

Competition and Selectivity during Rare Earth Element Adsorption at Aluminum Oxide-Water Interfaces

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Regolith-hosted deposits serve as major resources for rare earth elements (REEs). These deposits form via chemical weathering of granites and often display relative enrichment in the heavy REEs. Retention of REEs occurs primarily via adsorption to clay minerals, such as kaolinite, halloysite, and gibbsite, enabling recovery via mild chemical extractions. The underlying interfacial chemistry that controls the retention, fractionation, and extractability in these deposits remains unresolved. Strong retention suggests a ligand-exchange binding mechanism yet the ease of extractability may imply cation exchange, despite the predominance of clay minerals with limited capacity to bind elements via this process. Molecular-scale information on interfacial reaction mechanisms of REEs is challenging to access via traditional approaches, such as X-ray absorption spectroscopy, because of the disordered nature of REE first coordination shells and the weak spectral contributions of aluminum and silicon atoms. We have applied resonant anomalous X-ray reflectivity measurements to probe the comparative binding of a light (Nd), middle (Dy), and heavy (Yb) REEs to the (001) surface of aluminum oxide, a structural analog of gibbsite and kaolinite basal surfaces. Equimolar mixtures of the three REEs in a dilute NaCl fluid at pH 6.5 reveal near-complete suppression of Yb(III) adsorption via site competition while Nd(III) and Dy(III) bind at similar surface coverages. Yb(III) readily adsorbs in the absence of competition, and all REEs bind solely via inner-sphere coordination. Lowering the pH to 5.5 produces substantial Nd(III) adsorption, minor Dy(III) adsorption, and minimal Yb(III) adsorption. A dilute CaCl₂ solution at pH 6.5 completely suppresses Dy(III) and Yb(III) adsorption, with Nd(III) the only detectable REE on the surface. Citrate addition at pH 6.5 enhances Nd(III) adsorption and creates a second, outer-sphere species. These studies reveal that surface complexation at the aluminum oxide surface produces strong selectivity for light REEs, involves primarily ligand exchange, and is altered by organic acids and electrolyte cations. *Ab initio* molecular dynamics simulations will explore the mechanistic origin of the observed fractionation. Heavy REE enrichment in regolith-hosted deposits likely requires an adsorption mechanism distinct from surface complexation, such as cation exchange to permanently-charged