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ARTICLE

Geochemistry of rare earth elements in soils under different land uses in a typical karst area, Guizhou Province, Southwest China

Guilin Han, Zhaoliang Song, and Yang Tang

Abstract: Understanding soil erosion processes under different land uses is important for predicting and controlling watershed soil losses, especially in karst areas. Five soil profiles and 55 soil samples were collected from soils that were under different land uses in a typical karst catchment, Southwest China. The total contents of rare earth elements (REE) are significantly lower (<100 mg kg^{-1}) than the average value of soils in China (181 mg kg^{-1}). The enrichment degree of REE in heavy REE is much higher than that of light REE in all soil samples. A positive Ce anomaly (~1.4) and a slightly negative Eu anomaly (~0.95) were found. The enrichment and release of REE are partly controlled by pH, distribution of REE in bedrocks, contents, and adsorption ability of organic matters in weathering profiles.

Key words: rare earth elements, Y/Ho, land use, karst, Southwest China.

Résumé : Il est important de comprendre les mécanismes d'érosion du sol exploité à diverses fins pour prévoir et ralentir la perte de sol dans les bassins hydrographiques, surtout dans les régions karstiques. Les auteurs ont recueilli 55 échantillons de sols à vocation différente de cinq profils pédologiques dans un bassin hydrographique karstique caractéristique au sud-ouest de la Chine. La concentration totale de terres rares était nettement plus faible (<100 mg kg^{-1}) que la concentration moyenne relevée dans les sols chinois (181 mg kg^{-1}). Dans tous les échantillons, le taux d'enrichissement en terres rares était beaucoup plus élevé dans les sols à forte teneur en terres rares que dans les autres sols. Les auteurs ont relevé une aberration positive pour le cérium (~1,4) et une légère aberration négative pour l'europium (~0,95). Le taux d'enrichissement et de libération des terres rares dépend en partie du pH, de la distribution des terres rares dans le substrat rocheux ainsi que de la concentration et du potentiel d'adsorption de la matière organique dans les profils à météorisation. [Traduit par la Rédaction]

Mots-clés : terres rares, Y/Ho, vocation des terres, karst, sud-ouest de la Chine.

Introduction

The rare earth elements (REE) are a group of elements that have similar geochemical properties and have been used extensively to trace geochemical processes in natural systems because they possess similar atomic radii and oxidation states (Åström 2001; Welch et al. 2009). Because yttrium exhibits similar properties to the lanthanide family, it is also considered as one of this group of elements (Liu and Byrne 1995; Tyler 2004). Recently, the usage of REE has been increasing rapidly in industrial and agricultural applications (Zhang and Shan 2001; Wang and Liang 2015). Therefore, the biogeochemical cycles of REE and their ecological and environmental effects are greatly concerned by many researchers (Liu et al. 2016; Martín-García et al. 2016). Due to chemical weathering of the primary minerals in rocks, the redistribution of REE in weathering products has been the subject of attention for the past several decades (Hill et al. 2000; Patino et al. 2003). Although REE may accumulate on particulates or in certain size fractions of nano-colloids (Moraetis et al. 2011; Neubauer et al. 2013), it may lead to fractionation of specific elements in

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G. Han. School of Scientific Research, China University of Geosciences (Beijing), Beijing 100083, People's Republic of China.

Z. Song. Institute of the Surface-Earth System Science Research, Tianjin University, Tianjin 300072, People's Republic of China.

Y. Tang. The State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, People's Republic of China.

Corresponding authors: Guilin Han (email: hanguilin@cugb.edu.cn) or Zhaoliang Song (email: zhaoliang.song@tju.edu.cn).

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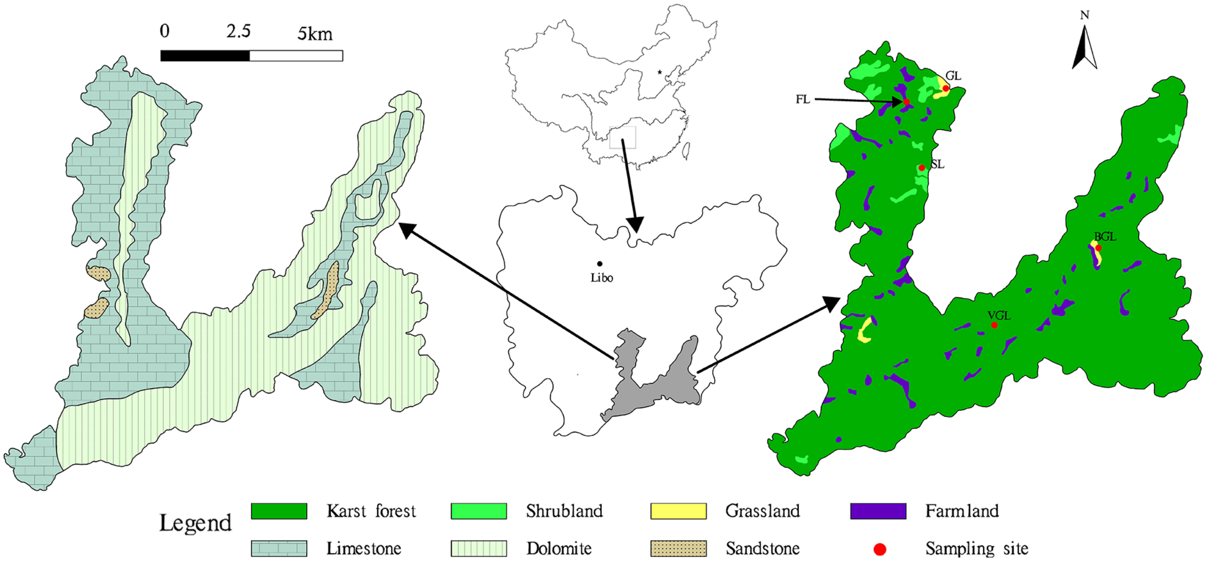
Fig. 1. The distribution of various land-use types with sampling sites in Guizhou Province, Southwest China.



particulate phases. REE fractionation has been observed within specific soil horizons (Germund 2004; Stille et al. 2006) and in carbonate-dominated areas (Johannesson et al. 1999). Under more alkaline conditions ($pH > 6$), naturally occurring nano-colloids have strong binding capacity for REE (Quinn et al. 2006; Marsac et al. 2013). Regarding REE migration, some studies have shown that REE are immobile during surface processes (Szczepanski and Ilnicki 2014). However, some researchers have found that the mobility of REE was controlled by pH values (Han et al. 2009; Pazand and Javanshir 2014) and REE was generally believed to be mobile at a lower pH value (Han and Liu 2007; Migaszewski et al. 2014). However, there is a paucity of study on the mobility of REE in soils influenced by different land-use strategies.

In karst regions of the Southwest (SW) China, the degradation of ecosystems has led to many ecological problems, such as karst rocky desertification. Locally high permeability at shallow depths in mature karst regions has caused an ecosystem associated with a soilless and water-scarce surface environment (LeGrand 1973). The different land uses and land cover of a given region can provide an environmental gradient to elucidate REE vertical transporting processes. However, only a few studies have investigated the changes of REE in modern soils at different depths and under different types of land use in karst areas (Zhu and Liu 2006; Han et al. 2015). The Maolan National Nature Reserve Park in the southeastern region of Guizhou Province is a typical forested area in SW China. Agricultural activity is one of the most important human inputs of potentially hazardous REE in this area. Since agricultural soil has both direct and indirect influences on public health via food production, it is of great importance to have a decent understanding of the accumulation and the spatial variability of REE in soils (Zhang and Shan 2001; Nakamaru et al. 2006; Wang et al. 2015).

This study explored the distribution pattern of REE in soil profiles along different landscapes in a karst catchment in SW China. The nature of plant cover (forest, grass, and crop) affects pedogenetic weathering and changes the soil organic matter and REE properties. Thus, in this work, the spatial variability (structure) of the soil variables and its controlling factors (soil parent material and agricultural practices) were investigated to explore the relationship among the REE characteristics in soils and soil properties [pH and organic matter (OM), Pardo et al. 2013]. This study aims to analyze the total REE contents in the typical karst ecosystem, to determine the potential effects of REE, and to assess REE ecological risk in soil using the enrichment factors.

Materials and Methods

Study area

The study area is located in the southeastern Guizhou Province (25°09′20″–25°20′50″N and 107°52′10″–108°05′40″E), which is approximately 200 km^2 (Fig. 1). The region is controlled by a subtropical and monsoonal climate, with a mean annual temperature of 17 °C and a mean annual precipitation of 1750 mm. The rock exposures in the study area are sedimentary formations of limestone, dolomite, sandstone, and clay of the early to middle carboniferous period (Han et al. 2015).

Samples collection and analysis

The sampling sites were chosen under different land uses within a small karst catchment in 2007

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(Han et al. 2015). Soil samples were collected at intervals of 10 cm from the surface to the boundary of soil and rock. A total of 55 soil samples were collected. Soil samples were collected from the park to represent the chronosequences of deforestation and land-use changes. The sampling strategy was designed to collect representative data from various landforms, land-use types, and areas with different conversion histories to cover a range of soil conditions. The sampling areas were selected based on field surveys and interviews with farmers and local experts. Five types of soil profiles were chosen for sampling during the summer of 2007. In addition to the virgin forest site, one sample site had been converted to intensive maize cropping, one site had been converted to shrubland (SL), and two sites had been converted to grassland (GL) in recent decades. The visible characteristics of the studied profiles are shown in Han et al. (2015). The GL, SL, burnt grassland (BGL), and virgin forest land (VFL) species profiles mainly contained C_3 plants. Maize, an important food crop that uses C_4 photosynthesis, was grown in the farmland profile.

Soil samples were air-dried and then sufficiently disaggregated by passing through a 2 mm sieve. Then, soil samples were entirely ground into powder in an agate mortar and sieved (mesh size, 75 μm). The powdered samples were then dried in an oven at 105 °C for 3 h before digestion. The methods used to digest the sample powders are as follows (Roy and Smykatz-Kloss 2007; Tang et al. 2015):

1. 100 mg of sample powder was digested with 1 mL HF and 2 mL HNO_3 in a PFA sample jar (Savillex, USA) at 140 °C for 7 d.
2. Samples were redissolved in 1 mL HF and 2 mL HNO_3 using the same treatment as in step 1. This process was repeated until the solution became clear.
3. After the samples were completely digested, 2 mL HNO_3 (1:1) was added two times to break up fluorine compounds. Then, samples were dried and vaporized on a hot plate.
4. Finally, the digested remainder was dissolved in a 100 mL volumetric flask, using 2% HNO_3.

The REE concentrations of the digested solutions were analyzed using an Agilent 7500a ICP-MS at the State Key Laboratory of Ore Deposit Geochemistry, Chinese Academy of Sciences, Guiyang, China. Quality control was performed using the national standard reference material of China (GBW07427). The testing error was ±3%. Analytical precision was estimated to be <5% for the heavy metals, based on duplicate analyses of samples and standards.

Data treatment

Since REE concentrations are naturally variable, the variation in REE compositions among samples was assessed by using the convention of concentrations normalized to post-Archaean Australian shale (PAAS) (McLennan 1989). Although normalizing data against a reference specific to the study system is preferred, such information is often unavailable. For the absence of a system specific reference, PAAS is widely used for normalizing REE concentrations (Laveuf and Cornu 2009).

We selected and calculated six REE variables, including ΣREE, light REE (LREE), middle REE (MREE), heavy REE (HREE), Ce anomaly, and Eu anomaly. ΣREE is the sum of the 15 REE. LREE includes La, Ce, Pr, Pm, and Sm; MREE includes Eu, Gd, Tb, and Dy; and HREE includes Gd, Tb, Dy, Ho, and Er (Germund 2004). The deviation of Ce and Eu relative to the neighboring elements is usually defined as the Ce and Eu anomalies. Ce and Eu anomalies (Sholkovitz et al. 1994; Han et al. 2009) are defined as follows:

$$\text{Ce anomaly} = 2 \times (\text{Ce}/\text{Ce}_N)/(\text{La}/\text{La}_N + \text{Pr}/\text{Pr}_N)$$

$$\text{Eu anomaly} = 2 \times (\text{Eu}/\text{Eu}_N)/(\text{Sm}/\text{Sm}_N + \text{Gd}/\text{Gd}_N)$$

where Ce_N, La_N, Pr_N, Eu_N, Sm_N, and Gd_N represent the concentrations of the respective REE in the PAAS. The Ce anomaly represents the deviation of the Ce concentrations from those expected by linear interpolation between the concentrations of La and Pr in the PAAS-normalized REE pattern of the samples. The Eu anomaly represents the deviation of the Eu concentrations from those expected by linear interpolation between the concentrations of Sm and Gd in the PAAS-normalized REE pattern of the samples. It is easy to distinguish the deviation (fractionation) of Ce and Eu from the expected (trivalent) REE. The negative Ce (Eu) anomalies or positive Ce (Eu) anomalies are defined as values of less or greater than 1, respectively.

Results and Discussion

REE contents in soil

REE concentrations of soils and bedrock are listed in Table S1.[1] The statistical parameters (six REE variables) are also shown. We can see that the REE contents of these soil samples are relatively low. The REE concentrations of most soil samples are lower than 100 mg kg^{-1}, whereas the REE contents of most samples from the surface soil are higher than those from the soil and rock boundary, such as the sample from the surface soil of the SL soil profiles (102.63 mg kg^{-1}). The ΣREE in this area is much lower than the average value in China (181 mg kg^{-1}; Hu et al. 2006), slightly higher than the REE in Japan (98 mg kg^{-1}; Yoshida et al. 1998),

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[1] Supplementary data is available with the article through the journal Web site at http://nrcresearchpress.com/doi/suppl/10.1139/cjss-2017-0043.

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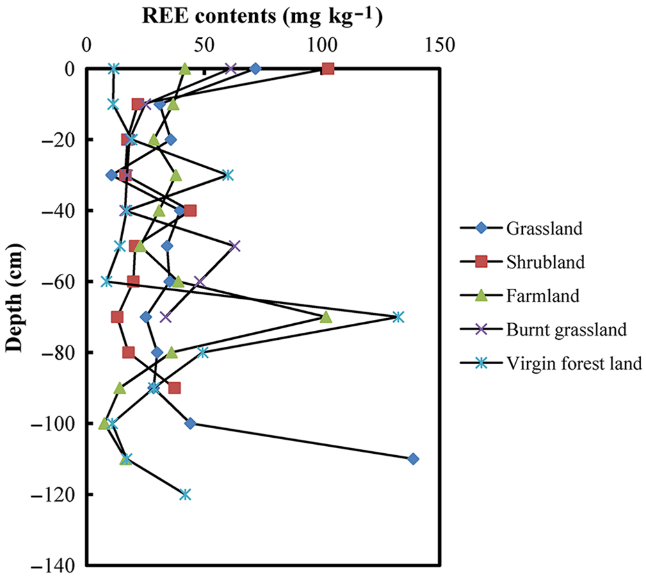
Fig. 2. Distribution of rare earth elements contents in the profile.



and similar to that in Australia (105 mg kg^{-1}; Diatloff et al. 1996).

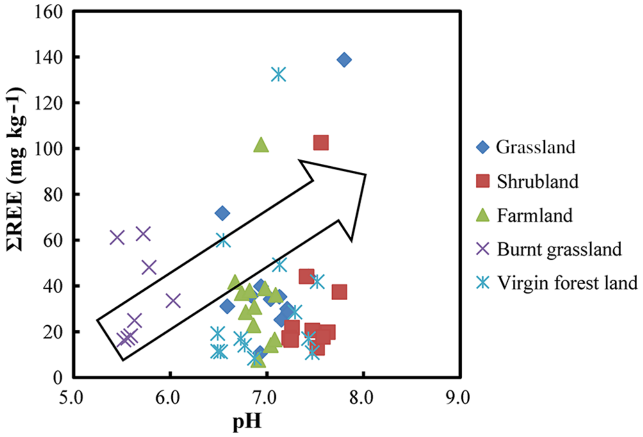
There is no significant difference of the REE contents among the five soil profiles, except the VFL, which were characterized by relatively low total REE concentrations, particularly at the surface (11.52 mg kg^{-1}, Table S1[1]). The changes in the total REE concentration with depth varied in a narrow range in each of the five soil profiles. The total REE concentrations decreased or increased in general with depth (Fig. 2). The REE content of surface soil in SL is the highest value.

The soil pH value is an important factor influencing the adsorption of REE. The adsorption of REE generally increases with increasing soil pH values, because the surface of the soil particles is charged with more OH^- ions and dissolved REE ions can easily form complexes. It can be seen that pH is positively correlated to the REE contents (Fig. 3).

REE fractionation

Although most soil samples show differences in the absolute concentration of REE, they have similar PAAS-normalized patterns. The PAAS-normalized pattern allows one to identify, within the typical sedimentary REE patterns, an enrichment or deficiency of a single element or group of elements (Henderson 1984). PAAS-normalized REE fractionation patterns are shown in Fig. 4 for the total soil samples. It is clear that these soil samples do not show a flat PAAS-normalized REE pattern. The PASS-normalized ratio of La/Yb is a common indicator to demonstrate the depletion of LREE over HREE. From Table S1[1] and Fig. 4, it can be seen that the $(La/Yb)_N < 1$ for all soil samples in all soil profiles, indicating that HREE enrichment is a dominant feature of the fractionation patterns in all soil profiles. In addition, the variations of REE fractionation patterns along the vertical profiles do not increase with depth, which demonstrated that there exists a pronounced inheritance between the bedrock and residual soil.

Fig. 3. Relationships between rare earth elements contents and pH.



Ce and Eu anomalies

Due to their special electron configuration in the outer shell, Ce and Eu occur as Ce (IV) and Eu (II), respectively. Most of the calculated Ce anomalies of our samples are positive (Ce* = 1.4, Table S1[1]). Slight negative Eu anomalies are also found in soil samples from all profiles (Eu = 0.94, Table S1[1]).

Table S1[1] and Fig. 5 show a consistent positive Ce anomaly (Ce anomalies > 1.4) in most of the soil samples from the soil profiles. This might be caused by Ce form Ce oxide hydrate retention in the surface profile in a hot and humid environment such as the Maolan catchment, migrate into the lower soil profile during the weathering processes, and enrich Ce in the soil samples. Usually, Eu depletion is inherited from bedrock rather than a result of surficial processes (Perri et al. 2013). The Eu does not show a significant positive anomaly (most Eu anomalies are about 1) because Eu^{2+} released during weathering is oxidized to Eu^{3+} and it hence behaves like other trivalent REE (Taylor and McLennan 1985).

Organic matter is abundant in the SL and GL soils. Numerous studies have investigated the influence of natural organic matter on REE retention and fractionation (Pourret et al. 2008). Pourret et al. (2008) demonstrated that REE were strongly complexed by humic substances at a near-neutral pH. As such, REE sorption to solid-phase humic substances is likely to have influence on REE behavior in the organic-rich soils examined in this study.

Y/Ho

In the process of weathering, the complex ability of Ho to coordinate with organic material or HCO_3^-

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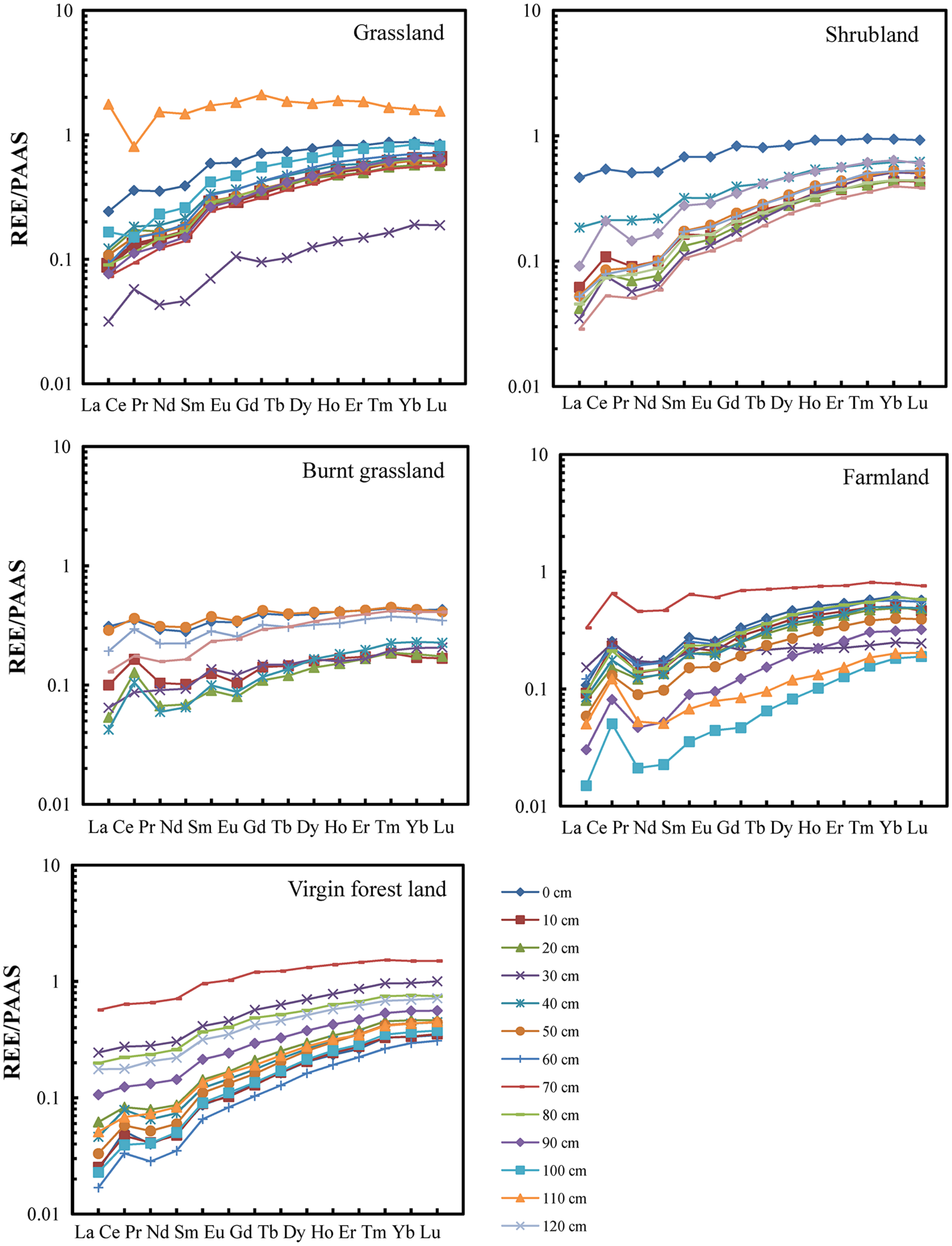
Fig. 4. Fractionation patterns of rare earth elements (post-Archaean Australian shale normalized) in soil profiles from the five land uses studied in Guizhou Province, Southwest China.



is greater than that of Y, and Y shows a stronger tendency to be adsorbed onto solid particles in the process of water–rock interaction (Kawabe et al. 1991). Ho is more easily lost due to leaching, resulting in an increase in the Y/Ho ratios of weathering profiles. The nonchondritic Y/Ho molar ratios in soil samples ranged from 26 to 81, with an average value of 42. Most of them are lower than the value of the continental rocks (Y/Ho = 52; Nozaki et al. 1997), and slightly higher than those of the source rock (Y/Ho = 39; Li et al. 1998). This may suggest the fractionation between these two elements due to weathering. Figure 6 shows that Y/Ho ratios for most samples are higher than those of the source rocks and continental rocks, and Y/Ho is positively related to La_N/Yb_N, suggesting that Ho is more rapidly removed from the water relative to Y. It is likely

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Fig. 5. Ce anomaly and Eu anomaly versus soil organic carbon (SOC). SOC data from Han et al. (2015).

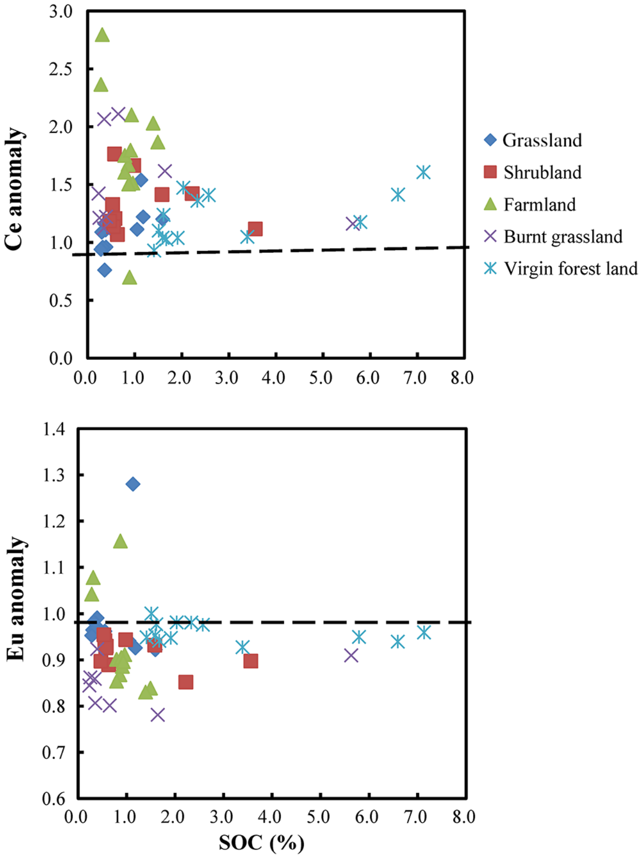
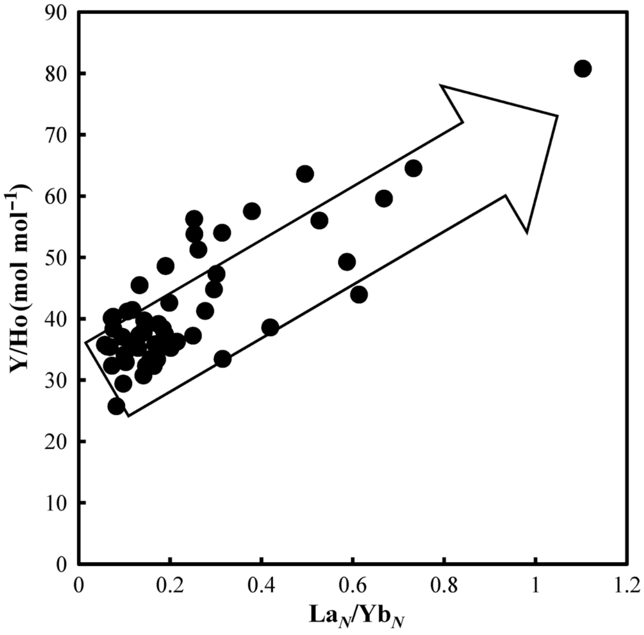


Fig. 6. Figure showing the covariation of Y/Ho versus La/Yb.



that Y distinctly deviated from Ho due to the competitive reactions during weathering processes (Byrne and Lee 1993).

Conclusions

The purpose of this study is to evaluate the geochemical behavior of REE in a typical karst alkaline environment. Compared with the research results of other regions, the patterns of REE in soils have a distinct regional characteristic in karst area. The contents of REE remain low (<100 mg kg^{-1}). The results of this study reveal a strong positive correlation between the concentrations of the REE enrichment and pH. The PAAS-REE normalized patterns showed that the HREE are enriched relative to the LREE. Y/Ho is positively related to the La/Yb, suggesting that Y distinctly deviates from Ho due to the competitive reactions during weathering processes. This suggests that a common soil fraction influences the enrichment of HREE relative to LREE. In alkaline systems, the stability constant for REE–organic complexes is greater for HREE than LREE. Compared with the research results of other regions, the patterns of REE in soils have a distinct regional characteristic in karst areas.

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References

Åström, M. 2001. Abundance and fractionation patterns of rare earth elements in streams affected by acid sulphate soils. Chem. Geol. **175**: 249–258. doi:10.1016/S0009-2541(00)00294-1.

Byrne, R.H., and Lee, J.H. 1993. Comparative yttrium and rare earth element chemistries in seawater. Mar. Chem. **44**(2–4): 121–130. doi:10.1016/0304-4203(93)90197-V.

Diatloff, E., Asher, C.J., and Smith, F. 1996. Concentrations of rare earth elements in some Australian soils. Aust. J. Soil Res. **34**: 735–747. doi:10.1071/SR9960735.

Germund, T. 2004. Vertical distribution of major, minor, and rare elements in a Haplic Podzol. Geoderma, **119**(3): 277–290. doi:10.1016/j.geoderma.2003.08.005.

Han, G., Li, F., and Tang, Y. 2015. Variations in soil organic carbon contents and isotopic compositions under different land uses in a typical karst area in Southwest China. Geochemical J. **49**(1): 63–71. doi:10.2343/geochemj.2.0331.

Han, G.L., and Liu, C.Q. 2007. Dissolved rare earth elements in river waters draining karst terrains in Guizhou Province, China. Aquat. Geochem. **13**(1): 95–107. doi:10.1007/s10498-006-9009-1.

Han, G.L., Xu, Z.F., Tang, Y., and Zhang, G.P. 2009. Rare earth element patterns in the karst terrains of Guizhou Province, China: implication for water/particle interaction. Aquat. Geochem. **15**(4): 457–484. doi:10.1007/s10498-009-9061-8.

Henderson, P. 1984. Rare earth element geochemistry. Elsevier, Oxford, UK. 510 pp.

Hill, I.G., Worden, R.H., and Meighan, I.G. 2000. Yttrium: the immobility-mobility transition during basaltic weathering. Geology, **28**(10): 923–926. doi:10.1130/0091-7613(2000)28<923:YTITDB>2.0.CO;2.

Hu, Z.Y., Haneklaus, S., Sparovek, S., and Schnug, E. 2006. Rare earth elements in soils. Commun. Soil Sci. Plant Anal. **37**: 1381–1420. doi:10.1080/00103620600628680.

Johannesson, K.H., Farnham, I.M., Guo, C., and Stetzenbach, K.J. 1999. Rare earth element fractionation and concentration

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variations along a groundwater flow path within a shallow, basin-fill aquifer, southern Nevada, USA. Geochim. Cosmochim. Acta, **63**(18): 2697–2708. doi:10.1016/S0016-7037(99)00184-2.

Kawabe, I., Kitahara, Y., and Naito, K. 1991. Non-chondritic yttrium/holmium ratio and lanthanide tetrad effect observed in pre-cenozoic limestones. Geochem. J. **25**: 31–44. doi:10.2343/geochemj.25.31.

Laveuf, C., and Cornu, S. 2009. A review on the potentiality of rare earth elements to trace pedogenetic processes. Geoderma, **154**(1–2): 1–12. doi:10.1016/j.geoderma.2009.10.002.

LeGrand, H.E. 1973. Hydrological and ecological problems of Karst regions: hydrological actions on limestone regions cause distinctive ecological problems. Science, **179**(4076): 859–864. doi:10.1126/science.179.4076.859. PMID:17832755.

Li, J., Zhu, L., and Chen, Y. 1998. Rare earth element distribution in weathering crusts of carbonate rocks, Guizhou Province. Carsol. Sin. **17**(1): 15–24 [In Chinese.].

Liu, G., Xiao, H., Liu, P., Zhang, Q., and Zhang, J. 2016. Using rare earth elements tomonitor sediment sources from a miniature model of a small watershed in the three gorges area of China. Catena, **143**: 114–122. doi:10.1016/j.catena.2016.03.044.

Liu, X., and Byrne, R.H. 1995. Comparative carbonate complexation of yttrium and gadolimium at 25 °C and 0.7 mol dm^{-3} ionic strength. Mar. Chem. **51**: 213–221. doi:10.1016/0304-4203(95)00067-4.

Marsac, R., Davranche, M., Gruau, G., Dia, A., Pédrot, M., Le Coz-Bouhnik, M., and Briant, N. 2013. Effects of Fe competition on REE binding to humic acid: origin of REE pattern variability in organic waters. Chem. Geol. **342**: 119–127. doi:10.1016/j.chemgeo.2013.01.020.

Martín-García, J.M., Sánchez-Marañón, M., Calero, J., Aranda, V., Delgado, G., and Delgado, R. 2016. Iron oxides and rare earth elements in the clay fractions of a soil chronosequence in Southern Spain. Eur. J. Soil Sci. **67**: 749–762. doi:10.1111/ejss.12377.

McLennan, S.M. 1989. Rare-earth elements in sedimentary rocks — influence of provenance and sedimentary processes. Rev. Mineral. Geochem. **21**: 169–200.

Migaszewski, Z.M., Galuszka, A., and Migaszewski, A. 2014. The study of rare earth elements in farmer's well waters of the Podwiśniówka acid mine drainage area (South-Central Poland). Environ. Monit. Assess. **186**: 1609–1622. doi:10.1007/s10661-013-3478-7. PMID:24122124.

Moraetis, D., Stamati, F., Kotronakis, M., Fragia, T., Paranychnianakis, N., and Nikolaidis, N.P. 2011. Identification of hydrologic and geochemical pathways using high frequency sampling, REE aqueous sampling and soil characterization at Koiliaris critical zone observatory, crete. Appl. Geochem. **26**: S101–S104. doi:10.1016/j.apgeochem.2011.03.055.

Nakamaru, Y., Tagami, K., and Uchida, S. 2006. Effect of nutrient uptake by plant roots on the fate of REEs in soil. J. Alloys Compd. **408–412**: 413–416. doi:10.1016/j.jallcom.2004.12.102.

Neubauer, E., Köhler, S.J., von der Kammer, F., Laudon, H., and Hofmann, T. 2013. Effect of pH and stream order on iron and arsenic speciation in boreal catchments. Environ. Sci. Technol. **47**(13): 7120–7128. doi:10.1021/es401193. PMID:23692297.

Nozaki, Y., Zhang, J., and Amakawa, H. 1997. The fractionation between Y and Ho in the marine environment. Earth Planet. Sci. Lett. **148**: 329–340. doi:10.1016/S0012-821X(97)00034-4.

Pardo, R., Vega, M., Barrado, E., Castrillejo, Y., and Sanchez, I. 2013. Three-way principal component analysis as a tool to evaluate the chemical stability of metal bearing residues from wastewater treatment by the ferrite process. J. Hazard Mater. **262**: 71–82. doi:10.1016/j.jhazmat.2013.08.031. PMID:24008000.

Patino, L.C., Velbel, M.A., Price, J.R., and Wade, J.A. 2003. Trace element mobility during spheroidal weathering of basalts and andesites in Hawaii and Guatemala. Chem. Geol. **202**(3): 343–364. doi:10.1016/j.chemgeo.2003.01.002.

Pazand, K., and Javanshir, A.R. 2014. Rare earth element geochemistry of spring water, north western Bam, NE Iran. Appl. Water Sci. **4**: 1–9. doi:10.1007/s13201-013-0125-y.

Perri, F., Critelli, S., Martin-Algarra, A., Martin-Martin, M., Perrone, V., Mongelli, G., and Zattin, M. 2013. Triassic redbeds in the Malaguide Complex (Betic Cordillera — Spain): petrography, geochemistry and geodynamic implications. Earth-Sci. Rev. **117**: 1–28. doi:10.1016/j.earscirev.2012.11.002.

Pourret, O., Davranche, M., Gruau, G., and Dia, A. 2008. New insights into cerium anomalies in organic-rich alkaline waters. Chem. Geol. **251**(1): 120–127. doi:10.1016/j.chemgeo.2008.03.002.

Quinn, K.A., Byrne, R.H., and Schijf, J. 2006. Sorption of yttrium and rare earth elements by amorphous ferric hydroxide: influence of pH and ionic strength. Mar. Chem. **99**(1): 128–150. doi:10.1016/j.marchem.2005.05.011.

Roy, P.D., and Smykatz-Kloss, W. 2007. REE geochemistry of the recent playa sediments from the Thar Desert, India: an implication to playa sediment provenance. Chem. Erde Geochem. **67**(1): 55–68. doi:10.1016/j.chemer.2005.01.006.

Sholkovitz, E.R., Landing, W.M., and Lewis, B.L. 1994. Oceanic particle chemistry: The fractionation of rare earth elements between suspended particles and seawater. Geochim. Cosmochim. Acta, **58**: 1567–1579. doi:10.1016/0016-7037(94)90559-2.

Stille, P., Steinmann, M., Pierret, M.C., Gauthier-Lafaye, F., Chabaux, F., Viville, D., Pourcelot, L., Matera, V., Aouad, G., and Aubert, D. 2006. The impact of vegetation on REE fractionation in stream waters of a small forested catchment (the Strengbach case). Geochim. Cosmochim. Acta, **70**(13): 3217–3230. doi:10.1016/j.gca.2006.04.028.

Szczepanski, J., and Ilnicki, S. 2014. From Cadomian arc to Ordovician passive margin: geochemical records preserved in metasedimentary successions of the Orlica-Śnieznik Dome in SW Poland. Int. J. Earth Sci. **103**: 627–647. doi:10.1007/s00531-013-0993-2.

Tang, Y., Han, G., Li, F., and Wu, Q. 2015. Natural and anthropogenic sources of atmospheric dust at a remote forest area in Guizhou karst region, southwest China. Geochem. Explor. Environ. Anal. **16**: 159–163. doi:10.1144/geochem2015-345.

Taylor, S.R., and McLennan, S.M. 1985. The continental crust: its composition and evolution. Blackwell, London, UK.

Tyler, G. 2004. Rare earth elements in soil and plant systems — a review. Plant Soil, **267**(1–2): 191–206. doi:10.1007/s11104-005-4888-2.

Wang, L., and Liang, T. 2015. Geochemical fractions of rare earth elements in soil around a mine tailing in Baotou, China. Sci. Rep. **5**: 12483. doi:10.1038/srep12483.

Wang, Q.-L., Chetelat, B., Zhao, Z.-Q., and Liu, X. 2015. Behavior of lithium isotopes in the Changjiang River system: sources effects and response to weathering and erosion. Geochim. Cosmochem. Acta, **151**: 117–132. doi:10.1016/j.gca.2014.12.015.

Welch, S.A., Christy, A.G., Isaacson, L., and Kirste, D. 2009. Mineralogical control of rare earth elements in acid sulfate soils. Geochim. Cosmochem. Acta, **73**(1): 44–64. doi:10.1016/j.gca.2008.10.017.

Yoshida, S., Muramatsu, Y., and Tagami, K. 1998. Concentrations of lanthanide elements, Th, and U in 77 Japanese surface soils. Environ. Int. **24**: 275–286. doi:10.1016/S0160-4120(98)00006-3.

Zhang, S., and Shan, X. 2001. Speciation of rare earth elements in soil and accumulation by wheat with rare earth fertilizer application. Environ. Pollut. **112**: 395–405. doi:10.1016/S0269-7491(00)00143-3. PMID:11291446.

Zhu, S., and Liu, C. 2006. Vertical patterns of stable carbon isotope in soils and particle-size fractions of karst areas, Southwest China. Environ. Geol. **50**(8): 1119–1127. doi:10.1007/s00254-006-0285-2.