Goldschmidt 2026 Abstract
https://doi.org/10.46427/gold2026.35059

In-situ Raman spectroscopy and DFT insights into tungsten behavior in hydrothermal and deep subduction zone fluids

NAOKO TAKAHASHI[1], MICHIHIKO NAKAMURA[1], SHIGERU YAMASHITA[2] AND HIROYUKI KAGI[3]

[1]Tohoku University
[2]Okayama University
[3]The University of Tokyo

The mobility of tungsten (W) in aqueous fluids has been documented in magmatic-hydrothermal ore deposits and serpentinized mantle peridotites in deep subduction zones. In recent years, the stable isotopes of the element have also gained attention as potential geochemical tracers for deciphering deep fluid–rock interactions. However, thermodynamic properties of aqueous metal complexes are predicted from low-temperature solubility experiments, and understanding their speciation in geological fluids under high-pressure and high-temperature conditions remains limited.

We examined the behavior of W(VI) in aqueous fluids up to 800 °C and 1 GPa using in situ Raman spectroscopy in an externally-heated hydrothermal diamond anvil cell, with the band assignment complemented by DFT calculations. The metal speciation changes with temperature, pH, and the presence of Na in the fluids. The changes are indicated by the appearance of a higher-frequency band than those of oxyanions above 400 °C, with an additional higher-frequency band appearing only in Na-free environments. Based on analogous Mo solution experiments, previous in-situ studies, and thermodynamic models, these high-*T* bands are assigned to mononuclear species rather than polynuclear anions. Our DFT vibrational frequency calculations indicate that several optimized structures of protonated tungstate anions and tungstic acid monomers qualitatively reproduce the observed high-frequency features, with tetrahedral or higher-coordinated species as plausible candidates. Finally, we compare our results with the existing thermodynamic modeling. These findings have implications for metal transport in hydrothermal and deep subduction-zone environments and the mechanisms of stable isotope fractionation between fluids and minerals.