

**Variations of Redox conditions across the Cambrian-Ordovician
GSSP (Green Point Formation) in western Newfoundland (Canada):
implications from the Mo-, U-, C- and N-isotope signatures**

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Variations of Redox conditions across the Cambrian-Ordovician GSSP (Green Point Formation) in western Newfoundland (Canada): implications from the Mo-, U-, C- and N-isotope signatures

Abstract

The organic-rich shales of the Green Point Formation rhythmites are believed to be the source rock of potential hydrocarbon reservoirs in western Newfoundland. No detailed studies have yet investigated the redox conditions of that section despite being the Cambrian-Ordovician GSSP. The proposed study will utilize the Mo- and U-isotope signatures of the shales and those of C- and N counterparts of the organic matter to evaluate the reducing conditions that dominated during the late Cambrian (SPICE event) and the Cambrian-Ordovician boundary in attempt to better understand the global distribution of organic matter around that time interval. The results are also expected to provide high-resolution isotope profiles that can be utilized for reliable global correlations.

1. Introduction

The study of redox conditions that dominated oceans through the Earth's history is a key factor for the evaluation of potential source rocks and understanding their global distribution patterns across the sedimentary basins. Hydrocarbon seepage has been documented in the Lower Ordovician St. George Group dolomites of Western Newfoundland and the porosity associated with dolomitization made those carbonates a potential reservoir rock (e.g., Lane, 1990; Cooper et al., 2001; Lavoie et al., 2005, Azmy et al., 2008, 2009; Conliffe et al., 2009; Azmy and Conliffe, 2010; Azomani et al., 2013; Olanipekun et al., 2014). The organic-rich shale (Green Point Formation of the Cow Head Group) and overlying impermeable layers (Table Point Formation limestone of the Table Head Group) are critical elements for the presence of an efficient hydrocarbon system with the St. George dolomitized facies as potential reservoir rocks; moreover, the Middle Devonian Acadian Orogeny resulted in the development of structural traps (Baker and Knight, 1993; Fowler et al., 1995; Stockmal et al., 1998; Cooper et al., 2001; Knight et al., 2008).

The Green Point Formation spans the GSSP section of the Cambrian-Ordovician boundary and the study of the included source rocks will provide significant information that will contribute to the exploration strategies not only in western Newfoundland but also on a global basis. Very few studies, almost only one, that investigated the geochemistry of TOC contents in the Green Point Formation shales around the Cambrian-Ordovician boundary in many locations in western Newfoundland (0.6 to 5.2 wt. %; Weaver et al., 1988).

Earlier studies indicated that global sealevel changes along the eastern Laurentian margin around the Cambrian-Ordovician boundary influenced seawater redox conditions and organic productivity (e.g., Terfelt et al., 2012, 2014; Azmy et al., 2014). Sealevel changes also influence riverine inputs into the oceans and consequently the contents of trace elements in marine deposits (e.g., Wignall and Twitchett, 1996; Murphy et al., 2000; Arnaboldi and Meyers, 2007; Wignall et al., 2007; Piper and Calvert, 2009). The drop of oxygen level in seawater and the spread of dysoxic/anoxic conditions are known to be associated with global reduction of primary productivity and consequently the total organic carbon contents (TOC) and C- and N-isotope compositions of organic matter (e.g., Quan et al., 2008; Herrmann et al., 2012; Quan et al., 2013). Changes in redox conditions are also associated with variations in the $\delta^{98}\text{Mo}$ and $\delta^{238}\text{U}$

values of marine carbonates and organic-rich mudrocks (e.g., Dahl et al., 2010a; Voegelin et al., 2010; Brennecke et al., 2011; Dickson et al., 2012; Romaniello et al., 2013). The main objective of the currently proposed study are (a) to evaluate the degree of preservation of the Mo- and U-isotope compositions of the marine sediments (shales and carbonates) and the C- and N-isotope compositions of their associated organic matter in the slope/deep shelf rhythmites of the Green Point Formation (Cambrian-Ordovician GSSP) and (b) to better understand the changes in, and extension of, the global oceanic paleoredox conditions that occurred around Cambrian-Ordovician boundary including the SPICE event (Upper Cambrian).

1. Geologic Setting

Paleozoic sediments of western Newfoundland in Canada (Fig. 1) were deposited on the eastern Laurentian margin. The Laurentian plate developed by active rifting around 570 to 550 Ma (Cawood et al., 2001), and a pre-platform shelf formed and was eventually covered by clastic sediments (James et al., 1989). A major transgression flooded the Laurentian platform margin and resulted in the accumulation of thick carbonate deposits (Wilson et al., 1992; Lavoie et al., 2013). These platform deposits (carbonate/shale slope deposits of the Cow Head Group) are dominated by high-energy carbonates that formed during the Middle and Late Cambrian, and were later buried under the low-energy carbonates of the St. George Group during the Early to earliest Middle Ordovician (cf. Knight et al., 2007, 2008; Lavoie et al., 2013).

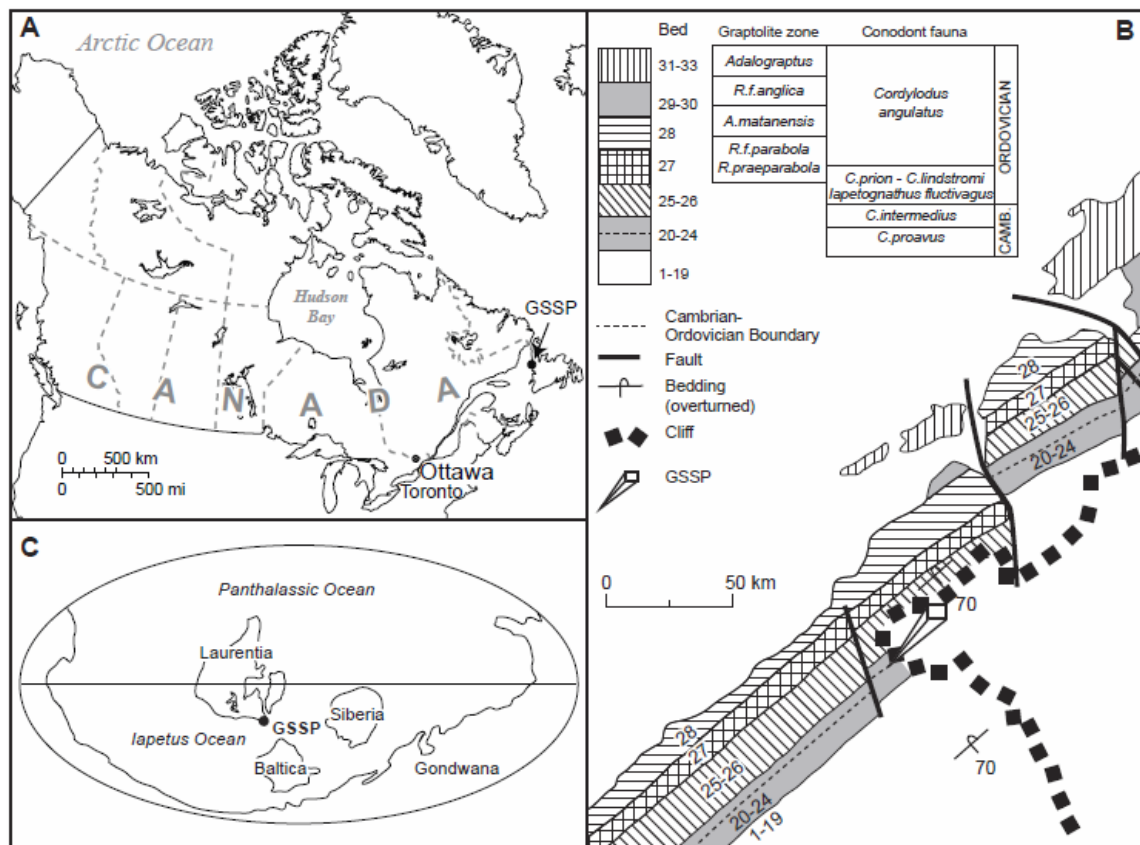


Fig. 1. Location map of Green Point, western Newfoundland, Canada showing (A) the location of the GSSP Cambrian-Ordovician boundary section in eastern Canada, (B) the distribution of outcrops of the beds covering the boundary interval (modified from Cooper et al., 2001), and (C) the position of the GSSP on the paleomap during the Cambrian-Ordovician time interval (based on Scotese, C. R., 2002, PALEOMAP Project, <http://www.scotese.com>).

2. Litho- and Biostratigraphy

The lithostratigraphy of the Cambrian–Ordovician boundary section, which is part of the Green Point Formation of the Cow Head Group (Fig. 2), has been studied and discussed in detail by James and Stevens (1986), and it will therefore be only summarized here. It consists of the uppermost Cambrian Martin Point and lowermost Ordovician Broom Point members, which are generally composed of dark grey to black fissile shale alternating with thin (~ 1 cm-thick) interbeds of ribbon limestone rhythmites. Siltstone interbeds (up to 1 cm thick) may co-occur with shale, and the limestone interbeds vary from isolated and thin to up to 20 cm thick. The conglomerate beds contain blocks of shallow water carbonates that were transported into deep-water facies along the slope of the Laurentian margin (James and Stevens, 1986).

The Cambrian–Ordovician GSSP section at Green Point spans the *Cordylodus intermedius* (Furongian, uppermost Cambrian) to the *Cordylodus angulatus* Zones (Tremadocian, Lower Ordovician) and is defined by the first appearance datum (FAD) of the conodont *Iapetognathus fluctivagus* (Fig. 2; Cooper et al., 2001). The current spike marking the Cambrian–Ordovician boundary in the GSSP section at Green Point (Fig. 2) is placed within Bed 23 (Cooper et al., 2001). Sometimes stratigraphic boundaries and sequences including GSSPs are difficult to correlate with others due to lack of key fossils (Cooper et al., 2001; Terfelt et al., 2012), which makes carbon isotope chemostratigraphy a valuable and important tool for GSSPs and their global correlation.

3. Methodology

Samples (Fig. 2) will be collected at high resolution (sampling intervals as small as 5 cm) from the Cambrian–Ordovician GSSP boundary section (49° 40' 51" N; 57° 57' 36" W) at Green Point, western Newfoundland (Fig. 1). Samples will be taken from both shales and laminated lime mudstone rhythmites to avoid allochthonous clasts. Thin sections of samples will be petrographically examined with a polarizing microscope and with a cathodoluminoscope, particularly for carbonates, to evaluate the degree of preservation of the carbonates. Cathodoluminescence (CL) observations will be performed using a Technosyn 8200 MKII cold cathode instrument operated at 8 kV accelerating voltage and 0.7 mA current.

For carbonates, a mirror-image slab of each thin section is also prepared and polished for microsampling. These polished slabs are washed with deionized water and dried overnight at 50 °C prior to isolating the finest grained lime mudstone free of secondary cements and other contaminants. Approximately 10 mg of carbonate are microsampled from the cleaned slabs using a low-speed microdrill under binocular microscope.

For shales, Molybdenum- and uranium-isotope measurements will be carried out at the W.M. Keck Foundation Laboratory for Environmental Biogeochemistry, School of Earth and Space Exploration, Arizona State University. The analytical protocol of acid digestion of shale powder for the isolation of Mo and U and measurements of the Mo- and U-isotope composition by multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS; Thermo Scientific Neptune) are described in detail by Kendall et al. (2013) and Dahl et al. (2010a,b). The $\delta^{98}\text{Mo}$ and $\delta^{238}\text{U}$ values are reported relative to the international standards as follows:

$$\delta^{98}\text{Mo} (\text{‰}) = \left[\left(\frac{{}^{98/95}\text{Mo}_{\text{sample}}}{{}^{98/95}\text{Mo}_{\text{STANDARD}}} \right) - 1 \right] \times 1000 \text{ and}$$

$$\delta^{238}\text{U} (\text{‰}) = \left[\left(\frac{{}^{238/235}\text{U}_{\text{sample}}}{{}^{238/235}\text{U}_{\text{STANDARD}}} \right) - 1 \right] \times 1000, \text{ respectively. The SD}$$

uncertainty of individual samples is based on sample replicate measurements.

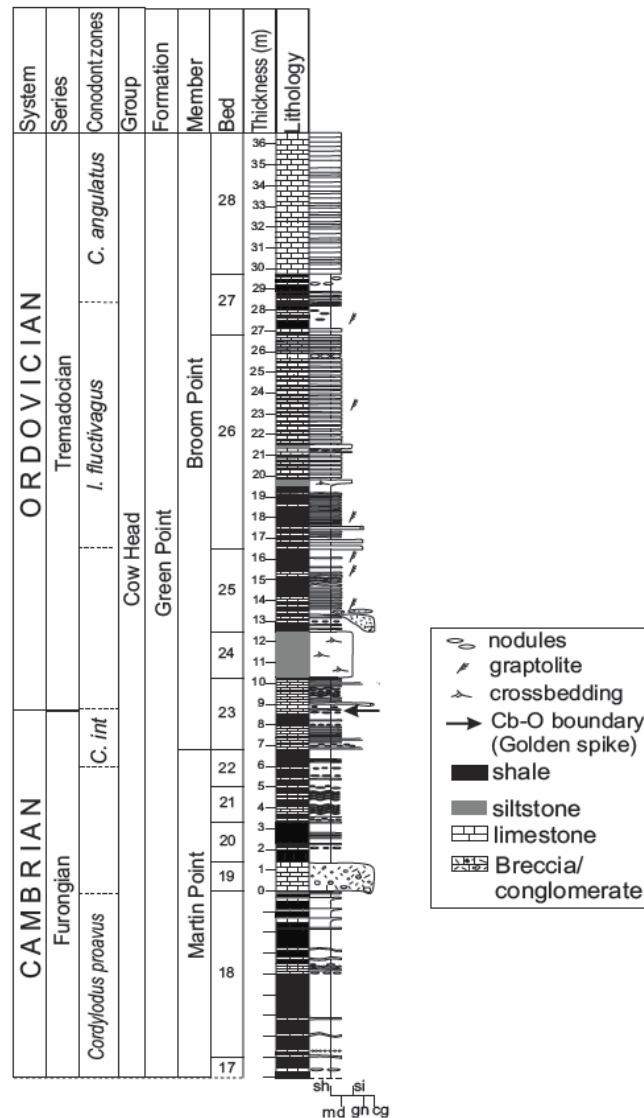


Fig. 2. Stratigraphic framework of the pilot study by Azmy et al. (2014) of the Cambrian–Ordovician GSSP boundary section in western Newfoundland, Canada showing the detailed measured upper part of the section and conodont zonation scheme (modified from Cooper et al., 2001). The proposed study will cover the shale intervals in the section and the carbonate and shale intervals in the lower sections below Bed 17 that span the upper Cambrian SPICE event.

For C- and O-isotope analyses of carbonates, about 220 μg of powder sample is reacted in an inert atmosphere with ultrapure concentrated (100%) orthophosphoric acid at 70 $^{\circ}\text{C}$ in a Thermo–Finnigan GasBench II. The liberated CO_2 is automatically delivered to a ThermoFinnigan DELTA V plus isotope ratio mass spectrometer in a stream of helium, where the gas is ionized and measured for isotope ratios. Uncertainties of better than 0.1‰ (2σ) for the analyses are determined by repeated measurements of NBS-19 ($\delta^{18}\text{O} = -2.20\text{‰}$ and $\delta^{13}\text{C} = +1.95\text{‰}$ vs. VPDB) and L-SVECS ($\delta^{18}\text{O} = -26.64\text{‰}$ and $\delta^{13}\text{C} = -46.48\text{‰}$ vs. VPDB). Organic carbon- and nitrogen-isotope ratios are measured on isolated kerogen after treatment with acid at the isotope laboratory of Memorial University of Newfoundland, using a Carlo Erba Elemental

Analyzer coupled to a ThermoFinnigan DELTA V plus isotope ratio mass spectrometer in a stream of helium, where the gas is ionized and measured for isotope ratios. The results are normalized to the standards IAEA-CH-6 ($\delta^{13}\text{C} = -10.43\text{‰}$), NBS18 ($\delta^{13}\text{C} = -5.04\text{‰}$), USGS24 ($\delta^{13}\text{C} = -15.99\text{‰}$), IAEA-N-1 ($\delta^{15}\text{N} = 0.43\text{‰}$), and IAEA-N-2 ($\delta^{15}\text{N} = 20.32\text{‰}$). The uncertainty calculated from repeated measurements is usually $\sim 0.2\text{‰}$.

For elemental analyses of carbonates, a subset of carbonate sample powder ($\sim 10\text{ mg}$ each) is digested in 5% (v/v) acetic acid for 70–80 min. and analysed for major, minor and rare earth elements (REE) using an Elan DRC II ICP-MS (Perkin Elmer SCIEX) at Memorial University of Newfoundland. The relative uncertainties of these measurements are usually less than 5%, and results are normalized to a 100 % carbonate basis (cf. [Azmy et al., 2014](#)).

4. Previous work

Although the Green Point Formation of the Cow Head Group in western Newfoundland is the Cambrian–Ordovician GSSP ([James and Stevens, 1986](#)), which is the international reference section for global correlations, no detailed study has yet investigated the redox conditions that dominated the ocean water during that time interval. The formation contains organic-rich shale, which is deemed to be a source rock for potential reservoirs (e.g., St. George Group carbonates) in the area. Very few studies shed the light on the geochemistry of the organic matter of the black shale (e.g., [Weaver et al., 1988](#)) and only one recent pilot study examined the c-isotope stratigraphy of the Cambrian–Ordovician boundary ([Azmy et al., 2014](#)), which did not cover the SPICE event of the late Cambrian (e.g. [Saltzman et al., 1998](#)).

5. Proposed Work

The proposed investigation will combine the petrographic and geochemical techniques to better understand the redox conditions that dominated during the late Cambrian to earliest Ordovician and to evaluate the preservation of primary geochemical signatures, which is the cornerstone of building reliable interpretations.

5.1. Petrographic approach

The Green Point Formation spans the Cambrian–Ordovician boundary and is dominated by limestone rhythmites with interbedded organic-rich shale and siltstone layers ([James and Stevens, 1986](#)). The establishment of petrographic preservation of carbonates will certainly reflect the preservation of shale and the associated organic matter, a significant issue in interpretation of their geochemical signatures re-construction of ancient redox conditions of seawaters.

The original sedimentary fabrics and degree of recrystallization are significant features for the evaluation of degree of textural preservation, which is also confirmed by examination under cold cathodoluminescence (CL). Luminescence in carbonates is mainly activated by high concentrations of Mn and quenched by high concentrations of Fe ([Machel and Burton, 1991](#)). Dull luminescence, in many cases, indicates relative preservation of primary geochemical signatures although altered carbonates might still exhibit no luminescence due to high Fe contents ([Rush and Chafetz, 1990](#)) and cathodoluminescence is, therefore, a single evaluation tool that has to be complemented by additional tests ([Brand et al., 2011](#)).

5.2. *Geochemical approach*

5.2.1. *Trace elements*

The evaluation of geochemical signatures of carbonates is a critical issue for the study because it will reflect the degree of preservation of the primary of isotopic signatures of the organic-rich shale and associated organic matter. Also, it allows the utilization of the $\delta^{13}\text{C}_{\text{carb}}$ for building the c-isotope stratigraphy particularly that of the late Cambrian (SPICE event), which will provide very important tool for global correlations with other sections worldwide and evaluation of the degree of connectivity of the basin in western Newfoundland to open ocean water at that time (e.g., Azmy et al., 2014). Diagenesis results mainly in depletion in Sr and $\delta^{18}\text{O}$ values of carbonates but enrichment in Mn and ΣREE counterparts (Veizer, 1983; Azmy et al., 2014). Therefore, the Mn/Sr values of marine carbonates, when correlated with their $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ counterparts, can be utilized for evaluating the degree of preservation (e.g., Derry et al., 1992; Kaufman and Knoll, 1995). The ΣREE contents of carbonates are sensitive to the slightest of alteration, significantly enriched by diagenesis, and have been proven a powerful tool in recognizing alteration in carbonates (e.g., Azmy et al., 2011, 2012). Variations in sealevel, particularly those associated with time events, are generally associated with changes in trace and rare earth element concentrations in sediments due to the inputs of terrestrial material and changes in redox conditions (e.g., Wignall and Twitchett, 1996; Murphy et al., 2000; Arnaboldi and Meyers, 2007; Wignall et al., 2007; Piper and Calvert, 2009; Śliwiński et al., 2010). Therefore, major $\delta^{13}\text{C}$ shifts of time events reflect relative changes in organic productivity and paleoredox.

Levels of oxygen in the water column influence the oxidation state of some elements and selectively control their solubility in seawater and consequently their enrichment in marine sediments (e.g., Wignall and Twitchett, 1996; Arnaboldi and Meyers, 2007; Wignall et al., 2007). The Ce-anomaly (Ce/Ce^*) values in ancient micritic/near-micritic sediments have been found to provide a proxy of the redox condition of seawater (e.g., Bau and Dulski, 1996).

5.2.2. *C- and N-isotopes of organic matter*

The c-isotope composition of organic matter ($\delta^{13}\text{C}_{\text{org}}$) combined with the amount of total organic carbon (TOC) contents provide valuable proxy to the paleoredox of marine environment and may reflect the influence of major extinction events through Earth's history (e.g., Lehnert et al., 2005). The C/N ratios combined with the N-isotope composition of organic matter ($\delta^{15}\text{N}_{\text{org}}$) may also reflect the influence of denitrification, and possibly stagnation, caused by sealevel rise (Quan et al., 2013) and the contributions from N_2 -fixing bacteria relative to inputs from terrestrial plants.

5.2.3. *Mo- and U-isotopes*

The isotopic composition and concentrations of Mo and U, expressed $\delta^{98/95}\text{U}$ and $\delta^{238/235}\text{U}$ ‰ relative to international standards, provide significant proxies of the reducing conditions that dominated during the Phanerozoic (e.g., Dahl et al., 2010a, 2014). The concentrations of Mo in marine sediments are controlled by the dissolved H_2S in seawater. In oxic oceans, Mo is soluble in form of molybdate (MoO_4^{-4}) whereas in anoxic water molybdate reacts with H_2S to precipitate as thiomolybdate ($(\text{MoO}_{4-x}\text{S}_x)^{-2}$). Thiomolybdates are ultimately converted into tetrathiomolybdate in strongly euxinic water and removed entirely to sediments, thus yielding sediment $\delta^{98}\text{Mo}$ almost identical to that of ambient seawater (Barling et al., 2001;

Arnold et al., 2004; Neubert et al., 2008) particularly with ocean water homogeneity (Nakagawa et al., 2008). The increase in reducing conditions leads to enrichment in $\delta^{98}\text{Mo}$ values of sediments relative to those of oxic shallow shelf seawaters (e.g., Poulson et al., 2006; Dickson et al., 2012).

U-isotope fractionation occurs during U reduction from U^{+6} to U^{+4} , which is associated with a decrease in U^{238} in ocean water and thus resulting in lowering in the $\delta^{238}\text{U}$ values of sediments with the enhancement of anoxic conditions (e.g., Brennecke et al., 2011; Dahl et al., 2010a). Therefore, the variations in the $\delta^{238}\text{U}$ profile across the Green Point Formation (organic-rich shale, and carbonates too, are expected to reflect the changes in the redox conditions particularly when combined with their $\delta^{98}\text{Mo}$ counterparts and will provide better understanding of how the anoxic conditions changed with sealevel and how severe the event was. This will allow better evaluation of the sediments as a source rock for the associated potential reservoirs in the area.

6. Economic Significance

The Green Point Formation of the Cow Head Group in western Newfoundland is deemed to be the source rock for potential carbonate reservoirs in the area such as those of the St. George dolomites. The most recent test production (315 barrels per day) from some of those carbonate reservoirs, by the CIVC in early 2007, indicates high API (50-56°) oil and significant volume of natural gas ($10^6 \text{ ft}^3/\text{day}$). However, there has been yet a detailed study of the redox conditions that dominated during the deposition of those source rocks although the section has been the Cambrian–Ordovician GSSP. The study of those rocks will provide better understanding of their origin and allow better understanding of their distribution.

7. Global Applications

Regardless the location of the studied sequence, the investigation of the redox conditions of the Green Point Formation sediments will allow modelling the paleoceanographic conditions on a global basis particularly because the investigated formation is the Cambrian–Ordovician GSSP, which adds to the value of the contributions of the study to understanding the global distribution of source rocks around that time interval. Also, the produced isotope and elemental geochemical profiles will contribute significantly to the global correlation of the investigated section with other source rocks of the same age from different basins and paleomasses.