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Controls of Fe-Mn (Hydr)oxides on Cerium Anomaly During Chemical Weathering: Implications for Ion-Adsorption Type REE Deposit Exploration in South China

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Cerium (Ce) exhibits unique redox-sensitive behavior compared to neighboring rare earth elements (REEs), making Ce anomaly (Ce/Ce*) useful for tracing the variation of redox conditions in soil, ocean and supergene deposits. Though previous studies have investigated the genesis of Ce anomaly by simulation experiments and theoretical calculations, field observations are still lacking, which limits its utilization as a geochemical tool. Here, we address this gap by investigating a 90-m weathering profile from the Huangshe ion-adsorption REE (iREE) deposit in South China, integrating geochemical and mineralogical analyses to unravel the supergene evolution of Ce.

Weathering degree, quantified by the variation of composition and texture, defines four horizons with distinct Ce anomalies: (1) topsoil (Ce/Ce* = 2.1–57.7), (2) completely weathered horizon (Ce/Ce* = 0.03–2.88), (3) semi-weathered horizon (Ce/Ce* = 0.90–1.34), and (4) parent rock (Ce/Ce* = 0.90). In the parent rock, Ce is primarily hosted in accessory minerals (allanite, titanite, apatite, bastnaesite-(Ce), parisite-(Ce), monazite, and rhabdophane-(Ce)). Initial weathering releases Ce through mineral dissolution, while Fe-bearing minerals decompose to form poorly crystalline goethite, which adsorbs Ce^{3+}, generating weak positive Ce anomalies.

As weathering progresses, Ce-Fe-Mn ternary mixed (hydr)oxides become prevailing in the lower completely weathered horizon. Fe (hydr)oxides transition from goethite/ferrihydrite to hematite, reducing hydroxyl group density and surface reactivity, thereby decreasing Ce retention. As for Mn (hydr)oxides, hausmannite promotes the oxidation of Ce^{3+} to Ce^{4+} via a direct redox reaction, giving rise to the formation of cerianite (CeO_2) in the Fe-Mn-Ce composite and increase of positive Ce anomaly. But in the advanced weathering stage, well crystallized hematite and cerianite segregate and accumulate in the topsoil, resulting in the obvious positive Ce anomaly.

The above results demonstrate that Fe-Mn (hydr)oxides govern Ce mobility through adsorption and oxidative scavenging. Unlike other REEs that are transported downward with groundwater, Ce remains isolated in the vadose zone without being involved in the downward groundwater flow, forming a positive Ce anomaly (Fig. 1). Therefore, the positive Ce anomaly can be utilized as a geochemical exploration indicator to identify iREE deposits hosted in mature regolith in South China and other regions of similar geology and climate globally.