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Impact of Fluoride and Phosphate on Mechanisms of Rare Earth Element Accumulation in Weathering Zones

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Regolith-hosted deposits are important rare earth element (REE) resources, with these critical minerals recovered via mild extraction. These deposits form during intense weathering of continental crust, which releases REEs from primary mineral hosts into pore water. The mechanisms controlling REE reaccumulation on the surfaces of weathering product minerals, such as clays or iron oxides, are not fully characterized. This study investigates the immobilization of Nd on the surface of goethite by both co-adsorption and precipitation with inorganic ligands. Fluoride and phosphate in particular are known to form aqueous complexes with REEs, and are constituents of secondary REE-bearing minerals identified in REE-rich regolith. We hypothesize that fluoride and phosphate increase REE uptake by iron oxide surfaces by forming ternary surface complexes. However, such complexes may also be precursors to the heterogeneous nucleation of secondary REE-bearing phases.

We measured Nd uptake in goethite suspensions with known initial concentrations of F and Nd to understand how thermodynamic saturation state with respect to NdF_3 impacts adsorption and nucleation at pH ~6. Results show that fluoride has a small, non-linear effect on total Nd uptake at lower initial NdF_3 saturation indices (SI) and timescales <48 hours, attributed to competition between neodymium-fluoride co-adsorption and aqueous complexation. We then subsampled goethite suspensions with the same initial Nd concentration and varying initial F concentration over 48 days. Whereas fluoride has a weak effect on Nd uptake by adsorption that occurs within the first 30 minutes of reaction, over longer timescales, elevated fluoride concentration also induces Nd precipitation. Nucleation rates are sensitive to saturation state, with an 8x increase in SI accelerating the onset of Nd-bearing secondary phase nucleation from more than 22 days of reaction time to less than 48 hours. The role of the goethite surface and Nd surface speciation in further accelerating nucleation is being studied. Results of Nd adsorption and mineral formation in phosphate-bearing systems will also be reported. This study reveals the kinetic controls on REE speciation in weathering zones, specifically the impact of SI and surface speciation on nucleation rates of secondary REE-bearing phases.