

Iron (Oxyhydr)oxide-Specific Inhibition of Palladium Adsorption by Chloride: Implications for Palladium Mobility during Weathering of Platinum-Group Element Deposits

EMILY G WRIGHT, OLWEN STAGG, ELAINE D FLYNN
AND JEFFREY G CATALANO

Washington University in St. Louis

Presenting Author: e.g.wright@wustl.edu

Weathering zones above ultramafic rock represent a promising new source for platinum-group elements, but the fundamental geochemical controls on the mobility and distribution of these elements are poorly understood. The mobilization and loss of palladium (Pd) during acidic, oxic weathering has been attributed to aqueous chloride complexation. However, some Pd is retained and associated with iron (oxyhydr)oxides in these weathering zones. Adsorption may be one mechanism by which Pd is retained, but the effect of chloride on this process is currently unknown. We studied the effect of chloride on Pd(II) adsorption to hematite, goethite, and 2-line ferrihydrite at pH 4 using macroscopic binding experiments and extended X-ray absorption fine structure (EXAFS) spectroscopy.

Increasing chloride concentration suppressed Pd adsorption to hematite. However, speciation modeling suggests that aqueous complexation effects cannot completely explain the adsorption differences observed. The EXAFS spectra of Pd adsorbed to hematite are consistent with a mixture of Pd-chloro and -hydroxy surface complexes, with increasing Pd-Cl ternary complexation as aqueous chloride increases.

Pd adsorption to ferrihydrite is similar to hematite at the same chloride concentration and the surface speciation is the same. However, Pd has a much greater affinity for goethite compared to hematite and ferrihydrite. Additionally, bimodal adsorption behavior is observed on goethite, indicating the presence of multiple surface species with varying binding affinities. While the EXAFS spectra of Pd adsorbed to goethite are also consistent with a mixture of Pd-hydroxy and -chloro surface complexes, an additional second shell feature unique to goethite was observed, suggesting that Pd incorporates into surface defects or forms polymeric surface complexes.

Our results demonstrate that under acidic, oxidizing conditions Pd will be mobilized as a chloride complex. Surface speciation differences are likely responsible for the observed variations in adsorption behavior. The greater affinity of Pd for goethite compared to the other two iron (oxyhydr)oxides studied indicates that this mineral is a key control on Pd mobility during weathering. Large scale controls on iron (oxyhydr)oxide mineralogy, such as climate, will affect Pd retention during weathering, with greater retention under conditions that favor goethite formation.