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Distribution of rare earth elements in agricultural soil and human body (scalp hair and urine) near smelting and mining areas of Hezhang, China

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Abstract: Rare earth elements (REEs) in recent decade are widely used and lead to the accumulation of REE in the environment and human body. The aim of this study was to evaluate the concentrations of REEs in soil and human body (scalp hair and urine) of people living in agricultural soil near smelting and mining areas in Hezhang County, China. The results showed that mean concentrations of determined REEs in agricultural soil from smelting areas were higher than background. However, concentration was slightly higher in soil in mining area. In addition, REEs concentrations of hair and urine in smelting areas were higher than those in mining areas. ΣREEs for soil in mining and smelting areas were 177.79 and 277.06 mg/kg, respectively. ΣREEs for hair in mining and smelting were 1.13 and 1.55 mg/kg, respectively, and ΣREEs for urine in mining and smelting were 0.58 and 0.59 μg/L, respectively. Results showed that La, Ce and Nd were enriched in soil, hair and urine. Eu in smelting area showed a positive anomaly. In smelting and mining areas, females were more likely than male to expose to REEs. The relationship between REEs concentration and age group showed that hair's high concentrations of REE existed in 18–40 years age for people from smelting areas and females from mining areas. While high concentrations distributed in the age of 41–65 for males from mining area. However, urine did not present similar distribution for different age group. Compared with hair and urine, soil showed the same distribution of REEs. And according to the Ce/Ce* value vs. La_N/Yb_N ratio showed that hair and soil tended to increase, with the stability of Ce/Ce* value. Thus the distribution of REEs in soil was closely related with the accumulation in human body. This is a preliminary study which may be suggested to the other research, and this study data may be useful for adding up the data pool on REEs levels in China.

Keywords: rare earth elements; soil; human exposure; anomaly; age groups

The demand of rare earth elements (REEs) assessment in recent decade has increased, because REEs are widely applied in industrial, medicine, pharmacology, agricultural[1,2] and high technology such as computer memory, rechargeable batteries, cell phone, etc. Recently rare earth and cerium oxide (CeO_2) particles doped ceria-based nanostructures are usually investigated because of their great properties[3,4] and cerium oxide is valuable tools used in many aspect of bio-medical field[5]. China has the largest reserve of REEs in the world and REEs were usually detected in fishery, agriculture and animal farming[6–8]. The increase of utilization of REEs prompted mining process, and mining process consequently lead to environmental pollution such as soil, water, food, animals and human health risks. The impacts of REEs have attracted many researchers especially those focused on human risks and those focused on environmental exposure[9–11]. He et al. revealed that REEs can have positive effects on growth of vegetable and animal with small quantity in environment[12]. REEs can accumulate in body by ingestion, inhalation or dermal contact. However, others showed that long term intake of REEs can cause chronic poisoning and damage liver and kidney. REEs may promote the calcification of blood vessel and lead to plaque formation[7,8,13]. What's more, REEs can cause hepatotoxic and neurotoxic effects and damage to human lung[14–18]. Zhu et al. showed that living in high background of REEs can affect children's intelligence[2]. Moreover, REEs can be accumulated in many parts of the body such as bone, saliva, nails, blood, hair, etc. and excreted via both feces and urine[19].

Hezhang is a county of Bijie City in Guizhou Province, located in southwest of China. Guizhou is a typical Karst area and covers 109084 square kilometers. It is known for abundant type of metals, such as Pb, Zn and Hg. Hezhang is formerly known as an artisan Zn smelting using indigenous methods in Guizhou for hundreds of years from at least the seventeenth century until 2004. However, large amounts of heavy metals[20] and REEs were spread throughout this area affecting environment. South China is renewed for karstic rock formation, according to Wang, several deposits in Guizhou Province are related

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with E'meishan basalt weathering crust[21]; many deposits were formed on weathering crust of the top basalt with high content such as Fe, Mn, Au, Cu, REEs. Geochemical analysis in Hezhang, Weining, Bijie City of the basalt weathering crust, have found REE mineralization. And according to Chen and Yang, three kinds of soil formed by the weathering of the basalt, the carbonate rock and the phosphorite in the REE-bearing phosphate mining area of Guizhou Province were all rich in REEs[22].

For biomonitoring the toxicity of REEs exposure, urine, scalp hair and soil samples were collected from agricultural land of studied areas. Urine and scalp hair are used as a biomarker, because of their conveniences for storage and transport to the laboratory for analysis. Inductively coupled plasma mass spectrometry (ICP-MS) was used to analyze REEs because it is powerful and fast technique for elemental determination[23]. Goullé et al.[24] and Amarasiriwardena et al.[25] reported that ICP-MS is a useful tool for analyzing intoxication in environmental component. The investigations about REEs in human caused by mining and smelting process from Hezhang were handled in this work. The main objective of this study was to (1) investigate the concentrations, assess the enrichment factor and correlation of REEs in the vicinity of agricultural soil near an active mine (MM) and earlier smelting areas (SM) in Hezhang County; (2) to study REEs assessment in urine and hair, and comparison with earlier published data; (3) to evaluate the age-related variation and gender difference in hair and urine for REEs; (4) to study the relation between soil sample and human (hair and urine).

1 Materials and methods

1.1 Study area setting

Hezhang County (104°10′E to 105°35′E, 26°46′N to 27°28′N) is in west of Guiyang, the capital of Guizhou China. Hezhang County has a typical subtropical humid monsoon climate, with an average temperature of 13.4 ºC and an average annual rainfall of 854 mm. Artisan Zn smelting using indigenous techniques was practiced from at least the seventeenth century to 2004. Guizhou is an essential coal production base where exists abundant coal resources in China[26]. These activities led to big quantities of heavy metals[20,27–29], and many other pollutants were spread through soil and air such as REEs. And according to Liu and Wei, the level of REEs in Guizhou depends on the distance of coal-forming environment from the land and REEs in coals are essentially continental origins, associated with Emeishan basalt[26]. The description of soil type and geology in this study were detailedly explained in existing research[20]. Several areas were selected for use in this study. Soil, urine and hair samples were collected from agricultural land around the mining and smelting areas that have been affected by mining activities and/or other anthropogenic activities. The study was focused on four regions including Shehucun (ZB), Shijiapo (ZBL), Haimeicun (LA), and Longjiayuan (ZZ), which are affected by smelting activities. And the study on hair and urine was focused only on Haimeicun and Shehucun that were well-known for artisan zinc smelting (SM). The data for these regions were compared with data for agricultural soil near an active mine Shangermachong (MM) in Hezhang, the sampling areas are presented in Fig. 1. Urine and hair donors were from 6 to 81 years age, and ages for hair and urine were divided to 4 groups (6–17, 18–40, 41–65 and ≥66) for female and male, respectively.

1.2 Sample collection and pre-treatment

Soil samples were collected from top soil 0–15 cm. Every sample was placed in a bag then each sample was dried at 45 ºC in an oven until constant weight. Then each sample was grounded by using an agate ball mill. Samples were then passed through a 200-mesh sieve to analyze REEs and 2-mm sieve to analyze soil pH[20].

A questionnaire based on analysis was collected during the sampling period. Urine and hair of participants were determined to assess the current status of REEs exposure. The criteria of the selection of urine and hair were that they were the residents of the areas. Besides, ages and genders were noted gradually during sampling. The concentrations of REEs in hair and urine of mining and smelting areas were divided into four age groups, including 6–17; 18–40; 41–65, and ≥66 years (Table 1).

Hair was taken by using stainless scissors and kept in zip bag. Urine samples were transferred into a plastic tube. Tubes were kept in fridge bag and transported to refrigerator until analysis. According to Feldmann et al., the urine samples were stored at 4 ºC without any addi-

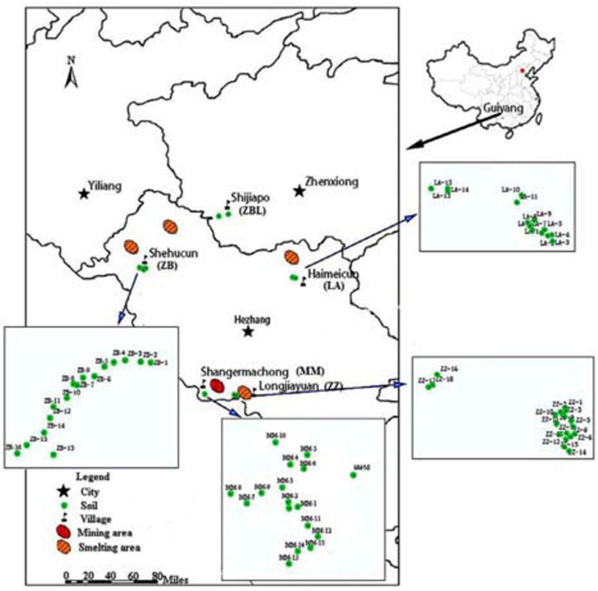

Fig. 1 Location of sites and soil sampling points collected in Hezhang

Table 1 Detail of number of male and female of each age group

Ages\Sexes	Hair of smelting areas (SM)		Hair of mining area (MM)		Urine of smelting areas (SM)		Urine of mining area (MM)	
	Male	Female	Male	Female	Male	Female	Male	Female
6–17	*n*=8	*n*=4	*n*=2	*n*=0	*n*=9	*n*=1	*n*=2	*n*=0
18–40	*n*=7	*n*=5	*n*=2	*n*=4	*n*=6	*n*=5	*n*=2	*n*=7
41–65	*n*=5	*n*=11	*n*=2	*n*=9	*n*=5	*n*=12	*n*=2	*n*=7
≥66	*n*=1	*n*=3	*n*=1	*n*=4	*n*=2	*n*=2	*n*=1	*n*=3

tives[30]. Hairs were cleaned by tap water and distilled water, then dried in an oven at 60 ºC overnight to avoid surface contaminants.

1.3 Sample analysis for REEs

All of the experiments were conducted at the State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences (Guiyang, China). 14 REEs concentrations (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) in soil, hair and urine samples were determined by quadrupole inductively coupled plasma mass spectrometry (ICP-MS, ELEMENT, Finnigan MAT). Soil, hair and urine analysis, detection limit, quality control, precision, and sensitivity of these analytical measurements and validation of the procedure were conducted following the procedure. Detailed procedures can be found in existing researches[20,31–33]. In brief, approximately 50 mg of hair sample was digested in microwave-assisted digestion using 2 mL conc. HNO_3 and 1 mL H_2O_2, and later analysis was performed by ICP-MS. The analysis of urine was performed in accordance with existing research[33]. Heating for 10 h to 90 ºC after the addition of 0.8 mL HNO_3 and 0.4 mL H_2O_2 to 2 mL of urine, and later analysis was performed by ICP-MS (ELEMENT, Finnigan MAT). The accuracy and precision of the analyses were monitored by performing reagent blank analyses. 10% of the samples were analyzed in duplicate[31].

The enrichment factors (EFs) in agricultural soils of studied areas were measured to determine the sources and anthropogenic influences of REEs in the studied areas. The measured method followed the same method of Briki et al.[20].

Briefly: EF=[X/Sc] sample/[X/Sc] baseline

EF denotes enrichment factor, X is the concentration of the element considered in the sample and Sc is the concentration of a reference element in the sample.

According to Loska and Wiechula, five contamination categories based on EFs have been defined, in case of EF<2 is minimal enrichment, EF=2–5 moderate enrichment, EF=5–20 significant enrichment, EF=20–40 very high enrichment, EF>40 extremely high enrichment[34].

2 Results and discussion

2.1 Concentration of REEs in soil

Statistical results of the average content, concentration of individual REEs in 85 samples of agricultural soil and PAAS shale are presented in Table 2. The average contents of all elements in soil were extremely variable, ranging from 0.53 (Lu) to 117.94 (Ce) in smelting areas (SM), and from 0.39 (Lu) to 83.09 (Ce) in mining area (MM) with total concentrations of 277.06 and 177.79 mg/kg respectively. It can be remarkably observed that smelting areas had higher concentrations in comparison with the values of mining area. And comparing concentrations between agricultural soil in smelting and mining areas from Hezhang County with planting soil in Wudang district of Guiyang city[35], results showed that values in this study were slightly higher.

The total concentration of REEs in agricultural soil of mining area (MM) was slightly higher than the background value of China soil[36] (154.95 mg/kg) but lower than background values in Guizhou[36], so REEs are slightly enriched in mining area (MM). However, total contents of smelting areas (SM) are remarkably higher than background values in China soil and Guizhou. Generally speaking, the region of smelting areas was polluted by REEs. The mean pH values are 5.82 in SM and 6.94 in mining area (MM). According to Jiang et al., both REEs concentrations and crustal abundance are much higher in near-neutral soils than values in acidic soils[37]. The main cause of high concentration of REEs is due to the earlier smelting process original rock rare earth mineral composition, mineralization process, agricultural process and alteration process of life and migration. And on the other hand, supergene action can prompt the accumulation of REEs. REEs can be adsorbed by ferric hydroxide colloid and clay mineral, resulting in a high REEs concentration in this region[38]. The average content of REEs in surface soil in smelting and mining areas followed this order: Ce>La>Nd>Pr>Sm>Gd>Dy>Er>Yb>Eu>Ho>Tb>Tm>Lu. This result followed the rules of Oddo-Harkins, i.e., the REEs' concentration was higher than odd numbers. With the increase of the atomic number, the abundance of elements generally decreased. The content of LREEs was larger than that of HREEs (Fig. 2).

The patterns plots eliminated by normalizing the concentration of individual REEs in smelting areas (SM) and mining area (MM) in every soil samples versus PAAS are drawn in Figs. 3 and 4 respectively. As shown by Figs. 3 and 4, the shale-normalized REEs distribution

Table 2 Statistical results of REEs in agricultural soil of Hezhang (mg/kg)

Elements	PAAS[a]	Smelting areas SM (n=68)		Mining area MM (n=17)		Background values in Chinese soil[b]	Background values in Guizhou[b]
		Mean	SD	Mean	SD		
La	38	56.08	17.03	35.69	7.55	37.4	41.2
Ce	80	117.94	23.33	83.09	23.2	64.7	95.5
Pr	8.9	13.48	4.29	7.85	1.78	6.67	8.08
Nd	32	50.47	15.06	27.74	6.21	25.1	30.5
Sm	5.6	9.4	2.43	5.09	1.17	4.94	6.13
Eu	1.1	2.35	0.52	1.09	0.28	0.98	1.17
Gd	4.7	8.49	2.03	4.94	0.98	4.38	5.47
Tb	0.77	1.29	0.31	0.73	0.17	0.58	0.79
Dy	4.4	7.28	1.81	4.47	1.05	3.93	5.29
Ho	1	1.45	0.36	0.95	0.22	0.83	1.12
Er	2.9	4.15	1.06	2.77	0.62	2.42	3.24
Tm	0.4	0.58	0.14	0.41	0.1	0.35	0.45
Yb	2.8	3.58	0.9	2.58	0.6	2.32	3.12
Lu	0.43	0.53	0.13	0.39	0.09	0.35	0.45
LREEs	165.6	249.72		160.55			
HREEs	17.4	27.35		17.24			
LREEs/HREEs	9.52	9.13		9.31			
ΣREE	183	277.06		177.79		154.95	202.51
La_N/Yb_N		1.17		1.02			
Gd_N/Yb_N		1.43		1.16			
Ce/Ce^*		1.01		1.14			
Eu/Eu^*		1.24		1.00			

SD denotes standard deviation, n denotes number of analyzed samples; [a] Post Archaean Australian Shale (PAAS), Taylor and, McLennan[56], [b]CNEMC[36]; ∑REE are the sum of La to Lu, LREEs are the sum of La to Eu, HREEs are the sum from Gd to Lu, $Ce/Ce^*=Ce_N/(La_N/Pr_N)^{0.5}$, $Eu/Eu^*=Eu_N(Sm_N/Gd_N)^{0.5}$, La_N/Yb_N, Gd_N/Yb_N, where N refers to PAAS value (see Taylor and McLennan[56])

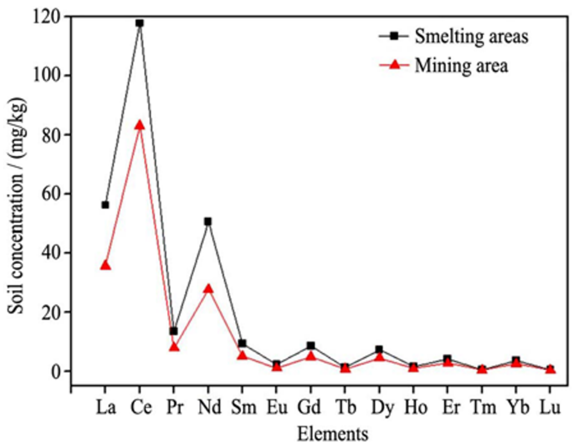

Fig. 2 Total REEs patterns for the soil from mining and smelting areas

patterns for the soil in mining and smelting areas were generally similar, indicating uniformity of geochemical distribution in PAAS shale[10]. However, the normalized patterns were completely different from mining and smelting areas. From the studied areas the REEs patterns were characterized by slight LREE enrichment and HREE depletion with downward trend. According to Chen and Yang, LREE could be easily absorbed by kaolinite grains, and LREE was fully enriched in the desorption process, migration and re-absorption, which formed a typical LREE soil[22].

In smelting areas, a strongly positive Eu anomaly is illustrated in Fig. 3. In mining area, there is a difference between samples to other samples especially for sample number MM-3, where Eu is clearly observed a negative anomaly. Eu elements was more abundant comparing to other REEs, which may have a greater accumulation originated not only from weathering but also soil contamination[10].

2.2 Enrichment factors of REEs

The calculated EFs of all fourteen REEs in soil are shown in Figs. 5 and 6. The EFs in mining area are lower than 2. According to the classification carried out on the basis EF, all the elements have minimal enrichment. The EFs in smelting areas are almost all the same (<2), and we can see that Eu element has the highest enrichment compared with other elements especially in Shehucun (ZB), Shijiapo (ZBL) and Longjiayuan (ZZ). However, it was found that EFs of REEs in Haimeicun (LA) area were all higher than 2, and according to the classification basis that Haimeicun (LA) has moderate enrichment. The EFs values for the fourteen REEs in soil originated mainly from natural sources, including the atmospheric dust from the weathered soils and rocks[39,40].

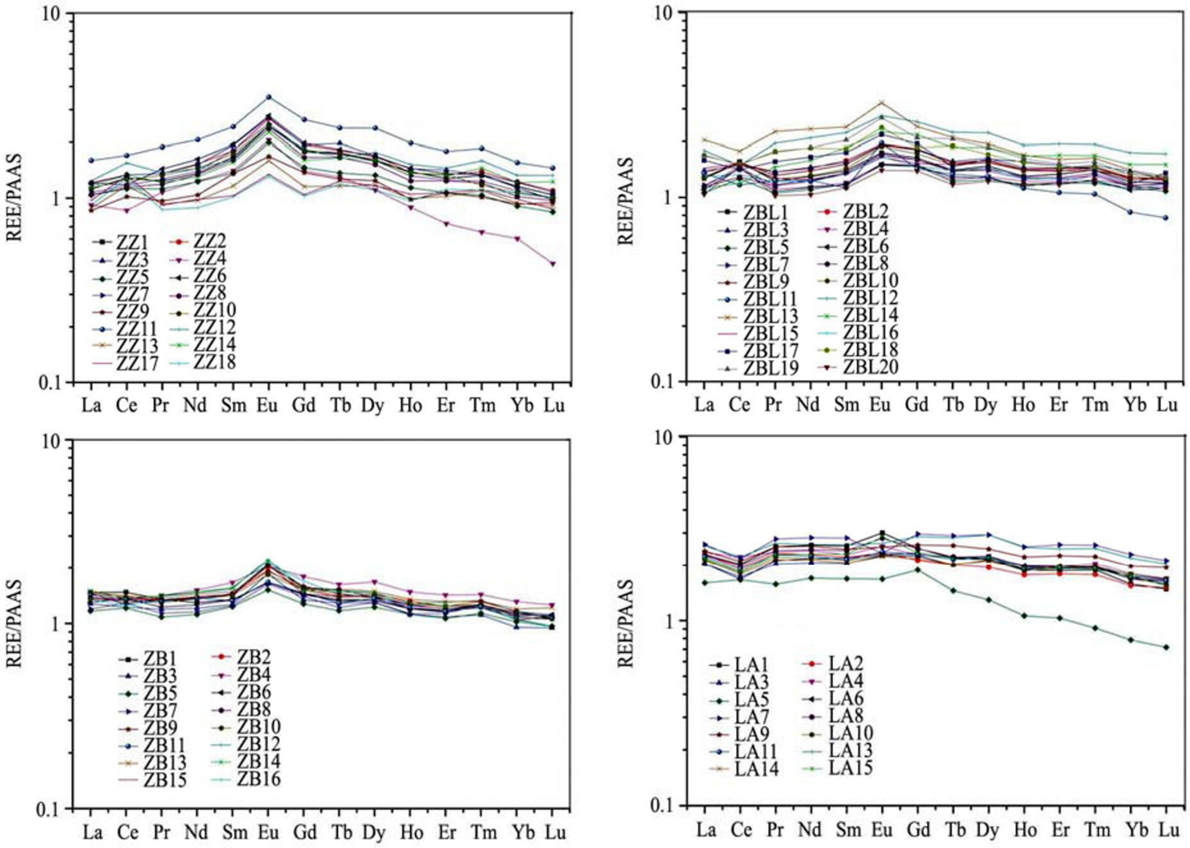

Fig. 3 Soil and PAAS - normalized patterns of average concentrations of REEs in smelting areas (ZZ, ZBL, ZB and LA)

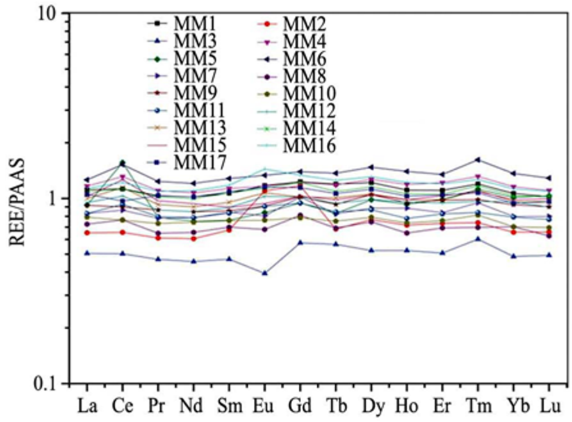

Fig. 4 Soil and PAAS - normalized patterns of average concentrations of REEs in mining area

2.3 Correlation analysis between REE in soil

The main objective of correlation analysis is to define the dependency relation, and the specific dependency relation can help to explore the relevant direction and the degree of correlation. The correlation of rare earth elements analysis results are shown in Table 3. It can be concluded that the correlations of REEs have the following characteristics: (1) a significant positive correlations can be found between REEs; (2) the relationship between Eu and other REEs is relatively poor; (3) in smelting the relationship between Ce and other REEs does not correlate; but in mining area Ce correlates with HREEs. The sources of Cu, Cd, Pb and REEs in mining area (MM) were different. Sources of Cu, Cd and Pb in mining area (MM) were mainly from transportation and mining process[20], and REEs mainly originated from rock and mineral weathering, erosion and soil parent material[41,42].

2.4 Concentrations of REEs in human hair and urine

44 hair samples (21 male, 23 female) were collected from smelting areas, and 24 (7 male, 17 female) from mining area. 42 urine samples (22 male, 20 female) were collected from smelting areas and 24 (7 male, 17 female) from mining area. Concentrations and comparison of individual REEs with others published data in human hair and urine are given in Table 4. The amount of ∑LREEs (including La, Ce, Pr, Nd, Sm and Eu), ∑HREEs (including Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) and ∑REEs are also presented. The mean concentrations of individual REEs of hair were variable, ranging from 0.001 mg/kg (Lu) to 0.74 mg/kg (Ce) in smelting areas (SM) and from 0.0003 mg/kg (Lu) to 0.52 mg/kg (Ce) in mining area (MM) respectively. The LREEs/HREEs ratios were 14.21 and 13.62 in smelting (SM) and mining (MM) areas respectively. LREEs comprised about 94% of total REEs contents in human hair in both smelting and mining areas. According to Bettinelli et al., HREEs are generally less abundant than LREEs in nature. Ce, La and Nd were considerably enriched in hair samples[43]. However, La, Ce and Nd are also enriched in the above cited authors' works[9,10,44]. Previous studies such as Feng et al.

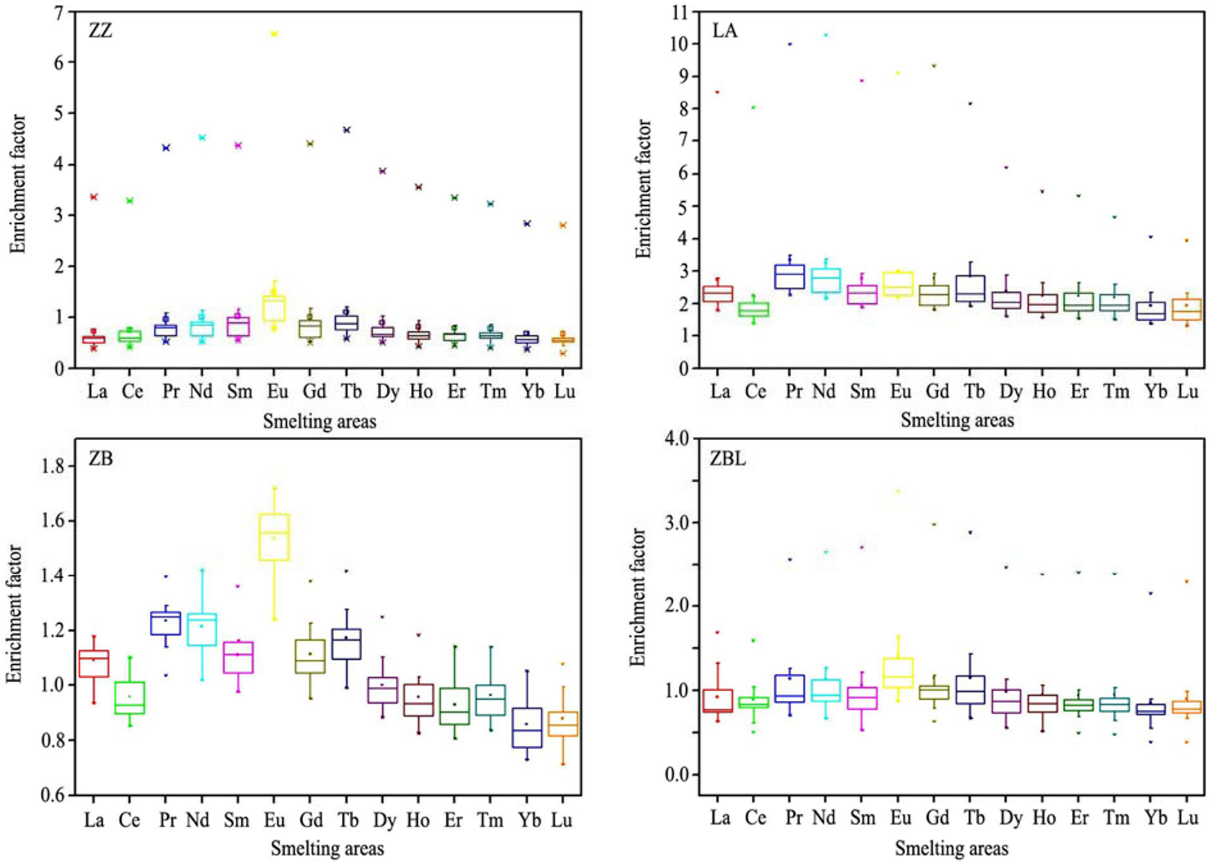

Fig. 5 Enrichment factor for REEs in agricultural soil of smelting areas (ZZ, LA, ZB and ZBL)

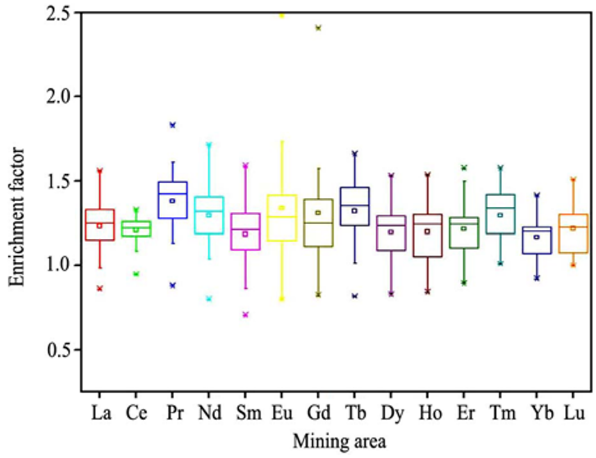

Fig. 6 Enrichment factor for REEs in agricultural soil of mining area

have reported that exposing to La compounds induced neurological damage, affecting mean intelligence quotient of children[45].

The mean concentrations of individual REEs in urine ranged from 0.004 μg/L (Lu) to 0.22 μg/L (Ce) in smelting areas and from 0.003 μg/L (Lu) to 0.22 μg/L (Ce). The LREEs/HREEs ratios were 4.38 and 5.13 for smelting and mining areas respectively. LREEs comprised about 81% and 84% of total REEs contents in human urine in SM and MM respectively. When comparing with HREEs, LREEs were higher. This might indicate that the environment in mining and smelting areas mainly derived from LREEs. Hao et al. found that mining area is polluted by REE[46].

Comparing with others' published data in Table 4, it can be seen that there was a trend that REEs concentrations in smelting areas (SM) and mining area (MM) of Hezhang were much higher than those from other places in China and other countries. For example, the values in hair in smelting and mining areas were higher than those reported in Lu et al.[9] and Li et al.[10]. However, comparing the residents hair of these study areas with those of miners who are still working in the Baiyunebo mine, values were lower in LREEs (La, Ce, Pr and Nd)[44]. However, except Lu, almost all HREEs elements were higher than other studied areas in this study, and Lu had the highest concentration in Fujian mining. In addition, concentrations of Er and Tm were similar to the level in Fujian mining area.

Moreover, urine concentrations in smelting areas and mining area were obviously different from normal values of unexposed population according to Bettinelli et al.[43]. Comparing to the population in mining area of Baiyun Obo, concentrations of Nb, Sm, Eu, Gd, Tb and Ho were higher in the population in Baiyun Obo. However, La, Ce and Er were higher in this study[46]. Besides, concentrations of Dy and Lu were higher in smelting areas (SM), and Tm and Yb were higher in mining area (MM) in this study. According to results of hair and urine, this might indicate that the studied areas were more seriously

Table 3 Correlations between LREE and HREE in soil of smelting (SM) and mining (MM) areas

Elements	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
La	1	0.828**	**0.991****	**0.985****	**0.966****	0.832**	0.828**	**0.972****	**0.980****	**0.971****	**0.981****	**0.951****	**0.968****	**0.965****
Ce	**0.910****	1	0.774**	0.747**	0.705**	0.601*	0.616**	0.746**	0.808**	0.818**	0.854**	0.879**	**0.902****	**0.919****
Pr	**0.975****	0.889**	1	**0.997****	**0.983****	0.849**	0.845**	**0.983****	**0.980****	**0.971****	**0.974****	**0.943****	**0.948****	**0.946****
Nd	**0.949****	0.862**	**0.994****	1	**0.990****	0.858**	0.851**	**0.983****	**0.977****	**0.967****	**0.966****	**0.931****	**0.936****	**0.930****
Sm	0.847**	0.769**	**0.937****	**0.965****	1	0.891**	0.883**	**0.980****	**0.970****	**0.961****	**0.950****	**0.917****	**0.918****	**0.906****
Eu	0.539**	0.443**	0.671**	0.730**	0.839**	1	**0.960****	0.872**	0.880**	0.865**	0.860**	0.792**	0.808**	0.802**
Gd	0.829**	0.785**	**0.915****	**0.941****	**0.969****	0.788**	1	0.867**	0.890**	0.884**	0.870**	0.825**	0.826**	0.820**
Tb	0.827**	0.773**	**0.910****	**0.934****	**0.967****	0.797**	**0.957****	1	**0.985****	**0.977****	**0.967****	**0.945****	**0.945****	**0.931****
Dy	0.858**	0.824**	**0.920****	**0.931****	**0.943****	0.726**	**0.959****	**0.975****	1	**0.992****	**0.993****	**0.968****	**0.976****	**0.968****
Ho	0.879**	0.850**	**0.927****	**0.931****	**0.923****	0.681**	**0.947****	**0.952****	**0.990****	1	**0.990****	**0.981****	**0.977****	**0.973****
Er	0.881**	0.865**	**0.921****	**0.916****	0.895**	0.604**	**0.922****	**0.930****	**0.975****	**0.987****	1	**0.973****	**0.985****	**0.984****
Tm	0.868**	0.874**	0.896**	0.886**	0.857**	0.574**	0.890**	**0.900****	**0.959****	**0.976****	**0.987****	1	**0.980****	**0.981****
Yb	0.857**	0.863**	0.884**	0.872**	0.841**	0.535**	0.875**	0.890**	**0.948****	**0.967****	**0.985****	**0.991****	1	**0.990****
Lu	0.830**	0.849**	0.846**	0.829**	0.790**	0.470**	0.838**	0.836**	**0.910****	**0.941****	**0.967****	**0.977****	**0.980****	1

The left lower part and right upper part represents the correlation coefficient correlation between the REE elements in agricultural soil of smelting area and the REE in agricultural soil of mining areas, respectively. ** Correlation is significant at the 0.01 level (2-tailed); * Correlation is significant at the 0.05 level (2-tailed)

Table 4 Concentrations of REEs of hair and urine and comparison of the elemental concentrations from Hezhang with other published data. Note urine samples are presented in μg/L and hair in mg/kg

Elements	Hair										Urine							
	In our study						Shandong[a]		Fujian[b]	Baiyunebo (Inner Mongolia)[c]	In our study						Baiyuan Obo[d]	Pesaro, Italy[e]
	Smelting area (SM)			Mining area (MM)			Mining	Control	Mining	Mining (miner)	Smelting area (SM)			Mining area (MM)			Mining area	Unexposed population
	Mean	SD	Median	Mean	SD	Median	Mean	Mean	Mean	Mean	Mean	SD	Median	Mean	SD	Median	Median	Mean
La	0.33	0.379	0.184	0.237	0.375	0.099	0.125	0.025	0.108	0.368	0.1	0.069	0.103	0.104	0.069	0.126	0.079	0.016
Ce	0.739	0.867	0.429	0.521	0.878	0.249	0.269	0.066	0.215	0.803	0.216	0.143	0.23	0.215	0.149	0.234	0.089	0.016
Pr	0.066	0.073	0.041	0.051	0.077	0.027	0.021	0.005	0.024	0.078	0.024	0.018	0.027	0.024	0.018	0.028	0.03	0.008
Nd	0.255	0.296	0.153	0.205	0.316	0.093	0.077	0.021	0.079	0.306	0.103	0.07	0.104	0.105	0.07	0.121	0.153	0.02
Sm	0.045	0.056	0.028	0.032	0.06	0.012	0.009	0.004	0.017	0.036	0.03	0.023	0.028	0.031	0.022	0.033	0.04	0.018
Eu	0.013	0.012	0.008	0.011	0.014	0.007	0.003	0.001	0.007	0.007	0.009	0.008	0.009	0.008	0.006	0.008	0.019	0.004
Gd	0.036	0.041	0.02	0.028	0.047	0.007	0.008	0.005	0.017	0.022	0.025	0.021	0.023	0.023	0.022	0.026	0.024	0.015
Tb	0.007	0.005	0.005	0.005	0.006	0.003	0.001	0.001	0.004	0.002	0.006	0.004	0.006	0.006	0.004	0.007	0.015	0.005
Dy	0.027	0.024	0.02	0.022	0.034	0.013	0.004	0.003	0.015	0.008	0.026	0.018	0.028	0.021	0.015	0.023	0.02	0.01
Ho	0.005	0.005	0.004	0.004	0.006	0.003	0.001	0.001	0.004	0.001	0.006	0.005	0.006	0.005	0.004	0.006	0.171	0.004
Er	0.011	0.011	0.008	0.009	0.016	0.004	0.002	0.001	0.011	0.04	0.019	0.015	0.018	0.016	0.011	0.018	0.011	0.008
Tm	0.002	0.003	0.001	0.001	0.003	0.001	0.0002	0.0001	0.002	0.0004	0.005	0.004	0.004	0.004	0.003	0.005	0.002	0.003
Yb	0.013	0.011	0.01	0.008	0.013	0.005	0.001	0.001	0.006	0.003	0.019	0.015	0.017	0.017	0.012	0.019	0.007	0.007
Lu	0.001	0.002	0.0003	0.0003	0.002	0.0003	0.0002	0.0001	0.002	0.0004	0.004	0.005	0.004	0.003	0.003	0.003	0.002	0.003
LREEs	1.45			1.06					0.45		0.48			0.49				
HREEs	0.1			0.08					0.06		0.11			0.1				
LREEs/HREEs	14.21			13.62					7.24		4.38			5.13				
ΣREE	1.55			1.13					0.51		0.59			0.58				

[a] Lu et al.[9]; [b] Li et al.[10]; [c] Wei et al.[44]; [d] Hao et al.[46]; [e] Bettinelli et al.[43]

influenced by REEs. These results might show that smelting (SM) and mining (MM) areas are influenced by REEs emission from smelting and mining process at earlier stages[47]. And these differences might be caused by prolonged intake of REEs through food chains[48]. Some authors have concluded that REEs have multiple pathways to affect human such as long-term ingestion via food chain, air inhalation, medicine treatment and/or water[48]. According to Zhu et al.[7], the toxicity through long time should not be negligible. According to Koeberl and Bayer[49] and Hobarth et al.[19], results revealed that ingestion of food and inhalation of dust particles were the major way of incorporation of REE in human body. However, our study showed that difference existed between the LREEs/HREEs ratio in urine and hair with higher LREEs/HREEs ratios in smelting areas than those of mining areas. However, urine in mining area showed a slightly higher value comparing to smelting areas for 5.13 and 4.38, respectively. This may be due to the time of exposure. Hirano and Suzuki[1] revealed that firmly attached REEs were excreted rapidly in urine. Hence, REEs toxicity of people living around mining should not be negligible, because the intake of small dose over time can affect human beings[8]. The total concentration values of REEs for male and female in smelting and mining areas are presented in Fig. 7. It can be seen that the highest total concentration was found in female for both urine and hair. In hair, concentrations for female and male in smelting areas were higher than female and male in mining area especially for Ce, La and Nd. In urine, especially for Ce, La and Nd, concentrations for female were higher than male in smelting and mining areas respectively. According to Zhang et al.[13], female are more likely exposed to fatty liver than male.

However, results in this study were different from those of many other works[13,44,46]. Others' research showed that males were more exposed to REEs than females, and the male tended to increase and female samples tended to decrease with prolonged REEs intake. This gender difference might be related to food intake, iron status, and hormonal's influences on absorption and bioavailability of metals[50]. And according to Gil et al., hair grew approximately 10 mm per month, so it can give information past and recent exposure, and female's hair was longer than males hair[51]. Higher REEs found in female hair might attribute to external contamination such as artificial hair treatment. And according to some authors such as Barbosa et al.[52] and Esteban et al.[53], the contents of metals in hair vary significantly according to hair color, hair care.

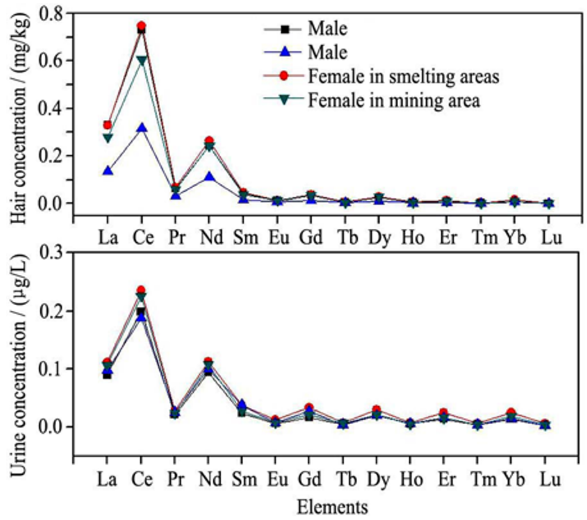

Fig. 7 Total REEs patterns for the urine and hair of male and female from mining and smelting areas

2.5 Age-related variation difference in hair and urine in REEs

The relationships between age and total LREE concentrations in hair and urine for males and females are presented Figs. 8 and 9, respectively. Fig. 8(a) and (a′) show the total REEs concentrations in males' hair for different age group. It can be seen that although concentrations in age of 18–40 varied widely among these areas, the total LREEs and total HREEs concentrations in hair from 6 to ≥66 years were higher in smelting than in mining. This might indicate that residents in age group of 18–40 years in SM were exposed and accumulated to higher amounts LREEs and HREEs. However, LREEs and HREEs in mining area were higher in the age group of 41–65. It is interesting to note that the concentration of total REEs in MM increases with age, but decreases in age group of ≥66 years. This may suggest that young people of this generation are more affected and sensitive to REEs than older generation. Fig. 8(b) and (b′) shows the total LREEs and HREEs concentration in females' hair vary among age groups in smelting and mining areas. The variation tendency of the value of total REEs concentrations in hair of females among age groups from both mining and smelting was different from the total REEs concentration of males especially in the age range of 18–40. In mining area, the total REEs (LREEs and HREEs) were higher than smelting areas. Besides, the concentration decreased rapidly with age. This may indicate that LREEs and HREEs affected female more seriously than male. Wei et al. showed that the young female had sensitive response to small quantity of REEs[44].

Fig. 9(a) and (a′) show the total LREEs and HREEs concentrations in urine males vary among age groups. It can be seen that urine's LREEs values were higher for the age of ≥66 years in smelting (SM) and mining (MM) areas. But comparing the concentrations between mining (MM) and smelting (SM) areas, concentration in mining area (MM) was higher. The high HREEs value was different from those of LREEs especially when comparing to ages and areas. It can be seen that the high value in mining area (MM) was in age groups of 6–17, and high value existed in age of 41–65 for smelting areas (SM). While it is remarkably shown by comparing total LREEs and HREEs in smelting (SM) and mining (MM) areas that the value were increasing with the ages. However, the concentration increased from 6–17 in mining area, decreased from 18–65 and finally increased in ≥66 years. In addition, REEs concentration in males' urine in mining area (MM) was higher than the value in smelting areas (SM) in all age groups, except for 41–65 years. Fig. 9(b) and (b′) show that the total LREEs and HREEs in females' urine vary among different age groups. The variation tendency of total REEs concentrations in females' urine among age groups from both mining (MM)

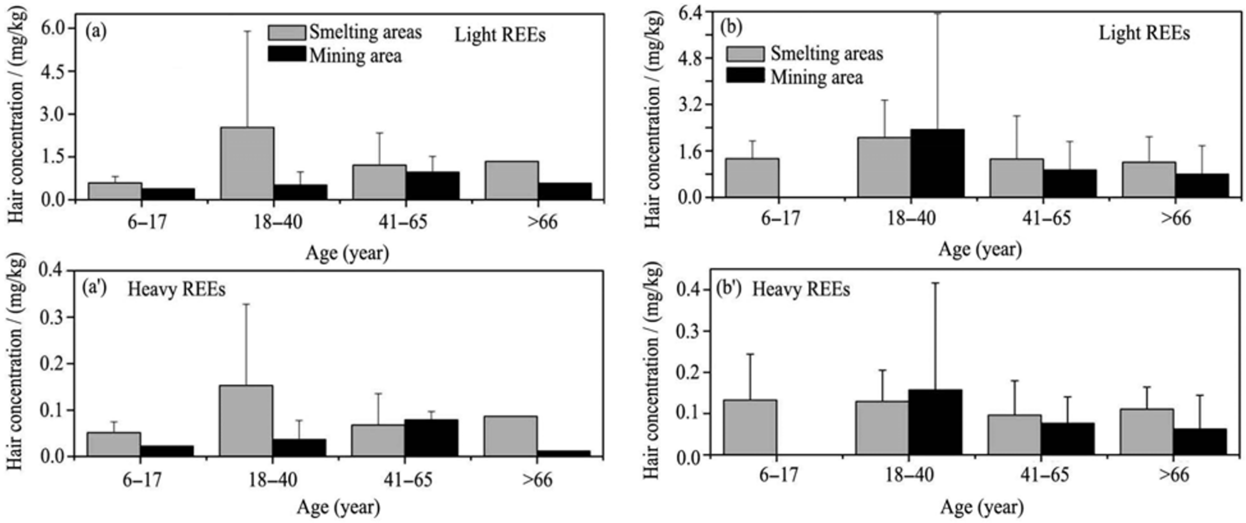

Fig. 8 Total light and heavy REEs in male hair vary among age groups (a, a′) and total light and heavy REEs in female hair vary among age groups (b, b′)

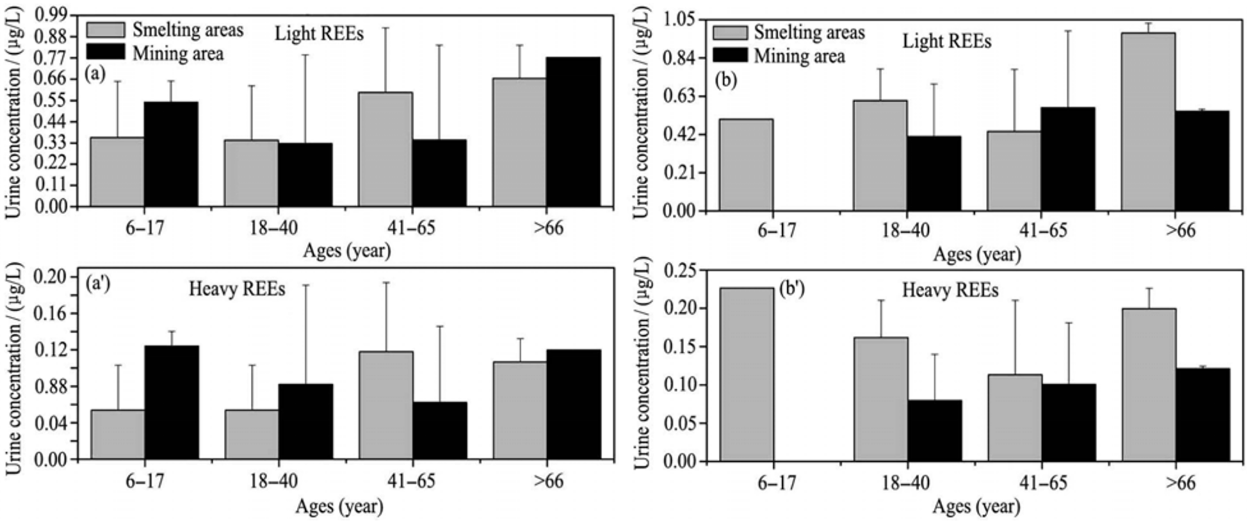

Fig. 9 Total light and heavy REEs in male urine vary among age groups (a, a′) and total light and heavy REEs in female urine vary among age groups (b, b′)

and smelting (SM) areas was different from the males' total REEs concentration of. In mining area, the highest total LREE concentrations were found in the age group of 41–65 years. While the highest total LREEs concentrations were found in ≥66 years in smelting areas. The highest total HREEs concentrations in hair were found in ≥66 years in mining area, while the value increased remarkably with the ages. However, the highest total HREEs concentrations were found in 6–17 years in smelting areas.

Overall the results of HREEs were different from LREEs, but LREEs were the highest. According to Koeberl and Bayer this fractionation performs during metabolism and deposition in the human body[49]. And Hao et al. revealed that smoking can increase the concentration of LREEs[46]. LREEs and HREEs in smelting areas age group of 18–40 years presented the highest value in hair for both male and female. However, concentrations for male and female in mining area (MM) were different with 41–65 and 18–40 for both LREEs and HREEs, respectively. Results of urine were completely different from that of hair. The similitude can be seen just in HREEs for male in smelting (SM) and mining (MM) areas in age group of 41–65. It was observed that hair grouping results were more stable similitude between the area and genders than those of urine. The degree of exposure differed between different areas. Tong et al. showed that human scalp hair can reveal REEs exposure level and distribution characteristics of the principal REEs exposure route[54].

2.6 Relation between soil sample and human (hair and urine)

In order to achieve the relation found between biological samples (hair and urine) and soils in terms of REE concentrations, Eu/Eu^* values vs. Gd_N/Yb_N ratios and Ce/Ce^* values vs. La_N/Yb_N ratios for soil, hair and urine from SM and MM areas are shown in Fig. 10(a) and (b) respectively. From Eu/Eu^* values vs. Gd_N/Yb_N ratios for soil, hair and urine, there is no clear relation between biological samples and soil.

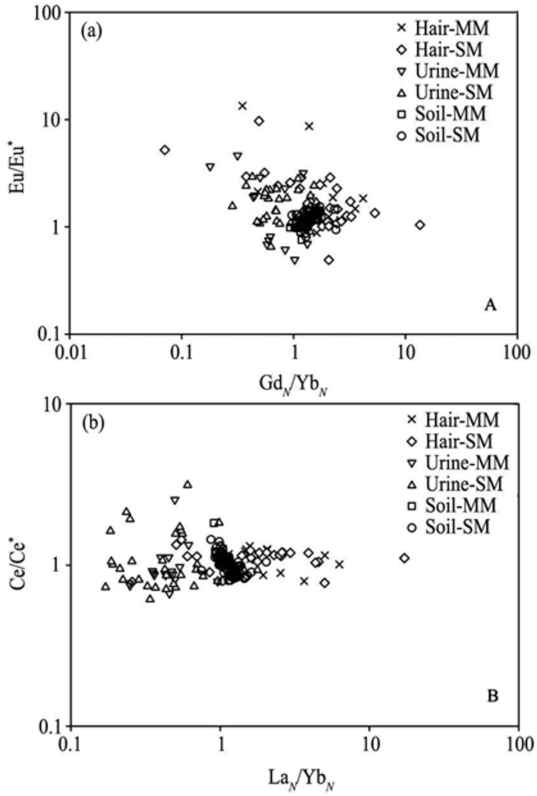

Fig. 10 Eu/Eu* value vs. Gd_N/Yb_N ratio (a) and Ce/Ce* value vs. La_N/Yb_N ratio (b) for soil, hair and urine from smelting (SM) and mining (MM) areas

As presented in Fig. 10(b), Ce/Ce* value vs. La_N/Yb_N ratio for soil, hair and urine from smelting (SM) and mining (MM) areas the ratios of La_N/Yb_N tend to increase, with the stability of Ce/Ce* value especially for hair and soil. The differentiation of soil and hair in smelting (SM) and mining (MM) are increasing with incensement of the ratio of La_N/Yb_N, this may be related to the long time life of metals in hair. According to Foo et al., hair can give information for past and recent exposure[55], and also related to the persistence of REEs in soil. However, the distribution of urine in smelting (SM) and mining (MM) is different from hair and soil with lower ratios of La_N/Yb_N, which can explain that REEs in urine may have other origin such as water and air. According to Zhang et al., REE proportion in soil was much higher than that in PM2.5, thus the contribution of atmospheric particles is not significant to the REEs in soil[57]. REE in urine has short time life and may be related to other constituent such as water (unpublished data showed that REEs concentration in most of samples in drinking water are below detection limit). But Ce/Ce* values of urine in smelting areas (SM) increased compared to urine in mining area (MM). Considering the higher concentration in soil relative to other environmental constituent and some unpublished data of REE in vegetables and drinking water, soil is the essential component affecting human.

3 Conclusions

The concentrations of rare earth elements (LREEs and HREEs) in agricultural soil, and human body (hair and urine) of smelting areas were higher than those from mining area. Furthermore, comparing agricultural soils of studied areas concentrations were higher than background values. When comparing human hair and urine from smelting and mining areas in this study, concentrations were higher than that of other mining area especially for HREEs. This enrichment of REEs was due to the earlier smelting processes and original rocks. Smelting areas showed positive Eu anomaly. EF levels in the studied areas ranged from low to moderate enrichment. Considerable positive correlations were found between most of the REEs in soil, and LREEs showed better correlation comparing to HREEs. And Eu had relatively poor relation with other REEs. The pollution of REEs was mainly caused by LREEs.

The mean concentrations of females' hair and urine were higher than those of males from mining and smelting areas. For most REEs, it was shown that hair's REEs concentrations were the highest in 18–40 years age group, and those of 6–17 were the lowest, but urine had different distribution of age group. Soil and hair showed that the relation increased with the increase of La_N/Yb_N ratios.

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