



## Research paper

# Linking the Acadian Orogeny with organic-rich black shale deposition: Evidence from the Marcellus Shale

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## ABSTRACT

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

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## 1. Introduction

Due to the recent boom in shale gas production in the Appalachian basin, United States, the natural gas-rich Marcellus Shale has drawn tremendous attention from the geoscience community. Well production data have shown that the ‘gas-rich’ zones within the Marcellus Shale are often associated with high total organic carbon (TOC) content (Milliken et al., 2013). Many studies have tried to understand the mechanisms of organic matter enrichment during black shale deposition (e.g., Ettensohn, 1985; Pedersen and Calvert, 1990; Sageman et al., 2003; Rimmer et al., 2004; Ver Straeten, 2009, 2010; Chen et al., 2015; Chen and Sharma, 2016). It has long been recognized that enrichment of organic matter in fine-grained

sediments such as shale is directly affected by several processes like 1) rate of sediment input, 2) water column redox conditions; and 3) primary productivity (e.g., Pedersen and Calvert, 1990; Werne et al., 2002; Sageman et al., 2003; Rimmer et al., 2004; Lash and Blood, 2014). In addition, a recent study Chen and Sharma (2016) also suggested that nutrient recycling is driven by alternating water column redox conditions might have also played a key role in the formation of the organic-rich zone in the Marcellus Shale.

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

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black shale in the Acadian foreland basin. Further, we tried to establish direct linkage (i.e., temporal and geochemical correlations) between these processes and sedimentary records preserved in the Marcellus Shale in our study area.

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

In terms of the tectonic control on black shale accumulation, a key piece of information still missing is a direct linkage between tectonics and sedimentary records that are independent of other variables (e.g., global sea-level change). Recent studies of volcanic ash layers in the Appalachian Basin reveal that the development of the Acadian Orogeny and the associated foreland basin during Early-Middle Devonian time was associated with multiple phases of volcanism/magmatism within the Acadian mountain (Murphy

et al., 1999; Ver Straeten, 2005; 2008). Based on the relative intensity of magmatism, the Acadian orogeny can be subdivided into three magmatic stages: a magmatic active period that lasted from early Emsian to lower-middle Eifelian (~400–395 Ma), followed by a relatively magmatic quiescent period between ~395 Ma and ~380 Ma which was then succeeded by another magmatic active period from ~380 Ma to ~370 Ma (Murphy et al., 1999).

Signals of the proposed Acadian magmatism were recorded by sediments deposited in the adjacent foreland basin (Hosterman and Whitlow, 1981). It has been found that the Middle to Late Devonian marine shales of the Appalachian Basin contain abundant smectite which is interpreted to be derived from weathered volcanic clast and phenocrystals, indicating a significant sediment contribution from igneous sources (Hosterman and Whitlow, 1981). If representative, the shale strata deposited within the Appalachian Basin may likely record the geochemical signals (e.g., trace and rare earth element content) of the Acadian magmatism. It has been shown that partial melting of crustal rocks during magmatism can cause enrichment of light rare earth elements (i.e., La-Sm) in the newly formed magma (Lipin and McKay, 1989), which later migrates upward toward the surface, forming intrusive or extrusive igneous rocks. Therefore, the newly formed igneous rocks should bear REE composition different from the source region. Weathering of these rocks would then transport the REE signals into the adjacent sedimentary basin. There is little fractionation of REE during weathering of parent rocks or during subsequent sediment transportation (e.g., Condie, 1991). As such, it is obvious that the REE compositions of fine-grained rocks formed by deposition and lithification of these weathered sediments would resemble the REE signature of their sediment source. Therefore, we hypothesized that if the OC-rich black shale deposition in the Appalachian foreland basin was directly related to the Acadian orogeny, we should observe a correlation between the Acadian magmatic signals and organic carbon enrichment in the shale.

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

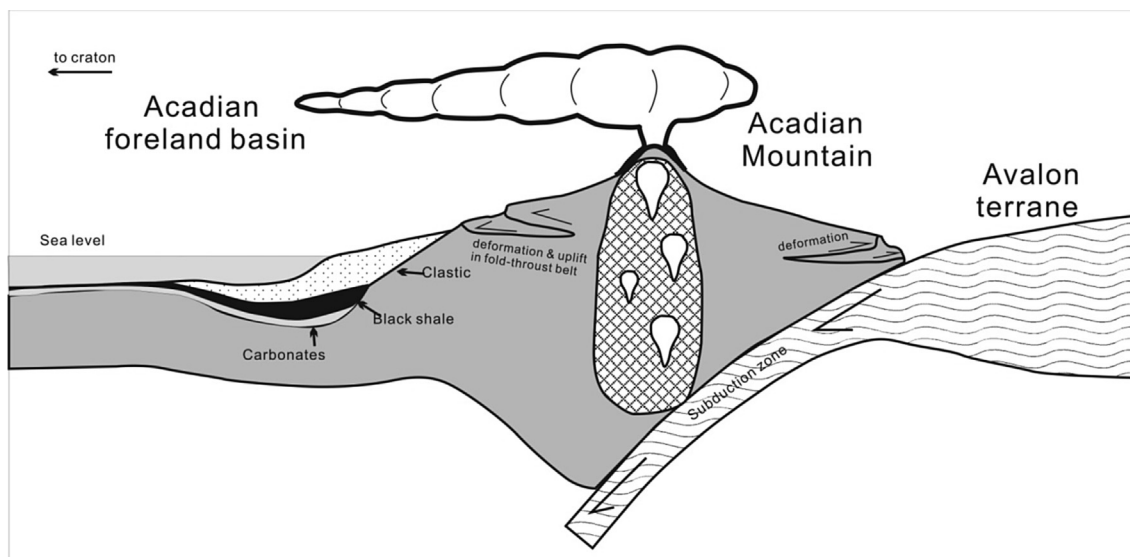


Fig. 1. A tectonic model of the Acadian Orogen and the associated foreland basin (modified from Ver Straeten, 2009).

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