

## **Enrichment and fractionation of rare earth elements (REEs) in ion-adsorption-type REE deposits: Constraints of an iron (hydr)oxide-clay mineral composite**

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### **ABSTRACT**

Ion-adsorption-type rare earth element (REE) deposits are the source of more than 90% of global heavy REEs (HREEs). Thus, understanding the ore genesis of REEs, particularly the distribution characteristics and enrichment mechanisms of HREEs, is vital for efficient exploration and mining of ion-adsorption-type REE deposits worldwide. The characteristics and petrogenesis of bedrock and the aqueous mobility of REEs are known to be important factors controlling REE accumulation and fractionation in the weathering crust of REE deposits. However, the effect of REE adsorption on secondary minerals, a crucial step in deposit formation, remains poorly understood. This problem was addressed by the study described herein, which involved a systematic analysis of the complete weathering profile (78 m) of the Renju ion-adsorption-type REE deposit in South China and a simulated adsorption experiment. Clay minerals and iron (Fe) (hydr)oxides are the dominant REE adsorbents in the weathering crust and most are micro-to-nanosized particles. Thus, the fine-particle fraction (<2 μm) was separated from field samples to disclose better their effects on the concentration and redistribution of REEs. Phase compositions and morphologies were characterized by X-ray diffraction, Mössbauer spectrometry, and scanning/transmission electron microscopy (SEM/TEM), which revealed that various clay minerals and Fe (hydr)oxides form composites along the profile of the deposit. Composites of ferrihydrite-kaolinite, goethite-kaolinite/halloysite, and hematite-kaolinite/halloysite were found to be distributed in the semi-weathered, completely weathered, and topsoil layers, respectively, with different sizes and shapes. The concentrations and partition patterns of REEs in different occurrence states were distinguished after sequential extraction. Ion-exchangeable-REEs were the major state and enriched in the upper completely weathered layer. These species were found to be adsorbed onto kaolinite and halloysite via electrostatic attraction without obvious fractionation. Fe (hydr)oxides were determined to comprise ca. 20% of REEs at most depths and over 50% of REEs in the topsoil and semi-weathered layer. It was found that Fe (hydr)oxides scavenge REEs through complexation and oxidation, resulting in HREE enrichment and a positive cerium (Ce) anomaly, respectively. In addition, compared with crystalline Fe (hydr)oxides, amorphous Fe (hydr)oxides immobilize more REEs but exhibit weaker preferential adsorption of HREEs. The above-described findings are consistent with the results of simulated experiments for REE adsorption onto a clay mineral-Fe (hydr)oxide composite (Bt-60d), which was obtained from hydrothermal processing of biotite.

Furthermore, the distributions and stabilities of LREEs and HREEs were distinguished by TEM-energy-dispersive spectroscopy (EDS) of Bt-60d before and after REE extraction by ammonium sulfate. The phase transformation pathways of clay minerals and Fe (hydr)oxides and their different enrichment and fractionation characteristics in REEs were also discussed in terms of the structure and surface properties of minerals, adsorption mechanisms, and variations in chemical properties across the REE group. The results shed new light on how clay minerals and Fe (hydr)oxides affect the enrichment and fractionation of REEs in ion-adsorption-type deposits.

**Keywords:** Ion-adsorption-type REE deposit, clay minerals, Fe (hydr)oxides, adsorption, fractionation, weathering