

Appendix:

Method in Li et al. (2019) for mineralogical and REE distribution analysis of the Zudong deposit

1. Quantitative XRD analysis

Quantitative estimates were made of the proportions of major minerals in the soil and rock samples using Rietveld refinement applied to XRD spectra collected at the Rock and Mineral Testing Center of Hunan Province, China, with a D8 Focus Bruker powder X-ray diffractometer. Finely ground powdered samples were X-rayed with non-monochromated Cu K α radiation (40 kV, 40 mA) from 2° to 70° 2 θ and diffractograms collected at a scanning speed of 2°/min. The XRD spectra were analyzed and refined using the JADE 6.5 software.

2. Sequential extraction experiments

A four-step sequential extraction was performed based on the methodology of Wenzel et al. (2001), Du et al. (2012), and Sanematsu et al. (2013). Step 1 targeted the exchangeable clay-adsorbed component, step 2 the Fe-Mn oxyhydroxide adsorbed component, step 3 the organic matter-bound component, and step 4 the strongly bound chemically adsorbed Fe-Mn oxyhydroxide component. Centrifuge tubes, containers, and flasks used in the extraction were soaked in 1 M HNO₃ for over 24 h and rinsed repeatedly with Milli-Q double deionized water (Ω = 18.2 M) before use to remove any contaminants. The extraction involved adding 40 mL of solution to 1 g of powdered sample and mechanically shaking for 16 h at room temperature. The solutions used in steps 1, 2, 3, and 4 were 0.5 M ammonium sulfate (adjusted to pH = 4 with H₂SO₄), 0.5 M hydroxylammonium chloride (adjusted to pH = 2 with HNO₃), 0.1 M sodium pyrophosphate, and a mixture of 0.2 M ammonium oxalate and 0.1 M ascorbic acid (adjusted to pH = 3), respectively. After each extraction, the solution was separated from the solid residue by centrifuging at 3,000 rpm for 20 min. The supernatant solution was collected for analysis by filtration using a cellulose acetate-type membrane filter (ϕ = 0.22 μ m), which was rinsed repeatedly with 50 mL of Milli-Q doubly deionized water to recover all the extracted solutions. In steps 2 and 3, the requisite solution (hydroxylammonium chloride and sodium pyrophosphate, respectively) was added to the solid residue of the preceding step, thereby making the extraction sequential. The experimental protocol was different for step 4, in which the reactants were mechanically shaken for 8 h followed by

heating in a water bath at 96°C for 1 h. The filtered solutions were acidified to 5% HNO₃ equivalent and stored at 4°C until analysis. The analysis was carried out with an Agilent 7900 ICP-MS at HKU with rhodium as an internal standard. Detection limits for the different elements were determined using the blank solutions. Both the accuracy and precision were better than 10% for all the analyzed elements.

References

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- Sanematsu, K., Kon, Y., Imai, A., Watanabe, K., and Watanabe, Y. (2013) Geochemical and mineralogical characteristics of ion-adsorption type REE mineralization in Phuket, Thailand. *Mineralium Deposita*, 48(4), 437-451.
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