The influence of thermal maturation on trace metal/total organic carbon ratios in black shales of the Bakken Formation, USA

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Marine biogeochemists commonly utilize trace metal/total organic carbon (TM/TOC) ratios in black shales to reconstruct trace metal budgets in ancient oceans. This approach is strongly rooted in studies of modern euxinic environments where TM/TOC ratios correlate with the concentration of TMs in seawater. However, TM/TOC ratios are susceptible to modification due to loss of carbon caused by burial diagenesis and thermal maturation processes. Because many black shales are petroleum source the expulsion of hydrocarbons should be a common and potentially significant mechanism for the alteration of TM/TOC ratios. This process would complicate the reconstruction of ancient seawater chemistry but could facilitate the exploration of energy resources.

Here we present TM/TOC ratios for black shales of the Late Devonian-Early Mississippian Bakken Formation of North Dakota and Montana. We sampled six drill cores [1] covering a range of burial depths and thermal maturities (immature to peak oil window) as indicated by vitrinite reflectance and programmed pyrolysis. We treat the TM/TOC of immature shales as representative of Late Devonian to Early Mississippian seawater such that variations of these ratios in thermally mature shales can be used as a potential indicator of hydrocarbon expulsion. In general we find little variation in TM/TOC ratios, consistent with the retentian of hydrocarbons, even in samples from the early to peak oil window. In one core, taken from near the Nesson Anticline we find clear enrichments in TM/TOC consistent with the expulsion of hydrocarbons and we can use TM/TOC ratios to calculate a carbon loss of ~30%. We propose that the TM/TOC ratios of immature Bakken shales are an appropriate baseline for all source rocks of Late Devonian to Early Mississippian age.

[1] Scott *et al.* (2017) *Chem Geol* **452**, 24-33.