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Characterization of nano-minerals and nanoparticles in supergene rare earth element mineralization related to chemical weathering of granites

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Abstract

Ion adsorption-type rare earth element (REE) ore deposits in South China are a major source of heavy rare earth elements (HREE) around the world, which are of considerable economic and strategic significance. In these ores, REE is enriched in the clay minerals, specifically kaolinite and halloysite, which are derived from their parent granitoid by the weathering process. However, the mechanisms of supergene REE mineralization remain unclear. We investigated the nature and origin of supergene REE mineralization, based on a nanoscale study of a typical REE-mineralized granite regolith profile (ΣREE_{max} = 1201 ppm) in the Dazhou super-large, ion adsorption-type REE deposit, Guangxi Province, South China. Bulk mineralogical and geochemical analyses, coupled with novel nano-characterization techniques [i.e., hollow fiber flow field-flow fractionation inductively coupled plasma-mass spectrometry (HF5-ICP-MS), scanning electron microscopy (SEM), and transmission electron microscopy (TEM)], were used to determine the nature of the nano-minerals and nanoparticles in the regolith samples. X-ray diffraction and SEM-EDS analyses revealed that ion-adsorption clay minerals are dominated by platy-shaped kaolinite and rod-like halloysite (10 and 7 Å) within the regolith. The average clay mineral contents decreased from 38 to 15% from the fully weathered horizon to the semi-weathered horizon, whereas the proportion of halloysite increased in the clay mineral fraction in the deep horizons. The REE-bearing nanoparticles consist predominantly of macromolecules of organic matter (2–5 nm) and clay minerals (5–40 and 40–80 nm) according to the HF5-ICP-MS analysis. There is a close association between REE and Al contents in particles with sizes of 5–40 nm in the semi-weathered horizons and 40–80 nm in the highly weathered horizons, which indicates that nanoscale clay minerals (halloysite and kaolinite, respectively) are important REE carriers. In addition, nanoscale secondary REE mineral phases, including oxide, silicate, and phosphate, were identified by the SEM and TEM observations. These phases are typically adsorbed onto the surfaces of clay minerals, specifically rod-like halloysite, but have different occurrences in the regolith profile. Cesium-oxide (cerianite) and Ce-silicate (cerite) occur mainly in the upper horizon of the regolith profile, whereas low-crystallinity REE phosphates [rhabdophane-(La)] occur mainly in the lower horizon of the profile. Our results indicate that nano-minerals and nanoparticles affect REE enrichment and fractionation during granite weathering. Migration and accumulation of REE-bearing nano-minerals were caused by leaching and neoformation of REE-bearing nano-minerals during secondary precipitation. These processes contribute to the formation of supergene REE mineralization in granite regolith.

Keywords: Granite regolith, rare earth element, halloysite, kaolinite, REE phosphate, nanoparticle, nano-mineral