A field, petrographic and preliminary S isotopic study of the Walt and Tyrala sediment-hosted barite occurrences (105O/7), and associated Ba-Zn-Pb mineralization, MacMillan Pass district, Yukon

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ABSTRACT

The MacMillan Pass district (map sheet 105O) located in east Yukon contains several sedimenthosted Ba ± Zn ± Pb deposits including the Tom and Jason deposits, as well as a multitude of 'barren' sediment-hosted barite occurrences. A classic sedimentary-exhalative (SEDEX) model has been postulated for these occurrences in which the barite horizons represent distal expressions of a hydrothermal vent system. Fieldwork was completed at the Walt and Tyrala barite occurrences that occur within the MacMillan Pass district in order to examine the deposit-scale geology and to sample undeformed barite horizons for subsequent geochemical analysis. Samples were also collected from drill core from the Hess barite occurrence. Barium mineralization occurs in both the Devonian Portrait Lake Formation (Lower Earn Group) and in underlying Ordovician-Silurian limestone of the Road River Group. A variety of textures were encountered that were indicative of both synsedimentary deposition of barite, as well as diagenetic to epigenetic barite mineralization. Base metal sulphides that are interpreted to post-date the barite mineralization were encountered at depth in drill core and are primarily hosted by Road River Group carbonates.

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INTRODUCTION

Sedimentary basins host some of the world's major base metal (Zn, Pb, Cu) mineral deposits e.g., McArthur Basin, Australia; the Zambian Copperbelt; and Rammelsburg, Germany. In particular, sedimentary-exhalative (SEDEX) deposits are an important source of these commodities. SEDEX deposits gain their name from the original model proposed by Carne and Cathro (1982), whereby fluids were "exhaled; and precipitated metals on the seafloor". In this model, fluids are sourced from deep within the basin and transported along structures such as synsedimentary faults to the sediment-seawater interface. Upon reaching the seafloor, the mineralizing fluids then interact with the water column, which is thought to be stratified into upper oxygenated and lower anoxic layers (Goodfellow, 1987). In this model, sulphide minerals, mostly occurring as sphalerite ((Zn,Fe)S) and galena (PbS), precipitate due to mixing of anoxic, reduced (H₂S_{ac}-rich) seawater with saline, metaliferous, oxidized $(H_2S_{ar}-poor)$ fluids. Barite (BaSO₄) is thought to represent the distal component of the hydrothermal vent associated with SEDEX mineralization, and is precipitated in the upper, oxygenated (SO₄²- rich) layer. Hence, stratification of the ocean is crucial for both sulphide mineralization and barite precipitation. Minerals precipitated as a result of these reactions, accumulate on the basin floor along with normal marine sediments to form stratiform deposits that contain sulphide-rich and sediment-rich laminations that can often display normal sedimentary features such as bedding and grading. Therefore, barite textures can be used to vector to the sulphide component of the SEDEX system.

One subset of SEDEX deposits is the vent-proximal type (Goodfellow *et al.*, 1993). The conduit for fluids in this case is thought to be a growth fault that creates relief on the sea-floor (Goodfellow and Lydon, 2007). The vent facies can be recognized in paleosystems by brecciation of the basinal units, and the replacement of the host rocks by sulphides and iron carbonates (Fig. 1).

An understanding of SEDEX fluid geochemistry is important for understanding the relationship, if any, between a sulphide ore deposit and possible hydrothermal 'exhalites' that may precipitate at a distance from their source. In Canada, the Selwyn basin, which is located in both Northwest Territories (NWT) and Yukon, contains several economic zinc-lead-silver resources that have been assigned a SEDEX deposit type. Additionally, the Selwyn basin is host to a number of sedimentary barite occurrences whose origins remain unknown. The major

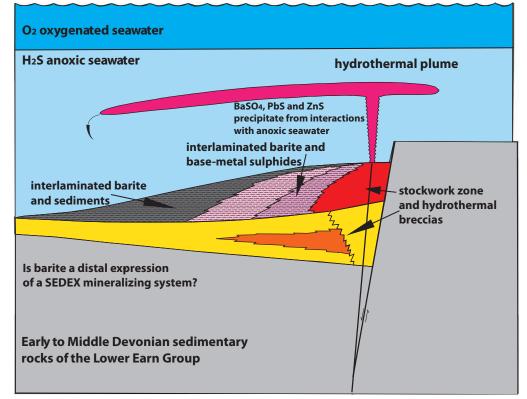


Figure 1. Idealized cross-section of a vent proximal SEDEX deposit (modified from Goodfellow and Lydon, 2007).

vent-proximal deposits of the Selwyn basin are thought to have formed in the late Devonian-Mississippian based on the age of host lithologies (Goodfellow and Lydon, 2007). Important sediment-hosted barite sequences that are found in both NWT (Fernandes *et al.*, 2010) and in the MacMillan Pass district, Yukon are interpreted to be in host rocks of the same age (e.g., Turner and Goodfellow, 1990). Barite occurrences and deposits that occur in the MacMillan Pass district include the Hess, Cathy, Walt and Tyrala showings and are found ~30 km northwest of the Tom Ba-Zn-Pb deposit which is also hosted in Lower Earn Group rocks.

This study represents part of a MSc project currently being completed at the University of Alberta, which is focussed on examining sediment-hosted barite mineralization occurring in the Devonian-Mississippian Earn Group in Northwest Territories and Yukon. In this contribution we present preliminary field and analytical results from the barite occurrences examined in Yukon.

Our main objectives of this study are:

- 1.To sample drill core from the Hess barite occurrence in order to understand the relationship between the barite and sulphide mineralization.
- 2. To investigate the Walt and Tyrala sediment-hosted barite occurrences (which include the Hess barite occurrence) in the MacMillan Pass district.
- 3. To analyse the S isotope compositions of sulphides in Hess barite samples in order to better constrain the relationship between sediment-hosted barite and Zn-Pb mineralization in the MacMillan Pass district.

BACKGROUND GEOLOGY

One of the best preserved and documented examples of an epicratonic sedimentary sequence is found in the Selwyn basin in northwestern Canada. This is interpreted to have formed on the passive margin of Ancient North America as a result of erosion of the crystalline basement during continental breakup initiated at ~760 Ma (Eisbacher, 1981). The oldest rocks exposed in the Selwyn basin consist of a thick (4-6 km) sequence of Hadrinian-Cambrian clastic sedimentary rocks of the Windermere Supergroup (Eisbacher, 1981). However, the Windermere Supergroup may also represent the basement to the Selwyn basin and current work by the Yukon Geological Survey (YGS) will refine its regional setting (J. Chakungal, *pers. comm.*, 2010). The Windermere Supergroup rocks are overlain by deepwater Cambrian-Ordovician carbonate rocks of the Sekwi Formation, which in turn are overlain by Late Ordovician-Silurian basinal facies chert and shale of the Road River Group (Cecile, 1982; Gordey *et al.*, 1982). The basinal sedimentary facies is bounded by the Mackenzie and Macdonald carbonate platforms to the east and north and dissected by the intrabasinal shelf facies of the Cassiar Platform in the south-central part. The regional stratigraphy is illustrated in Figure 2.

Sedimentation changed dramatically in late Devonian time when transgressive shale covered the platform and thick sequences of basin-derived clastic sediments accumulated in a number of submarine fan complexes to the west (Gordey *et al.*, 1982). This was followed by a sequence of arenites and debrites deposited in the early Mississippian. This group of Devonian-Mississippian rocks was first formally defined as the Earn Group in the Nahanni, Sheldon Lake, Niddery Lake and Sekwi Mountain map areas by Gordey *et al.* (1982). They divided the Earn Group into a lower and an upper unit, with the lower unit consisting of basinal siliceous shale, mudstone and shaley siltstone, and the upper unit containing coarser-grained turbiditic siliciclastic rocks.

The focus of this study are the units belonging to the sedimentary rocks of the Earn Group. The Earn Group is subdivided into the Lower Earn Group and the Upper Earn Group (Fig. 3). The Lower Earn Group; known as the Portrait Lake Formation in Yukon and as the Canol Formation in NWT, consists of a package of cherty mudstones, black, siliceous shales and grey siltstones that often weather to a characteristic silver colour.

The Upper Earn Group unconformably overlies the Canol/ Portrait Lake formation which is known as the Imperial Formation in NWT and the Prevost Formation in Yukon (more recently called the Itsi Member of the Earn Group (Abbott and Turner, 1990)). The Upper Earn Group comprises coarse-grained, brown debrites and sandstones. The MacMillan Pass district of Yukon also has a chert pebble conglomerate unit, the MacMillan Pass Member, which is not well-constrained stratigraphically, but is thought to occur in the middle of the Lower Earn Group (Fig. 3b; Gordey and Anderson, 1993). Further confusion occurs when reading older literature (e.g., Large, 1980) that originally used the Canol and Imperial Formation nomenclature in Yukon (Fig. 3c).

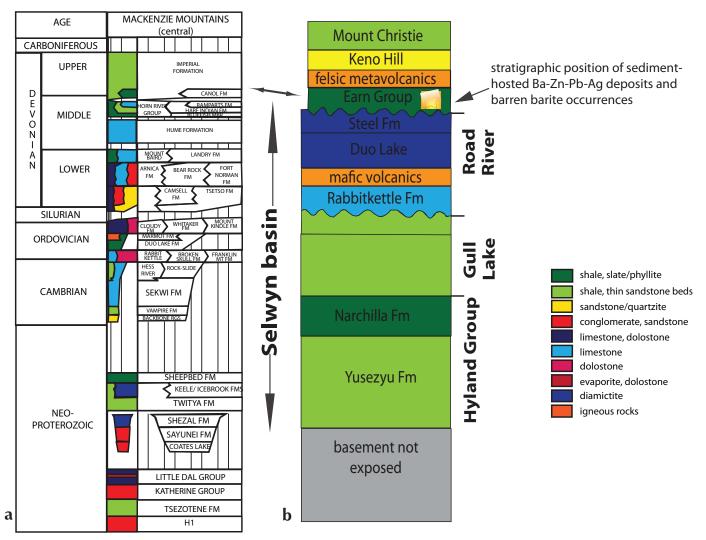


Figure 2. (a) Regional stratigraphy of the Mackenzie Mountains (modified after Dewing et al., 2006); (b) regional stratigraphy of the western Selwyn basin (modified after J. Chakungal, pers. comm., 2010)

For simplicity, we use Yukon stratigraphic nomenclature when describing the geological setting of the barite occurrences in the MacMillan Pass district; however, we recognize that this terminology is different from nomenclature used in NWT and that Portrait Lake Formation is interchangeable with the Canol Formation and that Itsi Member of the Portrait Lake Formation correlates to the Imperial Formation.

GEOLOGICAL SETTING OF STUDY AREA

The Hess occurrence (Yukon MINFILE 105O 021) is found in the MacMillan Pass district, east Yukon and is located in map sheet 105O (Fig. 4). Showing locations (Yukon MINFILE, 2010) are provided on a map of local geology (Fig. 5; J. Chakungal, *pers. comm.*, 2010). Abbott (1982) divided the MacMillan Fold Belt (MFB) into three tectonostratigraphic domains (North, Central and South blocks) based on style of Mesozoic structures present and distribution of Silurian-Devonian stratigraphy. The Nidd deposit, along with the Jason and Tom stratiform zinc-lead deposits, occur within the Central Block. This block is dominated by west-trending tight folds and steep faults. In the Central Block, lower Earn Group stratigraphy overlies basaltic flows and volcaniclastic rocks as young as late-middle Devonian (Turner and Rhodes, 1990).

Abbott *et al.* (1987) recognized three informal units within the Lower Earn Group: a lower member of carbonaceous chert, a middle turbidite member, and an upper member of carbonaceous siliceous shale. A thick conglomerate unit (MacMillan Pass Member; Fig. 3c) occurs within the middle turbidite member and reflects the development of a Devonian graben (Abbott, 1982). Also restricted to

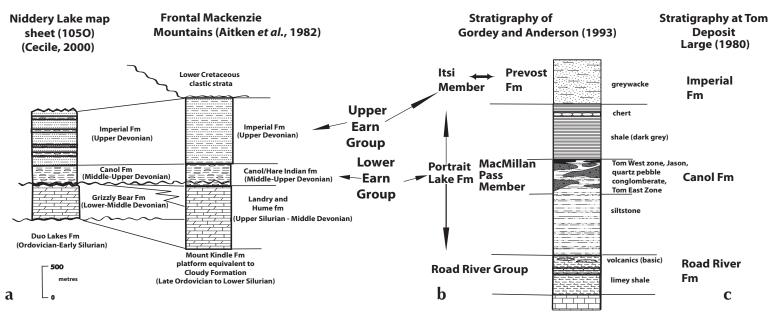


Figure 3. (a) Earn Group Stratigraphy in the Selwyn basin and Frontal Mackenzie Mountains (modified after Aitken et al., 1982; Cecile, 2000); (b) Earn Group stratigraphy in MacMillan Pass district (modified after Gordey and Anderson, 1993); (c) Earn Group stratigraphy at the Tom SEDEX deposit (modified after Large, 1980).

this graben are Silurian and Devonian volcanic rocks, late Devonian faults and upper Devonian stratiform zinc-lead mineralization. The Hess occurrence is located along the southern margin of the North Block, a domain intensely deformed by an imbricate package of south-directed thrust faults (Turner and Goodfellow, 1990).

HESS/WALT/CATHY/TYRALA SEDIMENT-HOSTED BARITE

The sediment-hosted barite showings correspond to Yukon MINFILE 105O 021 and 105O 022 and are located within the Walt and Tyrala claim blocks. These barite occurrences were drilled by Baroid of Canada in 1980, mapped and sampled by Cominco, and later, samples that were anomalous in zinc, lead and copper were re-examined by NDU Resources (Yukon MINFILE, 105O 021). Samples were collected from a single drillhole (Hess Barite) from Hess during fieldwork in 2009 and a field investigation was conducted on the claim blocks during summer of 2010.

FIELD RELATIONSHIPS

Sediment-hosted barite at all occurrences in the study area occurs within interbedded shale and siltstone of the Portrait Lake Formation, and in massive to brecciated limestone of the underlying Road River Group carbonates. The Itsi Member of the Portrait Lake Formation (Upper Earn Group) is absent in the study area. No sulphides were observed in outcrop samples.

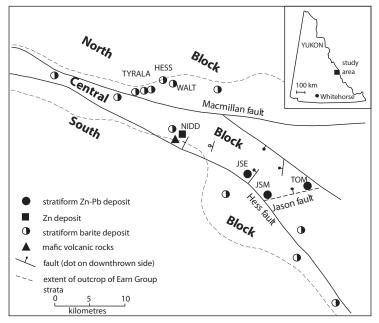
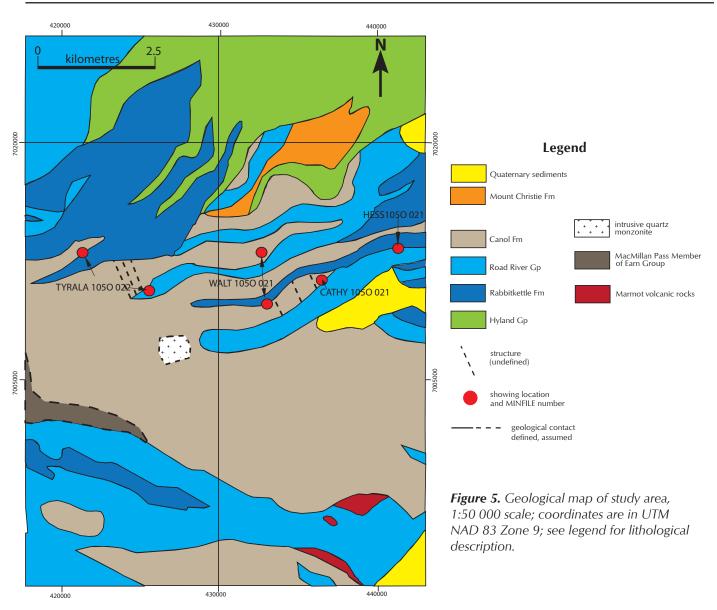


Figure 4. District map of the MacMillan Pass region illustrating major structural blocks, trends and deposits/showings. JSE = Jason Endzone, JSM = Jason Main zone (modified after Turner and Goodfellow, 1990).

YUKON GEOLOGICAL RESEARCH



Barite that is hosted in Portrait Lake Formation shale and mudstone occurs predominantly as fine laminations (Fig. 6a) or in minor, millimetre-sized nodules (Fig. 6b). Tight to isoclinal folding of barite laminations indicates a pre-fold and thrust deformation origin (Fig. 6c). Barite laminae vary from 0.5 to 2 mm in thickness, are dark grey in colour and organic rich. Barium-enriched laminae in the Road River Group carbonates are dark grey, weather to a pale cream colour, and are composed of fine-grained barium carbonate and barite (Fig. 6d). Barite nodules are round, roughly 1 mm in diameter, and are composed of sub-millimetre, radiating barite crystals which make up less than 2% of samples. These primary structures indicate syngenetic to early diagenetic deposition of barium minerals within the Road River Group and Portrait Lake Formation.

Within the study area, the greater majority of barite deposition occurred within the Road River Group carbonates and have a marked fault-related structural control punctuated by sharp contacts (Fig. 6e). X-ray diffraction (XRD) analyses of samples indicates the presence of both barite and numerous barium carbonates such as barytocalcite $(BaCa(CO_2)_2)$ and norsethite $(BaMg(CO_2)_2)$, in addition to variable amounts of calcite and dolomite. Massive, fine to medium-grained barium carbonate is the principal component of barite lenses, up to 20 m in thickness that form steep, resistant ridges. Barium carbonate breccias range from pale grey, angular to subrounded, and clast-supported, to large, subrounded pale grey clasts up to 50 cm in diameter in a finegrained, dark grey siliceous matrix (Fig. 6f). Clasts that are composed of fine-grained barium carbonates suggest coeval barium replacement of limestone and brecciation.

HESS BARITE DRILL CORE

Samples were collected from a weathered Cominco Ltd. drillhole at the Hess barite occurrence, which was drilled to a depth of 105.5 m. Textures associated with barium mineralization are similar to those observed in outcrop. Subsequent XRD analysis confirmed the presence of varying amounts of barite and barium carbonates with the Hess barite samples.

The Cominco drillhole was collared in deformed and locally brecciated, non-calcareous, black siltstone and mudstone of the Portrait Lake Formation (Fig. 7a). Minimal barite was observed from 0 to 39 m in the hole. Unmineralized siltstone and mudstone units are underlain (39 – 105.5 m) by increasingly altered, brecciated, and carbonate, sulphide and barite-rich lithologies.

The carbonate units contain barium minerals that exhibit similar epigenetic textures found in outcrop such as breccias (Fig. 7b). Barium minerals are overprinted by disseminated sulphides consisting of coarse-grained, euhedral pyrite and medium-grained galena crystals (Fig. 7c), which can occur as 0.5 cm-patches and as millimetre-thick veinlets that crosscut laminations (Fig. 7d). Sphalerite commonly occurs in these sulphide patches as fine-grained, light honey-brown anhedral crystals. One sample (~88.65 m depth) has thin laminations of sphalerite interlaminated with host carbonates (Fig. 7e). Late quartz veinlets also crosscut all host rocks and mineralization (Fig. 7f).

SULPHUR ISOTOPE GEOCHEMISTRY

Sulphur (S) is present in nearly all natural environments and is a critical component of ore deposits, where S is the dominant non-metal phase. Fractionation of S isotopes is highly dependent on the process of metal deposition, furthermore S variations in nature are caused by redox reactions involving the isotopic species.

Goodfellow and Lydon (2007) propose that the anoxic part of the seawater column is the source for S in sediment-hosted ore deposits. In this study, we will compare the δ^{34} S of the sulphides and sulphates from all showings examined to assess whether ore-bearing fluids are genetically related. The δ^{34} S values of hand-picked sulphides from drill core were analysed in order for future comparison with the δ^{34} S values of barite from the same locality. These will be compared against established δ^{34} S values for seawater and sediments during the respective

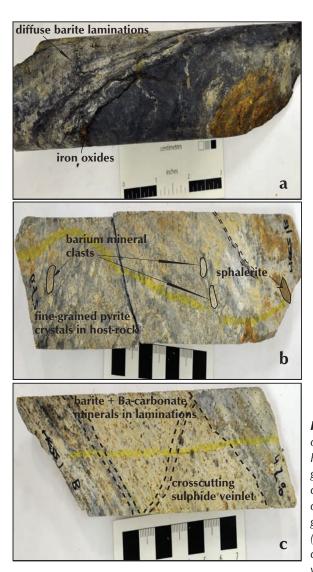


Figure 6. (a) Shale-hosted laminated barite mineralization (sample 10NF42F); *(b)* shale-hosted nodular barite mineralization (sample 10NF40A); *(c)* pre-deformation laminated barite wraps around a fold hinge; *(d)* laminate barium mineralization in Road River Group carbonates at Walt showing; *(e)* sharp contact between barite replacement of Road River Group carbonates at Cathy showing; and *(f)* barium carbonate breccias in Road River Group carbonates.

times of deposition for the Road River Group and Lower Earn Group (e.g., Claypool *et al.*, 1980)

ANALYTICAL TECHNIQUES

The sulphur isotope ratios of sulphides were determined using Continuous Flow Elemental Analyzer Isotope Ratio Mass Spectrometry (CF-EA-IRMS) at the University of Calgary. The instrumentation comprises a Carlo Erba NA 1500 elemental analyzer interfaced to a VG PRISM II mass spectrometer. Samples are packed in tin cups, which are dropped by auto sampler onto a quartz tube combustion reactor. The temperature of this column is maintained at 1020°C and 'flash-combustion' is achieved by injecting a pulse of O₂(gas) exactly at the time of sample drop. The eluent gases are then swept by the helium carrier stream through a gas chromatography column to achieve



separation of SO₂, CO₂ and NO_x's before being focussed through an open split into the ion source of the mass analyzer. δ^{34} S values are determined by comparing the respective sample peak areas, as [Amp-s], to a reference gas peak inlet from the DI reference bellows of the mass spectrometer during each sample run. Raw data was normalized to the Cody Diablo Troilite (CDT) reference scale. The precision of using the VG Prism II–CE EA1500 technique, is generally better than $\pm 0.25\%$ (n=10).

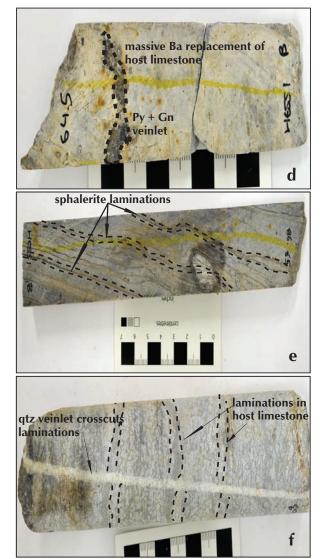


Figure 7. (a) Canol Fm mudstone with minor diffuse barite and iron oxide mineralization (depth = 27.05 m); (b) brecciation of host Road River Group limestone and replacement by barium carbonate, finegrained pyrite and sphalerite (depth = 57 m); (c) laminated barium carbonate mineralization in Road River Group carbonates, note disseminated pyrite throughout sample (depth = 42.8 m); (d) pyrite + galena veinlet crosscutting massive barium carbonate-rich rock (depth = 64.5 m); (e) sphalerite laminations in weakly barium carbonate-replaced limestone (depth = 86.85 m); (f) late quartz veinlet crosscuts laminated barium mineralization (depth = 89.5 m).

RESULTS

The δ^{34} S values for sulphides (vCDT) from drill core from the Hess barite occurrence range between +24.3 to +28.4‰ for pyrite, +23.4 to +26.2‰ for galena (one sample at +7.6‰), and 24.6‰ for a single sphalerite sample. Co-existing, intergrown sulphides display similar δ^{34} S values. These results are summarized in Table 1.

SUMMARY

Barium mineralization that occurs at the Walt and Tyrala mineral occurrences in the MacMillan Pass district of Yukon is hosted in carbonates of the Siluro-Ordovician Road River Group, and shale and mudstone belonging to the Portrait Lake Formation (*i.e.*, Lower Earn Group). Barite mineralization pre-dates the ductile deformation that is associated with formation of the MacMillan fold belt.

Barium minerals are predominantly found in the altered limestone lenses of the Road River Group, where they occur as barite and barium carbonates (barytocalcite, norsethite and witherite). These barium phases either massively replace host limestone, or are in the form of breccias, laminations or nodules.

Barite laminations may indicate either synsedimentary depositional textures, or may represent preferential replacement along pre-existing heterogeneities or chemically favourable horizons in the host rock. We consider the majority of the textures observed at these showings to be secondary (*i.e.,* replacing a pre-existing favourable host-rock). Replacement, brecciation and nodule formation are features of diagenetic to epigenetic mineralization that could have only taken place beneath the sediment water interface (SWI).

Additionally, our observations indicate that one protracted episode (or possibly two phases) of barium mineralization may have developed. This occurs by syngenetic to early diagenetic deposition of barite in the Portrait Lake Formation along with contemporaneous epigenetic barium mineral replacement in the Road River Group carbonates related to brittle deformation.

The Road River Group carbonate horizons are the primary host for sulphide mineralization. Sulphide minerals include intergrown coarse-grained pyrite and fine-grained galena ± sphalerite. Sulphide mineralization observed in the Hess barite occurs as disseminations in the host rock, or in crosscutting veins that post-date ductile deformation and barium mineralization.

The δ^{34} S values for sulphides fall within a very tight range from +24 to +28‰ which suggest that S in basemetal sulphides was derived from a single fluid source. Epigenetic sulphide mineralization in the Road River Group and Portrait Lake Formation has δ^{34} S values consistent with seawater evaporite values for the Late Devonian (e.g., Claypool *et al.*, 1980). However, as sulphide mineralization post-dates lithification of the Road River Group, the fluid(s) from which they derived their δ^{34} S values may not necessarily have been seawater, but possibly fluids

(e.g., pore waters) derived from basinal sediments.

Importantly, we note that the sedimentary units that host barite mineralization in the MacMillan Pass district are not restricted to the Lower Earn Group as was previously described (Turner and Goodfellow, 1990), but also include the Road River Group carbonates, where mineralization is epigenetic to host limestone.

Pyrite	δ ³⁴ S	Galena	δ ³⁴ S	Sphalerite	δ ³⁴ S
H45.0 PY	24.4	H45.0 GN	25.3	H64.5 SPH	24.3
H45.0 PY	24.6	H45.6 GN REP	24.6	H64.5 SPH REP	24.7
H45.0 PY	24.3	H61.6 GN	23.4		
H45.6 PY	23.1	H61.6 GN REP	23.8		
H46.2 LSTPY	24.5	H62.4 GN REP	25.4		
H46.2 SHLPY	24.4	H64.5 GN	7.6		
H57.3 PY	28.4	H66.7 GN	26.2		
H61.6 PY	25.1	H66.7 GN REP	26.0		
H62.4 PY	25.0				
H64.5 PY	25.3				

Table 1. Summary of δ 34S values for sulphides from Hess barite drillhole for pyrite, galena and sphalerite respectively. Number in sample name indicates relative depth of sample downhole. LST = limestone-hosted, SHL = shale-hosted.

FUTURE WORK

Future work will include detailed petrography and further stable isotope analysis of sulphides, sulphates and carbonates. The age of pyrite mineralization will also be determined using Re-Os dating techniques and compared to data from other sediment-hosted lead-zinc-barite deposits in the MacMillan Pass district. Petrography will focus on determining whether barite mineralization in the study area is a primary sedimentary event.

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