Hyper-enriched black shales: paleoredox conditions and late-stage metal mobility

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Hyper-enriched black shales (HEBS) are defined by weight percent levels of enrichment in metals, most notably, Ni, Mo, Zn and As, and anomalous concentrations of rare and precious metals. Researchers are divided on the genesis of these rocks, with some proposing metal derivation from ambient seawater and others venting of metal rich-hydrothermal fluids. The locally extreme concentrations of some metals, however, and the limited transport capacity of hydrothermal fluids for Ni call into question the validity of both of these models.

We consider that the conversion of solid kerogen to liquid oil may contribute to the mobilization and concentration of some metals. Geological investigation and preliminary whole rock chemical data from the Peel River HEBS locality in the Yukon, Canada, indicate that the mineralized horizon occurs as a thin (<15 cm), laterally extensive (10,000's km^2) sulphide-rich (60 % by volume) unit. Although the mineralogy is simple, there are complex textures suggesting multiple stages of metal enrichment. Average grades of 3.8 wt% Ni, 0.3 wt% Mo, 0.5 wt% Zn and 0.3 wt% As characterize the HEBS, whereas the host shales, on average, contain 280 ppm Ni, 70 ppm Mo, 640 ppm Zn and 30 ppm As.

Paleo-redox proxies suggest that the HEBS and the host shales were deposited under different conditions. High Mo concentrations in the HEBS horizon and pyritization of organic material suggest high concentrations of H_2S in the water column. However, Mo concentrations in the host shale imply that free H_2S was restricted to the pore waters. Vanadium, which should be enriched during water column euxinia, is depleted in the HEBS horizon relative to the host shale (220 vs 1350 ppm, respectively).

We propose that during hydrocarbon generation, V was mobilised from the HEBS horizon in a liquid oil, and now occurs in metre-scale pyrobitumen veins (4000 ppm V) in the overlying stratigraphy. Centimetre-scale pyrobitumen veins within the HEBS horizon are also enriched in V (~1400 ppm) and have micron thick selvages of millerite (NiS). The latter indicates late-stage Ni-sulphide precipitation, suggesting that hydrocarbon generation may also have played a role in the hyper-accumulation of Ni.