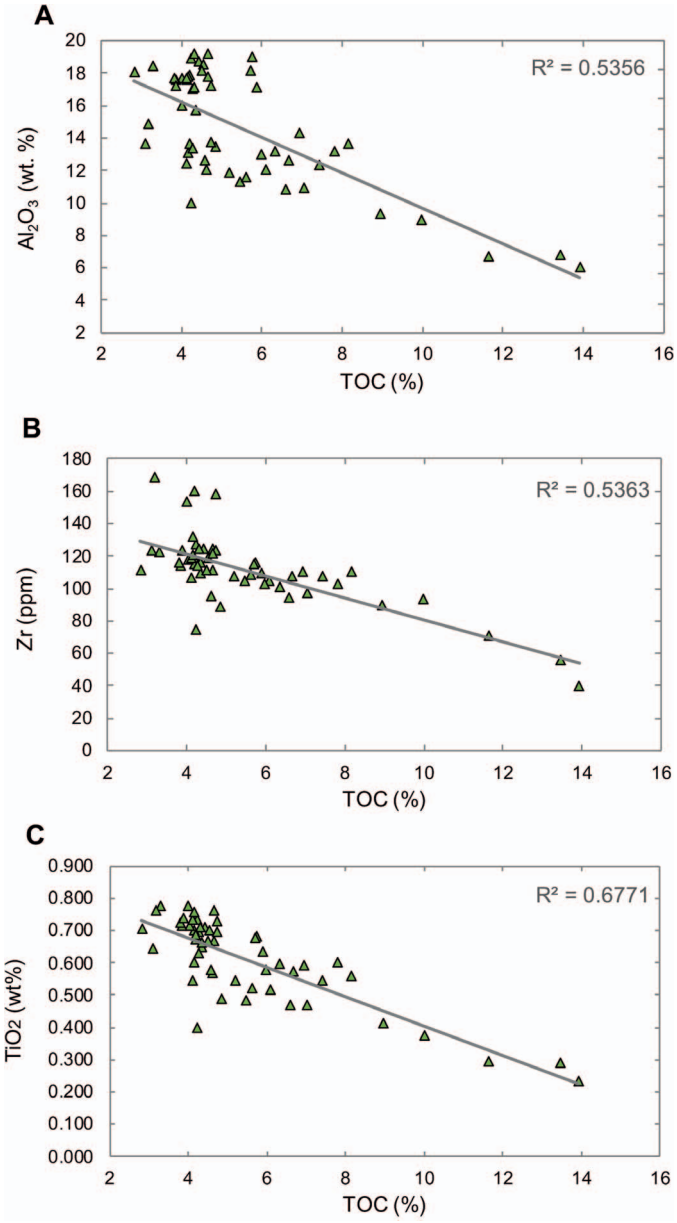

FIG. 4.—Cross-plots TOC versus **A)** Al_2O_3 , **B)** Zr, and **C)** TiO_2. Only data collected from the MIP-3H well are included because TOC data were not available for the WV-6 well. Green triangles represent Marcellus Shale samples; orange diamonds represent Mahantango Formation samples. Symbols are used in subsequent plots.

whereas data from the Mahantango Formation indicate mainly a dominantly felsic igneous source (Fig. 6). A few samples of the Marcellus Shale exhibited enrichment of Zr/Sc relative to Th/Sc, supporting minor sediment influx from a recycled sedimentary source (Fig. 8). The cross-plot of Th/Sc versus ε_{Nd} is also consistent with an upper-crust source (Fig. 10).

Raw SiO_2 averages of the noncalcareous samples from each formation yield averages of 53.7 and 56.3 for the Marcellus and Mahantango, respectively. These values could be interpreted as representing an intermediate igneous provenance. However, work by Roser and Korsch (1986) has shown that SiO_2 content often decreases with lessening grain size. Rocks of differing grain size derived from the same terrane have been found to display lesser SiO_2 content and greater K_2O/Na_2O ratios in fine-grained rocks (i.e., argillites) than coarse-grained rocks (i.e., graywackes; Roser and Korsch 1986). The results of Roser and Korsch (1986) supported the critical need to establish quantitative analyses to identify source-terrane type that could account for compositional variations related to grain size. In response, Roser and Korsch (1988) established the discriminant functions used in this study (D3 and D4) to identify source-rock composition regardless of grain size. Considering this, our interpretation of a dominantly felsic provenance for the units of the Hamilton Group is supported (Fig. 6).

The elemental geochemistry reveals a provenance signature consistent with two of the potential source terranes. The Superior Craton to the north-northwest of the basin is an older upper-crust source composed dominantly of granodioritic composition (Percival et al. 2012; Jaupart et al. 2014). The Acadian fold–thrust belt to the east would have produced a stronger signature of sediment recycling than what is observed in most Hamilton Group samples (Fig. 8). A few samples suggest derivation from a quartzose sedimentary source (Fig. 6), which indicates that the Acadian fold–thrust belt was a sediment source of the Hamilton Group deposits. A source of Acadian volcanic rocks into the basin could have generated a felsic signature also, but this source is ruled out by Sm-Nd isotopic evidence discussed below.

The Sm-Nd results of the Hamilton Group are consistent with a depleted-mantle model with upsection decreasing ages (τ_{DM}) ranging from 1.85 to 1.63 Ga (Fig. 10; Table 2). The calculated ages are much older than what would be generated by volcanic rocks of the Acadian arc and are even older than typical Grenville-associated rocks of the Acadian fold belt (Dickin and Higgins 1992). However, these ages are much younger than the τ_{DM} ages of $\sim$ 2.8 Ga reported for rocks of the Superior Craton (Fisher et al. 2010; Jaupart et al. 2014). Thus, a mixture of material derived from both the Acadian fold belt and Superior Craton is implicated by τ_{DM} ages of Hamilton Group deposits. The younger τ_{DM} ages of the Mahantango Formation compared to the older samples in the Marcellus Shale is interpreted to reflect increasing sediment flux derived from the Acadian fold–thrust belt over time (Tables 1, 2).

The ε_{Nd} values for the Hamilton Group samples which range from –11.74 to –7.06, are intermediate between Archean (Superior Craton) and Mid-Proterozoic (Grenville) crustal fields, suggesting a mixture of sediment derived from these two terranes (Fig. 11) (McCulloch and Wasserburg 1978; Marcantonio et al. 1990; Anderson and Sampson 1995). It is noteworthy that the single sample displaying an anomalous Sm abundance plots within the range of Grenville crustal rocks. Reported ε_{Nd} values of Acadian volcanics (+2.3 to +3.8) further exclude arc rocks as a likely source of clastic influx (Schoonmaker et al. 2011).

Provenance Model and Evolution

Geochemical and isotopic data of the Hamilton Group of West Virginia suggest that detritus was derived mainly from felsic igneous and upper-continental-crust source rocks. The lack of felsic source rocks with τ_{DM} ages roughly equal to those documented from the Hamilton Group suggests that detritus was derived from a mixture of source rocks, with input from both Archean Superior Craton and Grenville-associated sources. The Superior Craton is dominated by felsic plutonic rocks of Archean age (Percival et al. 2012) displaying τ_{DM} ages of $\sim$ 2.8 Ga. Rocks of the Acadian fold–thrust belt are slightly younger (τ_{DM} ages = $\sim$ 1.4–1.6 Ga; Dickin and Higgins 1992; Rainbird et al. 1997) and include rock units composed of detritus derived from the Grenville terrane (Anderson and Samson 1995; Thomas et al. 2014; Scott et al. 2016). Therefore, sediment eroded from the Acadian fold–thrust belt would likely be defined by a recycled-sedimentary-source geochemical signature. Thus, geochemical and isotopic signatures of Hamilton Group samples from north-central West Virginia are consistent with sediment derivation from the Superior Craton and the Acadian fold–thrust belt.

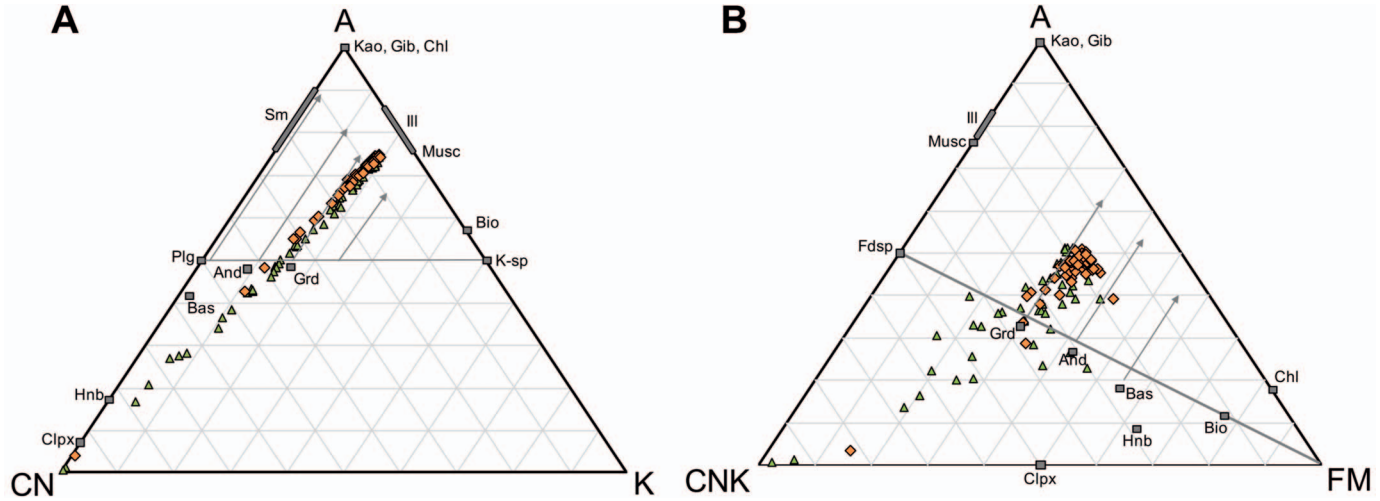

FIG. 5.—Ternary diagrams: **A)** $Al_2O_3 - (CaO + Na_2O) - K_2O$; **B)** $Al_2O_3 - (CaO + Na - {}_2O + K_2O) - (FeO_{total} + MgO)$. Abbreviations are as follows: And, andesite; Bas, basalt; Bio, biotite; Chl, chlorite; Clpx, clinopyroxene; Fdsp, feldspar; Gib, gibbsite; Grd, granodiorite; Hnb, hornblende; Ill, illite; Kao, kaolinite; K-sp, potassium feldspar; Musc, muscovite, Plg, plagioclase feldspar; Sm, smectite.

A one-dimensional mixing model using 1.53 Ga as representative τ_{DM} for the Grenville-dominated thrust belt (Dickin and Higgins 1992) and 2.8 Ga for the Superior Craton (Fisher et al. 2010; Jaupart et al. 2014) indicates that the mixture of sources was approximately 75–80% Acadian fold–thrust belt and 25–20% Superior Craton for deposits at the bottom of the Marcellus Shale. However, the Acadian fold–thrust belt may have accounted for as much as 91% of sediment deposited at the top of the Mahantango Formation, with the remaining 9% sourced from the Superior Craton (Fig. 9). The major shift in provenance occurs during early deposition of the Mahantango Formation; after this shift, the ~ 90/10 relative source contributions remains stable (Fig. 9). Decreasing τ_{DM} ages coincide with both higher Zr and TiO_2 concentrations in Hamilton Group mudrocks (Fig. 9), possibly indicating greater sediment influx from erosion of sedimentary rocks from the adjacent Acadian fold–thrust belt over time. However, increases in Zr and TiO_2 could be indicative of increasing depositional energy associated with sea-level fluctuations.

The observed τ_{DM} ages and ε_{Nd} values of the Hamilton Group samples suggest input from a slightly older source in north-central West Virginia compared to New York and Pennsylvania. Studies of Hamilton Group deposits of central and western New York have documented τ_{DM} ages ranging from 946 to 1689 Ma (Caesar et al. 2010a, 2010b) and suggested derivation of sediment from the Canadian Shield and fold–thrust-belt sediment transported westward via the Catskill Delta (Caesar et al. 2010b). The deposits analyzed by Caesar et al. (2010a, 2010b) may have been influenced by greater abundance of volcanic ashfall due to their more proximal location to the Acadian arc, resulting in a drawdown of τ_{DM} ages in the Marcellus Shale of New York. Gardiner et al. (2012) and Phan et al. (2018) documented τ_{DM} ages ranging from 1.38 to 1.61 Ga in the Marcellus Shale of Pennsylvania and New York suggesting a Grenville-aged source. However, $\varepsilon_{Nd(0)}$ values of –10.23 to –12.23 (Phan et al. 2018) fall between the ages of Archean (Superior Craton) and Mid-Proterozoic (Grenville-age) crust further supporting the idea of mixed model ages. These observations indicate the variability of detrital clay provenance along the basin axis, likely controlled by the spatial configuration of sediment transport systems along the eastern basin margin.

Oblique collision of the Avalonia micro-continent with the eastern margin of Laurentia was initiated at the St. Lawrence promontory of northern New England and southeastern Canada and gradually progressed southward (Ettensohn 1985). The earliest Marcellus deposits were dominated by intrabasinal sediments (e.g., radiolaria, pyrite framboids, pellets) to the basin from low-relief topography developed on the Superior Craton to the north along with subordinate clay shed westward off of the

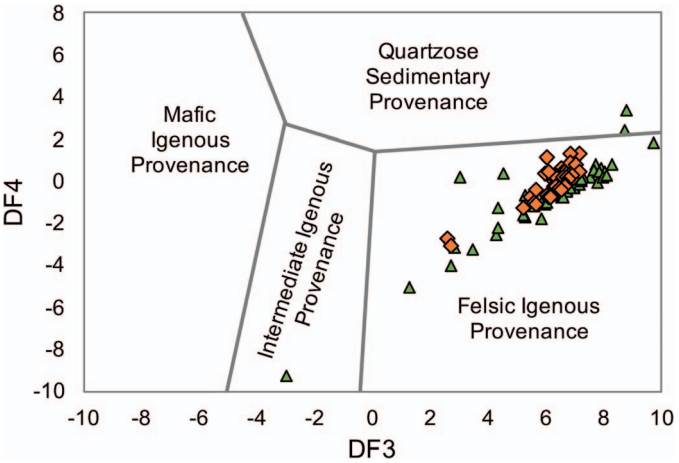

FIG. 6.—Major-element discrimination diagrams of functions D3 versus D4 developed by Roser and Korsch (1988) used to delineate source type.

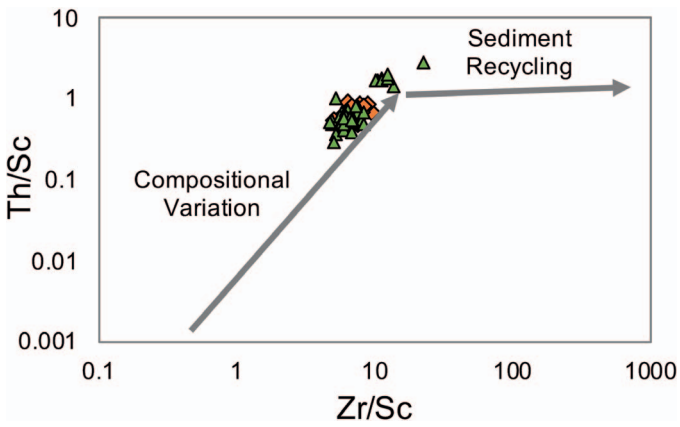

FIG. 7.—Cross-plot of Zr/Sc vs. Th/Sc.

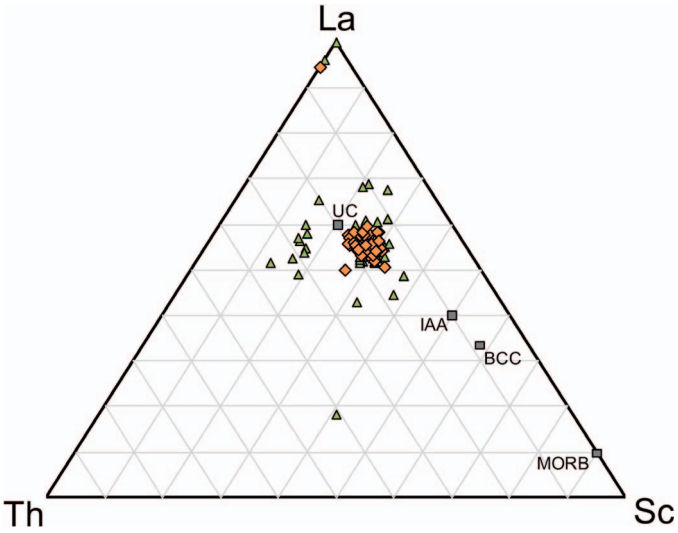

FIG. 8.—La-Th-Sc ternary diagram. Abbreviations are as follows: UC, upper crust; IAA, island-arc andesite; BCC, bulk-continental crust; MORB, mid-ocean-ridge basalt after McLennan et al. (1990) and Ma et al. (2015).

Acadian fold–thrust belt to the east. Superior Craton-derived sediments may have been routed through the modern Great Lakes region via depressions created by reactivation of Midcontinent rift structures (Van Schmus and Hinze 1985; Woodrow et al. 1988; Pinet 2016).

Increased relief related to the collision of Avalonia with the New York promontory induced increased erosion of the emerging fold–thrust belt, which supplied greater volumes of sediment to the Catskill Delta (Ettensohn 1985). Grenville-age rocks in the Acadian fold–thrust belt contributed a greater volume of sediment deposited in the Acadian Basin at this time, resulting in westward progradation of the delta system (Ver Straeten 2010). Progradation of the Catskill Delta and related transportation of clay and silt extended farther into the basin, including the modern location of north-central West Virginia. This progressive delivery of detritus from the Acadian fold–thrust belt resulted in reduced τ_{DM} ages in the lower Mahantango Formation, similar to the τ_{DM} ages documented from Marcellus Shale samples in New York (Caesar et al. 2010a, 2010b). As southward migration of the Avalonian–Laurentian suture continued to the south of the New York promontory, progradation of Acadian-derived sediment farther into the basin led to a greater proportion of Grenville-aged sediment, resulting in even younger depleted-mantle model ages and more negative ε_{Nd} in the Mahantango Formation as compared to the Marcellus Shale. Alternately, a greater structural distance of transport of the Acadian thrust-front south of the New York Promontory could have facilitated deltaic progradation and increased delivery of Acadian-derived clay and silt to north-central West Virginia.

Clastic flux to the basin could not have been dominated by contribution from the Acadian volcanic arc and associated synorogenic rocks along the eastern margin. Influx from the Acadian arc would cause a decrease in τ_{DM} and also be apparent from elemental discrimination diagrams. However, Walker and Harms (1971), in their investigation of facies changes in the Upper Devonian Catskill Formation of Pennsylvania, recognized sedimentation patterns suggesting that progradation of the eastern Devonian shoreline was dominantly influenced by accumulation of mud that had drifted along the shore from distant river mouths. Results of our work show that there was influx from the Archean crust to the north in addition to sediment delivered from the Acadian fold–thrust belt likely transported via the Catskill Delta system and associated distant river systems. Smaller transverse deltaic systems likely contributed sediment from the Acadian fold-thrust belt that mixed with sediment in the basin from the Catskill system. Comparisons of geochronologic data from Middle Devonian source terranes supports an evolving mixed model for the deposition of the Marcellus Shale and Mahantango Formation.

Provenance, Paleoclimate, and Controls on Organic-Matter Preservation

Consideration of paleoclimate fluctuations is key to interpreting clay production and its associated influence on organic-matter preservation. The Appalachian Basin was located approximately 25–30° south of the paleoequator in tropical to subtropical latitudes during the Acadian Orogeny (McKerrow and Scotese 1990). Devonian land-plant $\delta^{13}C$ values throughout the northern and central Appalachian Basin as well as a global $\delta^{18}O$ record of conodont apatite have been used to investigate pCO_2 and paleotemperature fluctuations throughout the Devonian (Joachimski et al. 2009; Wan 2012). These studies have indicated a drop in regional temperatures during the deposition of the Marcellus Shale from ~ 23.5°C to 21°C, most likely due to global cooling associated with organic-carbon burial and expansion of land plants, resulting in consequent drawdown of pCO_2. Temperatures continued to drop into the mid-Givetian and then rose, ranging from ~ 20°C to ~ 23.5°C during the deposition of the Mahantango Formation (Joachimski et al. 2009).

Weathering indices calculated from major-element geochemistry of the Hamilton Group are consistent with reconstructions of global and regional paleotemperature for the Devonian (Simon et al. 2007; Joachimski et al. 2009; Wan 2012). Specifically, upsection increases of CIA and CIW and diminishing ICV (Fig. 3) throughout the deposition of the Marcellus Shale are suggestive of increased chemical weathering intensity over time. Moreover, consistently higher CIA and CIW values through the Mahantango Formation may reflect stronger weathering intensity in the source region during this time. It is likely that the increase in influx of terrigenous clay to the basin from synorogenic sedimentation from the Acadian fold–thrust belt was enhanced by increased climate-driven chemical weathering of source rocks during this time.

Comparisons of elemental data with TOC suggest that detrital dilution exerted a strong control on organic-matter deposition in the Hamilton Group (Fig. 4). The negative covariation between TOC and geochemical proxies Al_2O_3 ($R^2 = -0.5356$), Zr ($R^2 = -0.5363$), and TiO_2 ($R^2 = -0.6771$) indicate that terrigenous clay influx from proximal sources in the Acadian fold–thrust belt negatively affected organic-matter accumulation over the duration of Hamilton Group deposition. Higher TOC concentrations of the Marcellus Shale were generated when Acadian synorogenic influx was suppressed compared to Acadian synorogenic influx to Mahantango Formation deposition. In summary, geochemical evidence suggests that organic-matter content of the Hamilton Group was in part influenced by dilution via terrigenous clastic sedimentation due to increased delivery of Acadian synorogenic sediment to the basin, likely as a result of progressive tectonism and shoreline regression aided by increased chemical-weathering intensity that enhanced sediment generation.

In contrast, deposition of the clastic sediment of the organic-rich Marcellus Shale was strongly influenced by longshore currents transporting mud from the Superior Craton. However, organic-matter accumulation in this unit is not only due to a relative "lack" of diluting sedimentation patterns, but rather a function of many factors. Production of organic matter is dependent on sufficient nutrient supply to sustain higher rates of primary productivity. Preservation of organic matter relies heavily on a stratified water body that produces anoxic bottom waters, lack of microbial degradation, and a balanced sediment supply that is great enough to bury organic matter before potential degradation or oxidation, yet low enough to not dilute it. For example, Lash and Blood (2014) conducted a thorough geochemical investigation on a Marcellus Shale core from southwestern Pennsylvania examining the role of detrital influx, redox conditions, and primary productivity on the TOC. Their results show how base-level

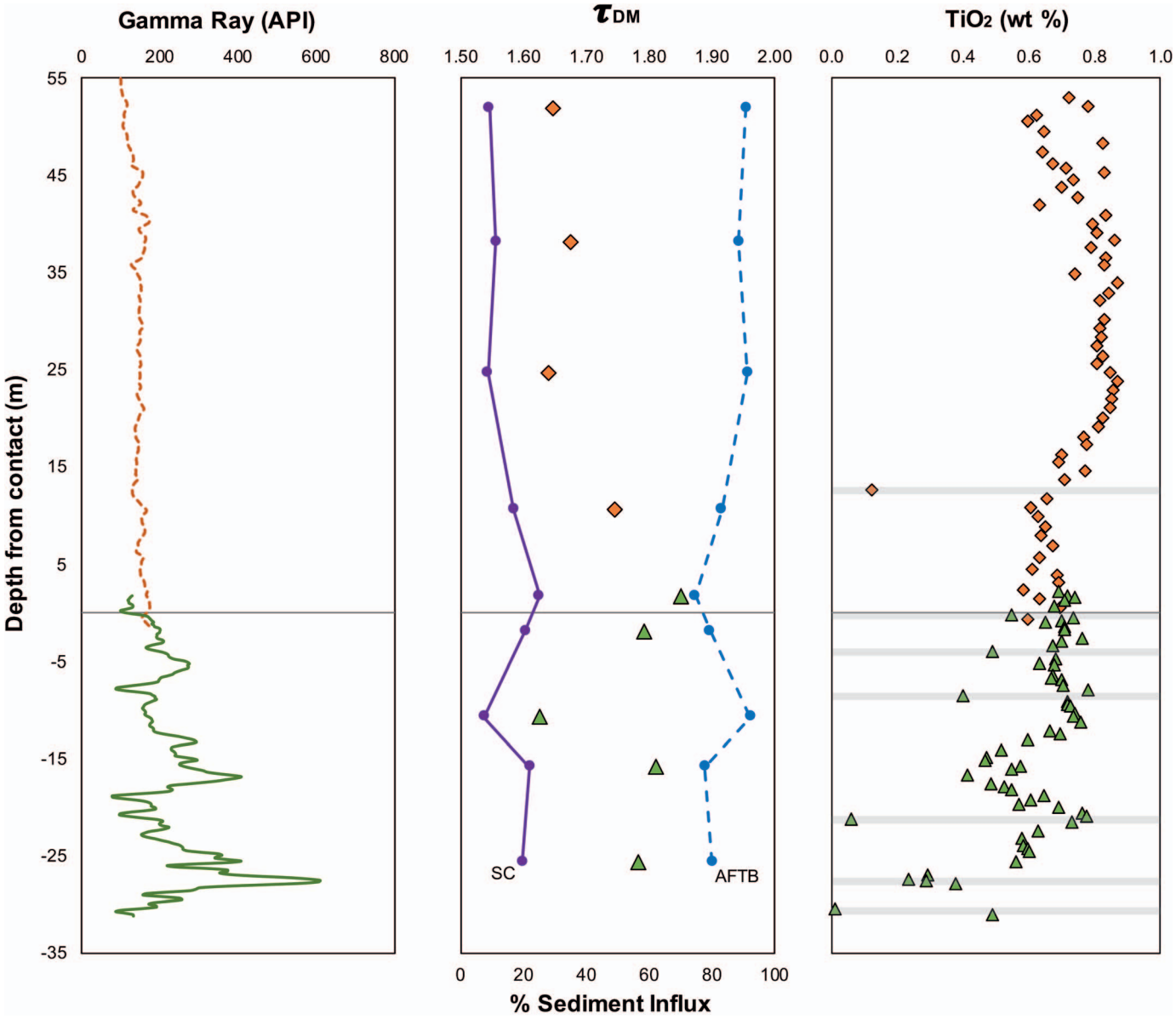

FIG. 9.—Stratigraphic trends of gamma-ray values, τ_{DM}, TiO_2, and approximate percentage of sediment influx from the two identified sources: the Superior Craton (SC; purple line) and Acadian fold–thrust belt (AFTB; dashed blue line). Note that the general trend of Zr concentration is highly correlative to that of TiO_2 shown here ($R^2 = 0.8034$). Gray bars in the TiO_2 plot indicate carbonate-rich intervals.

fluctuations throughout the deposition of the Marcellus Shale provided, at times, the ideal reducing conditions to facilitate organic-matter accumulation. Lash and Blood (2014) used Al content as a proxy for detrital influx; their results also indicate an increase in Al content correlative to lower TOC content in the upper Marcellus Shale. Results of their work are consistent with some of the interpretations presented within this study and emphasize the role of sea-level fluctuations on sedimentation and ultimately organic-matter accumulation.

CONCLUSIONS

This work provides new insight into the provenance of the Hamilton Group and its role in influencing organic-matter accumulation independent of allogenic influences of sedimentation. Geochemical provenance indicators suggest that the Marcellus Shale and the Mahantango Formation were sourced dominantly from granodioritic, felsic igneous source rocks supplemented by input from a recycled sedimentary source. Sm-Nd isotopic analysis yields ε_{Nd} values ranging from –7.06 to –11.74, with τ_{DM} ranging from 1.85 to 1.64 Ga. Together these data indicate a mixed-sediment-source model, including detritus sourced in both the Archean Superior Craton to the north and the Acadian fold–thrust belt to the east. Influx from the Acadian fold–thrust belt increased throughout the deposition of the Hamilton Group, causing τ_{DM} ages to decrease and Al_2O_3, TiO_2, and Zr content to increase upsection. Differences in organic-matter content between these two units were likely influenced by increased influx of detrital clay and consequent dilution rather than changing rates of organic production. Increased clay influx to the basin was driven by both increased chemical weathering due to warming paleoclimate and increased physical weathering from tectonic uplift and deposystem progradation during the Acadian Orogeny. Further investigation of provenance and

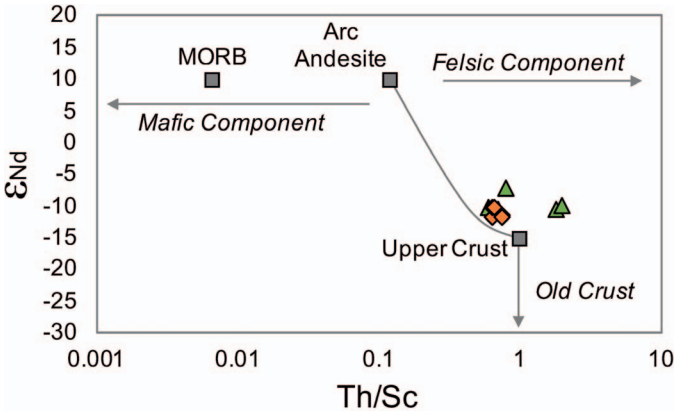

FIG. 10.—Th/Sc vs. ε_{Nd} values to identify type of source terrane. All ten data points plot near the upper-crust compositional end member.

paleoclimate signals through geochemical analysis of the Hamilton Group could better constrain our understanding of provenance and the controls on the distribution of organic-rich mudrock facies in the central Acadian Basin.

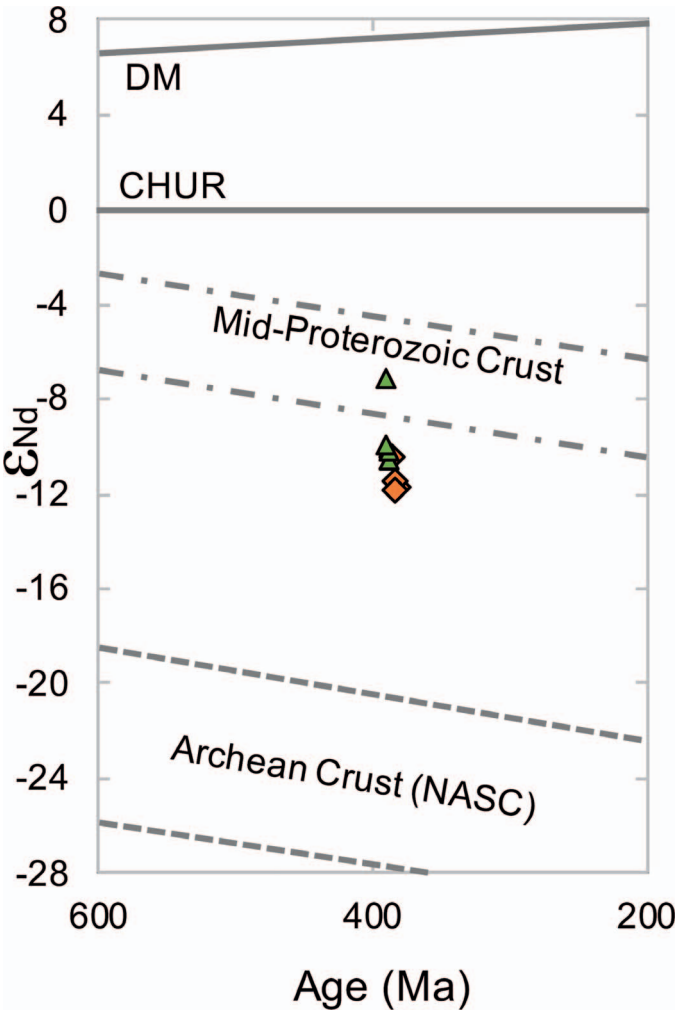

FIG. 11.—Plot of the age of Hamilton Group rocks versus ε_{Nd}. Adapted from McLennan et al. (1993) and Anderson and Samson (1995).

SUPPLEMENTAL MATERIAL

Appendices 1 and 2 are available from JSR's Data Archive: https://www.sepm.org/pages.aspx?pageid=229.

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REFERENCES

ANDERSON, C.B., AND SAMSON, S.D., 1995, Temporal changes in Nd isotopic composition of sedimentary rocks in the Sevier and Taconic foreland basins: increasing influence of juvenile sources: Geology, v. 23, p. 983–986.

ARTHUR, M.A., AND SAGEMAN, B.B., 2005, Sea-level control on source-rock development: perspectives from the Holocene Black Sea, the Mid-Cretaceous Western Interior Basin of North America, and the Late Devonian Appalachian Basin, *in* Harris, N.B., eds., The Deposition of Organic-Carbon-Rich Sediments: Models, Mechanisms, and Consequences: SEPM, Special Publication 82, p. 35–59.

BLAKEY, R., 2009, Middle Devonian North American Paleogeographic Map, accessed January 2016.

BOCK, B., MCLENNAN, S.M., AND HANSON, G.N., 1994, Rare earth element redistribution and its effects on the neodymium isotopes system in the Austin Glen Member of the Normanskill Formation, New York, USA: Geochimica et Cosmochimica Acta, v. 58, p. 5245–5253.

BRADLEY, D.C., 1983, Tectonics of the Acadian Orogeny in New England and adjacent Canada: The Journal of Geology, v. 91, p. 381–400.

CAESAR, W., MOSHER, D., REGAN, S.P., COUSENS, B.L., ASPLER, L.B., CHIARENZELLI, J., AND CHIARENZELLI, J.R., 2010a, Nd model ages and geochemistry of Devonian and Ordovician shales of western and central New York [Abstract]: Geological Society of America, Abstracts with Programs, v. 42, p. 71–72.

CAESAR, W., MOSHER, D., MURPHY, J.T., JR., AND CHIARENZELLI, J.R., 2010b, Nd TDM model ages of Upper and Middle Devonian and shales of western and central New York [Abstract]: Geological Society of America, Abstracts with Programs, v. 42, p. 288.

CAETANO, M., PREGO, R., VALE, C., DE PABLO, H., AND MARMOLEJO-RODRIGUEZ, J., 2009, Record of diagenesis of rare earth elements and other metals in a transitional sedimentary environment: Marine Chemistry, v. 116, p. 36–46.

CANIL, D., 2008, Canada's craton: a bottoms-up view: GSA Today, v. 18, p. 4–10.

CHAMLEY, H., 1989, Clay Sedimentology: Berlin, Springer-Verlag, 623 p.

CHEN, R., 2016, Dominant controls on organic-rich shale deposition: geochemical evidences from the Marcellus Shale in the Appalachian Basin [Ph.D. Thesis]: West Virginia University, 130 p.

CHEN, R., AND SHARMA, S., 2017, Linking the Acadian Orogeny with organic-rich black shale deposition: evidence from the Marcellus Shale: Marine and Petroleum Geology, v. 79, p. 149–158.

COLEMAN, J.L., JR., MILICI, R.C., COOK, T.A., CHARPENTIER, R.R., KIRSHBAUM, M., KLETT, T.R., POLLASTRO, R.M., AND SCHENK, C.J., 2011, Assessment of undiscovered oil and gas resources of the Devonian Marcellus Shale of the Appalachian Basin province: U.S. Geological Survey, Paper no. 2011-3092.

COX, R., LOWE, D.R., AND CULLERS, R.L., 1995, The influence of sediment recycling and basement composition on evolution of mudrock chemistry in Southwestern United States: Geochimica et Cosmochimica Acta, v. 59, p. 2919–2940.

DENNISON, J.M., AND HASSON, K.O., 1976, Stratigraphic cross-section of Hamilton Group (Devonian) and adjacent strata along the south border of Pennsylvania: American Association of Petroleum Geologists, Bulletin, v. 60, p. 278–298.

DENNISON, J.M., AND TEXTORIS, D.A., 1988, Devonian Tioga ash beds: 19th Annual Appalachian Petroleum Geology Symposium, Geology of Appalachian Basin Devonian Clastics: West Virginia Geological and Economic Survey, Circular C-42, p. 15–16.

DEPAOLO, D.J., 1988, Neodymium Isotope Geochemistry: An Introduction: Berlin, Springer-Vaerlag, 187 p.

DePaolo, D.J., and Wasserburg, G.J., 1976, Nd Isotopic Variations and Petrogenetic Models: Geophysical Research Letters, v. 3, p. 249–252.

Dickin, A.P., 1995, Radiogenic Isotope Geochemistry: Cambridge, UK, Cambridge University Press, 509 p.

Dickin, A.P., and Higgins, M.D., 1992, Sm/Nd evidence for a major 1.5 Ga crust-forming event in the central Grenville province: Geology, v. 20, p. 137–140.

Dickinson, W.R., Beard, L.S., Brakenridge, G.R., Erjavec, L.J., Ferguson, R.C., Inman, K.F., Knepp, R.A., Lindberg, F.A., and Ryberg, P.T., 1983, Provenance of North American Phanerozoic sandstones in relation to tectonic setting: Geological Society of America, Bulletin, v. 94, p. 222–235.

Enomoto, C.B., Olea, R.A., and Coleman, J.L., Jr., 2014, Characterization of the Marcellus Shale based on computer-assisted correlations of wireline logs in Virginia and West Virginia: U.S. Geological Survey, Scientific Investigations Report 2013–5131, 21 p.

Ettensohn, F.R., 1985, The Catskill Delta complex and the Acadian Orogeny: a model, *in* Woodrow, D.L., and Sevon, W.D., eds., The Catskill Delta: Geological Society of America, Special Paper 201, p. 39–50.

Ettensohn, F.R., and Lierman, T.R., 2013, Large scale tectonic controls on the origin of Paleozoic dark shale source rock basins: examples from the Appalachian foreland basin, eastern United States: American Association of Petroleum Geologists, Memoir 100, p. 95–124.

Faill, R.T., 1985, The Acadian orogeny and the Catskill Delta, *in* Woodrow, D.L., and Sevon, W.D., eds., The Catskill Delta: Geological Society of America, Special Paper 201, p. 15–38.

Fedo, C.M., Nesbitt, H.W., and Young, G.M., 1995, Unraveling the effects of potassium metasomatism in sedimentary rocks and paleosols, with implications for paleoweathering conditions and provenance: Geology, v. 23, p. 921–924.

Fisher, C.M., Loewy, S.L., Miller, C.F., Berquist, P., Van Schmus, W.R., Hatcher, R.D., Jr., Wooden, J.L., and Fullagar, P.D., 2010, Whole-rock Pb and Sm-Nd isotopic constraints on the growth of southeastern Laurentia during Grenvillian orogenesis: Geological Society of America, Bulletin, v. 122, p. 1646–1659.

Gardiner, J.B., Stewart, B.W., Capo, C., Phan, T.T., Sharma, S., and Toro, J., 2012, A neodymium isotope investigation of sediment sources for the Middle Devonian Marcellus Formation, Pennsylvania, USA [Abstract]: Geological Society of America, Abstracts with Program, v. 44, p. 314–315.

Gromet, L.P., Haskin, L.A., Korotev, R.L., and Dymek, R.F., 1984, The "North American shale composite": Its compilation, major and trace element characteristics: Geochimica et Cosmochimica Acta, v. 48, p. 2469–2482.

Harnois, L., 1988, The CIW index: a new chemical index of weathering: Sedimentary Geology, v. 55, p. 319–322.

Harper, J.A., and Piotrowski, R.G., 1978, Stratigraphy, extent, gas production, and future gas potential of the Devonian organic-rich shales in Pennsylvania: U.S. Department of Energy/Morgantown Energy Technology Center, Eastern Gas Shales Symposium, p. 310–329.

Harris, A.G., Stamm, N.R., Weary, D.J., Repetski, J.E., Stamm, R.G., and Parker, R.A., 1994, Conodont color alteration index (CAI) map and conodont-based age determinations for the Winchester 30′ × 60′ quadrangle and adjacent area, Virginia, West Virginia, and Maryland: U.S. Geological Survey, Miscellaneous Field Studies Map, MF-2239, 1 sheet, scale 1:100,000.

Hayward, J.M., 2012, Zircon geochronology of ash beds in the Marcellus Shale of the Appalachian basin [MS Thesis]: West Virginia University, Morgantown, West Virginia, 96 p.

Hibbard, J.P., van Staal, C.R., and Rankin, D.W., 2010, Comparative analysis of the geological evolution of the northern and southern Appalachian orogeny Late Ordovician–Permian, *in* Tollo, R.P., Bartholomew, M.J., Hibbard, J.P., and Karabinos, P.M., eds., From Rodinia to Pangea: The Lithotectonic Record of the Appalachian Basin: Geological Society of America, Memoir 206, p. 51–69.

Hupp, B.N., and Donovan, J.J., 2018, Quantitative mineralogy for facies definition in the Marcellus Shale (Appalachian Basin, USA) using XRD-XRF integration: Sedimentary Geology, v. 371, p. 16–13.

Jaupart, C., Mareschal, J.C., Bouquerel, H., and Phaneuf, C., 2014, The building and stabilization of an Archean Craton in the Superior Province, Canada, from a heat flow perspective: Journal of Geophysical Research, Solid Earth, v. 119, p. 9130–9155.

Joachimski, M.M., Breisig, S., Buggisch, W., Talent, J.A., Mawson, R., Gereke, M., Morrow, J.R., Day, J., and Weddige, K., 2009, Devonian climate and reef evolution: insights from oxygen isotopes in apatite: Earth and Planetary Science Letters, v. 284, p. 599–609.

Johnson, J.G., 1974, Shorelines of epeiric seas: American Journal of Science, v. 274, p. 465–470.

Lash, G.G., and Blood, D.R., 2014, Organic matter accumulation, redox, and diagenetic history of the Marcellus Formation, southwestern Pennsylvania, Appalachian basin: Marine and Petroleum Geology, v. 57, p. 244–263.

Lash, G.G., and Engelder, T., 2011, Thickness trends and sequence stratigraphy of the Middle Devonian Marcellus Formation, Appalachian Basin: implications for Acadian foreland basin evolution: American Association of Petroleum Geologists, Bulletin, v. 95, p. 61–103.

Ma, P., Wang, L., Wang, C., Wu, X., Wei, Y., 2015, Organic-matter accumulation of the lacustrine Lunpola oil shale, central Tibetan Plateau: controlled by the paleoclimate, provenance, and drainage system: International Journal of Coal Geology, v. 147–148, p. 58–70.

Marcantonio, F., McNutt, R.H., Dickin, A.P., and Heaman, L.M., 1990, Isotopic evidence for the crustal evolution of the Frontenac arch in the Grenville province of Ontario, Canada: Chemical Geology, v. 83, p. 297–314.

McCulloch, M.T., and Wasserburg, G., 1978, Sm-Nd and Rb-Sr chronology of continental crust formation: Science, v. 200, p. 1003–1011.

McKerrow, W.S., and Scotese, C.R., 1990, Palaeozoic Palaeogeography and Biogeography: Geological Society of London, Memoir 12, 431 p.

McLennan, S.M., Taylor, M.T., McCulloch, M.T., and Maynard, J.B., 1990, Geochemical and Nd-Sm isotopic composition of deep-sea turbidites: crustal evolution and plate tectonic associations: Geochimica et Cosmochimica Acta, v. 54, p. 2015–2050.

McLennan, S.M, Hemming, S., McDaniel, D.K., and Hanson, G.N., 1993, Geochemical approaches to sedimentation, provenance, and tectonics *in* Johnsson, M.J., and Basu, A., eds., Processes Controlling the Composition of Clastic Sediments: Geological Society of America, Special Paper 284, p. 21–40.

Milici, R.C., and Swezey, C.S., 2014, Assessment of Appalachian basin oil and gas resources: Devonian gas shales of the Devonian Shale–Middle and Upper Paleozoic Total Petroleum System: U.S. Geological Survey, Professional Paper 1708, 81 p.

Mosher, D., Caesar, W., O'Brien, N.R., Leone, J., and Chiarenzelli, J.R., 2010, Geochemical and isotopic characterization of potential gas bearing units of the Utica and Marcellus Shale, New York [Abstract]: Geological Society of America, Abstracts with Programs, v. 42, p. 63.

Murphy, A.E., Sageman, B.B., and Hollander, D.J., 2000, Black shale deposition and faunal overturn in the Devonian Appalachian basin: clastic starvation, seasonal water-column mixing, and efficient biolimiting nutrient recycling: Paleoceanography, v. 15, p. 280–291.

Nesbitt, H.W., and Young, G.M., 1984, Prediction of some weathering trends of plutonic and volcanic rocks based on thermodynamic and kinetic considerations: Geochimica et Cosomochimica Acta, v. 48, p. 1523–1534.

Nesbitt, H.W., and Young, G.M., 1989, Formation and diagenesis of weathering profiles: The Journal of Geology, v. 97, p. 129–147.

Paronish, T., 2018, Meso- and macro-scale facies and chemostratigraphic analysis of Middle Devonian Marcellus Shale in northern West Virginia, USA [MS Thesis]: West Virginia University, Morgantown, West Virginia, 382 p.

Parrish, C.B., 2013, Insights into the Appalachian Basin Middle Devonian depositional system from U-Pb zircon geochronology of volcanic ashes in the Marcellus Shales and Onondaga Limestone [MS Thesis]: West Virginia University, Morgantown, West Virginia, 149 p.

Pedersen, T.F., and Calvert, S.E., 1990, Anoxia vs. productivity: What controls the formation of organic-carbon-rich sediments and sedimentary rocks?: American Association of Petroleum Geologists, Bulletin, v. 74, p. 454–466.

Percival, J.A., Sanborn-Barries, M., Skulski, T., Stott, G.M., Helmstaedt, H., and White, D.J., 2006, Tectonic evolution of the western Superior Province from NATMAP and lithoprobe studies: Canadian Journal of Earth Sciences, v. 43, p. 1085–1117.

Percival, J.A., Skulski, T., Sanborn-Barrie, M., Stott, G.M., Leclair, A.D., Corkery, M.T., and Boily, M., 2012, Geology and tectonic evolution of the Superior Province, Canada, Chapter 6, *in* Percival, J.A., Cook, F.A., and Clowes, R.M., eds., Tectonic Styles in Canada: The Lithoprobe Perspective: Geological Association of Canada, Special Paper 49, p. 321–378.

Phan, T.T., Gardiner, J.B., Rosemary, C.C., and Stewart, B.W., 2018, Geochemical and multi-isotopic ($^{87}Sr/^{86}Sr$, $^{143}Nd/^{144}Nd$, $^{238}U/^{235}U$) perspectives of sediment sources, depositional conditions, and diagenesis of the Marcellus Shale, Appalachian Basin, USA: Geochimica et Cosmochimica Acta, v. 222, p. 187–211.

Pin, C., and Zalduegui, J.S., 1997, Sequential separation of light rare-earth elements, thorium and uranium by miniaturized extraction chromatography: application to isotopic analyses of silicate rocks: Analytica Chimica Acta, v. 339, p. 79–89.

Pinet, N., 2016, Far-field effects of Appalachian orogenesis: a view from the craton: Geology, v. 44, p. 83–86.

Potter, P.E., and Pryor, W.A., 1961, Dispersal centers of Paleozoic and later clastics of the Upper Mississippi Valley and adjacent area: Geological Society of America, Bulletin, v. 72, p. 1195–1249.

Rainbird, R.H., McNicoll, V.J., Theriault, R.J., Heaman, L.M., Abbott, J.G., Long, D.G.F., and Thorkelson, D.J., 1997, Pan-continental river system draining Grenville Orogen recorded by U-Pb and Sm-Nd geochronology of Neoproterozoic quartzarenites and mudrocks, northwestern Canada: Journal of Geology, v. 105, p. 1–17.

Rast, N., and Skehan, J.W., 1993, Mid-Paleozoic orogenesis in the North Atlantic: the Acadian Orogeny, *in* Roy, D.C., and Skehan, J.W., eds. The Acadian Orogeny: Recent Studies in New England, Maritime Canada, and the Autochthonous Foreland: Geological Society of America, Special Paper 275, p. 1–25.

Repetski, J.E., Over, J.D., and Enomoto, C.B., 2013, Conodont-based correlation of the Marcellus/Millboro formations in the Central Appalachian Basin [Abstract]: Geological Society of America, Abstracts with Programs, v. 45, p. 529.

Richard, P., Schimizu, N., and Allegre, C.J., 1976, $^{143}Nd/^{146}Nd$ a natural tracer: an application to oceanic basalts: Earth and Planetary Sciences Letters, v. 31, p. 269–278.

Roden, M.K., Parrish, R.R., and Miller, D.S., 1990, The absolute age of the Eifelian Tioga Ash Bed, Pennsylvania: Journal of Geology, v. 98, p. 282–285.

Roen, J.B., and Hosterman, J.W., 1982, Misuse of the term "bentonite" for ash beds of Devonian age in the Appalachian basin: Geological Society of America, Bulletin, v. 93, p. 921–925.

Roser, B.P., and Korsch, R.J., 1986, Determination of tectonic setting of sandstone–mudstone suites using SiO_2 content and K_2O/Na_2O ratio: The Journal of Geology, v. 94, p. 635–650.

Roser, B.P., and Korsch, R.J., 1988, Provenance signatures of sandstone–mudstone suites determined using discriminant function analysis of major-element data: Chemical Geology, v. 67, p. 119–139.

Sageman, B.B., and Lyons, T.W., 2003, Geochemistry of fine-grained sediments and sedimentary rocks, *in* MacKenzie F., ed., Treatise on Geochemistry, v. 7, p. 115–158.

Sageman, B.B., Murphy, A.E., Werne, J.P., Ver Straeten, C.A., Hollander, D.J., and Lyons, T.W., 2003, A tale of shales: the relative roles of production, decomposition, and dilution in the accumulation of organic-rich strata, Middle–Upper Devonian, Appalachian basin: Chemical Geology, v. 195, p. 229–273.

Schoonmaker, A., Kidd, W.S.F., Reusch, D.N., Dorais, M.J., Gregg, T., and Spencer, C., 2011, Stratigraphic context, geochemical, and isotopic properties of magmatism in the Siluro-Devonian inliers of northern Maine: implications for the Acadian Orogeny: American Journal of Science, v. 311, p. 528–572.

Scott, B.E., Garver, J.I., and Kidd, W.S.F., 2016, Provenance of detrital zircon in Taconic Foreland flysch, in the Hudson and Mohawk Valleys of eastern New York [Abstract]: Geological Society of America, Abstracts with Programs, v. 48, no. 30-7.

Selleck, B.W., Chiarenzelli, J., Kratzmann, D.J., Christoffersen, P., and Durham, A., 2014, Detrital zircon geochronology and provenance of Middle and Upper Devonian strata, northern Appalachian Basin of New York State [Abstract]: Geological Society of America, Abstracts with Programs, v. 46, p. 98.

Selleck, B., Ver Straeten, C., Chiarenzelli, J.R., and Holzman, E., 2016, Provenance evolution during assembly of the Acadian/Neoacadian Orogen: detrital zircon data from the Devonian of New York [Abstract]: Geological Society of America, Abstracts with Programs, v. 48, paper no. 30-10.

Simon, L., Goddéris, Y., Buggisch, W., Strauss, H., and Joachimski, M.M., 2007, Modeling the carbon and sulfur isotope composition of marine sediments: climate evolution during the Devonian: Chemical Geology, v. 246, p. 19–38.

Sinha, A.K., Thomas, W.A., and Hatcher, R.D., 2010, Ordovician to Devonian magmatism associated with Taconic collisional tectonics in the Central Appalachians [Abstract]: an example of an orogenic cycle: Geological Society of America, Abstracts with Programs, v. 42, p. 98.

Soeder, D.J., Enomoto, C.B., and Cermak, J.A., 2014, The Devonian Marcellus Shale and Millboro Shale: Geological Society of America, Field Guide 35, p. 129–160.

Thomas, W.A., Mueller, P.A., and Gehrels, G.E., 2014, Detrital-zircon record of provenance of Ordovician–Devonian sandstones in the Appalachian Foreland [Abstract]: Geological Society of America, Abstracts with Program, v. 46.

Tucker, R.D., Bradley, D.C., Ver Straeten, C.A., Harris, A.G., Ebert, J.R., and McCutcheon, S.R., 1998, New U-Pb zircon ages and the duration and division of Devonian time: Earth and Planetary Science Letters, v. 158, p. 175–186.

Van Schmus, W.R., and Hinze, W.J., 1985, The Midcontinent Rift System: Annual Review of Earth and Planetary Sciences, v. 13, p. 345–383.

van Staal, C.R., Barr, S.M., Whalen, J.B., and White, C.E., 2011, Constraints on the tectonic setting of Devonian magmatism and orogenesis [Abstract]: Geological Society of America, Abstracts with Programs, v. 43, p. 158.

Ver Straeten, 1995, Stratigraphic synthesis and tectonic and sequence stratigraphic framework, upper Lower and Middle Devonian, northern and central Appalachian Basin [Ph.D. Thesis]: University of Rochester, Rochester, New York, 824 p.

Ver Straeten, C.A., 2004, K-bentonites, volcanic ash preservation, and implications for Early to Middle Devonian volcanism in the Acadian orogen, eastern North America: Geological Society of America, Bulletin, v. 116, p. 474–489.

Ver Straeten, C.A., 2010, Lessons from the foreland basin: northern Appalachian basin perspectives on the Acadian orogeny, *in* Tollo, R.P., Bartholomew, M.J., Hibbard, J.P., and Karabinos, P.M., eds., From Rodinia to Pangea: The Lithotectonic Record of the Appalachian Region: Geological Society of America, Memoir 206, p. 251–282.

Ver Straeten, C.A., and Sageman, B.B., 1999a, Elemental geochemistry of mudrocks, Middle to Upper Devonian Appalachian foreland basin: implications for source province and Acadian unroofing [Abstract]: Geological Society of America, Abstracts with Programs, v. 31, p. 76.

Ver Straeten, C.A., and Sageman, B.B., 1999b, Mudrock geochemistry, Devonian Appalachian Foreland Basin [Abstract]: implications for source provenance, and unroofing of the Acadian Orogeny: Geological Society of America, Abstracts with Programs, v. 31, p. 375.

Walker, R.G., and Harms, J.C., 1971, The "Catskill Delta": a prograding muddy shoreline in central Pennsylvania: The Journal of Geology, v. 79, p. 381–399.

Wan, Z., 2012, Stable Carbon and Nitrogen Isotopic Studies of Devonian Land Plants: An Indicator of Paleoclimate and Paleoenvironmental Changes [Ph.D. Thesis]: University of Cincinnati, Cincinnati, Ohio, 156 p.

Wang, G., and Carr, T.R., 2013, Organic-rich Marcellus Shale lithofacies modeling and distribution pattern analysis in the Appalachian Basin: American Association of Petroleum Geologists, Bulletin, v. 97, p. 2173–2205.

Woodrow, D.L., Dennison, J.M., Ettensohn, F.R., Sevon, W.T., and Kirchgasser, W.T., 1988, Middle and Upper Devonian stratigraphy and paleogeography of the central and southern Appalachians and eastern Midcontinent, USA, *in* Devonian of the World: 2nd International Symposium on the Devonian System, Regional Syntheses, Proceedings, Memoir 14, v. 1, p. 277–301.

Yu, W., 2015, Developments in modeling and optimization of production in unconventional oil and has reservoirs [Ph.D. Thesis]: University of Texas at Austin, Austin, Texas, 264 p.

Zhou, C.H., and Keeling, J., 2013, Fundamental and applied research on clay minerals: from climate and environment to nanotechnology: Applied Clay Science, v. 74, p. 3–9.

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