



Rare earth elements in human hair from a mining area of China

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ABSTRACT

Rare earth minerals have been mined for more than 50 years in Inner Mongolia of China. In the mining area rare earth elements (REE) may be significantly accumulated in humans. Therefore, the aim of this paper is to characterize the REE concentrations in hair of local residents. REE concentrations in hair of 118 subjects were determined. The results showed that the mean concentrations of the determined REE in the hair of both females and males were usually higher from mining area than from control area. The mean concentrations of all the fifteen REE were much higher in hair of males than in hair of females from mining area. This suggested that males might be more sensitive to REE than females. In addition, the mean contents of the REE in hair of miners, particularly light REE (La, Ce, Pr and Nd), were usually much higher than the values in hair of non-miners from both mining area and control area, indicating that the miners were exposed to higher concentrations of REE in occupational environment. Among age groups, the relationships between REE concentrations and age groups showed that more and more concentrations of light REE accumulated in body of both females and males with age until 60 years, while heavy REE concentrations decreased with age in males who were exposed to low concentrations of heavy REE.

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1. Introduction

Rare earth elements (REE) usually refer to the elements spanning atomic numbers 57 (lanthanum) to 71 (lutetium). They have very similar physicochemical properties, and thus they form a chemically coherent group of elements. Sometimes, Yttrium is also included in the group (Ryu et al., 2007). In recent decades, REE were widely applied in agricultural, industrial and medicine field, hightechnology industries and others (Evans, 1990; Hirano and Suzuki, 1996). The increasing applications of REE and mining of rare earth mineral may emit abundant REE into environment. Consequently, enrichment of the REE induced environmental contamination, including soil contamination, hydrosphere contamination and biosphere contamination (Sultan and Shazili, 2009; Perez-Lopez et al., 2010; Tranchida et al., 2011; Delgado et al., 2012). Therefore, significant growths of interest in REE geochemistry have come out (Ryu et al., 2007).

Meanwhile, human health risk caused by environmental exposure to REE has obtained more and more attention in recent years. Low dose of REE have been shown to have the positive effects on the growth performance of animals and vegetables (He et al., 2003). It has been reported that REE exposure can improve the activity of telomerase and increase the percentage of cells in the

S-phase and G2/M-phase, and has no influence on the apoptosis of PBMCs (Yu et al., 2007). However, animal experiments have indicated that in animals fed with REE diet, the REE can be absorbed through the digestive tract and can enter blood circulation. The REE can travel across the membrane into the erythrocytes (Wu et al., 2002). Chen et al. (2001) reported that REE could enter the cell and cell organelles and mainly be bound with biological macromolecules. Some functions of the cell in the human body may be deduced by REE (Chen et al., 2001). REE can induce low total serum protein (TSP), albumin, globulin, glutamic pyruvic transaminase, serum triglycerides, and immunoglobulin, but high cholesterol of blood. In addition, the influence of REE on males is a one-way irreversible process, whereas females show a strong ability of restoration (Zhang et al., 2000). Furthermore, it is reported that toxicity of REE varies from low to moderate levels. REE are non-essential elements for living systems. The long-term consumption of food contaminated with REE may cause chronic poisoning (Seishiro et al., 1996; Jiang et al., 2012). REE may be also accumulated in organs of human by ingestion, inhalation and dermal contact, and may induce some diseases. Long-term intake of low dose REE from environment may induce accumulation of REE in the bone structure. This may change the bone tissue and increase bone marrow micronucleus rate. Moreover, REE accumulated in bone can induce generation of genetic toxicity in bone marrow cell (Chen and Zhu, 2008; Zaichick et al., 2011). Zhuang et al. (1996) showed that the concentrations of Th, La, Ce, Gd, and Lu were significantly higher in tumor tissues

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compared with the normal brain tissues. This indicated that REE might be associated with tumor cells. In addition, REE can be accumulated in human brain through blood circulation, which can induce neurotoxic effects. Long-term ingestion of low dose REE can decrease the intelligence quotient of children and hinder the conduction of adult nervous centralis (Chen, 2005). Samochocka et al. (1984) suggested that REE are able to cross placental barrier and blood brain barrier. The infants can absorb abundant REE through breast milk (Samochocka et al., 1984). Therefore, the biological effects and distribution patterns of REE in the human body should be investigated.

Human biomonitoring does not provide comparative information on health before and after exposure, but it is much more accurate than environmental monitoring in providing data on health effects within the continuum “source emissions–environmental concentrations–exposure–human biomonitoring–health effects” (Reis et al., 2007; Li et al., 2012). Biomonitoring is therefore a useful complement to environmental monitoring for estimating the level of REE exposure. In recent studies, body fluids or tissues (saliva, blood, urine, hair, nails, etc.) have been widely used in the biomonitoring of heavy metals in large cohorts (Li et al., 2012, 2013). Compared with other biological specimen, such as blood and urine, hair is considered less invasive, more convenient for storage and transport to the laboratory for analysis, and less hazardous to handle. Many studies considered that the concentrations measured in hairs are not only the elements absorbed by organisms but also the elements adsorbed on the hair surface (Frisch and Schwartz, 2002; Harkins and Susten, 2003; Noguchi et al., 2012). Although there is a controversy on hair as biological indicators, hairs are an attractive biomonitoring substrate, at least superficially because of less invasive, more convenient. However, up to now, scientific data for REE in hairs is rather limited.

Within the context of the perspectives mentioned above, human health risk assessment of REE should be based on toxicology assessment and REE exposure of population assessment. Several studies have reported the concentrations of REE in human body (Chen et al., 2001; Yu et al., 2007). However, the reports about exposure of population assessment are rare (Arvela, 1979). Several investigations have shown that REE concentration in human hair can be defined as the index of REE exposure, which reflects the absorbed dose and load capacity of human body (Zhou et al., 1994). The investigations about REE in the human body and environment caused by a mining area from Inner Mongolia of China were hardly found at present. The rare earth mineral is mined through strip mining. Thus, the mining process can emit abundant REE into the environment. These REE can enter human body through environmental exposure to REE. The health of local residents may be influenced by these elements. Therefore, in order to characterize the REE concentrations in hair of residents and assess human health risk of REE from the mining area in Inner Mongolia, compared investigation of REE contents in human hair from the mining area and control area is conducted in this paper.

2. Materials and methods

2.1. Study area

The REE mining area, namely Baiyunebo iron-rare earth mineral deposit, was located in the central of the Inner Mongolia Autonomous Region of China and located in the northern of Baotou city (Fig. 1). The minerals exploited iron, REE, niobium and many other valuable mineral (Li, 2003). Approximately 54% of rare earth mineral over the world originate from Baiyunebo iron-rare earth mineral deposit (Li, 2008). The rare earth mineral mainly included monazite and bastnaesite, particularly enriched in light La, Ce, Pr and Nd (Gao, 2009). The area of the mining area was about 328 km². The mine has been operated since 1957. At present, mineral annual output is as high as 11 million tons.

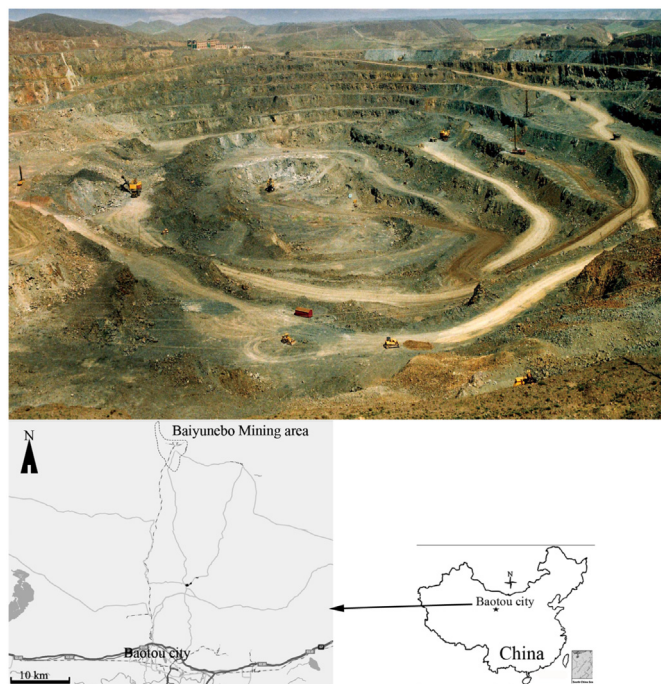


Fig. 1. The map of the study area.

2.2. Sampling

60 residents (33 females and 27 males) living in the vicinity of Baiyunebo mining area in Inner Mongolia of China were selected for hair sampling. The area was defined as mining area. The control area is located in the western part of Baotou city, which is about 200 km away from the Baiyunebo mining area (Fig. 1). The residents in the control area were hardly influenced by REE derived from the rare earth mine. 41 subjects (20 females and 21 males) living in the control area were selected for hair sampling. Moreover, another 17 subjects (13 males and 4 females), who are working in Baiyunebo mining area, were also selected for hair sampling. They are also living in the mining area. The ages of the individual are in the range of 11–77 years old. All of the subjects were living in the local area.

All of the subjects agreed to participate in this study. Additionally all recipients were informed that their hair will be used for REE determination. Therefore, hair sample was cut and collected from the nape of the head (close to the scalp) with scissors for each subject. Each collected hair sample was put into a paper envelope and labeled for the test.

2.3. Analysis methods

All the reagents were of analytical reagent grade or chromatographic grade. For dilution and wash, high-purity deionized water provided by a Milli-Q Plus filter apparatus (Millipore, MA, USA) was used throughout. All implements that came into contact with the samples had been prewashed using 5% nitric acid solution.

The individual hair samples were washed with detergent solution (2% non-ionic liquid detergent) and flushed with sufficient deionized water to remove exogenous matter. Then, the clean hair samples were dried in an oven for 10 h at 65 °C. The dried hair sample was cut into small pieces of 0.5–1 cm length. Approximately 0.2 g of each hair sample was weighed for digestion.

The weighed hair samples were digested with 3 ml concentrated nitric acid in cleaned glass tube at room temperature overnight. Then, the sample was further digested and heated at 100 ± 5 °C until no residue remained in the solution. The digested samples were cooled to room temperature and diluted to 25 ml with deionized water for further analysis. The blank was prepared in the same way but without the hair sample. All the reagents used were of ultrahigh purity. All the processes were conducted in clean laboratory.

The concentrations of the 15 REE, including lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), lutetium (Lu) and yttrium (Y), were determined by inductively coupled plasma mass spectrometry (ICP-MS). Considering the importance of quality assurance, a parallel routine check of the accuracy of quantified results was ensured through the use of Certified Reference Material (CRM, human hair powder GBW 09101 received from the National standard Sample Study Center, China). The contents of elements estimated in the CRM were found to be consistent with the values of elements reported in the CRM. The details of the method were

shown by Wang et al. (2000). The recoveries of standard samples for the elements are listed in Table 1.

3. Results and discussion

3.1. REE concentrations in hair of resident

The REE concentrations in hair of females from Baiyunebo rare earth mining area and control area are represented in Table 2. It can be seen in the table that the mean concentrations of the determined REE in the hair of females from mining area were usually higher than from control area except for Pr, Nd and Er. Similarly, the highest contents of REE in the hair of females from mining area were also much higher. The Student's *t*-test showed that the mean concentrations of Eu and Tm were significantly different between the two areas (Table 2).

Table 3 showed the statistical data of REE concentrations in hair of males from Baiyunebo rare earth mining area and control area. The results of Student's *t*-test are also listed in the table. The results indicated that the mean concentrations of all the determined REE in hair of males were much higher in the mining area than in the control area. The highest mean values of the REE were mainly found in the hair of males from the mining area.

The results in both Tables 2 and 3 showed that the mean concentrations of the determined REE in human hair were mainly

higher in the mining area than in the control area. This may indicate that the environment (water, air and soil) in mining area has been significantly influenced by REE emitted from rare earth mining process. Residents in the mining area might be exposed to higher concentrations of REE in the environment. Consequently, higher amounts of REE were accumulated in humans in the mining area. The main pathways of REE entering human body may be ingestion, inhalation, and dermal contact. Moreover, REE may also be transmitted from the environment into the food chain. Thus, REE may also be accumulated in humans through food chain.

Comparing the results in Table 2 with Table 3, it can be seen that the mean concentrations of all the 15 REE were usually higher in hair of males than in hair of females from the mining area. However, the mean concentrations of the determined REE varied slightly among hair of males and hair of females from control area. The features suggested that males might be more sensitive to REE than females. Males absorbed higher dose of REE through environmental exposure to REE. Moreover, males might be more exposed than females to REE through their life habits. Zhang et al. (2000) also has reported that the effect of REE intake was a one-way irreversible process for males, while the females are capable of self-restoring after a sensitive response to REE.

3.2. REE concentrations in hair of miners

The statistical data of REE concentrations in hair of miners who are still working in the Baiyunebo mine at present is listed in Table 4. The results of *t*-test, the concentrations of REE between miners and non-miners were also listed in the table. The *t*-values indicated that the mean concentrations of REE were significantly higher in hair of miner than in hair of non-miners from both mining area and control area. In addition, the mean contents of the REE in hair of miners, particularly La, Ce, Pr and Nd, were usually much higher than the values in hair of males and females from both mining area and control area, except for Tm, Yb and Lu. The rare earth mineral in Baiyunebo mainly contained La, Ce, Pr and Nd (Gao, 2009). This may induce extreme higher concentrations of the elements in hair of miners. The results reflected that humans absorb much higher amounts of REE through occupational exposure to REE than environmental exposure to REE. Therefore, higher contents of REE were accumulated in humans through occupational exposure to REE.

Table 1

The recovery of standard samples for the elements (*N*=10).

Element	Recovery of standard samples (%)	Standard value (ng/g)	Determination value (ng/g)	Standard deviation
La	102.60	13.6	13.95	1.51
Y	98.58	8.04	7.93	0.91
Ce	103.27	19.5	20.137	2.62
Pr	99.59	2.2	2.19	0.22
Nd	99.10	8.31	8.24	0.87
Sm	106.14	1.45	1.54	0.34
Eu	102.05	0.78	0.80	0.07
Gd	103.88	1.7	1.77	0.24
Tb	105.00	0.18	0.19	0.04
Dy	95.21	1.19	1.13	0.19
Ho	101.82	0.22	0.22	0.05
Er	102.63	0.76	0.78	0.09
Tm	96.92	0.13	0.13	0.02
Yb	97.64	0.89	0.87	0.15
Lu	102.00	0.2	0.20	0.03

Table 2

Statistical data of REE concentrations in hair of female (ng/g).

Element	Mining area (<i>N</i> =33)				Control area (<i>N</i> =20)				<i>T</i> -value
	Range	Mean	Median	SE	Range	Mean	Median	SE	
La	35.47–732.45	161.00	143.04	22.08	59.32–295.92	146.45	127.56	15.98	−0.534
Y	7.72–85.74	25.40	19.11	2.93	9.99–47.88	19.88	17.85	2.19	−1.513
Ce	112.32–1396.98	402.28	312.06	55.39	140.52–653.18	312.05	296.24	28.43	−1.449
Pr	7.07–150.84	32.76	27.64	4.66	10.10–125.53	33.55	27.33	5.62	0.108
Nd	28.99–575.94	131.45	110.63	18.10	40.89–788.65	153.62	129.06	35.52	0.556
Sm	6.26–70.16	19.37	16.26	2.33	5.53–29.77	15.57	12.58	1.53	−1.365
Eu	1.47–14.66	4.80	3.96	0.53	1.20–6.63	3.49	3.27	0.31	−2.164*
Gd	3.98–50.56	12.92	9.51	1.76	4.45–35.16	11.86	10.52	1.62	−0.445
Tb	0.39–4.13	1.22	1.02	0.12	0.43–2.81	1.02	0.81	0.14	−1.006
Dy	1.37–20.84	5.57	4.67	0.68	1.76–9.28	4.05	3.49	0.45	−1.874
Ho	0.30–3.29	0.96	0.67	0.12	0.24–1.59	0.72	0.63	0.08	−1.754
Er	4.30–63.16	17.14	16.52	1.72	4.90–63.78	20.83	18.37	2.76	1.064
Tm	0.10–0.98	0.34	0.29	0.04	0.09–0.47	0.24	0.21	0.03	−2.169*
Yb	0.59–7.66	2.05	1.62	0.24	0.61–2.97	1.53	1.50	0.15	−1.850
Lu	0.06–1.44	0.30	0.22	0.04	0.10–0.80	0.26	0.27	0.03	−0.765

* *P* < 0.05.

Table 3
Statistical data of REE concentrations in hair of male (ng/g).

Element	Mining area (N=27)				Control area (N=21)				T-value
	Range	Mean	Median	SE	Range	Mean	Median	SE	
La	38.26–830.42	194.68	176.61	28.61	54.16–505.19	148.28	102.87	25.40	-1.213
Y	7.40–90.13	30.33	23.82	4.06	9.60–66.57	21.75	17.90	3.17	-1.667
Ce	134.88–1460.24	483.50	420.86	59.91	138.94–1053.65	351.14	247.70	47.69	-1.729
Pr	8.40–158.75	39.66	32.36	6.13	11.00–105.66	29.73	19.23	5.20	-1.235
Nd	32.57–603.72	158.84	121.86	23.52	45.19–436.89	121.19	70.61	22.74	-1.151
Sm	4.19–99.89	24.92	20.81	3.87	5.53–56.25	17.93	13.56	2.91	-1.443
Eu	0.95–12.60	4.29	3.65	0.58	1.20–9.72	3.62	2.37	0.52	-0.849
Gd	3.37–45.67	14.88	12.14	1.89	5.18–46.64	13.65	7.92	2.62	-0.382
Tb	0.37–6.38	1.56	1.04	0.26	0.44–4.25	1.28	0.82	0.22	-0.828
Dy	0.98–19.17	6.54	5.32	0.89	1.89–27.31	5.84	3.37	1.34	-0.431
Ho	0.26–5.36	1.22	0.96	0.19	0.31–3.24	0.88	0.57	0.16	-1.383
Er	5.77–109.08	37.21	23.02	6.17	7.90–88.40	29.49	21.65	4.92	0.978
Tm	0.10–4.08	0.54	0.33	0.15	0.09–1.39	0.37	0.22	0.07	-1.069
Yb	0.80–11.48	2.60	1.77	0.49	0.28–9.03	2.04	1.42	0.43	-0.872
Lu	0.10–3.06	0.50	0.29	0.11	0.07–2.31	0.35	0.21	0.10	-0.961

Table 4
Statistical data of REE concentrations in hair of miner (ng/g).

Element	Range	Mean	Median	SE	T1	T2
La	38.26–1554.73	367.60	222.34	111.69	2.946**	2.845**
Y	7.40–84.89	34.15	25.36	5.32	1.234	1.117
Ce	172.69–2857.86	802.78	529.84	201.69	3.561**	2.789**
Pr	8.40–317.39	78.43	42.81	21.98	3.087**	3.151**
Nd	32.57–1229.96	306.11	183.18	84.38	2.698*	3.124**
Sm	4.19–129.68	36.03	26.11	8.40	3.243**	2.356*
Eu	1.04–26.69	6.94	4.58	1.68	2.906**	2.074**
Gd	3.37–81.17	22.48	15.84	5.44	2.302**	2.321**
Tb	0.37–6.47	2.00	1.58	0.42	2.512*	1.796
Dy	0.98–22.26	8.38	6.79	1.58	2.251	1.796
Ho	0.26–2.97	1.29	1.10	0.19	2.668	0.912
Er	5.77–168.19	40.35	22.16	10.61	1.856**	1.721**
Tm	0.10–1.17	0.42	0.33	0.06	1.518	-0.156
Yb	0.47–6.81	2.56	2.20	0.39	1.713	0.562
Lu	0.10–1.17	0.38	0.35	0.07	0.877	-0.083

T1=The value of *t*-test between mean concentrations of REE in hair of miner and residents from control area; and T2=The value of *t*-test between mean concentrations of REE in hair of miner and residents from mining area.

* $P < 0.05$.

** $P < 0.01$.

3.3. Comparing REE concentrations in this paper with that in previous one

Table 5 represents some values of REE in human hair from different areas. The mean contents of REE in hair of infants (0–3 years old), children (11–15 years old) and adults from Shandong and Jiangxi were usually higher in the mining area than in the control area. The results of the present study also showed the same trend.

Comparing the table with Tables 2–4, it can be seen that the mean concentration of each REE from rare earth mining area was extremely higher in hair of infants than in hair of adults in this study and Shandong. The values were also much higher than that in youth. However, the REE concentrations in hair of infants were usually lower than that in hair of children and adults of this paper. The REE concentrations in control area were much lower for infants and children than for adults. These data indicated that higher amounts of REE might be absorbed by infants and children who were exposed to high concentrations of REE in environment in the mining area. The accumulation capacity of adults might be lower than that of infant and children. Moreover, the varied REE concentrations in hair might be attributed to the different

bioavailability of REE between the different regions. The data may also suggest that REE can be accumulated in human body.

In addition, the concentrations of La, Y and Ce in human hair from a city of Sweden have been determined. The results showed that the mean contents of La, Y and Ce in hair of urban resident were 35, 23, 39 ng/g (Rodushkin and Axelsson, 2000). The values were similar with mean concentrations in human hair from Shandong, while they were usually lower than the values in human hair from both mining area and control area of this paper. This indicated that urban residents were exposed to very low concentrations of REE in the environment.

3.4. Variation of REE concentrations among age groups

If the REE concentrations in hair of local residents from the mining area and the control area vary with age, the resident population was divided into three age groups, including < 40 (control area: 6 females, 5 males; mining area: 9 females, 9 males), 41–60 (control area: 7 females, 7 males; mining area: 17 females, 9 males), and > 60 years (control area: 7 females, 9 males; mining area: 7 females, 9 males). The relationships between age and total light REE and heavy REE concentrations for males and females are represented in Figs. 2 and 3, respectively.

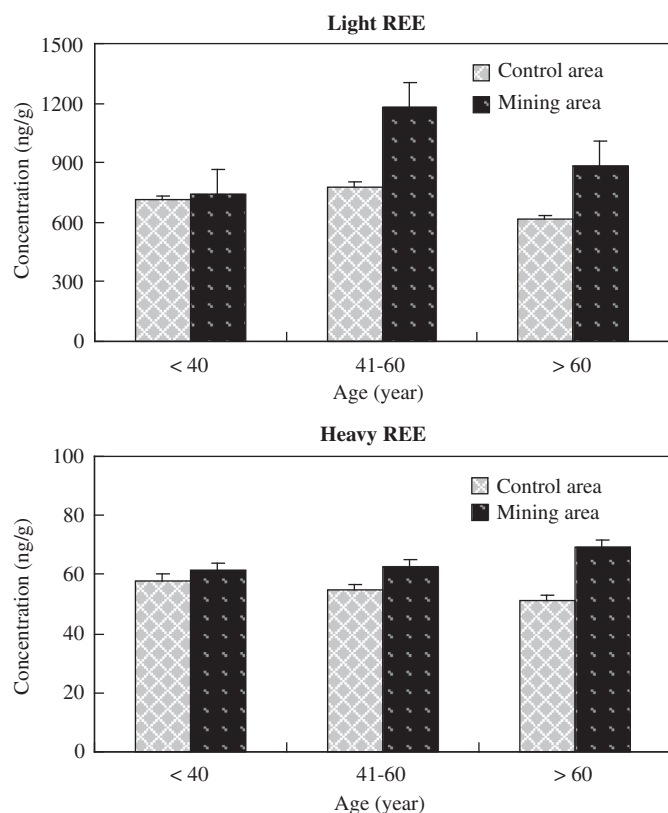
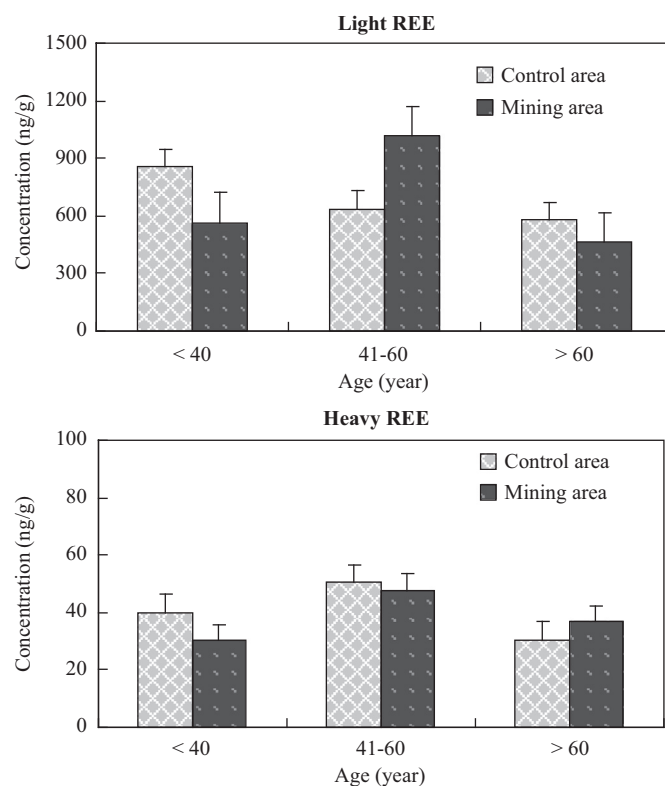
Fig. 2 shows the total light REE and heavy REE concentrations in hair of males vary among age groups in both mining area and control area. It can be seen that the total light REE and heavy REE concentrations in hair of the age groups of 41–60 and > 60 years were higher from mining area than from control area, while the values in the age groups of < 40 varied slightly among the two areas. This might indicate that the residents were exposed to higher concentrations of light and heavy REE in environment from mining area than that from control area. In mining area, the total light REE concentrations in males were highest in the age group of 41–60 years, indicating higher amounts of light REE were accumulated in body of the age group. In addition, the total heavy REE concentrations increased with the age groups, indicating higher amounts of heavy REE were accumulated in body of males with age. However, the total light REE concentrations in hair of males from control area varied slightly among the age groups. Interestingly, the total heavy REE concentrations in males from control area decreased gradually with age. This may suggest that heavy REE accumulated in males who were exposed to lower concentrations of heavy REE may be not associated with age.

The total light and heavy REE concentrations in hair of females vary among age groups in both mining area and control area are shown in Fig. 3. The variation tendency of total REE

Table 5

REE concentrations in human hair in previous paper (ng/g).

Element	Jiangxi (0–3 years)		11–15 years		Sweden	Shandong	
	Mining	Control	Mining	Control	Urban	Mining	Control
La	1370.59	78.11	450.0	120.0	35	124.9	25.1
Y	201.55	38.72	71.2	82.3	23	19.6	16.0
Ce	581.24	113.06	340.0	220.0	39	269.2	65.6
Pr	302.34	18.74	80.0	30.0		21.4	5.2
Nd	1111.44	70.92	280.0	120.0		77.2	21.2
Sm	196.71	15.23	40.0	30.0		9.3	3.9
Eu	20.04	0.97	6.0	3.7		2.5	1.1
Gd	151.97	14.79	30.6	23.7		8.4	4.6
Tb	18.09	1.98	3.3	3.4		0.8	0.5
Dy	71.59	10.44	15.1	18.2		4.2	3.1
Ho	11.22	1.90	2.3	3.1		0.7	0.5
Er	28.13	4.95	15.9	8.5		2.3	1.4
Tm	2.87	0.64	0.6	1.1		0.2	0.1
Yb	17.31	3.35	3.6	6.6		1.4	1.3
Lu	2.31	0.33	0.5	0.8		0.2	0.1
Reference	Peng et al. (2002)		Tong et al. (2004)		Rodushkin and Axelsson (2000)	Lu et al. (2007)	

**Fig. 2.** Total light and heavy REE concentrations in hair of males vary among age groups.**Fig. 3.** Total light and heavy REE concentrations in hair of females vary among age groups.

concentrations in hair of females among age groups from both mining area and control area was different from that of males. In mining area, the total highest light REE concentrations were found in the age group of 41–60 years, while the value decreased rapidly in control area. This may indicate that light REE were rapidly accumulated in females who were exposed to high concentration of light REE in environment until 60 years old. For heavy REE, the highest concentrations were found in the age group of 41–60 years in both mining area and control area. The features may indicate that heavy REE were rapidly accumulated in females who were exposed to high and low concentration of heavy REE in environment until 60 years old.

4. Conclusions

According to the REE concentrations in hair of males and females from mining area and control area, it can be concluded that the environment in mining area has been usually influenced by REE emitted from rare earth mining process. Residents in the mining area might be exposed to higher concentrations of REE in the environment. The mean concentrations of all the 15 REE were usually higher in hair of males than in hair of females from the mining area, indicating that males may be more sensitive to REE than females. The REE concentrations in hair of miners reflected that much higher amounts of REE was absorbed by humans

through occupational exposure to REE than through environmental exposure to REE. The relationships between REE concentrations and age groups showed that more and more concentrations of light REE accumulated in body of both females and males with age until 60 years, while heavy REE concentrations decreased with age in males who were exposed to low concentrations of heavy REE.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.ecoenv.2013.05.031>.

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