Tungsten transport in ore-forming fluids: insights from *ab initio* molecular dynamics simulations

Yuan Mei[1], Weihua Liu[1], Xin-Song Wang[2,3], A.E. Williams-Jones[2]
[1] *CSIRO Mineral Resources, Clayton, Victoria, 3168, Australia*
[2] *Earth and Planetary Sciences, McGill University, 3450 University Street, Montreal H3A 0E8, Canada*
[3] *State Key Laboratory of Ore Deposits Geochemistry, Institute of Geochemistry, China Academy of Sciences, Guiyang 550005, China*
yuan.mei@csiro.au
https://orcid.org/0000-0001-6251-3483

Tungsten is a strategic metal mined mainly from hydrothermal tungstate minerals in which the tungsten is in both tetravalent (e.g., tungstenite, $WS_{2(s)}$) and hexavalent (e.g., scheelite, $CaWO_{4(s)}$, and ferberite, $FeWO_{4(s)}$) oxidation states. To understand the transport of tungsten in ore-forming fluids and develop geochemical models for the formation of these deposits, we need reliable information on the speciation and thermodynamic properties of tungsten complexes in aqueous fluids over wide ranges of temperature, pressure and chemical composition. In the past four decades, there have been a limited number of experimental studies on W solubility and speciation in hydrothermal fluids (Bali et al., 2012; Redkin and Kostromin, 2010; Wesolowski et al., 1984; Wood and Samson, 2000; Wang et al., 2019). However, there has been no direct molecular-level study of the mechanism of tungsten complexation under hydrothermal conditions, and thus the role of chloride, sulfur and fluorine in aqueous tungsten species are poorly understood.

In this study, we used *ab initio* molecular dynamic (MD) simulations to calculate the speciation and geometries of tungsten W(VI) in chloride, sulfur and fluorine bearing brines up to 600ºC, 2kbar. We also used the thermodynamic integration method to also determine the acidic constants of tungstic acid, the stability constants of possible W(VI)-S and W(VI)-F complexes at temperatures up to 600 ºC. The derived thermodynamic properties enable better understanding and quantitative modelling of tungsten mobility in hydrothermal systems.

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