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Geochemical characteristics of rare earth elements (REEs) in soils developed on different parent materials, in the Baoshan area, Yunnan Province, SW China

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Abstract: The geochemistry of rare earth elements (REEs) was studied in rock samples from host formations, ore samples from two mineral deposits (the Hetaoping Cu-Pb-Zn mine: HTP and the Heiyanao Fe-Cu-Pb-Zn mine: HYA) and the overlying or nearby soils to better understand REE concentrations, distributions and behaviour during weathering from different parent materials at the regional scale, Baoshan area, Yunnan Province, SW China. The mudstone and sandstone formations have the highest total REE (ΣREE) contents. Chondrite-normalized diagrams for rocks and ores show significant light REEs (LREEs) enrichments and Eu depletion (except for ores in HYA). Cerium displays an obvious negative anomaly in carbonate rocks (Є-3-R, C-R, D-R, T-1-R and T-2-R). Soils overlying carbonate rock formations (T-1-S, C-S and Є-3-S) have the highest ΣREE contents, while soils overlying basalts have the lowest ΣREE contents. Soils show enrichments in LREEs with negative Eu anomalies and slight Ce anomalies in the studied soils. Soils with high ∑LREE/∑heavy REE (HREE) values may result from the preferential absorption of LREEs by organic matter. Negative Eu anomalies in soils occur for parent materials in the study area lacking feldspar, especially soils developed from carbonates. Compared to the parent materials, most soils show REE enrichment because alkali metals are removed and REEs are concentrated by low mobility in surficial processes and positive Ce anomalies because of weathering dissolution of other trivalent REEs with ionic radii similar to that of Ca^{2+}.

Keywords: rare earth elements (REEs); principal component analysis (PCA); compositional data analysis (CoDA); parent materials; Baoshan; SW China

Supplementary material: Additional data (Tables S1 and S2) and sample locations (Fig. S1) are available at https://doi.org/10.6084/m9.figshare.c.5303140

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The rare earth elements (REEs) are a group of 16 elements with identical physical and chemical properties and similar behaviour in the environment; these elements are yttrium (Y) and the 15 lanthanide elements: lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb) and lutetium (Lu); Pm does not occur naturally in the Earth's crust (Henderson 1984; Tyler 2004; Hu *et al.* 2006; Loell *et al.* 2011; Aide and Aide 2012; Jaireth *et al.* 2014; Aysha Masood *et al.* 2017). These elements are commonly divided into two groups based on their atomic numbers and masses: light REEs (LREEs: La-Eu) and heavy REEs (HREEs: Gd-Lu (Y)) (Tyler 2004; Hu *et al.* 2006; Walters *et al.* 2010; Long *et al.* 2012; Sadeghi *et al.* 2013; Davranche *et al.* 2016; Alfaro *et al.* 2018). However, REEs are not as rare in nature as the name suggests. For example, the abundance of cerium in the crust is similar to that of Cu and Zn (Haxel *et al.* 2002; Tyler 2004; Loell *et al.* 2011). These elements are present in more than 200 minerals, mainly phosphates, carbonates, silicates, fluorides, and iron and manganese oxides (Braun *et al.* 1993; Chakhmouradian 1996; Ivanova *et al.* 1996; Sabourdy *et al.* 1997; Alex *et al.* 1998; Gramaccioli *et al.* 1999; Bauluz *et al.* 2000; Masau *et al.* 2000; Buhn *et al.* 2002; Kanazawa and Kamitani 2006; Laveuf and Cornu 2009; Aide and Aide 2012; Boni *et al.* 2013; Hanilçi 2013; Radusinović *et al.* 2017). Generally, they occur as trivalent ions, while Ce can also be tetravalent and Eu can be divalent (Tyler 2004; Mihajlovic and Rinklebe 2018).

Soils are mainly composed of complex mixtures of weathered geologic materials (M. Li *et al.* 2008). The abundances of REEs in soils are influenced by their parent materials, texture, weathering history, pedogenic processes, organic matter contents and reactivity, and anthropogenic disturbances (Aide and Aide 2012). REEs and their occurrence patterns (especially the LREE/HREE ratio and δEu and δCe) are good indicators of soil processes for researchers in environmental sciences (Henderson 1984; Tyler 2004), and they are crucial for understanding the geochemical characteristics of a specific region (Zhang *et al.* 1998; Egashira *et al.* 2004; C. Li *et al.* 2008). Interest in the geochemical behaviour of REEs during rock weathering and soil formation has grown steadily in the past several decades (Nesbitt 1979; Öhlander