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Ligand and pH Controls on Pt(II) Adsorption to Iron (Oxyhydr)oxides: Pathway-Dependent Mobility during Weathering of Platinum-Group Element Deposits

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Platinum-group elements (PGEs), critical minerals indispensable as catalysts, have a low natural abundance but are concentrated in weathering zones above ultramafic rock. Geochemical controls on PGE behavior during weathering are poorly understood. Platinum (Pt) displays lower mobility during weathering than palladium (Pd) and is commonly associated with iron (oxyhydr)oxides. It may be retained via adsorption, but the effects of complexation and pH on this behavior are unknown. Available thermodynamic data predicts Pt-chloro and -hydroxy complexes under weakly acidic conditions, with increasing ammine complexation as pH increases. We studied the impacts of pH and two ligands, chloride and ammonia, on Pt(II) adsorption to hematite and goethite using macroscopic binding experiments and extended X-ray absorption fine structure (EXAFS) spectroscopy.

At pH 4, increasing chloride concentration suppresses Pt(II) adsorption to both minerals. Less inhibition occurs than was previously observed for Pd(II), and Pt(II) displays greater overall adsorption. The EXAFS spectra of adsorbed Pt at pH 4 are consistent with Pt-Cl ternary surface complexation. Pt displays a greater affinity for goethite and forms inner-sphere species only on this mineral. These differences with hematite are induced by distinct surface structures. Increasing the pH in chloride-bearing fluids generally increases Pt(II) adsorption.

In more complex solutions containing both chloride and ammonia, Pt(II) adsorption shows pathway dependence indicating non-equilibrium behavior. When Pt(II) is introduced as a Pt-Cl solution followed by ammonia addition, Pt(II) readily adsorbs and displays no variation in binding with ammonia concentration, despite existing thermodynamic data predicting abundant Pt(II)-ammine complexation. However, when Pt(II) is added as a Pt-NH_3 solution which is then mixed with dissolved chloride, negligible adsorption is observed. These distinct adsorption behaviors in identical final fluid compositions are consistent with prior work showing that Pt(II)-ammine complexes are kinetically inert.

Our results demonstrate that chloride has a smaller effect on Pt(II) mobilization compared to Pd(II) despite still forming ternary surface complexes. Greater retention of Pt(II) compared to Pd(II) is expected in chloride-rich fluids under weakly-acidic to circumneutral conditions. Fluids that promote the formation of ammine complexes create an unreactive and highly mobile Pt(II) pool that remains even if such species later become thermodynamically unstable.