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Metal transport by liquid hydrocarbons: Evidence from metal-rich black shales and pyrobitumen veins, Selwyn Basin, Yukon, Canada

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Black shales hyper-enriched in metals occur within the Selwyn Basin, Yukon, Canada as thin (~3cm) laterally extensive layers within Late Devonian strata. These shales contain an average of 5 wt % Ni, 0.7% wt Zn, 770 ppb PGE + Au as well as anomalous concentrations of Se, As, Mo, P Ba and U. This mineralization shows many similarities to that of the metalliferous shales of early Cambrian age exposed in the Guizhou and Hunan provinces of China. The origin of these high metal concentrations in black shales is strongly debated and a variety of models have been put forward. It has been proposed that the metals are derived from seawater and they become hyper-enriched because of the isolation of the seawater in sediment starved, stratified euxinic basins (Lehmann et al., 2007). Other proposals include hyper-enrichment due to remobilization by hydrothermal fluids after initial enrichment by seawater (Large et al., 2012) and hyper-enrichment because of hydrothermal venting into accumulating organic-rich shales. A major problem for the models involving hydrothermal fluids, is that Ni is extremely insoluble in aqueous liquids. By contrast, a process that has not been considered and does not suffer this problem is mobilization by hydrocarbon liquids. These liquids are produced during diagenesis as the sediment enters and passes through the oil window, and most significantly for the present context, are known to be commonly enriched in Ni, V, Zn and the PGE. In the case of Ni and V, it is well-established that this is due to the formation of stable metalloporphyrins; the speciation of the other metals is not known. Thus, it is possible that hyper-enrichment of the metals referred to above could be due to their transport by liquid hydrocarbons along select bedding planes in black shales.

Pyrobitumen is present within the metal-enriched shale layer as spherical to lenticular droplets (30 – 150 µm diameter) and as numerous late stage veinlets that cross-cut early stage sulfide mineralization. Nickel-sulfide mineralization commonly surrounds the pyrobitumen veinlets, occurring as minor selvages. The veinlets are typically 10 µm wide and can extend across the entire sample (~3.5 cm). Pyrobitumen also occurs as much thicker veins in the surrounding shale packages. A difference between the veinlets in the metal-enriched shale layer and the thicker veins is that the former are not enriched in metals, whereas the one vein that has been analyzed to date contains 8000 ppm Zn, 2000 ppm Ni, 3700 ppm V, 220 ppm Mo and anomalous concentrations Au and PGE's. The vein textures vary from being massive to highly fractured. The fractures reach a maximum width of 50 µm and are infilled by quartz and carbonate. Compositionally, the carbonate ranges from calcite to Fe-rich ankerite and concentrations of magnesium and manganese are below the level of detection with an electron microprobe. Abundant sphalerite is present in the fracture network and rarely as inclusions in the organic phase. The presence of nickel and vanadium bearing phases within pyrobitumen veins is consistent with the notion of metal-transportation by liquid hydrocarbons.