# Paleozoic black shale deposition: A lithological, stratigraphical, and geochemical analysis of the Upper Devonian Kettle Point Formation in southwestern Ontario

*Nikole Bingham-Koslowski[1] (nbingham@uwo.ca); Cameron Tsujita[1]; Jisuo Jin[1]; Karem Azmy[2]*

*[1]Department of Earth Sciences, Western University, London, ON, N6A 5B7*

*[2]Department of Earth Sciences, Memorial University, St. John's, NL, A1B 3X9*

## Summary

Despite the recent interest in black shales as alternative hydrocarbon reservoirs, the ancient depoformational environments of these rocks remains enigmatic because of a general lack of modern analogs. This study aims to help elucidate the mechanisms behind the deposition of black shales by using the Upper Devonian Kettle Point Formation as a case study. Detailed core and thin section analyses divulged that the Kettle Point Formation can be subdivided into three lithofacies: interlaminated black shales interbedded with greyish green mudstones and separated by thick intervals of non-interlaminated black shales. Subsurface correlation of the Kettle Point, using gamma ray logs, has revealed thickness variations of these lithofacies that suggest the influence of local tectonic features on their depositional patterns. Major variations in lithology within the succession are attributed to changes in the intensity and vertical extent of anoxia in the marine water column that culminated in the deposition of the thick packages of non-interlaminated black shales during the acme of anoxia. Interbedded interlaminated black shales and greyish green mudstones record lower intensities of oxygen deficiency overall, but fluctuating at a finer level between anoxic and dysoxic conditions respectively. Geochemical analysis based on sulphur isotopes is currently being conducted to further resolve the redox conditions of the paleo-basin. Integration of the lithological, stratigraphical, and geochemical data will result in the determination of the depositional environment of the Kettle Point Formation. This information can then be extrapolated and applied to other syndepositional black shales, contributing to the understanding of possible black shale depositional environments and aiding in the interpretation of ancient global climate change patterns.

## Introduction

Organic-rich, siliciclastic mudrocks, informally called black shales, have traditionally been considered hallmarks of anoxic, deep-water marine conditions (Ozaki et al. 2011); however, recent studies have demonstrated their deposition in a range of aquatic environments from deep to shallow water (Schlanger and Jenkyns 1976; Schieber 1994; 1998; Ozaki et al. 2011). This novel insight has raised questions regarding both the nature and scale of causative factors of large-scale anoxia, as recorded by black shales. It is generally agreed that an abundant source of organic matter and the development of anoxic conditions are required for the formation of black shales (Tourtelot 1979; Arthur and Sageman 1994; Ozaki et al. 2011; Jenkyns 2010), but the relative significance of, and nature of interplay between, these environmental factors in the deposition of organic-rich sediments (ultimately preserved as black shales) remains poorly understood. Furthermore, although the deposition of black shales was relatively common and geographically widespread at various times in the geologic past, particularly during the Paleozoic, modern analogs of such a depositional motif are lacking (Schlanger and Jenkyns 1976; Arthur and Sageman 1994; Jenkyns 2010).

Due to the anoxic requirements of black shales, their presence in the rock record used to automatically be interpreted as reflecting deposition in deep, stagnant, marine waters. Studies have since disproved this outdated notion and demonstrated that, although anoxia can readily form in deep water environments, it is by no means restricted to it. To better understand the conditions and mechanisms required for shallow-water black shale deposition, this study investigates one of the largest, stratigraphically continuous, black shale deposits in Ontario; The Kettle Point Formation. The Kettle Point Formation is a succession of Upper Devonian black shale known from local outcrops in its type area and found throughout the subsurface of southwestern Ontario. The formation was deposited in an epeiric sea during the Acadian Orogeny and is paleogeographically situated between the Appalachian and Michigan Basins, in the Chatham Sag, bounded by the Algonquin and Findlay Arches. The formation contains 40-150 cm in diameter, carbonate concretions called Kettles, after which the formation is named.

## Methods

In order to resolve subsurface stratigraphic architecture and to determine possible vertical lateral relationships among discernible lithofacies, eight cores containing the Kettle Point Formation were logged in detail at the Oil, Gas and Salt Resources Library in London, Ontario. Core analysis focused on lithological, sedimentological and paleontological aspects of the Kettle Point sediments, recording the thickness of multiple lithological units and noting the presence of any visible fossils and/or sedimentary features. Nine samples were collected from core ARGOR 65-1, eight of which were converted into thin sections for micro-sedimentary analysis. The ninth sample was used for scanning electron microscope (SEM) imaging to analyze minute *Tasmanites* fossils found throughout the Kettle Point Formation, as well as to document any other nano-scale features present.

Geophysical data (gamma ray and density logs) was obtained from the Oil, Gas and Salt Resources Library for nineteen cores containing the Kettle Point Formation. Schmocker (1981) (and reiterated by Russell in 1985), demonstrated that gamma ray logs can be used to interpret lithology in Devonian black shales as natural radioactivity correlates to organic content. This relationship was verified in this study when gamma ray signatures were superimposed over detailed core logs and the highs and lows in the gamma ray logs corresponded to organic-rich and organic-poor lithologies respectively. Using this association, it became possible to determine the presence and thickness of the Kettle Point lithofacies in each well and how they varied across the depositional region. Gamma ray signatures were then correlated to create a suite of cross sections through southwestern Ontario using the software Petra.

Additional samples were collected from core OGS KP-18 and are currently being analyzed for stable isotopes in Dr. Karem Azmy's Stable Isotope Lab (CREAIT Network - TERRA Facility) at Memorial University.

## Results

Detailed core and thin section analysis shows that the Kettle Point Formation can be subdivided into three distinct lithofacies: greyish green mudstones, interlaminated black shales, and non-interlaminated black shales. Greyish green mudstones occur interbedded with interlaminated black shales and alternate with thick packages of non-interlaminated black shales. Gamma ray cross sections illustrate that the overall thickness and the spatio-temporal facies continuity of the formation was largely controlled by the presence of two local tectonic arches: the Algonquin and Findlay arches. Furthermore, the correlation of geophysical data, and supported by core analysis, exposed three arch-related trends. (1) the thickness of the Kettle Point Formation increases towards the deepest sections of the Chatham Sag and thins towards the northeast and southwest with increasing proximity to the arches; (2) the abundance of greyish green mudstones is greatest towards the arches; and (3) greyish green units become thicker and more continuous archwards.

The core and geophysical data are here interpreted to reflect changing paleoenvironmental conditions, especially regarding the onset and intensification of anoxia. Anoxic conditions for the Kettle Point black shales are inferred from the high total organic carbon content, the presence of sulphide nodules reflecting sulphur reduction in the absence of oxygen, the preservation of laminations, and fluctuations in the abundance of *Tasmanites*, cysts that would have floated throughout the water column. Periods of maximum, basin-wide anoxia, correspond to thick, continuous packages of non-interlaminated black shales, whereas increases in the abundance, thickness and continuity of greyish green mudstones are inferred to represent a shift to dysoxic conditions.

Preliminary data from 50 samples spread throughout the formation have been collected and the values plotted against the core log. The results show a largely consistent background value for the black shales around -20 $\delta^{34}S$, punctuated by substantial positive excursions (up to 12.87) correlating to significant intervals of greyish green mudstones. A similar positive excursion has been documented earlier in correlation with the Frasnian-Famennian event (e.g. Faure and Mensing, 2005). This enrichment is interpreted as reflecting a significant reduction in primary productivity that resulted in a drop in sulfate reduction by bacteria in oceans. Further analysis is to be conducted to refine the sulphur isotope curve and paleoenvironmental interpretations.

Paleozoic black shales are not limited to North America, but can be found worldwide, suggesting that the conditions required for their formation existed globally (Schlanger and Jenkyns 1976; Arthur and Sageman 1994; Jenkyns 2010). Thick intervals of black shales, often in excess of 1 km, likely represent extended periods of global anoxia (Tourtelot 1979; Negri et al. 2009a;b). The combination of factors that led to such extensive anoxia and widespread black shale deposition are still contested; however, stable high temperatures during the Paleozoic would have lowered oxygen solubility leading to a decrease in dissolved oxygen in the water column (Meyer and Kump 2008). Furthermore, these pervasive greenhouse conditions likely resulted in sluggish, stratified oceans that were prone to anoxia (Schlanger and Jenkyns 1976; Hotinski et al. 2001; Ozaki et al. 2011).

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