

Tungstate polymerization and its role in sorption on iron and aluminum oxyhydroxides

E.A. LORENZ¹, H. HUR² AND R.J. REEDER^{1*}

¹Dept. of Geosciences, Stony Brook Univ., Stony Brook, NY 11794 USA (*correspondence: rjreeder@stonybrook.edu)

²Dept. of Chemistry, Stony Brook Univ., Stony Brook, NY 11794 USA

Tungsten, although largely unregulated as an environmental pollutant, is now identified as an emerging contaminant, partly as a consequence of its widespread use in commercial, industrial, and military applications. Interaction with mineral substrates is considered an important process governing the mobility of dissolved tungsten species in aquatic and soil systems. We examined the uptake of tungstate species by iron and aluminum oxyhydroxide phases in model systems. Results indicate that W(VI) uptake is strongly dependent on pH and W concentration. The pH dependence determined from batch studies (pH 4-8) shows sorption behavior typical of anions, with only minor dependence on ionic strength. Sorption isotherms of tungstate on iron and aluminum oxyhydroxide phases show Langmuir-like uptake at low W(VI) concentrations, but increasing uptake at higher concentrations. Solution speciation calculations suggest that a monomeric tungstate species dominates at pH > 7, with formation of polymeric tungstate species favored at lower pH and with increasing W concentration. W L₃-edge EXAFS and W L₁-edge XANES of tungstate solutions are consistent with a monomeric tungstate species at pH 8 and at least one polymeric tungstate species present in solution at pH 4, which is consistent with speciation calculations. EXAFS and XANES of tungstate sorbed on goethite over the pH range 4-8 and at W concentrations 25-1000 µM show spectra that are similar and suggest that tungstate polymerization occurs at the surface, either forming a polytungstate sorption complex or a surface precipitate. This conclusion is supported by differential pair distribution function data, which show correlations extending to 11 Å that are likely attributable to the W-W pair correlations present in polytungstates. EXAFS and XANES spectra of tungstate sorbed onto bohemite over similar pH and W concentrations show differences in uptake mechanism not observed for goethite. Desorption experiments reveal limited reversibility of uptake, consistent with formation of a surface precipitate. These initial findings emphasize the need for additional research to assess the importance of sorption in limiting the mobility of dissolved tungstate in the environment.

Talvivaara Ni deposit and ore potential of Palaeoproterozoic black shale formations in Finland

K. LOUKOLA-RUSKEENIEMI^{1*}, E. HYVÖNEN², H. ARKIMAA¹, M.-L. AIRO¹, J. VANNE³, J. LERSSI³ AND S. VUORIAINEN¹

¹Geological Survey of Finland, P.O. Box 96, FI-02151 Espoo, Finland

(*correspondence: kirsti.loukola-ruskeeniemi@gtk.fi)

²Geological Survey of Finland, P.O. Box 77, FI-96101 Rovaniemi, Finland

³Geological Survey of Finland, P.O. Box 1237, FI-70211 Kuopio, Finland

The black-shale-hosted Talvivaara deposit contains more than 1 000 Mt of low-grade Ni-Cu-Co-Zn-Mn ore. The two ore bodies are from 20 m to > 450 m thick, less than 2 km long and almost 0.5 km wide. The textures, mineralogy and geochemistry of the black shales have been studied earlier [e.g. 1, 2].

Talvivaara black shales are characterized by high organic C and S concentrations with median values of 7.6% and 9%, respectively, and the occurrence of horizons with Mn₂O₃ ≥ 0.8%. Nickel precipitated in organic-rich mud from Ni-rich bottom waters in an epicontinental stratified marine basin. The Mn-rich horizons were probably deposited on the margins of the euxinic basin or, alternatively, Mn was derived via upwelling from oxygen-minimum zones.

The ore potential of black shale formations in Finland was first evaluated by nation-wide airborne geophysical surveys, because the geophysical properties of black shales can be used for preliminary classification [3, 4]. Textures, mineralogy, geochemistry and petrophysical properties were studied from altogether 800 black shale samples. Concentrations of organic C and S were as high as at Talvivaara in many localities in eastern and northern Finland, but Ni-Cu-Co-Zn and/or Mn concentrations were lower. High Pd and Pt concentrations were found in some prospects.

A mass extinction for 2 Ga ago has been suggested for the origin of the high C in certain thick (> 50 m) black shale formations in eastern and northern Finland [5].

[1] Loukola-Ruskeeniemi & Heino (1996) *Econ. Geol.* **91**, 80–110. [2] Loukola-Ruskeeniemi (2011) *Geological Survey of Finland, Special Paper* **51**. [3] Arkimaa *et al.* (2000) Black Shale Map 1, 1 000 000. Geological Survey of Finland. [4] Airo & Loukola-Ruskeeniemi (2004) *Ore Geology Reviews* **24**, 67–84. [5] Loukola-Ruskeeniemi (2000) *Geol. Soc. of America. Abstracts with Programs* **32(7)** A-5.