

The critical role of hydrothermal activity in forming hyperenriched deposits of metals in black shales

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Introduction

Certain black shale-hosted deposits contain exceptional metal values that are several orders of magnitude greater than average black shale (which typically contains, for example, 300 ppm Zn; 10 ppm Mo)^{1,2}. In Illinois and Indiana, for example, bed B of the Carboniferous Mecca Quarry Shale Member^{3,4} contains an average of 1100 ppm Mo as well as erratic values for Zn that average 3000 ppm but in some cases even exceed 10,000 ppm. Elsewhere, the Ni-Mo sulphide beds in Cambrian shales of southern China contain more than four weight per cent Mo and nearly as much Ni^{5,6}. We suggest that mineralized beds containing such highly concentrated deposits of metals be called "hyperenriched". Known examples of such deposits are all located in exceptionally metal-rich geological environments (i.e. in the Mississippi Valley of North America, the rich ancient mining areas of southern China in Guizhou and Hunan or are adjacent to *bona fide* sedex deposits⁷).

Origins of Hyperenriched Deposits

Although hyperenriched deposits of metals in black shales have been studied since the days of Goldschmidt's early 20th Century work on the Kupferschiefer, a consensus on the mode (or modes) of origin has yet to emerge. Workers have variously attributed black shale-hosted deposits to a wide range of agents including syngenetic or epigenetic hydrothermal activity, bolide impact, or accumulation from sea water. We note, however, that the hyperenriched deposits in black shales that we cite are associated regionally with coeval hydrothermal ore systems that have left evidence in the form of hot saline fluid inclusions found in association with the shales. For these reasons, we infer that the metalliferous black shale deposits, such as the Late Paleozoic American black shales, and the unusual Ni-Mo deposits of China, primarily owe their origins to hydrothermal processes.

Conclusions

Besides the evidence cited above, we and others⁸ note the absence of a clear modern analog for deposition of hyperenriched enriched deposits directly from sea water as has been proposed by some other workers. We conclude, therefore, that hyperenriched deposits result from hydrothermal sources.

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Influence of salinity on methanogenesis in the Alberta oil sands region

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This study examined the relationship between water chemistry and methanogenic microbial activity in the Alberta oil sands using a bench-scale experiment. The terminal redox process, methanogenesis, is common in many shallow hydrocarbon reservoir systems and is thought to be a central process in the geological history of Alberta's oil sands. The biodegradation of light oil over geological time via methanogenesis has been proposed to be a primary formation process of the oil sands reserves in western Canada [1]. Shallow hydrocarbon reservoir environments are favourable to methanogenic communities that require moderate temperature, pH and reducing geochemical conditions to conduct their metabolic processes. In the McMurray formation, the predominant Athabasca oil sands reservoir, formation water geochemistry is variable and salinities vary from fresh to brine. Furthermore, quaternary-aged glacial channels have brought fresh groundwater into contact with oil sands deposits since the last glaciation [2], possibly stimulating increased methanogenic activity in the sedimentary basin [3]. Therefore the relationship between microbial processes and aqueous geochemistry requires investigation to gain insight into potential biodegradation mechanisms and rates of oil sands.

Laboratory cultures of methanogenic communities grown on an oil sands substrate were prepared using waters with three different geochemical compositions and salinities ranging from fresh to saline. Methane generation rates, microbial community composition and stable isotope geochemistry of carbon and sulphur systems were determined over eight months to assess the influence of variable salinity on biodegradation of oil sands via methanogenesis.

Microbial methane generation was variable among replicates with similar chemical water compositions. However, mean methane generation rates were higher in brackish and freshwater cultures than in saline cultures. Carbon isotope measurements indicated that neither CO₂ reducing, nor acetoclastic methanogens were dominant, and that a mixed methanogenic community was most likely active in all three geochemical variants. Sulphur isotope data suggested that bacterial sulphate reduction (BSR) is a likely process in the saline cultures where sulphate concentrations were elevated. However, in the cultures with active BSR, methanogenesis was not inhibited. Increasing concentrations of acetate in all cultures suggest syntrophic fermenting bacteria play a dominant role in the microbial ecosystem under all geochemical conditions tested.

These preliminary results indicate that both CO₂ reduction and acetoclastic methanogenesis are potential processes for oil sands biodegradation under laboratory conditions, and may also be active in modern oil sands reservoirs.

[1] Jones et al. (2008) *Nature* 451, 176-180.

[2] Lemay (2002) *Alberta EUB/AGS Geo-Note 2002-03*.

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