

# **Base-metal Enrichment in Stage-5 (mid-Cambrian) Black Shale of the Hess River Formation, Misty Creek Embayment, Selwyn Basin**

**E.C. Turner**

*Department of Earth Sciences / Mineral Exploration Research Centre  
Laurentian University, ON  
eturner@laurentian.ca*

## **Abstract**

Deep-water turbiditic limestone of the Cambrian Hess River Formation in the Misty Creek Embayment (Mackenzie Mountains, Northwest Territories), a poorly known and economically underexplored part of the sedimentary exhalative/clastic-dominant (SEDEX/CD)-hosting Selwyn Basin, contains a >20 m-thick black shale interval with elevated base metal and barium content and geochemical evidence of hydrothermal venting. Carbon isotope stratigraphy of the formation in its type area shows that its deposition in the Cambrian spanned from at latest early Stage 5 to mid-Paibian, and that its upper, conformable contact with the Rabbitkettle Formation, as originally defined lithostratigraphically, is coincident with the Sauk II-III boundary in the chemostratigraphic reference curve. The black shale addressed by this study was deposited in latest Stage 5, and a further ~50 m may exist under scree above the studied interval, probably extending into the early Drumian. This depositional age may be identical to that of host strata of mineralisation in the Anvil District, Yukon, but the depositional age of host rocks and mineralisation in the latter are not well constrained. The newly established depositional age of the Hess River Formation in the Misty Creek Embayment identifies significant dating and correlation problems in the broader Selwyn Basin. Biostratigraphic data from base of the overlying Rabbitkettle Formation in its type area indicate a Drumian depositional age, yet the top of the Hess River Formation in its type area is Paibian (i.e. 9 m.y. of overlap with depositional span of Hess River Formation in its type area). This conflict highlights the difficulty of mapping, picking contacts in, and correlating monotonous deep-water successions with little biostratigraphically useful content, subtle differences among formations, and diachronous changes in sedimentation regimes in a basin that was tectonically active. Although it is not field-friendly, carbon isotope stratigraphy may be the only viable tool that can be applied to deciphering the Selwyn Basin's tectonic, stratigraphic, and metallogenic history.

## **Introduction**

The Selwyn Basin, a Cambrian to Silurian deep-water region flanking the northwestern margin of Laurentia, contains SEDEX/CD past-producing deposits and showings at several stratigraphic levels (Goodfellow, 2007). The past-producing Anvil District was hosted by Cambrian deep-water strata (Pigage,

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2004; Goodfellow, 2007), but the exact age of the host rocks (Mount Mye and Vangorda formations) is not well constrained. Mid-Ordovician (or possibly Silurian-Devonian) deep-water strata contain the Vulcan showing (Mako and Shanks, 1984), which, although not a past-producing deposit, is significant because it records a temporally distinct episode of syndepositional base-metal mineralisation in a different part of the basin from the better known mining and exploration camps. Early Silurian deep-water strata host the Howards Pass deposits (Norford and Orchard, 1985). Younger SEDEX/CD deposits of the MacMillan Pass area are hosted by Devonian deep-water strata belonging to an unrelated, younger basin regime and, although in the same geographic region as the older deposits, are not considered here to be part of the Selwyn Basin.

The Selwyn Basin spans both the Yukon-Northwest Territories boundary and a geographic range in which Cordilleran deformation intensifies southwestward. This region encompasses the lower to middle Paleozoic northwestern margin of Laurentia, comprising several geographically complex embayments that are inferred to have resulted from anomalous extension during early to mid-Paleozoic passive-margin subsidence. The most northwestern of the embayments in the Selwyn Basin system is the Misty Creek Embayment (MCE; Figure 1), which is in the less-deformed, better-exposed eastern zone of the northern Canadian Cordillera. Owing to its remoteness, the MCE has not been extensively studied to unravel its geologic history, nor extensively explored to evaluate its economic potential.

The established understanding of the MCE is dominated by the regional stratigraphic synthesis of Cecile (1982), in which the thick and previously poorly known “Road River Group” was subdivided into formal stratigraphic units: the Hess River, Rabbitkettle, Duo Lake, and Cloudy formations, which together form the lower to middle Paleozoic deep-water succession in the MCE and other parts of the Selwyn Basin. The Hess River, Duo Lake, and Cloudy formations were defined in, and have type sections in, the MCE, whereas the Rabbitkettle Formation’s type section is farther south in the Mackenzie Mountains (Gabrielse et al., 1973), a geographic disparity that poses problems for defining the units’ contacts in the field.

The regional distribution of the MCE’s deep-water units relative to surrounding shallow-water carbonate-dominated environments was established (Figure 1), and the depositional evolution of the basin outlined by Cecile (1982). A number of representative sections were documented at reconnaissance scale, and biostratigraphic constraints were established as best as possible, given the dearth of fossil material. Depositional ages of the younger stratigraphic units were adequately constrained biostratigraphically (Cecile, 1982) but the depositional age of the Hess River Formation remained enigmatic owing to poor biostratigraphic control. This meant that the formation’s role in basin evolution could not be adequately characterised, and its relationship to metalliferous strata elsewhere in the Selwyn Basin has not been established.

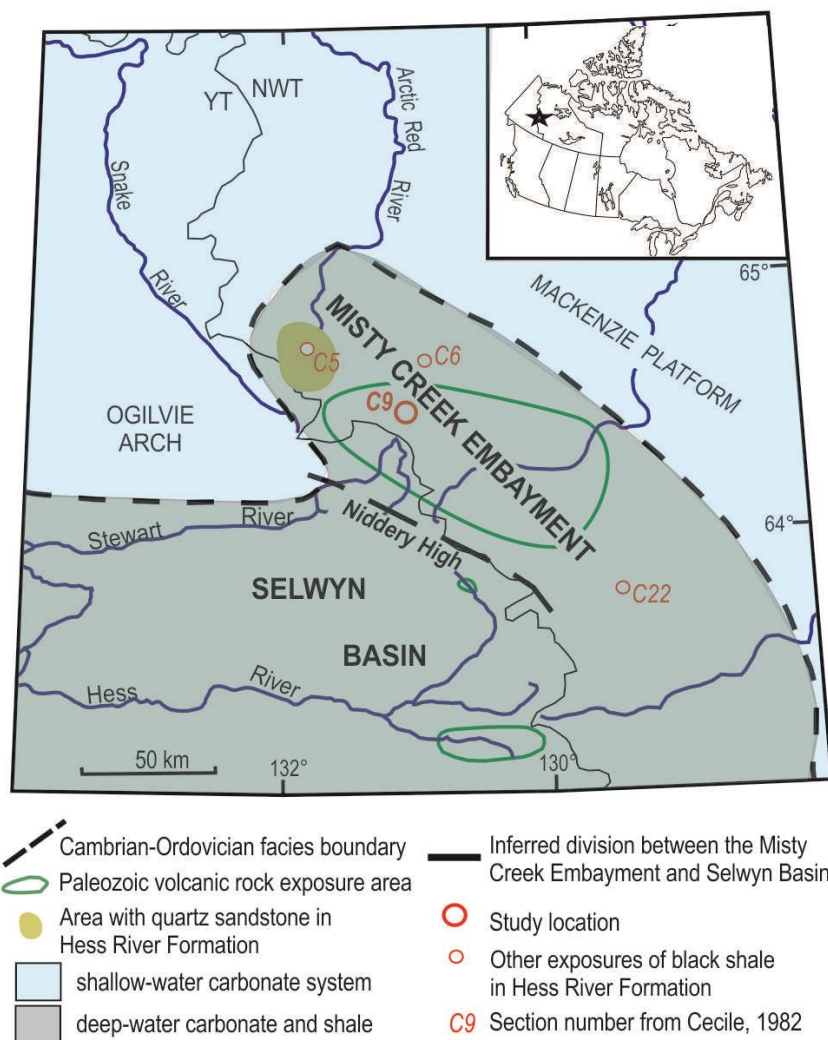


Figure 1. Location map of the deep-water Misty Creek Embayment and coeval, surrounding shallow-water environments, the study location (C9), and other stratigraphic sections mentioned in the text. Location C6 is the type section of the Hess River Formation.

The present work is part of a detailed sedimentological-stratigraphic study of one of the thickest and deepest-water sections originally documented by Cecile (1982), and is intended to follow up in greater detail on the depositional environments, processes, age, and base-metal prospectivity of the MCE. For this study, one very thick and continuous section through the deepest-water part of the embayment was measured and sampled in detail. The lowest part of the succession is not exposed at this location. Results of the field study (Chevrier and Turner, 2013a, b) showed that the Hess River and Rabbitkettle formations in the centre of the MCE are dominated by silt- and mud-grade material derived from contemporaneous shallow-water carbonate environments and deposited by very fine-grained turbidity currents on a gently sloping basin floor. Sedimentation was strongly carbonate-dominated during deposition of the Hess River and

Rabbitkettle formations, but became shale and chert-dominated when the Duo Lake Formation was deposited (Late Ordovician – Early Silurian), returning to carbonate-dominated deposition during accumulation of the Silurian Cloudy Formation.

Among the objectives of this study has been to identify, date, and evaluate any black shales in the succession. Four of the stratigraphic sections of Cecile (1982) depict black shale intervals in the lower part of the Hess River Formation in the Misty Creek Embayment. Fritz (1976, 1978, 1979) documented recessive intervals of “dark shale and platy limestone” that overlie the Lower Cambrian Sekwi Formation throughout a broader region of the western Mackenzie Mountains in NT. Although it is unclear whether any of these generalised intervals includes distinctly black shale like that addressed by the present study, they suggest the possibility of regionally distributed black shale in the lower Hess River Formation.

Analytical work for this project component has focussed on (a) establishing a carbon isotope curve for lower Paleozoic strata of the MCE, in order that its depositional history be better temporally constrained than has been possible using sparse biostratigraphic data, and so that the depositional age of any intervals of potential economic interest is known, and (b) analysing the geochemistry of a hitherto untested black shale interval in the lower Hess River Formation. This paper reports on the results of this analytical work.

## **Results/Data Analysis**

### ***Methods***

A detailed stratigraphic section was documented at decimetric scale through approximately 3 km of lower to middle Paleozoic strata (Figure 2; Chevrier and Turner, 2013a, b) at the location of a previously measured reconnaissance section in the middle of the MCE (Cecile, 1982, section 9; Figure 1). Hand samples were collected approximately every 2-5 m for stable isotope analysis. Black shale was sampled where present by excavating pits (depth ~50-80 cm) through the shale scree to reach intact rock, which was then sampled using a pen knife.

The material sampled for stable isotope analysis consisted of well-preserved lime mudstone with little recrystallisation, no petrographic evidence of diagenetic alteration, and little to no tectonic veining. Samples were prepared from mud-grade parts of thin-section offcuts using a tungsten-carbide dental bur. The stable isotope analyses were performed at the GG Hatch isotope Laboratory at University of Ottawa following their standard protocol. Oxygen isotope results show little variation throughout the section, supporting the understanding of the succession as little altered and bearing near-depositional (original) stable isotope values.

Twelve samples from the black shale interval were subjected to whole-rock geochemical analysis at Acme Labs (Vancouver, British Columbia) using their standard aqua regia and lithium fusion inductively coupled plasma-mass

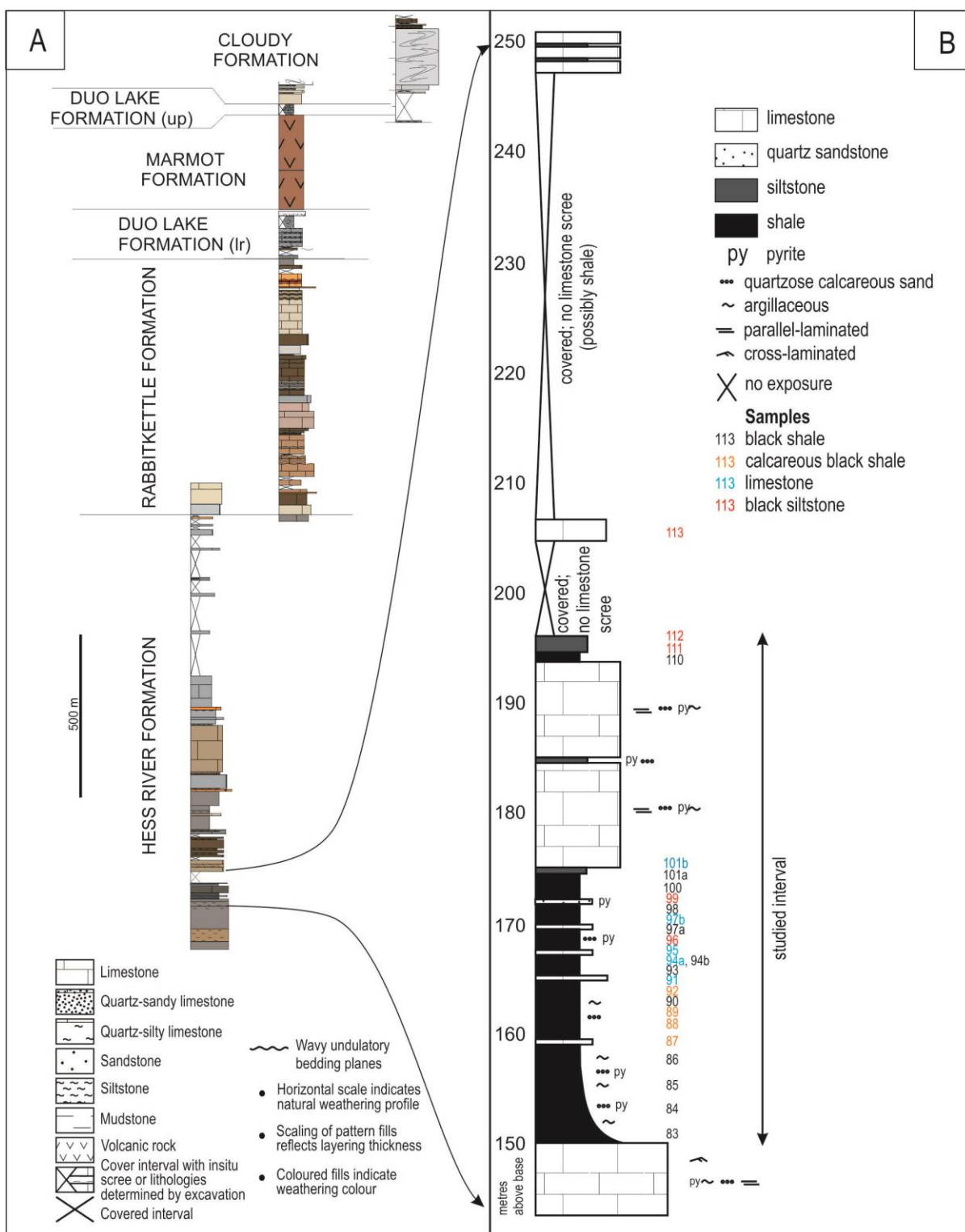


Figure 2. (A) Stratigraphic log for the entire lower to middle Paleozoic deep-water succession in the centre of the Misty Creek Embayment (after Chevrier and Turner, 2013a,b), measured in three increments. (B) Expanded log for the black shale interval in the lower Hess River Formation.

spectrometry (ICP-MS) protocols. Analytical results are normalised to the upper continental crust shale-equivalent standard “Mud of Queensland” (MUQ; Kamber et al., 2005). The possibility of BaO influencing Eu values was dismissed using inter-element correction.

Several samples were analysed for total organic carbon using Rock-eval pyrolysis at GSC-Calgary. One black shale sample was analysed for mineralogy using X-ray diffraction (XRD) at the Central Analytical Facility at Laurentian University.

## **Discussion/Models**

### ***Hess River Formation lithostratigraphy and sedimentation***

The lithostratigraphy and sedimentology of the Cambrian part of the MCE succession (Figure 3; Hess River Formation and lower half of Rabbitkettle Formation; Chevrier and Turner, 2013a, b) record a predominantly deep-water environment dominated by carbonate mud to sand delivered to the deep basin-floor by turbidity currents from a coeval shallow-water carbonate environment in which the carbonate material had originally precipitated. The Hess River Formation, the subject of this study (~1370 m thick; basal contact not exposed), consists of lime mudstone with sparse laminae of peloidal calcarenite together with trace to (rarely) dominant fine-grained quartz sand (Figure 3F) to silt and abundant pyrite, and shale seams that separate limestone layers (Figure 3E). The coarser laminae (silt- to rarely fine-sand-sized) are graded and exhibit rare cross-lamination and micro load-casts. Quartz silt to sand, a minor but pervasive component of the Hess River Formation, co-occurs with carbonate material of the same grain-size (i.e. coarser than most of the carbonate material in the formation) in millimetric laminae, and so the coarser quartz (i.e. silt-sand, rather than clay-sized) is interpreted as having been delivered in carbonate-dominated turbidity currents. Interpreting the quartz sand/silt's ultimate origin is beyond the scope of the present study.

The black shale interval is in the lower part of the exposed Hess River interval at the study site (Figure 3B-D), and is underlain and overlain by turbiditic lime mudstone to calcisiltite. The shale is very recessive, and contains sparse centimetre- to decimetre-thick argillaceous lime mudstone intervals. Minor rusty-weathering quartzose and calcareous silt laminae like those in the carbonate-dominated parts of the Hess River Formation are also present in the shale.

### ***Depositional age using carbon isotope stratigraphy***

A carbon isotope curve generated for the Hess River to lower Rabbitkettle formations (Figure 4) compares favourably to a global compilation curve for the Cambrian (Saltzman and Thomas, 2012) and especially well to details of the lower Paleozoic curve generated for southwestern Laurentia (Saltzman, 2005). This strong relationship to the well-constrained global and regional curves allows



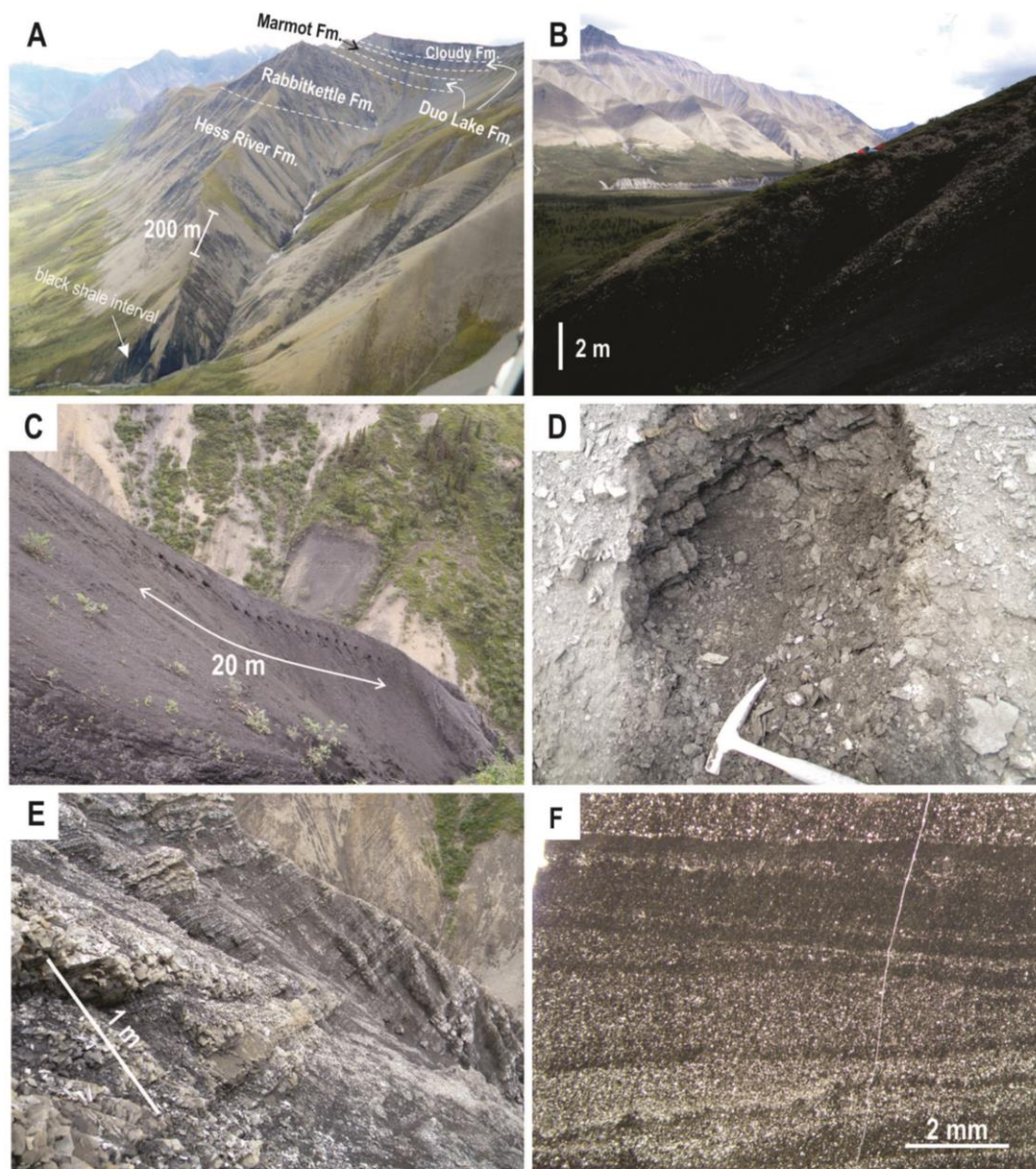


Figure 3. (A) Lower part of measured section, including Hess River Formation and its black shale interval. (B) Upper part of the black shale exposure. (C) Lower part of the black shale exposure, showing a series of shallow pits excavated for sampling of intact shale beneath a veneer of shale scree. Strata dip to the left. (D) A pit excavated for shale sampling. Upper centre shows intact shale layers that were sampled; sides show thin veneer of shale scree; lower centre is loose material produced by excavation. (E) Typical exposure of Hess River Formation limestone turbidites with minor argillaceous interbeds. (F) Thin section view in PPL of typical Hess River fine-grained graded beds with sharp contacts, silt-grade calcareous and quartzose material at layer bases, and evidence of pulsing tractional flow (repeated graded laminae).

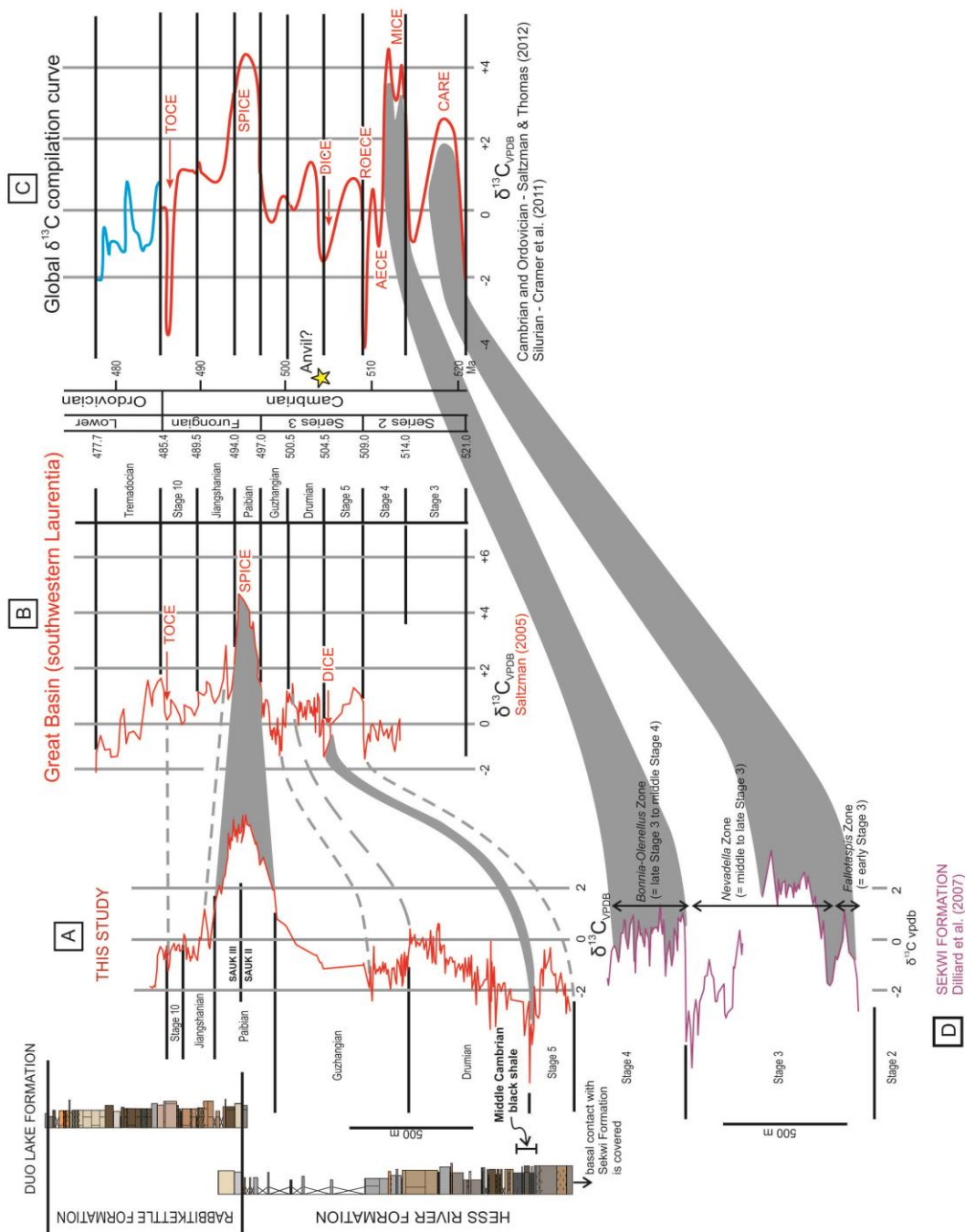


Figure 4. Carbon isotope curve for the Hess River and Rabbitkettle formations at the study site (A), compared to (B) detailed curve for southeastern Laurentia (Saltzman, 2005), (C) global composite curve (Saltzman and Thomas, 2012), and (D) curve for the underlying Sekwi Formation (Dilliard et al., 2007). Hess River Formation black shale interval may be temporally equivalent to host rock of the Anvil district in the Selwyn Basin of Yukon (yellow star).



the Cambrian part of the MCE succession to be assigned confidently to global stages (Figure 4). The high accumulation rates in deep water attest to the robust capacity of Phanerozoic carbonate factories to produce carbonate particulates in shallow-marine environments and export them voluminously elsewhere. Given the sedimentology of the succession and the understanding of Phanerozoic carbonate dynamics, it is clear that the carbonate material preserved in the deep-water MCE initially formed under shallow-water conditions, where it could acquire the carbon isotopic signal of the uppermost water column, which was well mixed with global marine water, before being transported to and deposited in a deep-water environment that may not have been fully exchanged with the global water mass (Figure 5A).

Carbon isotope stratigraphy indicates that the black shale interval in the lower Hess River Formation was deposited in (Cambrian) late Stage 5, just prior to the negative  $\delta^{13}\text{C}$  excursion known as the Drumian carbon isotope excursion (DICE), which marks the beginning of the Drumian (Figure 4; Saltzman and Thomas, 2012). Field evidence strongly suggests that black shale continues above the interval studied (possibly another ~50 m; Figure 2), which would indicate black shale depositional conditions that persisted into the early Drumian.

The time constraints placed on Hess River Formation deposition in the MCE using carbon isotope stratigraphy are generally compatible with the existing biostratigraphic data for the unit (Figure 6; Cecile, 1982), but with some serious caveats regarding the age and identification of the formation's lower and upper contacts. Fritz (1976) and Cecile (1982) suggested that the contact of the Hess River Formation with the underlying Sekwi Formation is diachronous. Chemostratigraphic data for the Sekwi Formation (Dilliard et al., 2007; Figure 4) do not contain two major Stage 4 (late Early Cambrian) carbon isotope excursions (Archeocyathan Extinction Carbon Isotope Excursion (AECE) and Redlichiid-Olenellid Extinction Carbon isotope excursion (ROECE)), and these anomalies are also absent from the lowermost exposed Hess River Formation in the present study, which could indicate a non-diachronous relationship involving a sedimentary hiatus. The basal contact of the Hess River Formation is not exposed at the study site, but at another section known to contain a black shale in the lower Hess River Formation (Cecile 1982, section 6) the lowest metre of Hess River Formation consist of quartz sandstone with sparse, 'floating' clasts of Sekwi Formation limestone, which suggests that base of the Hess River Formation may not be conformable. Furthermore, those sections of Cecile (1982) that contain a black shale interval depict variable thicknesses of Hess River Formation limestone below the black shale, which suggests that, if the black shale does indeed represent a temporally meaningful episode in basin history, the onset of accumulation of the underlying Hess River Formation turbiditic limestone varied temporally and geographically. Owing to the lack of any other reliable way to date these successions, the time relationship of the Sekwi – Hess River contact will probably only be solved with application of carbon isotope stratigraphy.

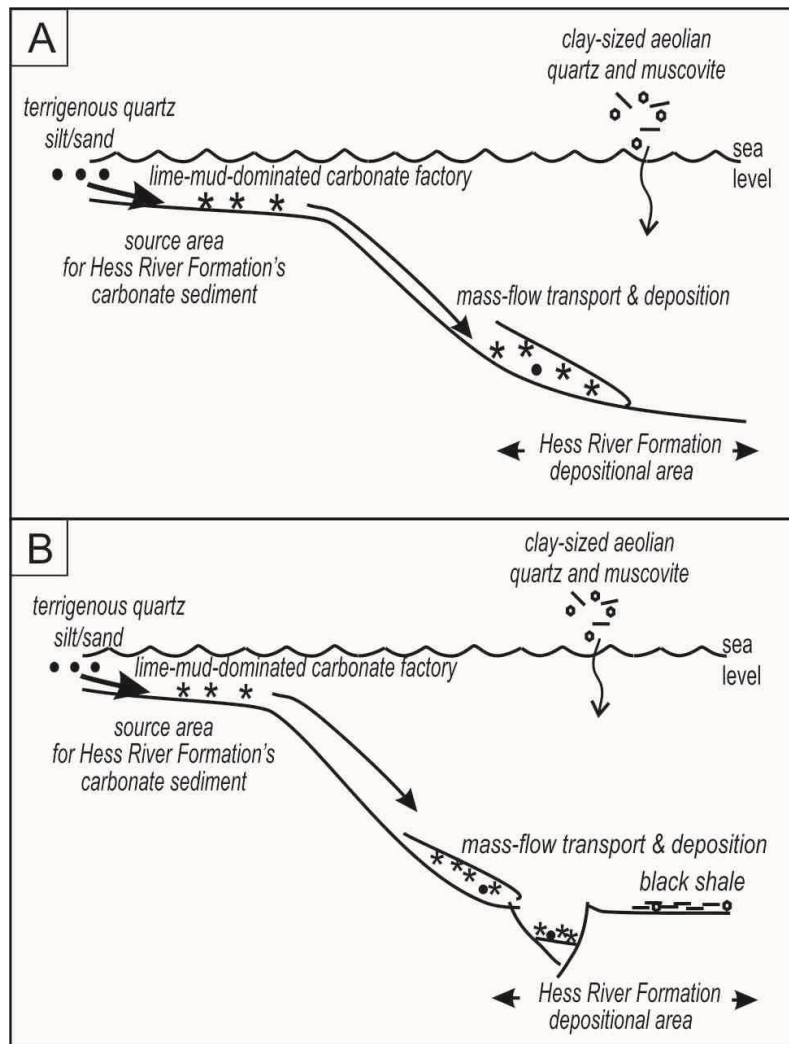


Figure 5. Depositional model for the Hess River Formation. (A) Background clay-sized aeolian sediment (hemipelagic quartz and muscovite) is fairly constantly supplied. Mud- to silt-sized carbonate material is supplied from a coeval, nearby, shallow-water carbonate factory that may be similar to the possibly contemporaneous Franklin Mountain Formation (Turner, 2011), and is delivered to the deep-water environment as fine-grained turbidity currents. Carbonate production and export to the deep-water basin was prolific, and almost always overwhelmed the background hemipelagic supply of clay-sized terrigenous silicate particles (shale seams). Silt-sized and coarser quartz was delivered to the basin floor along with carbonate mud to silt, but is not known to be present in possibly contemporaneous shallow-water formations. The (comparatively) coarser quartz may have been locally derived from uplifted blocks of older terrigenous strata (Windermere or Mackenzie Mountains supergroups). (B) Later, during black shale deposition, delivery of shallow-water-derived carbonate material to the study site ceased; given that there is no other evidence that the nearby carbonate factory may have been defunct at this time, a physical impediment that blocked or diverted sediment delivery is envisaged.

The contact between Hess River and overlying Rabbitkettle formations in Hess River Formation's type area in the MCE (Cecile, 1982) is placed at "the base of the first very thick succession (>10 m) of thin bedded limestone or silty limestone above which shale is a subordinate lithology within the Rabbitkettle Formation". The basal contact of the Rabbitkettle Formation in its type area, over 400 km south-southeast of the Hess River Formation's type area and well beyond the MCE, is an unconformity (Gabrielse et al., 1973). Trilobite biostratigraphic data for the Rabbitkettle Formation in its type area indicate that Rabbitkettle Formation deposition started in the Drumian (Figure 6; Pratt, 1988), yet in the MCE, where the Hess River Formation was established, the chemostratigraphic evidence shows that the Hess River-Rabbitkettle contact, as defined lithostratigraphically by Cecile (1982) is in the mid-Paibian, almost exactly equivalent to the Sauk II-III boundary (Figure 4). This substantial discrepancy in the position of the Hess River - Rabbitkettle contact (~9 m.y. difference) almost certainly results from the necessity of picking formation contacts in the field using lithostratigraphic evidence, in a biostratigraphically impoverished succession that is notoriously difficult to differentiate in the field and that probably had regionally variable timing in subtle sedimentation changes. The fact that changes in lithostratigraphic character seem to have been diachronous throughout the Selwyn Basin will continue to hamper stratigraphic correlation and comparison among the various parts of the basin system. Although it is not field-friendly, carbon isotope stratigraphy is probably the best way to define and correlate a succession that has subtle but important geographic variations in its sedimentological character, and which lacks biostratigraphic evidence that can be easily obtained and used in the field by non-specialists.

Using the new time-depositional constraints on Cambrian strata in the MCE to compare its stratigraphy to the stratigraphic record of base-metal mineralisation in the established mineral districts of the Selwyn Basin is complicated by the reality that the MCE succession is now better temporally constrained than the presumed coeval succession in the established exploration and mining camps (e.g. Pigage, 2004). The inferred depositional age of the oldest known base-metal depositional episode in the Selwyn Basin (middle Cambrian(?) Mount Mye Formation; Anvil district; Pigage, 2004), may correspond to the black shale interval at the study location in the MCE (Figure 4). Conversely, the >20-m-thick black shale interval in the MCE (Chevrier and Turner, 2013a,b) is now known to be early Stage 5 to Drumian (middle Middle Cambrian), an age for which no well-dated black shale episode or base-metal enrichment is known elsewhere in the peri-cratonic, deep-water, lower Paleozoic system in northwestern Canada. This depositional age is, however, identical to that of the Burgess shale Lagerstätte (British Columbia). The temporal coincidence of Burgess shale (Stephen Formation) deposition at the foot of a submarine escarpment and deposition of the lower Hess River Formation in an excessively subsiding basin 1750 km along strike to the north supports the well-established interpretation that the middle Cambrian was a time of exaggerated extension and subsidence throughout northwestern Laurentia.

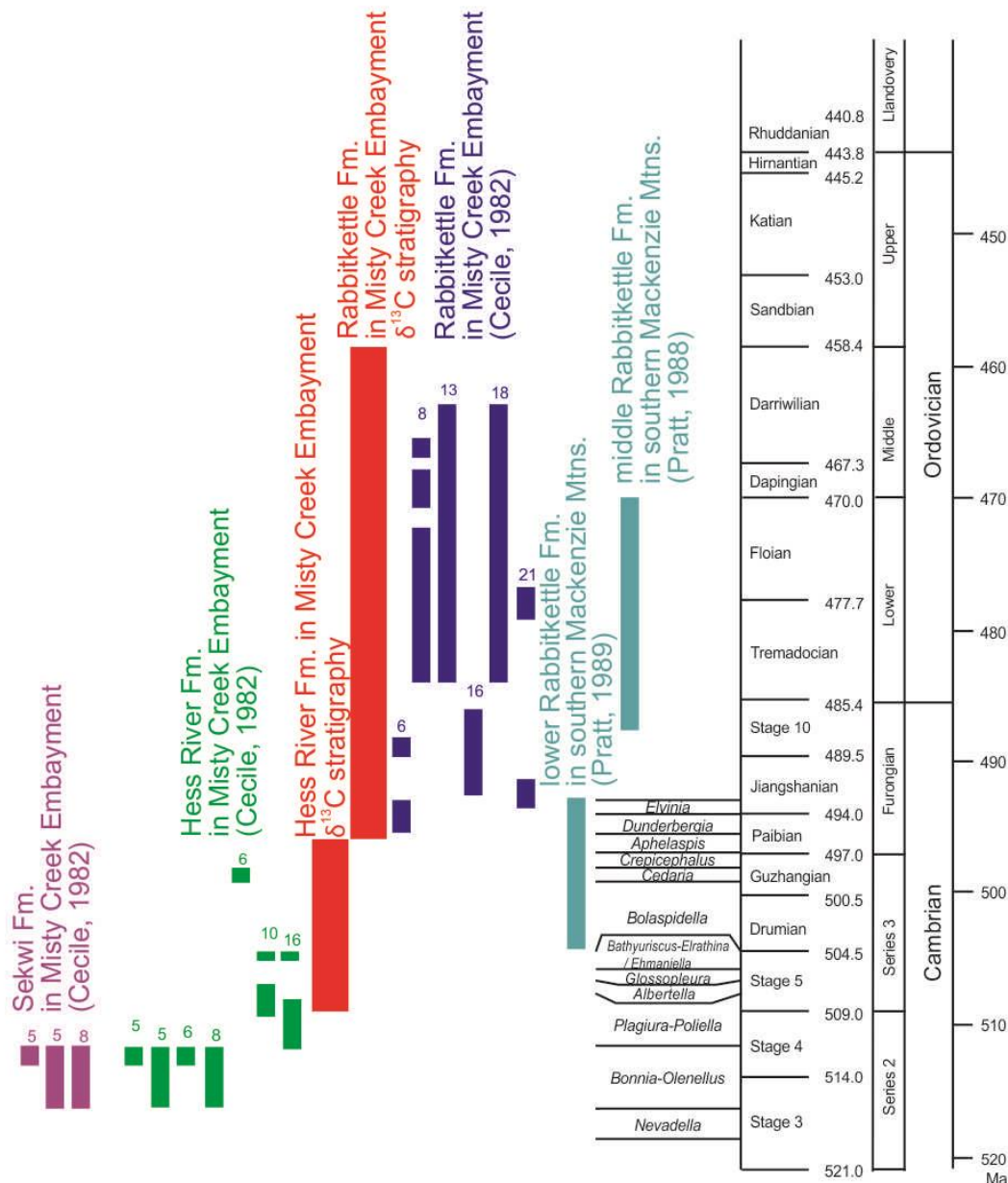


Figure 6. Comparison of temporal span of Hess River and Rabbitkettle formations in the MCE, based on biostratigraphic (Cecile, 1982) and chemostratigraphic (this study) data. The chemostratigraphic data (red) are compatible with biostratigraphic data (all other colours) for the MCE if the Sekwi and Hess River formations are interpreted to have a conformable contact in the *Bonnia-Olenellus* Zone (late Early Cambrian). The chemostratigraphic data, however, allow a more detailed temporal subdivision of the formations than do the sparse biostratigraphic data. Correlation into the southern Mackenzie Mountains (teal-coloured biostratigraphic data at right) is problematic, probably owing to unintentional placement of the Hess River-Rabbitkettle contact at different lithostratigraphic positions in the two respective type areas. Small numerals refer to section numbers in the cited material. Relevant Cambrian trilobite biozones are listed adjacent to the time scale.

### ***Black shale petrography and mineralogical composition***

No silicate, sulphide, or carbonate particles are discernible in Hess River Formation black shale thin sections under plane light. The mineralogical composition of one representative sample (ARR 90), determined by XRD, is quartz-dominated with significant muscovite and accessory jarosite and albite; the absence of clay minerals is to be expected, given the formation's pre-Devonian age (prior to the appearance of biologically active soil). The extremely recessive exposure in the black shale interval therefore reflects its very fine grain size rather than its mineralogical composition. The clay-grade quartz and muscovite that make the shale are interpreted as background sediment that was supplied steadily through time, probably by wind, upon which was superimposed, most of the time, the voluminous carbonate component transported by fine-grained mass-flow from a contemporaneous shallow-water carbonate factory such as that described by Turner (2011) for roughly contemporaneous shallow-water strata east of the MCE.

During Hess River Formation black shale deposition, carbonate delivery to the study location stopped almost completely. The carbon isotope curve shows that the shale's depositional interval was not protracted enough to eliminate, at the study site, any part of the carbon isotope record as established elsewhere in Laurentia (Figure 4; Saltzman, 2005). The geographic and temporal extent of the black shale episode in the MCE remain unknown, although the presence of shale at possibly equivalent stratigraphic positions in several sections of Cecile (1982) suggests that the shale depositional area may have had a regional extent of at least 50 km along and strike (possibly as much as 150 km; Figure 1), and at least 25 km perpendicular to the embayment's long axis. The temporary, late Stage 5 to early Drumian suspension of carbonate delivery to the study site, and possibly more broadly, could represent either (a) an episode of no carbonate deposition in the nearby carbonate factory (source area), such that no material was available to be exported to the deep-water setting (e.g. subaerial exposure during sea-level lowstand; development of geochemically unfavourable conditions in shallow water), or (b) appearance of a temporary physical impediment to the continued delivery of carbonate material at this site. The continued, rare delivery of silt-grade material that is both quartzose and calcareous, to form millimetric laminae in the black shale, however, suggests that both carbonate production and minor delivery of non-aeolian (i.e. comparatively coarse) quartz were maintained in the nearby shallow-water environment. The suspension of carbonate delivery to deep water therefore probably indicates the presence of a physical impediment that developed between the shallow-water carbonate source and the study site during the black shale depositional interval. Given that the basin is understood to have been episodically tectonically active, it is probable that a tectonic impediment such as an uplifted fault block or intervening graben may have appeared somewhere between the sediment production area and the study site, and temporarily diverted the influx of shallow-water-derived material elsewhere (Figure 5B).



### ***Shale Geochemistry***

Whole-rock geochemical results for a subset of samples from the newly identified Stage 5 black shale interval yielded the following results.

Given the mineralogical composition provided by XRD, silicon - aluminium ratios between 0.45 and 0.66 (Figure 7) indicate quartz: muscovite ratio of approximately 3:1; a slight stratigraphic decrease in this value reflects a greater proportion of phyllosilicates to quartz up-section. The proportion of Al in this Cambrian shale is significantly lower than that of the MUQ (modern, oxic) shale-equivalent standard (Kamber et al., 2005) used for comparison in this study, presumably owing to the Hess River shale's pre-Devonian, and therefore pre-clay, age. Zr/Hf, Nb/Ta, and Nb/Th ratios are relatively constant stratigraphically, with one anomalously high Zr/Hf value (sample 94b) that may reflect a coarser grain size in the quartz component (a quartz silt lamina may have been included in the sample inadvertently); although its Si/Al ratio is unremarkable, the sample also has elevated CaO, and so the high Zr probably reflects a small influx of coarser quartz delivered with the carbonate from shallow-water, both superimposed on the background of extremely fine-grained, presumably aeolian quartz and muscovite.

A ternary plot of oxides (Figure 8) shows that the shales'  $\text{Al}_2\text{O}_3/\text{MgO}$  ratios resemble those of black shale standard USGS SDO-1 ([http://crustal.usgs.gov/geochemical\\_reference\\_standards](http://crustal.usgs.gov/geochemical_reference_standards)), but have variably higher CaO content, which reflects carbonate content (also noted in the field; Figure 2). The steady ratio of the non-calcareous oxides, however, indicates that the terrigenous material supplied to the basin had a consistent composition, and therefore that detrital silicate composition is not responsible for variable base and precious metal concentrations. Given the mid-Cambrian age of the material (prior to abundant radiolaria),  $\text{SiO}_2$  content is assumed to be entirely terrigenous, and the total terrigenous content (sum of  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ , and  $\text{TiO}_2$ ; Figure 7) is comparatively steady at 65-78%; the lower total terrigenous values correspond to elevated CaO and presumed carbonate content, supplied, as deduced based on sedimentological constraints, as particulate carbonate from a nearby shallow-water carbonate factory. There is no correspondence between MgO and CaO, which reflects the calcitic, rather than dolomitic, composition of the carbonate component.

Rock-eval pyrolysis analysis of eleven shale samples (a different subset from that used for whole-rock analysis) yielded fairly constant total organic carbon (TOC) values between 1 and 2 wt% (Figure 7), which is considerably higher than background values in carbonate-dominated intervals of the MCE succession.

Total rare earth element (REE) content increases crudely up-section (Figure 7), but does not always covary with phyllosilicate (Si/Al) nor calcite (CaO), so it is unclear what drove the modestly increasing  $\Sigma\text{REE}$  trend. Black shale REE profiles (Figure 9) depict similar overall values and shapes. The light REE (LREE) are in general slightly enriched relative to middle REE (MREE) ( $\text{La}/\text{Gd} =$

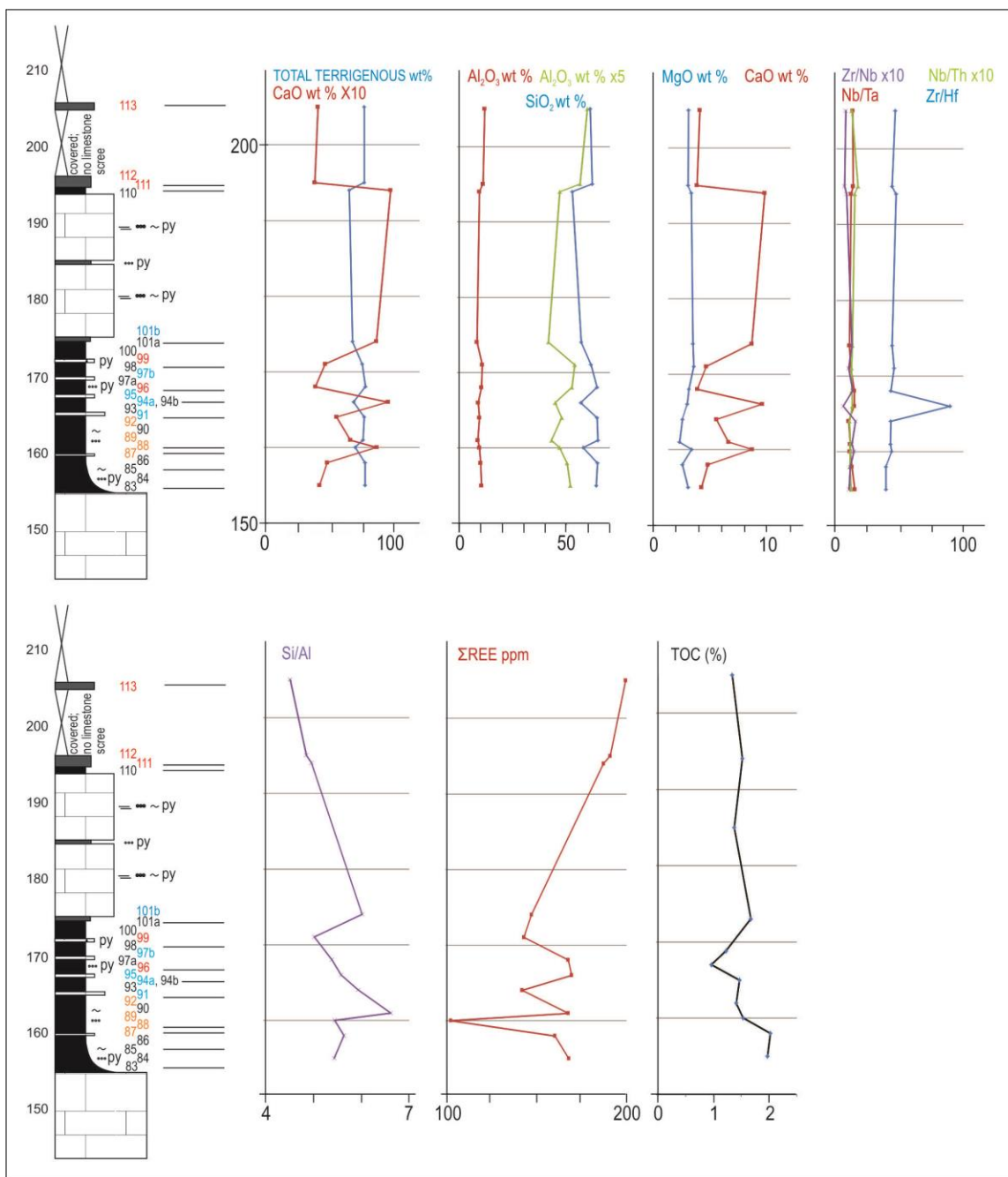


Figure 7. Stratigraphic patterns in major elements and terrigenous proxies. See text for interpretation.

1.1 to 1.3), but MREE are slightly depleted relative to heavy REE (HREE) ( $Gd/Lu < 1$ ), yielding profiles that are subtly dish-shaped and slightly negatively sloped. Such REE profiles indicate that the MCE's bottom water was not well exchanged with an open-marine water mass.  $La/La^*$  and  $Gd/Gd^*$  are near or above 1, and

Y/Ho is superchondritic ( $>26$ ) indicating that although the MCE bottom water had evolved away from a 'normal marine' REE profile, its origin had originally been marine. Pr/Yb ratios are less than 1, except for the stratigraphically uppermost two values, indicating a restricted basin that may have become slightly better connected with the global ocean as time progressed.

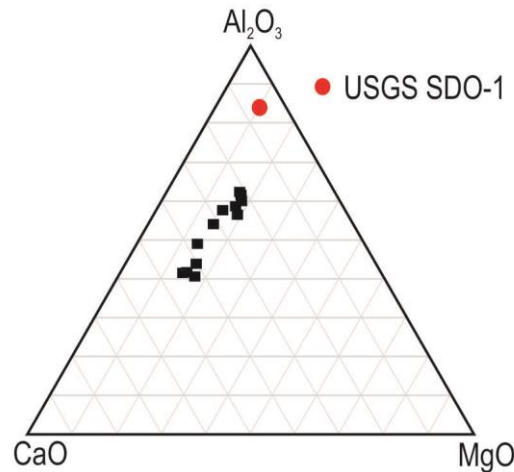


Figure 8. Ternary plot of major oxides. Hess River shale samples have a consistent ratio of  $\text{Al}_2\text{O}_3$  to  $\text{MgO}$ , but variable  $\text{CaO}$  that is well above that of black shale standard USGS SDO-1. The steady ratio of Al to Mg indicates a compositionally consistent source of silicate material during black shale deposition. The difference in  $\text{CaO}$  concentration reflects the variable but ongoing contribution of shallow-water-derived carbonate to the basin floor even during the time of seeming sediment starvation recorded in the black shale.

All samples have pronounced negative Y anomalies and flat to subtly positive  $\text{Ce}/\text{Ce}^*$ , suggesting mild anoxia (Figure 9). TOC values (Figure 7) are uniformly  $<2.5$ , putting them in the low-oxygen oxic region (Algeo and Maynard, 2004). Enrichment factors (EF) for the redox-sensitive elements As (7.2-10.5), U (3.5-6.4), and V (3.8-11.2) are moderately and variably elevated, but  $\text{Ce}/\text{Ce}^*$  values are only barely anomalous (between 1 and 1.1), suggesting that anoxia was not pervasive (Figure 10).  $\text{As}_{\text{EF}}$  strongly covaries with  $\text{Ce}/\text{Ce}^*$ , but  $\text{U}_{\text{EF}}$ ,  $\text{V}_{\text{EF}}$ , and  $\text{Cr}_{\text{EF}}$  covary less strongly with  $\text{Ce}/\text{Ce}^*$ , suggesting that these redox-sensitive elements had distinctive behaviours in the generally low-oxygen environment. The enrichment factor for Mo is generally high (40-113), but does not coincide with the Ce anomalies, suggesting that sulphidic conditions may have developed only below the sediment-water interface.

Zn (as enrichment factors normalised to MUQ; Kamber et al., 2005) is strongly elevated in several levels ( $\text{Zn}_{\text{EF}}=40$  to 113; maximum concentration 520 ppm; Figure 10). Copper ( $\text{EF}=2-4$ ), Pb ( $\text{EF}=1.5-2.8$ ), and Ag (191-655 ppb) covary with Zn and are modestly elevated at the same stratigraphic levels. Stratigraphic levels with highest  $\text{Mo}_{\text{EF}}$  or with highest  $\text{Ce}/\text{Ce}^*$ , however, do not correspond to

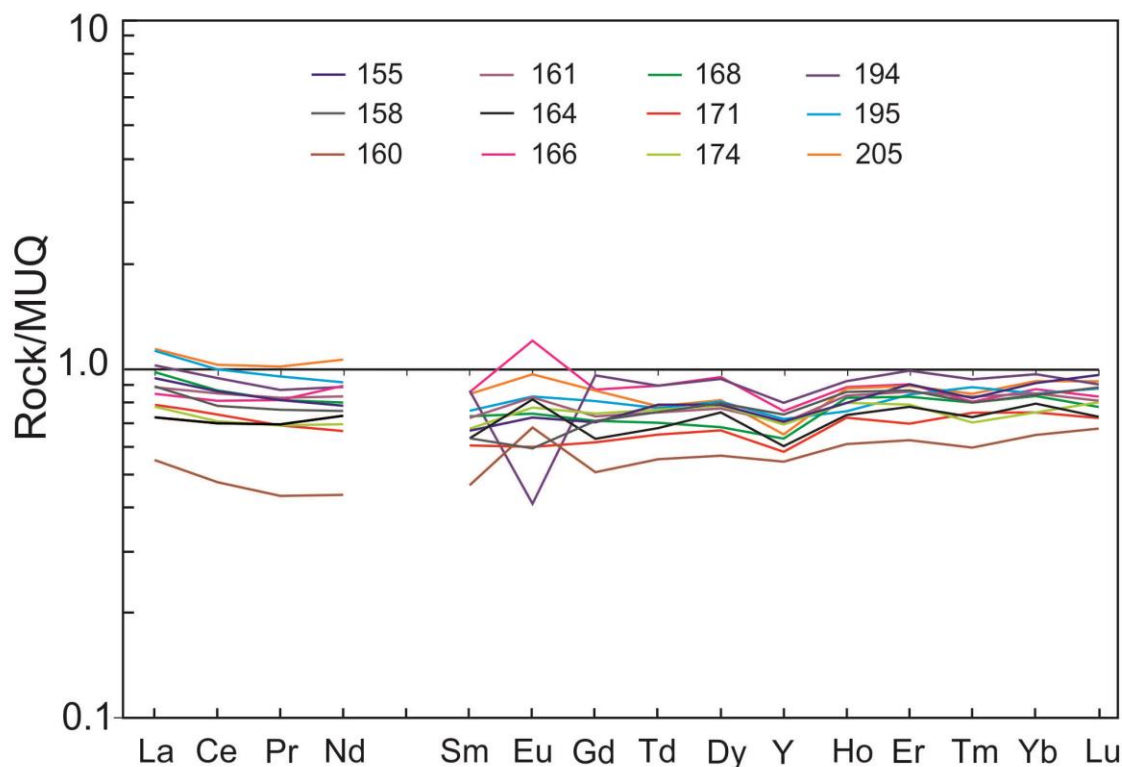


Figure 9. REE+Y in Hess River Formation black shale; samples are labelled by stratigraphic elevation. Slightly dish-shaped, slightly negatively sloped profiles indicate basin restriction and bottom-water evolution away from a 'normal-marine' signal. Cerium is very slightly positively anomalous in most samples, and Y is consistently negatively anomalous, suggesting mild anoxia. Positive Eu anomalies in most samples suggest the influence of hydrothermal sea-floor venting. Results are normalised to the upper continental crust shale-equivalent standard MUQ (Kamber et al., 2005).

elevated base-metal values, suggesting that base metal deposition did not strongly depend on euxinia or even anoxia. Base metal enrichment does not covary with CaO content (proxy for carbonate), and no relationship is evident with TOC.

The most notable of the black shale REE results are in Eu behaviour. Five of the 12 samples exhibit strongly positive  $\text{Eu}/\text{Eu}^*$ , and another five are moderately positive, which may reflect hydrothermal venting (Figure 10). Stratigraphic levels with the most positive  $\text{Eu}/\text{Eu}^*$  values, however, do not correspond to levels with highest EFs for base metals, and so the relationship between inferred venting and base metal concentration remains unclear. One negative Eu anomaly may reflect a transient episode of enhanced basin restriction.

Barium is enriched in the black shale, with particularly strong enrichment evident at 174 and 194 m; very little of the Ba is present in silicate phases, as shown by contrasting aqua regia and lithium fusion results. Although the Ba-rich samples are, predictably, not samples that exhibit elevated base metal content, and the Ba

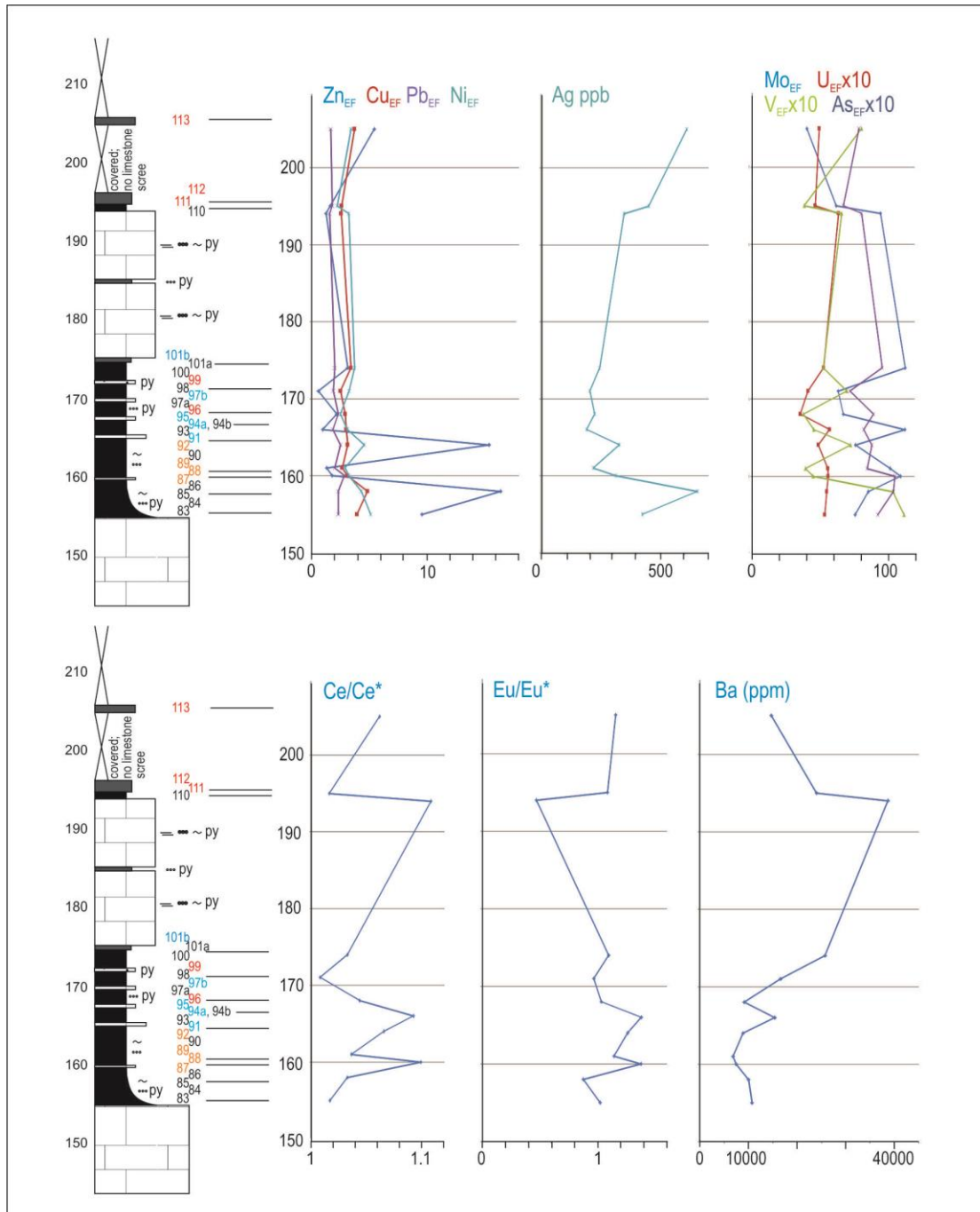


Figure 10. Stratigraphic patterns in base metal enrichment factors, [Ag], redox-sensitive elements, BaEF, paleoredox proxy  $Ce/Ce^*$ , and hydrothermal proxy  $Eu/Eu^*$ . Base metal enrichment factors generally covary, and Zn is conspicuously enriched. Base metal enrichment does not generally covary with RSEs or  $Ce/Ce^*$ , suggesting that paleoredox conditions were not a strong control on base metal content. Seafloor venting of hydrothermal fluids is suggested by generally positive  $Eu/Eu^*$ , but Eu anomalies do not coincide with levels of base-metal enrichment, suggesting that base-metal behaviour was not strongly linked to venting intensity. Enrichment factors for Ba are markedly elevated and antithetical to base-metal enrichment, but do not covary with proxies for paleoredox status of bottom waters or with  $Eu/Eu^*$ .



content does not covary with  $\text{Eu}/\text{Eu}^*$  (a proxy for venting), Ba concentration does appear to covary with the euxinia proxy  $\text{Mo}_{\text{EF}}$ , which is perplexing given that barite forms under oxic conditions. It is possible that the elevated Ba concentrations reflect barite that precipitated from vent-related fluid that had diffused both geographically away from its vent source and upward in the water column to a more oxidised level where barite could precipitate, and then settle as particulates to the sea-floor. Under such conditions,  $\text{Ba}_{\text{EF}}$  would not necessarily be expected to record the geochemical conditions that prevailed near the sea-floor, and might mix with unrelated sediment containing a more sea-floor, vent-related, and possibly less oxic geochemical signature.

### **Implications for Exploration**

The middle Cambrian (Series 3) stratigraphic succession in the Misty Creek Embayment shows strong evidence of characteristics that are known to be associated with SEDEX/CD deposits: (1) synsedimentary tectonic instability; (2) sediment starvation leaving only black shale to accumulate through deposition of aeolian material; (3) restricted exchange of bottom water with the global marine reservoir; (4) proxy evidence of poorly oxygenated to anoxic conditions; (5) proxy evidence for synsedimentary sea-floor venting, and (6) elevated base and precious metal concentrations at some stratigraphic levels. Dating using carbon isotope stratigraphy shows that a shale interval in the lower Hess River Formation may have the same depositional age as the host rocks of the Anvil District, suggesting the possibility of a regional black shale and venting episode in late Stage 5 to early Drumian. The MCE is remote and has received very little exploration attention, but its litho- and chemostratigraphic characteristics are strongly encouraging with respect to its potential to contain SEDEX/CD mineralisation.

### **Future Work**

The results reported here are from a focussed approach to a single stratigraphic transect in a stratigraphically and geochemically poorly known basin. The propitious geochemical results of the present, limited study suggest that the MCE may have SEDEX/CD potential. Further work to establish the regional dynamics of lower Paleozoic sediment deposition and the geology, chronology, and geochemical attributes of the Selwyn Basin's carbonate and non-carbonate strata is warranted. Once the geologic history of the basin and its embayments is better understood, perhaps with the use of carbon isotope stratigraphy, comparing the regions and their economic potential will become possible, and intervals of potential economic interest can be more clearly identified and studied in better detail. The pursuit of these objectives has not been possible because a functional temporal framework for the basin's evolution is lacking.

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Field sections were measured by T. Chevrier and K. Hahn. B Fischer and E. Martel of Northwest Territories Geoscience Office are gratefully acknowledged for field support and lively discussion. A. Macdonald and W. Zhe are thanked for assistance and insight in XRD analysis. This is NTGO contribution 85.

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