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Provenance of the Hamilton Group: A Study of Source-to-Sink Relationships within the Middle Devonian Central Appalachian Basin

Brittany N. Hupp

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**Provenance of the Hamilton Group: A study of source-to-sink
relationships within the Middle Devonian central Appalachian
Basin**

Brittany N. Hupp

**Thesis submitted
to the Eberly College of Arts and Sciences
at West Virginia University**

in partial fulfillment of the requirements for the degree of

**Master of Science in
Geology**

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Joe Donovan, Ph.D.
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Department of Geology and Geography

**Morgantown, West Virginia
2017**

**Keywords: Marcellus Shale, Mahantango Formation, Hamilton Group, mudrock,
provenance**

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ABSTRACT

Provenance of the Hamilton Group: A study of source-to-sink relationships within the Middle Devonian central Appalachian Basin

Brittany N. Hupp

Little is known of the provenance of detrital clays in the Hamilton Group, which contains one of the most lucrative unconventional shale gas plays in the world. The Hamilton Group consists of both the organic-rich Marcellus Shale and the overlying, clay-rich Mahantango Formation. This research, in collaboration with the Marcellus Shale Energy and Environmental Laboratory (MSEEL) project, aims to constrain the provenance of the two units within the Hamilton Group and evaluate paleoclimate indicators in order to better understand the role of clastic influx on organic-matter production and preservation within the Middle Devonian Acadian foreland basin.

Geochemical and petrographic analysis of 121 samples from two different wells in Monongalia Co., West Virginia indicate slight changes in provenance throughout the deposition of the Marcellus Shale into the Mahantango Formation. Major and trace element geochemistry indicates a felsic igneous, upper-continental crust sediment source of granodioritic composition with additional influx from a quartzose recycled sedimentary source. Nine samples throughout the Hamilton Group underwent Sm-Nd isotopic analysis, yielding ϵ_{Nd} values ranging from -7.06 to -11.75 and Nd depleted mantle model ages (τ_{Nd}) ranging from 1.63-1.85 Ga, with ages becoming younger up-section. Mineralogical data acquired from x-ray diffraction analysis found the dominant mineral phases to be illite, muscovite, and quartz with fairly consistent mineralogy found throughout the Mahantango Formation and slightly more heterogeneous mineralogy found throughout the Marcellus Shale. Weathering indices including the CIA, CIW, and ICV all indicate increased weathering throughout the deposition of the Marcellus Shale followed by constant moderate rates of weathering during deposition of the Mahantango Formation.

These results suggest that the extrabasinal detrital sediments of the Hamilton Group came from a mixed sediment source with clay influx from both the Superior Craton to the north ($\tau_{\text{Nd}} > 2.7$ Ga) and Grenville-sourced sediments of the adjacent Acadian fold-thrust belt to the east (~1.0-1.3 Ga). Older model ages, felsic composition, and evidence of sediment recycling suggest little to no influx from the Acadian volcanic arc, aside from the volcanic air fall tuffs of the Tioga Ashes. Model ages and trace element geochemistry indicate increased sediment influx from the fold-thrust belt during the deposition of the Hamilton Group, with the highest sediment influx having occurred during Mahantango Formation deposition. Petrographic and geochemical analyses suggest that variations in organic-content throughout the Hamilton Group is due to dilution of organic-matter by increased influx of detrital clays during its deposition, particularly within the Mahantango Formation. Consistent clay mineralogy and weathering indices suggest that this influx of detrital sediment is not a function of climate fluctuations at this time, but rather may be influenced by increased tectonic activity and fluvial progradation during the second tectophase of the Acadian Orogeny.

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INTRODUCTION

1.1 Research Purpose

1.1.1 Marcellus Shale Energy and Environmental Laboratory (MSEEL)

The Marcellus Shale Energy and Environmental Laboratory, MSEEL, is a collaborative project between West Virginia University, Ohio State University, and the Department of Energy- National Energy Technology Laboratory (NETL). The focus of the MSEEL project is to “provide a long-term field site to develop and validate new knowledge and technology to improve recovery efficiency and minimize environmental implications of unconventional resource development” (MSEEL, 2015). Funding and resources for portions of this thesis were provided through the MSEEL project. This thesis aims to contribute to the characterization of the inorganic mineralogical constituents (i.e. clays, silts, etc.) within the Marcellus Shale from a geochemical, sedimentological, and petrographic perspective and to further the understanding of the source-to-sink relationships that produced this organic-rich, lucrative unconventional shale gas play. Three wells were drilled and monitored under the MSEEL project: one vertical well, the MIP-SW or “science well”, and two horizontal wells, the MIP-3H and MIP-5H. Samples from the MIP-3H well were used to characterize and evaluate the Marcellus Shale, whereas the Mahantango Formation was explored using samples from the WV-6 well that was part of the DOE Eastern Gas Shales Program.

1.1.2 Research Objectives

The Middle Devonian Hamilton Group of the central Appalachian Basin in north-central West Virginia contains two stratigraphic sub-units: the Marcellus Shale and the

overlying Mahantango Formation. The Marcellus Shale contains organic-rich mudrock facies. While the Mahantango Formation is also composed primarily of mudrock, it does not contain abundant organic matter. Although organic matter in the Marcellus Shale has been studied extensively due to its relevance to hydrocarbon production (i.e. Harper and Piotrowski, 1978; Morshed and Tatham, 2013; Wang and Carr, 2013; Enomoto *et al.*, 2014; Yu, 2015), little work has been done to understand the source-to-sink relationships that produced the inorganic sediments in the Marcellus Shale and associated mudrock formations.

Determining the source of the extrabasinal clastic sediment within the Hamilton Group has implications for understanding the spatial and temporal distribution of organic-matter accumulation within clay-rich depositional environments, and could aid in understanding organic-matter distribution in other potential unconventional mudrock reservoirs. Organic 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; Fig. 1). Warmer, humid climates lead to increased secondary clay production primarily through hydrolysis of feldspars (Chamley, 1989; Zhou and Keeling, 2013), which can lead to increased clay-sized clastic sediment supply. Similarly, changes in source lithology due to uplift, unroofing, or drainage capture, can also alter clastic sediment flux volumes. Input of nutrients, such as nitrogen or phosphorus, are often supplied from terrestrial sediment influx to the basin, leading to increased primary biologic production. If anoxic/euxinic bottom waters exist, preservation of abundant organic matter in basin deposits can occur. However, increased terrestrial flux can also increase clay

Figure 1. Model showing the dominant processes that influence both the production and preservation of organic matter (OM) in marine sediments (Sageman *et al.*, 2003). The focus of this study is primarily on the “dilution” portion of this model by contributing to the understanding of mechanisms influencing clastic influx to the basin, specifically provenance and paleoclimate.

sedimentation in the basin, which can dilute organic-matter concentration and limit the hydrocarbon potential of mudrock deposits (Fig. 1). In addition, distance from the shoreline and fluctuations in water depth can also control the distribution of organic-matter deposition.

The Hamilton Group provides an excellent opportunity to explore the relationships between the controls on organic production/preservation in mudrock-dominated strata through a comparison between the geochemical compositions of the organic-rich Marcellus Shale with the clay-rich Mahantango Formation. This up-section decrease in organic-matter content leads to the question: is the decrease in organic-matter deposition in the Hamilton Group controlled by a change in provenance that led to an increase in clay delivery to the basin? The objectives of this research are as follows: 1) to establish the provenance of clastic detritus in the Middle Devonian Hamilton Group of

the central Appalachian Basin region and 2) to test the hypothesis that a change in clay provenance resulted in the decrease in organic-matter deposition and preservation within the stratigraphic units of the Hamilton Group.

1.2 Geologic Background

1.2.1 Tectonic Setting

The Hamilton Group is part of an eastward-southeastward thickening clastic wedge that was deposited in the retroarc foreland basin that developed due to the Acadian Orogeny (Ettensohn, 1985; Ver Straeten, 2010). Collision of the Avalonia micro-continent along the eastern margin of Laurentia from the Late Ordovician to Early Mississippian produced an orogenic belt that extended from southeastern Canada to Tennessee, and potentially as far south as Alabama (Ver Straeten, 1995; Hibbard *et al.*, 2010; Lash and Engelder, 2011). Thrust loading, subsidence, and uplift related to the Acadian orogeny produced a foreland basin inundated by the Kaskaskia Sea, in which the Hamilton Group was deposited (Ettensohn, 2011; Ettensohn and Lierman, 2012; Ettensohn and Lierman, 2013; Fig. 2-4).

1.2.2 Stratigraphy of the Acadian Basin

The Middle Devonian fine-grained sediments within the Acadian Basin vary greatly in nomenclature and surface/subsurface expression across the eastern United States. Nomenclature for these units vary throughout the Appalachian region, but is most commonly recognized as the Hamilton Group (Fig. 5). The Hamilton

Figure 2. Cross-section of Acadian Orogeny basin model showing the formation of the foreland basin and subsequent deposition of Middle Devonian mudrock units (Ver Straeten, 2010).

Figure 3. Map view of Acadian Orogeny tectonic model during the Middle Devonian showing plate movement and syn-orogenic deposits (Lash and Engelder, 2011).

Figure 4. Paleogeographic reconstruction of Laurentia during the Middle Devonian (385 Ma) in relation to the paleoequator with the approximate location of Monongalia County, WV marked by a red star (From Blakey, 2009).

System	Ohio	West Virginia	W. Pennsylvania	NW New York	Stage
U. Devonian		Brailer Formation			Frasnian
	Olentangy Shale	Harrell Shale	Harrell Shale	Genesee Formation	
		Tully Limestone	Tully Limestone	Tully Limestone	
	?????	Mahantango Formation	Mahantango Formation	Moscow Shale	Givetian
	Prout Limestone			Ludlowville Shale	
	Plum Brook Shale			Skaneateles Shale	
	Delaware Limestone	Marcellus Shale	Marcellus Shale	Marcellus Shale	
	Columbus Limestone	Huntersville Chert	Seinsgrove LS	Onondaga Limestone	Eifelian
L. Devonian	Bois Blanc Limestone				
		Needmore Shale	Needmore Shale	Bois Blanc Formation	Emsian

383 Ma

388 Ma

393 Ma

Figure 5. Stratigraphic column showing nomenclature differences and formation correlations within the Appalachian Basin Middle Devonian system with overlying and underlying units included. The Middle Devonian Hamilton Group and the units it contains are shown in color. Modified from Milici and Swezey (2014).

Group extends from eastern West Virginia and western Pennsylvania into Maryland and Virginia. Across West Virginia, these strata are mainly found buried in the subsurface of the Appalachian basin (Fig. 6); however, the units outcrop in the Appalachian Valley and Ridge Province of eastern West Virginia, Maryland, and northern Virginia.

Regionally, the Hamilton Group overlies the Lower Devonian (Upper Emsian to Lower Eifelian) Needmore Shale in eastern WV, Maryland, and western PA, the Huntersville Chert in WV, the Seinsgrove Limestone in eastern PA, or the Onondaga Limestone in western WV, central PA, and NY (Cleaves *et al.*, 1968; Harris *et al.*, 1994; Milici and Swezey, 2014). Overlying the Hamilton Group in the study area of north-central WV is the Tully Limestone and Harrell Shale (also referred to as the Genesee Formation in New York; Dennison and Hasson, 1976; Milici and Swezey, 2014, Soeder *et al.*, 2014).

Within the study area, the Hamilton Group is approximately 250 ft. thick and contains the Marcellus Shale (~100 ft.) and Mahantango Formation (~150 ft.; Fig. 5). The Marcellus Shale is a gray to black, thinly-laminated, organic-rich shale. The Tioga Ashes, also referred to as the Tioga Bentonites, are found interbedded within the basal part of the Marcellus Shale (Roen and Hosterman, 1982; Dennison and Textoris, 1988; Ver Straeten, 2004). The Marcellus Shale is gradationally overlain by the Mahantango Formation, a gray, thickly laminated, interbedded silty shale and siltstone-dominated unit (Fig. 7, 8; Dennison and Hasson, 1976; Soeder *et al.*, 2014). The contact between these two units is difficult to identify and is often marked in well logs as a transition from high gamma ray signature of the organic-rich Marcellus Shale compared to low clay-rich gamma ray signature of the Mahantango Formation (Soeder *et al.*, 2014; Fig. 9).

Figure 6. A: Map showing the extent and distribution of the Marcellus Shale and Millboro Formation (gray) throughout the Appalachian Basin, outlined in red. Black lines are isopachs showing the thickness of the Marcellus Shale in feet. Hachures along these isopachs indicate direction of thinning. The approximate location of the study area, Monongalia Co., WV, is indicated by the yellow box. Adapted from Milici and Swezey (2014). B: Map of Monongalia County, WV showing the location of the two wells sampled in this study.

Figure 7. Images of the gray, silty shale dominated Mahantango Formation outcropping near Grant, WV (A and B) as well as a picture of the WV-6 core at 7314 ft (C).

Figure 8. Image of core collected from 7546-7550 ft the MIP-3H well showing the dark black, organic-rich Marcellus Shale (A; Courtesy of Tom Paronish, 2016). Picture of the Marcellus Shale outcropping near Huntersville, WV (B).

Conodont biostratigraphy of interbedded carbonates sampled from outcrops in Pocahontas County, WV indicate the Marcellus Shale was deposited during the Eifelian to early Givetian (*hemiansatus* zone) and the Mahantango Formation during the Givetian (Harris *et al.*, 1994; Repetski *et al.*, 2013). However, zircon U-Pb ages from the Tioga Ashes sampled from wells in Taylor, Wetzel, and Harrison counties in West Virginia, yielded ages ranging from 394 to 389 Ma, indicating late Emsian to Late Eifelian deposition of the Marcellus Shale (Parrish, 2013). Based on these age estimates, the Hamilton Group records approximately 11 million years of deposition during the Devonian time period.

In north-central West Virginia, the Hamilton Group overlies the Onondaga Limestone. Within the MIP-3H core obtained through the MSEEL project, this contact

Figure 9. Well logs from the MIP-3H well, showing the Mahantango Formation and Marcellus Shale intervals. Well logs from left to right include caliper, gamma ray, resistivity, neutron porosity, density porosity, neutron-density separation, and photoelectric. The black dots marked to the right of the gamma ray indicate where core plugs were collected as part of the MSEEL project. Note the distinct differences in both the gamma-ray and TOC logs between the Marcellus Shale and overlying Mahantango Formation. Logs courtesy of T. Paronish (2017).

appears as a lithologic transition from fossiliferous limestone of the Onondaga Limestone to the overlying black shale of the Marcellus Shale. The contact between the Marcellus Shale and Mahantango Formation in both sampled wells was determined by the distinct transition from high to low gamma ray. The Tully Limestone gradationally overlies the Mahantango Formation and is identified in the WV-6 core by the transition into a lighter-colored carbonate-rich lithology.

1.2.3 Devonian Paleoclimate

Paleoclimate is often indicated as a primary control on the deposition of organic matter in the Hamilton Group (Sageman *et al.*, 2003; Emmanuel, 2014). Several studies have characterized global temperature variations throughout the Devonian. Joachimiski *et al.* (2009) measured $\delta^{18}\text{O}$ from hundreds of Devonian conodonts across Europe, North America, and Australia (Fig. 10). These measurements support the interpretation of warm, tropical temperatures ($\sim 30^\circ\text{C}$) globally during the Early Devonian (Lochkovian), to cooler temperatures during the Middle Devonian ($\sim 23\text{-}25^\circ\text{C}$) recognized by an enrichment in $\delta^{18}\text{O}$, followed by a temperature increase back to 30°C at the Frasnian-Famennian transition. Carbon cycle modeling of organic carbon burial and atmospheric CO_2 based on $\delta^{13}\text{C}$ and $\delta^{34}\text{S}$ measurements of marine carbonates from central and southern Europe and marine sulfates from Canada, Australia, Russia, Ukraine, Belgium, France, and Bulgaria indicate Early Devonian temperatures ranged from 27° to 30°C , Middle Devonian temperatures ranged from 25° to 28°C , and Late Devonian temperatures ranged from 26° to 29°C (Simon *et al.*, 2007). Simon *et al.* (2007) attributed the average $\sim 2^\circ\text{C}$ cooling to organic carbon burial and silicate weathering, leading to a

Figure 10. Paleotemperature reconstruction from Paleozoic conodont apatite $\delta^{18}\text{O}$ measurements-1‰ VSMOW. The period of deposition for the Hamilton Group has been denoted by the red box. Note the decrease in global temperatures throughout the Eifelian into the Early Givetian, followed by an abrupt increase in global temperatures from the Middle to Late Givetian. (Joachimski *et al.*, 2009).

drawdown in atmospheric CO_2 . The aforementioned studies support global cooling during the Eifelian into the beginning of the Givetian during deposition of the Hamilton Group. This cooling period was followed by global climate warming throughout the middle Givetian into the Frasnian.

In the region of the study area, $\delta^{13}\text{C}$ composition of Devonian land plants have been extensively studied throughout the northern and central Appalachian Basin, including outcrops from north-central Pennsylvania, eastern New York, and northern Ohio (Wan, 2012). Several paleoclimate study localities as far north as Quebec and New Brunswick, and as close as 50 miles south of the study area as Elkins, West Virginia,

provide insight into paleoclimate fluctuations within the north-central Middle Devonian Acadian Basin. Results indicate that on average, the $\delta^{13}\text{C}$ values were 3-4 ‰ higher during the Middle Devonian than the Early and Late Devonian (Wan, 2012). This trend implies lower atmospheric CO_2 and a cooler climate during the Middle Devonian compared to the Early and Late Devonian. During the deposition of the Marcellus Shale, temperatures dropped from $\sim 23.5^\circ\text{C}$ to 21°C (Wan, 2012). Temperatures continued to drop into the mid-Givetian and then rose, ranging from $\sim 20^\circ\text{C}$ to $\sim 23.5^\circ\text{C}$ during the deposition of the Mahantango Formation. Overall, these paleotemperatures are consistent with the sub-tropical paleolatitudinal interpretation of the basins paleogeographic location, approximately $25\text{-}30^\circ$ south of the paleoequator (McKerrow and Scotese, 1990).

1.3 Previous Studies

1.3.1 Provenance Terranes surrounding the Middle Devonian Acadian Basin

Epeiric seas occupied regions west of the Acadian Basin and were dominated by carbonate deposition (Johnson, 1974; Blakey, 2009); thus, there was likely minimal input of detrital clay from western sources. Instead, provenance of the Hamilton Group could have been associated with three potential sediment sources, or provenance terranes adjacent to the Acadian Basin: 1) the Acadian arc to the east, 2) the Acadian fold-thrust belt to the east, and 3) the Superior Craton to the north (Table 1). Additionally, sediment influx could have been sourced from the Grenville and Taconic orogenic rocks exposed in the remnants of the Taconic Highlands. These potential source terranes vary in lithology, age, and geochemical compositions.

Table 1. Table summarizing the geochemical signatures of each potential terrane within the Acadian foreland basin system. Note that it is possible that the provenance of the detrital sediments within the Hamilton Group could be from a mix of these sources.

Potential Terranes	Terrane Type	ϵ_{Nd}	Predicted τ_{DM}	Th/Sc	Major Elements	Additional Signatures	General Composition
Superior Craton	Old Upper Continental Crust (OUC)	≤ -10	>2.7 Ga	$= 1.0$	High CIA and Si/Al	Minor signs of sediment recycling	Felsic Igneous
Acadian Fold- Thrust Belt	Recycled Sedimentary Rocks (RSR)	≤ -10	$\sim 1.0\text{-}1.3$ Ga	≥ 1.0	High CIA and Si/Al	High Zr and Hf as signs of sediment recycling	Felsic Igneous or Quartzose Sedimentary
Acadian Volcanic Arc	Young Differentiated Arc (YDA)	$\geq +5$	$\sim 400\text{-}420$ Ma	Variable	Lower CIA than other OUC/RSR	Progressively older ages up-section	Felsic to Intermediate Igneous

The Acadian arc was located to the east of the Acadian Basin during the Middle Devonian (Fig. 2-4). Ash beds, known as the Tioga Ashes, found intermittently throughout the lower Marcellus Shale and underlying Onondaga Limestone, show air-fall volcanic input from this coastal volcanic arc during time of deposition. U-Pb zircon ages from these ash layers show periodic volcanic activity ranging from the Late Emsian (~394 Ma) to Late Eifelian (~389 Ma) (Tucker *et al.*, 1998; Ver Straeten, 2002; Parrish, 2013). In addition to distributing ashes across the southeastern surface of Laurentia, the Acadian arc magmatism generated internal felsic to intermediate melts (van Staal *et al.*, 2011; Parrish, 2013). Syn-orogenic magmatic granitoid rocks formed from the partial melting of subducted fore-arc material associated with flat slab subduction and show U-Pb zircon ages ranging from approximately 420-400 Ma (van Staal *et al.*, 2009; Sinha *et al.*, 2010). Sm-Nd studies of syn-orogenic volcanic rocks in Maine yielded τ_{DM} ages ranging from ~403-417 Ma (Schoonmaker *et al.*, 2011). Weathering and unroofing of the Acadian arc would produce sediment with geochemically felsic to intermediate composition. Erosion of Acadian volcanic and plutonic rocks would yield first-cycle sediment with low CIA values compared to sediment derived from highly-weathered cratonic or recycled sedimentary rocks.

Sediment influx from the Acadian fold-thrust belt would show a recycled sedimentary source rock geochemical signature. The Acadian fold-thrust belts lay to the east-northeast of the basin and extended from New Brunswick to Alabama (Fig. 2-4). Early Devonian (~400 Ma) to Grenville aged (~1250 Ma) rocks were thrust westward during the Acadian Orogeny (Fig. 2 and 11). The Acadian fold-thrust belt consists of Precambrian through Devonian strata; however, much of the Lower Paleozoic strata are

carbonate rocks which could not supply a significant influx of clay minerals to the Acadian foreland. The Taconic foreland basin deposits that formed during the Ordovician are primarily quartzolitic in composition. Detrital zircon analysis and Sm-Nd isotopic analysis from Taconic flysch indicate sediment input from erosion of rocks from the Grenville terrane (~1.0-1.3 Ga; Anderson and Samson, 1995; Scott *et al.*, 2016). Silurian and Early Devonian sandstones (e.g., Tuscarora Sandstone, Rose Hill Formation, Keefer Sandstone, Oriskany Sandstone) also show detrital-zircon provenance indicating dominantly Grenville (1330-1560 Ma) sediment sources, though a few 553 Ma zircon grains within the Tuscarora Sandstone indicate younger Neoproterozoic rocks of peri-Gondwanan origin also provided sediments (Thomas *et al.*, 2014). These rocks uplifted in the Acadian fold-thrust belt would generate a recycled orogenic source provenance signature (Dickinson *et al.*, 1983).

Overall, erosion of rocks from the adjacent fold-thrust belt to the east of the Acadian basin would generate sediment with highly-evolved major element abundances (McLennan *et al.*, 1993). Sediment influx from the fold-thrust belt would yield higher CIA and Si/Al values than first-cycle sediment derived from granitic or metamorphic rocks. The ϵ_{Nd} values for recycled sedimentary rock sources (RSR) typically are ≤ -10 (McLennan *et al.*, 1993). Input from a RSR source would also likely show enrichment of elements associated with refractory heavy minerals that typically survive multiple episodes of weathering and erosion; for example, abundant zircon would cause abundant Zr and Hf.

Cratonic sources to the north-northwest serve as the last potential source terrane. The Superior Craton lies north of the Devonian Acadian Basin and has been tectonically

stable since the Archean (Canil, 2008). The Superior Craton formed primarily as crust-derived granodioritic plutons during the Archean (Percival *et al.*, 2012; Jaupart *et al.*, 2014). Sm-Nd isotopic dating of the craton has yielded depleted mantle model (τ_{DM}) ages

Figure 11. Stratigraphy of the Valley and Ridge Province of the Appalachian Mountains, showing Lower Paleozoic sedimentary units that were likely part of the Acadian fold-thrust belt. The dashed line indicates the probable décollement of these thrust sheets. Red arrows indicate activity along the eastern margin of Laurentia throughout the Lower Paleozoic, while the blue arrow indicates an extended period of eastern Laurentia being a passive margin. Adapted from Sak *et al.* (2012).

Figure 12. Generalized map of Proterozoic and older terranes of eastern North America, established through U-Pb zircon ages and Sm-Nd (T_{DM}) depleted mantle model ages. Abbreviated terranes are as follows: AD-Adirondacks; BG-Baltimore Gneiss; CO-Crab Orchard; CG- Corbin Gneiss; GL-Goochland terrane; OH- Old Hickory; HU-Honeybrook; RM-Roan Mountain, SFM-St. Francois Mountains; SM-Sauratown Mountain window; TD-Toxaway dome; TF-Tallulah Falls dome; TR- Trimont Ridge; VBR-Virginia Blue Ridge (Fisher *et al.*, 2010) Note the location and age of Grenville terranes along the eastern side of the basin and Superior Craton terrane to the north of the paleo-basin. The study area for this research is indicated by the red box.

ranging from 2.7 to 3.1 Ga, with an average τ_{DM} age of ~2.8 Ga (Fig. 12; Percival *et al.*, 2006; Fisher *et al.*, 2010; Percival *et al.*, 2012). The Superior Craton serves as an old upper-continental crust source (OUC), likely exhibiting highly-evolved major elements

(i.e. Si/Al ratios) which would reflect both the dominantly granodioritic composition and intense weathering history associated with the older age of the source. Overall, these rocks tend to display signatures of felsic/granitic composition with additional signs of sediment recycling and old depleted mantle model ages of >2.7 Ga (Fisher *et al.*, 2010; Percival *et al.*, 2006; Percival *et al.*, 2012).

1.3.2 Previous provenance analysis of Acadian syn-orogenic sediments

Only one previous study has investigated provenance of the Marcellus Shale in the central Appalachian Basin region. Gardiner *et al.* (2012) sampled a core drilled in Greene County of southwestern Pennsylvania to conduct Sm-Nd isotopic dating on the detrital sediments and U-Pb dating on zircons within the ash beds of the Marcellus Shale. Their results yielded Nd depleted mantle model ages of 1.4 to 1.6 Ga to which they attributed to detrital sediments being dominantly sourced from Acadian orogenic highlands to the east. Zircon crystals in the ash exhibited inherited cores that yielded U-Pb ages of ~1.0 Ga, suggesting the volcanic magmatic system assimilated rocks of Grenville basement (Gardiner *et al.*, 2012). Zircon from ash beds of the lower Marcellus in West Virginia were similarly found to contain inherited cores with Grenville U-Pb ages (Parrish, 2013; Hayward, 2012).

Many studies have evaluated provenance of the Hamilton Group in New York given the subsurface thickness and abundant surface exposures of this unit throughout the state. Ver Straeten and Sageman (1999a, 1999b) investigated 600 m of mudrock-dominated core from the Middle Eifelian Onondaga Limestone to the Upper Fammenian Gowanda Shale from western New York. Average elemental geochemical compositions were similar to upper-continental crust with few samples suggesting an andesitic to

basaltic source rock. Elemental trends reflected an increasing felsic input up-section. Ver Straeten and Sagemen (1999a, 1999b) attribute the origin of these fine-grained sediments to the unroofing of the Acadian arc with recycled input from the adjacent hinterland. Middle and Upper Devonian shales of western and central New York were analyzed by Caesar *et al.* (2010a, 2010b) for major, trace, and rare earth element chemistry, as well as Sm-Nd isotopic composition. The results of their analyses yielded model ages (τ_{DM}) ranging from 946 Ma for the Union Springs Member, the lowest member of the Marcellus Shale, to 1504 Ma in the Marcellus Shale itself (Caesar *et al.*, 2010a; Caesar *et al.*, 2010b). Both the older τ_{DM} model ages and evidence of a highly-weathered and well-mixed source from REE and trace element geochemistry led Caesar *et al.* (2010a) to interpret their data as supporting a dominantly Archean Canadian Shield sediment influx from the north, with input from the Catskill Mountains to the east. Mosher *et al.* (2010) conducted a similar study on the Union Springs member of the Marcellus Shale in New York, establishing the major, minor, and trace elemental chemistry with Nd-model ages that indicate a Precambrian source rock (1504-1689 Ma; Mosher *et al.*, 2010).

Detrital zircons sampled from the Marcellus Shale of New York were found to be dominantly 950-1350 Ma (Grenville orogeny) or 400-450 Ma (Taconic/early Acadian), with minor populations of 550-700 Ma (Brasiliano/Pan-African), 1400-1500 Ma (Granite-rhyolite Province), 1800-1950 Ma (Trans-Hudson/Penokean Provinces), and 1600-1800 Ma (Yavapai/Mazatzal; Selleck *et al.*, 2014). Selleck *et al.* (2014) suggested that the Marcellus Shale was deposited during early stages of basin-filling due to input from both cratonic and reworked passive margin sources. Grenville zircons found within their older sampled strata showed a bias toward younger Grenville ages, providing

evidence for potential unroofing of the Grenville terrane during the deposition of the Marcellus Shale (Selleck *et al.*, 2014). Additional detrital zircon provenance analysis of the Marcellus Subgroup in the Catskill region of New York suggested that the provenance of the Marcellus Shale was dominated by Laurentian source rocks, with younger Grenville zircons from the Ottawa Orogeny (1080-1020 Ma) being the most abundant (Selleck *et al.*, 2016). In comparison, the younger Givetian clastics of the Manorkill Formation in the Catskill region, which are correlative to the upper Mahantango Formation, were also dominated by Grenville zircon ages, but showed a larger population of syn-orogenic zircon from the Acadian Orogen (470-420 Ma).

RESEARCH

2.1 Sampling

Two wells were sampled in order to analyze both the Marcellus Shale and the Mahantango Formation. Only samples from the Marcellus Shale were available from the MIP-3H well of the MSEEL project. Therefore, the nearest well with available core, WV-6, was used to sample throughout the Mahantango Formation.

2.1.1 MSEEL: MIP-3H

The MIP-3H horizontal well was drilled near Morgantown, Monongalia County, West Virginia along the western side of the Monongahela River (Fig. 6). Sixty-two samples were collected from side-wall plugs from the MIP-3H well (API # 47061017050000) as part of the MSEEL drilling project (Fig. 13-14). Side wall plugs ranged in weight from ~10-50 g and were collected at variable intervals, ranging from every 0.5-8.5 ft., with an average sampling interval of 1.7 ft., throughout the entire 108 ft. of sampled section. Of the 62 samples, 6 were collected from the bottom of the Mahantango Formation, whereas the other 56 were from the Marcellus Shale. Aliquots of all 62 samples were analyzed by XRD for bulk mineralogy and XRF for major and trace elemental composition, 25 were made into thin-sections, and 6 were analyzed for Sm-Nd whole-rock isotopic analysis (Fig. 14).

2.1.2 WV-6

Fifty-nine samples were collected from core recovered from the WV-6 well (API #: 47061003700000) that is archived by the West Virginia Geological Survey. The WV-6

Figure 13. Drone image of the MSEEL site, just south of Morgantown, WV. (mseel.org, 2015)

well was drilled within Monongalia Co. approximately four miles toward the north from the MIP-3H well (Fig. 6). These samples ranged from ~30-100 g and were collected approximately every 3 ft. throughout the Mahantango Formation (58 samples) and includes one sample from the uppermost Marcellus Shale. All 59 samples were analyzed via XRD bulk mineralogy and XRF for major and trace element geochemistry, 11 were made into thin-sections, and 4 were analyzed for Sm-Nd whole rock isotopic dating (Fig. 14). The Marcellus Shale section of the WV-6 well has been extensively sampled for various geochemical analyses (stable isotopes, major and trace elements, REE, etc.) and studied by Chen (2016).

Figure 14. Two graphs showing the sampling distribution for various analyses collected from both the MIP-3H well (left) and the WV-6 well (right). Contacts separating the Marcellus Shale (MS) and Mahantango Formation (MF) are indicated by the black horizontal lines.

2.2 Methods

2.2.1 Thin-section Petrography

A total of thirty-six thin sections were made for petrographic analysis to characterize mineralogy and texture of the various petrofacies present throughout the sampled section of the Hamilton Group. Twenty-five thin-sections were made from 1-inch diameter sidewall plugs selected from the MIP-3H well. Thin-section sampling was limited to those core plugs which were large enough for thin-sectioning. Eleven standard thin-sections were made from core samples collected from the WV-6 well approximately every 15 feet throughout the Mahantango Formation (Fig 14). All thin-sections were made by National Petrographic Services, Inc. to the standard thickness of 30 microns. Two microscopes were used for thin-section petrography, an Olympus SZX10 (6.3-2000x magnification) and an Olympus BX53 (6.3-63x magnification), in order to view a range of details within each thin-section.

Petrofacies were established from these thin sections and were characterized by differences in color, grain size, grain assemblages, and detrital versus authigenic components. Each sample was given a descriptive name based off of the Picard (1971) classification of fine-grained rocks if it was dominated by clay and larger clasts ($\geq$ silt). The Milliken (2014) classification system for fine-grained sedimentary rocks was used if the sample was dominated by mud and contained the grain types or components used in this classification. Note that many of the claystones from the Picard (1971) classification could be crossed-classified as tuffs within the Milliken (2014) classification scheme. End-member components within each thin-section were estimated and plotted on the ternary classification diagrams of Picard (1971) and Milliken (2014). Additionally, petrofacies

interpretations were examined within their stratigraphic context. Thin-section petrofacies from samples of the MIP-3H well were compared to a core log and gamma-ray log established by Paronish (2017).

2.2.2 X-ray Diffraction Analysis (XRD)

All 121 samples were analyzed using x-ray diffraction (XRD) in order to determine bulk mineralogy. The samples were ground for approximately 4 to 6 minutes using an A Spex Shatterbox with steel grinding containers until powdered. Powdered samples were pressed into chemplex pellets and analyzed using the PANalytical X'Pert Pro X-ray Diffractometer at West Virginia University Shared Research Facilities. Samples were analyzed at 2θ angles between 5° and 75° , with a step time of ~ 75 seconds, for a total sample analysis time of approximately 13.5 minutes. CuK_2 x-ray beams were concentrated and shot through a 20 mm brass opening onto an XceleratorTM detector. Peaks were identified using the PDF2 reference library as part of the X'pert HighScore Plus Program (Appendix I). Mineral percentages were initially determined semi-quantitatively using reference intensity ratios (RIR). RIR interpretations allowed for identification of the mineral suites present, absences of specific minerals, and the relative abundances of different mineral phases (Appendix II and IV). However, the abundances are subject to uncertainties related to the choice of the reference standard.

Mineral assemblage interpretation was then quantified using the XRF elemental data to stoichiometrically constrain phase abundances within the mineral assemblage (Appendix III and V). Based on RIR identification of the mineral suite, the abundance of

each mineral phase was calculated based on the stoichiometries of the PDF2 reference phases using the following assumptions:

1. All K is in muscovite/illite.
2. The calculated abundance of muscovite represents combined abundance of illite and muscovite.
3. All Fe is in either pyrite and/or chlorite.
4. All Na is in albite.
5. Ca is present in calcite, gypsum, and/or dolomite. Distribution of Ca among calcite and dolomite phases is assumed to be proportional to the XRD mineral peak height ratios from the diffractograms in the Marcellus Shale, where gypsum was absent. A similar approach was used to determine abundances of calcite, gypsum, and dolomite within the Mahantango Formation.
6. Mg is present in both chlorite and dolomite. Distribution of Mg among these two phases is assumed to be proportional to the respective peak height ratios.
7. Barite is present as a strontian-barite, which contains both Ba and Sr, inferred from the XRF results.
8. Si is present in quartz, albite, and muscovite. Quartz concentrations were calculated from the remaining SiO_2 after albite and muscovite/illite concentrations were calculated.
9. The sum of crystalline components does not include organic matter and was normalized to 100%.

Mineralogical data was statistically analyzed using PAST 3.0 software in order to identify patterns via Euclidean cluster analysis.

2.2.3 X-ray Fluorescence Geochemical Analysis (XRF)

X-ray fluorescence (XRF) analysis was performed on all 121 samples to establish the abundance of both major and trace elements. Samples were analyzed using a Thermo ARL Perform'X X-ray Fluorescence Spectrometer located at the Hamilton College Analytical Laboratory. Elemental compositions ranging from C to U on the periodic table can be detected and are reported as weight percentages of oxides for major elements or as parts per million (ppm) for trace elements. Samples were also powdered in preparation for XRF analysis. The same powders used for XRD analysis of the MIP-3H samples were used for XRF analysis. Samples from the WV-6 well were ground in aluminum ceramic grinding containers at the Hamilton College Analytical Lab in preparation for XRF analysis. A second aliquot of all powders was subjected to serial loss on ignition (LOI) at temperatures of 600°C and 900°C in order to remove and quantify organic matter and carbonates from the sample. Powders were fused into glass beads prior to XRF analysis (Appendix VI).

Oxide abundances from XRF analysis were converted to moles in order to calculate the chemical index of alteration (CIA; Eq. 1; Nesbitt and Young, 1984; Fedo *et al.*, 1995).

$$\text{Eq. 1} \quad \text{CIA} = [\text{Al}_2\text{O}_3 / (\text{Al}_2\text{O}_3 + \text{CaO}^* + \text{K}_2\text{O} + \text{Na}_2\text{O})] \times 100$$

$$\text{CaO}^* = \text{mol CaO} - \text{mol CO}_{2\text{cc}} - (0.5 \times \text{mol CO}_2)_{\text{dol}} - [(10/3) \times \text{mol P}_2\text{O}_5]_{\text{ap}}$$

cc = calcite; dol = dolomite; ap = apatite

High CIA values ($>\sim 75$) are associated with increased chemical weathering, whereas low CIA values ($<\sim 50$) indicate decreased chemical weathering alteration (Nesbitt and Young, 1984; McLennan *et al.*, 1993; Lee, 2002; Potter *et al.*, 2005).

The chemical index of weathering (CIW) was also calculated using molar concentrations and can be interpreted similarly to CIA trends with respect to weathering. The CIW is a useful way to identify if the calculated CIA weathering trends have been influenced by mobile potassium. Potassium is absent from this equation, so that weathering trends independent of potential K-metasomatism could be identified (Eq. 2; Harnois, 1988).

Eq. 2.
$$\text{CIW} = [\text{Al}_2\text{O}_3 / (\text{Al}_2\text{O}_3 + \text{CaO}^* + \text{Na}_2\text{O})] \times 100$$

The index of compositional variability (ICV) was calculated using the oxide weight percentages to provide insight into provenance by recognizing enrichment of heavy minerals present (Eq. 3; Cox *et al.*, 1995). The CIA and CIW weathering indices are dependent upon relative abundances of clays versus feldspars, whereas the ICV provides a better index for discriminating geochemical modification of the parent rock lithology by evaluating the abundances of Fe and Mg (Cox *et al.*, 1995; Potter *et al.*, 2005).

Eq. 3
$$\text{ICV} = (\text{CaO} + \text{K}_2\text{O} + \text{Na}_2\text{O} + \text{Fe}_2\text{O}_{3\text{total}} + \text{MgO} + \text{MnO} + \text{TiO}_2) / \text{Al}_2\text{O}_3$$

Decreasing ICV values reflect increasing modification by chemical weathering.

Calculating the ICV helps to identify oxide weathering trends influenced by non-clay silicate minerals (Cox *et al.*, 1995; Potter *et al.*, 2005).

In addition, elemental ratios and ternary diagrams were used to evaluate geochemical composition of the rock samples and interpret sediment source composition (Roser and Korsch, 1988; Zhang *et al.*, 1998; Baïoumy, 2004; Table 2). Roser and Korsch (1998) determined a technique to identify sediment source composition, independent of grain size, through discriminant function analysis using major element geochemistry. Four discrimination equations were established from their work in order to identify source rock composition independent of biogenic influence (D1 and D2) and for rocks influenced by biogenic sedimentation (D3 and D4). The following equations were used to calculate discrimination factors DF1, DF2, DF3, and DF4 and recognize compositional variation of the source rock, specifically among mafic igneous, intermediate igneous, felsic igneous, and mature quartzose sedimentary rocks (Eq. 4-7):

$$\text{Eq 4. } DF1 = -1.773 \text{ TiO}_2 + 0.607 \text{ Al}_2\text{O}_3 + 0.76 \text{ Fe}_2\text{O}_3 \text{ (t)} - 1.5 \text{ MgO} + 0.616 \text{ CaO} + 0.509 \text{ Na}_2\text{O} - 1.22 \text{ K}_2\text{O} - 9.09$$

$$\text{Eq 5. } DF2 = 0.445 \text{ TiO}_2 + 0.07 \text{ Al}_2\text{O}_3 - 0.25 \text{ Fe}_2\text{O}_3 \text{ (t)} - 1.142 \text{ MgO} + 0.438 \text{ CaO} + 1.426 \text{ K}_2\text{O} - 6.861$$

$$\text{Eq 6. } DF3 = [30.638 \text{ TiO}_2 - 12.541 \text{ Fe}_2\text{O}_3 \text{ (t)} + 7.32 \text{ MgO} + 12.031 \text{ Na}_2\text{O} + 35.402 \text{ K}_2\text{O}] / \text{Al}_2\text{O}_3 - 6.382$$

$$\text{Eq 7. } DF4 = [56.50 \text{ TiO}_2 - 10.879 \text{ Fe}_2\text{O}_3 \text{ (t)} + 30.875 \text{ MgO} - 5.404 \text{ Na}_2\text{O} + 11.112 \text{ K}_2\text{O}] / \text{Al}_2\text{O}_3 - 3.89$$

Table 2. Geochemical evaluation of provenance and paleoclimate signals.

Weathering Indices	Proxies for weathering intensity	References
Chemical Index of Alteration (CIA)	High CIA=greater weathering	Nesbitt and Young, 1984
Chemical Index of Weathering (CIW)	High CIW = greater weathering	Harnois, 1988
Index of Compositional Variability (ICV)	High ICV= less weathering	Cox <i>et al.</i> , 1995
Ratios		
Si/Al	Proxy for clay influence, lower value=more clay input	McLennan <i>et al.</i> , 1993
Ti/Al	Proxy for terrestrial clastic influence; higher value= more terrestrial clastic input	Murphy <i>et al.</i> , 2000
Th/Sc and Th/U	Specific ratio ranges are tied to general terrane types	McLennan <i>et al.</i> , 1993
Cross-plots		
Zr/Sc vs. Th/Sc	Identifies signs of sediment recycling	McLennan <i>et al.</i> , 1993
Th/Sc vs. ϵ_{Nd}	Differentiates source terrane types	McLennan <i>et al.</i> , 1993
Ternary Plots		
Al_2O_3 -(CaO+Na ₂ O)-K ₂ O	Both ternaries identify composition of source material by recognizing weathering trends	Nesbitt and Young, 1984
Al_2O_3 -(CaO+Na ₂ O+K ₂ O)-(FeO _{total} +MgO)	Differentiates terrane type	Nesbitt and Young, 1989
La-Th-Sc		McLennan <i>et al.</i> , 1990
Discrimination Diagrams		
	Differentiates source terrane composition; specifically between felsic, intermediate, and mafic igneous, and quartzose sedimentary sources	Roser and Korsch, 1988

2.2.4 Samarium-Neodymium (Sm-Nd) Isotopic Analysis

Sm-Nd isotopic analyses were used to calculate Nd-model ages. Radiogenic isotopes were measured for 10 whole rock samples by ultra-high precision (<20 ppm) thermal ionization mass spectrometry (TIMS) at Geochronex Analytical Services Ltd. Samples taken from the depths of 7448, 7460, 7505, and 7544 feet were sent to Geochronex Analytical Services as 5 g rock chips. These rock chips were powdered, spiked with a ^{149}Sm - ^{150}Nd solution, and dissolved in a mixture of HF, HNO₃, and HClO₄. The 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 consisting of 10 g were collected from depths of 7225, 7270, 7314, 7360, 7489, and 7538 feet were powdered in a jasper mortar. Following powdering, samples were spiked with a ^{149}Sm - ^{150}Nd trace solution. The mixture then decomposed in a Hf+HNO₃ (3:1) solution at 140°C for 2 days, followed by baking in HNO₃ at 250°C for 2 hours within a Milestone Ultra Clave high pressure microwave oven. Separation of Sm and Nd was done through two-stage ion exchange and extraction chromatography (Richard *et al.*, 1976; Pin and Zalduegui, 1997). Isotope abundance measurements were done using a ThermoFisher Triton TI mass spectrometer.

Depleted mantle (τ_{DM}) model ages were calculated from Sm-Nd isotopic analysis results (Eq. 8; Dickin, 1995; DePaolo, 1998). Additionally, measured $^{143}\text{Nd}/^{144}\text{Nd}$ ratios can be compared to bulk-earth ratios of the chondritic uniform reservoir (CHUR). This ratio comparison is the ϵ_{Nd} notation (Eq. 9; DePaolo and Wasserburg, 1976). $^{143}\text{Nd}/^{144}\text{Nd}$ evolved through radioactive decay of original ^{147}Sm and ^{146}Sm to ^{143}Nd and ^{142}Nd ,

respectively at a constant decay rate. The ϵ_{Nd} notation describes this evolution of the sample with respect to the original chondritic reservoir at any point specific point in time:

Eq. 8.

$$\tau_{DM} = \frac{1}{\lambda} \ln \left(\frac{{}^{143}\text{Nd}/{}^{144}\text{Nd}_{\text{sam}} - {}^{143}\text{Nd}/{}^{144}\text{Nd}_{DM}}{{}^{147}\text{Sm}/{}^{144}\text{Nd}_{\text{sam}} - {}^{147}\text{Sm}/{}^{144}\text{Nd}_{DM}} + 1 \right)$$

$$\epsilon_{\text{Nd}} = \left[\frac{({}^{143}\text{Nd}/{}^{144}\text{Nd})_{\text{sample}} - ({}^{143}\text{Nd}/{}^{144}\text{Nd})_{\text{CHUR}}}{({}^{143}\text{Nd}/{}^{144}\text{Nd})_{\text{CHUR}}} \right] \times 10000$$

Eq. 9.

where ${}^{143}\text{Nd}/{}^{144}\text{Nd}_{DM}=0.51315$, ${}^{147}\text{Sm}/{}^{144}\text{Nd}_{DM}=0.2137$, ${}^{143}\text{Nd}/{}^{144}\text{Nd}_{CHUR}=0.512638$, and

${}^{147}\text{Sm}$ decay constant (λ) = 6.54×10^{-12} (Dickin, 1995).

RESULTS

3.1 Petrographic Results

Petrographic analysis of thirty-six thin-sections from the two wells led to the differentiation of four primary petrofacies end members that characterize the heterogeneity of lithofacies throughout the sampled section (Fig. 15-22; Appendix VII).

3.1.1 Petrofacies 1: Tarly claystone

The rocks of the tarly claystone petrofacies appear light brown to darkish brown in color and contain grains ranging from clay-size to silt-size (Fig. 19). The matrix of this petrofacies is dominated by detrital clays, specifically illite and muscovite (Fig. 19A). These matrix components show strong alignment horizontal to bedding as indicated by their anisotropy. Silt-sized grains include authigenic euhedral pyrite crystals (Fig. 19F-G), detrital quartz grains, and detrital micas. Intrabasinal grains include clay pellets or peloids (Fig. 19B), agglutinated foraminifera (Fig. 19C), radiolarians, and tasmantid algae (Fig. 19E). Large grains of woody organic matter and black organic stringers are present within the matrix (Fig. 19D). Planar laminations are visible at low magnification and can be identified by transitions in color, from dark brown to light brown. Thin fractures also run parallel to the linear fabric of the rock. These rocks have been classified as tarly claystones due to their abundant clay-rich matrix. This petrofacies is most common within the Mahantango Formation and upper Marcellus Shale.

Figure 15. Ternary diagram showing the uppermost triangle of the Picard (1971) classification of fine-grained rocks and sediments with twenty samples plotting within this classification scheme. Eleven of the samples were from the Marcellus Shale (blue triangles) and nine from the Mahantango Formation (green diamonds). Of these thin-sections, seven (2 MF, 5 MS) fell within the silty claystone field and thirteen (7 MF, 7 MS) fall within the claystone field.

Figure 16. Ternary diagram showing the Milliken (2014) classification for fine grained sedimentary rocks. Fifteen samples plotted within this classification scheme with two samples from the Mahantango Formation (green diamonds) and thirteen from the Marcellus Shale (blue triangles).

Figure 17. Stratigraphic context of petrographic analysis of all thirty-six thin-sections throughout the Mahantango Formation (MF; green diamonds) and Marcellus Shale (MS; blue triangles). The Marcellus-Mahantango contact within the MIP-3H well is indicated by the horizontal line.

Figure 18. Comparison of petrofacies identification of the MIP-3H samples in comparison to the core log and gamma-ray log prepared by Paronish (2017). Note how the argillaceous sarls and bio-siliceous tarls correlate strongly with the presence of black shale and high gamma-ray values.

Figure 19. Thin section images from MIP-3H 7448 in the lower Mahantango Formation showing the early claystone petrofacies to demonstrate diversity of the grain assemblage. A: Larger scale view of the petrofacies; B: Clay pellet; C: Agglutinated foraminifera; D: Woody organic matter allochem (red); E: Tasmanid algae; F and G: Euhedral pyrite crystals (red arrows). Images A, C, F, and G were all taken in both transmitted and reflected light, whereas images B, D, and E were all taken in only transmitted light.

3.1.2 Petrofacies 2: Organic-rich argillaceous sarl

This petrofacies is characteristically black to dark brown in color (Fig. 20). The matrix is primarily composed of illite and organic matter. Larger, silt-size grains are dominated by compressed/collapsed radiolarians composed of microcrystalline silica (Fig. 20B-E). Radiolarians are found abundantly throughout these sarls and show preferential alignment with the horizontal plane along the long axis of their ovoid tests. In some cases, radiolarians also show euhedral pyrite crystals making up part of their in-fill cement (Fig. 20E). Larger authigenic quartz crystal cements can be found, as well as in-fill or replacement of moldic porosity (Fig. 20F). In reflected light, pyrite framboids are abundant throughout this petrofacies. Laminations are delineated by radiolarian-rich layers (Fig. 20A). Planar fractures are also common within this petrofacies. Due to the abundance of silicified radiolarians and organic-rich matrix, this petrofacies is described as an organic-rich, argillaceous sarl. This petrofacies is most commonly found within the lower Marcellus Shale (Fig. 17-18).

Figure 20. Images of the organic-rich argillaceous sarl petrofacies. A: Laminations formed from intrabasinal; B: Image of compressed radiolarians. Some radiolarians have spins preserved (red arrows) while others have pyritic infill (blue arrows); C: Image of clay- and organic-dominated matrix (brown) with many microcrystalline silica-rich radiolarians (white grains); D: Compressed radiolarian with spin preserved; E: Radiolarian with euhedral pyrite infill. F: Image of moldic porosity infill, potential of tasmanitid algae. G: Polycrystalline authigenic quartz cement. All images except for C and G were taken in transmitted light. Image C was taken in both reflected and transmitted light. Image G was taken in cross-polarized light. Images were taken from the MIP-3H 7544 sample from the lower, organic-rich stratigraphic region of the Marcellus Shale.

3.1.3 Petrofacies 3: Styliolinid Carl

Only one of the thirty-six thin-sections are classified within the styliolinid carl petrofacies (Fig. 21). However, this sample exhibited similar XRD-derived mineralogical composition as lithologies in the middle to lower Marcellus Shale, suggesting that this thin-section may represent a petrofacies that is sparsely interbedded within the Marcellus Shale and not a single anomaly.

The styliolinid carl petrofacies is named from its abundance of styliolinid fossils and clay-calcite matrix. These rocks appear dark brown to gray in color and contain clay to medium sand-sized grains (Fig. 21). The matrix is composed of clay and displacive calcite. The bulk of grains are dominated by styliolinids and thin-walled mollusc shells. Calcite cements are found in much of the intragranular and shelter porosity as well as fractures. However, fossilized shells do not exhibit evidence of recrystallization. Fossils display both drusy and blocky cement within the larger intragranular pores.

Figure 21. Thin-section images of the styliolinid carl petrofacies from sample MIP-3H 7554 of the lower Marcellus Shale. A: Large scale image of whole-rock fabric; B: Styliolinid cut along the long-axis showing several generations of calcite cement. Image is in transmitted light; C: Large blocky calcite-filled fracture runs perpendicular to orientation of fossiliferous grains; D: Same view as image B in cross-polarized light; E: A thin-walled mollusc (larger circle) and cross-section of a styliolinid (small, calcite filled circle). All images in plane-polarized light, except for D, which was taken in cross-polarized light.

3.1.4 Petrofacies 4: Silty Tarly Claystone

This petrofacies is found throughout the Mahantango Formation and differs from the tarly claystone by having a higher proportion of extrabasinal sediment absent from the Marcellus Shale. The silty tarly claystone is light to dark brown and consists of a clay-dominated matrix, primarily illite (Fig. 22). Detrital quartz silt is the dominant grain type throughout these rocks (Fig. 22D-E). The quartz silt grains are angular and often define the laminations within these rocks. Organic matter is also a common grain type, often appearing as fine silt-sized grains that partially define the darker brown laminations (Fig. 22C). This petrofacies is classified as a silty tarly claystone because of the clay-dominated matrix and abundant detrital quartz silt content.

Figure 22. Images of the silty tarry claystone petrofacies. A: Silt-rich versus organic-rich laminations show and distinguished by light brown versus darker brown layers; B: Closer view of silty areas and fossil (?) present (red arrow); C: Image showing grains of organic matter (blue arrows); D and E: Angular detrital quartz silt-rich areas. All images were taken of the WV-6 7221 sample of the Mahantango Formation and are in plane-polarized light. \

3.2 Geochemical Results

3.2.1. X-ray Diffraction Results

X-ray diffraction analysis of the MIP-3H samples indicate a mineral suite of up to nine minerals including quartz, illite, muscovite, chlorite, pyrite, albite, calcite, dolomite, and barite (Fig. 23, Appendices II-V). Illite and muscovite were interpreted as one mineral via initial RIR interpretations due to difficulty in peak discrimination.

Mineralogical trends show that quartz, illite+muscovite, and albite covary and are inversely correlated with calcite and dolomite (Fig 24). Of the Mg-bearing minerals, chlorite dominates the upper part of the sampled section, whereas dolomite dominates the lower part of the sampled section, with a thin interval between 7488-7500 feet in which both minerals are present in the middle of the sampled section. The barite found within the MIP-3H well is interpreted as a strontian-barite, as both Sr and Ba are elevated and strongly correlate within the XRF data (Fig 24C).

Euclidean cluster analysis of all 62 samples revealed seven different distinct clusters (Fig. 25). Each cluster either represents a stratigraphic region of the sampled section (i.e. lower Mahantango Fm.-upper Marcellus Sh.) or samples that were enriched in an anomalous mineral phase (i.e. calcite or barite). Cluster analysis has shown that the upper (>7497 ft.), middle (~7503 ft. -7514 ft.), and lower (<7515 ft.) Marcellus Shale all have mineralogically distinct facies, with the primary difference being a slight decrease in calcite content up-section. The greatest mineralogical heterogeneity is found within the lower Marcellus Shale stratigraphic interval.

Figure 23. Mineralogical trends from the MIP-3H samples for all mineral phases identifiable through quantification of XRD analysis.

Figure 24. A: Cross-plot of calcite vs. illite+muscovite showing a strong negative correlation. B: Cross-plot of quartz vs. illite+muscovite showing a positive correlation. C: Ba vs. Sr showing a very strong correlation supporting the interpretation that barite within the sampled section is Sr-barite.

Figure 25. Euclidean cluster analysis of mineralogical data from the MIP-3H well. Seven distinct clusters (C1-C7) were identified and their average breakdown of mineralogical constituents identified. Pie charts for C2-C7 are found on the following page. Clinocllore is the specific form of chlorite present and the areas labeled muscovite represent the percentage of both illite and muscovite. Note that each cluster either encompasses many samples from a stratigraphic section of the sampled interval or a mineralogical anomaly.

Figure 25. *continued.*

X-ray diffraction analysis of the WV-6 samples identified the same nine mineral phases as found within the Marcellus Shale, with the addition of gypsum (Fig. 26).

Quartz, muscovite, illite, and chlorite are the dominant mineral phases throughout the Mahantango Formation and displayed similar trends. The minor mineral phase albite commonly followed the trends of the dominant mineral phases. Calcite and dolomite are less abundant in the Mahantango Formation than in the Marcellus Shale. However, gypsum appeared consistently throughout the sampled section ranging from ~0.5-6.5%. Chlorite is the only mineral that displayed a consistent increase up-section.

Euclidean cluster analysis of the WV-6 samples revealed five clusters composed of 56 of the samples, with three outliers (Fig. 27). The three outliers were all enriched in a specific mineral phase, drastically increasing their Euclidean distance from the other samples. These phases included calcite (66.43% at 7354.4 ft.), pyrite (13.39% at 7388.1 ft.), and quartz (50.25% at 7360.5 ft.). Of the five clusters identified, two clusters represent stratigraphic sections of the Mahantango Formation (i.e. Cluster 2=middle to upper Mahantango Fm. and Cluster 5=lower Mahantango Formation.) The middle-upper Mahantango Formation differs from the lower Mahantango Formation by exhibiting slight enrichments in clay minerals and gypsum and decreases in quartz up-section. The remaining three clusters identify groups that are rich in carbonates and gypsum, poor in carbonates, or represent an intermediate between the mineralogical facies of the middle-upper Mahantango Formation and the lower Mahantango Formation. In all clusters except for C3 (carbonate-poor cluster), mineralogical averages yielded minimum calcite, dolomite, barite, and gypsum percentages of at least 0.18%.

Figure 26. Mineralogical trends from the WV-6 samples for all mineral phases identifiable through quantification of XRD analysis.

Figure 27. Euclidean cluster analysis of mineralogical data of 56 samples from the WV-6 well. Five distinct clusters (C1-C5) were identified and their average breakdown of mineralogical constituents identified. Pie charts for C1-C5 are found on the following page. Note that most clusters either encompasses many samples from a stratigraphic section of the sampled interval or a mineralogical anomaly.

Figure 27.
continued.

3.2.2 X-ray Fluorescence Results

Elemental composition data was collected from both the MIP-3H and WV-6 wells in order to establish a high-resolution chemostratigraphic record of the Marcellus Shale (n=57) and the Mahantango Formation (n=64). Major and trace elements for each suite of samples were determined by XRF (Appendices VIII-XIII). Major element trends were examined as proxies for sediment influx. Si/Al ratios within the Marcellus Shale showed a distinct increase up-section. Ti/Al ratios show a fluctuating cyclic pattern (Fig 28). Within the Mahantango Formation, elemental trends are less clear. Si/Al ratio increases to ~3.9 within the lower and upper portions of the formation, but are fairly uniform at ~3.0 throughout the middle section of the unit (Fig. 28).

Si/Al and Ti/Al from the Marcellus Shale were examined in comparison to TOC log data in order to further evaluate the relationship between organic content and clay or clastic influx to the basin (Fig. 29A-B). A cross-plot of TOC vs. Ti/Al showed no evidence of correlation ($R^2=0.0007$). However, a cross-plot of TOC vs. Si/Al shows a positive correlation ($R^2=0.4477$) indicating that increased clay sedimentation to the basin is correlated to lower total organic content values.

Cross-plots of other major elements as well as Zr were compared to TOC in attempt to identify potential relationships with content of organic matter (Fig. 30). TOC was compared to both P_2O_5 and FeO to evaluate the effects of limiting nutrient input on

Figure 28. Gamma ray from the MIP-3H (blue) and the WV-6 (orange) wells in comparison to major element ratios, specifically Si/Al and Ti/Al. The contacts separating the Marcellus Shale from the overlying Mahantango Formation in each well are indicated by the gray horizontal lines. The gray dots represent major element pXRF counts ratios.

Figure 29. Cross-plots of TOC vs. Ti/Al (A) and vs. Si/Al (B) comparing organic content to sedimentation proxies within the MIP-3H samples.

primary production as reflected by organic-matter content (Fig. 30A-B) No correlation was exhibited within either of these cross-plots (P_2O_5 , $R^2=0.0055$; FeO , $R^2=0.0505$), suggesting that production may not have been the limiting factor in controlling organic content but rather the preservation played a more important role. A cross-plot of TOC vs.

Figure 30. Cross-plots comparing TOC as a proxy for organic matter content to (A) P₂O₅, (B) FeO, and (C) Zr. The TOC and cross-compared data are all from the MIP-3H due to a range in organic matter content ranging from ~3-16 wt%. P₂O₅ and FeO serve as proxies for available nutrient input to the basin for primary production. Zr serves as a proxy for heavy-mineral influx to the basin, which is typically a sign of sedimentation for a recycled sedimentary rock source.

Zr shows a negative correlation ($R^2=0.3687$) suggesting that increases in influx of recycled sediment directly correlates to decreases in content of organic matter.

Weathering indices for all samples throughout both formations were examined within both the carbonate and siliciclastic facies. However, cross-plots of calcite in comparison to each of the weathering indices, using the MIP-3H samples, show a strong correlation indicating high calcite content negatively correlates to lower CIA ($R^2=0.697$) and CIW ($R^2=0.6503$) values and higher ICV values ($R^2=0.7241$; Fig. 31). Thus, calcite influenced the weathering indices to show lower weathering intensities in carbonate-rich samples, accounting for outliers among the trends. This relationship was explored using data from the MIP-3H due to its higher abundance of carbonate layers compared to Mahantango Formation sampled from the WV-6 well.

The Marcellus Shale shows CIA values ranging from 0.67 to 74.13 (Fig. 32; Appendix X). For the entire Marcellus Shale sample suite, the average CIA was 54.95 ± 18.19 ($n=59$). When removing carbonate-rich (calcite+dolomite >10 %) samples from the suite ($n=51$; 8 removed), the siliciclastic facies (Clusters 1-4) had an average CIA of 60.56 ± 11.32 . CIW values for the Marcellus Shale ranged from 0.68 to 91.63, with a full sample suite average of 65.90 ± 23.51 and the siliciclastic CIW average of 73.01 ± 15.49 . Both the CIA and CIW values show an increasing trend up-section within the Marcellus Shale. ICV values within the Marcellus Shale averaged 3.29 ± 11.78 within the full suite, with an average siliciclastic fraction ICV of 1.04 ± 0.36 . Values ranged between 0.69 and 81.99 and show a decreasing trend up-section.

Figure 31. Cross-plots of CIA (A), CIW (B), and ICD (C) versus calcite to show the strong correlations indicating that calcite-rich samples will yield weathering index values that indicate lower weathering intensities within all three indices.

Figure 32. Weathering indices calculated for the WV-6 and MIP-3H samples. From left to right is the gamma-ray log, chemical index of alteration (CIA; blue/orange), chemical index of weathering (CIW; gray), and index of compositional variability (ICV).

Siliciclastic facies within the Mahantango Formation (n=62) had CIA values averaging 69.51 ± 6.47 and CIW values averaging 84.43 ± 9.14 (Fig. 32; Appendix XI). CIA values ranged from 4.05 to 74.96, while CIW values ranged from 4.08 to 92.13. There was only one carbonate-rich (calcite+dolomite = ~72%) sample found within the Mahantango Formation suite, making the full sample suite (n=63) average CIA value 68.47 ± 10.45 and average CIW value 83.16 ± 13.59 . ICV values for the Mahantango Formation averaged at 0.82 ± 0.14 within the silicate fraction, and 1.06 ± 1.88 within the full sample suite. The Mahantango Formation does not show any great variation or trends in regards to weathering indices compared to the indices indicating increased weathering intensity found up-section throughout the Marcellus Shale (Fig. 32).

Element comparisons in various discrimination and ternary diagrams help to determine mudstone provenance. The Al_2O_3 -($\text{CaO}+\text{Na}_2\text{O}$)- K_2O ternary diagram depicts the relationships between major element abundances used to calculate CIA (Fig. 33; Nesbitt and Young, 1984, 1989; McLennan, 1993). Both the Marcellus Shale and Mahantango Formation samples tend to follow the typical weathering trend of a granodiorite. Similarly, Al_2O_3 -($\text{CaO}+\text{Na}_2\text{O}+\text{K}_2\text{O}$)-(FeO_{total}+MgO) (Nesbitt and Young, 1984, 1989; McLennan, 1993) indicate Marcellus Shale and Mahantango Formation samples follow a granodioritic weathering trend (Fig. 34). Discrimination diagrams calculated from major element composition data established by Roser and Korsch (1988) helped to further delineate source type by differentiating between a quartzose sedimentary source, felsic igneous source, intermediate igneous source, and mafic igneous source. The Marcellus Shale composition indicated a felsic igneous source with

Figure 33. A-CN-K (Al_2O_3 -($\text{CaO}+\text{NaO}$)- K_2O) ternary diagram showing how major element chemistry data collected from the Mahantango Formation (green diamonds) and Marcellus Shale (blue triangles). Note that samples from both formations on average follow a granodioritic weathering trend.

Figure 34. A-CN-K $[Al_2O_3-(CaO+NaO+K_2O)-(FeO^*+MgO)]$ ternary diagram showing how major element chemistry data collected from the Marcellus Shale (blue triangles) and Mahantango Formation (green diamonds) to help in identifying composition of the original source rock. The rocks of the Mahantango Formation consistently show a granodiorite weathering trend, whereas the Marcellus Shale data shows greater compositional variability.

some minor influence from a quartzose sedimentary source, whereas the Mahantango Formation mainly reflects dominance of a felsic igneous source (Fig. 35).

Trace element ternary diagrams, such as La-Th-Sc further constrain provenance terrain type (McLennan *et al.*, 1990; Ma *et al.*, 2015). Both the Mahantango Formation and Marcellus Shale plot nearest to an upper crust source, though, the Marcellus Shale shows more compositional variability than the Mahantango Formation (Fig. 36). Cross-plots of Zr/Sc vs. Th/Sc were used to identify signs of sediment recycling (McLennan *et al.*, 1993; Fig. 37). The Marcellus Shale showed some influence of sediment recycling, whereas the Mahantango Formation showed no signs of influence from a recycled sedimentary source.

Elemental evaluation of the Marcellus Shale suggested a dominantly felsic igneous, granodioritic source with additional input from a recycled quartzose sedimentary source. The Mahantango Formation consistently showed geochemical composition indicating sediment influx from weathering of a granodioritic, felsic igneous source.

Figure 35. Discrimination diagrams used to determine the composition of the source rock for the Mahantango Formation (orange) and the Marcellus Shale (blue). Differential functions DF1 and DF2 are to evaluate rocks independent of biogenic influence, whereas DF3 and DF4 are to evaluate source composition of rocks that have been influenced by biogenic sedimentation.

Figure 36. La-Th-Sc trace element ternary diagrams from the Mahantango Formation (green diamonds) and the Marcellus Shale (blue triangles) are shown above. Abbreviations within each diagram are as follows: UC= Upper Crust; IAA= Island Arc Andesite; BCC= Bulk Continental Crust; MORB= Mid-Ocean Ridge Basalt. Note that both the Mahantango Formation and Marcellus Shale plot dominantly within the upper crustal source region of the diagram.

Figure 37. Trace element cross-plots of Zr/Sc vs. Th/Sc relationships with data from the Mahantango Formation (A) and Marcellus Shale (B). The plots help to show if there are signs of a recycled sedimentary source through zirconium enrichment for each of the two formations.

3.2.3 Sm-Nd Isotopic Dating Results

Of the ten samples that were analyzed for Sm-Nd radiogenic isotopes, only nine samples presented valid results. One anomalous sample recorded an ϵ_{Nd} value of -7.06, whereas the remaining nine samples ranged from -9.85 to -11.74 (Table 3, Fig. 38, Appendix XIV). Depleted mantle model ages (τ_{DM}) were calculated, resulting in model ages ranging from 1.85-1.64 Ga, with the anomalous sample providing a model age of 5.33 Ga. Cross-plots of Th/U vs. ϵ_{Nd} values further indicate an upper crustal composition of the source rock (Fig 39).

Table 3. Sm-Nd isotopic data from ten samples throughout the Mahantango Formation (blue; n=5) and Marcellus Shale (brown; n=5) including the well they were collected from, sample depth, ϵ_{Nd} values, τ_{DM} model ages, LOI at 600°C as a proxy for organic-matter content, and mineralogical cluster. In some samples, LOI was not reported.

Well	Depth (ft.)	ϵ_{Nd}	τ_{DM} (Ga)	LOI	Min. Cluster
WV-6	7225.3	-11.65	1.65	5.6	WV6-C2
WV-6	7270.3	-11.47	1.67	6.5	WV6-C2
WV-6	7314.7	-11.74	1.64	6.5	WV6-C2
WV-6	7360.5	-10.38	1.74	6.9	Qtz-rich outlier
MIP-3H	7448.35	-10.34	1.85	7.89	MIP3H-C2
MIP-3H	7460.2	-10.51	1.79	unkn	MIP3H-C2
MIP-3H	7489.06	-10.55	1.63	7.62	MIP3H-C2
MIP-3H	7505.93	-10.18	1.81	11.20	MIP3H-C4
MIP-3H	7538.15	-9.85	1.78	unkn	MIP3H-C3
MIP-3H	7544.85	-7.06	5.34	11.03	MIP3H-C1

One of ten Sm-Nd data points (7544.85 ft.) yielded extreme ϵ_{Nd} and calculated τ_{DM} due to the depletion of Nd within the sample. Studies of other Paleozoic shales have found anomalous Sm-Nd data that have led to erroneous model ages, and there are many possible mechanisms for this depletion (McLennan *et al.*, 1990; Bock *et al.*, 1994). One possibility could be early diagenesis in which the breakdown of unstable minerals could cause REEs to be released and subsequently collected into phosphate minerals within the organic-rich layers. Within the 7544.85 sample, TOC is greater than 17%, and has a higher concentration of Sr-barite at 32%. Thus, based on XRD mineralogy results, phosphate bearing-minerals are not observed in the study samples, ruling out influence of REEs from phosphatic minerals. A second, more probable possibility is that these upper crustal sourced sediments experience mixing with LREE-depleted volcanic ashes that were falling intermittently at this time. Tioga ashes can be found throughout the lower Marcellus Shale. However, further examination of the MIP-3H core shows there are not any ash beds stratigraphically near this sample.

Figure 38. ϵ_{Nd} values for nine samples, excluding the anomalous data point, throughout the Hamilton Group. Note the general decrease in epsilon values up section.

Figure 39. Cross-plot of Th/Sc vs. ϵ_{Nd} values to identify source rock type. All ten data points plot near the upper crust compositional end-member.

DISCUSSION

4.1 Constraints on sediment influx from Hamilton Group petrography and mineralogy

Five mineralogically defined petrofacies were established using cluster analysis of extrabasinal and intrabasinal mineralogical phases along with bulk geochemical compositions and organic matter abundance. Organic matter abundance was determined from gamma ray wireline logs, LOI at 600°C, and TOC (Fig. 40; meesl.org). The continuous gamma-ray derived TOC log shows uranium-predicted TOC, whereas the measurements were collected by the DOE-National Energy Technology Laboratory in Morgantown, WV using a source rock analyzer (SRA; mseel.org). TOC SRA measurements were collected at the bottom of each 3 ft. break in the core. The SRA TOC measurements from the core were cross-plotted with the geophysical gamma ray log in order to establish an equation to calculate a continuous TOC log.

Clay-rich petrofacies are characterized by samples with greater than 70% illite+muscovite, but do not have any chlorite. TOC values are ~4-14%. These petrofacies are most abundant in the lower and middle Marcellus Shale, and comprise ~35% of the Marcellus Shale. The clay-rich petrofacies forms the organic-rich section of the lower Marcellus Shale. Most thin-sections in this petrofacies are identified as argillaceous sarls and claystones, with minor silty claystones. Two samples of bio-siliceous tarl lithofacies are contained within the clay-rich petrofacies and show abundant radiolarians, providing evidence of clear surface waters and sufficient nutrient flux to support primary biologic productivity that would allow these pelagic zooplankton to thrive (Milliken *et al.*, 2012). These conditions likely contributed to increased production of organic matter. Although XRD data indicates illite and muscovite making up much of

the matrix, this additional input from extrabasinal sources did not cause substantial dilution of organic matter. Instead, deposition was dominated by relatively higher rates of pelagic sedimentation compared to hemipelagic sedimentation.

The chlorite-rich petrofacies were characterized by samples with high concentrations of illite, muscovite, quartz, and chlorite. Chlorite in this petrofacies averages 7.1% ($\pm 0.8\%$), whereas it is absent in all other petrofacies. TOC abundances are overall lower in this petrofacies, ranging from ~2-6%. The chlorite-rich petrofacies of the upper Marcellus Shale and Mahantango Formation units are mainly composed of organic-poor lithofacies, and thin-sections primarily claystones and silty claystones. Thus, the lower organic-matter content within these lithofacies is due to deposition of hemipelagic detrital clay influx in low oxygen, low energy bottom waters. Organisms such as the highly-efficient agglutinated foraminifera observed in thin-sections, suggest that the benthic environment was characterized by suboxic conditions (Fig. 20). Abundance of clay pellets and authigenic pyrite crystals indicate epifaunal invertebrate detrital feeders and sulfur-fixing bacteria were also present in this dysoxic environment. Although bottom-water conditions were dysoxic, benthic organisms were able to persist, producing the intrabasinal grains found throughout this petrofacies. However, the concentration of organic matter in the chlorite-petrofacies has been diluted by detrital clay influx to the basin.

Approximately 20% of the analyzed samples have mineralogical compositions distinctive from the clay-rich and chlorite-rich petrofacies. These samples were grouped into three petrofacies dominated by non-organic intrabasinal phases. These petrofacies seem to characterize thin intervals of the Hamilton Group that are interbedded within the

more abundant chlorite-rich and clay-rich petrofacies. The barite-rich petrofacies is defined by samples containing >20% barite. Two samples interbedded in the clay-rich petrofacies of the lower Marcellus Shale are identified as barite-rich petrofacies. The carbonate-rich petrofacies is defined as samples with calcite and dolomite composing 10-70% of their overall mineralogical make-up. Seven samples were found interbedded throughout both the clay-rich and chlorite-rich petrofacies of the Marcellus Shale. The limestone/calcareous mudstone petrofacies differs from the carbonate-rich petrofacies in that greater than 70% of its mineral constituents are composed of calcite and dolomite. Just two samples of the limestone/calcareous mudstone are found interbedded in the clay-rich petrofacies of the lower Marcellus Shale. TOC values for the carbonate-rich and limestone/calcareous mudstone petrofacies are typically lower than in the deposits immediately above and below these beds.

Overall, mineralogy of the Hamilton Group mudrocks includes both intrabasinal and extrabasinal sedimentation components. Intrabasinal phases include calcite, dolomite, gypsum, barite, pyrite, and authigenic or biogenic silica recrystallized into quartz. Samples that contain >30% intrabasinal mineral phases were typically found in the lower Marcellus Shale, where TOC values are low (<~3%) and constitute the barite-rich, calcite-rich and limestone/calcareous mudstone petrofacies. Extrabasinal phases included quartz when associated with quartz silt grains observed in thin-section, illite, muscovite, chlorite, and albite. These phases form the bulk of the clay-rich and chlorite-rich petrofacies that dominate the upper Marcellus Shale and lower Mahantango Formation, where $\geq 70\%$ or more of the mineralogical constituents composed of non-authigenic/non-biogenic quartz, muscovite, illite, chlorite, and/or albite. The upper Marcellus Shale to

lower Mahantango Formation contained a higher percentage of extrabasinal sediment at 89% than what is found within the middle (84%) or lower (81%) Marcellus Shale.

Mineralogical and petrographic observations suggest transitions in environmental conditions during deposition of the studied formations influenced sedimentation patterns and preservation of organic matter. Petrographic investigation of the lower Marcellus Shale indicated sufficient nutrient flux to support high primary productivity and subsequent organic matter deposition. In contrast, bottom-water conditions during the deposition of the upper Marcellus Shale and the Mahantango Formation were characterized by dysoxic marine bottom-water conditions and increased terrigenous influx to the basin. Sedimentation patterns were thus controlled by pelagic processes throughout the deposition of the Marcellus Shale and hemipelagic processes throughout the deposition of the Mahantango Formation leading to a decrease in organic matter preservation via terrigenous clastic dilution found up-section throughout the Hamilton Group.

4.2 Source rock lithology from geochemical composition

Mineralogy and elemental abundances indicate a mainly upper crustal, granodioritic source rock supplied sediment to the study area throughout deposition of the Hamilton Group (Table 4; Fig. 33-36). Discrimination diagrams for major and trace element composition of the Mahantango Formation indicate a felsic igneous source, whereas data from the Marcellus Shale suggests a dominantly felsic igneous source with a few samples exhibiting minor influence from quartzose sedimentary sources (Fig. 35). A few samples of the Marcellus Shale exhibited enrichment of Zr/Sc relative to Th/Sc

Table 4. Summary table of the geochemical provenance proxies used in this study and their results for both the Marcellus Shale and Mahantango Formation.

Geochemical Proxies	Marcellus Shale	Mahantango Formation
Weathering Indices		
Chemical Index of Alteration (CIA)	Increases up-section	Stays fairly constant; No clear trends
Chemical Index of Weathering (CIW)	Increases up-section	Stays fairly constant; No clear trends
Index of Compositional Variability (ICV)	Decreases up-section	Stays fairly constant; No clear trends
Ratios		
Si/Al	Decrease up-section	No clear trends
Ti/Al	Cyclic trend, with high Ti/Al correlative to low TOC	Higher Ti/Al in middle portion of formation
Th/Sc and Th/U	Avg. Th/Sc=0.792; Th/U=0.734	Avg. Th/Sc =0.668; Th/U=2.53
Cross Plots		
Zr/Sc vs. Th/Sc	Minor signs of sediment recycling	No signs of sediment recycling
Th/Sc vs. ϵ_{Nd}	Upper Crust Source	Upper Crust Source
Ternary Plots		
$Al_2O_3-(CaO+Na_2O)-K_2O$	Granodiorite Source Composition	Granodiorite Source Composition
$Al_2O_3-(CaO+Na_2O+K_2O)-(FeO_{total}+MgO)$	Granodiorite Source Composition	Granodiorite Source Composition
La-Th-Sc	Upper Continental Crustal Source	Upper Continental Crustal Source
Discrimination Diagrams		
	Felsic Igneous Provenance with minor input from a Quartzose Sedimentary source	Felsic Igneous Provenance
Sm-Nd Radioisotopic Data		
ϵ_{Nd}	Range from -9.85 to -10.55 (anomalous point=-7.06)	Range from -10.34 to -11.74
T_{Nd}	Range from 1.81-1.63 Ga (anomalous point=5.34 Ga)	Range from 1.64-1.85 Ga

(Fig. 37), supporting minor sediment influx from a recycled sedimentary source. The cross-plot of Th/Sc vs. ϵ_{Nd} is also consistent with an upper crustal source (Fig. 39).

There are two terranes that would produce these signatures when weathered. The Superior Craton to the north-northwest of the basin is an older upper crustal source of primarily granodioritic composition. The Acadian fold-thrust belt to the east would also produce a felsic igneous signature when weathered. However, this terrane would also produce signs of sediment recycling, accounting for influence from quartzose sedimentary source indicated within the discrimination diagrams (Fig. 35).

4.3 Source area age characterization

The Sm-Nd results for the Hamilton Group yield depleted mantle model ages (τ_{DM}) ranging from 1.85 to 1.63 Ga and τ_{DM} ages appear to gradually decrease up-section (Fig. 38; Table 3). The ϵ_{Nd} values for the Hamilton Group samples ranged from -12 to -7, which falls between values from Archean to Mesoproterozoic crustal rocks in North America; however, ϵ_{Nd} values of the Hamilton Group are lower than the values for Mesoproterozoic Grenville rocks, with only the anomalous sample with ϵ_{Nd} of -7 falling within the range of Mesoproterozoic crustal rocks (Fig. 41). Ashes from the Acadian arc would have shown ϵ_{Nd} of +2.3 to +3.8, making it highly unlikely that there was any major input from this source (Shoonmaker *et al.*, 2011).

Because there are no source rocks with the observed τ_{DM} ages and ϵ_{Nd} values of the Hamilton Group, a mixture of possible sources is required. The data suggests a mixed sediment source, with input from both Archean and Mid-Proterozoic age sources.

Results from this study suggested greater input from a slightly older source than what has been found in previous studies. Studies from central and western New York have found τ_{DM} ranging from 946-1689 Ma (Caesar *et al.*, 2010a, 2010b). Caesar *et al.*, (2010a, 2010b) concluded that these ages reflected sediment influx from rocks of the Canadian Shield, recycled older sedimentary units, or distal, non-North American pre-Grenville rocks, but was likely a reflection of mixing of two or more these sources. The ages reported by Caesar *et al.* (2010a, 2010b) could have been influenced by influx from the Acadian arc, leading to sediment mixing that would result in a drawdown of τ_{DM} ages in comparison to τ_{DM} ages within this study. A study from southwestern PA found τ_{DM} ages

Figure 41. Graph showing the geologic age of Hamilton Group rocks versus ϵ_{Nd} values in order to show sediment mixing from both Mesoproterozoic (Grenville) and Archean (Superior Craton) aged sediment sources. Adapted from Anderson and Samson (1995) and McLennan *et al.* (1993).

ranging from 1.4-1.6 Ga (Gardiner *et al.*, 2012) within the Marcellus Shale, which fall between the ages of Archean and Mesoproterozoic crust.

4.4 Paleoclimate influence

Climate signals are not apparent in the geochemical composition of the Hamilton Group deposits. Clay mineralogy within the Hamilton Group was fairly homogeneous and likely modified by diagenesis. Samples are dominated by illite and muscovite with minor amounts of chlorite appearing in the upper Marcellus Shale and into the Mahantango Formation (Fig 24-27). The dominance of illite and muscovite could have two possible implications: 1) The abundance and uniform frequency of illite throughout the Hamilton Group could imply contribution of illite from erosion under stable climate conditions (Chamley, 1989). 2) Alternately, illite and muscovite could have formed from decomposition of original kaolinite.

4.5 Provenance Model and Evolution

The geochemical and petrographic data indicate erosion of primarily felsic igneous and upper-continental crustal source, with Sm-Nd τ_{DM} ages ranging from 1.6-1.8 Ga and negative ϵ_{Nd} values indicating primary crustal origin of the parent source rock. Together these data are consistent with sediment influx to the basin from the old continental crust of the Superior Craton exposed to the north. Although the Superior Craton has a wide range of lithologies, it is dominated by felsic plutonic rocks of Archean age (Percival *et al.*, 2012). However, Sm-Nd analysis requires additional sediment input from a rock bearing younger Sm-Nd τ_{DM} ages and more positive ϵ_{Nd} values. Rocks of the

Acadian fold-thrust belt have slightly younger Sm-Nd τ_{DM} ages (~1.0-1.3 Ga; Fisher *et al.*, 2010). Provenance of the units within the Acadian fold-thrust belt is dominated by Grenville terrane (Anderson and Samson, 1995; Thomas *et al.*, 2014; Scott *et al.*, 2016). Erosion of the Acadian fold-thrust belt produced a recycled sedimentary source signature.

Figure 42. Map of the Middle Devonian Acadian Basin and location of provenance terranes including the Superior Craton, Acadian arc, and Acadian fold-thrust belt along with geochronologic ages. Black dots indicate the approximate location of previous studies and Nd depleted mantle model ages yielded from those studies. Larger black dots indicate more than one study conducted in the area. The red star and associated τ_{DM} age represents the results of this study. Gray arrows indicate the approximate wind direction as interpreted from the distribution of Tioga Ashes within the Acadian Basin. Red arrows show how detrital clay sediments were generally transported to the central Acadian Basin. Note how Nd depleted mantle model ages are older the farther from the Catskill Delta. MCR=Mid-continent rift. Data compiled from Blakey, 2009; Caesar *et al.*, 2010a, 2010b; Gardiner *et al.*, 2012; Fisher *et al.*, 2010; Schoonmaker *et al.*, 2011.

Synthesis of petrological, mineralogical and geochemical data indicates variable volumes of sediment influx from northern and eastern sources controlling the lithologies of the Hamilton Group in north-central WV. In particular, Sm-Nd depleted model ages of the Hamilton Group requires mixing of older material from the Superior craton with younger material of the Acadian fold-thrust belt. The younger τ_{DM} ages of the Mahantango Formation compared to the older samples in the Marcellus Shale indicate the flux of sediment derived from the Acadian fold-thrust belt increased over time (Fig 43-45). A one-dimensional mixing model using 1.25 Ga as representative τ_{DM} for the Grenville-dominated thrust belt (Tollo *et al.*, 2004) and 2.8 Ga for the Superior Craton (Fisher *et al.*, 2010; Jaupart *et al.*, 2014) has helped to further constrain mixed provenance evolution throughout the deposition of the Hamilton Group (Figure 43; Table 5). The model indicates that the mixture of sources transitioned from approximately 65% Acadian fold-thrust belt and 35% Superior Craton for deposits at the bottom of the Marcellus Shale, to 75% influx from the Acadian fold-thrust belt and 25% sediment influx from the Superior Craton at the top of the Mahantango Formation. Increasingly younger depleted mantle model ages coincide with both higher Zr and TiO₂ concentrations in Hamilton Group mudrocks (Fig. 44-45). These trends supported the interpretation of greater sediment influx from erosion of sedimentary rocks with younger Sm-Nd ages in the adjacent Acadian fold-thrust belt over time. Mineralogical trends further support increased influx from the Acadian fold-thrust belt. Chlorite appears within the upper Marcellus Shale and increases up-section into the Mahantango Formation, but is completely absent from the middle and lower Marcellus Shale of the sampled section, suggesting this is a primary extrabasinal mineral phase (Fig. 23). Appearance of chlorite

could further support the interpretation of sediment influx from metasedimentary rocks incorporated in Acadian thrust-sheets. Chlorite could also be representative of hydrothermal alteration of muscovite, influenced by Mg-rich brines that have been noted within the Marcellus Shale (Haluszczak *et al.*, 2013). However, it is unlikely that Mg-rich brines would only drive chlorite formation in the upper part of the formation and not affect muscovite buried just 10's of feet deeper within the section.

Oblique collision of the micro-continent Avalonia with the eastern margin of Laurentia began with initial contact with the St. Lawrence Promontory in northern New

Figure 43. Graph showing the fluctuations in the mixing of sediment influx from both the Superior Craton and the Acadian fold-thrust belt. Note the increased influence from the Acadian fold-thrust belt, throughout the deposition of the Mahantango Formation.

Table 5. Results of the one-dimensional mixing model showing the proportion of sediment influx coming from the Acadian fold-thrust belt and Superior Craton throughout the deposition of the Hamilton Group.

Depth (ft)	ϵ_{Nd}	T_{DM}	% Fold-Thrust Belt	% Superior Craton
7225.3	-11.65	1.65	74.49	25.51
7270.3	-11.47	1.67	72.62	27.38
7314.7	-11.74	1.64	74.83	25.17
7360.5	-10.38	1.74	68.11	31.89
7448.35	-10.34	1.85	61.29	38.71
7460.20	-10.51	1.79	65.09	34.91
7489.06	-10.55	1.63	75.75	24.25
7505.93	-10.18	1.81	63.83	36.17
7538.15	-9.85	1.78	65.73	34.27

England and southeastern Canada and gradually progressed southward (Ettensohn, 1985). Initial deposition of the Marcellus Shale was greater influenced by intrabasinal sediments, with limited detrital clay influx eroded and transported from the Superior Craton to the north. Sediment was transported longitudinally southward along the eastern coast of the basin. At this time, Avalonia was colliding with the New York Promontory, allowing for increased clay influx from the adjacent fold-thrust belt to be deposited into the Catskill Delta region, thus contributing to a sediment mixture that would yield younger Nd depleted mantle model ages than found within the Superior Craton and less negative ϵ_{Nd} values in the Marcellus Shale in north-central WV, similar to what was observed in Marcellus Shale samples New York (Caesar *et al.*, 2010a, 2010b). As collision continued southward into the Virginia Promontory, the Mahantango Formation was deposited, with increased sedimentation from the adjacent Acadian fold-thrust belt to the east and greater contribution of Acadian-derived deposits caused even younger Nd

Figure 44. Concentrations of Zr (ppm) and TiO₂ (wt %) in comparison to the depleted mantle model ages (τ_{DM}). Note that younger Sm-Nd model ages occur more frequently where there are high concentrations of Zr and Ti which are signatures of influx from a recycled sedimentary source and housed within heavy minerals such as zircon and rutile.

Figure 45. Cross-plots showing the relationships between Zr, TiO₂, and τ_{DM} . Note the negative correlations between both Zr and TiO₂ versus τ_{DM} , further supporting the correlation between younger depleted mantle model ages and increased influx from a recycled sedimentary source. The strong correlation between Zr and TiO₂ further support that these chemical signatures are influenced by the same sink mechanism.

depleted mantle model ages and less negative ϵ_{Nd} in the Mahantango Formation. Ver Straeten (2010) explains the influx of coarser detrital sediment within the upper Middle Devonian shales of New York as being due to overfilling of proximal margin deposition, resulting in deltaic progradation into the basin and deposition of the detrital clays and silt. Alternately, structural advance of the Acadian thrust-front could have caused deltaic progradation to deliver greater flux of Acadian-derived material to north-central WV.

Previous interpretations of the Acadian foreland basin model relied on the assumption that clastic influx to the basin was dominantly from the adjacent fold-thrust belt with potential contribution from the unroofing of the Acadian volcanic arc. Influx from the Acadian arc would cause a drawdown in τ_{DM} and also be apparent within elemental discrimination diagrams. However, results from this work show that there was greater influx from the Archean crust to the north likely transported via the Catskill delta system. Smaller transverse deltaic systems contributed sediment from the Acadian fold-thrust belt that mixed in the basin with sediment from the Catskill system.

4.6 Provenance, paleoclimate, and controls on organic-matter preservation

Results suggested that the differences in organic-matter preservation between the Marcellus Shale and Mahantango Formation is due to dilution of organic matter, initially due to detrital clay sedimentation, and later by silt sedimentation. Although there was an increase in global temperatures throughout the deposition of the Mahantango Formation, evidence of this climatic transition is not evident within the provenance signatures interpreted by this study. It is likely that the increase in influx of clay to the basin is not primarily climate driven, but rather representative of increased tectonic influence and

related physical weathering of source rocks during this time, resulting in increased sediment influx from the Acadian fold-thrust belt.

Comparisons of elemental data to TOC further support the story of dilution. A positive correlation between Si/Al and TOC ($R^2=0.4477$; Fig. 29) indicates that greater clay influx to the basin resulted in less organic matter being preserved. Additionally, a negative correlation between Zr and TOC ($R^2=0.3687$; Fig. 30) further supports the relationship between the provenance model previously described and dilution of organic matter content. Greater deposition from the Acadian fold-thrust belt, as indicated by the increases in Zr, resulted in lower TOC concentrations. Petrographic trends showing a transition from the organic-rich argillaceous sarks of the lower Marcellus Shale into the tarry claystones and silty tarry claystones of the upper Marcellus Shale and Mahantango Formation help to provide visual evidence of the dilution of organic matter throughout the Hamilton Group. In summary, geochemical and petrographic evidence suggest that organic-matter content within the Hamilton Group was primarily controlled by dilution via terrigenous clastic sedimentation. This sedimentation was initially dominated by abundant clay deposition, followed by silt deposition throughout the deposition of the Hamilton Group.

CONCLUSIONS

Geochemical and petrographic provenance indicators suggest that the Marcellus Shale and Mahantango Formation were sourced from a mix of the northern Archean Superior Craton and Grenville-sourced sediments of the Acadian fold-thrust belt to the east. Recycled sediment influx from the adjacent fold-thrust belt increased throughout the deposition of the Hamilton Group as indicated by Sm-Nd depleted mantle model ages, mineralogy, and trace element geochemistry. Differences in organic content between these two units is due to dilution of organic matter by influx of detrital clay sedimentation followed by coarser silt deposition and lower rates of organic production throughout the accumulation of the Mahantango Formation. Increased clay influx to the basin does not appear to be climate driven, but rather appears to be indicative of increased physical weathering related to evolving tectonic activity and fluvial progradation during the Acadian Orogeny. Results of this study alter the previously assumed Acadian foreland basin depositional model for the Marcellus Shale by suggesting greater influx from older upper-continental crustal sources from the north, likely transported by the Catskill Delta river system. Investigation of provenance and paleoclimate signals through geochemical and petrographic analysis of the Hamilton Group have helped to further constrain our understanding of Acadian basin-fill architecture and the controls on organic-rich versus clay-rich facies within mudrock-dominated foreland basin systems.

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APPENDIX I. Table containing mineral identification information relevant to the X'pert HighScore Plus identification system including the common name, compound name, reference code, chemical formula, and reference intensity ratio of all the mineral phases identified within the Hamilton Group.

Common Name	Compound Name	Reference Code	Chemical Formula	Reference Intensity Ratio (RIR)
Albite	Albite, ordered	00-009-0466	NaAlSi ₃ O ₈	2.10
Barite	Barite	01-089-7357	BaSO ₄	2.78
Calcite	Calcite	01-083-0578	CaCO ₃	3.21
Chlorite	Clinochlore 1Mla	01-089-2972	Mg _{2.5} Fe _{1.65} AlO ₁₀ (OH) ₈	1.06
Dolomite	Dolomite (1687)	01-073-2409	CaMg(CO ₃) ₂	2.42
Gypsum	Gypsum, syn	00-033-0311	CaSO ₄ ·2H ₂ O	1.83
Muscovite	Muscovite 2\ITM\RG#1	01-082-0576	KAl ₂ (AlSi ₃)O ₁₀ (OH) ₂	0.38
Pyrite	Pyrite	01-071-1680	FeS ₂	0.89
Quartz	Quartz, low	00-005-0490	SiO ₂	3.6

APPENDIX II. RIR interpretation of bulk mineralogy for samples collected from the MIP-3H well. Samples collected from the Marcellus Shale (MS) are colored in blue, with samples from the Mahantango Formation (MF) are colored in brown.

Depth (ft)	Quartz	Muscovite	Chlorite	Pyrite	Albite	Calcite	Dolomite	Barite
7447.20	32	46	9	9	2	1	1	0
7448.35	31	49	9	9	3	0	0	0
7449.25	32	45	8	12	3	0	0	0
7450.20	35	44	7	11	3	0	0	0
7451.00	34	43	6	13	2	1	1	0
7452.22	28	52	8	9	3	0	0	0
7455.00	28	36	14	3	2	14	3	0
7456.16	21	55	11	10	3	0	0	0
7457.15	33	44	7	13	2	0	1	0
7459.13	14	51	27	4	5	0	0	0
7460.20	31	47	7	11	3	0	0	0
7463.10	34	46	9	8	3	0	0	0
7464.05	33	44	8	11	3	0	0	0
7465.30	30	45	8	14	3	0	0	0
7467.30	24	33	7	10	2	22	2	0
7470.05	32	47	7	12	3	0	0	0
7471.13	32	43	7	11	2	2	1	2
7472.09	26	50	8	13	3	0	0	0
7475.12	27	46	8	12	3	2	0	3
7476.15	30	43	9	13	2	4	0	0
7477.07	13	57	14	8	4	4	0	0
7479.05	30	50	7	9	3	1	0	0
7480.05	34	47	7	9	3	1	0	0
7482.12	13	37	8	8	2	28	5	0
7484.11	34	48	6	8	3	0	0	0
7485.03	34	47	6	9	3	0	1	0
7485.60	31	52	7	8	3	0	0	0
7488.15	29	51	7	7	3	1	3	0
7489.06	34	44	6	11	2	0	2	0
7491.22	33	46	6	11	3	1	1	0
7492.06	30	44	6	10	3	1	2	4
7494.20	35	45	5	9	3	1	1	0
7497.39	25	38	5	19	2	8	1	1
7500.60	31	42	3	10	3	7	1	3
7503.04	36	47	0	10	2	3	2	0
7505.93	34	45	0	16	3	1	1	0
7506.99	30	55	0	8	3	2	1	0
7509.01	31	39	0	16	2	11	1	
7512.01	37	45	0	13	3	1	1	0

7513.08	19	60	0	6	6	4	6	0
7514.10	38	43	0	13	2	3	1	0
7515.80	28	49	0	11	3	8	1	0
7517.23	35	41	0	11	3	9	1	0
7519.05	27	40	0	19	3	6	2	4
7520.13	33	41	0	9	3	3	3	0
7522.05	34	50	0	8	3	4	1	0
7523.03	34	51	0	4	3	8	1	0
7523.89	4	0	0	5	5	79	0	8
7524.90	34	48	0	3	3	11	2	0
7528.01	32	46	0	11	3	8	1	0
7530.15	23	57	0	10	4	3	0	3
7533.02	19	59	0	10	4	10	1	0
7534.04	35	43	0	12	3	7	1	0
7534.89	36	47	0	11	3	3	0	0
7538.15	32	47	0	15	3	2	1	0
7542.93	23	35	0	15	2	24	1	0
7544.37	18	41	0	16	5	4	1	16
7544.85	19	43	0	21	3	4	1	10
7545.77	24	50	0	16	3	4	2	0
7554.33	22	0	0	8	0	66	0	3
7556.15	26	51	0	6	3	12	2	0

APPENDIX III. XRF-quantified interpretation of bulk mineralogy for samples collected from the MIP-3H well. Samples collected from the Marcellus Shale (MS) are colored in blue, with samples from the Mahantango Formation (MF) are colored in brown.

Sample	Quartz	Muscovite	Chlorite	Pyrite	Albite	Calcite	Dolomite	Barite
7447.20	48.01	29.09	7.10	8.86	5.12	1.21	0.35	0.25
7448.35	47.78	30.34	7.46	8.66	4.89	0.68	0.00	0.20
7449.25	45.99	30.36	7.49	9.95	5.40	0.57	0.00	0.23
7450.20	48.38	29.32	7.23	8.80	5.36	0.69	0.00	0.21
7452.22	49.82	27.98	6.95	9.21	5.34	0.48	0.00	0.20
7455.00	32.60	17.51	9.51	10.17	2.62	25.62	1.79	0.18
7456.16	42.99	33.52	7.64	9.20	5.58	0.79	0.00	0.28
7457.15	46.02	30.90	6.74	9.59	5.49	0.91	0.00	0.36
7457.37	48.11	27.62	7.20	10.23	5.10	1.56	0.00	0.18
7459.13	42.54	32.37	8.04	10.62	5.31	0.83	0.00	0.28
7460.20	43.21	33.47	8.21	9.04	5.26	0.54	0.00	0.27
7463.10	44.35	33.21	7.84	7.94	5.45	0.69	0.00	0.52
7464.05	42.91	32.93	7.86	8.35	5.26	2.42	0.00	0.28
7465.30	43.00	31.71	7.58	10.35	5.62	1.05	0.00	0.69
7467.30	31.33	22.74	5.91	8.56	3.54	26.21	1.48	0.23
7470.05	44.26	33.44	7.52	8.25	5.49	0.78	0.00	0.25
7471.13	43.06	31.54	6.60	8.84	5.17	2.88	0.68	1.24
7472.09	42.57	33.57	7.66	8.72	5.42	0.69	0.00	1.36
7475.12	40.70	32.20	7.34	9.22	5.31	2.18	0.00	3.04
7476.15	40.83	32.75	7.34	9.44	5.11	4.26	0.00	0.27
7477.07	40.73	31.66	7.14	11.86	4.82	3.55	0.00	0.23
7479.05	44.66	33.14	7.02	8.06	5.64	1.23	0.00	0.26
7480.05	45.75	32.75	7.02	7.49	5.68	1.00	0.00	0.32
7482.12	29.62	17.73	5.10	8.49	3.40	29.93	3.78	1.94
7484.11	46.78	32.16	7.40	7.04	5.62	0.74	0.00	0.25
7485.03	46.83	32.26	6.76	6.88	5.76	0.48	0.78	0.25
7485.60	46.39	31.61	7.36	8.11	5.50	0.78	0.00	0.26
7488.15	47.15	31.63	4.51	7.57	5.37	0.41	3.10	0.26
7489.06	45.55	31.59	6.52	8.39	5.46	0.85	1.40	0.24
7491.22	44.78	32.07	6.96	8.26	5.74	1.21	0.70	0.28
7492.06	41.49	29.58	6.18	8.62	5.36	1.11	1.34	6.32
7494.20	45.93	31.68	6.18	7.38	5.56	1.49	1.56	0.23
7497.39	39.31	26.54	5.32	13.64	4.90	7.73	0.97	1.59
7500.60	46.03	23.53	3.76	8.67	5.26	6.55	2.04	4.16
7503.04	56.90	22.64	0.00	7.91	4.63	2.85	4.89	0.18
7503.98	57.42	22.05	0.00	7.56	4.83	2.44	5.50	0.21
7505.93	53.58	25.17	0.00	11.95	5.25	0.79	4.63	0.20
7506.99	56.22	25.60	0.00	7.93	5.15	0.06	4.85	0.19
7509.01	45.74	18.60	0.00	10.88	3.97	15.83	4.79	0.19

7512.01	56.44	23.31	0.00	9.61	5.33	0.28	4.80	0.23
7513.08	52.28	25.12	0.00	8.51	4.92	2.28	6.67	0.21
7514.10	54.11	25.06	0.00	8.30	4.70	2.54	5.09	0.20
7515.80	49.02	27.66	0.00	8.15	5.14	4.55	5.28	0.20
7517.23	47.33	26.24	0.00	6.42	5.63	9.59	4.57	0.22
7519.05	38.94	22.55	0.00	11.27	4.79	6.48	6.70	9.27
7520.13	45.69	28.06	0.00	6.95	5.81	3.09	10.17	0.23
7522.05	47.38	30.56	0.00	7.23	6.74	2.45	5.35	0.29
7523.03	45.30	31.71	0.00	4.41	5.74	7.62	4.92	0.31
7523.89	5.98	1.62	0.00	3.76	0.88	75.88	0.00	11.87
7524.90	42.74	27.37	0.00	3.84	5.59	13.76	6.41	0.29
7528.01	49.02	27.31	0.00	7.11	5.30	6.04	5.01	0.21
7530.15	49.27	26.55	0.00	10.28	5.58	3.87	0.00	4.45
7533.02	47.09	26.79	0.00	7.19	5.26	9.05	4.40	0.21
7534.04	48.47	27.38	0.00	7.08	5.71	6.41	4.68	0.28
7534.89	55.25	28.37	0.00	7.03	5.83	3.32	0.00	0.19
7538.15	48.64	29.58	0.00	9.91	6.09	0.19	5.74	0.23
7542.93	39.91	14.88	0.00	8.96	4.44	28.24	3.38	0.20
7544.37	30.41	13.76	0.00	9.81	5.36	5.14	3.98	31.54
7544.85	34.31	15.12	0.00	14.59	5.44	4.17	3.48	22.90
7545.77	49.77	21.86	0.00	13.20	4.52	3.55	6.86	0.25
7554.33	23.29	0.58	0.00	0.60	0.00	75.46	0.00	0.07
7556.15	46.99	23.26	0.00	6.58	4.96	10.67	7.34	0.19

APPENDIX IV. RIR interpretation of bulk mineralogy for samples collected from the WV-6 well. Samples collected from the Mahantango Formation are colored in brown, with the sample from the Marcellus Shale colored in blue.

Depth (ft)	Quartz	Ill. + Musc.	Chlor.	Pyrite	Albite	Calcite	Dol.	Gyp.
7222.3	12	44	23	0	5	6	2	8
7225.3	15	54	21	1	4	1	0	3
7228.1	19	56	18	2	5	0	0	0
7229.9	17	59	16	2	6	0	0	0
7233.3	15	54	25	1	6	0	0	0
7237.3	13	52	26	2	6	0	1	0
7240.2	17	56	16	5	5	0	0	3
7244.4	15	57	18	1	5	1	0	3
7245.8	15	61	18	1	4	0	0	0
7247.6	15	54	20	1	5	0	2	4
7249.9	13	50	24	2	5	0	0	7
7252.2	12	49	22	2	6	3	1	6
7255.8	14	60	18	3	5	0	0	0
7258.3	19	56	16	3	4	0	0	2
7261.9	20	57	14	2	4	0	0	4
7264.6	13	53	21	1	5	0	0	7
7267.8	19	58	12	3	4	0	0	3
7270.3	25	54	11	5	3	0	0	2
7272.7	16	58	14	4	5	0	0	4
7275.9	14	58	16	2	5	0	0	4
7278.6	12	44	21	3	6	0	0	14
7281.7	18	57	14	3	4	1	0	3
7284.7	15	60	15	3	4	0	0	3
7287.8	15	59	16	2	5	0	0	3
7290.5	14	59	17	2	4	0	0	5
7296.9	18	57	15	3	4	0	0	3
7299.9	17	60	13	3	4	0	0	3
7303	19	58	14	2	4	0	0	3
7305.8	19	55	13	3	3	1	2	3
7309.2	15	59	16	2	4	0	0	4
7311.9	13	51	22	2	5	0	2	5
7314.7	31	50	10	3	3	0	0	2
7317.8	35	47	10	3	3	0	0	2
7320.7	21	57	12	3	4	0	0	3
7323.5	13	57	18	2	5	0	0	5
7326.7	12	50	21	1	5	1	2	7
7330.3	24	51	13	4	3	1	1	2
7333.1	25	52	13	1	3	1	2	3

7336.5	26	46	12	3	2	5	4	2
7338.9	22	54	12	4	3	1	1	3
7342.3	35	49	7	3	3	0	0	3
7344.9	27	52	10	5	3	0	0	4
7347.8	34	50	7	4	3	0	0	2
7351	35	44	9	8	3	0	0	2
7354.4	11	24	9	13	0	37	6	0
7357.3	29	50	9	6	3	0	0	3
7360.5	17	54	12	3	3	3	4	4
7363.4	17	56	12	3	3	3	1	4
7366.9	19	57	11	3	4	2	0	3
7369.9	17	54	13	2	4	3	2	5
7373.1	13	51	18	2	5	0	0	11
7377.2	17	57	12	4	5	0	0	5
7381.1	18	52	12	6	3	3	2	4
7383.2	21	58	8	7	4	0	0	3
7385.7	21	57	8	7	4	0	0	3
7388.1	20	41	11	12	2	9	1	4
7391.2	34	46	6	9	3	0	0	2
7394.2	29	52	6	8	3	0	0	2
7397.8	14	53	14	8	4	3	0	6

APPENDIX V. XRF-quantified interpretation of bulk mineralogy for samples collected from the WV-6 well. Samples collected from the Mahantango Formation are colored in brown, with the sample from the Marcellus Shale colored in blue.

Depth (ft)	Qtz	Ill.+ Musc.	Chlor.	Pyrt.	Alb.	Calc.	Dol.	Bar.	Gyp.
7222.3	43.37	27.46	7.50	5.72	4.41	7.35	2.06	0.15	1.97
7225.3	44.19	30.67	9.69	7.10	5.04	1.33	0.00	0.15	1.84
7228.1	44.02	32.97	10.29	6.28	6.27	0.00	0.00	0.18	0.00
7229.9	51.17	27.52	8.40	7.00	5.77	0.00	0.00	0.14	0.00
7233.3	47.15	30.76	10.20	6.64	5.09	0.00	0.00	0.15	0.00
7237.3	48.13	29.40	9.03	7.49	5.09	0.00	0.73	0.14	0.00
7240.2	44.42	30.01	8.61	10.03	5.84	0.00	0.00	0.15	0.95
7244.4	46.54	30.64	9.29	6.38	5.23	0.98	0.00	0.15	0.78
7245.8	46.49	32.16	9.52	6.51	5.16	0.00	0.00	0.16	0.00
7247.6	46.22	28.04	9.64	6.63	4.94	0.00	1.04	0.15	3.34
7249.9	45.05	31.47	9.56	6.98	5.67	0.00	0.00	0.15	1.12
7252.2	43.50	29.77	9.17	7.21	5.12	2.93	0.49	0.15	1.65
7255.8	44.29	34.27	8.79	7.12	5.34	0.00	0.00	0.18	0.00
7258.3	40.63	27.36	10.10	13.84	4.55	0.00	0.00	0.22	3.30
7261.9	43.99	30.27	9.31	7.46	5.12	0.00	0.00	0.17	3.68
7264.6	43.67	30.69	9.11	8.12	4.91	0.00	0.00	0.17	3.33
7267.8	44.62	32.15	8.93	8.01	5.20	0.00	0.00	0.18	0.92
7270.3	45.29	32.28	8.77	7.70	5.18	0.00	0.00	0.18	0.61
7272.7	43.81	31.06	8.84	9.92	5.15	0.00	0.00	0.17	1.06
7275.9	45.52	31.72	9.13	7.05	5.44	0.00	0.00	0.18	0.96
7278.6	45.22	31.39	9.15	7.66	5.07	0.00	0.00	0.17	1.33
7281.7	40.69	27.90	10.07	7.79	4.02	2.74	0.00	0.16	6.62
7284.7	45.43	31.71	9.20	7.50	5.10	0.00	0.00	0.18	0.89
7287.8	45.53	31.33	9.51	7.09	5.39	0.00	0.00	0.18	0.98
7290.5	44.69	30.62	9.67	7.91	5.26	0.00	0.00	0.17	1.67
7296.9	44.93	30.62	9.80	7.89	4.93	0.00	0.00	0.17	1.67
7299.9	46.16	31.14	9.13	7.41	4.94	0.00	0.00	0.17	1.05
7303	45.82	30.64	9.50	7.30	4.77	0.00	0.00	0.17	1.80
7305.8	44.04	29.72	8.30	8.35	4.64	0.92	1.36	0.18	2.50
7309.2	44.81	30.79	9.72	7.88	5.03	0.00	0.00	0.17	1.59
7311.9	44.60	29.74	9.65	8.14	4.60	0.00	1.04	0.16	2.06
7314.7	46.05	31.05	9.05	7.31	4.98	0.00	0.00	0.18	1.37
7317.8	45.83	30.88	9.08	7.26	4.90	0.00	0.00	0.18	1.88
7320.7	45.38	31.32	9.32	7.31	4.73	0.00	0.00	0.18	1.76
7323.5	45.46	31.58	9.06	7.43	5.00	0.00	0.00	0.18	1.29
7326.7	45.04	30.98	8.80	7.03	4.56	0.48	1.09	0.18	1.84
7330.3	44.94	31.85	8.42	6.96	4.95	0.99	0.55	0.18	1.16

7333.1	43.28	32.12	8.88	6.58	4.56	0.86	0.95	0.18	2.58
7336.5	40.64	26.27	8.82	7.89	3.64	7.58	1.98	0.19	2.99
7338.9	45.92	31.16	8.07	7.24	4.96	0.35	0.43	0.17	1.70
7342.3	47.91	29.55	8.19	7.10	4.89	0.00	0.00	0.18	2.19
7344.9	48.61	29.33	8.17	6.45	4.92	0.00	0.00	0.17	2.35
7347.8	48.89	30.53	8.00	6.35	4.98	0.00	0.00	0.19	1.07
7351	47.82	30.13	8.15	7.03	4.56	0.00	0.00	0.20	2.11
7354.4	10.69	3.88	3.32	9.12	0.52	66.43	5.54	0.50	0.00
7357.3	48.18	29.51	7.98	7.49	4.49	0.00	0.00	0.20	2.15
7360.5	50.25	26.56	5.00	7.02	4.42	2.17	2.43	0.16	1.99
7363.4	49.17	27.78	7.12	6.62	4.49	1.97	0.83	0.17	1.85
7366.9	50.26	28.48	7.79	6.21	4.53	1.24	0.00	0.18	1.31
7369.9	50.26	28.45	6.34	6.79	4.79	0.96	1.18	0.17	1.06
7373.1	49.03	30.11	7.67	7.13	4.69	0.00	0.00	0.18	1.20
7377.2	50.14	27.62	7.43	8.62	4.63	0.00	0.00	0.17	1.39
7381.1	44.47	28.36	7.27	8.71	4.23	1.98	1.86	0.17	2.95
7383.2	49.12	29.39	7.43	8.29	4.92	0.00	0.00	0.18	0.67
7385.7	48.15	30.11	7.59	8.42	4.94	0.00	0.00	0.19	0.59
7388.1	34.70	26.17	6.96	13.39	3.40	9.79	0.75	0.17	4.66
7391.2	46.76	30.37	7.75	9.36	4.76	0.00	0.00	0.19	0.82
7394.2	44.32	33.81	8.14	8.31	4.37	0.00	0.00	0.21	0.84
7397.8	41.56	30.31	7.82	11.66	4.14	1.03	0.00	0.19	3.30

APPENDIX VI. Image of prepared samples for XRF analysis.

APPENDIX VII. Petrographic analysis estimates of classification scheme end members and rock identification assigned to each sample. Samples from the Mahantango Formation are scripted in brown, with Marcellus Shale samples indicated by blue script.

Depth (ft)	Well	Milliken (2014)			Picard (1971)			Name
		Terr./ Volc.	Cal c. all.	Bio- sil. all.	Clay	Sand	Silt	
7221	WV6				74	1	25	Silty claystone
7237	WV6				85		15	Claystone
7251	WV6				98		2	Claystone
7268	WV6				94	1	5	Claystone
7284	WV6				85		15	Claystone
7299	WV6				75		25	Silty claystone
7314	WV6				80		20	Claystone
7330	WV6	97		3				Tarl
7347	WV6	90		10				Bio-siliceous tarl
7363	WV6				90		10	Claystone
7381	WV6				90		10	Claystone
7448	M3H				90		10	Claystone
7451	M3H	90		10				Bio-siliceous tarl
7457	M3H				95		5	Claystone
7460	M3H				99		1	Claystone
7464	M3H	90		10				Bio-siliceous tarl
7467	M3H	92	8					Tarl
7472	M3H				75		25	Silty Claystone
7475	M3H	80		20				Bio-siliceous tarl
7505	M3H				90		10	Claystone
7514	M3H				98		2	Claystone
7515	M3H	70		30				Argillaceous sarl
7522	M3H	73	7	20				Argillaceous sarl
7528	M3H				65		35	Silty claystone
7530	M3H				60		40	Silty claystone
7533	M3H				80		20	Claystone
7534	M3H	75		25				Argillaceous sarl
7542	M3H	70	10	20				Bio-siliceous tarl
7544	M3H	60		40				Argillaceous sarl
7554	M3H	30	70					Carl
7556	M3H	60	10	30				Argillaceous sarl

APPENDIX VIII. Major element concentrations (weight percent) of the samples collected from the MIP-3H well. Samples collected from the Marcellus Shale (MS) are colored in blue, with samples from the Mahantango Formation (MF) are colored in brown. FeO* indicates the total iron expressed as FeO.

Depth (ft)	SiO ₂	TiO ₂	Al ₂ O ₃	FeO*	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	LOI
7447.20	58.54	0.691	16.52	5.86	0.022	1.40	0.86	0.67	3.97	0.079	9.20
7448.35	57.98	0.718	17.18	5.71	0.019	1.38	0.42	0.63	4.13	0.066	9.60
7449.25	57.34	0.737	17.50	6.66	0.019	1.41	0.36	0.71	4.20	0.062	9.49
7450.20	59.40	0.708	16.73	5.84	0.020	1.34	0.43	0.70	4.02	0.070	8.90
7452.22	60.10	0.674	15.72	6.03	0.019	1.28	0.30	0.69	3.78	0.067	8.58
7455.00	40.83	0.545	12.41	6.82	0.073	2.23	16.68	0.35	2.43	0.062	13.52
7456.16	53.01	0.734	18.86	6.03	0.017	1.40	0.49	0.72	4.54	0.074	11.90
7457.15	55.14	0.697	17.03	6.18	0.018	1.37	0.55	0.70	4.12	0.074	10.49
7457.37	59.77	0.648	15.68	6.89	0.022	1.36	0.98	0.68	3.84	0.092	9.24
7459.13	53.09	0.708	18.71	7.05	0.017	1.49	0.52	0.69	4.44	0.073	11.67
7460.20	53.53	0.708	19.12	5.97	0.017	1.52	0.33	0.68	4.56	0.077	12.11
7463.10	55.76	0.761	19.12	5.33	0.018	1.47	0.43	0.72	4.60	0.085	9.81
7464.05	53.12	0.700	18.50	5.52	0.019	1.45	1.49	0.68	4.49	0.073	10.94
7465.30	53.21	0.673	17.88	6.81	0.017	1.40	0.65	0.73	4.31	0.067	12.14
7467.30	39.31	0.490	13.40	5.75	0.064	1.48	16.98	0.47	3.16	0.068	15.88
7470.05	54.87	0.683	18.99	5.46	0.017	1.40	0.48	0.72	4.57	0.067	11.37
7471.13	51.90	0.633	17.11	5.73	0.019	1.36	1.97	0.66	4.22	0.066	12.08
7472.09	51.59	0.678	18.17	5.62	0.016	1.38	0.42	0.69	4.47	0.075	12.89
7475.12	49.81	0.670	17.74	5.99	0.018	1.34	1.33	0.68	4.32	0.298	12.93
7476.15	50.75	0.666	18.13	6.25	0.021	1.36	2.64	0.67	4.48	0.060	11.64
7477.07	50.69	0.699	17.78	7.90	0.018	1.33	2.21	0.63	4.36	0.068	11.78
7479.05	53.43	0.704	18.07	5.15	0.019	1.26	0.73	0.71	4.38	0.057	10.75
7480.05	56.48	0.778	18.40	4.95	0.019	1.30	0.62	0.74	4.47	0.062	9.53
7482.12	35.33	0.398	9.95	5.44	0.056	1.80	19.15	0.43	2.34	0.069	17.29
7484.11	57.21	0.715	17.63	4.62	0.017	1.36	0.45	0.73	4.36	0.059	10.76
7485.03	56.92	0.716	17.56	4.49	0.018	1.42	0.55	0.74	4.35	0.067	10.35
7485.60	57.79	0.724	17.63	5.43	0.018	1.38	0.49	0.73	4.37	0.059	9.79
7488.15	57.15	0.739	17.16	5.01	0.022	1.58	1.30	0.70	4.32	0.055	9.85
7489.06	56.22	0.736	17.52	5.57	0.021	1.55	1.00	0.71	4.33	0.054	9.77
7491.22	55.26	0.757	17.67	5.45	0.019	1.45	0.98	0.75	4.37	0.059	10.81
7492.06	52.84	0.663	17.08	5.87	0.021	1.51	1.17	0.72	4.16	0.062	11.75
7494.20	55.85	0.696	17.20	4.83	0.019	1.51	1.43	0.72	4.29	0.059	11.32
7497.39	48.22	0.594	14.31	9.00	0.026	1.22	5.09	0.64	3.62	0.082	11.54
7500.60	53.90	0.517	12.07	5.55	0.026	1.15	4.59	0.66	3.11	0.063	12.30
7503.04	60.00	0.470	10.90	4.74	0.017	1.07	3.08	0.55	2.80	0.075	13.37
7503.98	60.20	0.468	10.79	4.49	0.018	1.19	3.01	0.57	2.71	0.085	13.75
7505.93	59.08	0.575	12.59	7.41	0.014	1.05	1.00	0.64	3.22	0.074	13.20
7506.99	59.95	0.545	12.32	4.77	0.014	1.06	1.51	0.61	3.18	0.077	13.58
7509.01	51.75	0.412	9.30	6.97	0.025	1.12	11.04	0.50	2.46	0.181	11.23
7512.01	58.44	0.484	11.27	5.60	0.013	1.02	1.57	0.61	2.81	0.107	16.73
7513.08	53.85	0.522	11.53	4.94	0.015	1.41	3.20	0.56	3.01	0.088	17.50
7514.10	56.98	0.545	11.84	4.95	0.014	1.11	2.96	0.55	3.08	0.097	15.32
7515.80	54.51	0.643	13.59	5.07	0.018	1.20	4.32	0.63	3.55	0.111	12.25
7517.23	53.86	0.603	13.02	4.05	0.017	1.05	7.12	0.70	3.42	0.084	11.87
7519.05	46.23	0.568	12.01	7.40	0.020	1.61	6.21	0.62	3.06	0.078	15.16

7520.13	51.52	0.688	13.66	4.32	0.023	2.31	5.01	0.71	3.60	0.100	14.91
7522.05	53.18	0.761	14.88	4.43	0.018	1.20	3.07	0.81	3.87	0.100	14.41
7523.03	53.02	0.774	15.93	2.85	0.024	1.16	6.22	0.73	4.23	0.087	11.59
7523.89	6.72	0.058	1.13	2.30	0.027	0.60	43.41	0.11	0.20	0.092	33.37
7524.90	49.83	0.728	13.75	2.46	0.026	1.50	10.34	0.71	3.63	0.131	12.97
7528.01	54.91	0.629	13.32	4.45	0.018	1.14	5.12	0.65	3.53	0.077	13.41
7530.15	55.29	0.576	12.58	6.42	0.013	0.95	2.26	0.69	3.42	0.069	13.24
7533.02	54.36	0.580	13.00	4.62	0.018	1.03	6.88	0.67	3.56	0.065	13.25
7534.04	54.88	0.597	13.12	4.45	0.018	1.07	5.26	0.71	3.55	0.066	13.34
7534.89	59.84	0.601	13.14	4.26	0.013	1.02	1.88	0.70	3.55	0.100	12.58
7538.15	53.01	0.558	13.62	5.96	0.013	1.26	1.65	0.72	3.68	0.073	17.12
7542.93	41.87	0.293	6.65	5.24	0.016	0.72	16.44	0.51	1.80	0.078	18.58
7544.37	32.00	0.233	6.02	5.52	0.022	0.82	3.84	0.59	1.60	0.065	14.47
7544.85	36.60	0.289	6.75	8.42	0.016	0.73	3.27	0.62	1.80	0.078	17.30
7545.77	49.49	0.375	8.96	7.41	0.011	1.41	3.82	0.50	2.53	0.076	22.42
7554.33	19.53	0.011	0.44	0.30	0.015	0.37	35.48	0.03	0.06	0.310	33.73
7556.15	51.79	0.490	10.12	4.06	0.009	1.65	8.45	0.60	2.96	0.103	16.31
MF Average	58.67	0.71	16.73	6.02	0.02	1.36	0.47	0.68	4.02	0.07	9.16
MS Average	51.15	0.59	13.98	5.41	0.02	1.29	5.14	0.63	3.51	0.09	13.74

APPENDIX IX. Major element concentrations (weight percent) of the samples collected from the WV-6 well. Samples collected from the Mahantango Formation (MF) are colored in brown, with samples from the Marcellus Shale colored in blue. FeO* indicates total iron expressed as FeO.

Depth (ft)	SiO ₂	TiO ₂	Al ₂ O ₃	FeO*	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	LOI
7222.3	55.75	0.720	17.28	4.78	0.042	1.99	4.40	0.61	3.95	0.096	7.6
7225.3	56.28	0.781	18.63	5.83	0.034	1.84	1.34	0.67	4.29	0.114	7.9
7228.1	52.89	0.623	18.93	4.93	0.027	1.81	0.54	0.77	4.27	0.101	12.4
7229.9	62.24	0.594	16.23	5.43	0.025	1.54	0.24	0.75	3.72	0.071	8.1
7233.3	55.25	0.644	16.99	5.14	0.055	1.79	4.68	0.63	3.98	0.086	8.0
7237.3	60.08	0.822	17.77	5.97	0.036	1.88	0.98	0.67	4.08	0.118	5.9
7240.2	54.08	0.639	17.10	7.31	0.029	1.55	0.42	0.74	3.99	0.053	12.6
7244.4	58.30	0.670	18.16	5.23	0.028	1.74	0.71	0.69	4.24	0.082	8.8
7245.8	58.96	0.714	19.47	5.41	0.031	1.81	0.29	0.69	4.50	0.085	6.8
7247.6	59.14	0.827	17.48	5.56	0.051	2.11	1.94	0.67	3.97	0.117	6.0
7249.9	57.30	0.735	19.01	5.68	0.030	1.80	0.52	0.75	4.37	0.093	8.1
7252.2	55.97	0.698	18.20	5.90	0.037	1.88	2.02	0.69	4.21	0.089	7.9
7255.8	55.18	0.746	20.04	5.62	0.026	1.63	0.58	0.70	4.69	0.078	8.7
7258.3	50.67	0.629	17.27	10.17	0.029	1.87	1.50	0.59	3.73	0.094	10.2
7261.9	56.15	0.831	18.46	6.04	0.042	1.77	1.72	0.69	4.25	0.081	7.7
7264.6	54.76	0.791	18.32	6.38	0.037	1.71	1.53	0.65	4.24	0.097	8.9
7267.8	55.53	0.806	19.15	6.23	0.030	1.66	0.42	0.68	4.41	0.087	9.1
7270.3	56.52	0.860	19.29	6.04	0.028	1.64	0.28	0.68	4.45	0.088	8.2
7272.7	53.82	0.788	18.18	7.38	0.037	1.62	0.48	0.66	4.20	0.085	10.7
7275.9	56.90	0.832	18.98	5.63	0.029	1.70	0.44	0.71	4.36	0.083	8.3
7278.6	55.46	0.828	18.48	5.95	0.029	1.68	0.60	0.66	4.25	0.087	9.9
7281.7	51.69	0.739	16.99	6.34	0.048	1.91	4.83	0.54	3.91	0.112	7.5
7284.7	56.36	0.866	18.95	5.91	0.028	1.71	0.41	0.67	4.34	0.089	8.4
7287.8	57.74	0.842	19.23	5.77	0.031	1.80	0.45	0.72	4.36	0.090	6.9
7290.5	55.36	0.815	18.25	6.19	0.033	1.78	0.76	0.68	4.16	0.091	9.2
7296.9	56.54	0.826	18.66	6.31	0.033	1.84	0.77	0.65	4.25	0.095	7.5
7299.9	57.29	0.816	18.50	5.87	0.029	1.70	0.48	0.65	4.28	0.084	8.2
7303	57.61	0.819	18.46	5.91	0.032	1.79	0.83	0.63	4.27	0.094	7.0
7305.8	55.11	0.804	17.91	6.49	0.041	1.90	2.20	0.62	4.13	0.092	7.1
7309.2	56.55	0.823	18.84	6.31	0.034	1.83	0.73	0.67	4.28	0.092	7.8
7311.9	56.94	0.804	18.70	6.59	0.043	2.11	1.33	0.62	4.20	0.088	6.0
7314.7	57.16	0.847	18.52	5.80	0.032	1.69	0.63	0.65	4.27	0.083	8.2
7317.8	56.85	0.868	18.37	5.77	0.032	1.69	0.86	0.64	4.25	0.096	8.4
7320.7	56.71	0.856	18.88	5.86	0.032	1.75	0.81	0.63	4.34	0.094	7.6
7323.5	56.49	0.849	18.82	5.88	0.031	1.69	0.59	0.66	4.34	0.097	8.4
7326.7	57.02	0.845	19.01	5.72	0.042	1.95	1.55	0.61	4.37	0.089	6.0
7330.3	56.73	0.823	19.33	5.60	0.035	1.73	1.36	0.66	4.46	0.089	6.4

7333.1	55.46	0.811	19.80	5.46	0.044	1.95	2.10	0.62	4.56	0.085	6.0
7336.5	50.76	0.767	15.99	6.24	0.072	2.16	6.85	0.48	3.66	0.114	8.9
7338.9	56.77	0.773	18.27	5.65	0.032	1.61	1.14	0.65	4.29	0.095	8.1
7342.3	56.98	0.698	16.70	5.39	0.026	1.48	0.97	0.62	3.93	0.090	11.9
7344.9	59.41	0.688	17.05	5.10	0.026	1.52	1.07	0.64	4.01	0.083	8.9
7347.8	59.10	0.769	17.57	4.97	0.024	1.47	0.48	0.64	4.13	0.080	9.3
7351	58.76	0.710	17.53	5.53	0.026	1.52	0.97	0.60	4.16	0.084	8.2
7354.4	10.77	0.122	2.76	5.28	0.177	1.62	35.61	0.06	0.44	0.185	28.4
7357.3	57.96	0.652	16.84	5.71	0.022	1.47	0.97	0.58	3.99	0.086	10.4
7360.5	58.70	0.605	14.94	5.04	0.033	1.48	3.00	0.56	3.55	0.092	9.1
7363.4	58.06	0.627	15.74	4.99	0.026	1.48	2.28	0.57	3.71	0.083	10.4
7366.9	59.80	0.648	16.17	4.82	0.022	1.42	1.34	0.58	3.83	0.073	9.2
7369.9	59.16	0.636	16.02	5.01	0.023	1.42	1.44	0.61	3.79	0.088	10.0
7373.1	58.31	0.671	17.00	5.39	0.020	1.39	0.53	0.60	4.03	0.072	10.0
7377.2	59.56	0.631	15.77	6.35	0.020	1.35	0.62	0.59	3.71	0.081	9.6
7381.1	54.54	0.608	16.79	6.56	0.034	1.81	3.22	0.56	3.91	0.084	9.3
7383.2	58.70	0.685	16.76	6.13	0.020	1.35	0.30	0.63	3.95	0.070	9.8
7385.7	56.60	0.691	16.85	6.12	0.019	1.36	0.26	0.62	3.97	0.064	11.9
7388.1	41.79	0.581	14.65	9.40	0.039	1.45	8.28	0.44	3.51	0.061	10.1
7391.2	53.94	0.633	16.33	6.60	0.018	1.36	0.50	0.59	3.92	0.077	13.6
7394.2	51.41	0.696	18.11	6.00	0.017	1.43	0.36	0.54	4.38	0.078	15.2
7397.8	49.83	0.594	16.86	8.34	0.022	1.42	2.10	0.53	4.05	0.072	13.3
MF Average	55.52	0.73	17.56	5.94	0.03	1.69	2.01	0.63	4.07	0.09	9.15

APPENDIX X. Table summarizing weathering proxies, major element ratios, loss on ignition data, and averages of each from the MIP-3H well. Samples in brown were collected from the Mahantango Formation (MF), whereas the samples in blue were collected from the Marcellus Shale (MS).

Sample	CIA	CIW	ICV	Si/Al	Ti/Al	LOI
7447.20	70.33	86.09	0.82	3.54	0.042	9.20
7448.35	73.27	90.51	0.76	3.37	0.042	9.60
7449.25	73.33	90.57	0.81	3.28	0.042	9.49
7450.20	72.70	89.66	0.78	3.55	0.042	8.90
7452.22	73.15	90.38	0.81	3.82	0.043	8.58
7455.00	27.01	28.65	2.35	3.29	0.044	13.52
7456.16	72.99	90.12	0.74	2.81	0.039	11.90
7457.15	72.08	88.83	0.80	3.24	0.041	10.49
7457.37	68.94	84.37	0.92	3.81	0.041	9.24
7459.13	73.10	89.98	0.80	2.84	0.038	-
7460.20	74.13	91.69	0.72	2.80	0.037	-
7463.10	73.33	90.66	0.70	2.92	0.040	9.81
7464.05	68.02	82.82	0.78	2.87	0.038	10.94
7465.30	71.76	88.27	0.82	2.98	0.038	12.14
7467.30	27.65	29.75	2.12	2.93	0.037	15.88
7470.05	73.04	90.22	0.70	2.89	0.036	-
7471.13	64.96	78.58	0.85	3.03	0.037	12.08
7472.09	72.98	90.57	0.73	2.84	0.037	12.89
7475.12	68.37	83.40	0.81	2.81	0.038	12.93
7476.15	62.79	75.46	0.89	2.80	0.037	11.64
7477.07	64.51	77.83	0.97	2.85	0.039	11.78
7479.05	71.39	87.83	0.72	2.96	0.039	10.75
7480.05	71.93	88.73	0.70	3.07	0.042	9.53
7482.12	20.73	21.89	2.98	3.55	0.040	-
7484.11	72.35	89.71	0.69	3.24	0.041	10.76
7485.03	71.70	88.77	0.70	3.24	0.041	10.35
7485.60	72.14	89.44	0.74	3.28	0.041	9.79
7488.15	67.70	83.02	0.80	3.33	0.043	9.85
7489.06	69.50	85.39	0.80	3.21	0.042	9.77
7491.22	69.54	85.44	0.78	3.13	0.043	10.81
7492.06	68.62	83.78	0.83	3.09	0.039	-
7494.20	67.14	81.99	0.78	3.25	0.040	11.32
7497.39	50.16	58.14	1.41	3.37	0.041	11.54
7500.60	48.52	56.12	1.29	4.47	0.043	12.30
7503.04	53.33	62.62	1.17	5.51	0.043	13.37
7503.98	53.60	62.73	1.15	5.58	0.043	-
7505.93	66.44	81.42	1.10	4.69	0.046	13.20
7506.99	63.12	76.63	0.95	4.86	0.044	13.58

7509.01	28.30	30.79	2.42	5.57	0.044	11.23
7512.01	61.99	74.44	1.08	5.19	0.043	-
7513.08	53.54	63.07	1.19	4.67	0.045	17.50
7514.10	55.16	65.32	1.12	4.81	0.046	15.32
7515.80	51.64	60.48	1.14	4.01	0.047	12.25
7517.23	42.24	48.01	1.30	4.14	0.046	11.87
7519.05	43.46	49.37	1.62	3.85	0.047	-
7520.13	49.07	57.07	1.22	3.77	0.050	14.91
7522.05	57.25	68.25	0.95	3.57	0.051	14.41
7523.03	48.26	56.03	1.00	3.33	0.049	11.59
7523.89	1.40	1.41	41.41	5.96	0.052	33.37
7524.90	36.52	40.78	1.41	3.62	0.053	12.97
7528.01	48.39	56.18	1.17	4.12	0.047	-
7530.15	58.44	70.59	1.14	4.39	0.046	13.24
7533.02	42.69	48.86	1.34	4.18	0.045	13.25
7534.04	47.39	55.03	1.19	4.18	0.045	13.34
7534.89	61.01	74.23	0.91	4.55	0.046	12.58
7538.15	62.52	76.49	1.02	3.89	0.041	-
7542.93	16.91	17.79	3.76	6.29	0.044	18.58
7544.37	38.28	43.02	2.10	5.32	0.039	14.47
7544.85	43.09	49.22	2.25	5.43	0.043	17.30
7545.77	46.01	53.56	1.79	5.53	0.042	22.42
7554.33	0.68	0.68	81.99	44.14	0.025	33.73
7556.15	34.11	38.24	1.80	5.12	0.048	16.31
MF Avg	72.55	89.44	0.79	3.51	0.042	9.16
MS Avg	54.77	65.68	3.33	4.58	0.042	13.68

APPENDIX XI. Table summarizing weathering proxies, major element ratios, loss on ignition data, and averages of each from the WV-6 well. Samples in brown were collected from the Mahantango Formation, whereas the sample in blue was collected from the Marcellus Shale.

Sample	CIA	CIW	ICV	Si/Al	Ti/Al	LOI
7222.3	56.59	65.78	0.95	3.23	0.042	7.56
7225.3	69.47	84.04	0.79	3.02	0.042	7.87
7228.1	73.34	89.33	0.69	2.79	0.033	12.35
7229.9	74.05	90.72	0.76	3.83	0.037	8.14
7233.3	55.08	64.02	1.00	3.25	0.038	7.97
7237.3	70.87	86.02	0.81	3.38	0.046	5.94
7240.2	73.06	89.61	0.86	3.16	0.037	12.63
7244.4	72.13	88.21	0.73	3.21	0.037	8.75
7245.8	74.85	92.12	0.69	3.03	0.037	6.80
7247.6	66.22	79.10	0.87	3.38	0.047	5.98
7249.9	73.33	89.71	0.73	3.01	0.039	8.05
7252.2	66.04	79.12	0.85	3.08	0.038	7.92
7255.8	73.34	90.09	0.70	2.75	0.037	8.66
7258.3	69.05	82.37	1.07	2.93	0.036	10.23
7261.9	67.61	81.29	0.83	3.04	0.045	7.74
7264.6	68.45	82.64	0.84	2.99	0.043	8.89
7267.8	74.23	91.06	0.74	2.90	0.042	9.12
7270.3	74.96	92.23	0.72	2.93	0.045	8.17
7272.7	73.66	90.28	0.83	2.96	0.043	10.71
7275.9	73.93	90.57	0.72	3.00	0.044	8.35
7278.6	73.19	89.50	0.76	3.00	0.045	9.91
7281.7	55.00	63.73	1.08	3.04	0.044	7.48
7284.7	74.37	91.18	0.73	2.97	0.046	8.39
7287.8	74.09	90.58	0.73	3.00	0.044	6.94
7290.5	72.26	87.95	0.79	3.03	0.045	9.15
7296.9	72.52	88.29	0.79	3.03	0.044	7.54
7299.9	73.78	90.52	0.75	3.10	0.044	8.19
7303	72.00	87.83	0.77	3.12	0.044	7.00
7305.8	65.37	78.12	0.90	3.08	0.045	7.06
7309.2	72.73	88.56	0.78	3.00	0.044	7.78
7311.9	70.05	84.45	0.84	3.05	0.043	6.03
7314.7	73.03	89.31	0.75	3.09	0.046	8.15
7317.8	71.80	87.52	0.77	3.09	0.047	8.36
7320.7	72.39	88.29	0.76	3.00	0.045	7.55
7323.5	73.32	89.75	0.75	3.00	0.045	8.43
7326.7	68.99	83.27	0.79	3.00	0.044	6.02
7330.3	69.75	84.45	0.76	2.94	0.043	6.36

7333.1	66.94	80.35	0.79	2.80	0.041	6.00
7336.5	48.15	54.68	1.27	3.17	0.048	8.93
7338.9	70.12	85.31	0.77	3.11	0.042	8.14
7342.3	70.36	85.72	0.78	3.41	0.042	11.86
7344.9	69.91	85.05	0.77	3.48	0.040	8.93
7347.8	73.29	90.09	0.71	3.36	0.044	9.33
7351	70.75	86.45	0.77	3.35	0.040	8.24
7354.4	4.05	4.08	15.69	3.90	0.044	28.42
7357.3	70.52	86.11	0.80	3.44	0.039	10.38
7360.5	59.37	70.06	0.96	3.93	0.040	9.06
7363.4	63.33	75.55	0.87	3.69	0.040	10.37
7366.9	68.20	82.64	0.78	3.70	0.040	9.18
7369.9	67.48	81.59	0.81	3.69	0.040	9.98
7373.1	72.91	89.69	0.74	3.43	0.039	10.03
7377.2	72.06	88.24	0.84	3.78	0.040	9.58
7381.1	60.42	71.27	0.99	3.25	0.036	9.29
7383.2	74.13	91.39	0.78	3.50	0.041	9.83
7385.7	74.44	91.85	0.77	3.36	0.041	11.86
7388.1	42.81	48.15	1.62	2.85	0.040	10.07
7391.2	72.73	89.69	0.83	3.30	0.039	13.63
7394.2	74.22	92.13	0.74	2.84	0.038	15.22
7397.8	65.03	78.28	1.01	2.96	0.035	13.28
MF	68.12	82.62	1.08	3.19	0.042	9.15
Average						

APPENDIX XII. Trace element concentrations (ppm) of the MIP-3H samples. The Mahantango Formation (MF) is recorded in brown, with the Marcellus Shale (MS) recorded in blue. “ND” indicates elements which could not be determined reliably within the presence of >3 wt% barium.

Depth (ft)	Ni	Cr	V	Sc	Cu	Zn	Ga	Ba	Rb	Cs	Sr
7447.20	105	104	398	16	93	41	21	1496	187	10	124
7448.35	124	105	441	18	97	36	22	1172	197	17	130
7449.25	135	102	385	15	105	41	23	1382	202	11	124
7450.20	96	100	361	17	97	33	22	1278	193	16	119
7452.22	98	87	315	17	86	35	22	1185	177	10	111
7455.00	28	54	111	15	22	29	17	907	105	6	266
7456.16	170	94	343	21	110	348	26	1676	219	16	134
7457.15	179	96	436	19	125	224	23	2138	200	16	135
7457.37	135	89	322	18	113	36	20	1097	181	11	124
7459.13	165	119	444	19	132	39	25	1722	222	18	128
7460.20	165	103	421	20	115	48	27	1588	228	16	136
7463.10	118	92	277	19	92	207	27	3292	225	16	161
7464.05	144	90	272	20	144	71	25	1656	217	14	151
7465.30	144	96	286	15	165	52	24	4270	206	15	161
7467.30	104	62	189	15	124	39	20	1310	145	6	240
7470.05	153	100	365	18	86	64	27	1520	229	15	127
7471.13	180	89	389	18	134	44	23	7634	200	13	229
7472.09	198	94	499	19	142	350	26	8395	217	18	221
7475.12	184	85	346	17	151	139	26	19000	204	12	386
7476.15	163	88	301	22	157	447	24	1599	215	15	140
7477.07	155	88	329	23	180	46	25	1362	208	14	162
7479.05	160	100	347	20	130	893	25	1497	210	16	106
7480.05	118	98	285	19	98	62	25	1988	214	17	121
7482.12	52	52	94	7	83	20	13	11800	103	3	420
7484.11	142	85	332	19	105	37	25	1508	206	13	118
7485.03	121	89	291	19	91	2965	24	1502	202	15	117
7485.60	113	85	254	18	79	75	22	1587	207	13	118
7488.15	85	84	189	19	79	43	24	1560	199	13	118
7489.06	106	92	217	18	68	37	22	1430	198	13	122
7491.22	120	93	250	20	83	34	24	1669	198	12	130
7492.06	152	89	220	19	99	102	26	41600	196	11	605
7494.20	124	94	282	19	103	71	24	1379	196	14	126
7497.39	171	84	291	20	140	62	20	10000	162	12	281
7500.60	193	79	448	17	143	446	16	25700	136	11	435
7503.04	181	81	477	16	137	270	16	909	126	11	132
7503.98	177	73	461	14	134	877	16	1110	123	10	125
7505.93	154	80	412	15	134	55	17	1108	146	14	112
7506.99	166	78	459	14	139	31	18	1025	143	12	118
7509.01	175	56	261	17	148	50	14	1000	107	7	192
7512.01	77	81	507	15	51	31	16	1170	127	7	122
7513.08	224	81	622	19	142	436	16	1069	132	10	137
7514.10	188	81	529	17	147	35	17	995	135	9	146
7515.80	207	85	472	18	136	27	20	1048	155	10	171
7517.23	196	91	661	20	154	183	19	1085	139	12	257

7519.05	189	99	665	15	153	26	22	59000	131	7	751
7520.13	190	130	732	23	187	696	20	1248	151	12	146
7522.05	199	123	656	21	197	135	20	1590	159	11	147
7523.03	120	121	404	22	130	130	21	1760	171	10	211
7523.89	46	0	17	0	35	29	ND	70200	9	ND	1064
7524.90	84	107	224	19	113	378	19	1568	141	11	282
7528.01	160	93	563	16	88	22	18	1098	151	6	164
7530.15	179	72	510	14	103	25	19	26800	143	7	464
7533.02	188	88	571	18	107	247	19	1149	148	10	207
7534.04	166	78	491	17	99	146	19	1531	149	11	182
7534.89	169	90	492	17	102	243	18	1022	148	12	128
7538.15	323	108	1106	17	161	1435	20	1253	156	13	124
7542.93	251	61	713	14	151	1129	10	804	68	5	332
7544.37	243	23	889	8	166	121	ND	172000	58	ND	2224
7544.85	220	40	777	7	173	57	ND	128000	68	ND	1676
7545.77	466	102	1274	13	231	986	16	1193	99	5	158
7554.33	21	0	52	0	6	53	0	102	3	0	261
7556.15	304	89	1083	14	224	257	16	930	116	9	248
MS Avg.	163	84	437	17	124	266	20	11301	159	11	281
MF Avg.	112	100	380	16	96	37	22	1303	191	13	121

Depth (ft)	Y	Zr	Hf	Nb	Mo	La	Ce	Nd	Th	U	Pb ≥
7447.20	36	119	2	11	32	39	77	36	11	8	31
7448.35	31	122	5	11	56	40	75	31	12	9	29
7449.25	32	124	4	12	53	38	71	32	12	8	33
7450.20	31	120	3	12	25	37	71	36	11	6	32
7452.22	27	114	4	10	26	34	71	27	13	7	33
7455.00	76	106	3	11	3	48	94	47	7	4	7
7456.16	29	127	4	13	119	39	65	30	12	15	26
7457.15	32	116	4	9	89	35	69	30	13	13	36
7457.37	32	109	4	11	53	33	68	32	11	7	33
7459.13	33	124	4	11	72	37	72	36	12	17	24
7460.20	37	124	4	12	107	39	78	37	11	19	26
7463.10	38	124	5	12	95	43	76	41	13	16	30
7464.05	35	119	3	11	90	42	83	36	13	16	32
7465.30	30	118	3	12	99	38	69	30	11	20	33
7467.30	123	88	2	9	94	51	97	57	9	23	19
7470.05	26	116	3	11	110	34	64	31	11	21	23
7471.13	32	109	1	9	155	36	71	34	12	17	31
7472.09	30	115	3	11	143	35	79	34	13	24	31
7475.12	63	111	3	11	129	40	92	57	11	30	33
7476.15	35	111	2	10	111	38	74	40	11	22	32
7477.07	33	115	4	12	99	40	88	36	13	19	35
7479.05	23	111	4	11	121	36	68	30	12	15	29
7480.05	26	122	5	12	59	35	66	26	11	11	27
7482.12	62	74	3	7	12	24	52	29	5	7	18
7484.11	28	117	4	11	114	34	67	29	14	15	27
7485.03	31	114	4	10	105	34	68	33	10	15	26
7485.60	29	116	4	11	97	34	68	34	13	16	28

7488.15	31	123	3	11	91	40	72	36	12	10	23
7489.06	32	118	4	10	94	35	76	31	13	11	27
7491.22	35	131	5	12	112	34	78	34	10	14	24
7492.06	35	116	3	12	107	29	64	29	11	16	19
7494.20	35	123	5	12	116	32	65	30	11	14	27
7497.39	43	110	4	11	129	35	68	40	9	28	37
7500.60	38	105	4	9	153	30	73	29	9	24	33
7503.04	39	97	2	8	146	30	55	33	9	24	26
7503.98	38	94	4	7	137	28	52	31	7	23	7
7505.93	39	107	3	9	133	37	65	34	9	23	34
7506.99	40	107	3	9	181	29	62	35	10	21	32
7509.01	108	90	3	7	177	37	79	61	6	47	36
7512.01	45	104	4	9	132	33	59	36	9	47	5
7513.08	48	108	3	8	266	32	56	36	9	46	26
7514.10	50	107	3	9	179	34	64	40	10	31	34
7515.80	33	123	4	11	181	34	57	30	11	25	33
7517.23	37	120	3	10	148	35	63	31	8	14	30
7519.05	28	121	2	12	114	21	45	21	5	15	20
7520.13	31	159	6	12	129	30	55	29	9	17	29
7522.05	31	168	4	12	97	36	74	34	11	18	36
7523.03	37	153	4	13	21	42	83	40	11	10	18
7523.89	21	16	1	5	10	9	ND	ND	0	1	ND
7524.90	46	158	5	14	6	40	81	40	12	5	11
7528.01	37	114	3	9	75	37	63	31	9	16	12
7530.15	25	95	3	10	91	24	65	21	8	18	37
7533.02	38	103	3	8	126	34	61	27	9	16	27
7534.04	33	100	3	10	106	38	57	28	8	18	24
7534.89	32	102	3	9	120	29	54	28	10	28	28
7538.15	38	110	3	9	225	29	52	31	9	60	17
7542.93	84	70	2	7	130	38	64	43	4	44	26
7544.37	29	40	1	11	101	3	ND	ND	8	28	ND
7544.85	37	55	3	9	80	10	ND	ND	6	33	ND
7545.77	46	93	2	5	317	27	46	32	7	71	41
7554.33	54	1	0	1	24	15	32	26	1	7	2
7556.15	31	122	3	8	308	17	29	16	7	32	34
MS Avg.	40	108	3	10	116	33	67	34	9	21	26
MF Avg.	31	120	3	11	39	38	73	33	12	8	32

APPENDIX XIII. Trace element concentrations (ppm) of the WV-6 samples. The Mahantango Formation (MF) is recorded in brown, with the Marcellus Shale recorded in blue.

Depth (ft)	Ni	Cr	V	Sc	Cu	Zn	Ga	Ba	Rb	Cs	Sr
7222.3	48.3	112.2	163.2	18.2	32.7	49.1	23.8	855.1	176.3	9.1	148.8
7225.3	92.0	117.6	304.4	18.0	72.3	1511.5	24.8	874.6	196.3	13.6	117.3
7228.1	100.2	149.4	657.5	18.2	113.7	83.1	23.9	978.8	199.0	13.5	126.1
7229.9	119.5	108.2	420.7	16.0	79.7	42.6	23.2	797.5	172.3	12.1	102.3
7233.3	81.2	101.9	223.6	18.5	53.1	84.8	21.7	813.9	177.2	11.9	110.8
7237.3	59.2	110.1	196.5	17.9	30.8	60.9	24.8	823.9	184.1	10.7	102.6
7240.2	141.4	124.3	240.3	16.3	66.1	58.6	24.6	867.8	189.3	12.2	99.0
7244.4	104.6	121.1	536.1	18.1	56.3	118.9	24.7	878.2	197.0	12.0	105.6
7245.8	74.7	115.6	320.5	17.9	64.5	206.0	27.2	966.0	208.7	12.0	109.4
7247.6	51.0	102.7	175.3	18.5	27.8	50.8	22.9	856.3	182.1	9.0	124.7
7249.9	102.9	113.2	474.9	18.5	55.6	317.8	25.7	903.1	200.9	12.9	111.7
7252.2	83.8	109.6	255.7	20.0	60.9	57.0	24.3	867.7	193.3	11.8	124.0
7255.8	75.1	108.4	299.4	19.2	75.2	202.4	27.7	1076.3	224.2	16.0	125.3
7258.3	123.8	90.0	240.7	16.1	61.4	305.4	22.8	1300.5	172.3	11.9	139.2
7261.9	52.4	95.2	154.3	18.7	49.2	48.7	25.9	981.4	201.6	12.4	135.8
7264.6	80.9	95.7	168.5	18.7	57.7	53.7	24.6	971.1	201.3	9.2	131.7
7267.8	78.8	98.1	217.6	18.4	54.2	49.6	26.8	1030.7	209.9	12.0	122.1
7270.3	67.8	99.5	208.6	17.7	45.3	48.7	27.1	1056.4	213.6	12.6	123.7
7272.7	86.2	96.5	209.8	17.9	57.7	110.6	24.5	988.0	200.9	11.2	117.9
7275.9	57.8	96.3	190.1	18.6	41.0	90.7	26.2	1023.2	208.4	11.6	120.2
7278.6	69.6	95.7	186.9	18.6	43.4	111.2	25.0	1001.8	203.6	15.4	124.3
7281.7	66.4	83.9	177.1	23.6	47.2	130.4	22.8	928.6	184.6	13.6	140.1
7284.7	66.1	93.8	177.6	18.2	42.5	74.1	26.5	1052.5	209.0	13.6	124.9
7287.8	47.4	94.5	192.9	18.9	34.0	87.8	25.9	1042.5	209.5	13.2	122.8
7290.5	65.6	92.9	195.1	18.4	44.8	80.2	25.1	998.2	197.1	12.7	121.5
7296.9	65.3	94.2	197.6	18.2	42.2	57.5	25.7	1011.3	201.8	11.1	122.9
7299.9	66.8	95.5	213.7	17.9	38.2	104.6	25.4	1006.6	205.6	13.1	114.4
7303.0	71.7	97.3	231.4	18.1	63.9	1206.4	25.3	1026.5	203.0	15.8	121.2
7305.8	82.5	93.2	202.6	18.7	65.6	249.9	25.1	1027.1	195.0	9.8	133.8
7309.2	61.4	97.0	199.0	18.7	42.2	53.4	25.2	1022.9	203.5	13.5	125.7
7311.9	51.6	95.1	189.5	18.3	39.5	71.0	25.6	969.8	195.9	13.6	118.2
7314.7	69.5	101.4	203.9	17.9	50.2	84.3	26.1	1043.9	203.0	11.2	121.1
7317.8	59.4	99.5	205.3	17.2	40.7	61.6	24.4	1037.0	202.0	12.3	124.4
7320.7	70.5	104.9	215.4	18.3	35.4	51.9	24.6	1057.9	206.0	12.1	124.1
7323.5	74.5	100.4	200.5	18.4	41.3	164.4	26.4	1025.8	204.1	12.5	120.5
7326.7	53.6	102.4	180.9	18.5	45.8	51.5	26.7	1052.1	205.1	12.9	135.0
7330.3	74.4	100.0	209.7	17.8	56.5	120.1	26.6	1069.3	209.0	13.8	136.9
7333.1	38.1	102.7	175.8	17.7	28.4	46.2	26.9	1112.9	212.8	10.7	135.1

7336.5	57.5	91.0	137.1	18.0	67.4	45.1	21.0	1075.2	166.4	6.6	175.6
7338.9	83.1	97.8	203.1	18.4	81.6	114.6	25.0	996.9	202.5	13.1	119.0
7342.3	82.2	94.5	307.1	17.0	64.0	51.3	22.8	981.8	189.4	11.2	128.5
7344.9	92.3	92.4	276.0	17.3	75.0	88.2	23.9	979.5	192.5	13.1	123.1
7347.8	77.7	99.2	284.5	16.4	63.4	508.0	23.6	1078.4	199.4	12.3	118.8
7351.0	85.4	100.5	292.7	17.2	77.8	45.1	24.3	1206.3	197.9	12.2	124.8
7354.4	24.0	13.6	56.3	0.0	18.0	11.1	3.3	2385.9	17.8	0.1	304.5
7357.3	101.3	97.1	349.2	16.6	92.5	50.1	24.1	1203.1	191.9	12.8	112.8
7360.5	89.5	83.5	272.2	16.7	74.6	151.7	19.7	885.4	167.5	10.4	121.0
7363.4	106.8	89.2	374.3	19.3	96.7	122.8	21.9	960.1	176.7	13.5	133.7
7366.9	106.6	90.7	363.4	15.6	86.4	65.5	20.9	1011.6	184.2	10.9	126.7
7369.9	121.8	91.0	404.0	16.5	84.0	3156.0	22.2	979.9	180.7	20.3	122.6
7373.1	108.6	92.5	397.6	16.3	92.1	39.9	23.5	1033.4	192.3	12.6	113.3
7377.2	107.5	90.1	352.6	16.1	92.2	35.3	22.6	953.5	177.1	12.7	113.4
7381.1	94.7	96.4	311.2	20.8	119.3	37.3	23.0	987.9	184.1	10.5	158.6
7383.2	99.4	94.2	303.9	16.9	85.8	34.7	23.7	1041.8	194.2	13.2	114.4
7385.7	121.2	94.5	342.2	17.2	115.1	90.5	25.2	1070.5	193.3	12.4	115.8
7388.1	113.3	79.1	157.6	17.5	114.5	1364.5	19.0	907.6	165.9	13.1	191.5
7391.2	186.3	93.2	363.1	16.5	120.4	2432.4	22.2	1064.8	193.6	19.1	113.4
7394.2	165.9	100.7	399.0	18.3	144.6	52.2	26.7	1192.2	218.7	14.5	119.1
7397.8	153.1	89.1	295.0	21.1	154.9	46.5	23.5	1057.3	197.2	12.6	126.8
MF Avg.	85.0	98.0	261.9	17.7	65.7	252.5	24.0	1024.6	192.3	12.3	127.8

Depth (ft)	Y	Zr	Hf	Nb	Mo	La	Ce	Nd	Sm	Dy	Yb
7222.3	29.4	140.2	4.29	11.94	0.75	37.67	73.67	31.70	5.87	4.66	1.77
7225.3	30.3	138.8	3.90	12.83	18.03	38.01	70.54	32.53	6.23	5.02	5.48
7228.1	24.6	117.4	3.71	10.32	15.97	33.97	72.80	33.35	5.91	3.88	2.91
7229.9	22.5	103.8	2.69	9.83	16.51	28.10	58.33	23.92	4.45	3.43	3.43
7233.3	27.5	107.6	2.88	10.31	18.39	33.44	66.24	27.41	4.83	4.46	4.27
7237.3	35.0	169.0	5.41	14.81	1.33	41.40	77.29	36.27	6.36	5.51	1.42
7240.2	22.5	110.5	3.44	9.87	1.76	32.34	57.99	28.64	5.20	3.35	2.91
7244.4	25.3	116.1	3.22	10.41	30.30	30.67	57.56	24.50	4.79	3.96	6.17
7245.8	26.8	123.4	3.39	11.57	14.39	38.66	69.05	30.39	5.46	4.14	5.17
7247.6	38.2	175.1	5.32	14.62	0.76	35.40	74.41	34.74	6.74	6.07	7.12
7249.9	29.3	129.4	3.71	12.99	35.82	33.50	65.41	28.76	5.01	4.55	2.69
7252.2	31.6	119.9	3.72	12.54	15.61	36.33	72.65	31.96	6.13	5.02	2.23
7255.8	29.4	125.8	3.69	11.79	14.74	37.87	81.82	33.91	5.99	4.61	1.20
7258.3	26.1	106.8	3.44	10.41	42.44	31.40	58.91	27.15	5.25	4.16	3.17
7261.9	30.4	142.9	4.75	14.90	4.75	40.87	78.48	33.80	6.42	4.75	2.51
7264.6	32.8	136.0	3.95	12.49	25.54	39.60	81.31	37.21	6.52	5.14	2.02
7267.8	29.4	137.3	4.40	13.75	26.68	40.79	77.92	32.91	5.50	4.58	0.00
7270.3	33.4	146.9	4.08	13.89	13.34	39.74	79.84	37.70	6.48	5.28	4.26

7272.7	30.1	135.4	3.15	12.87	18.10	37.18	72.56	32.68	6.03	4.77	3.33
7275.9	30.9	140.0	3.51	13.77	10.45	41.14	75.34	34.57	6.29	4.81	3.88
7278.6	32.4	145.7	4.54	13.72	30.90	39.71	82.24	36.98	6.54	5.00	3.54
7281.7	36.8	128.4	3.46	11.86	21.94	35.86	73.30	35.39	6.44	5.88	5.70
7284.7	32.6	149.6	4.53	14.41	18.75	44.62	84.63	38.06	6.47	5.17	2.12
7287.8	32.6	147.6	4.04	15.12	5.07	41.97	86.10	38.40	7.04	5.16	6.76
7290.5	32.5	145.8	4.21	13.65	10.53	42.50	79.32	36.82	6.59	5.04	3.76
7296.9	33.8	147.7	3.73	14.27	10.54	40.57	80.68	36.19	6.72	5.22	4.29
7299.9	31.0	142.3	4.91	14.45	23.71	41.58	77.24	34.73	6.48	4.91	3.70
7303.0	33.1	140.0	4.69	13.33	18.49	41.85	83.61	37.54	6.76	5.16	4.69
7305.8	37.9	141.6	4.60	13.04	15.67	42.49	83.11	36.02	7.13	6.00	6.57
7309.2	32.7	144.4	3.81	13.59	9.68	41.22	82.07	35.73	6.79	5.12	3.63
7311.9	33.2	135.8	3.98	14.04	5.22	37.65	83.28	38.51	7.02	5.12	2.37
7314.7	30.9	147.5	4.45	13.71	7.78	41.42	79.22	37.90	6.30	4.82	2.78
7317.8	34.1	152.7	4.99	15.16	11.47	42.63	87.10	38.00	7.21	5.27	2.68
7320.7	32.6	145.8	4.20	14.64	11.57	43.56	85.15	36.47	6.81	5.04	2.80
7323.5	31.6	144.7	4.53	13.21	17.09	40.55	80.27	38.24	6.65	5.08	4.06
7326.7	32.9	144.4	4.17	13.66	1.99	40.13	85.85	39.08	7.02	5.22	1.52
7330.3	30.0	139.5	4.06	13.70	13.51	40.54	76.92	35.15	6.43	4.82	3.59
7333.1	30.7	142.0	4.55	13.76	0.76	40.42	78.57	36.72	6.55	4.93	4.08
7336.5	40.8	137.6	3.95	12.50	4.78	40.27	76.68	35.49	7.36	6.53	4.14
7338.9	28.8	129.8	3.80	12.60	29.38	36.42	73.31	32.99	5.93	4.63	4.36
7342.3	29.4	119.5	3.29	11.65	23.57	37.99	72.68	31.49	5.96	4.54	3.02
7344.9	30.8	117.9	3.49	11.67	28.68	37.60	72.26	35.85	6.53	4.87	3.59
7347.8	29.6	131.1	4.03	12.53	24.70	39.89	72.00	33.12	5.86	4.67	2.01
7351.0	29.4	119.7	4.07	11.85	23.15	35.83	74.07	32.87	6.20	4.54	3.43
7354.4	40.9	20.0	1.76	1.96	10.42	15.03	28.57	15.37	5.69	6.70	3.52
7357.3	28.2	111.4	2.98	10.67	40.70	37.08	67.56	33.19	6.06	4.34	3.62
7360.5	35.0	103.8	3.58	10.10	37.18	31.86	60.14	29.29	5.88	5.51	1.74
7363.4	34.9	107.0	3.53	9.86	54.34	34.27	65.55	33.18	6.33	5.52	1.99
7366.9	31.7	109.1	3.02	10.53	56.34	35.63	64.40	32.52	6.05	4.86	3.57
7369.9	32.3	108.4	3.09	10.54	69.06	31.71	59.15	30.71	5.72	5.00	2.54
7373.1	27.8	113.0	3.54	10.25	40.83	33.57	63.51	29.21	5.53	4.35	2.90
7377.2	28.7	106.7	3.10	10.40	36.67	37.40	66.68	31.38	5.93	4.56	4.10
7381.1	39.6	104.4	2.84	9.98	27.29	37.82	72.89	37.18	7.23	6.32	4.03
7383.2	28.4	118.0	3.55	11.82	27.56	36.20	69.22	33.84	6.37	4.46	4.64
7385.7	24.9	119.4	3.64	11.47	50.84	35.02	59.47	26.58	4.62	3.73	3.20
7388.1	46.6	99.7	3.43	9.48	17.60	36.38	67.07	36.56	8.12	7.13	4.24
7391.2	32.9	107.7	3.39	9.05	92.77	32.55	64.22	31.33	6.27	5.13	4.09
7394.2	36.4	119.0	3.76	11.79	96.73	36.74	69.47	36.83	6.58	5.72	3.67
7397.8	44.2	100.5	3.58	10.05	61.34	40.63	77.07	41.68	8.13	6.90	2.97
MF Avg.	31.8	127.3	3.8	12.1	24.0	37.4	72.7	33.6	6.3	5.0	3.5

Depth (ft)	U	Tl	Pb >=	Bi
7222.30	5.87	2.98	5.69	2.05
7225.30	4.46	1.30	20.82	0.00
7228.10	10.41	0.62	11.65	0.71
7229.90	5.19	3.06	42.75	1.21
7233.30	3.16	2.69	24.34	0.65
7237.30	3.42	1.90	17.09	0.57
7240.20	3.44	2.20	29.61	0.97
7244.40	8.29	3.22	22.75	0.92
7245.80	7.90	3.67	24.74	1.51
7247.60	3.23	1.80	16.14	0.47
7249.90	10.39	1.21	18.46	0.00
7252.20	4.65	1.58	31.40	0.00
7255.80	8.57	1.01	31.97	0.00
7258.30	4.80	3.89	35.02	1.18
7261.90	2.14	3.07	29.61	1.21
7264.60	4.59	2.02	38.95	0.00
7267.80	3.85	2.66	35.02	0.83
7270.30	5.28	3.52	33.16	0.56
7272.70	5.49	3.87	37.18	1.62
7275.90	3.51	3.70	26.35	0.65
7278.60	6.09	4.36	23.54	1.91
7281.70	6.07	1.87	27.73	0.65
7284.70	3.33	1.94	29.56	0.37
7287.80	3.19	2.54	21.78	1.78
7290.50	1.92	2.84	30.50	0.64
7296.90	5.22	1.49	43.19	0.37
7299.90	4.26	1.67	23.25	0.19
7303.00	4.32	1.60	24.49	0.47
7305.80	3.75	0.84	32.64	0.00
7309.20	3.16	4.93	32.57	2.14
7311.90	3.60	2.66	18.12	0.57
7314.70	3.89	4.08	25.85	1.67
7317.80	3.51	3.51	19.23	1.76
7320.70	4.57	2.98	19.77	0.19
7323.50	2.22	3.42	23.00	1.02
7326.70	4.46	1.23	19.26	0.76
7330.30	3.69	0.85	23.06	0.09
7333.10	2.37	2.85	15.09	1.90
7336.50	3.59	0.00	30.71	0.00
7338.90	6.30	1.30	34.66	0.37
7342.30	5.60	3.38	27.93	0.09
7344.90	6.25	4.60	24.73	0.64

7347.80	7.14	1.46	24.79	0.46
7351.00	4.54	1.85	28.33	0.00
7354.40	2.37	0.00	4.06	0.00
7357.30	6.24	3.62	28.22	0.00
7360.50	6.15	2.39	26.81	0.18
7363.40	9.31	2.26	22.33	0.00
7366.90	8.61	4.49	25.10	0.92
7369.90	10.36	3.54	21.17	0.09
7373.10	8.17	3.36	25.95	0.45
7377.20	5.93	5.02	29.37	1.19
7381.10	11.26	2.93	25.09	0.00
7383.20	7.64	2.09	28.92	0.00
7385.70	8.36	4.71	31.64	0.00
7388.10	9.30	4.24	30.33	2.08
7391.20	12.97	7.83	32.46	0.87
7394.20	15.89	6.92	33.58	0.17
7397.80	15.90	1.57	33.90	0.00
MF Avg.	5.9	2.8	26.4	0.7

APPENDIX XIV. Radiogenic Samarium-Neodymium isotopic data.

Well	Depth (ft)	Unit	Sm (ppm)	Nd (ppm)	$\frac{^{147}\text{Sm}}{^{144}\text{Nd}}$	$\frac{^{143}\text{Nd}}{^{144}\text{Nd}}$	ϵNd	τ_{Nd}
WV-6	7225.3	MF	5.99	32.5	0.1112	0.512041	-11.65	1.65
WV-6	7270.3	MF	7.27	38.6	0.1138	0.51205	-11.47	1.67
WV-6	7314.7	MF	7.03	38.5	0.1104	0.512036	-11.74	1.64
WV-6	7360.5	MF	6.96	34.3	0.1227	0.512106	-10.38	1.74
MIP-3H	7448.35	MF	4.27	20.13	0.1281	0.512108	-10.34	1.85
MIP-3H	7460.2	MS	6.85	33.25	0.1245	0.512099	-10.51	1.79
MIP-3H	7489.06	MS	6.9	36.2	0.1152	0.512097	-10.55	1.63
MIP-3H	7505.93	MS	5.57	26.53	0.1269	0.512116	-10.18	1.81
MIP-3H	7538.15	MS	6.65	31.7	0.1269	0.512133	-9.85	1.78
MIP-3H	7544.85	MS	5.19	16.6	0.1891	0.512276	-7.06	5.34