Speciation and mobility of tungsten in modern euxinic system: Determination of acid catalyzed thiotungstates formation and kinetics

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The presence of acid in aqueous systems generally has a large impact on speciation as well as on mobility of trace elements. In our present study, we investigated the effect of acid on tungsten (W) sulfidation process as well as developed the Brønsted acid relationship, which provides a tool to predict the effect of acids on the kinetics of the thiolation reaction of W in natural waters. The results of laboratory experiments 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". The modeling results show that full thiolation of Mo requires ca. 110 days, whereas full thiolation of W requires ca. 50 years under a persistent euxinic condition such as the Black Sea. In addition, acid-catalyzed thiolation rates of W can be estimated from the Brønsted acid relationship. Specifically, the results show that different acids enhance the reaction rates to the different extent. For example, bicarbonate-catalyzed thiolation rate of W is faster than ammonium-catalyzed thiolation rate of W. Although acid greatly enhance the W thiolation process, full thiolation of W still requires much more time than that of Mo. Our results indicate that the longer the period of euxinia, the higher chance of WS_4^{2-} species in solutions and subsequently be incorporated into euxinic sediments as W-S species. Thus, an important product of this research will be an improved mechanistic understanding of the speciation and mobility of W shown in our study, which provides insight into the bioavailabilities of W in the paleocean and subsequently enhance our ability to reconstruct paleoredox during major Earth-life transitions.