

Tungsten in Petroleum Systems: A Potential Paleo-Environment Indicator

Karen Johannesson, Dept. Earth and Environmental Sciences, Tulane University

Narrative Report

During the past 12 months we have been studying the kinetics of tungstate (WO_4^{2-}) sulfidation in the presence of dissolved sulfides. Our goal was to evaluate the factors that control formation of thiotungstate anions in euxinic waters to better understand tungstate thiolation occurred by first order kinetics or kinetic reactions of different order, and how tungstate and dissolved sulfide concentrations as well as solution pH influenced the rates of tungstate thiolation. The kinetic investigations were specifically undertaken to help test my hypothesis that W is more stable in euxinic waters than its “geochemical twin” Mo owing, in part, to its lower sulfidation constants and slower reaction kinetics. Furthermore, I hypothesized that slow kinetics of W thiolation would only lead to W accumulations in sediments deposited in restricted basins with long water residence times and little to no ventilation. If this is correct, then source rocks deposited in upwelling environments along continental margins that experience seasonal or variable anoxia will not accumulate W.

Over the past 12 months we investigated the effect of acid on tungsten (W) sulfidation processes as well as quantified Brønsted acid relationships for various weak acids, which now provides a tool to predict the effect of weak acids on the kinetics of the thiolation reaction of W in natural waters. These kinetic experiments were conducted in solutions buffered with ammonium, hydrogen sulfide, and carbonic acid, which allowed us to develop the Brønsted acid relationships (Fig. 1). The results of laboratory experiments also show that thiotungstate formation is first order with respect to both H_2S and WO_4^{2-} concentrations, and is catalyzed by acids. Therefore, low pH and high H_2S concentrations both favor W thiolation. However, compared to molybdenum (Mo), thiolation of W is kinetically “sluggish”. Moreover, the acid-catalyzed thiolation rates of W can be estimated from the Brønsted relationships. Specifically, the results show that

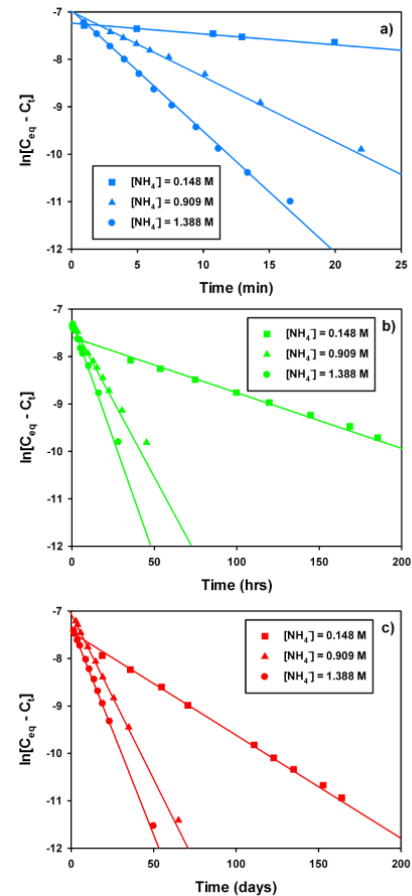


Figure 1. Results of kinetic experiments of W thiolation reactions for different NH_4^+ concentrations. Panel (a) shows results for the reaction $\text{WO}_3\text{S}_2^{2-} + \text{H}_2\text{S} \leftrightarrow \text{WO}_2\text{S}_2^{2-} + \text{H}_2\text{O}$, panel (b) are the data for the reaction $\text{WO}_2\text{S}_2^{2-} + \text{H}_2\text{S} \leftrightarrow \text{WOS}_3^{2-} + \text{H}_2\text{O}$, (c) shows the data for the reaction $\text{WOS}_3^{2-} + \text{H}_2\text{S} \leftrightarrow \text{WS}_4^{2-} + \text{H}_2\text{O}$. Experimental conditions: NaCl 0.7 M; $\Sigma\text{W} = 1$ mM; $\Sigma\text{S}^{\text{II}} = 160$ mM; $T = 25^\circ\text{C}$. On the ordinates of each panel, C_t (mol L^{-1}) and C_{eq} (mol L^{-1}) represent the amounts of thiotungstate species at time, t (min), and at equilibrium, respectively.

different acids enhance the reaction rates to the different extents. For example, the bicarbonate-catalyzed thiolation rate of W is faster than the ammonium-catalyzed thiolation rate of W, which reflects the lower pK_a of carbonic acid compared to the pK_a for ammonium. Although acids greatly enhance the W thiolation process, full thiolation of W still requires for more time than that of Mo for the same pH conditions. Our results indicate that the longer the period of euxinia, the higher chance of WS_4^{2-} species in solutions.

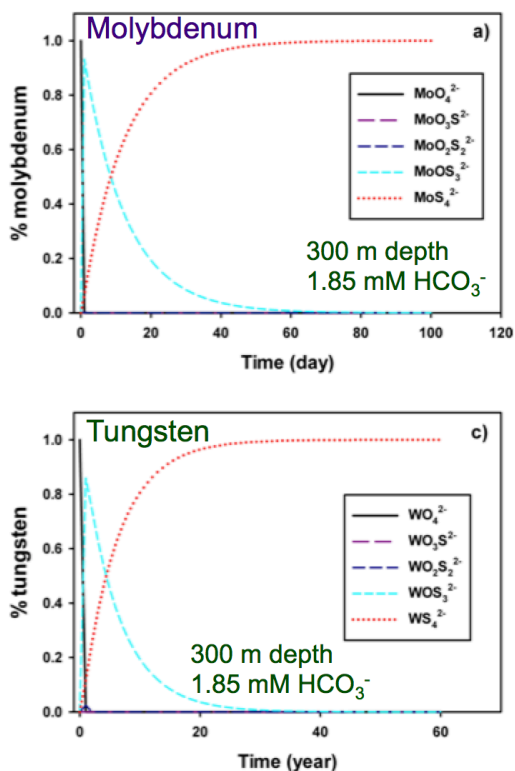


Figure 2. Results of speciation and kinetic modeling for Mo (top panel) and W (bottom panel) in the euxinic water column of the Black Sea. Kinetic data for W used in the modeling are from the current study.

The Brønsted acid relationships then allowed us to develop geochemical models for W thiolation kinetics in the Black Sea, and to compare these results with those for Mo that were modeled using previously determined rate constants (Fig. 2). Our geochemical modeling shows that full thiolation of Mo requires ca. 138 days in the euxinic water column of the Black Sea, whereas full thiolation of W requires ca. 60 years. Again, the modeling assumes that current euxinic conditions of the Black Sea are persistent. The kinetic study has been submitted for review in the journal *Geochimica et Cosmochimica Acta*. Also, I presented the results of the kinetic geochemical modeling as part of my Keynote talk at the 2018 Goldschmidt Conference. My PhD student (Dr. Minming Cui) whose research was funded by the project also presented an abstract at the Goldschmidt Conference where he presented the details of the kinetic experiments. Dr. Cui is now a post-doctoral scholar at the Johns Hopkins University.

In summary, the study provides an improved mechanistic understanding of the speciation and mobility of W in euxinic environments, including additional insight into the bioavailability of W in the paleocean and subsequently enhances our ability to reconstruct paleoredox during major Earth-life transitions.