

# EXPLORING THE SUITABILITY OF THE MIDDLE-LATE DEVONIAN ANTRIM SHALE, MICHIGAN BASIN, FOR ORGANIC CARBON ISOTOPIC ANALYSIS

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## INTRODUCTION

### Motivation

The Middle-Late Devonian is distinguished by widely acknowledged biotic phenomena attributed to marine anoxia and perturbations in the carbon cycle (Berner et al., 1995). While these events have been extensively documented in strata of the North American Appalachian Basin (Sageman et al., 2003; Zambito et al., 2016a), more attention needs to be directed toward discerning analogous global biotic occurrences within the neighboring Michigan Basin. To accomplish this, stable isotope geochemistry, more specifically organic carbon isotopes ( $^{12}\text{C}$  and  $^{13}\text{C}$ ), can be applied to establish periods of global warming and cooling (Mackensen et al., 2019). During photosynthesis,  $^{12}\text{C}$  and  $^{13}\text{C}$  are fractionated as plants convert  $\text{CO}_2$  and sunlight into energy. It requires less energy for a plant to incorporate an atom of the lighter isotope  $^{12}\text{C}$  than it does an atom of  $^{13}\text{C}$ ; therefore, the  $\delta^{13}\text{C}$  ratio of materials such as carbonate and organic matter can be used to reconstruct changes to the carbon cycle. However, before such experimental techniques are pursued, the carbon fluxes within an isotope system must be understood. This investigation aims to determine the suitability of  $\delta^{13}\text{C}$  values from organic carbon in Middle-Late Devonian black shale deposits within the Antrim Formation for carbon cycle reconstruction. Since black shale organic matter (OM) is possibly a combination of marine and terrestrial sources, the first step is to utilize elemental proxies for sedimentation to understand terrestrial OM input to the basin. Ultimately, a detailed understanding of local detrital fluxes into the Michigan Basin and potential terrestrial organic carbon input to marine settings is

necessary to place the Michigan Basin carbon isotopic profile within the global framework.

### Background

Black shales are fine-grained, dark-colored, organic carbon-rich sedimentary rocks that are generally composed of clay minerals, quartz silt, organic matter, and kerogen. Most black shales are found in marine settings (Potter et al., 1980), but they can also form in lacustrine depositional systems (Bohacs et al., 2000). Their black color is due to the presence and abundance of organic matter and pyrite; therefore, the reducing environments where pyrite forms suggest black shales require anoxic water column conditions (Sageman et al., 2003). Moreover, carbonates precipitate either directly or indirectly by organic processes. For instance, direct precipitation occurs when animals or plants secrete lime skeletons, while indirect precipitation happens when biochemical changes in water precipitate carbonate as individual crystals (Selley, 2005). Most ancient carbonate deposition takes place in shallow water depths (<10-20 m) as lime-producing organisms require photosynthesis in oxic environments. Additionally, deposition generally arises in environments with low abundances of siliciclastic input as high abundances disrupt light penetration into waters.

The identified transitions between black shales and carbonates across the Michigan Basin indicate changes between these anoxic (black shales) and oxic (carbonates) environmental conditions. Furthermore, depositional transitions between black shales and carbonates are not exclusive to the Michigan Basin, as the Appalachian Basin underwent similar changes in lithologies associated with marine sequences (Brett

and Baird, 1996). While the primary factors directing these cycles are a matter of debate, they are commonly related to eustatic variations, including glacial melt and growth prompted by global climate changes (Johnson et al., 1985). The research undertaken by Gutschick and Sandberg (1991a and 1991b) summarizes the biostratigraphy and depositional history of the Middle-Late Devonian sequence within the Michigan Basin. These studies suggest that depositional events in the Michigan Basin are linked to Devonian eustatic sea-level fluctuations, aligning with Acadian orogenic tectophases and the deposition of the Catskill Delta in the Appalachian Basin.

## GEOLOGIC SETTING

The overall stratigraphy of the Michigan Basin is attributed to a failed rift that occurred ~1.1 bya (Hinze and Chandler, 2020). This process caused weakening in the surrounding lithosphere, and as time progressed, sediment deposition resulted in mass subsidence initiating the formation of the basin. The Late Devonian Michigan Basin emerged as one of several local depressions within the Eastern Interior seaway (Gutschick and Sandberg, 1991a). This body of water occupied the North American craton between the Acadian Mountains and the Transcontinental Arch (Fig. 1). Subsequent basin construction began toward the end of the Middle Devonian due to subsidence driven by the Traverse Group carbonates. The Middle-Late Devonian is characterized by anoxic events associated with perturbations in the global carbon cycle as increased organic carbon production overwhelms the oxygenation of seawater developing organic-rich mud that lithifies to black shale (He et al., 2022). Consequently, units of carbonates and shales transition across the basin and vary in thickness due to accommodation and surrounding terrestrial input (Howell and van der Pluijm, 1999).

This research focuses on the description of the State Chester Welch 18 core within the Middle-Late Devonian Traverse Group and Antrim Formation strata, deposited in the Michigan Basin during the Givetian, Frasnian, and Famennian stages (approximately 385.3 to 359.3 million years ago; Becker et al., 2020). Extracted from the northcentral region of the basin (Fig. 2), the depth of the core

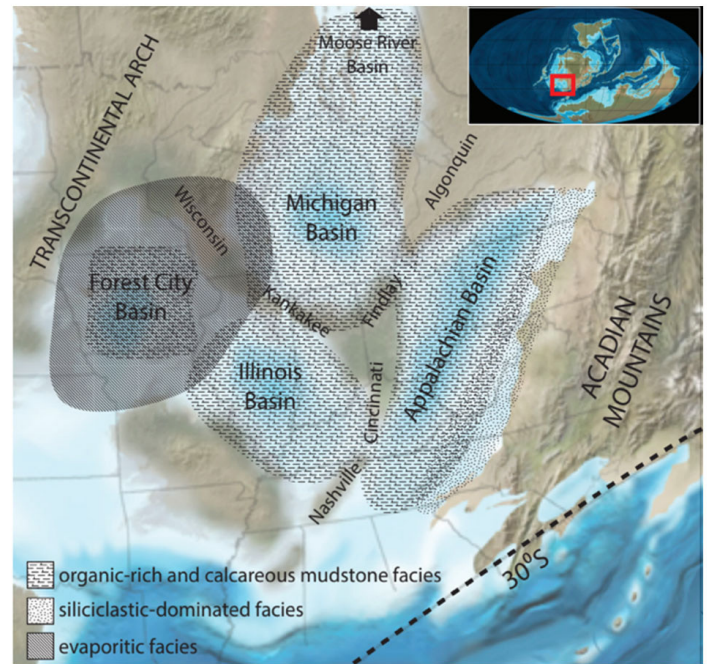


Figure 1. Paleoenvironmental map of the Middle-Late Devonian showcasing various lithologies and depositional locations of the Michigan Basin and surrounding areas. Paleogeographic maps are adapted from Blakey (2013) and Zambito and Voice (this volume).

interval studied ranges from 1,435.1 feet to 1,684.15 feet, with a total length of 249.05 feet.

## METHODS

### Lithology

Core measurements and detailed lithological observations were made at the Michigan Geological Repository for Research and Education (MGRRE). The description of the State Chester Welch 18 involved examination at the macroscopic level, refined to a scale of one-tenth of a foot. Subsequent analysis focused on delineating facies based on criteria including color, effervescence, fossil abundance, mineral assemblage, bioturbation, and diagenetic features. Following this initial characterization, the core was sampled at three-foot (approximately 1 meter) intervals. A Dremel equipped with a diamond-tipped drill bit (model 7123) operating at ~2,000 revolutions per minute (rpm) was employed to cleanse the core's exterior to mitigate potential contamination introduced during the coring process. A total of 79 samples from the State Chester Welch 18 were systematically extracted from the pre-determined locations along the core using a Dremel outfitted with

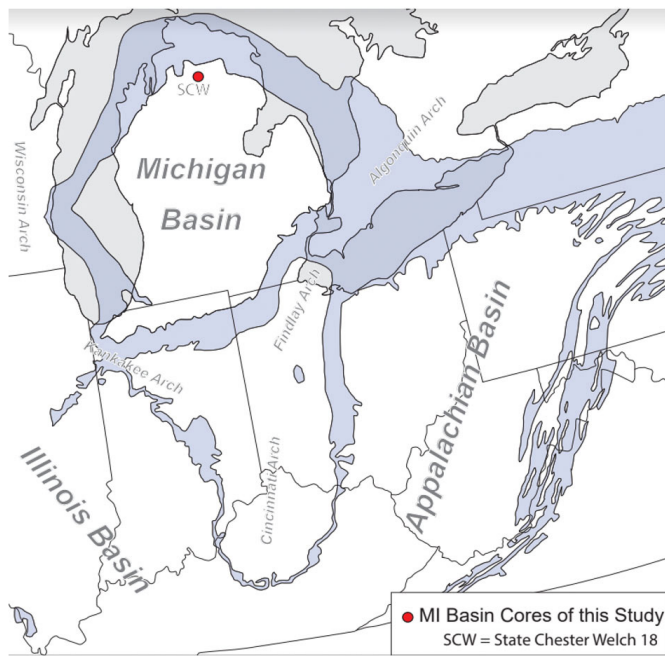


Figure 2. Location of the State Chester Welch 18 drill core used in this study. Purple-gray areas represent the Devonian outcrop belt. Adapted from Zambito and Voice (this volume).

a tungsten carbide drill bit (model 9906) operating at ~5,000 rpm and carefully packaged in 2.0mL plastic vials to preserve their integrity for further analytical procedures.

## Geochemistry

Portable x-ray fluorescence (pXRF) analysis was conducted at the Beloit College Department of Geology to discern the elemental composition of the samples obtained from the core utilizing the Thermo Fisher Scientific Niton XL3t GOLDD+ Handheld XRF Analyzer (see methods in Zambito et al., 2016b). To ensure accurate measurements, calibration of the elemental compositions of each sample was executed following the protocol outlined in Rowe et al. (2012) using standards from the pXRF manufacturer, NIST, and the USGS. Elemental proxies for siliciclastic influx (Si, Si/Al, and K) were used to understand changes in detrital influx through time. Individual powdered samples were prepared at Beloit College for future determination of total organic carbon (TOC) and organic stable carbon isotope ratio ( $\delta^{13}\text{C}$ ).

## RESULTS

### Lithology

The stratigraphy of St. Chester Welch 18 core consists of ~249.05 ft of marine sediments transitioning between black shale and carbonate lithologies (Fig. 3). The sequence begins with ~10 ft of the light gray Traverse Group limestone which hosts many fossils (e.g., corals, crinoids, bryozoan, brachiopods, and stromatoporoid) along with various degrees of bioturbation. The Traverse Group's contact with the "Squaw Bay Formation" is at ~1,674.75 ft. The "Squaw Bay" lithology is represented by shifts between light and dark gray where light gray shales host minor evidence of bioturbation and fossils, few pyrite inclusions, and silt laminations. At ~1,645.5 ft, the "Squaw Bay Formation" transitions into the Antrim Shale. The Antrim Shale in this core is further separated into three members: Norwood, Paxton, and Lachine members. The Norwood Member extends for ~44.35 ft and it is the first of the black shales to be observed. This member is very black in color, has trace amounts of pyrite, and exhibits minor interbedded silt laminations. The contact of the Norwood Member with the Paxton Member is at ~1,601.15 ft. This lithology is generally light gray in color with minor transitions between dark gray, has pyrite inclusions, concretions, small bioturbations, and silt laminations. The contact of the Paxton Member with the Lachine Member is at ~1,560 ft. The Lachine Member is mostly black in color with a slight transition into dark grey towards the top of the member. Throughout the member, there are pyrite inclusions, silt laminations, and a minor bioturbated interval. The contact of the Lachine Member with the Ellsworth Formation is at ~1,478 ft. The Ellsworth Formation is light to dark grey, has abundant silt laminations, and transitions to a dark brown towards the end.

### Geochemistry

Elemental analysis was performed on all 79 powdered core samples at approximately three-foot intervals across the "Squaw Bay Formation", Antrim Shale (Norwood, Paxton, and Lachine), and Ellsworth Formation. Concentrations of elements of interest (Silicon, Aluminum, and Potassium) collected using pXRF were used to make graphs for sedimentation rate proxies, while Total Organic Carbon (TOC) was originally measured and provided by Dellapenna

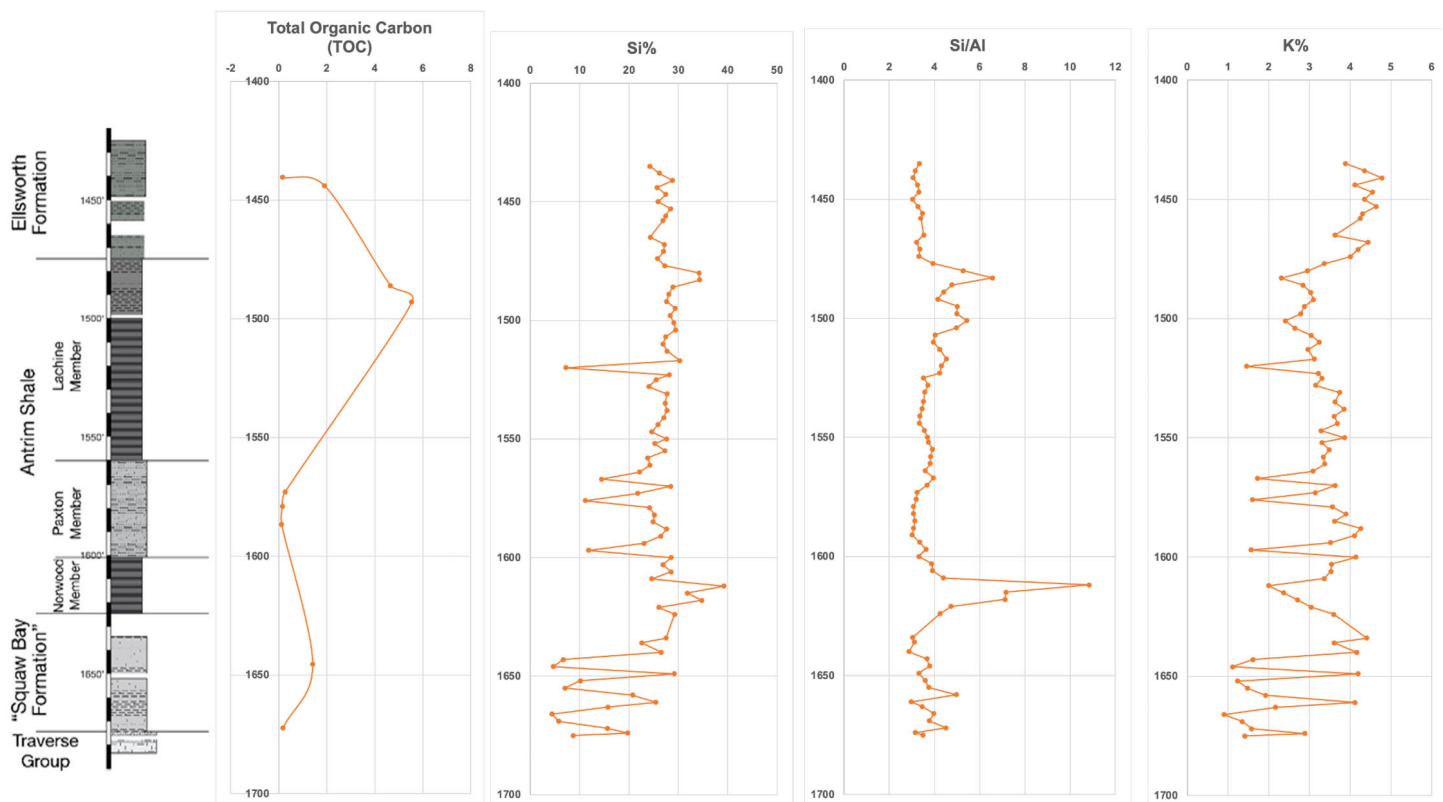


Figure 4. Lithostratigraphy after Zambito and Voice (this volume), Total Organic Carbon (TOC) from Dellapenna (1991), and pXRF trends of the State Chester Welch 18 core showing Si%, Si/Al, and K%.

(1991) as shown in Figure 3. In the “Squaw Bay Formation”, TOC initially increases then gradually decreases around 1%, Si% readily fluctuates between 5% and 30% with an increasing trend overall, Si/Al has minor fluctuations confined to ~3 and 4, and K% has many fluctuations between 1% and 5% with a sharp decrease at the end. In the Norwood Member, TOC decreases gradually, Si% increases to 40% then sharply decreases to ~25%, Si/Al spikes to ~11 and drops back down to 4, and K% decreases to 2% before rapidly increasing to ~4%. In the Paxton Member, TOC continues to decrease until 0% and begins to increase, Si% fluctuates between 10% and 30%, Si/Al is consistently between 3 and 4, and K% fluctuates between 1.5% and 4.25%. In the Lachine Member, TOC continues to increase to ~6% before decreasing, Si% remains relatively consistent between 25% and 30% with a spike down to ~8%, Si/Al stays consistently between 3 and 4 as it increases to ~6.5 and sharply decreases to ~3, and K% has minor fluctuations as it decreases to ~2% with one spike down to 1.5%. In the Ellsworth Formation, TOC continues to decrease before reaching ~0%, Si% is consistently 25% with slight fluctuations, Si/Al is relatively stable around 3, and K% increases to ~4.5% and continues to

have slight fluctuations between 3.5% and 5%.

## DISCUSSION

St. Chester Welch 18 is one of two drill cores analyzed both lithologically and geochemically for organic carbon isotope analytical suitability: the second being the Krocker 1-17 (Giehler et al., this volume). Identical lithological and geochemical methodologies were conducted on the Krocker 1-17 samples. Utilizing the same elemental proxies for detrital input dynamics, initial pXRF analysis shows similar trends in sedimentation rate proxies between the two core locations, suggesting that basin-fill dynamics are spatially consistent.

First, TOC provides context on the depositional environment and the conditions under which sediments were deposited. Second, silica content (Si%) provides a measure of the overall abundance of silicate minerals present (e.g., quartz, feldspar, clay). Third, silica to aluminum ratio (Si/Al) is useful for determining the source rock composition and weathering conditions. For instance, aluminum is commonly found in feldspars and clays, which are

susceptible to weathering, while silica is resistant to weathering. Therefore, high Si/Al ratios suggest minimal weathering and a primary source of silicate material, whereas low ratios suggest intense weathering and removal of aluminum-rich minerals. Fourth, potassium content (K%) gives insight into the overall abundance of potassium-bearing minerals in the detrital sediment (e.g., feldspars). Together, these proxies provide valuable insight into the detrital input dynamics of the Michigan Basin further to identify the suitability of organic carbon isotopic analysis.

In the Norwood, Si%, Si/Al, and K% mostly correspond suggesting predominantly clay mineral deposition, though an anomalously high interval of Si%, Si/Al, and TOC (and low K%) is interpreted as high paleoproductivity and biogenic silica production (radiolarians). In the Paxton, all elemental proxies for sedimentation are relatively consistent through time, indicating minimal detrital flux changes. This suggests that the Paxton is an ideal unit to conduct organic carbon isotopic analysis because of the relative stability of detrital influx within that unit as it does not experience any spikes. This stability facilitates distinguishable differences in future isotope ratio analysis as detrital influx does not contaminate the marine signal.

In the Lachine, the overall trend of increasing Si% and Si/Al and corresponding decreasing K and TOC suggests increased detrital input through time. pXRF data highlights different sources of detrital influx between the Lachine and Ellsworth units. This difference was also noticeable in lithologic results, with a visible difference in color and composition between the two units- the Lachine being a darker, pyritic shale and the Ellsworth having thick, interfingering bands of coarser-grained material. Consistent trends in both cores indicate these patterns are similar across the basin, therefore, this study is more reproducible using additional cores. Ultimately, these trends provide the necessary baseline for future work interpreting organic carbon isotopic data.

## FUTURE WORK

The preliminary lithological and geochemical investigation of the St. Chester Welch 18 core

compared with the Krocker 1-17 core in the Michigan Basin show detrital input dynamics are consistent across time and space. These patterns provide a promising baseline for interpreting organic carbon isotopic data and necessitate further analysis. Ultimately, future work will utilize Total Organic Carbon (TOC) and stable organic carbon isotopes for further assessment of both the Krocker 1-17 and State Chester Welch 18, by conducting isotope ratio mass spectrometry at UC Davis Stable Isotope Facility.

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