Linking the Acadian Orogeny with Organic-Rich Black Shale Deposition: Evidence from the Marcellus Shale

Abstract

The trace and rare earth elements (REE) analyses were conducted on samples collected from a 30-m core of the Marcellus Shale obtained from Greene County, southwestern Pennsylvania. Our results suggest that organic matter enrichment trends in the Marcellus Shale can be directly linked with the Acadian Orogeny. The Acadian Orogeny has been recognized as a main sediment source for the Marcellus Shale. Synthesis of tectonic history and recent ash bed geochronology, reveals that deposition of the organic carbon-rich (OR) zone (characterized by TOC >4%; located between 2393 m and 2406.5 m core depth) in the studied Marcellus Shale core was coincident with tectonically active and magmatic quiescent period of the Acadian orogeny (ca. 395-380 Ma). This time period also corresponds to the highest rate of mountain building in the Acadian Orogeny. The light rare earth (LREE) and selected trace elemental (e.g., Ta, Cs) composition of the OR zone sediments is similar to that of the bulk continental crust, supporting the lack of magmatic activity in the source area (i.e. Acadian Orogeny). In contrast, subsequent deposition of the organic carbon-poor (OP) sediments (characterized by TOC <4%; located between 2376 m and 2393 m core depth) in the upper Marcellus Shale occurred synchronously with a magmatic active phase (ca. 380-370 Ma) during the Acadian orogeny. The OP zone sediments have LREE and trace elemental composition similar to the average of the upper continental crust, suggesting intrusion of granodiorite rocks during a magmatic active period of Acadian Orogeny. The temporal and geochemical correlation between the Acadian orogenesis and the Marcellus deposition provide evidence for the role of tectonism in the enrichment of organic matter in the Marcellus Shale.

1. Introduction

Due to the recent boom in shale gas production in the Appalachian basin, United States, the natural gas-rich Marcellus Shale has drawn tremendous attention from the geoscience community. Well production data have shown that the ‘gas-rich’ zones within the Marcellus Shale are often associated with high total organic carbon (TOC) content. Many studies have tried to understand the mechanisms of organic matter enrichment during black shale deposition (e.g., Ettensohn, 1985; Pedersen and Calvert, 1990; Sageman et al., 2003; Rimmer et al., 2004; Ver Straeten, 2009, 2010; Chen et al., 2015; Chen and Sharma, 2016). It has long been recognized that enrichment of organic matter in fine-grained sediments such as shale is directly affected by several processes like 1) rate of sediment input, 2) water column redox conditions; and 3) primary productivity (e.g., Pederson and Calvert, 1990; Werne et al., 2002; Sageman et al., 2003; Rimmer et al., 2004; Lash and Blood, 2014). In addition, a recent study Chen and Sharma (2016) also suggested that nutrient recycling is driven by alternating water column redox conditions might have also played a key role in the formation of the organic-rich zone in the Marcellus Shale.

However, the underlying mechanism that caused the widespread deposition of black shale in the Acadian foreland basin is still debated. The tectonostratigraphic model proposed by Ettensohn (1985) suggests that deposition of organic carbon (OC)-rich black shales in the Appalachian basin was controlled by tectonic forces of Acadian orogeny, whereas recent studies demonstrate that global sea-level change may have also played a key role (Arthur, 2005; Sageman et al., 2003; Werne et al., 2002). Thus, the objective of this study is to understand the processes (i.e., tectonism) that might have contributed to this widespread deposition of black shale in the Acadian foreland basin. Further, we tried to establish direct linkage (i.e., temporal

and geochemical correlations) between these processes and sedimentary records preserved in the Marcellus Shale in our study area.

According to Ettensohn's model (Fig. 1), widespread carbonates (e.g., the Onondaga Limestone) beneath OC-rich shale formations (e.g., the Marcellus Shale) represents deposition in shallow open marine environments with little to no terrigenous clastic input. The onset of the Acadian orogeny led to crustal bending and subsidence within the adjacent foreland basin (Ettensohn, 1985). Subsequent cratonward advancement of the Acadian orogenic front created fold-thrust sheets that uplifted the old sedimentary and low-grade metamorphic rocks in the Acadian mountain and recycled them to the foreland basin (Ettensohn, 1985; Ver Straeten, 2009). High erosion rates during the active orogenesis generate high sedimentation rates and low oxygen availability, resulting in anoxic bottom water conditions and enhanced organic carbon burial (Galy et al., 2007). Although several modifications have been made to this model (e.g., Bradley, 2000; Ettensohn, 1987), it still remains one of the most widely accepted model as it explains some basic observations in the sedimentary records. However, recent studies suggest that global sea-level change may have also played a key role in organic matter enrichment because deposition of OC-rich black shales in the Appalachian Basin generally coincides with the periods of global sea-level transgressions (Arthur, 2005; Sageman et al., 2003; Werne et al., 2002). It is well known that global sea-level rise can mitigate sediment 'dilution' effect by reducing terrestrial weathering and the amount of sediments transported into the basin (e.g., Sageman et al., 2003; Werne et al., 2002). Rising of sea-level reduces the efficiency of water-column mixing, creating more reducing bottom water conditions that are favorable for organic matter preservation (Arthur, 2005).

In terms of the tectonic control on black shale accumulation, a key piece of information still missing is a direct linkage between tectonics and sedimentary records that are independent of other variables (e.g., global sea-level change). Recent studies of volcanic ash layers in the Appalachian Basin reveal that the development of the Acadian Orogeny and the associated foreland basin during Early-Middle Devonian time was associated with multiple phases of volcanism/magmatism within the Acadian mountain (Murphy et al., 1999; Ver Straeten, 2005, 2008). Based on the relative intensity of magmatism, the Acadian orogeny can be subdivided into three magmatic stages: a magmatic active period that lasted from early Emsian to lower-middle Eifelian (~400-395 Ma), followed by a relatively magmatic quiescent period between ~395 Ma and ~380 Ma which was then succeeded by another magmatic active period from ~380 Ma to ~370 Ma (Murphy et al., 1999).

Signals of the proposed Acadian magmatism were recorded by sediments deposited in the adjacent foreland basin (Hosterman and Whitlow, 1981). It has been found that the Middle to Late Devonian marine shales of the Appalachian Basin contain abundant smectite which is interpreted to be derived from weathered volcanic clast and phenocrystals, indicating a significant sediment contribution from igneous sources (Hosterman and Whitlow, 1981). If representative, the shale strata deposited within the Appalachian Basin may likely record the geochemical signals (e.g., trace and rare earth element content) of the Acadian magmatism. It has been shown that partial melting of crustal rocks during magmatism can cause enrichment of light rare earth elements (i.e., La-Sm) in the newly formed magma (Liping and McKay, 1989), which later migrates upward toward the surface, forming intrusive or extrusive igneous rocks. Therefore, the newly formed igneous rocks should bear REE composition different from the source region. Weathering of these rocks would then transport the REE signals into the adjacent

sedimentary basin. There is little fractionation of REE during weathering of parent rocks or during subsequent sediment transportation (e.g., Condie, 1991). As such, it is obvious that the REE compositions of fine-grained rocks formed by deposition and lithification of these weathered sediments would resemble the REE signature of their sediment source. Therefore, we hypothesized that if the OC-rich black shale deposition in the Appalachian foreland basin was directly related to the Acadian orogeny, we should observe a correlation between the Acadian magmatic signals and organic carbon enrichment in the shale.

Figure 1: A tectonic model of the Acadian Orogen and the associated foreland basin (modified from Ver Straeten, 2009).

Here we report major, trace and rare earth elemental data from the Marcellus Shale samples collected from a well core from southwestern Pennsylvania, USA. Shale samples are grouped as organic-rich (OR) and organic-poor (OP) categories with the purpose of establishing the possible link between the Acadian magmatism and temporal variation in organic matter content during Marcellus Shale deposition.

Figure 2: Location and stratigraphic column of the studied Marcellus Shale core plotted with biostratigraphic and ash-bed age constraints (Bergström, 1970; Hayward, 2012; Parrish, 2013). Filled star: depositional age from dating of volcanic ash layers; unfilled star: depositional age estimated using sediment accumulation rates (Hayward, 2012; Parrish, 2013). The timing of the Acadian magmatism is from Murphy et al. (1999). The Middle Devonian paleogeography map was modified after Blakey (2013).

2. Sampling and Analytical Methods

2.1. Study area and sampling

The Marcellus Shale is the basal unit of the Hamilton Group of the Appalachian basin, underlain by the Onondaga Limestone and overlain by the Mahantango Shale (i.e., Ettensohn, 1985). The Marcellus Shale well core used in this study is the Whipkey State #1 (WS) and was cored in September 2008 by Eastern American Energy Corporation, API number 3705924715. The surface location of this well is in Greene County (Latitude: 39.92, Longitude: -80.00), southwestern Pennsylvania (Fig. 2). The studied Marcellus interval is divided into two zones based on total organic carbon (TOC) content: a ~12 m thick organic-rich (OR) zone (2404 to 2392 m core depth) and a ~18 m thick organic-poor (OP) zone (2392 to 2374 m core depth). The OR zone is characterized by high TOC content (range from 5 to 9 wt.%, average = 7 wt.%) and high gamma-ray log response (average = ~300 API). In contrast, the OP zone has lower TOC content (range from 2 to 4 wt.%, average = 3 wt.%) and lower gamma-ray log response (average = ~200 API) (Fig. 2). The OR zone consists of the entire Union Spring Shale Member and lower part of the Oatka Creek Shale Member while the OP zone corresponds to upper part of the Oatka Creek Shale Member (Fig. 2). Both the OR and OP zones are dominated by black shale interbedded with gray mudstone, siltstone, and limestone. The Purcell Limestone and Cherry Valley Limestone occur as distinct interbeds within the OP and OR zones, respectively.

A total of 26 rock samples were collected from the Marcellus interval of the WS core for elemental analyses, with an average sampling interval of ~1 m. Samples from the carbonate-rich intervals were not included as they are primarily authigenic and hence would not reflect REE signals of the source area. Samples were collected from the inner part of the core using chisel and hammer. Thin rock chips were further ground to homogenous powders prior to geochemical analyses. Thirteen of the samples are chosen from the OR zone and the rest are from the OP zone

(Fig. 2). Notable sampling gaps beneath the Purcell and Cherry Valley limestone beds are due to lack of core material associated with low core recovery.

2.2. Analytical methods

Major, trace and rare earth elemental concentrations were measured at Activation Laboratory in Canada using sodium peroxide fusion method. For each sample, 200 mesh, 0.5 g powders were oxidized and fused with sodium peroxide (Na_2O_2). The fused samples are diluted and analyzed using a PerkinElmer SCIEX ELAN 6000 ICP/MS. Controls and standards fused with samples are run every 22 samples. Fused duplicates are run every 10 samples. International standards of GXR-4 and OREAS 101a were used to monitor analytical quality. The precision of measurements is better than 1% for all major elements. For trace and rare earth elements, the accuracy and precision were estimated to be better than 10%. Based on the atomic number, light rare earth elements (LREE) in this study includes La, Pr, Nd, Sm, and the heavy rare earth elements (HREE) include Gd, Tb, Dy, Ho, Er, Tm, and Yb. All measured elemental abundances are corrected for dilution effect caused by varying total organic carbon (TOC) contents, using an ash basis equation:

$$\text{Ash content (\%)} = -1.0834 [\text{TOC (\%)}] + 94.981$$

This equation was developed to estimate the correlation between carbon content and ash content from a study of bulk, trace, and rare earth elements in 300 coal and shale samples (NETL unpublished data source: https://edx.netl.doe.gov/ree/?page_id=1602).

3. Results

The ash basis-major and trace elemental data are shown in Table 1 (raw data are shown in Table S1), with the values, normalized to the Upper Continental Crust (UCC) standard (Fig. 3) (McLennan, 2001). Samples from the OP zone are characterized by very similar UCC-normalized major- and trace elemental patterns, whereas samples in the OR zone display much variable concentration patterns (Fig. 3). Generally, samples from the OR Zone are relatively depleted in Al, K, Fe, Mg, Ti, Rb, Cs, and Th but enriched in Ca.

Sample	Si wt%	Al wt%	K wt%	Fe wt%	Mg wt%	Ca wt%	Ti wt%	Rb ppm	Cs ppm	Ta ppm	Th ppm
WS-7795	26.5	11.9	4.6	6.8	1.0	0.4	0.5	247.5	18.0	1.0	14.5
WS-7801	26.5	10.2	3.9	5.0	1.0	1.2	0.4	204.5	13.8	0.9	11.8
WS-7807	23.6	9.5	3.7	9.3	1.0	4.6	0.4	201.6	14.0	0.7	10.1
WS-7811	26.8	10.4	3.9	6.8	1.0	2.7	0.4	217.1	15.4	0.7	11.8
WS-7813	27.5	11.1	4.3	6.5	1.0	0.6	0.5	240.4	17.3	0.8	12.5
WS-7818	28.4	11.3	4.4	6.2	1.0	0.5	0.5	247.5	17.8	1.0	14.0
WS-7828	30.0	10.2	3.9	4.2	1.0	0.8	0.5	207.8	13.2	1.1	12.6
WS-7833	30.1	11.2	4.3	4.4	1.3	1.6	0.5	235.4	22.2	0.9	11.9
WS-7838	28.5	10.7	4.1	4.8	1.0	0.5	0.5	212.1	14.6	1.1	11.1
WS-7843	30.1	10.0	3.9	4.4	1.0	0.8	0.4	224.0	15.3	0.9	12.1
WS-7846	19.5	8.4	3.5	4.2	0.9	1.7	0.4	174.6	12.1	0.5	10.6
WS-7849	31.4	8.8	3.5	4.8	0.9	1.3	0.4	178.4	12.0	0.7	8.8
WS-7851	31.4	8.6	3.5	4.2	0.9	1.6	0.4	184.0	12.8	0.8	9.6
WS-7854	31.9	8.5	3.5	4.7	0.8	1.0	0.4	163.5	11.3	0.8	9.8
WS-7858	29.8	8.5	3.5	5.0	0.9	1.5	0.4	187.8	14.5	0.7	10.6
WS-7860	25.3	7.5	2.9	9.7	0.9	1.6	0.4	156.2	12.0	0.5	8.4
WS-7863	29.8	6.7	2.7	3.4	1.0	5.0	0.3	141.6	10.6	0.5	8.9
WS-7865	27.9	5.4	2.2	2.4	0.9	10.0	0.3	113.9	8.3	0.6	9.8
WS-7866	25.5	8.3	3.4	3.9	1.0	1.6	0.4	157.5	11.7	0.9	11.8
WS-7873	31.6	8.0	3.3	4.7	0.7	1.6	0.4	162.9	12.0	0.7	9.0
WS-7877	30.4	7.5	3.1	4.4	0.8	2.5	0.4	172.6	12.6	0.7	9.6
WS-7878	28.2	7.1	3.0	3.5	0.6	5.3	0.4	143.9	10.6	0.7	9.4
WS-7887	15.2	1.4	0.6	1.9	0.4	11.4	0.1	25.1	1.9	< 0.2	1.7
WS-7891	28.6	4.2	1.8	6.6	1.0	3.9	0.2	79.7	5.7	0.5	6.2
WS-7893	35.0	3.6	1.6	3.3	0.5	1.2	0.2	76.4	5.1	0.2	4.4
WS-7895	22.4	7.8	3.1	2.8	1.5	6.0	0.4	77.9	5.2	< 0.2	2.8

Table 1: Selected major and trace element concentrations in the WS core. Trace element data has

been corrected per sample on an ash basis.

Figure 3: Selected major and trace elements normalized to UCC (McLennan, 2001) for the WS core samples.

Total abundance of ash basis- REE values varies from 69.3 to 235.6 ppm in the studied samples (Table 2, Fig. 4). Raw data of REEs are shown in Table S2. The OP zone contains a higher abundance of REE than that of the OR zone, with values, ranging from 183 to 235.6 ppm (average =199 ppm) for the OP zone, and 69.3 to 220 ppm (average =165.8 ppm) for the OR zone. REE data are normalized to Post-Archean Australian Shale (PAAS) standard (Fig. 4) (McLennan, 1989). Samples in the OP zone are characterized by remarkably similar patterns of LREE and moderately variable HREE content (Fig. 4). In comparison, both LREE and HREE patterns are highly variable in samples from the OR zone (Fig. 4).

Figure 4: PAAS-normalized REE distribution patterns of the WS core samples. The REE values of PAAS are from McLennan et al. (1980a).

Sample	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	ΣREE
WS-7795	41.3	74.7	10.0	40.7	6.9	1.4	5.5	1.0	4.5	1.3	3.7	0.5	3.3	194.7
WS-7801	40.2	76.1	10.1	36.8	8.4	1.7	8.6	1.2	6.9	1.3	3.9	0.5	3.2	199.0
WS-7807	45.5	74.3	12.0	49.6	11.7	2.8	13.4	1.9	10.8	2.1	5.8	0.9	4.8	235.6
WS-7811	42.2	68.1	10.9	42.0	8.9	1.9	9.0	1.2	7.6	1.4	4.2	0.7	3.7	201.7
WS-7813	42.4	69.4	10.2	37.7	7.1	1.5	6.3	1.0	6.0	1.2	3.6	0.5	3.3	190.2
WS-7818	43.6	69.8	9.9	36.8	5.9	1.3	4.7	0.8	4.8	1.1	3.1	0.4	2.9	185.2
WS-7828	42.6	79.8	10.2	37.3	7.1	1.4	6.6	0.9	5.7	1.2	3.5	0.5	3.0	199.9
WS-7833	42.5	71.4	11.0	41.9	8.5	1.7	8.4	1.1	7.1	1.4	3.9	0.7	3.6	203.0
WS-7838	41.2	65.4	9.9	35.6	7.0	1.3	6.9	1.0	6.1	1.2	3.7	0.5	3.4	183.0
WS-7843	44.7	70.9	10.8	42.4	7.8	1.7	7.7	1.1	7.0	1.5	4.2	0.7	3.8	204.4
WS-7846	40.6	73.3	10.2	38.2	8.9	2.1	10.0	1.3	7.9	1.5	4.5	0.7	3.7	202.9
WS-7849	38.7	62.6	10.1	38.1	7.7	1.7	8.0	1.1	7.0	1.4	4.1	0.7	3.6	184.9
WS-7851	42.1	68.0	11.1	43.9	9.6	2.1	10.2	1.3	8.3	1.6	4.8	0.8	4.2	208.0
WS-7854	38.0	65.2	8.9	31.9	6.9	1.5	7.4	1.0	6.2	1.4	3.8	0.6	3.3	176.0
WS-7858	42.7	68.7	11.2	44.6	9.8	2.0	9.4	1.3	8.2	1.7	4.7	0.7	4.0	209.3
WS-7860	41.5	58.6	9.6	38.2	7.5	1.5	7.7	1.0	6.3	1.2	3.4	0.6	2.7	179.9
WS-7863	37.3	51.7	9.1	39.9	8.3	1.8	8.5	1.2	6.9	1.3	4.0	0.6	3.2	173.8
WS-7865	43.5	68.3	11.8	48.8	10.9	2.2	10.6	1.5	9.3	1.8	5.4	0.8	5.0	220.0
WS-7866	38.9	66.6	9.9	39.3	8.9	1.8	9.3	1.2	7.2	1.5	4.2	0.6	3.5	192.8
WS-7873	29.7	42.6	6.5	22.8	4.0	0.9	4.5	0.7	4.3	0.9	2.7	0.4	2.5	122.4
WS-7877	32.2	47.8	7.5	29.1	6.4	1.3	6.4	0.9	5.8	1.2	3.5	0.6	3.2	146.0
WS-7878	38.8	68.7	9.8	38.3	8.9	2.0	10.4	1.3	8.4	1.7	4.9	0.7	4.2	198.1
WS-7887	44.6	54.8	9.3	38.6	9.4	2.4	14.5	2.0	13.9	3.1	9.6	1.4	9.2	212.7
WS-7891	27.9	45.1	7.9	33.1	8.8	1.6	10.7	1.4	8.9	1.9	5.2	0.7	4.2	157.3
WS-7893	18.2	31.3	5.3	21.4	4.7	1.0	5.0	0.7	4.3	0.8	2.4	0.3	2.0	97.4
WS-7895	14.9	18.8	3.9	14.7	3.4	0.8	3.9	0.6	3.5	0.7	2.1	0.4	1.8	69.3

Table 2: REE contents of the Marcellus Shale for the WS core (ppm). Data has been corrected per sample on an ash basis.

4. Discussion

4.1. Sediment provenance of the Marcellus Shale

The chondrite-normalized LREE distribution pattern has been widely used as a sensitive indicator for determining the sediment source of the sedimentary rocks (McLennan et al., 1980b; Paikaray et al., 2008). Felsic sources are represented by North American Shale Composite

(NASC) and mafic sources are represented by Mid-Ocean Ridge Basalt (MORB) (Fig. 5) (McLennan et al., 1980a; Totten and Hanan, 1998). The samples from NASC and MORB have distinctly different LREE patterns while their HREE patterns do not show much variation. In our studied interval, the samples from the OP zone display very small ranges of LREE values that closely overlap with the NASC standard, which indicates that the sediments were mostly derived from sources that have similar REE compositions as the NASC. Samples from the OR zone are characterized by variable LREE patterns (Fig. 5). Furthermore, a few samples are distributed in the middle of NASC and MORB, indicating a relatively high proportion of mafic igneous rocks compared to those in the OP zone. Overall, the REE patterns suggest an increasing contribution of felsic sources during the deposition of the Marcellus Shale in our study unit.

Figure 5: Chondrite-normalized REE distribution patterns of the WS core samples. The REE values of chondrite are from McLennan et al. (1980).

4.2. Correlation between organic matter enrichment in Marcellus Shale and Acadian orogeny

As previously discussed, the hypothesis that deposition of organic-rich and organic poor zones in the Marcellus Shale might be related to tectonic activities of the Acadian Orogeny can be tested by temporal and chemostratigraphic correlation of Acadian orogenic and magmatic events with geochemical signals recorded by the shale strata.

4.2.1 Temporal correlation

Previously, the depositional age of the Marcellus Shale was only loosely constrained at Middle Devonian (Eifelian-Givetian) based on conodont biostratigraphy (e.g., Bergström, 1970) (Fig. 2). However, with the recent dating of the Tioga ash layers in the basal part of the Marcellus Shale and development of high-resolution U-Pb zircon dating techniques, depositional ages of Marcellus strata have been more accurately determined (Hayward, 2012; Parrish, 2013). Dating of zircon grains from the Tioga ash layers shows that onset of the Marcellus deposition likely occurred diachronously in the Acadian foreland basin with estimated depositional age of the basal Marcellus spanning an interval of 394 ± 5 Ma to 389 ± 3 Ma (Parrish, 2013). In the studied core (i.e., St. Whipkey #1) in southeastern PA, the dating of two ash layers suggests deposition of the Marcellus Shale likely started at between 389 ± 5.8 Ma and 395 ± 5.7 Ma (average = 392 ± 4.1 Ma) (Parrish, 2013). The estimated depositional ages from our study well is consistent with the ash bed ages obtained from the adjacent wells (i.e., EQT 511391, Coldstream #1, Winner 4-8, Fortuna FEI Thomas; see Parrish, 2013 for well locations), which shows an average age of basal Marcellus at 392.8 ± 1.6 Ma (range = ~ 397 - ~ 387 Ma). It is worth noting that currently, radiometric ages are only available from the basal part of Marcellus strata where volcanic ash layers were discovered, and depositional ages for the middle and upper Marcellus

can only be derived using estimated shale accumulation rates (Hayward, 2012). The average sedimentation rates calculated in this study were based on dates obtained from ash layers reported from all the wells near the study area. For example, the Coldstream #1 well in Clearfield, Pennsylvania contains two ash beds (i.e., ash bed #1 Cold2, 7157.2', 391.3 ± 4.8 Ma; and ash bed #2 Cold4, 7162.4', 393.4 ± 5.5 Ma), which are separated by 5.2 feet of Marcellus Shale interval with an average of 2.1 Ma age difference. Thus, the compacted sedimentation rate for the well was calculated at ~ 2.5 ft/m.y. (Table. 3). Based on the sedimentation rates from all the adjacent wells, we estimate the average sedimentation rates for the Marcellus shale in the study area to be ~ 4.3 ft/m.y. However, it is worth noting that current precision of the SIMS U-Pb zircon dating method is at between plus and minus 2 to 5 Ma (Deloule et al., 2002). Therefore, uncertainties associated with the zircon dating technique make it difficult to resolve short timescale variations. In addition, there is a paucity of ash layers in the upper Marcellus hence most U-Pb ages are from volcanic ash layers (Tioga ash beds) found near the base of the Marcellus Shale. Therefore, the estimated average sedimentation rates most likely represent the depositional conditions during the deposition of the basal part of the Marcellus Shale. This part of the Marcellus Shale is highly organic-rich with average TOC values close to 8.5% (Fig. 2) and deposition of such high TOC units is usually linked to the extremely low clastic influx. Further, the low concentrations of trace metals (Fig. 6) and Al and Ti contents (Fig. 8) also support that the clastic influx was extremely low during the beginning of the Marcellus Shale deposition. As a result, the low sedimentation rates (i.e., 4.3 ft/m.y.) were expected in our study area.

In the WS core, the base of the Marcellus Shale has an average age at 392 ± 4.1 Ma (Parrish, 2013). Using the estimated average shale compacted sedimentation rates (i.e., 4.3 ft/m.y.), the age of top of the OR zone is likely at between 385 Ma and 377 Ma if uncertainty in

the ash ages is considered. Temporal correlation of the Marcellus Shale deposition and the Acadian magmatism (Fig. 1), reveals that deposition of the OR zone sediments was generally coincident with the magmatic quiescent period of the Acadian orogeny which lasted from ~395 to ~380 Ma (Murphy et al., 1999). Tectonic synthesis show that the magmatic quiescence stage which lasted from ~395 to ~380 Ma was accompanied by extensive crustal shortening (>600 km), and orogenic activities related to convergence between the North America plate and Avalon terrane (Murphy et al., 1999). Coupling of the sub-ducted and overlying plates led to significant thickening of continental crust and inhibited the penetration of mantle plume into the continental crust, which accounts for the lack of magmatism in the Acadian mountain during this time (Murphy et al., 1999). It has been suggested that the initial coupling of the subducting and overriding plates led to rapid uplift of the Acadian mountain and by inference, rapid subsidence and deepening of the adjacent Acadian foreland basin (Murphy et al., 1999). This suggests that the rise of the Acadian orogen was coincident with the initiation of organic-rich shale deposition of the Marcellus Formation (i.e., the OR zone).

The subsequent deposition of the overlying OP zone sediments most likely initiated at ~382 - 374 Ma, which coincides with the period of magmatic reactivation in Acadian Orogeny lasting from 380-370 Ma (Murphy et al., 1999). During this time period, there was a progressive thermal erosion of continental crust by the mantle plume, thus, the crust was exposed to hot asthenosphere (Murphy et al., 1999). In addition, reactivation of Acadian magmatism was accompanied by the intrusion of extensive granitoid batholiths and continued convergence and deformation along the North America plate margin. This led to extensive cratonward migration of the Acadian organic belt, providing voluminous felsic sediments into the adjacent Acadian foreland basin (Murphy et al., 1999).

Tioga Ash Ages and Sedimentation Rates					
Well Name County, State	Sample ID	Ash # (depth in ft.)	Avg. $^{238}\text{U}/^{206}\text{Pb}$ Age (Ma)	Measured interval (ft.)	Compacted sedimentation rate (ft/my)
EQT 511391	EQT1	1 (7114.9)	394.2 ± 5.4	7117.05-7114.9	1.2
	EQT2	2 (7117.05)	396.7 ± 5.0		
Armstrong #1	Arm1	1 (7755.27)	388.1 ± 5.1	7771.9-7755.27	2.5
	Arm4	4 (7771.9)	390.6 ± 2.7		
St. Whipkey #1	Whip2	2 (7893.6)	395.1 ± 5.7		
	Whip4	4 (7897.5)	388.7 ± 5.8		
Coldstream #1	Cold2	2 (7157.2)	391.3 ± 4.8	7162.4 - 7157.2	2.5
	Cold4	4 (7162.4)	393.4 ± 5.5	7163.5 - 7162.4	0.35
	Cold5	5 (7163.5)	396.5 ± 5.6	7163.5 - 7157.2	1.2
Winner 4-8	Win23	1 (8023.5)	387.4 ± 7.8	8035.4 - 8023.5	3.5
	Win35	3 (8035.4)	390.8 ± 9.4	8041.5 - 8035.4	8.5
	Win41	4 (8041.5)	391.5 ± 8.4	8041.5 - 8023.5	4.5
Tunnelton CV1	Tun52	1 (7852.0)	387.3 ± 2.5	7862.5 - 7852.0	14
	Tun62	2 (7862.5)	388.0 ± 3.0	7865.7 - 7862.5	2.3
	Tun65	3 (7865.7)	389.3 ± 3.3	7865.7 - 7852.0	6.5

Table 3: Dated ash samples and calculated sedimentation rates in the study area. All data were obtained by Parrish (2013).

4.2.2. Chemostratigraphic correlation

Temporal correlation of Acadian orogeny with organic-rich shale deposition in the Marcellus Formation suggest that onset of Acadian orogeny played a key role in the onset of deposition of the OR zone. Further, as rare earth and trace element ratios of sedimentary rocks reflect geochemical signatures of their sediment source (e.g., Condie, 1991), chemostratigraphic studies can provide further evidence of this linkage. The previous study of magmatic zircons from the Tioga ash beds shows that the rare earth and trace element compositions of zircon grains are consistent with the continental granitoid origin (Hayward, 2012). Here, we plotted LREE and selected trace elements of shale samples that are least affected by weathering and

diagenetic process (Figs. 6 and 7). Average elemental compositions of bulk crust and upper crust (similar to granodiorite) (Taylor and McLennan, 1995), were also plotted for comparison with the shale composition. The plots show that trace elements (Th, Rb, Cs and Ta) (Fig. 6) and LREE (La, Pr, Nd, and Sm) (Fig. 7) contents of the studied shale interval display an upward increasing trend. The values in the OR zone are relatively low and scattered and similar to that of the bulk crust. In contrast, the LREE and trace element contents in the OP zone are significantly higher and become more stable with values more similar to that of the average composition of the granodiorite. In addition, it is widely accepted that the volatile trace elements (e.g., Rb) and refractory elements (e.g. Th, REE) are significantly enriched in volcanic plumes, their abundance is governed by magmatic degassing of sulfate/halide compounds (Moune et al., 2006). It is clear that there was a compositional shift of sediment source during the course of the Marcellus Shale deposition. The OR zone shale samples were more likely sourced from the old continental crust, the ‘non-magmatic signal’ preserved in the OR zone can be correlated to the period of magmatic quiescence between ~395 and ~380 Ma. In contrast, the OP zone shale samples have more “granodiorite-like” composition, suggesting significant input from new formed igneous sources. Therefore, the “magmatic signal” preserved in the OP zone can be correlated to the magmatic active period that lasted from ~380 to ~370 Ma. Together, the geochemical signature provides further evidence of the linkage between the Acadian tectonics and organic carbon concentration in the Marcellus Shale.

It is worth noting that the LREE contents are highly variable in the OR zone (Fig. 7). These fluctuations may relate to the development of finer-scale depositional cycles/tectophases in the Appalachian Basin. Orogenic events may have caused changes in sediment source, resulting in variable LREE patterns in the sediment record. A recent study (Chen and Sharma,

2016), suggested that the bottom water redox conditions were alternating between suboxic and anoxic during the deposition of OR zone shale. These alternating redox conditions may reflect the finer-scale water-depth changes primarily controlled by Acadian Orogeny. However, it is difficult to assess the existence of these finer-scale tectophases because a large part of the Acadian mountain has been eroded or tectonically overprinted, especially in the central to southern Appalachian basin (Ver Straeten, 2009).

Figure 6: Selected trace elements for the WS core.

Figure 7: LREE profiles for the WS core.

Chemical weathering could potentially alter the LREE and trace element concentrations in the studied shale (Buggle et al., 2011; Clift et al., 2014) and it is necessary to evaluate the variations of chemical weathering intensity at the time of deposition. “Chemical Index of Alteration” (CIA) has been used as a good indicator of chemical weathering for many studies (e.g., Clift et al., 2014; Jian et al., 2013; Nesbitt and Young, 1982; Paikaray et al., 2008). The CIA is calculated from Al, Ca, Na and K contents (Nesbitt and Young, 1982), however, Na contents are not detectable due to using sodium peroxide (Na_2O_2) fusion as a pretreatment in our study. In this study, we report the ratios of K/Cs and K/Rb, which show very similar patterns as CIA and can be used as chemical weathering indicators (Cliff et al., 2014). Alkali elements, including K, can be categorized as soluble cations and are relatively mobile in water, while Cs and Rb are often regarded as immobile elements due to their large ionic radius (e.g., Buggle et al.,

2011; Cliff et al., 2014). The ratios K/Cs and K/Rb slightly decrease upward in the WS core (Fig. 8), suggesting enhanced chemical weathering during the time of deposition. Consequently, we conclude that the sediments in the OP zone reflect a higher degree of chemical alteration and the original trace element contents of the sediments were probably higher than the present values (Fig. 6). Therefore, the observed compositional differences between the OR and OP zones are likely to be underestimated if we take the effects of potential chemical weathering into consideration.

It is also important to note that increased clastic input could also cause higher trace element and LREE concentrations observed in the OP zone. Ti and Al are treated as essentially immobile due to their low solubility of the oxides and hydroxides in low-temperature aqueous solutions (Hayashi et al., 1997; Paikaray et al., 2008),). They can therefore be considered extremely resistant to weathering (Cliff et al., 2014; Chen et al., 2013; Chen et al., 2015). Ti is highly concentrated in heavy minerals and Al mostly resides in clays and residual feldspars, which are all detrital components (Murray and Leinen, 1996). Therefore, the concentrations of Ti and Al serve as good proxies for tracing sedimentary transportation processes in our study site. Thus higher concentrations of Ti and Al in the OP zone may also suggest a higher supply of siliciclastic materials to the basin compared to the OR zone (Fig. 8).

Figure 8: Temporal evolution in proxies linked to chemical weathering and clastic input intensities.

4.3. Roles of tectonics and erosion on organic matter enrichment in the Marcellus Shale

During the period of OR zone deposition (ca. 395-380 Ma), mountain building of the Acadian Orogeny was at its highest rate (Murphy et al., 1999; Ver Straeten, 2009, 2010). During this time, the northwestern migration of the deformation front contributed to the development of a flat-slab beneath the Appalachians, causing Lamaride-style orogenic activities (Murphy et al., 1999). Active mountain building of the Acadian orogeny also resulted in increased subsidence in the Acadian foreland basin (Ver Straeten, 2009, 2010). The $\delta^{13}\text{C}_{\text{org}}$ values of samples from the OR zone (ca. -30.5‰) suggest organic matter deposited during this period were primarily marine in origin (Chen and Sharma, 2016), reflecting a land-ward shift of environments accompanying a relative deepening of basin water depth (Ettensohn, 1985). During the tectonically active period, uplift of the Acadian Mountain could have acted as a barrier to the moisture-laden east wind,

causing rain shadow effect on the western side of the Acadian Mountain (Ettensohn and Barron, 1981). The rain shadow effect would have reduced sediment input from rivers into the Appalachian Basin. The lower Ti and Al concentrations in the OR zone (Fig. 8) may reflect the lower influx of land-derived sediments in the basin. Reduced clastic influx combined with deepening of the Acadian foreland basin, would have promoted the accumulation and preservation of organic matter during the tectonically active period (coincident with the magmatic quiescent period), resulting in widespread deposition of OC-rich black shales throughout the basin.

The magmatic quiescent period was abruptly terminated by a magmatic active period marked by the widespread intrusion of granodiorite rocks during the period of ca. 380 - 370 Ma (Murphy et al., 1999). In the sedimentary record, this is reflected by the high LREE and selected trace element contents preserved in the OP zone. The higher LREE and trace element contents could also possibly suggest higher clastic input. Higher concentrations of Ti and Al in the OP zone also suggest increased influx of siliciclastic materials into the basin during this time period. During periods of tectonic quiescence and magmatic activity, the Acadian Mountain might have slowly lowered due to continued weathering and erosion, resulting in reduced rain shadow effect on the western side of the mountain (Ettensohn and Barron, 1981). The reduced rain shadow effect would have permitted more moisture-laden east wind to cross the mountain, causing more precipitation and increased clastic input into the basin. Furthermore, magmatism within the Acadian orogen may have produced voluminous felsic rocks in the source area which could be a plausible source of sediments during the deposition of the OP zone. The higher clastic input would have probably caused dilution effect resulting in lower organic matter concentration in the OP zone sediments. In the meantime, subsidence would have decreased in the basin's foredeep,

resulting in shallower water depth and suboxic/oxic bottom water condition (Werne et al., 2002; Sageman et al., 2003; Arthur, 2005). Chen and Sharma (2016), suggested that the bottom water redox conditions were dominantly suboxic during the deposition of the OP zone, which is consistent with this interpretation. The higher clastic influx accompanied by faster rates of organic matter oxidation would have decreased the relative organic carbon concentration in sediments and poor preservation of organics, resulting in deposition of organic-poor shale zone.

5. Conclusions

The tectonics of the Acadian Orogeny has long been linked with organic matter enrichment in the shale deposited in the Appalachian Basin. This study attempts to provide the direct link between the Acadian Orogeny and organic-rich shale deposition. Temporal and geochemical correlation of the Acadian magmatism and magmatic signals preserved in the Marcellus Shale, reveals that the OR zone sediments were mainly formed during the period of tectonically active and magmatic quiescent period of the Acadian Orogeny. In contrast, the higher LREE and selected trace elements in the OP zone sediments indicate deposition during the period of magmatic reactivation of the Acadian Orogeny. In addition, the sediment source indicates a shift from intermediate (mixed of felsic and mafic) to felsic upward throughout the section, also supporting the trend towards higher magmatic activities. Reduced basin subsidence combined with higher sediment influx led to oxic bottom water conditions and organic matter dilution, both of which were not favorable for organic matter preservation in the OP zone of the Marcellus Shale.

Acknowledgements

The research was supported by two National Science Foundation grants to Dr. Sharma (NSF EAR-1205596 and NSF DEB-1342732). We would like to thank Drs. Toro, Banks, Carr, Weislogel, and Shang for helpful discussions.

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