The importance of thermal maturity for molybdenum geochemistry in black shale: Implications for the paleo – proxy

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This study investigates the distribution and speciation of molybdenum (Mo) at various thermal maturities in the Upper Ordovician Utica Shale from southern Quebec, Canada. Samples display maturity ranging from peak oil window (Ro ~ 1%) to dry gas zone (Ro ~ 2%). While our data show significant correlation between total organic carbon (TOC) and Mo (R^2 = 0.45, n = 43) at lower thermal maturity, this correlation gradually deteriorates with increasing thermal maturity. Certain intervals within the thermally over-mature Utica section contain higher levels of Mo (20 – 81 ppm). Surprinsingly, these Mo-rich intervals are characterized by co-variance with calcium (Ca). Petrographic evidence suggests these intervals have undergone thermal sulfate reduction (TSR) along with production of recrystallized pyrite.

We used x-ray absorption fine structure spectroscopy (XAFS) to determine the oxidation state and molecular coordination environment of Mo in samples from these intriguing intervals ([Mo] > 30 ppm) [1]. Our results show that the average oxidation state of Mo is +V, and that Mo is distributed between two phases: molybdenite Mo(IV)S_2 (30±5 %) and Mo(VI)-Organic Matter (70±5 %) [2].

This new evidence suggests that at higher thermal maturities, sulfide released by TSR triggers a series of processes (e.g. organic matter oxidation, Mo remobilization, molybdenite formation). These processes could potentially co-precipitate with later stage TSR-derived carbonate and change the original Mo signal in sedimentary records, challenging its use as a paleo redox proxy in some black shales where Mo speciation is not investigated.

[1] Dahl *et al*. (2013) *GCA* **103** *213-231,* [2] Chappaz *et al*. (2014) *GCA* **126** *112-122*.