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Kinetic Influences on Platinum Adsorption to Iron Oxides: Speciation-Dependent Mobility during Weathering of Platinum Group Element Deposits

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Iron (oxyhydr)oxide-rich weathering zones concentrate platinum and could serve as a potential future resource for this critical mineral. However, the fundamental processes that control the retention of Pt during the formation of these resources are poorly understood. The frequent association of Pt with iron (oxyhydr)oxides suggests that these minerals could play an important role in controlling the mobility of Pt. However, the effects of Pt aqueous speciation on retention by these minerals is unknown. Existing thermodynamic data suggests that Pt should be highly complexed in the environment, primarily by chloride and ammonia. We studied the effects of these two ligands on Pt(II) adsorption to hematite and goethite over a several month reaction period.

Initial experiments reveal persistent Pt disequilibrium between pH 4 and 8. Reaction of $Pt(NH_3)_4^{2+}$ with hematite and goethite shows negligible adsorption after several months of aging because this complex is kinetically inert. Addition of chloride has no effect despite predictions that ligand competition should partially dissociate Pt(II)-NH_3 complexes. Pt(II)-Cl complexes undergo substantial adsorption, with uptake progressively increasing over several months. Ammonia addition inhibits this increased Pt binding during aging but effects only occur after 6 to 10 days of reaction, reflecting the slow formation of Pt(II)-ammine species. Complex ligand and adsorption dynamics thus control Pt behavior, with initial Pt(II) speciation and slow reaction rates determining the mobility and accumulation of Pt in weathering zones and soils. Notably, ammonium generation via organic matter mineralization will create a highly mobile pool of Pt(II)-ammine complexes.

Despite its solubilizing effect, ammonia addition has no detectable impact on Pt surface speciation. On both minerals, Pt initially forms inner-sphere Pt(II)-Cl ternary surface complexes. However, while adsorbed Pt on goethite displays little variation over 2 months, Pt adsorbed to hematite progressively loses Cl ligands and oxidizes to Pt(IV). These findings reveal that mineralogy also influences the speciation of Pt. Hematite-rich environments will produce oxidized Pt(IV) over time, while Pt(II) more readily persist in goethite-rich regions.