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ORIGINAL ARTICLE

Effects of topography and vegetation on distribution of rare earth elements in calcareous soils

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Abstract This study investigated the impact of topography and vegetation on distribution of rare earth elements (REEs) in calcareous soils using methods of single extraction and mass balance calculation. The purposes of the study were to set a basis for further research on the biogeochemical REE cycle and to provide references for soil–water conservation and REE-containing fertilizer amendments. The results show a generally flat Post-Archean Average Australian Shale—normalized REE pattern for the studied calcareous soils. REE enrichment varied widely. The proportion of acid-soluble phases of heavy REEs was higher than that of light REEs. From top to bottom of the studied hills, dominant REE sources transitioned from limestone in-situ weathering to input from REE-containing phases (e.g., clay minerals, amorphous iron, REE-containing fluids). Our results indicate that the REE content of calcareous soils is mainly controlled by slope aspect, while the enrichment degree of REEs is related to geomorphological position and vegetation type. Furthermore, the proportion of acid-soluble phases of REEs is mainly controlled by geomorphological position.

Keywords REE distribution · Weathering and pedogenesis · Topography and vegetation · Calcareous soils

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1 Introduction

Rare earth elements (REEs), a group of metallic elements with chemically similar behavior, have a special significance in tracing material sources and evolution processes of various geochemical systems (Sadeghi et al. 2013). Much attention has been paid to the biogeochemical REE cycle in terrestrial ecosystems and its controlling factors (Mihajlovic et al. 2014).

Rock weathering and pedogenesis, which are important sources of ecosystem REEs and key processes in the global biogeochemical REE cycle, vary with climate (Chadwick et al. 2003), lithology (Ji et al. 2004; Song et al. 2006), topography, and vegetation. Research about the influence of these factors on the differentiation, enrichment, and migration of REEs during weathering and pedogenesis may help determine the environmental characteristics of weathering and soil formation and improve understanding of the biogeochemical REE cycle (Ji et al. 2004; Song et al. 2006). However, there are few systematic reports on the impact of topography and vegetation on calcareous soil formation and related REE behavior.

Calcareous soils are extensively developed on carbonate rocks in karst regions of the world (Ji et al. 2004). Through analysis of calcareous soils in the Yangzhong catchment in Huaxi, Guizhou Province, China, this study investigated the impact of topography and vegetation on sources and distribution of soil REEs to better understand the mechanisms controlling the biogeochemical REE cycle.

2 Materials and methods

Guizhou Province contains the largest continuously distributed mountainous karst plateau in tropical and subtropical regions. The study area is in Yangzhong karst basin (Fig. S1). The lithology of the basin is Triassic limestone and the local soil is black calcareous soil. Dominant plants in the study area are *Cotinus coggygria* and *Pyracantha fortuneana* with a coverage of 60%–80%.

Surface calcareous soils under *C. coggygria* on the sunny side of Yangzhong basin were sampled from the bottom of the slope to the top (Fig. S1; Table S1). Surface calcareous soils were also sampled under *C. coggygria* and *P. fortuneana* on the shady slope (Fig. S1; Table S1).

Soil samples were air dried and ground to less than 200 mesh with an agate mortar prior to elemental analysis. The major element analysis was performed using conventional wet chemical methods. REE content was determined with inductively coupled plasma mass spectrometry (ICP-MS, Finnigan MAT, British) using rhodium as the internal standard after acid ($HNO_3 + HF$) digestion of soil samples in polytetrafluoroethylene tanks. The quality of analysis was monitored with standard samples of limestone (GBW07120) and calcareous soil (GBW07404). The analysis precision of major elements and REEs were better than 2% and 8%, respectively. Acid-soluble major elements and REEs were extracted with 0.50-M NH4Ac-HAc at pH 4.74 and analyzed by inductively coupled plasma-optical emission spectroscopy (ICP-OES, Perkin Elmer, USA) and ICP-MS, respectively. The REE distribution pattern was normalized to Post-Archean Average Australian Shale (PAAS) (McLennan 1989). The element enrichment factor of element X (EF_X) was calculated as follows (Taylor and McLennan 1985):

$$EF_X = X_{sample}/X_{UCC}$$

where X_{sample} and X_{UCC} are the contents of element X in sample and in upper continental crust (UCC), respectively.

3 Results

The contents of Al_2O_3, Fe_2O_3, and REEs had decreasing trends in calcareous soils under *C. coggygria* on the sunny slope from bottom to top of the hill, while the CaO content and La/Yb ratio presented increasing trends (Table S1). Al_2O_3, Fe_2O_3, and REE contents as well as La/Yb ratios and other parameters of calcareous soils on the sunny slope were nearly equivalent to those on the shady slope under *C. coggygria*. The CaO contents of calcareous soils under *C. coggygria* on the sunny slope were lower than those under *P. fortuneana* on the shady slope.

In general, the REE distribution patterns among all samples were relatively flat. On the sunny slope, the REE distribution patterns of calcareous soils were very flat (Fig. 1a–c). Heavy REEs (HREEs) in most calcareous soils under both *C. coggygria* and *P. fortuneana* on the shady slope had slight loss (or slight enrichment of light REE (LREE)) compared with soils sampled on the sunny slope (Fig. 1d, e).

EF_{LREE}, EF_{HREE}, and EF_{REE} in calcareous soils were very similar and decreased from bottom (higher than 1) to top of the hill (lower than 1) (Fig. 2). EF_{LREE} was higher than EF_{HREE} in the calcareous soils. EF_{LREE}, EF_{HREE}, and EF_{REE} in the calcareous soils under *C. coggygria* were higher than 1, but varied significantly under *P. fortuneana* (Fig. 2b).

The extraction ratios (ERs) of LREEs, HREEs, and REEs in the calcareous soils by 0.5-M NH_4Ac-HAc (pH 4.74) were calculated based on single extraction results (Fig. 3). On the whole, ER_{HREE} was higher than ER_{LREE}, indicating that HREEs had a higher bioavailability and mobility than LREEs. ER_{LREE}, ER_{HREE}, and ER_{REE} on the sunny slope ranged from 0.28% to 2.56%, 0.41% to 4.49% and 0.30% to 2.75%, respectively, and decreased from bottom to top of the hill (Fig. 3a). ER_{LREE}, ER_{HREE}, and ER_{REE} under different slopes, elevation, and vegetation ranged from 0.55% to 4.96%, 0.91% to 6.96%, and 0.59% to 5.16%, respectively (Fig. 3b). Under *P. fortuneana* on the shady slope, ER_{LREE}, ER_{HREE}, and ER_{REE} showed increasing trends from bottom to mid-slope.

4 Discussion

4.1 Sources and distribution of rare earth elements in calcareous soils

According to field geological investigation and biogeochemical studies of trace elements in calcareous soils (Song et al. 2006; Song 2006), the parent rock of the study area is continuously distributed limestone and the calcareous soils developed from in situ limestone weathering. Furthermore, the consistency of the REE pattern and La/Yb ratio in different calcareous soils show that the calcareous soils came from the same material source.

To better understand REE sources and distribution in calcareous soils, we calculated the element mobility factor (Middelburg et al. 1988) ($MF_X = (X/TiO_2)_{sample}/(X/$

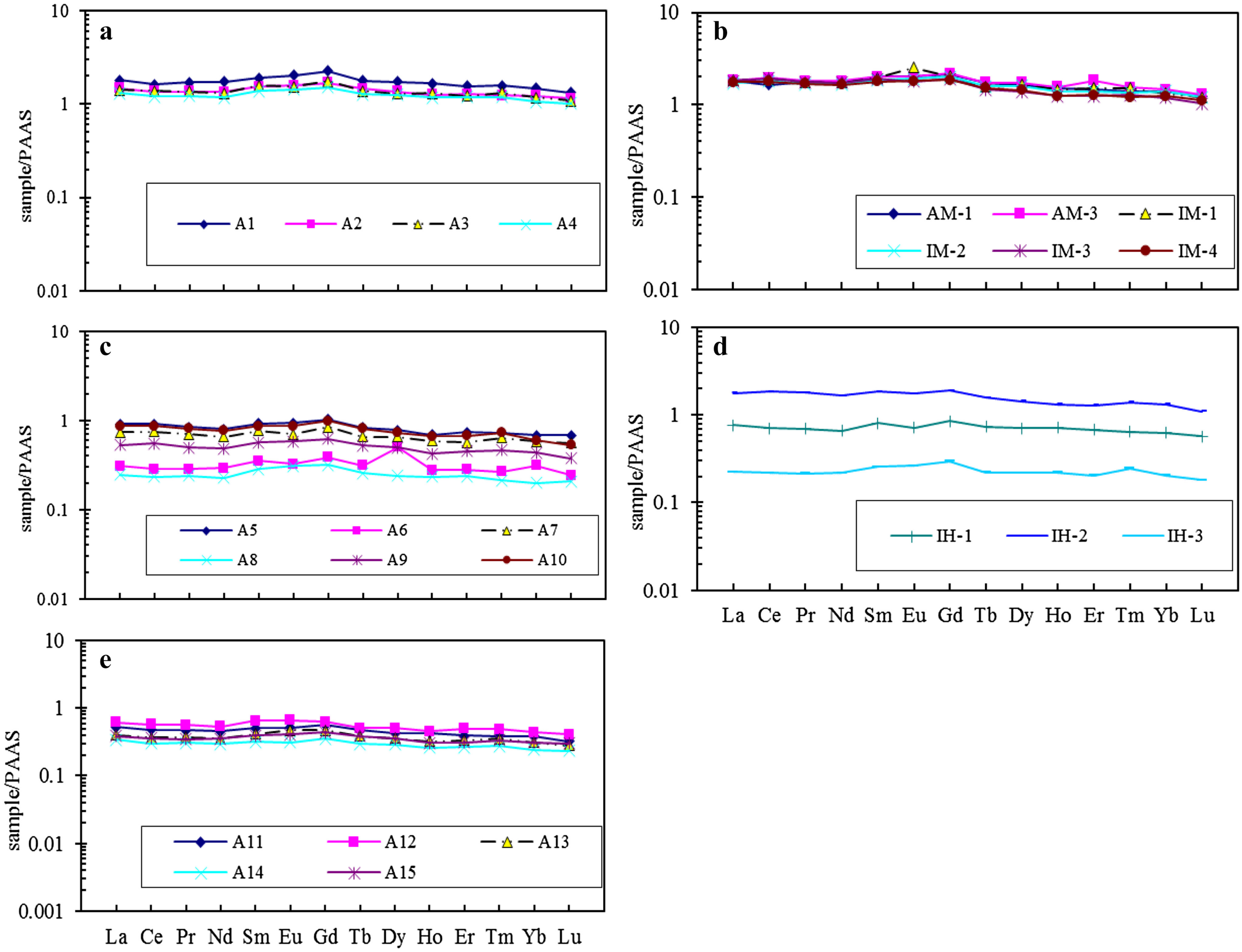

Fig. 1 PAAS-normalized REE distribution pattern of calcareous soils. Sunny **a** lower, **b** middle, and **c** upper slopes covered by *C. coggygria*; shady **d** lower and **e** middle-upper slopes covered by *C. coggygria* and *P. fortuneana*

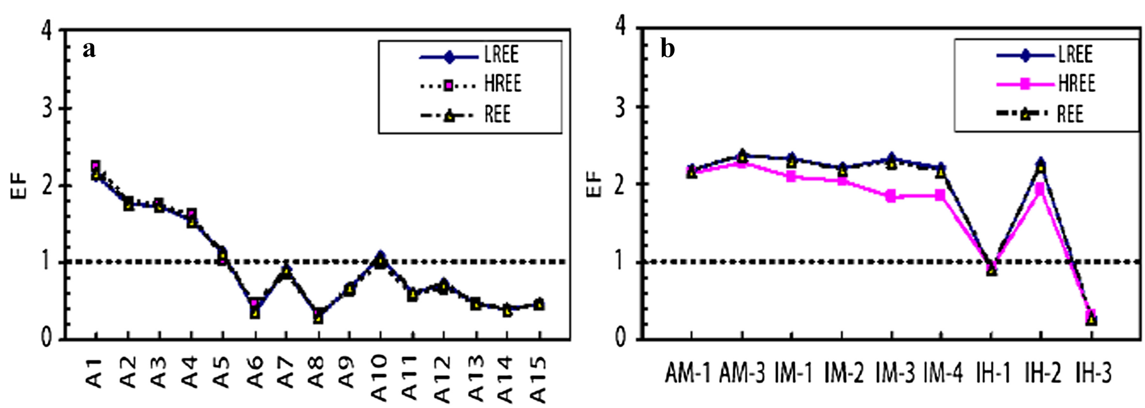

Fig. 2 Enrichment factor (EF) of LREEs, HREEs, and REEs overall in calcareous soils relative to upper continental crust: **a** from bottom to top of the sunny slope of the studied hill; **b** under different slope aspects and vegetation conditions

$TiO_2)_{\text{parent rock}}$, where $(X/TiO_2)_{\text{sample}}$ and $(X/TiO_2)_{\text{parent rock}}$ are the mass ratios of *X* and TiO_2 in samples and parent rocks, respectively). Considering the stages of limestone weathering and pedogenesis (Song 2006), we used the average composition of relatively low developed calcareous soil samples A13 to A15 to replace the limestone rocks.

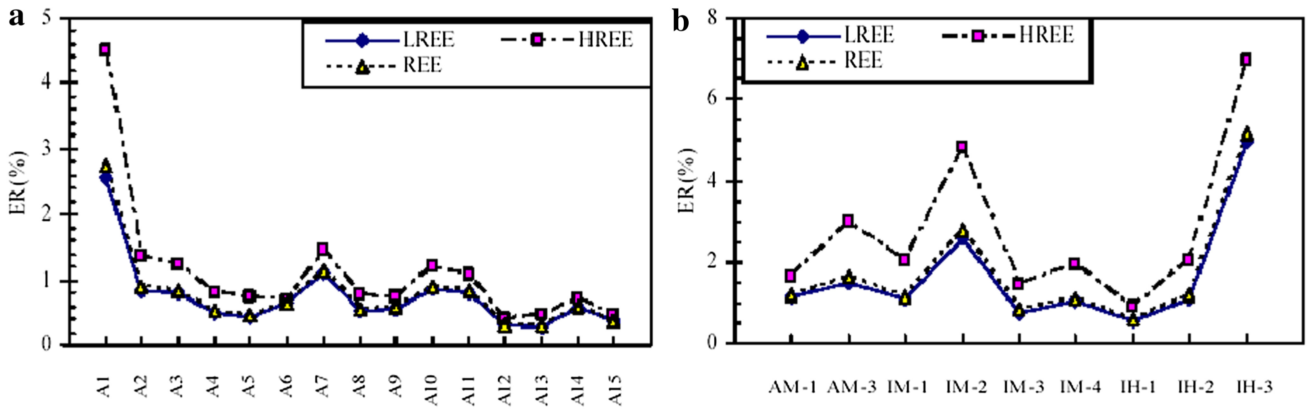

Fig. 3 Extraction ratio (ER) of calcareous soils with 0.5-M NH_4Ac-HAc (pH 4.74): **a** from bottom to top of the sunny slope of the studied hill; **b** under different slope aspects and vegetation conditions

The MF_{REE} value was higher than 1, except for samples A11 and IM-3, and had a close relationship with MF_{Al} and MF_{Fe} (Fig. 4), indicating that the migration and enrichment of REEs in calcareous soils (Fig. 2) are mainly related to the input of REE-containing phases (i.e. clay minerals) or to the deposition and enrichment mechanisms of REEs (Song et al. 2006). The study of biogeochemical cycles of trace elements in soil profiles developed on carbonate rocks (Song 2006) has shown that clay from calcareous soil substance and fluid immigration mechanisms mainly occurs in depositional landforms. However, the deposition and enrichment mechanism mainly occurs in erosional landforms. In this study, REEs at the deposition area mainly came from REE-containing phases (e.g., clay minerals, amorphous iron, and REE-containing fluids) from higher positions. By contrast, the REEs at hilltop erosion positions mainly came from in situ limestone weathering. Furthermore, REEs at mid-slope erosion-accumulation transforming positions derived from both of the two sources mentioned above. The different source ratios depended on the relative intensity of erosion and accumulation at different positions.

4.2 The factors controlling rare earth element distribution in calcareous soils

The development processes of calcareous soils can be divided into two stages: calcium and magnesium removal with aluminum, silicon, and potassium enrichment; and silicon removal with aluminum, silicon, and potassium enrichment. However, the development degree of calcareous soils at different sites varies with geomorphological position and vegetation type (Song 2006). According to the contents of CaO, Al_2O_3, and K_2O and the distribution of MF_{Ca} and MF_{Al} in calcareous soils (Table S1; Fig. 4), the calcareous soils at the study site were in the first stage.

From top to bottom on the sunny slope of the studied hill, the degree of calcium removal increased (Table S1; Fig. 4a). Simultaneously, REE enrichment and proportion of acid-soluble REEs also increased (Figs. 2a, 3a). These

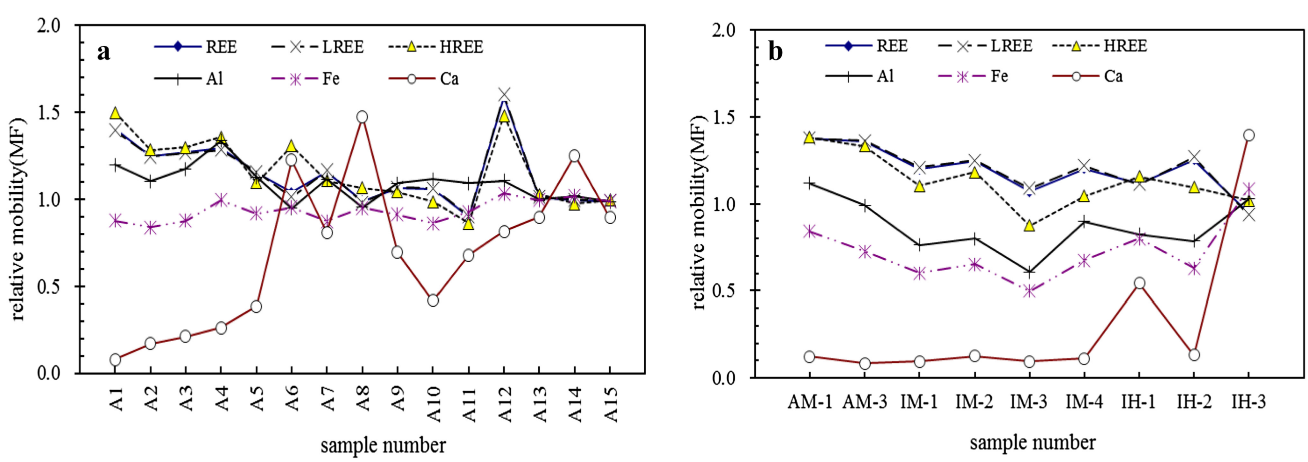

Fig. 4 Variation of relative mobility of REEs, LREEs, HREEs, Al, Fe, and Ca for calcareous soils: **a** from bottom to top of the sunny slope of the studied hill; **b** under different slope aspects and vegetation conditions

phenomena were related to the increasing migration of REE-containing materials from top to bottom of the studied hill (Fig. 4a). However, the REE distribution patterns of calcareous soils in different geomorphological positions were generally flat due to the flat distribution of REEs in the parent materials (Fig. 1a–c) and to the migration behaviors of LREEs and HREEs (Fig. 4a).

HREE loss and emigration of REEs, Fe, and Al in calcareous soils were greater on the shady slope than on the sunny slope at corresponding locations under *C. coggygria* (Figs. 1a–d, 2a, b, 4a, b). These results were related to lower emigration from the top of the hill of REE-containing phases on the shady slope relative to those on the sunny slope. The degree of enrichment of soil REEs (Figs. 2a, b), the ratio of acid-soluble REEs (Figs. 3a, b), and the emigration degree of Ca (Figs. 4a, b) on the shady slope were similar to those on the sunny slope.

At the bottom and mid-slope of the shady slope, the calcareous soils under *C. coggygria* had lower CaO contents, and higher REE enrichment (Fig. 2b) and Ca emigration (Fig. 4b) than those under *P. fortuneana* (Table S1). These results were related to the stronger water retention capacity and in situ chemical weathering (i.e., development degree) of soils under *C. coggygria* than of those under *P. fortuneana*. As leaf $\delta^{13}C$ values correlate positively with plant water use efficiency, the higher leaf $\delta^{13}C$ values for *C. coggygria* ($-27.99‰ \pm 0.37‰$) than for *P. fortuneana* ($-29.09‰ \pm 0.45‰$) from the same karst research area (Yang et al. 2007) partly support the above explanation. Calcareous soils under *C. coggygria* and *P. fortuneana* had similar REE distribution patterns (Fig. 1d, e).

5 Conclusion

PAAS-normalized REE patterns of the studied calcareous soils were generally flat. The enrichment degree of REEs varied widely, but was generally comparable to UCC. The proportion of acid-soluble phases of HREEs was higher than that of LREEs: 0.41%–6.96% and 0.28%–4.96%, respectively. At the bottom of the hill, REEs derived mainly from the movement of REE-rich phases (such as clay minerals) from the top. At the erosion site of the hilltop, REEs derived mainly from the weathering of surrounding limestone. At the erosion-accumulation transitional positions of the hillside, REEs were from both of the above two sources, with the proportion of the two related to the erosion/accumulation degree of the location. Our results indicate that REE patterns of calcareous soils are mainly related to slope aspect; the enrichment degree of REEs is related to the geomorphological position and vegetation type; and the proportion of acid-soluble phases of REEs is mainly controlled by geomorphological position. However, it is necessary to compare REE behavior in calcareous soil profiles from different areas with different slope aspects, geomorphological positions, and vegetation types to improve understanding of the effects of topography and vegetation on REE behavior in calcareous soils.

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Complinace with ethical standards

Conflict of interest We declare no conflict of interest.

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