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Canol Formation chronostratigraphy: $\delta^{13}C_{org}$ stable isotope results from the Richardson Mountains, north Yukon

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Summary

*This paper presents stable carbon isotope ($\delta^{13}C_{org}$) data from a 227m thick section of Canol Formation exposed in the east Richardson Mountains in north Yukon. This technique was used to refine the age of the formation and to correlate the existing intra-formational chemostratigraphic zonation scheme into a chrono and sequence stratigraphic framework. A negative $\delta^{13}C_{org}$ excursion and heavy metal enrichment immediately below the basal Canol contact is tentatively linked to the Kačák-*otomari *event, suggesting that the base of the formation may approximate the Eifelian-Givetian boundary. The upper contact with the Imperial Formation is correlated to the base of the middle Frasnian* jamieae *condont zone. Intra-formational positive $\delta^{13}C_{org}$ excursions (including the '*punctata*' event) correspond well to chemostratigraphic zones, and are probably linked to Frasnian sequences 1-4, with the base of each excursion related to sea-level rise and deepwater renewal in the restricted Canol basin. These $\delta^{13}C_{org}$ results are anticipated to facilitate future outcrop and subsurface stratigraphic correlation of the Canol Formation and its lateral equivalents within, between and beyond north Yukon petroleum basins.*

Introduction

In 2013, Yukon Geological Survey initiated the 'North Yukon Upper Palaeozoic Shale Project'. The project's aim is to further the understanding of the petroleum potential of Devonian-Carboniferous shale strata in north Yukon. The Middle to Upper Devonian Canol Formation was targeted as the first priority for lithological characterisation, refinement of age and stratigraphic relationships, and assessment of source rock and shale gas reservoir potential. Petroleum potential analytical results from outcrop and diamond drillhole core work undertaken in 2012 and 2013 (Fraser *et al.* 2012 and Fraser & Hutchison 2014) suggest the formation is highly prospective as a dry gas source rock in north Yukon (e.g. %Ro>1.8, 4.3 wt.% average TOC).

Interpretation of high-resolution sedimentological and lithogeochemical data from measured sections in north Yukon indicate that Canol Formation siliceous shales and chert were deposited in a silled, restricted basin with euxinic deepwater (Hutchison & Fraser 2015). Organic richness was enhanced by minimal terrigenous influx, however fluctuating productivity resulted in significant biogenic silica enrichment that reduced porosity. The formation was also divided into four regionally correlatable chemostratigraphic zones (A-D). Each zone was characterised by up-section profiles of: decreasing biogenic silica enrichment, increasing proportions of siliceous shale relative to chert, decreasing redox-sensitive Mo, U and V enrichment factors and decreasing Mo/TOC ratios. An overall decrease in Mo/TOC ratios suggests increasing basinal restriction over time associated with relative sea-level fall.

Previous attempts to refine the formation's age in north Yukon using palynological or microfossil (radiolarian) dating techniques have met with little success primarily due to the high maturity of the shales. Therefore, in order to relate these new chemostratigraphic and palaeohydrographic observations to a sequence stratigraphic framework and to further constrain the absolute age of the formation's contacts, high resolution $\delta^{13}C_{org}$ stable isotope analysis was undertaken and compared to published $\delta^{13}C_{org}$ and sea-level curves.

Background

The Canol Formation has been reported as Givetian-Frasnian at its type locality in the Northwest Territories by Gal *et al.* (2009), and limited conodont data from the District of Mackenzie suggests that the formation spans the *Palmatolepis punctata*, *P. hassi* and *P. jamieae* Zones (Montagne Noir Zones 6-10; McLean & Klapper 1998). The formation is coeval with, and may have been laterally continuous with, other stratigraphic units in Yukon, including the Earn Group of Selwyn basin, the McCann Hill Chert in southern Kandik basin and eastern Alaska, and the Horn River Group in Liard basin suggesting an extensive, possibly interconnected system of basins in northwestern North America during the Middle to Upper Devonian. In Yukon, the Canol Formation typically overlies either Middle Devonian platform carbonates of the Ogilvie Formation or Road River Group limestone and shales in the Richardson Mountains. The nature of the formation's basal contact is currently unclear, but has previously been interpreted as both conformable and unconformable (Pugh 1983). At several locations, this contact is marked by metre-scale carbonate concretions and Mo-Ni-Zn-PGE mineralisation (e.g. Hulbert *et al.* 1992). Recent (2014) field observations in the Richardson Mountains also highlighted the presence of a thin, lithologically distinctive shale unit between the Road River Group and Canol Formation that may correlate to strata of the lower Hare Indian Formation in the Northwest Territories (Hutchison & Fraser 2015). Both sets of observations suggest a more regionally-complex basal stratigraphic architecture to the formation than previously recognised. At its upper contact, the Canol Formation is conformably overlain by clastic strata of the Upper Devonian to Lower Carboniferous Imperial and Ford Lake Shale formations.

Data & methodology

In Yukon, the Canol Formation has been mapped at surface between 65^{o} and 67^{o}N, and is documented in oil and gas wells in and near the exploration regions of Eagle Plain basin, Peel Plateau and Plain basins and northeast Kandik basin. Data for this study are taken from one outcrop section (Trail River) measured in 2013, accessed via helicopter in the east Richardson Mountains. The Canol Formation at Trail River is 227.3m thick. Palynomorphs recovered from the uppermost Road River Group and lowermost Imperial Formation at this section indicate a Middle? Devonian to Frasnian age for Canol Formation strata (Dolby 2013).

Systematic rock chips were collected through 2m intervals to form a composite sample, then powdered, homogenised and analysed for whole rock lithogeochemistry at ACME Laboratories Ltd in Vancouver before being dispatched for destructive $\delta^{13}C_{org}$ stable isotope analysis by Chemostrat Canada Ltd in Calgary. Prior to isotopic analysis, carbonate was removed by placing samples in a bath of hydrochloric acid – the weight loss from this process was then used to estimate the total organic carbon content of the material. Individual samples were heated to 1700^{o}C and carbon dioxide produced by this process was passed through a Europa Scientific 20-20 Isotope Ratio Mass Spectrometer. Results have been compared to several well-established reference standards and normalized to the Vienna Peedee Belemnite (V-PDB). Analytical precision (1σ) was estimated to be better than ±0.2‰ for $\delta^{13}C_{org}$.

Results

Canol Formation $\delta^{13}C_{org}$ values lie between -27.7 and -30.4‰, with an average value of -29.5‰ and baseline values of approximately -30 to -29‰. The formation's lower contact at 19.7m is preceded by a negative $\delta^{13}C$ excursion and heavy metal enrichment (e.g. Co and Cs) tentatively correlated to the global anoxic Kačák-*otomari* event that occurred prior to the Eifelian-Givetian (E-G) boundary (e.g. van Hengstum & Gröcke 2008, Ellwood *et al.* 2011). These observations suggest that the base of the Canol Formation may approximate the E-G boundary, and that the blue-grey to black, highly radioactive, heavy metal enriched shale unit underlying this contact is potentially the Bluefish Member of the Hare Indian Formation (c.f. Pyle *et al.* 2014) deposited during the Kačák-*otomari* event. The Canol to Imperial Formation contact at 246m is marked by a rise in $\delta^{13}C$ values – a signal that has been interpreted as a positive excursion occurring near the base of the *jamieae* Zone (Yans *et al.* 2007). These upper and lower age constraints suggest an approximate depositional timespan for the Canol Formation of 11 Ma (Cohen *et al.* 2013).

Four intra-formational $\delta^{13}C$ positive excursions are recorded, with bases at approximate depths of 90, 150, 180 and 205m measured stratigraphic thickness. The 180m horizon is correlated to the base of the mid-Frasnian *punctata* conodont zone (McLean & Klapper 1998), with $\delta^{13}C$ trends above this bearing similarity to the '*punctata*' excursion observed in $\delta^{13}C_{carb}$ curves from Devonian strata in northeast and western Alberta (e.g. Holmden *et al.* 2006 and Śliwiński *et al.* 2011), northeastern Europe (Yans *et al.* 2007) and China (Ma *et al.* 2008). Three of these four $\delta^{13}C$ positive excursions (90, 150 and 180m) also correlate well with chemostratigraphic zone boundary depths reported in Hutchison & Fraser (2015). Each zone boundary was interpreted as a flooding surface resulting in deepwater renewal in the restricted Canol basin, with each zone becoming more restricted up-section. Zone B (between 90-150m) was interpreted as the least restricted on the basis of relatively high Mo/TOC ratio values, and was therefore representative of the highest sea-levels during Canol deposition. Correlation to conodont zones via the $\delta^{13}C$ curve suggest that deposition of zone B occurred during the 'Frasnian 1' sequence of Haq & Schutter (2008), and this sequence also records the highest mean sea-level during the Middle to Late Devonian. The $\delta^{13}C$ isotope framework subsequently facilitated correlation of zones C and D to the 'Frasnian 2' and 'Frasnian 3 and 4' sequences respectively, with the $\delta^{13}C$ positive excursion at 205m dividing zone D deposition between the latter two sequences. The lowest Canol zone (A – 19.7 to 90m) was therefore correlated to 'Givetian 1 to 7' sequences. Increasing overall basin restriction during Canol deposition was supported by falling mean sea-levels during the middle to late Frasnian.

These $\delta^{13}C_{org}$ results from Trail River will facilitate future outcrop and subsurface chrono and sequence stratigraphic correlation of the Canol Formation and its lateral equivalents within, between and possibly beyond north Yukon petroleum basins. Additional $\delta^{13}C_{org}$ stable isotope analysis results are pending for four potential Canol Formation sections measured during 2013-2014 summer fieldwork in the Richardson, Northern Ogilvie and Wernecke mountains, including one section in which samples across the Mo-Ni-Zn-PGE mineralised ?Bluefish-Canol contact zone are currently being dated via Re-Os isotope analysis.

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