Please ensure that your abstract fits into one column on one page and complies with the *Instructions to Authors* available from the Abstract Submission web page.

Tungsten in sulfidic waters: Implications for paleoceanography and the origins of life

KAREN H. JOHANNESSON[1*], MINMING CUI[1, 2], AND GEORGE R. HELZ[3]

[1]Department of Earth and Environmental Sciences, Tulane University, New Orleans, LA, USA, kjohanne@tulane.edu (*presenting author)
[2]Department of Earth and Planetary Sciences, Johns Hopkins University, Baltimore, MD, USA
[3]Department of Geology, University of Maryland, College Park, MD, USA

Although both tungsten (W) and molybdenum (Mo) react with dissolved sulfide in euxinic waters, conversion of tungstate, $W^{VI}O_4^{2-}$, to tetrathiotungstate, $W^{VI}S_4^{2-}$, requires higher dissolved sulfide concentrations than the analogous thiolation of molybdate ($\Sigma S^{-II} \geq 60$ μmol kg^{-1} vs. ca. 11 μmol kg^{-1}, respectively) [1-3]. Thiotungstate formation is first order with respect to both H_2S and $W^{VI}O_4^{2-}$concentrations, and is catalysed by acids [4]. Thus, decreasing pH and increasing H_2S concentrations both favor W thiolation. However, compared to Mo, thiolation of W is kinetically "sluggish". For example, calculations using newly determined rate constants [4] suggest that formation of $W^{VI}S_4^{2-}$ in deep waters of the Black Sea requires approximately of 50 years, whereas the analogous formation of $Mo^{VI}S_4^{2-}$ takes ca. 110 days [2, 3]. Hence, $W^{VI}S_4^{2-}$ should only accumulate to appreciable amounts in poorly ventilated, permanently anoxic waters (e.g., restricted basins). In contrast, $W^{VI}O_4^{2-}$, or partially thiolated oxothiotungstate anions, will predominate in seasonally anoxic environments, or natural waters that experience relatively short-lived euxinia (e.g., multi-year as opposed to multi-decade or longer periods). The slow kinetics in conjunction with the lower "particle reactivity" of $W^{VI}S_4^{2-}$ compared to $Mo^{VI}S_4^{2-}$ with respect pyrite [5] supports our previous investigation of sulfidic, salt marsh porewaters where W is apparently more stable in solution than its "chemical twin" Mo [3]. These differences in W and Mo behavior in sulfidic waters may have important consequences for paleoceanography, the antiquity of W-based enzymes, and hence, early life.

[1] Erickson and Helz (2000) *Cosmochim Acta* **64**, 1149, [2] Mohajerin et al. (2014) *Geochim. Cosmochim Acta* **144**, 157, [3] Mohajerin et al. (2016) *Cosmochim Acta* **177**, 105, [4] Cui and Johannesson (in review) *Geochim. Cosmochim Acta*, [5] Cui and Johannesson (2017) *Chem. Geol*. **464**, 57.

This abstract is too long to be accepted for publication. Please revise it so that it fits into the column on one page.