

Geology, Geochemistry and Mineralogy of Hyper-Enriched Black Shale Deposits, Yukon

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ABSTRACT

Hyper-enriched black shale (HEBS) deposits are a globally important resource for base-, strategic- and precious-metals. In northern Yukon, thin (3 to 40 cm-thick) HEBS deposits occur sporadically over 1000s of km² at the Road River Group-Canol Formation contact. The deposits in each location share lithological and geochemical characteristics (particularly Ni-Zn-Mo-PGE enrichment). Despite decades of research, there is little consensus on how these formed. Exploration for HEBS mineralization is hampered due this poor understanding; however, through ongoing research, we aim to develop a genetic model that accounts for the salient features within these deposits.

INTRODUCTION

Hyper-enriched black shales (HEBS; also referred to as polymetallic metalliferous shales) are an important global resource for Zn, Ni, Cu, Mo, Se, U, V, ± Cr, Co, Ag, Au, PGE and REE (Jowitt and Keays, 2011). These deposits are thin (<10 cm) and laterally widespread, covering 1000s of km² (e.g., Cambrian, Yangtze Platform, China; Devonian, Mackenzie Platform, Yukon). Canada hosts some of the best examples globally (e.g., Nick deposit, Yukon; Hulbert et al., 1992). The Nick deposit was discovered in 1981 by Cominco geologists by following up a Geological Survey of Canada stream sediment survey (Garrett et al., 1977; Carne, 1989). The Ni sulphide horizon is very thin (3 to 10 cm) and discontinuously crops out over a strike length of 100 km (Carne, 1989). This style of mineralization has been recognized in many localities across northern Yukon (Figure 1), indicating that there is significant potential for further discoveries. However, exploration is currently hindered by a lack of understanding of how these deposits formed. Current genetic models are myriad and include: seafloor hydrothermal; ambient seawater/phosphogenesis/high organic productivity; and impact-related (e.g., Hulbert et al., 1992; Lehmann et al., 2007; Goodfellow et al., 2010). Basic questions that remain unresolved for the Yukon HEBS deposits include the age and duration of the mineralizing event(s) and the host phase(s) of PGE. The goal of our research is to develop a cogent, internally consistent genetic model for HEBS deposits using bulk and micro-analytical geochemical data.

REGIONAL GEOLOGY

The HEBS deposits are located within basinal strata equivalent to those of the Selwyn Basin to the south (Figure 1). These rocks are characterized by a thick (>100 m) succession of fine-grained, carbonaceous siliciclastic rocks of the Ordovician to Early Devonian Road River Group. The Canol Formation overlies

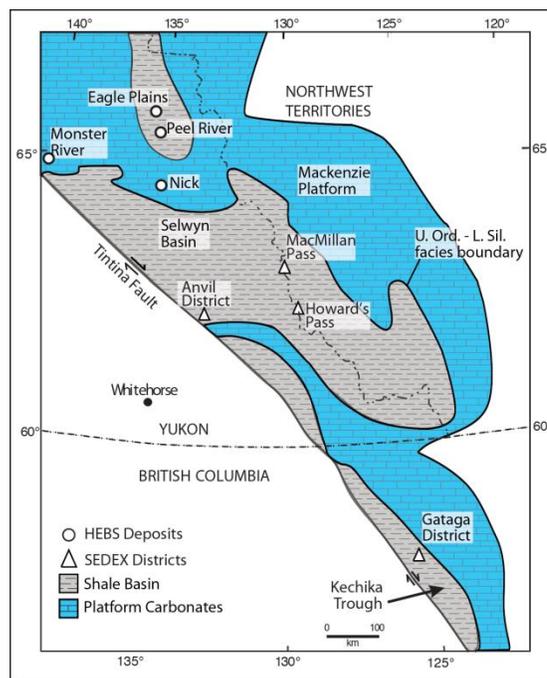


Figure 1: Map of ancestral North American passive continental margin displaying locations of key HEBS deposits and SEDEX districts.

Road River Group sedimentary rocks, and consists of up to ca.220 m of Middle Devonian to Early Late Devonian siliceous carbonaceous shale (at the Trail River section; Hutchison and Fraser, 2015). The nature of the contact between the Road River Group and overlying Canol Formation is unclear as it has been documented as both conformable and unconformable (Hutchison and Fraser, 2015; Pugh, 1983); however, a thin (3 to 40 cm-thick) Ni-Zn-PGE-rich HEBS layer at this contact is documented in many localities throughout northern Yukon (Figures 1, 2).

Locally, each of the HEBS deposits possesses nearly identical stratigraphy. From the base upward (Figure 2), the section is comprised of: 1) a conspicuous unit comprised of 1 to 1.5 m-diameter calcareous concretions within carbonaceous shale; this so-called “limestone ball” member is 2 to 20 m thick. Shale beds drape around the concretions, and bedding is preserved within some concretions; 2) siliceous, carbonaceous shales with cm-scale barite and/or calcite concretions. This unit is up to 250 cm thick; 3) Ni-sulphide HEBS layer that is 3 to 40 cm thick; 4) carbonaceous, siliceous shale to black-cherty shale in sharp contact with the underlying HEBS mineralization.

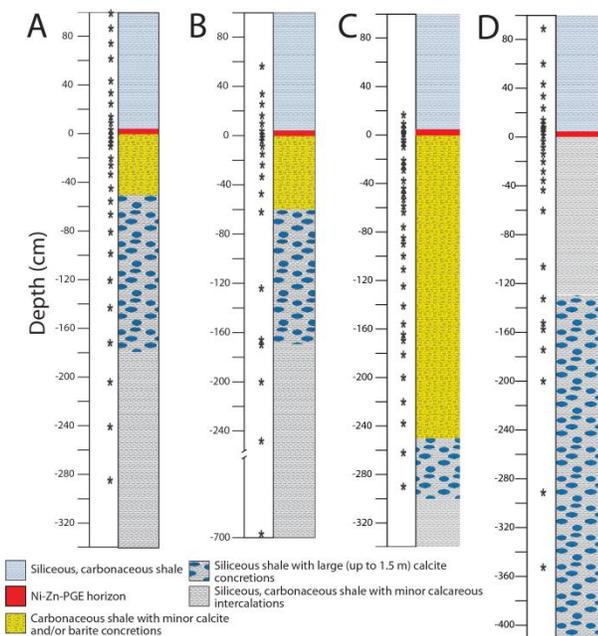


Figure 2: Schematic stratigraphic sections of: A) Eagle Plains, B) Peel River, C) Monster River and D) Nick HEBS localities, Yukon. Note: asterisks indicate sample locations in Figure 3.

Horan et al. (1994) conducted Re-Os isotope analyses of HEBS and host black shales at the Nick deposit. They found that Re-Os-PGE enrichment occurred during or shortly after deposition, and mineralization is a maximum of 380 Ma to a minimum of 367 Ma. Goodfellow et al. (2010) recovered conodont elements from the limestone-ball unit a few metres below HEBS mineralization at Peel River that yielded Emsian to Middle Eifelian (i.e., Middle Devonian) ages; however, no conodont elements were recovered from the HEBS deposits. Radiolarians recovered from the shales 40 cm above the HEBS layer yield Middle Frasnian to Early Famennian ages (Goodfellow et al., 2010). There is no chronostratigraphic or biostratigraphic information for the other HEBS localities, but they are surmised to be contemporaneous based on their nearly identical stratigraphy and bulk geochemistry.

GEOCHEMISTRY, MINERALOGY AND MINERAL CHEMISTRY OF THE HEBS MINERALIZATION

The HEBS layer possesses striking enrichments in a broad suite of elements relative to the enclosing sedimentary rocks (Figure 3). Values range up to: Fe (21 wt.%), S (28.9 wt.%), Ni (7.0 wt.%), Mo (0.33 wt.%), Zn (2.3 wt.%), Pt (511 ppb), Pd (202 ppb), Ir (10.9 ppb), Ru (12 ppm), Re (25.8 ppm), Se (0.57 wt.%) and As (1.1 wt.%).

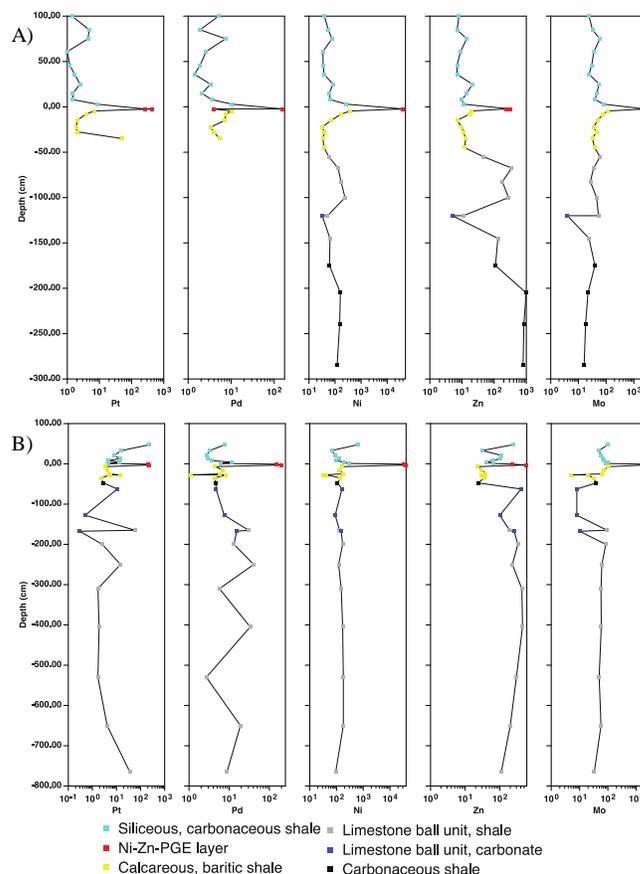


Figure 3: Geochemical profiles of stratigraphic sections at A) Eagle Plains and, B) Peel River. Note that Pt and Pd are ppb and Ni, Zn and Mo are ppm.

The mineralogy among the different HEBS localities is relatively uniform. Broadly, the sulphide mineralogy comprises pyrite, Ni-sulphides—millerite (NiS), vaesite (NiS₂) and gersdorffite (NiAsS)—and sphalerite, whereas non-sulphide minerals are predominantly quartz, barite, apatite, pyrobitumen and trace to minor hyalophane (Ba-K feldspar) and K feldspar. The mineralization is ≈ 60% sulphide minerals and 40% non-sulphide gangue minerals (Hulbert et al., 1992). Vaesite is the main Ni sulphide mineral at Nick, whereas millerite predominates at the Peel River, Monster River and Eagle Plains localities.

At the Nick deposit, vaesite is anhedral and forms encrustations on, and is interstitial to, pyrite (Figures 4A, 4B). Electron probe

microanalysis (EPMA) indicates that the average major and minor element composition of vaesite is 44.8 ± 1.3 wt.% Ni, 50.1 ± 0.6 wt.% S and 1.5 ± 0.6 wt.% Se, <0.1 to 0.95 wt.% As, 0.6 to 1.8 wt.% Fe, <0.1 to 0.26 wt.% Cu and 0.15 to 0.26 wt.% Tl. Millerite at the Peel River, Monster River and Eagle Plains HEBS occurrences is subhedral, but otherwise shares the same textural associations with pyrite in that millerite is generally either interstitial to pyrite grains (Figures 4C–E) or encrusts pyrite nodules (Figure 4F). EPMA data indicate that the major element composition of millerite is 60.5 to 64 wt.% Ni, 29.8 to 36.4 wt.% S and 0.24 to 9.5 wt.% Se; millerite also contains <0.1 to 0.14 wt.% As, <0.1 to 2.8 wt.% Fe and <0.1 to 0.18 wt.% Tl. Gersdorffite is a relatively rare mineral in the Yukon HEBS deposits and is most commonly encountered at the Peel River locality. There, 10 to 20 μm -thick veneers of euhedral gersdorffite mantle 50 to 100 μm -diameter grains of millerite and/or sphalerite (Figure 4D). These sulphide minerals are enclosed within minute, enigmatic Ba-K feldspar ellipsoidal structures that may be of biogenic origin. The major element composition of gersdorffite is 34.8 ± 0.5 wt.% Ni and 19.4 ± 0.5 wt.% S, 43.6 ± 0.6 wt.% Ni and 2.1 ± 0.3 wt.% Se.

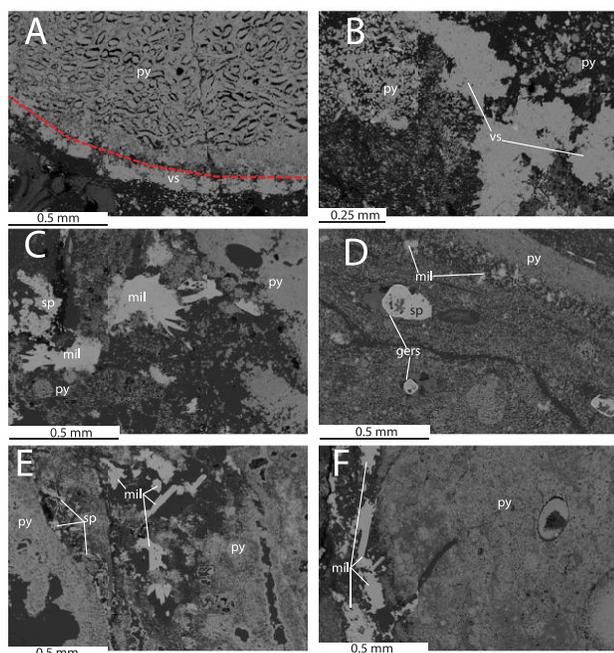


Figure 4: Back-scattered electron detector (BSE) images of: A) Vaesite mantling pyrite. The pyrite texture suggests that it is replaced organic matter (Nick Deposit); B) Anhedra to subhedral vaesite with framboidal pyrite and microcrystalline pyrite and sphalerite (Nick Deposit); C) Acicular to subhedral millerite with sphalerite and framboidal and microcrystalline pyrite (Peel River showing); D) Euhedral gersdorffite associated with sphalerite, millerite and Ba-rich feldspar within a matrix of semi-massive to laminated framboidal and microcrystalline pyrite (Peel River showing); E) Acicular millerite within microcrystalline pyrite and minor sphalerite (Eagle Plains showing); F) Acicular millerite at outer margin of fine-grained pyrite mass (Monster River showing). Vs = vaesite; py = pyrite; sp = sphalerite; mil = millerite; gers = gersdorffite.

Pyrite in the HEBS layers has varied and complex textures. The textures are similar at all of the occurrences, and include framboids (<0.003 to ca. 0.1 mm in diameter; Figures 4A–D), minute crystals (0.01 to 0.1 mm; Figure 4B, D), replacements of organic remains (Figure 4A) and anhedral masses (Figure 4B, E, F). Individual grains and masses commonly possess two to three textural varieties, suggesting that pyrite formed during several stages. For the sake of brevity, pyrite EPMA data will be presented as framboidal and non-framboidal. The major element composition of framboidal pyrite is homogeneous across the HEBS occurrences, with 45.6 ± 0.4 wt.% Fe and 52.8 ± 0.6 wt.% S; framboids also contain <0.1 to 0.77 wt.% Ni and <0.1 to 0.18 wt.% As. The major element composition of non-framboidal pyrite is 44.7 ± 1.12 wt.% Fe and 52.7 ± 0.48 wt.% S; non-framboidal pyrite also contains <0.1 to 4.5 wt.% Ni, <0.1 to 1.41 wt.% As and <0.1 to 1.96 wt.% Se.

Pyrobitumen grains from the HEBS layer at the Peel River locality were extracted and analyzed using laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS). These preliminary data reveal that a minor proportion of metals and metalloids are contained within the altered organic matter (Figure 5). The most abundant metal is V, with a mean value of 2200 ppm. Nickel and Fe are also relatively abundant, with mean values of 463 and 265 ppm, respectively. The mean values of all of the other trace elements are below 10 ppm. PGE are mostly absent, but mean Au and Re values are 38 and 118 ppb, respectively.

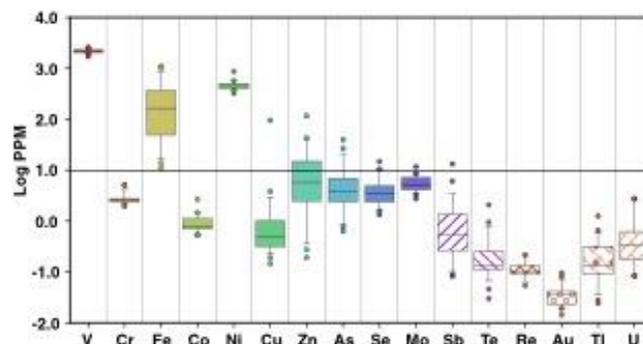


Figure 5: Trace element compositions of pyrobitumen from the HEBS layer at the Peel River locality.

DISCUSSION

Age of HEBS Deposits

Determination of absolute age information for the HEBS deposits has proven extremely difficult. Although Horan et al. (1994) were able to obtain Middle to Late Devonian model Re-Os dates for the Nick deposit, Re-Os dating attempts at the other HEBS localities have proven fruitless (due to post-depositional remobilization of Os; Beranek pers. comm. 2016). We attempted to liberate conodont elements from the sulphide/shale matrix of the shales by electric pulse disaggregation and also by chemical dissolution. Neither technique provided optimal results, but small rock fragments with visible conodont elements were handpicked and analyzed using scanning micro-tomography. The 3D volumetric models of conodont elements derived from

x-ray micro-tomographic data for the Peel River HEBS locality are shown in Figure 6. Although the computer-generated images are coarse (voxelated), the conodont elements are tentatively identified as *Polygnathus varcus* or *Polygnathus ensensis* (S. Gouwy pers. comm. 2017). That these conodont elements can be identified from their voxel models suggests that this method is viable for samples that are otherwise unfit for weak acid digestion methods (i.e., indurated siliceous shales). These conodont elements span from Early to Middle Devonian, indicating a maximum age of Early Late Devonian. Goodfellow et al. (2010) proposed that the age of the HEBS deposits coincided with the Frasnian-Fammenian boundary in the Late Devonian; however, our conodont ages contradict this because they are consistent with the Road River Group-Canol Formation age of Late Middle Devonian (Hutchison and Fraser, 2015). Additional data are required to establish whether the same conodont species are present in HEBS from the other localities. This is necessary to elucidate the number and duration of HEBS-forming event(s). Moreover, the controls on thickness variations in the HEBS layer (e.g., up to 40 cm-thick at Peel River compared with 3 cm-thick elsewhere) are poorly understood (Hulbert et al., 1992).

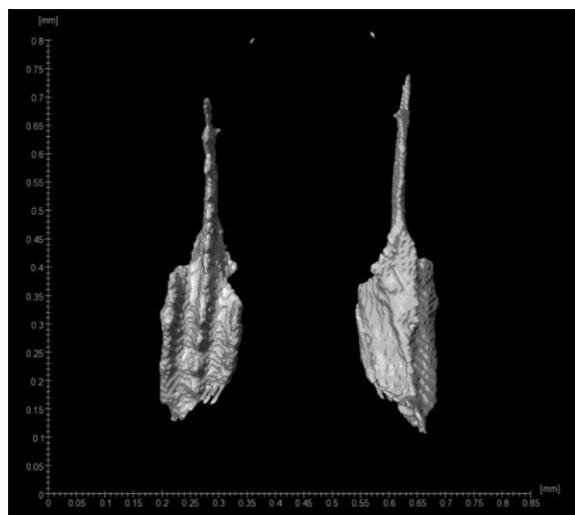


Figure 6: X-ray micro-tomography-generated 3D models of conodont elements within semi-massive sulphides of the HEBS layer at Peel River.

Genetic Models

Hulbert et al. (1992) suggest that the mineralization was formed from a seafloor-hydrothermal system, whereby carbonaceous shales underlying the HEBS layer supplied metalliferous brines. These brines were subsequently discharged into carbonaceous oozes within a euxinic, stratified water mass. Steiner et al. (2001) suggests a similar origin for the Cambrian Chinese HEBS deposits; however, other researchers favour formation by quantitative scavenging of metals from seawater by organic matter under biologically productive, sediment-starved basinal conditions (Lehmann et al., 2007; Lingang et al., 2011). Goodfellow et al. (2010) proposed that the Yukon HEBS deposits are of extraterrestrial origin. They suggest that the underlying limestone-ball member is a tsunami deposit that was generated by a large bolide impact. These authors also suggest

that the laterally widespread mineralized horizon and pronounced Ir anomaly are best accounted for by an impacting Fe meteorite, and that the impacting event perhaps coincided with the Frasnian-Fammenian extinction interval.

The residence site(s) of the PGE has yet to be identified. EPMA and LA-ICP-MS analyses of sulphide minerals and pyrobitumen, respectively, have not revealed the mineral host. EPMA analysis of sulphides failed to identify PGE, and LA-ICP-MS analysis of pyrobitumen indicates that PGE do not reside within this mineraloid. We are presently performing LA-ICP-MS analyses of sulphide minerals to determine if the PGE are hosted within them.

CONCLUSIONS

There is still much to be learned from the Yukon HEBS Ni-Zn-Mo-PGE deposits, and it is our goal to elucidate how these deposits formed. Ongoing research aims to identify the geochemical, chronostratigraphic and mineralogical controls on the enrichment of metals in this thin HEBS horizon.

REFERENCES

- Carne, R., 1989, Nick Property, Yukon Territory Assessment Report, 8 p.
- Garrett, R. G., W. Goodfellow, and N.G. Lund, 1977, Uranium reconnaissance program national stream sediment + water geochemical reconnaissance data northern Yukon Territory: Geological Survey of Canada, Open File 418, 1-15.
- Goodfellow, W., H.H.J. Geldsetzer, K. Pride, T. Uyeno, and C. Gregoire, 2010, Geochemistry and origin of geographically extensive Ni-(Mo, Zn, U)-PGE sulphide deposits hosted in Devonian black shales, Yukon, TGI-3 Workshop: Public Geoscience in Support of Base Metal Exploration, 15-18.
- Horan, M. F., J.W. Morgan, R.I. Grauch, J. Coveney, J.B. Murowchick, and L.J. Hulbert, 1994, Rhenium and osmium isotopes in black shales and Ni-Mo-PGE-rich sulfide layers, Yukon Territory, Canada, and Hunan and Guizhou provinces, China: *Geochimica et Cosmochimica Acta*, 58, 257-265.
- Hulbert, L. J., R.C. Carne, D.C. Gregoire, and D. Paktunc, 1992, Sedimentary nickel, zinc, and platinum-group-element mineralization in Devonian black shales at the Nick Property, Yukon, Canada; a new deposit type: *Exploration and Mining Geology*, 1, 39-62.
- Hutchison, M. P. and T.A. Fraser, 2015, Paleoenvironment, paleohydrography and chemostratigraphic zonation of the Canol Formation, Richardson Mountains, north Yukon, in K.E. MacFarlane, M.G. Nordling, and P.J. Sack, eds., *Yukon Exploration and Geology 2014*, Yukon Geological Survey, 73-98.
- Jowitt, S. M. and R.R. Keays, 2011, Shale-hosted Ni-(Cu-PGE) mineralisation: a global overview: *Transactions of the Institution*

of Mining and Metallurgy, Section B-Applied Earth Science, 120, 187-197.

Lehmann, B., T.F. Nägler, H.D. Holland, M. Wille, J. Mao, J. Pan, D. Ma, and P. Dulski, 2007, Highly metalliferous carbonaceous shale and early Cambrian seawater: *Geology*, 35, 403.

Lingang, X., B. Lehmann, M. Jingwen, Q. Wenjun, and D. Andao, 2011, Re-Os age of polymetallic Ni-Mo-PGE-Au mineralization in Early Cambrian black shales of South China—A reassessment: *Economic Geology*, 106, 511-522.

Pugh, D. C., 1983, Pre-Mesozoic geology in the subsurface of Peel River map area, Yukon Territory and District of Mackenzie: *Geological Survey of Canada Memoir* 401, 61 p.

Steiner, M., E. Wallis, B.D. Erdtmann, Y. Zhao, and R. Yang, 2001, Submarine-hydrothermal exhalative ore layers in black shales from South China and associated fossils — insights into a Lower Cambrian facies and bio-evolution: *Palaeogeography, Palaeoclimatology, Palaeoecology*, 169, 165-191.