

Controls of rare earth elements fractionation during competitive adsorption on corundum surfaces

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Rare earth elements (REEs) bound to kaolinite, halloysite, and gibbsite surfaces in ion adsorption-type deposits (IADs) are currently the main source for heavy REEs. The fundamental adsorption mechanisms of REEs on these clay minerals are unclear. Despite their large retention by clay minerals under intense weathering, the REEs in IADs can be easily extracted through chemical leaching methods, indicating relatively weak binding. In order to construct a comprehensive picture of REE adsorption mechanisms, we applied synchrotron-based X-ray reflectivity (XR) and resonant anomalous X-ray reflectivity (RAXR) to probe the competitive adsorption behavior of light (Nd), middle (Dy), and heavy (Yb) REEs. These studies utilized the corundum (001) surface, which is isostructural to the kaolinite, gibbsite, and halloysite aluminol basal planes and, therefore, enables the investigation of generalized adsorption mechanisms. Our results show that the corundum (001) surface exhibits strong selectivity for light REE adsorption across a wide range of geochemical conditions, including varied REE concentrations, different pH values, and the presence of citrate. In all competitive adsorption experiments without citrate, REEs only adsorbed as inner-sphere complexes residing $\sim 1.6\text{-}2.1$ Å above the terminal oxygens. The height of adsorbed REEs decreases with increasing atomic number, consistent with contraction of the ionic radius across the REE series. The presence of citrate forms additional adsorption species, likely as citrate-REE ternary complexes, substantially increases adsorption capacity but still favoring the LREEs. A change from a NaCl to a CaCl₂ background salt results in a suppression of LREE adsorption, likely from competition with Ca²⁺ for surface binding sites, while slightly increasing adsorption heavier REEs. Our results demonstrate that REE surface complexes on kaolinite, gibbsite, and halloysite under an array of geochemical conditions would produce fractionation patterns similar to LREE IADs. The relative selectivity of mineral surfaces for REEs and the amount adsorbed on clay mineral basal planes may be strongly regulated by the pore fluid chemistry.