Title: Role of alternating redox conditions in the formation of organic-rich interval in the Middle Devonian Marcellus Shale, Appalachian Basin, USA

Ruiqian Chen^a, Shikha Sharma^{a*}

^a Department of Geology and Geography, West Virginia University, Morgantown, WV 26506

*E-mail: shikha.sharma@mail.wvu.edu; Phone: +1 304-293-6717

Keywords:

► Marcellus shale ► alternating redox ► nutrient regeneration ► stable isotopes ► geochemical characteristics

ABSTRACT

Geochemical, isotopic and petrographic analyses were performed on a 30-m core of the Marcellus Shale obtained from Greene County, Pennsylvania, to understand the dominant controls on organic matter deposition in the black shale study units. Our study suggests that the regeneration of nutrients, such as nitrogen (N) and phosphorous (P), may have played a key role in the formation of organic carbon (OC)-rich intervals in the Marcellus Shale. The decomposition of organic matter is likely to have released N and P into the water column, and the episodic upward mixing of these nutrient-enriched waters enhanced primary production. The ratios of C_{org}/N_{bulk} and C_{org}/P_{tot} are significantly higher in the OC-rich zone of the core (i.e., defined as $TOC > 4\%$ and located between 2393 and 2406.5 m depth). The high C_{org}/P_{tot} and C_{org}/N_{bulk} ratios of the preserved organic matter may reflect the release of N and P by microbial processes, indicating the recycling of nutrients during deposition of the OC-rich interval. In addition, our data show a positive relationships between the C_{org}/P_{tot} and C_{org}/N_{bulk} ratios and the organic carbon content, which indicate that the recycled nutrients may have promoted primary

productivity, resulting in higher OC accumulation in some intervals. The geochemical and stable isotopic results also suggest that the alternating redox conditions in the water mass were favorable for nutrient regeneration. Highly variable trace metal concentrations (e.g., U, Mo, V) in the OC-rich zone and a wide range of $\delta^{15}\text{N}$ and $\delta^{34}\text{S}_{\text{pyr}}$ values towards the top of the OC-rich zone suggest fluctuations between anoxic and suboxic water conditions. Finally, sedimentary features and agglutinated benthic foraminifera in the OC-rich zone support the existence of short-term fluctuations between suboxic and anoxic conditions near the sediment-water interface. Multiple lines of evidence suggest that nutrient regeneration due to alternating redox conditions may have played an important role in the formation of OC-rich intervals in the Marcellus Shale.

1. Introduction

Organic carbon-rich (OC-rich) shales or “black shales” are dark-colored shales containing organic matter and silt- to clay-sized mineral grains (Swanson, 1961; Aller, 1994). OC-rich shales have been found around the world and are known to have high hydrocarbon-generating potential. The dominant factors that control the deposition of organic matter in black shales, however, are still highly debated. Previously, most discussions have primarily focused on “productivity” versus “preservation” models (e.g., Demaison and Moore, 1980; Pedersen and Calvert, 1990). The “preservation” model suggests that bottom-water anoxia and consequent organic matter accumulation are induced by a permanently stratified water column (e.g., Demaison and Moore, 1980; Tyson, 2005), whereas the “productivity” model suggests that high organic matter concentration primarily result from elevated primary productivity. In the productivity model, anoxic bottom water conditions are, therefore, the consequence rather than the cause of organic matter enrichment (e.g., Pedersen and Calvert, 1990; Calvert et al., 1992). However, numerous recent studies have demonstrated that the deposition of organic matter in

black shales is controlled by the interplay of multiple factors, including primary productivity, bottom water redox conditions, rate of clastic influx and the activity of degradation processes (e.g., Murphy et al., 2000b; Werne et al., 2002; Sageman et al., 2003; Pichevin et al., 2004; Rimmer et al., 2004; Tuite and Macko, 2013; Lash and Blood, 2014). Thus, it is unlikely that either the “preservation” or “production” model alone can account for the organic matter accumulation and preservation in black shales.

The Middle-Late Devonian period marks the initiation of an extensive colonization of land by higher plants that possibly enhanced physical/chemical-weathering rates (Algeo and Scheckler 1998). Berner (1997) suggested that an increasing abundance of higher plants would have enhanced the removal of CO₂ from the atmosphere, resulting in significantly higher silicate and carbonate mineral weathering rates. This would have increased land-derived nutrient influx into sedimentary basins, resulting in higher primary productivity and a subsequent increase in OC burial during this geological period (Algeo et al., 1995; Sageman et al., 2003). However, the actual mechanism that promoted the deposition of OC-rich intervals and controlled the temporal heterogeneity still remains contentious and poorly understood in the Marcellus Shale.

The OC-rich shales in the Appalachian Basin have been studied for many years and are considered to have been deposited in anoxic-sulfidic water conditions under a permanent pycnocline (e.g., Byers, 1977; Ettensohn and Barron, 1981; Ettensohn, 1985a, b; Brett et al., 1991; Murphy et al., 2000a, b). However, evidence from recent studies suggests that the water column stratification principally resulted from seasonal thermoclines rather than a permanent pycnocline (e.g., Werne et al., 2002; Macquaker et al., 2009; Schieber, 2009; Boyce and Carr, 2010). The basin was at shelfal depths and had an open connection with the global ocean. The maximum water depth was approximately 100 meters, but it shallowed considerably towards the

71 southwestern and western margins of the Appalachian Basin (probably to a few tens of meters),
72 and silled margins existed in these areas (Schieber, 1994; Algeo et al., 2007). Extensive drilling
73 of the Marcellus Shale over the last eight years has resulted in the availability of a large number
74 of cores and subsurface data. This provides an opportunity to better understand the factors that
75 control the distribution of organic matter in our study units.

76 Werne et al. (2002) and Sageman et al. (2003) employed geochemical methods (e.g.,
77 carbon isotope, trace elements) to study the Marcellus Shale preserved in cores recovered from
78 western New York. However, the Union Springs Shale (i.e., the lower shale unit within the
79 Marcellus Shale) is largely missing in western New York because the shale member pinches out
80 in western Ohio, northeastern Pennsylvania and western New York due to sea-level fluctuations
81 and the paleo-topography inherited from the underlying Onondaga Limestone (Kohl et al., 2014).
82 Therefore, Werne et al. (2002) and Sageman et al. (2003) primarily focused on depositional
83 processes within the Oatka Creek Shale (i.e., the upper shale unit within the Marcellus Shale).
84 Here we study a Marcellus Shale core recovered from southwestern Pennsylvania (Fig. 1) in
85 which the Union Springs Shale is thicker (~10 m), providing a higher resolution record of
86 paleoredox changes during the transition from the Onondaga Limestone to the Marcellus Shale.
87 Additionally, in contrast to previous studies, we utilized nitrogen and sulfur isotopes and
88 integrated sedimentary and petrographic characteristics to provide critical constraints for
89 understanding processes that might have played a key role in organic matter production and
90 preservation.

91 It has been suggested that nitrogen (N) and phosphorous (P) are preferentially released
92 relative to carbon under alternating redox conditions (Aller, 1994; Anderson et al., 2001; Werne,
93 2007). Episodic mixing of nutrient (N and P)-enriched waters can potentially lead to enhanced

photoc zone productivity. Here we employ multiple proxies, including carbon/nitrogen/sulfur isotopes, redox sensitive elements (e.g., Mo, U, V), and sedimentary and petrographic characteristics to assess the potential role of nutrient recycling and alternating redox conditions in the accumulation of organic matter within the Marcellus Shale.

2. Regional stratigraphy

The Marcellus Shale overlies the Onondaga Limestone and is overlain by the Mahantango Shale in most of western and central Pennsylvania (Fig. 1). The Marcellus Shale is a predominantly gray-black to black thinly laminated fissile pyritic OC-rich shale (Boyce and Carr, 2010). TOC values range from 0.3 to 11 weight percent (wt %) (Nyahay et al., 2007). The Marcellus Shale is divided into two shale members, the lower Union Springs Shale and the upper Oatka Creek Shale, which are separated by the Purcell/Cherry Valley Limestone (Werne et al., 2002; Segaman et al., 2003). The Union Springs Shale, the most organic-rich and gas-productive part of the Marcellus Shale (Soeder et al., 2014), consists of black shale, gray mudstone, siltstone, and limestone (Cooper, 1930). The Oatka Creek Shale contains less organic matter but has a higher clay content than the Union Springs Shale, and commonly contains abundant siderite concretions (Engelder, 2008; Bruner and Smosna, 2010). Carbonate concretions can be observed in both shale members (Lash and Blood, 2014). Lash and Engelder (2008, 2011) interpret the Purcell and Cherry Valley limestones to be equivalent; however, de Witt et al. (1993) and Werne et al. (2002) show that the Purcell and Cherry Valley limestones are separate members. In our studied core, the Purcell Limestone and Cherry Valley Limestone are separate members: the Cherry Valley Limestone (~2401 m) lies between the Union Springs and Oatka Creek shales, whereas the Purcell Limestone is within the Oatka Creek Shale (~ 2383 to 2384 m), dividing it into upper and lower Oatka Creek Shale units (Fig. 1). Conodont biostratigraphy

for the Marcellus Shale in the outcrop belt indicates a mid-upper Eifelian to lower Givetian age (398-392 Ma) (Becker et al., 2012). However, our volcanic ash ages near the base of the Marcellus range from 396 ± 2 Ma to 389 ± 3 Ma, which indicates that the basal Marcellus Shale in our study units was deposited diachronously in the basin (Parrish, 2013).

Fig. 1. The location and the stratigraphic column for the WS core, Pennsylvania. The stratigraphic column shows the gamma-ray log and the sampled intervals for the petrographic analysis of the core. Note: There was an approximate 9-foot (~2.7 meter) difference between the well log depth and the core depth due to stretching of the drill string during drilling operations. Well log depths have been corrected to core depths in this study.

3. Sampling and analytical procedures

3.1. Site location and sample preparation

We obtained core samples from the 30-m-thick Whipkey State #1 (WS) core that was drilled in September 2008 by Eastern American Energy Corporation, API number 3705924715. This core is currently curated by the West Virginia University Department of Geology and Geography. The surface location of this well is in Greene County (Latitude: 39.9235415, Longitude: -80.0033923), in southwestern Pennsylvania. In the WS core, 30 samples were collected for carbon and nitrogen isotope and geochemical analyses based on lithological characteristics and well log characteristics, such as abrupt changes in the gamma ray, as well as the changes in rock types, color, hardness and physical characteristics of the core. The presence of notable gaps in the sample record, particularly below the Purcell and Cherry Valley limestones is because those sections are missing from the core due to incomplete core recovery. Samples were collected from the inner part of the core using a chisel and hammer. The samples were ground to homogenous powder prior to stable isotope and geochemical analyses.

3.2. Analytical methods

Carbon and nitrogen isotope analyses were performed by the Stable Isotope Laboratory at West Virginia University. Carbon isotopic compositions of carbonate were measured using a GasBench Device online with a Delta Advantage gas isotope ratio mass spectrometer. For the organic carbon and nitrogen isotope measurement, the finely ground samples were treated with 1 mol/L hydrochloric acid (HCl) to remove the carbonate component. The acidified samples were rinsed 6–7 times with distilled water followed by centrifugation and were then dried in an oven at a temperature of 50°C. The dual C and N isotope analysis was conducted on a Costech ECS

4010 combustion elemental analyzer (EA), coupled to a Delta Advantage isotope ratio mass spectrometer via a ConFlo IV interface. The measurement precision was assessed by a replicate analysis of samples and internal lab standards and was better than $\pm 0.1\text{‰}$ for $\delta^{13}\text{C}$ and $\pm 0.2\text{‰}$ for $\delta^{15}\text{N}$. The $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values of the internal laboratory normalization and check standards were calibrated against their respective IAEA standards (i.e., NBS 18, NBS 19 and LSVEC for the $\delta^{13}\text{C}$ of carbonates; USGS 40 and USGS 41 for the $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ of organics), and the values are reported in per mil (‰) relative to V-PDB and AIR, respectively.

The nitrogen and organic carbon concentrations (N_{bulk} and C_{org}) were also measured using a Costech ECS 4010 combustion EA with the decarbonated samples. The C_{org} and N_{bulk} contents were determined with a precision of $\pm 0.5\%$ for C_{org} and $\pm 0.1\%$ for N_{bulk} .

Measurements of trace elements were performed by Activation Laboratory in Canada. The elements were measured using the peroxide fusion method. In this method, the sample is oxidized by sodium peroxide (Na_2O_2). Fused samples are diluted and analyzed using a PerkinElmer SCIEX ELAN 6000 ICP/MS. A fused blank is run in triplicate for every 22 samples. Controls and standards fused with samples are run after the 22 samples. Fused duplicates are run every 10 samples. The instrument is recalibrated every 44 samples. International standards of GXR-4 and OREAS 101a were used to monitor the analytical quality. The accuracy was estimated to be less than 8% for all elements except for Ni (16%). The precision of the measurement was better than 5% for all elements except for Cr (10%).

For measuring the sulfur isotopic composition of both pyrite ($\delta^{34}\text{S}_{\text{pyr}}$) and carbonate-associated sulfate ($\delta^{34}\text{S}_{\text{CAS}}$), 16 samples (~3 g) were selected for extraction. Samples were selected based on gamma ray logs, lithological characteristics and TOC. The sulfur extraction

procedure was followed according to the method of “chromium reduction” (Canfield et al., 1986). A brief protocol is provided here. (1) Elemental sulfur was removed within 24 hours in a Soxhlet apparatus at 50°C with dichloromethane (DCM) and copper pellets. Next, the residual DCM-extracted sediments were placed in an oven for 48 hours. (2) The samples were further slowly treated with 20 ml of 6N HCl while bubbling the solution with argon and stirring with a magnetic stirrer bar. This process aimed to remove the acid-volatile monosulfides (AVS extraction). (3) For the sulfate sulfur determination ($\delta^{34}\text{S}_{\text{CAS}}$), the sediment and HCl mixture from the AVS extraction were centrifuged. The filtered solution was then placed in a clean beaker, and the pH was raised to 10 by adding NaOH pellets on a hot plate and then left to stand overnight. (4) The solution was filtered to remove irons, iron oxides, etc. (5) Several drops of concentrated HNO_3 were added to the filtered solution to lower the pH to 4, then 5 ml of 0.2 M $\text{Ba}(\text{NO}_3)_2$ was slowly added and stirred. This solution was allowed to stand for several hours until no more white precipitate (BaSO_4) formed. Filtered and dried BaSO_4 precipitate was retained for sulfate sulfur analysis. (6) Finally, the filtered sediments from the AVS extraction were prepared for pyrite sulfur ($\delta^{34}\text{S}_{\text{pyr}}$) analysis. The sediment residue was treated with a mixture of 20 ml of 12N HCl and 20 ml of 1 M CrCl_3 under argon to dissolve the pyrite. The silver sulfide precipitate was placed in an oven to dry and then weighed to determine the final mass. Isotope analysis was performed by the Environmental Isotope Laboratory at the University of Arizona. The results were reported versus the Canyon Diablo Troilite (CDT) meteoritic sulfur standard and were generally reproducible within $\pm 0.15\%$.

Ten samples from this core were selected for petrographic analysis based on their variations in lithological characteristics, TOC and isotope results (Fig. 1). Polished, thin sections for this study were prepared by a commercial lab, McCrone Microscopes & Accessories, in

Westmont, Illinois. The thin sections were studied using a Nikon Optiphot petrographic microscope and a Leica M-series microscope. Pyrite framboid diameters were analyzed in 7 thin sections under reflected light using NIS-Elements Basic Research software. The diameters of at least 100 framboids from each sample were measured. In each sample the minimal, maximal and average diameter of framboids were measured, the standard deviation of the diameters was calculated and the percentage of pyrite framboids with a diameter $\geq 10 \mu\text{m}$ was calculated.

4. Geochemical proxies-background

4.1. Productivity and nutrient recycling proxies

Provided that samples preserve a primary marine carbonate carbon isotopic signature ($\delta^{13}\text{C}_{\text{carb}}$) is useful to evaluate the primary productivity (e.g., Arthur et al., 1988; Louis-Schmid et al., 2007; van Hengstum and Grocke, 2008; Spofforth et al., 2010; DeBond et al., 2012; Chen et al., 2015). The higher photosynthetic rates would preferentially remove lighter ^{12}C from the surface water, leaving the dissolved inorganic carbon (DIC) pool enriched in ^{13}C , resulting in a higher $\delta^{13}\text{C}$ of the precipitating carbonate. Alternatively, oxidation and remineralization of organic matter release lighter ^{12}C back into inorganic carbon reservoir, resulting in lower $\delta^{13}\text{C}$ of the precipitating carbonate (Freeman, 2001). In addition to the biological factors noted above, $\delta^{13}\text{C}_{\text{carb}}$ is also influenced by ocean margins and continental-type seaways (Holmden et al., 1998). The inorganic carbon near the basin margin can be easily influenced by input from groundwater and surface waters that are typically depleted in ^{13}C relative to open marine carbon (Freeman, 2001; Chen et al., 2015). However, diagenetic influences can also affect $\delta^{13}\text{C}_{\text{carb}}$ signature, particularly microbial cycling of methane, which is strongly depleted in ^{13}C relative to other carbon substrates (see Section 6.3.).

Carbon isotopic values of organic carbon ($\delta^{13}\text{C}_{\text{org}}$) can also be used to evaluate the primary productivity (e.g., Arthur et al., 1988; Bonis et al., 2010; DeBond et al., 2012). Higher productivity in the photic zone decreases the isotopic fractionation between DIC and marine organic matter, resulting in higher $\delta^{13}\text{C}_{\text{org}}$ values. However, the higher $\delta^{13}\text{C}$ in organic matter could be attributed to the changes in organic matter sources. During the Devonian period, marine organic matter are believed to have lighter $\delta^{13}\text{C}_{\text{org}}$ values of approximately -30.5‰ compared to terrestrial organic matter (-25‰ to -26‰) (Maynard, 1981; Jaminski et al., 1997, 1998).

Significant increases in C/N or C/P ratios suggest either variations in the organic matter source (marine versus terrestrial-dominated organic matter) or the preferential release (remineralization of bio-limiting nutrients) of N and P from the sediments to the water column (e.g., Ingall et al., 1993; Ingall and Jahnke, 1994, 1997; Clark et al., 1998; Algeo and Ingall, 2007; Tuite and Macko, 2009, 2013). This is plausible because marine phytoplankton incorporate N, P and C into their biomass at an approximate ratio of 106C:16N:1P (Redfield, 1942). Previous studies (e.g., Aller, 1994; Anderson et al., 2001; Benitez-Nelson et al., 2004; Ingall et al., 2005; Werne, 2007) suggested that under alternating redox conditions, N and P are preferentially released relative to C and remineralized into inorganic N and P. This mechanism appears to be related to the prevention of sorption of inorganic N and P species to clays in sediments under alternating redox conditions (Werne, 2007). The lower sorption of the inorganic N and P species onto clay particles preclude their preservation in sediments. Episodic water-column mixing makes nutrients (released from sediment) available for biological utilization, contributing to higher primary production and the increased delivery of organic matter to the sediment-water interface.

4.2. Redox proxies

Bulk sedimentary nitrogen isotopic compositions ($\delta^{15}\text{N}_{\text{bulk}}$) can indirectly reflect the redox conditions of the water column at the time of deposition (e.g., Altabet and Francois, 1994; Ganeshram et al., 1995, 2000, 2002; Calvert et al., 2001; Jenkyns et al., 2001; Kienast et al., 2002; Altabet, 2006; Quan et al., 2008; Sigman et al., 2009; Quan et al., 2013a,b). Nitrogen fixation, nitrification, nitrogen assimilation, denitrification and anammox are the primary nitrogen reactions that occur under different redox conditions (Sigman et al., 2009). Because denitrification and anammox both remove nitrogen from the water column under similar redox conditions (Sigman et al., 2009; Quan et al., 2013a, b), we refer to both reactions simply as “denitrification”. In brief, water column denitrification is predominant under suboxic conditions and the isotope fractionation factor associated with this reaction is relatively large, resulting in enriched $\delta^{15}\text{N}$ values of residual nitrate (Altabet, 2006; Quan et al., 2008, 2013b). Under anoxic conditions, nitrification is minimal, thus the amount of denitrification is very low. Therefore, $\delta^{15}\text{N}$ values are similar to that of nitrogen fixation, which has small fractionation resulting in slightly depleted $\delta^{15}\text{N}$ values in the produced organic matter (Quan and Falkowski, 2009; Quan et al., 2013b; Tuite and Macko, 2013). Oxic conditions inhibit denitrification, and other nitrogen reactions (nitrification, nitrogen fixation and nitrogen assimilation) are predominant, resulting in lower $\delta^{15}\text{N}$ values in the organic matter (Talbot, 2001; Altabet, 2006; Quan et al., 2008, 2013b).

Numerous studies indicate that the $\delta^{34}\text{S}$ values of syngenetic pyrite ($\delta^{34}\text{S}_{\text{pyr}}$) faithfully record the bottom water redox conditions during shale deposition (e.g., Berner, 1978; Berner and Petsch, 1998; Lyons et al., 2009). Sulfate reduction under anoxic conditions is the principle pathway of pyrite formation in marine sedimentary environments. As the fractionation associated with the formation of pyrite from sulfide is less than 1‰ (Price and Shieh, 1979), the sulfur

isotopic composition of preserved pyrite primarily reflects the $^{34}\text{S}/^{32}\text{S}$ ratios of the sulfide produced during sulfate reduction (Böttcher et al., 1998, 2003). For syngenetic pyrite, uniformly light $\delta^{34}\text{S}_{\text{pyr}}$ values reflect sulfate reduction in the presence of an infinite reservoir of sulfate found in sediments deposited in anoxic waters (Calvert et al., 1996; Lyons 1997; Lyons et al., 2003). In such conditions, sulfate reduction occurs within the anoxic/euxinic water column, as well as below the sediment-water interface (Suits and Wilkin, 1998; Böttcher et al., 2006), and a large fractionation can occur even when the rate of sulfate reduction is high (Gautier, 1986). In contrast, under fluctuating redox conditions the rate of pyrite sulfur burial is less than the estimated rate for the re-oxidation of dissolved sulfides, resulting in more positive and variable values of $\delta^{34}\text{S}_{\text{pyr}}$ (Gautier, 1986; Beier and Hayes, 1989). However, diagenetic pyrite is formed within the sediment and hence is not a reliable indicator of the bottom water conditions (Large et al., 2014).

Several trace elements, including U, Mo, Ni, Cu, and V, are considered to be redox-sensitive and have been extensively studied (e.g., Crusius et al., 1996; Dean et al., 1997; Rimmer et al., 2004; Algeo and Lyons, 2006; Tribovillard et al., 2006, 2012; Calvert and Pedersen, 2007; Algeo and Maynard, 2008; Quan et al., 2008; Algeo and Tribovillard, 2009; Lyons et al., 2009; Algeo and Rowe, 2012; Quan et al., 2013a, b). These trace metals are usually strongly enriched under anoxic/euxinic bottom water conditions and are also correlated with a high TOC content (e.g., Calvert and Piper, 1984; Calvert and Pedersen, 1993; Morford and Emerson, 1999; Zheng et al., 2000; Algeo and Maynard, 2004; Tribovillard et al., 2006; Calvert and Pedersen, 2007; Algeo and Rowe, 2012). Under anoxic conditions, U is removed from the water column close to or at the sediment-water interface and is precipitated as insoluble forms (UO_2 , U_2O_7 and U_3O_8) (e.g., Algeo and Tribovillard, 2009; Morford et al., 2009). Mo, Ni and Cu may be incorporated in

the insoluble forms, e.g., MoS_2 , NiS and CuS , and preserved in the sediments. In particular, the enhanced Mo uptake by marine sediment is accelerated under sulfidic bottom water conditions (e.g., Algeo and Maynard, 2004; Lyons and Severmann, 2006; Tribovillard et al., 2006, 2012; Algeo and Tribovillard, 2009). V/Al is also a useful indicator of paleoredox conditions in bottom water as V uptake by marine sediment is favored under anoxic conditions (Calvert and Piper, 1984; Dill, 1986; Tribovillard et al., 2006; Algeo and Maynard, 2008).

The size distribution of pyrite framboids in ancient sediments is a reliable measure of paleoredox conditions during the time of deposition (e.g., Bond and Wignall, 2010; Wang et al., 2012; Lash and Blood, 2014; Blood and Lash, 2015). Syngenetic pyrite framboids are considered to be deposited under anoxic/euxinic conditions and usually have smaller diameters ($<6\ \mu\text{m}$), and less variable size distributions. However, larger pyrite framboids ($>10\ \mu\text{m}$), having a more variable size distribution, are formed in diagenetically altered sediments under oxic or dysoxic conditions (Wang et al., 2012; Lash and Blood, 2014; Blood and Lash, 2015). These authors also suggested that the rapid alteration between anoxic and suboxic conditions are recorded as “time-averaged framboid size distribution” composed of abundant small framboids and a small number of larger framboids (e.g., Bond and Wignall, 2010; Blood and Lash, 2015).

5. Results

5.1. Organic carbon and bulk nitrogen content (C_{org} & N_{bulk})

The C_{org} values are very high in the basal part of the Marcellus Shale, with a maximum value of 9 wt % (Table S1, Fig. 2). At a depth of 2393 m, both the C_{org} and N_{bulk} values increase sharply. The highest C_{org} values of this interval are between 2393 and 2406.5 m core depths, which corresponds to the interval with the highest gamma ray values. Therefore, this interval is

defined as the OC-rich zone in the WS core. In the OC-rich zone, the Cherry Valley Limestone (~2401 m) has a relatively low organic carbon content ($C_{org} = 4.9$ wt %) and low gamma ray, thus separating the OC-rich zone into lower (Unit 1, at 2406.5-2401 m) and upper zones (Unit 2, at 2401-2393 m). The C_{org} values decrease markedly and are relatively stable at approximately 3 wt % in the non OC-rich zone (Unit 3, at 2393-2375 m). The N_{bulk} values are less variable but are slightly higher in Units 1 and 2 (ranging from 0.2 to 0.5 wt %, averaging 0.3 ± 0.1 wt %), whereas the N_{bulk} values in Unit 3 range from 0.1 to 0.3 wt % (average = 0.2 ± 0.1 wt %) (Table S1, Fig. 2)

Fig. 2. Organic carbon content (C_{org}), bulk nitrogen content (N_{bulk}), C_{org}/N_{bulk} and C_{org}/P_{tot} profiles for the WS core. On = Onondaga Limestone; US = Union Springs; CV = Cherry Valley Limestone; OC = Oatka Creek; P.Ls = Purcell Limestone.

5.2. C/N/P ratios

The C_{org}/N_{bulk} ratios are relatively high but variable in Units 1 and 2, ranging from 14.3 to 30.6 and averaging 21.3 ± 5.1 (Table S1, Fig. 2). A high value of 29.9 is observed in Unit 1 at 2405.2 m and a second peak appears Unit 2 at 2396 m. In contrast, the C_{org}/N_{bulk} ratios are stable and consistently low in Unit 3, ranging from 6.8 to 15.6 (average = 11.2 ± 2.5). The C_{org}/P_{tot} ratios for the shale samples from Units 1 and 2 are highly variable with average C_{org}/P_{total} ratios of approximately 200 (Table S1, Fig. 2), which is significantly higher than the average C/P ratio of 106 for marine phytoplankton (Redfield, 1942). The C_{org}/P_{total} values display a greater range in Unit 2. The C_{org}/P_{tot} ratios in Unit 3 are much lower compared to those of Units 1 and 2 (Fig. 2; Table S1).

5.3. Stable isotopes

Stable isotope data are listed in Table S2 and plotted against depth in Fig. 3. Carbon isotopic values of carbonate ($\delta^{13}C_{carb}$) are relatively high in Units 1 and 2, which is similar to the trend of the C_{org} values. In the basal part of the Marcellus Shale, $\delta^{13}C_{carb}$ values are relatively high with a maximum of -1.9‰ , and the values decrease abruptly to -10.2‰ at 2404 m and to -9.2‰ at 2396 m (Fig. 3). In Unit 3, the $\delta^{13}C_{carb}$ curve generally trends in a negative direction (averaging $-6.7 \pm 3.3\text{‰}$).

Fig. 3. Isotopic profiles for the WS core. On = Onondaga Limestone; US = Union Springs; CV= Cherry Valley Limestone; OC = Oatka Creek; P.Ls = Purcell Limestone; CAS = carbonate-associated sulfate.

The carbon isotopic composition of organic carbon ($\delta^{13}\text{C}_{\text{org}}$) exhibits slightly lower values in Unit 1 (averaging $-30.5 \pm 0.3\text{‰}$). The curve shifts towards higher values ranging from -30.8 to -30.1‰ in Unit 2 at ~ 2398.2 m. In Unit 3, the $\delta^{13}\text{C}_{\text{org}}$ values are slightly heavier (averaging $-29.8 \pm 0.4\text{‰}$). In particular, the values are much higher in the Purcell Limestone member (-28.9‰) (Fig. 3).

The bulk nitrogen isotopic compositions ($\delta^{15}\text{N}_{\text{bulk}}$) are more scattered in Unit 2 (averaging $0.6 \pm 1.2\text{‰}$) relative to those in Unit 1 (averaging $0.9 \pm 0.4\text{‰}$). There are few organic-rich intervals within Unit 2 that have lower $\delta^{15}\text{N}_{\text{bulk}}$ values of approximately -1.5‰ . The $\delta^{15}\text{N}_{\text{bulk}}$

increases in Unit 3, averaging $1.7 \pm 1.3\text{‰}$. In particular, above ~ 2390 m, the $\delta^{15}\text{N}_{\text{bulk}}$ values are relatively stable and as high as 3.6‰ (Fig. 3).

The isotopic compositions of pyrite ($\delta^{34}\text{S}_{\text{pyr}}$) range from -30.8‰ to 1.7‰ (Fig. 3). The $\delta^{34}\text{S}_{\text{pyr}}$ values are relatively lower in the bottom of Unit 1 (average = $-18.0 \pm 4.7\text{‰}$). A greater range of $\delta^{34}\text{S}_{\text{pyr}}$ values is observed in Unit 2 (average = $-11.8 \pm 9.4\text{‰}$), where the values reach to a maximum of 1.7‰ at approximately 2397.6 m. The $\delta^{34}\text{S}_{\text{pyr}}$ values in Unit 3 are slightly lower than those in the lower succession; however, they increase abruptly to -10.3‰ at the top of the Marcellus (Fig. 3).

The isotopic compositions of sulfates ($\delta^{34}\text{S}_{\text{CAS}}$) range from -16.1‰ to 4.9‰ (Fig. 3). The sulfates obtained from Units 1 and 2 display uniformly high $\delta^{34}\text{S}_{\text{CAS}}$ values (average = $3.0 \pm 2.1\text{‰}$). In Unit 3, the $\delta^{34}\text{S}_{\text{CAS}}$ profile trends to lower values upward throughout the core (average = $-6.4 \pm 6.7\text{‰}$).

5.4. Trace element geochemistry

Profiles for Al, Ti, U, Mo, Ni, Cu, and V are shown in Fig. 4 with values listed in Table S3. To eliminate the effect of varying clastic input, the concentrations of U, Mo, Ni, Cu and V are all divided by Al contents. The Al and Ti contents show a steady increase from the bottom to the top of the Marcellus Shale. The values for U, Mo, Ni, Cu and V/Al sharply increase at the bottom (from 2403 to 2406 m) of Unit 1. The trace metal concentrations decrease sharply in the Cherry Valley Limestone, followed by another increase in Unit 2. Although the enrichment of trace elements is not consistent across the entire unit, the values are relatively high. The Al-normalized element ratios exhibit a distinct decline in concentrations at ~ 2393 m, above which they maintain consistently low values (Fig. 4).

Fig. 4. Al, Ti, U, Mo, Ni, Cu and V/Al profiles for the WS core. On = Onondaga Limestone; US = Union Springs; CV= Cherry Valley Limestone; OC = Oatka Creek; P.Ls = Purcell Limestone;

5.5. Sedimentary features and petrography

The Marcellus Shale in the WS core consists of silty black shales and interbedded fossiliferous limestones and gray shales. The analyzed samples from the Marcellus Shale display a great range of textural and compositional variation. In general, the OC-rich deposits are strongly laminated though some display of subtle bioturbation. Some intervals of OC-rich gray shales or black shales are associated with thin layers of limestones. There is an abundance of angular to sub-angular carbonate skeletal fragments (bioclasts) at the base of the Marcellus Shale (Fig. 5a). Alternating laminae of gray shales and limestones with slight variations in thickness were observed near a depth of 2396 m in Unit 2. Lateral tracing of these alternating layers reveals subtle discontinuities (Fig. 5b).

Under microscopic examination, we observed pyrite grains in black shale and marls with some variation in the amount. In general, the pyrite grains in our samples are abundant small frambooids (<6 μm diameter) with a relatively small number of relatively large frambooids (>10

μm diameter) (Fig. 5f). The average diameter of the 823 framboidal pyrites measured is 5.3 μm, and only 3.8% of all sampled framboids had a diameter greater than 10 μm (Table S4). Pyrite framboid diameter data is presented as box-and-whisker plots (Fig. 6; Wignall and Newton, 1998). The whiskers define the minimum and maximum values, and the boxes range from the quartile Q=0.25 to quartile Q=0.75 of the data population. The average values of the data population are designed by vertical lines drawn through the boxes. A high proportion of agglutinated benthic foraminifera were found in samples WS-7865 and WS-7887 (Fig. 5c and d). These benthic foraminifera appear fine-crystalline cherty and are randomly distributed throughout the samples. The estimated percentages of foraminifera in samples WS-7865 and WS-7887 are 25% and 30%. Schieber (2009) suggested that these foraminifera first accumulate random grains, then they incorporate fine-grained quartz silts into new chambers. Lenticular bodies of quartz silt grains indicate the collapse of their tests, which took place during burial and compaction. Black and gray shale samples recovered from Unit 3 show discontinuous lamination, a likely expression of strong bioturbation. These samples contain a higher proportion of quartz silt grains and organic-poor materials (Fig. 5e).

Fig. 5. (A) Abundant bioclasts at the base of the Marcellus Shale. The white arrow points to a bryozoan fragment. (B) The upper image shows alternating beds of gray shales and limestones; the lower image is the lateral tracing of these discontinuous laminae. (C) Image WS-7865. Partial replacement of collapsed benthic foraminifera (white arrows) by quartz. (D) Image WS-7887. Photomicrograph of collapsed benthic foraminifera under higher magnification. Fine-grained

quartz silt can be observed along the chambers. Partial internal fill in the lenticular bodies prevented complete collapse. (E) Image WS-7828. Silty, pyritic black shale. (F) Image WS-7865. Pyrite grains under reflected light. White arrows point to the large pyrite framboids.

Fig. 6. Box-and whisker plots of pyrite framboid diameter data of the WS core samples. Note: “n” refers to the number of pyrite framboids analyzed.

6. Discussion

6.1. The OC-rich zone (Units 1 and 2)

OC-rich black shales of the Devonian Appalachian Basin have long been considered classic examples of stagnant, euxinic basin deposits (Byers, 1977; Ettensohn, 1992). However, recent work has shown that not all Devonian black shales were deposited under stagnant water column conditions (Murphy et al., 2000a, b; Werne et al., 2002; Sageman et al., 2003; Algeo et al., 2007; Lash and Blood, 2014). The presence of alternating redox conditions during the accumulation of OC-rich deposits in the WS core site is evidenced by (1) a wide range of $\delta^{15}\text{N}$ and $\delta^{34}\text{S}_{\text{pyr}}$ values in Unit 2; (2) highly variable trace metal concentrations; and (3) high $\text{C}_{\text{org}}/\text{N}_{\text{bulk}}$ and $\text{C}_{\text{org}}/\text{P}_{\text{tot}}$ ratios in Units 1 and 2.

The $\delta^{15}\text{N}_{\text{bulk}}$ values are relatively low in Units 1 and 2, in particular, the values are more consistent (average = $0.9 \pm 0.5\text{‰}$) in Unit 1 and then shift to a broader range (average = $0.7 \pm 1.2\text{‰}$) in Unit 2. Previous studies (e.g., Ganeshram et al., 1995, 2000; Calvert et al., 2001; Jenkyns et al., 2001; Quan et al., 2008, 2013b) suggested that increases in $\delta^{15}\text{N}_{\text{bulk}}$ values indicate a shift to suboxic conditions, in which denitrification removes isotopically light nitrate, leaving residual nitrate enriched in ^{15}N . However, decreases in $\delta^{15}\text{N}_{\text{bulk}}$ values can either indicate a shift from suboxic to oxic conditions or a shift from suboxic to anoxic conditions because both nitrification and nitrogen fixation processes result in lower $\delta^{15}\text{N}$ values in organic matter. The deposition of OC-rich black shale is unlikely to occur under oxic water column conditions; hence the decreases in $\delta^{15}\text{N}_{\text{bulk}}$ values in our study probably reflect a shift from suboxic to anoxic conditions. Therefore, the variable $\delta^{15}\text{N}_{\text{bulk}}$ values through Unit 2 (Fig. 3) most likely indicate that sediments in this interval were deposited under alternating redox conditions. It is also possible that the lower $\delta^{15}\text{N}_{\text{bulk}}$ values in Units 1 and 2 may produced by greater N fixation by microorganisms (Talbot, 2001; Quan et al., 2008; 2013b; Sigman et al., 2009). The higher $\text{C}_{\text{org}}/\text{N}_{\text{bulk}}$ and $\text{C}_{\text{org}}/\text{P}_{\text{tot}}$ ratios in the same units (Fig. 2) may suggest greater nutrients available for the growth of

microorganisms, which could have promoted N fixation during the time of deposition. However, further investigations are needed to better understand the microbial activities during the deposition of the Marcellus Shale.

In our study, most of the pyrite grains are considered syngenetic in origin (pyrite framboid size presented in Section 5.5.) and can therefore serve as good indicators of bottom water conditions. At the base of Unit 1 the $\delta^{34}\text{S}_{\text{pyr}}$ values show a decrease upward (Fig. 3). This suggests that at the very beginning of the Marcellus Shale deposition, the oxygen concentration in the bottom water decreased abruptly, and water conditions became primarily anoxic with high sulfide burial rates accompanied by only slight shifts in redox conditions. By contrast, the samples from Unit 2 display relatively higher and highly variable $\delta^{34}\text{S}_{\text{pyr}}$ values (Fig. 3), suggesting that sediments were probably deposited in episodically suboxic to anoxic bottom water conditions.

The alternating redox conditions during the deposition of Units 1 and 2 are also supported by highly variable trace metal concentrations (Fig. 4). The U/Al and V/Al ratios in Unit 1 increase sharply from ~4 to 36 and from ~85 to 360. The Mo/Al ratios increase abruptly from ~16 to 72, followed by a negative shift. The Ni/Al and Cu/Al ratios exhibit similar trends of increasing values to the middle of Unit 1 (Fig. 4). The rapid increase of these trace metal ratios suggests the bottom water redox conditions shifted from oxic to anoxic at the beginning of the Marcellus Shale deposition, perhaps as a consequence of a rapid sea-level rise. Algeo and Rowe (2012) suggested that rate changes in the trace metal concentrations in response to sea-level fluctuations can be quite rapid in restricted basins. The trace metal ratios decreased in the Cherry Valley Limestone, and remained relatively stable with low values up to ~2397 m. The ratios increase and reach another peak at ~2395 m, followed by a negative shift (Fig. 4). Such

fluctuations suggest that oxic/suboxic bottom water conditions existed during deposition of the Cherry Valley Limestone and became variably suboxic and anoxic during the accumulation of overlying sediments. Furthermore, the variable trace metal ratios correlate with a high C_{org} content and high gamma ray (Figs. 2 and 4), suggesting that the alternating redox conditions during this time interval enhanced the burial of organic matter.

The relatively high C_{org}/P_{tot} and C_{org}/N_{bulk} ratios in Units 1 and 2 may have been induced by alternating redox conditions that favored the release of N and P back to the water column (Fig. 2). Water column mixing would have made these nutrients available for biological utilization, resulting in the enhanced primary production and, consequently, increased delivery of organic matter to the sediment (Werne et al., 2002). This supports the hypothesis that a “productivity-anoxia feedback” mechanism may have contributed to a high level of OC production and sequestration in the Devonian black shales in the northern part of the Appalachian Basin (Ingall et al., 1993; Murphy et al., 2000a, b; Sageman et al., 2003). The ratios show a small decline at the Cherry Valley Limestone and then increase upward in Unit 2 (Fig. 2). We suggest that the low C_{org}/N_{bulk} and C_{org}/P_{tot} ratios in the Cherry Valley Limestone may reflect a transition to relatively shallow, suboxic water. The generally higher ratios above the limestone could have resulted from continued sea-level rise, which ultimately drowned out carbonate production and produced the organic-rich shale deposits in Unit 2. During the sea-level rise, a gradual increase in the intensity and/or duration of anoxic periods induced by thermal stratification could have produced the alternating anoxic/suboxic redox conditions (Werne et al., 2002), contributing to higher C_{org}/N_{bulk} and C_{org}/P_{tot} ratios in Unit 2.

Another possible cause of the variable C_{org}/N_{bulk} and C_{org}/P_{tot} ratios could be changes in the source of organic matter. Marine organic matter sources have C_{org}/N_{bulk} ratios in the range of

4 to 10 (Gray and Biddlestone, 1973). In contrast, organic matter from terrestrial sources is difficult to decompose and tends to have C_{org}/N_{bulk} ratios greater than 20 (Prah et al., 1994). C_{org}/P_{tot} ratios of modern terrestrial organic matter have a significantly higher C/P ratio (i.e., 300–1300) than modern marine organic matter (i.e., 7–80) (Ruttenberg and Goñi, 1997; Rimmer et al., 2004). A comparison of Fig. 2 and 3 shows that although C_{org}/N_{bulk} and/or C_{org}/P_{tot} ratios are high in Unit 1, this is not due to a large concentration of terrestrial organic matter; in fact, the $\delta^{13}C_{org}$ values are lower in this unit (i.e., suggests mostly marine organic matter, see Section 6.2.). Overall, there appears to be no significant relation between C/N/P ratios and $\delta^{13}C_{org}$ values throughout the section, arguing against the possibility that the observed variations in C/N/P ratios could be due to changes in organic matter sources. Hence, we suggest that the high C/N/P ratios seen in these sediments might have been controlled by nutrient regeneration rather than changes in organic matter sources.

Under most sedimentary conditions during early diagenesis, a modest increase in C_{org}/N_{bulk} and C_{org}/P_{tot} ratios are seen, independent of changes in organic matter sources (Arthur and Sageman, 2005; Junium and Arthur, 2007). However, high ratios are typical of low-oxygen, high paleo-productivity environments. When C_{org}/N_{bulk} and C_{org}/P_{tot} ratios are plotted against the C_{org} (Fig. 7), an increase in OC content from 2 to approximately 10 percent is accompanied by an increase in C_{org}/N_{bulk} and C_{org}/P_{tot} ratios. The positive correlations of OC content and C_{org}/N_{bulk} and C_{org}/P_{tot} ratios suggest that nutrient recycling and productivity might have played an important role in controlling OC accumulation in the Marcellus Shale.

Fig. 7. (A) A positive correlation between OC content and C_{org}/N_{bulk} ratios, (B) A positive correlation between OC content and C_{org}/P_{tot} ratios

6.2. The non-OC-rich zone (Unit 3)

Sediments preserved in Unit 3 were deposited under suboxic conditions, as suggested by (1) low trace metal ratios; (2) high $\delta^{15}N_{bulk}$ values; and (3) low C_{org}/N_{bulk} and C_{org}/P_{tot} ratios in this unit. Low trace metal ratios throughout Unit 3 most likely reflect suboxic bottom water conditions during the deposition of these sediments (Fig. 4), perhaps as a result of a falling sea level. However, these ratios slightly increase above the Purcell Limestone, possibly indicating a decline in clastic influx (Scott and Lyons, 2012). In a recent paper, Lash and Blood (2014) described a similar pattern of increase in Al concentrations upward throughout the Marcellus Shale accompanied by reduced OC content and diminished gamma ray response. The general increase in Al and Ti concentrations upward throughout Unit 3 might indicate the dilution of OM by clastics due to a higher clastic influx associated with a lowering sea level (Fig. 4). Some studies also suggest that an increase in clastic influx might also be associated with higher freshwater influx (Nash, 1994; Jaminski et al., 1998). As freshwater plumes generally strengthen

the pycnocline, this could have reduced the upward mixing of nutrient-rich deepwaters, potentially decreasing primary productivity and OC burial (Garvine, 1984).

Higher $\delta^{15}\text{N}_{\text{bulk}}$ values in Unit 3 also suggest suboxic bottom water conditions associated with enhanced denitrification (Fig. 3). However, previous studies suggest that diagenetic alteration of organic matter under various bottom water redox conditions could result in differential fraction of nitrogen isotope (e.g., Lehmann et al., 2002; Boudou, 2008; Quan et al., 2013b). In general, oxic and suboxic degradation leads to enrichment of ^{15}N while anoxic degradation leads to depletion of ^{15}N (Lehmann et al., 2002). Hence the higher $\delta^{15}\text{N}_{\text{bulk}}$ values observed in Unit 3 may be related to diagenetic alteration of organic matter under suboxic conditions, that is consistent with our previous interpretation. Together, the higher $\delta^{15}\text{N}_{\text{bulk}}$ values in combination with low $\text{C}_{\text{org}}/\text{N}_{\text{bulk}}$ and $\text{C}_{\text{org}}/\text{P}_{\text{tot}}$ ratios throughout Unit 3 provide further evidence of suboxic conditions during this time interval (Fig. 2). These conditions were not favorable for the periodic release of N and P, resulting in a reduced rate of primary productivity and relatively low OC contents in this unit.

The higher $\delta^{13}\text{C}_{\text{org}}$ in Unit 3 could be attributed to the changes in organic matter sources (Fig. 3): terrestrial organic matter is predominantly derived from the lignin fraction of wood, thus its isotopic composition is very close to that of coal, whereas marine organic matter is derived from marine phytoplankton (Goni et al., 1997). During the Devonian period, the marine and terrestrial organic matter are believed to have $\delta^{13}\text{C}_{\text{org}}$ values of approximately -30.5‰ , and -25‰ to -26‰ , respectively (Maynard, 1981; Jaminski et al., 1997, 1998). The lower $\delta^{13}\text{C}_{\text{org}}$ values of the samples from Units 1 and 2 indicate that the primary contribution was from marine organic matter sources. However, the samples from Unit 3 have higher $\delta^{13}\text{C}_{\text{org}}$ values indicating they received a contribution from both marine and terrestrial organic matter sources (Fig. 3). The

higher TOC intervals also tend to contain a higher percentage of marine organic matter compared to the low TOC intervals as reported in other studies (e.g., Jaminski et al. 1997, 1998). Alternatively, increases of $\delta^{13}\text{C}_{\text{org}}$ values may also record the withdrawal of ^{13}C -depleted water from the basin in response to a lowering sea level (Chen et al., 2013; Lash and Blood, 2014). Lash and Blood (2014) recorded very similar $\delta^{13}\text{C}_{\text{org}}$ variations in a Marcellus Shale core recovered from southwestern Pennsylvania (see Fig. 10). In this curve, the higher $\delta^{13}\text{C}_{\text{org}}$ values were observed in the Oatka Creek member, which is the organic-poor interval in the Marcellus Shale. They suggested that an overturn of the water mass could have emplaced the isotopically light CO_2 onto a shallow shelf of the Marcellus Basin. The cooling trend during the late Middle Devonian could have shifted the deep-water source from middle to high altitudes, disrupting the stable stratification of the oceans (Wilde and Berry, 1984; Murphy et al., 2000c). In our study, the lowering sea level could have reduced the oceanic overturn effect, thus less ^{12}C -enriched water was driven upward to the surface water, contributing to isotopically heavy $\delta^{13}\text{C}_{\text{org}}$ values. However, more research needs to be performed in the future to better understand the oceanic overturn model during the early period of the Marcellus Shale deposition.

6.3. Diagenetic influences

It is necessary to consider the possibility that $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{34}\text{S}_{\text{CAS}}$ values in the carbonates could have been altered during post-depositional diagenesis. The $\delta^{13}\text{C}_{\text{carb}}$ values documented in our study (ca. -2 to -13‰) are lower compared to the average marine $\delta^{13}\text{C}_{\text{carb}}$ values reported for the Middle Devonian carbonates (ca. 0 to 1‰) (Saltzman, 2005), suggesting that the carbonate present in our samples is likely of diagenetic origin (Fig. 3). Lash and Blood (2014) suggested that the carbonates in the Marcellus Shale display diagenetic effects related to the diffusion of biogenic methane through succession. Methane-derived authigenic carbonates are

commonly precipitated in the sulfate reduction zone, when there is a large rise in alkalinity. These reactions occur where downward migrating seawater sulfate encounters upward diffusing methane (e.g., Himmler et al., 2011; Lash and Blood, 2014; Drake et al., 2015). The isotopically light CO₂ derived from methane oxidation can provide light carbon to the system, which precipitates out as carbonate with low $\delta^{13}\text{C}_{\text{carb}}$ values (Whiticar and Faber, 1986; Suess and Whiticar, 1989).

The $\delta^{34}\text{S}_{\text{CAS}}$ values of the primary seawater sulfate during the Middle Devonian are reported to be between 15 and 25 ‰ (Kampschulte and Strauss, 2004). However, our values (ca. -16 to +5 ‰) are strongly biased toward lighter values (Fig. 3), reflecting the incorporation of isotopically light sulfur. Several studies have suggested that oxidized H₂S or sulfur oxidation intermediates within the diagenetic environment and could provide isotopically light sulfur to the system, resulting in sulfate reservoirs with depleted ^{34}S values relative to seawater (e.g., Canfield and Teske, 1996; Lyons, 1997; Canfield, 2001; Lyons et al., 2003; Konssow et al., 2015). This is consistent with the evidence of the precipitation of authigenic carbonates in our study units as secondary phases. Therefore, the $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{34}\text{S}_{\text{CAS}}$ values in the WS core reflect diagenetic alterations and cannot be used to interpret the primary seawater records, such as the rates of primary productivity and changes in water column redox conditions during the time of deposition.

6.4. Alternating redox conditions evidenced by sedimentary and petrographic features

Sedimentary features and petrographic characteristics provide supporting evidence to constrain the depositional conditions of the Marcellus Shale at the WS core site. The presence of bioclasts in Unit 1 (Fig. 5a) may suggest bottom current activity and consequent water column

592 mixing during the beginning of the Marcellus Shale deposition. The angular to sub-angular
593 outline of these fragments suggests that the energy of transporting currents was strong enough to
594 carry them to the basin. The strong current was probably caused by strong base flows associated
595 with storms that might have reworked bioclasts from the shallow platform (probably from the
596 underlying Onondaga Limestone). Gray shale interbedded with limestone in the Unit 2 suggests
597 that bottom water conditions alternated between anoxic and oxic during deposition. In addition,
598 subtle discontinuous laminae across the core might have resulted from bottom currents (Schieber,
599 2003), which allowed for the transfer of remineralized N and P from the sediments into the
600 photic zone. The circulation pattern within the basin is unknown, but the seasonal circulation and
601 associated episodic mixing could have played a key role in the temporal depositional
602 heterogeneity throughout the WS core.

603 Several studies (e.g., Bernhard and Reimers, 1991; Bernhard et al., 2003; Schieber,
604 2009) suggest that benthic foraminifera require at least some oxygen to persist at the seafloor.
605 Thus, the presence of agglutinated benthic foraminifera in the sediments indicates that the short-
606 lived dysoxic or oxic conditions occurred during the deposition of the OC-rich intervals in the
607 Marcellus Shale. Further, the abundant small pyrite framboids are considered as evidence of
608 sulfide precipitation under anoxic conditions, whereas a small proportion of larger framboids
609 may suggest brief periods of bottom water oxygenation during the deposition of the Marcellus
610 Shale at the WS core site. Variable redox conditions might have been produced by bottom
611 current activity and/or episodic mixing, which is consistent with the interpretation of the
612 sedimentary features. These observations are also consistent with a depositional model proposed
613 by Jaminski et al. (1997, 1998), who suggested that the organic matter accumulation in the
614 Appalachian Basin was subject to episodic fluctuations in freshwater runoff and clastic influx at

timescales of a few thousand years. These alternating paleoredox conditions might have been critical for N and P regeneration, resulting in higher primary productivity and high burial fluxes of OC. The abundant agglutinated benthic foraminifera documented from Unit 1 may be a manifestation of the higher organic matter flux related to elevated primary productivity. Enhanced organic matter flux from the surface water and the higher degradation of organic matter would provide a higher nutrient supply for foraminifera (Pedersen et al., 1988; Herguera and Berger, 1991). In contrast, Unit 3 deposits reflect a greater flux of siliciclastic sediment, which would have diluted the organic matter supply, thus reducing the nutrient supply for foraminifera. Such a scenario would not have been favorable for the persistence of benthic foraminifera at the seabed.

6. Conclusions

Temporal variations in the C/N/P ratios, C/N/S stable isotope compositions, trace element concentrations, and sedimentary and petrographic characteristics were utilized to reconstruct the changes in the paleo-redox conditions during the deposition of the Marcellus Shale at the WS core site. The multiple lines of evidence from our study suggest that the regeneration of bio-limiting nutrients under alternating redox conditions might have played a key role in sustaining high levels of primary productivity, resulting in the accumulation of OC-rich deposits. At the base of the Marcellus Shale, the higher concentrations of trace elements indicate a shift to anoxic conditions at the beginning of its deposition, resulting in a higher preservation of organic matter. Fluctuating $\delta^{15}\text{N}_{\text{bulk}}$ and $\delta^{34}\text{S}_{\text{pyr}}$ values and trace metal ratios throughout Unit 2 are suggestive of episodic suboxic conditions, possibly due to short-term sea-level changes. Overall, the redox water conditions were predominantly alternating between anoxic and suboxic during the deposition of sediments in Units 1 and 2. Higher C/N/P ratios throughout these units suggest that

the release of nutrients (N and P) from the organic matter might have sustained higher OC production. The C_{org}/P_{tot} and C_{org}/N_{bulk} profiles co-vary closely with the TOC contents in Units 1 and 2, suggesting a positive relationship between the nutrient release and higher burial of organic matter. The presence of bioclasts and discontinuous laminae observed in Units 1 and 2 suggests the possibility of bottom currents and water column mixing during that time of deposition. We suggest that this mixing could be the internal mechanism responsible for in-situ nutrient recycling, resulting in the increased productivity and higher OC concentration in the Marcellus Shale in Units 1 and 2 of our studied units. However, in Unit 3, lower trace metal ratios and higher $\delta^{15}N_{bulk}$ and $\delta^{13}C_{org}$ values likely reflect suboxic water conditions during deposition. The marked change in bottom water conditions from Units 1 and 2 to the overlying Unit 3 might have been caused by the falling sea-level resulting in higher siliciclastic input, as suggested by the higher Ti and Al contents and abundant siltstones.

Acknowledgements

The research was supported by two National Science Foundation grants to Dr. Sharma (NSF EAR-1205596 and NSF DEB-1342732). The work was also partly funded by a collaborative initiative of the National Energy Technology Laboratory's Regional University Alliance (NETL-RUA) RES contract DEFE0004000. We would like to thank Pete Sullivan from ECA, and Drs. Carr and Toro for giving us the core and the pertinent well log data. We also thank Drs. Kammer, Benison and Weislogel for their help with fossil identification. Dr. Ajay Warriar from the WVU Stable Isotope is acknowledged for providing help with sample analysis. We are grateful to Dr. Thomas Algeo and two anonymous reviewers for their constructive comments and suggestions.

660 REFERENCES

- 661 Algeo, T. J., Berner, R. A., Maynard, J. B., and Scheckler, S. E., 1995, Late Devonian oceanic
 662 anoxic events and biotic crises: “rooted” in the evolution of vascular land plants? *GSA*
 663 *Today*, v. 5, p. 64-66.
- 664 Algeo, T. J., and Scheckler, S. E., 1998, Terrestrial-marine teleconnections in the Devonian:
 665 links between the evolution of land plants, weathering processes, and marine
 666 anoxic events: *Royal Society of London Philosophical Transactions (B): Biological*
 667 *Sciences*, v. 353, p. 113-130.
- 668 Algeo, T. J., and Maynard, J. B., 2004, Trace-element behavior and redox facies in core shales of
 669 Upper Pennsylvanian Kansas-type cyclothems: *Chemical Geology*, v. 206, no. 3–4, p.
 670 289-318.
- 671 Algeo, T. J., and T. W. Lyons., 2006, Mo–total organic carbon covariation in modern anoxic
 672 marine environments: Implications for analysis of paleoredox and paleohydrographic
 673 conditions: *Paleoceanography*, 21, PA1016.
- 674 Algeo, T. J., and Ingall, E., 2007, Sedimentary Corg:P ratios, paleocean ventilation, and
 675 Phanerozoic atmospheric pO₂: *Palaeogeography, Palaeoclimatology, Palaeoecology*, v.
 676 256, no. 3–4, p. 130-155.
- 677 Algeo, T. J., Lyons, T. W., Blakey, R. C., and Over, D. J., 2007, Hydrographic conditions of the
 678 Devonian–Carboniferous North American Seaway inferred from sedimentary Mo–TOC
 679 relationships: *Palaeogeography, Palaeoclimatology, Palaeoecology*, v. 256, no. 3–4, p.
 680 204-230.
- 681 Algeo, T. J., and Maynard, J. B., 2008, Trace-metal covariation as a guide to water-mass
 682 conditions in ancient anoxic marine environments: *Geosphere*, v. 4, no. 5, p. 872-887.
- 683 Algeo, T. J., and Tribouillard, N., 2009, Environmental analysis of paleoceanographic systems
 684 based on molybdenum–uranium covariation: *Chemical Geology*, v. 268, no. 3–4, p.
 685 211-225.
- 686 Algeo, T. J., and Rowe, H., 2012, Paleoceanographic applications of trace-metal concentration
 687 data: *Chemical Geology*, v. 324–325, p. 6-18.
- 688 Aller, R. C., 1994, Bioturbation and remineralization of sedimentary organic matter: effects of
 689 redox oscillation: *Chemical Geology*, v. 114, no. 3–4, p. 331-345.
- 690 Altabet, M. A., and Francois R., 1994, Sedimentary nitrogen isotopic ratio as a recorder for
 691 surface ocean nitrate utilization: *Global Biogeochemical Cycles*, v. 8, p. 103–116.
- 692 Altabet, M. A., 2006, Isotopic Tracers of the Marine Nitrogen Cycle: Present and Past, in the
 693 *Handbook of Environmental Chemistry*, p. 251-293.

694 Anderson, L. D., Delaney, M. L., and Faul, K. L., 2001, Carbon to phosphorus ratios in
695 sediments: Implications for nutrient cycling: *Global Biogeochemical Cycles*, v. 15, no.
696 1, p. 65-79.

697 Arthur, M. A., Dean, W. E., and Pratt, L. M., 1988, Geochemical and climatic effects of
698 increased marine organic carbon burial at the Cenomanian/Turonian boundary: *Nature*,
699 v. 335, no. 6192, p. 714-717.

700 Arthur, M. A., and Sageman, B. B., 2005, Sea-level control on source-rock development:
701 Perspectives from the Holocene Black Sea, the Mid-Cretaceous Western Interior Basin
702 of North America, and the Late Devonian Appalachian Basin, Special Publication
703 SEPM Soc. Sediment. Geol., v. 82, p. 35–59.

704 Becker, R. T., Gradstein, F. M., and Hammer, O., 2012, Chapter 22 - The Devonian Period, *in*
705 Gradstein, F. M., Schmitz, J. G. O. D., and Ogg, G. M., eds., *The Geologic Time Scale*:
706 Boston, Elsevier, p. 559-601.

707 Beier, J. A., and Hayes, J. M., 1989, Geochemical and isotopic evidence for paleoredox
708 conditions during deposition of the Devonian-Mississippian New Albany Shale,
709 southern Indiana: *Geological Society of America Bulletin*, v. 101, no. 6, p. 774-782

710 Berner, R. A., 1978, Sulfate reduction and the rate of deposition of marine sediments: *Earth and*
711 *Planetary Science Letters*, v. 37, no. 3, p. 492-498.

712 Berner, R. A., 1997, The rise of plants and their effect on weathering and atmosphere CO₂:
713 *Science*, v. 276, p. 544-546.

714 Berner, R. A., and Petsch, S. T., 1998, The Sulfur Cycle and Atmospheric Oxygen: *Science*, v.
715 282, no. 5393, p. 1426-1427

716 Bernhard, J. M., and Reimers, C. E., 1991, Benthic Foraminiferal Population Fluctuations
717 Related to Anoxia: Santa Barbara Basin: *Biogeochemistry*, v. 15, no. 2, p. 127-149

718 Bernhard, J. M., P. T. Visscher, S. S. Bowser , 2003, Sub-millimeter life positions of bacteria,
719 protists, and metazoans in laminated sediments of the Santa Barbara Basin: *Limnology*
720 *and Oceanography*, v. 48, p. 813-828.

721 Benitez-Nelson, C. R., O'Neill, L., Kolowith, L. C., Pellechia, P. J., Thunell, R. C., 2004,
722 Phosphonates and particulate organic phosphorus cycling in an anoxic marine basin:
723 *Limnology and Oceanography*, v. 49, p. 1593–1604.

724 Blood, D. R., and Lash, G. G., 2015, Dynamic redox conditions in the Marcellus Shale as
725 recorded by pyrite framboid size distributions: *Geological Society of America Special*
726 *Papers*, v. 515.

727 Bond, D. P. G., and Wignall, P. B., 2010, Pyrite framboid study of marine Permian–Triassic
728 boundary sections: A complex anoxic event and its relationship to contemporaneous
729 mass extinction: *Geological Society of America Bulletin*, v. 122, p. 1265-1279.

- 730 Bonis, N. R., Ruhl, M., and Kürschner, W. M., 2010, Climate change driven black shale
731 deposition during the end-Triassic in the western Tethys: *Palaeogeography*,
732 *Palaeoclimatology*, *Palaeoecology*, v. 290, no. 1–4, p. 151-159.
- 733 Böttcher, M. E., Smock, A., and Cypionka, H., 1998, Sulfur isotope fractionation during
734 experimental precipitation of iron(II) and manganese(II) sulfide at room temperature:
735 *Chemical Geology*, v. 146, p. 127-134.
- 736 Böttcher, M.E., Rinna, J., Warning, B., Wehausen, R., Howell, M.W., Schnetger, B., Stein, R.,
737 Brumsack, H.-J., and Rullkötter, J., 2003, Geochemistry of sediments from the
738 connection between the western and eastern Mediterranean Sea (Strait of Sicily, ODP
739 Site 963): *Palaeogeography*, *Palaeoclimatology*, *Palaeoecology*, v. 190, p.165–194.
- 740 Böttcher, M. E., Hetzel, A., Brumsack, H.-J., and A. Schipper, A., 2006, Sulfur-iron-carbon
741 geochemistry in sediments of the Demerara Rise. *Proceedings of Ocean Drilling*
742 *Program*, *Scientific Results Volumn 207: Ms207SR-108* (1-23).
- 743 Boudou, J.-P., Schimmelmann, A., Ader, M., Mastalerz, M., Sebito, M., and Gengembre, L.,
744 2008, Organic nitrogen chemistry during low-grade metamorphism: *Geochimica et*
745 *Cosmochimica Acta*, v. 72, no. 4, p. 1199-1221.
- 746 Boyce, M. L., and Carr, T. R., 2010, Lithostratigraphy and Petrophysics of the Devonian
747 Marcellus Interval in West Virginia and Southwestern Pennsylvania, in T. R. Carr and
748 N. C. Rosen, eds., *Unconventional Resources: Making the Unconventional*
749 *Conventional*, Gulf Coast Section SEPM, Publication that is the product of the 29th Bob
750 F. Perkins Research Conference, December 6-8, 2009 in Houston, Texas, USA. p. 254-
751 281,
- 752 Brett, C. E., Dick, V. B., Baird, G.C., 1991: Comparative taphonomy and paleoecology of
753 Middle Devonian dark gray and black shales facies from western New York in *Dynamic*
754 *Stratigraphy and Depositional Environments of the Hamilton Group (Middle Devonian)*
755 *in New York State*, Part II: *New York State Museum Bulletin*, v. 469, p. 5 –36.
- 756 Bruner, K., and Smosna, R., 2010, A Comparative Study of the Mississippian Barnett Shale, Fort
757 Worth Basin, and Devonian Marcellus Shale, Appalachian Basin: *National Energy*
758 *Technology Laboratory report*, 106 p.
- 759 Byers, C. W., 1977, Biofacies patterns in euxinic basins: a general model in *Deep Water*
760 *Carbonate Environments*. *Society of Economic Paleontologists and Mineralogists: Tulsa*,
761 p. 5 – 17.
- 762 Calvert, S. E., and Piper, D. Z., 1984, Geochemistry of ferromanganese nodules from Dorganic
763 matterES site a, Northern Equatorial Pacific: Multiple diagenetic metal sources in the
764 deep sea: *Geochimica et Cosmochimica Acta*, v. 48, no. 10, p. 1913-1928.
- 765 Calvert, S. E., Bustin, R. M., and Pedersen, T. F., 1992, Lack of evidence for enhanced
766 preservation of sedimentary organic matter in the oxygen minimum of the Gulf of
767 California: *Geology*, v. 20, no. 8, p. 757-760.

- 768 Calvert, S. E., and Pedersen, T. F., 1993, Geochemistry of Recent oxic and anoxic marine
769 sediments: Implications for the geological record: *Marine Geology*, v. 113, no. 1–2, p.
770 67–88.
- 771 Calvert, S. E., Thode, H. G., Yeung, D., and Karlin, R. E., 1996, A stable isotope study of pyrite
772 formation in the Late Pleistocene and Holocene sediments of the Black Sea:
773 *Geochimica et Cosmochimica Acta*, v. 60, no. 7, p. 1261–1270.
- 774 Calvert S. E., Pedersen T. F., and Karlin R. E., 2001, Geochemical and isotopic evidence for
775 post-glacial palaeoceanographic changes in Saanich Inlet, British Columbia: *Marine*
776 *Geology*, v. 174, p. 278–305.
- 777 Calvert S. E., Pedersen T. F., 2007, Elemental proxies for palaeoclimatic and
778 palaeoceanographic variability in marine sediments: Interpretation and application:
779 *Methods in Late Cenozoic Paleoceanography*. Elsevier, New York, p. 567–644.
- 780 Canfield, D. E., Raiswell, R., Westrich, J. T., Reaves, C. M. and Berner, R. A., 1986, The use of
781 chromium reduction in the analysis of reduced inorganic sulfur in sediments and shales.
782 *Chemical Geology*, v. 54, p. 149–155.
- 783 Canfield, D. E., and Teske, A., 1996, Late Proterozoic rise in atmospheric oxygen concentration
784 inferred from phylogenetic and sulphur-isotope studies: *Nature*, v. 382, no. 6587, p. 127–
785 132.
- 786 Canfield, D. E., 2001, Biogeochemistry of Sulfur Isotopes: *Reviews in Mineralogy and*
787 *Geochemistry*, v. 43, no. 1, p. 607–636.
788
- 789 Chen, D., Wang, J., Racki, G., Li, H., Wang, C., Ma, X., Whalen, M., 2013, Large sulphur
790 isotopic perturbations and oceanic changes during the Frasnian-Famennian transition of
791 the Late Devonian: *Journal of the Geological Society*, v. 170, p. 465–476.
- 792 Chen, R., Sharma, S., Bank, T., Soeder, D., and Eastman, H., 2015, Comparison of isotopic and
793 geochemical characteristics of sediments from a gas- and liquids-prone wells in
794 Marcellus Shale from Appalachian Basin, West Virginia: *Applied Geochemistry*, v. 60,
795 p. 59–71.
- 796 Clark L. L., Ingall, E.D. and Benner, R. 1998, Marine phosphorus is selectively remineralized.
797 *Nature* 393:426.
- 798 Cooper, G. A., 1930, Stratigraphy of the Hamilton Group of New York, part I: *American Journal*
799 *of Science*, 5th series, v. 19, no. 110, p. 116–134.
- 800 Crusius, J., Calvert, S., Pedersen, T., and Sage, D., 1996, Rhenium and molybdenum
801 enrichments in sediments as indicators of oxic, suboxic and sulfidic conditions of
802 deposition: *Earth and Planetary Science Letters*, v. 145, no. 1–4, p. 65–78.
- 803 Dean, W. E., Gardner, J. V., and Piper, D. Z., 1997, Inorganic geochemical indicators of glacial-
804 interglacial changes in productivity and anoxia on the California continental margin:
805 *Geochimica et Cosmochimica Acta*, v. 61, no. 21, p. 4507–4518.

- 806 DeBond, N., Oakes, R. L., Paytan, A., and Wortmann, U. G., 2012, Early Aptian carbon and
807 sulphur isotope signatures at ODP Site 765: Isotopes in Environmental and Health
808 Studies, v. 48, no. 1, p. 180-194.
- 809 Demaison, G. J., and Moore, G. T., 1980, Anoxic environments and oil source bed genesis:
810 Organic Geochemistry, v. 2, no. 1, p. 9-31.
- 811 de Witt, Wallace, Jr., Roen, J.B., and Wallace, L.G., 1993, Stratigraphy of Devonian black shales
812 and associated rocks in the Appalachian basin, IN Roen, J.B., and Kepferle, R.C., eds.,
813 Petroleum geology of the Devonian and Mississippian black shale of eastern North
814 America: U.S. Geological Survey Bulletin, 1909-B, p. B1-B57.
- 815 Dill, H., 1986, Metallogenesis of early Paleozoic graptolite shales from the Graefenthal Horst
816 (northern Bavaria-Federal Republic of Germany): Economic Geology, v. 81, no. 4, p.
817 889-903.
- 818 Drake, H., Astrom, M. E., Heim, C., Broman, C., Astrom, J., Whitehouse, M., Ivarsson, M.,
819 Siljestrom, S., and Sjoval, P., 2015, Extreme ^{13}C depletion of carbonates formed
820 during oxidation of biogenic methane in fractured granite: Nature Communications, v.
821 6.
- 822 Engelder, T., 2008, Structural geology of the Marcellus and other Devonian gas shales: AAPG-
823 SEG Eastern Section Meeting Field Trip (Oct. 11-12, 2008).
- 824 Ettensohn, F. R., Barron, L.S., 1981, Depositional model for the Devonian–Mississippian black
825 shales of North America: a paleoclimatic–paleogeographic approach. In: Roberts, T.C.
826 (Ed.), Geological Society of America Cincinnati '81 Field Trip Guidebooks, Volume II:
827 Economic Geology, p. 344–361.
- 828 Ettensohn, F. R., 1985a, The Catskill Delta complex and the Acadian Orogeny: a model. In:
829 Woodrow, D.L., Sevon, W.D. (Eds.), The Catskill Delta: Geological Society of America
830 Special Paper, v. 201, p. 39– 49.
- 831 Ettensohn, F. R., 1985b, Controls on development of Catskill Delta complex basin-facies. In:
832 Woodrow, D.L., Sevon, W.D. (Eds.), The Catskill Delta: Geological Society of America
833 Special Paper, v. 201, p. 65– 77.
- 834 Ettensohn, F. R., 1992, Controls on the origin of the Devonian-Mississippian oil and gas shales,
835 east-central United States: Fuel, v. 71, no. 12, p. 1487-1492.
- 836 Freeman, K. H., 2001, Isotopic Biogeochemistry of Marine Organic Carbon: Reviews in
837 Mineralogy and Geochemistry, v. 43, no. 1, p. 579-605.
- 838 Ganeshram R. S., Pedersen T. F., Calvert S. E. and Murray J. W., 1995, Large changes in
839 oceanic nutrient inventories from glacial to interglacial periods: Nature, v. 376, p. 755–
840 758.
- 841 Ganeshram R. S., Pedersen T. F., Calvert S. E., McNeill G. W. and Fontugne M. R., 2000,
842 Glacial–interglacial variability in denitrification in the world’s oceans: causes and
843 consequences: Paleoceanography, v. 15, p. 361–376.

844 Ganeshram R. S., Pedersen T. F., Calvert S. E. and Francois R., 2002, Reduced nitrogen fixation
845 in the glacial ocean inferred from changes in marine nitrogen and phosphorus
846 inventories: *Nature*, v. 415, p. 156–159.

847 Garvine, R. W., 1984, Radial spreading of buoyant surface plumes in coastal waters: *Journal of*
848 *Geophysical Research*, v. 89, p. 1989-1996.

849 Gautier, D. L., 1986, Cretaceous shales from the western interior of North America:
850 Sulfur/carbon ratios and sulfur-isotope composition: *Geology*, v. 14, no. 3, p. 225-228

851 Goni, M. A., Ruttenger, K. C., and Eglinton, T. I., 1997, Sources and contribution of
852 terrigenous organic carbon to surface sediments in the Gulf of Mexico: *Nature*, v. 389,
853 no. 6648, p. 275-278.

854 Gray, K. R. and Biddlestone, A. J., 1973, Composting process parameters: *The Chemical*
855 *Engineer*, v. 2, p. 71-76.

856 Herguera, J. C., and Berger, W. H., 1991, Paleoproductivity from benthic foraminifera
857 abundance: Glacial to postglacial change in the west-equatorial Pacific: *Geology*, v. 19,
858 no. 12, p. 1173-1176.

859 Himmler, T., Brinkmann, F., Bohrmann, G., and Peckmann, J., 2011, Corrosion patterns of seep-
860 carbonates from the eastern Mediterranean Sea: *Terra Nova*, v. 23, no. 3, p. 206-212.

861 Holmden, C., Creaser, R. A., Muehlenbachs, K., Leslie, S. A., and Bergström, S. M., 1998,
862 Isotopic evidence for geochemical decoupling between ancient epeiric seas and
863 bordering oceans: Implications for secular curves: *Geology*, v. 26, no. 6, p. 567-570.

864 Ingall, E. D., Bustin, R. M. and Van Cappellen, P., 1993, Influence of water column anoxia on
865 the burial and preservation of carbon and phosphorus in marine shales: *Geochimica et*
866 *Cosmochimica Acta*, v. 57, p. 303-316.

867 Ingall, E. and Jahnke R., 1994, Evidence for enhanced phosphorus regeneration from sediments
868 overlain by oxygen depleted waters: *Geochimica et Cosmochimica Acta*, v. 58, p.
869 2571-2575.

870 Ingall E. and Jahnke R., 1997, Influence of water column anoxia on the elemental fractionation
871 of carbon and phosphorus during sediment diagenesis: *Marine Geology*, v. 139, p. 219-
872 229.

873 Ingall, E. Kolowith, L., Lyons, T. and Hurtgen, M. 2005, Sediment carbon, nitrogen and
874 phosphorus cycling in an Anoxic Fjord, Effingham Inlet, British Columbia: *American*
875 *Journal of Science*, v.305, p. 240-258.

876 Jaminski, J., Algeo, T.J., Maynard, J.B., and Hower, J.C., 1997, Climatic origin of dm-scale
877 compositional cyclicity in the Upper Devonian Cleveland Member of the Ohio Shale,
878 central Appalachian Basin. In: Algeo, T.J., and Maynard, J.B. (Eds.), 1997. *Cyclic*
879 *Sedimentation of Appalachian Devonian and Midcontinent Pennsylvanian Black Shales:*
880 *Analysis of Ancient Anoxic Marine Systems—A Combined Core and Field Workshop:*

- 881 Joint Meeting of Eastern Section AAPG and The Society for Organic Petrography
882 (TSOP), Lexington, Kentucky, Sept. 27-28, 1997, p. 26-62.
- 883 Jaminski, J., Algeo, T.J., Maynard, J.B., and Hower, J.C., 1998, Climatic origin of dm-scale
884 compositional cyclicity in the Cleveland Member of the Ohio Shale (Upper Devonian),
885 Central Appalachian Basin, USA. In: Schieber, J., Zimmerle, W., and Sethi, P.S., eds.,
886 Shales and Mudstones, v. 1: Stuttgart, Schweizerbart'sche, p. 217-242.
- 887 Jenkyns H. C., Grocke D. R., and Hesselbo S. P., 2001, Nitrogen isotopic evidence for water
888 mass denitrification during the early Toarcian (Jurassic) oceanic anoxic event:
889 Paleocyanography, v. 16, p. 593–603.
- 890 Junium, C. K., and Arthur, M. A., 2007, Nitrogen cycling during the Cretaceous, Cenomanian-
891 Turonian Oceanic Anoxic Event II: Geochemistry, Geophysics, Geosystems, v. 8, n. 3.
- 892 Kampschulte, A., and Strauss, H., 2004, The sulfur isotopic evolution of Phanerozoic seawater
893 based on the analysis of structurally substituted sulfate in carbonates: Chemical Geology,
894 v. 204, no. 3–4, p. 255-286.
- 895 Kienast S. S., Calvert S. E., and Pedersen T. F., 2002, Nitrogen isotope and productivity
896 variations along the northeast Pacific margin over the last 120 kyr: surface and
897 subsurface paleocyanography: Paleocyanography, v. 17, PA1055.
- 898 Knossow, N., Blonder, B., Eckert, W., Turchyn, A., Antler, G., and Kamysny, A., 2015, Annual
899 sulfur cycle in a warm monomictic lake with sub-millimolar sulfate concentrations:
900 Geochemical Transactions, v. 16, no. 1, p. 7.
- 901 Kohl, D., Slingerland, R., Arthur, M., Bracht, R., and Engelder, T., 2014, Sequence stratigraphy
902 and depositional environments of the Shamokin (Union Springs) Member, Marcellus
903 Formation, and associated strata in the middle Appalachian Basin: American
904 Association of Petroleum Geologists Bulletin, v. 98, no. 3, p. 483-513.
- 905 Large, R. R., Halpin, J. A., Danyushevsky, L. V., Maslennikov, V. V., Bull, S. W., Long, J. A.,
906 Gregory, D. D., Lounejeva, E., Lyons, T. W., Sack, P. J., McGoldrick, P. J., and Calver,
907 C. R., 2014, Trace element content of sedimentary pyrite as a new proxy for deep-time
908 ocean–atmosphere evolution: Earth and Planetary Science Letters, v. 389, p. 209-220.
- 909 Lash, G. G., and T. Engelder, 2008, Marcellus Shale subsurface stratigraphy and thickness
910 trends: Eastern New York to northeastern West Virginia (abs.): American Association of
911 Petroleum Geologists Eastern Section Meeting: http://www.papgrocks.org/lash_p.pdf
912 (accessed September 18, 2009).
- 913 Lash, G. G., and T. Engelder. 2011, Thickness trends and sequence stratigraphy of the Middle
914 Devonian Marcellus Formation, Appalachian Basin: Implications for Acadian foreland
915 basin evolution. American Association of Petroleum Geologists Bulletin, v. 95, p. 61-
916 103.

- 917 Lash, G. G., and Blood, D. R., 2014, Organic matter accumulation, redox, and diagenetic history
918 of the Marcellus Formation, southwestern Pennsylvania, Appalachian basin: *Marine and*
919 *Petroleum Geology*, v. 57, p. 244-263.
- 920 Lehmann, M. F., Bernasconi, S. M., Barbieri, A., and McKenzie, J. A., 2002, Preservation of
921 organic matter and alteration of its carbon and nitrogen isotope composition during
922 simulated and in situ early sedimentary diagenesis: *Geochimica et Cosmochimica Acta*,
923 v. 66, no. 20, p. 3573-3584.
- 924 Louis-Schmid, B., Rais, P., Schaeffer, P., Bernasconi, S.M., and Weissert, H., 2007, Plate
925 tectonic trigger of changes in pCO₂ and climate in the Oxfordian (Late Jurassic):
926 Carbon isotope and modeling evidence: *Earth and Planetary Science Letters*, v. 258, p.
927 44-60.
- 928 Lyons, T. W., 1997, Sulfur isotopic trends and pathways of iron sulfide formation in upper
929 Holocene sediments of the anoxic Black Sea: *Geochimica et Cosmochimica Acta*, v.
930 61, no. 16, p. 3367-3382.
- 931 Lyons, T. W., Werne, J. P., Hollander, D. J., and Murray, R. W., 2003, Contrasting sulfur
932 geochemistry and Fe/Al and Mo/Al ratios across the last oxic-to-anoxic transition in the
933 Cariaco Basin, Venezuela: *Chemical Geology*, v. 195, no. 1-4, p. 131-157.
- 934 Lyons, T. W., and Severmann, S., 2006, A critical look at iron paleoredox proxies: New insights
935 from modern euxinic marine basins: *Geochimica et Cosmochimica Acta*, v. 70, no. 23,
936 p. 5698-5722.
- 937 Lyons, T. W., Anbar, A. D., Severmann, S., Scott, C., and Gill, B. C., 2009, Tracking Euxinia in
938 the Ancient Ocean: A Multiproxy Perspective and Proterozoic Case Study: *Annual*
939 *Review of Earth and Planetary Sciences*, v. 37, no. 1, p. 507-534.
- 940 Maynard, J. B., 1981, Carbon isotopes as indicators of dispersal patterns in Devonian-
941 Mississippian shales of the Appalachian Basin: *Geology*, v. 9, no. 6, p. 262-265.
- 942 Macquaker, J., McIlroy, D., Davies, S. J., Keller, M. A., 2009, Not Anoxia! How Do You
943 Preserve Organic Matter Then? *American Association of Petroleum Geologists Annual*
944 *Convention and Exhibition*, Denver, Colorado, June 7-10, 2009.
- 945 Morford, J. L., and Emerson, S., 1999, The geochemistry of redox sensitive trace metals in
946 sediments: *Geochimica et Cosmochimica Acta*, v. 63, no. 11-12, p. 1735-1750.
- 947 Morford, J. L., Martin, W. R., François, R., and Carney, C. M., 2009, A model for uranium,
948 rhenium, and molybdenum diagenesis in marine sediments based on results from
949 coastal locations: *Geochimica et Cosmochimica Acta*, v. 73, no. 10, p. 2938-2960.
- 950 Murphy, A. E., Sageman, B. B., and Hollander, D. J., 2000a, Eutrophication by decoupling of the
951 marine biogeochemical cycles of C, N, and P: A mechanism for the Late Devonian
952 mass extinction: *Geology*, v. 28, no. 5, p. 427-430.
- 953 Murphy, A. E., Sageman, B. B., Hollander, D. J., Lyons, T. W., and Brett, C. E., 2000b, Black
954 shale deposition and faunal overturn in the Devonian Appalachian Basin: *Clastic*

955 starvation, seasonal water-column mixing, and efficient biolimiting nutrient recycling:
 956 *Paleoceanography*, v. 15, no. 3, p. 280-291.

957 Murphy, A. E., Sageman, B. B., Hollander, D. J., Straeten Ver, C. A., 2000c, Organic carbon
 958 burial and faunal dynamics in the Appalachian basin during the Devonian
 959 (Givetian-Famennian) greenhouse: an integrated paleoecological/ biogeochemical
 960 approach. In: Huber, B., MacLeod, K., Wing, S. (Eds.): *Warm Climates in Earth
 961 History*, Cambridge University Press, p. 351-385.

962 Nash, D. B., 1994, Effective sediment-transporting discharge from magnitude-frequency analysis:
 963 *Journal of Geology*, v. 102, p. 79-95.

964 Nyahay, R., Leone, J., Smith, L. B., Martin, J. P., Jarvie, D. J., 2007, Update on Regional
 965 Assessment of Gas Potential in the Devonian Marcellus and Ordovician Utica Shales of
 966 New York: AAPG Eastern Section Meeting, September 16-18, Lexington, Kentucky

967 Parrish, C. B., 2013, Insights into the Appalachian Basin Middle Devonian Depositional System
 968 from U-Pb Zircon Geochronology of Volcanic Ashes in the Marcellus Shale and
 969 Onondaga Limestone, unpublished master's thesis.

970 Pedersen, T. F., and Calvert, S. E., 1990, Anoxia vs productivity; what controls the formation of
 971 organic-carbon-rich sediments and sedimentary rocks?: *AAPG Bulletin*, v. 74, no. 4, p.
 972 454-466.

973 Pedersen, T. F., Pickering, M., Vogel, J. S., Southon, J. N., and Nelson, D. E., 1988, The
 974 response of benthic foraminifera to productivity cycles in the eastern equatorial Pacific:
 975 Faunal and geochemical constraints on glacial bottom water oxygen levels:
 976 *Paleoceanography*, v. 3, no. 2, p. 157-168.

977 Pichevin, L., Bertrand, P., Boussafir, M., and Disnar, J.-R., 2004, Organic matter accumulation
 978 and preservation controls in a deep sea modern environment: an example from
 979 Namibian slope sediments: *Organic Geochemistry*, v. 35, no. 5, p. 543-559.

980 Prah, F. G., Ertel, J. R., Goni, M. A., Sparrow, M. A., and Eversmeyer, B., 1994, Terrestrial
 981 organic carbon contributions to sediments on the Washington margin: *Geochimica et
 982 Cosmochimica Acta*, v. 58, no. 14, p. 3035-3048.

983 Price, F. T., and Shieh, Y. N., 1979, Fractionation of sulfur isotopes during laboratory synthesis
 984 of pyrite at low temperatures: *Chemical Geology*, v. 27, no. 3, p. 245-253.

985 Quan, T. M., van de Schootbrugge, B., Field, M. P., Rosenthal, Y., and Falkowski, P. G., 2008,
 986 Nitrogen isotope and trace metal analyses from the Mingolsheim core (Germany):
 987 Evidence for redox variations across the Triassic-Jurassic boundary: *Global
 988 Biogeochemical Cycles*, v. 22, no. 2, p. GB2014.

989 Quan, T. M., and Falkowski, P. G., 2009, Redox control of N: P ratios in aquatic ecosystems:
 990 *Geobiology*, v. 7, p. 124-139.

- 991 Quan, T. M., Wright, J. D., and Falkowski, P. G., 2013a, Co-variation of nitrogen isotopes and
992 redox states through glacial–interglacial cycles in the Black Sea: *Geochimica et*
993 *Cosmochimica Acta*, v. 112, no. 0, p. 305-320.
- 994 Quan, T. M., Adigwe, E. N., Riedinger, N., and Puckette, J., 2013b, Evaluating nitrogen isotopes
995 as proxies for depositional environmental conditions in shales: Comparing Caney and
996 Woodford Shales in the Arkoma Basin, Oklahoma: *Chemical Geology*, v. 360–361, no.
997 0, p. 231-240.
- 998 Redfield, A. C., 1942, The processes determining the concentration of oxygen, phosphate and
999 other organic derivatives within the depths of the Atlantic Ocean, Cambridge, Mass.,
1000 Massachusetts Institute of Technology ;, Contribution ... from the Woods Hole
1001 Oceanographic Institution ;.
- 1002 Rimmer, S. M., Thompson, J. A., Goodnight, S. A., and Robl, T. L., 2004, Multiple controls on
1003 the preservation of organic matter in Devonian–Mississippian marine black shales:
1004 geochemical and petrographic evidence: *Palaeogeography, Palaeoclimatology,*
1005 *Palaeoecology*, v. 215, no. 1–2, p. 125-154.
- 1006 Ruttenberg, K. C., and Goñi, M. A., 1997, Phosphorus distribution, C:N:P ratios, and $\delta^{13}\text{C}_{\text{org}}$ in
1007 arctic, temperate, and tropical coastal sediments: tools for characterizing bulk
1008 sedimentary organic matter: *Marine Geology*, v. 139, no. 1–4, p. 123-145.
- 1009 Sageman, B. B., Murphy, A. E., Werne, J. P., Ver Straeten, C. A., Hollander, D. J., and Lyons, T.
1010 W., 2003, A tale of shales: the relative roles of production, decomposition, and dilution
1011 in the accumulation of organic-rich strata, Middle–Upper Devonian, Appalachian basin:
1012 *Chemical Geology*, v. 195, no. 1–4, p. 229-273.
- 1013 Saltzman, M. R., 2005, Phosphorus, nitrogen, and the redox evolution of the Paleozoic oceans:
1014 *Geology*, v. 33, no. 7, p. 573-576.
- 1015 Schieber, J., 1994, Evidence for episodic high energy events and shallow water deposition in the
1016 Chattanooga Shale, Devonian, central Tennessee, U.S.A: *Sedimentary Geology*, v. 93,
1017 p. 193-208.
- 1018 Schieber, J., 2003, Simple gifts and hidden treasures – Implications of finding bioturbation and
1019 erosion surfaces in black shales: *The Sedimentary Record*, v. 1, p. 4-8.
- 1020 Schieber, J., 2009, Discovery of Agglutinated Benthic Foraminifera in Devonian Black Shales
1021 and Their Relevance for the Redox State of Ancient Seas. *Paleogeography,*
1022 *Paleoclimatology, Paleoecology*, v. 271, p. 292-300.
- 1023 Scott, C. T., and Lyons, T. W., 2012, Contrasting molybdenum cycling and isotopic properties in
1024 euxinic versus non-euxinic sediments and sedimentary rocks: Refining the paleoproxies:
1025 *Chemical Geology*, v. 324-325, p. 19-27.
- 1026 Sigman, D. M., Karsh, K. L., and Casciotti, K. L., 2009, Ocean process tracers: Nitrogen
1027 isotopes in the ocean: *Encyclopedia of ocean science*, 2nd edn. Elsevier, Amsterdam.

- 1028 Soeder, D. J., Enomoto, C. B., and Chermak, J. A., 2014, The Devonian Marcellus Shale and
1029 Millboro Shale: GSA Field Guides, v. 35, p. 129-160.
- 1030 Spofforth, D.J.A., Agnini, C., Pálke, H., Rio, D., Fornaciari, E., Giusberti, L., Luciani, V.,
1031 Lanci, L. and Muttoni, G., 2010, Organic Carbon Burial following the Middle Eocene
1032 Climatic Optimum (MECO) in the central - western Tethys: *Paleoceanography*, v. 25,
1033 PA3210.
- 1034 Suess, E., and Whiticar, M. J., 1989, Methane-derived CO₂ in pore fluids expelled from the
1035 Oregon subduction zone: *Paleogeography, Paleoclimatology, Paleoecology*, v. 71, p.119-
1036 136.
- 1037 Suits, N. S., and Wilkin, R. T., 1998, Pyrite formation in the water column and sediments of a
1038 meromictic lake: *Geology*, v. 26, no. 12, p. 1099-1102.
- 1039 Swanson, V. E., 1961, *Geology and geochemistry of uranium in marine black shales : a review*,
1040 Washington, U.S. Govt. Print. Off., Uranium in carbonaceous rocks.
- 1041 Talbot, M., 2001, Nitrogen Isotopes in Palaeolimnology, in Last, W., and Smol, J., eds.,
1042 *Tracking Environmental Change Using Lake Sediments, Volume 2*, Springer
1043 Netherlands, p. 401-439.
- 1044 Tribouvillard, N., Algeo, T. J., Lyons, T., and Riboulleau, A., 2006, Trace metals as paleoredox
1045 and paleoproductivity proxies: An update: *Chemical Geology*, v. 232, no. 1-2, p. 12-32.
- 1046 Tribouvillard, N., Algeo, T. J., Baudin, F., and Riboulleau, A., 2012, Analysis of marine
1047 environmental conditions based on molybdenum–uranium covariation—Applications to
1048 Mesozoic paleoceanography: *Chemical Geology*, v. 324–325, p. 46-58.
- 1049 Tuite, M. L., and Macko, S. A., 2009, Terrestrial P and Reactive N and Marine Productivity in
1050 the Late Devonian Appalachian Basin: AGU Fall Meeting Abstracts 12/2009.
- 1051 Tuite, M. L., and Macko, S. A., 2013, Basinward nitrogen limitation demonstrates role of
1052 terrestrial nitrogen and redox control of $\delta^{15}\text{N}$ in a Late Devonian black shale: *Geology*,
1053 v. 41, no. 10, p. 1079-1082.
- 1054 Tyson, R. V. (2005). The "productivity versus preservation" controversy: cause, flaws, and
1055 resolution. *SPECIAL PUBLICATION-SEPM*, 82, 17-33.
- 1056 van Hengstum, P. J., and Gröcke, D. R., 2008, Stable isotope record of the Eifelian–Givetian
1057 boundary Kačák– otomari Event (Middle Devonian) from Hungry Hollow, Ontario,
1058 Canada: *Canadian Journal of Earth Sciences*, v. 45, n. 3, p. 353-366
- 1059 Wang, L., Shi, X., and Jiang, G., 2012, Pyrite morphology and redox fluctuations recorded in the
1060 Ediacaran Doushantuo Formation: *Palaeogeography, Palaeoclimatology, Palaeoecology*,
1061 v. 333–334, p. 218-227.
- 1062 Werne, J. P., Sageman, B. B., Lyons, T. W., and Hollander, D. J., 2002, An integrated
1063 assessment of a “type euxinic” deposit: Evidence for multiple controls on black shale

1064 deposition in the middle Devonian Oatka Creek formation: American Journal of
1065 Science, v. 302, no. 2, p. 110-143.

1066 Werne, J. P., 2007, Effects of Variable Redox Conditions on Nutrient Regeneration during
1067 Organic Matter Remineralization: 23rd International Meeting on Organic Geochemistry,
1068 Torquay, England. September, 2007.

1069 Whiticar, M. J., and Faber, E., 1986, Methane oxidation in sediment and water column
1070 environments: Organic Geochemistry, v. 10, p. 759-768.

1071 Wilde, P., and Berry, W. B. N., 1984, Destabilization of the oceanic density structure and its
1072 significance to marine “extinction” events: Palaeogeography, Palaeoclimatology,
1073 Palaeoecology, v. 48, no. 2–4, p. 143-162.

1074 Wignall, P. B., and Newton, R., 1998, Pyrite framboid diameter as a measure of oxygen
1075 deficiency in ancient mudrocks: American Journal of Science, v. 298, p. 537-552.

1076 Zheng, Y., Anderson, R. F., van Geen, A., and Kuwabara, J., 2000, Authigenic molybdenum
1077 formation in marine sediments: a link to pore water sulfide in the Santa Barbara Basin:
1078 Geochimica et Cosmochimica Acta, v. 64, no. 24, p. 4165-4178.

1079