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ICP-MS measurement of uranium and thorium contents in minerals in China

Liang-Liang Yin[1] · Qing Tian[1] · Xian-Zhang Shao[1] · Bao-Ming Shen[1] · Xu Su[1] · Yan-Qin Ji[1]

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Abstract The activity levels of long-lived radionuclides in minerals have received more and more concern for the public health. The inductively coupled plasma mass spectrometry was used to measure the content of uranium and thorium in 60 mineral samples collected from 16 mines of seven provinces in China. The contents of uranium and thorium ranged 0.17 ± 0.04 μg g^{-1} to 15.3 ± 2.39 μg g^{-1}, and 0.19 ± 0.04 μg g^{-1} to 19.6 ± 7.56 μg g^{-1}, respectively. The highest levels of U and Th contents were found in aluminum ore, whereas the lowest was found in antimony and copper ores.

Keywords Uranium · Thorium · Raw minerals · Specific radioactivity

1 Introduction

Naturally occurring radioactive materials (NORM) are ubiquitous in the environment. The NORM contents in most natural substances are low [1], but higher contents may arise as the result of human activities, such as mineral extraction and processing, phosphate fertilizer application, forest products and thermal electric production [2–4]. High activity levels of NORM may increase risks to human health and the environment, causing high exposure level to workers or the public, for example, typical occupational exposure is 16 mSv a^{-1} in part of non-ferrous metal underground mines, but it exceeds the occupational dose limit of 20 mSv a^{-1} in a large percentage of the mines. As the result of human activities, rising level of public exposure to NORM radiation is 0.07 mSv a^{-1} per person, and collective dose is 7.98×10^4 Sv a^{-1} per person, which is 2.82 % of the total radiation dose [5].

The long-lived radioactive elements, e.g., uranium, thorium and their radioactive decay products, such as radium and radon in minerals, receive more concern for the human health [6–9], particularly in some regions of China [10, 11]. A common terrestrial radiation source is radon gas, which comes from uranium in the soil and accumulates in buildings. Radon inhaled into the pulmonary system may cause cancer. The α-ray it emits is a particle specie of big linear energy transfer, generating high concentration of biologically harmful OH radicals, which damage cell membranes by oxidation and any other cell constituents that are vital for complex and correct cell functions.

However, there are limited data which can be used to evaluate the U and Th contents in minerals and to establish a regulatory framework to reduce potential dangerous exposure to workers. In this paper, inductively coupled plasma mass spectrometry (HR-ICP-MS), with its advantages of multielement characteristics, speed of analysis and low detection limits [12], is used to measure U and Th contents in 60 material samples from 16 mines in China.

2 Materials and methods

2.1 Sample collection and preparation

A total of 60 mineral samples were collected from 16 active mines according to the requests of GB/T 1868-1995

Liang-Liang Yin, Qing Tian, Xian-Zhang Shao, Bao-Ming Shen, Xu Su and Yan-Qin Ji have contributed equally to this study.

✉ Yan-Qin Ji
jiyanqin@nirp.cn

[1] National Institute for Radiological Protection, Chinese Center for Disease Control and Prevention, Beijing 100088, China

and GB 14263-1993. The raw materials of different minerals were directly sampled in the mine area. The collected samples were packed in polyethylene bags and stored hermetically until analysis. Finally, the samples were air-dried for several days and sieved to 2 mm.

2.2 Apparatus and reagents

The ICP-MS is Element II (Thermo Finnigan, Bremen, Germany) of sector field and high resolution. Ultrapure water (18.2 MΩ cm) from a Milli-Q system (Millipore, MA, USA) was used. Multistandards solution of Th and U was obtained from Spex Industries. Before measurement, ^{209}Bi (Spex, USA; 10 μg mL^{-1}) was added to all solutions as internal standard. All acids used for the chemical analysis were of ultrapure grade (Merck, HNO_3 65 % v/v, HF 40 % v/v and HCl 37 % v/v) and checked for possible trace metal contamination.

Extreme care was taken to avoid contamination in preparing and analyzing the samples. All the materials were soaked overnight in HNO_3 20 % (v/v). They were rinsed with ultrapure water and air-dried with special care before use. A reagent blank was prepared for each digestion to assess possible contamination from the sample preparation.

2.3 Microwave digestion

The microwave vessels were acid-washed in nitric acid/water before use. Two replicate samples each weighing ~0.1000 g (±0.0004 g) were added in two microwave vessels with 4 mL HNO_3, 2 mL HCl and 2 mL HF and were subjected to a 15-min ramp to 205 °C, kept for 15 min and a 30 min cooling down. The resulting digestion was allowed to cool to room temperature. The clear colorless solution was brought to PFA cup, heated at 150 °C to almost dryness, for dispose of HF. Then the solution was brought to volume in a 100-mL volumetric flask with ultrapure water. A blank digestion was carried out in the same way.

2.4 Analysis

The HR-ICP-MS was performed under the following conditions: carrier gas flow rate, 0.98 mL min^{-1}; auxiliary gas flow rate, 0.8 mL min^{-1}; cooling gas flow rate, 16.0 mL min^{-1}; and RF power, 1200 W. Sensitivity and resolution of the apparatus were checked in advance with standards offered by Thermo Company. A six-point calibration curve from 10 to 10,000 ng L^{-1} was created for each analysis.

In order to validate the accuracy, reliability and sensitivity of the methods to determine the U and Th contents, certified reference materials (CRMs) GBW 07430 (soil) and GBW 07114 (dolomite) were used to check the experimental procedures. The soil CRM was provided by Institute of Geophysical and Geochemical Exploration, China, and the dolomite CRM by National Research Center for Geoanalysis, China. The CRMs were stored under specified controlled conditions to ensure its stability. As shown in Table 1, the results are in good agreement with the certified values of the CRMs.

3 Results and discussion

The 60 samples collected from 16 active mines include coal and mineral ores of iron, copper, tin, zinc, manganese, nickel, gold, mercury, antimony and aluminum. The analytical results are given in Table 2. The content ranges are as follows: U, 0.17 ± 0.04–15.3 ± 2.39 μg g^{-1}, averaged at 3.17 ± 3.95 μg g^{-1}; and Th, 0.19 ± 0.04–19.6 ± 7.56 μg g^{-1}, averaged at 4.03 ± 4.67 μg g^{-1}. The radioactivity of U and Th was calculated by their natural abundance (U^{238}, 99.2745 %; U^{235}, 0.7200 %; U^{234}, 0.0055 %; and Th^{232}, 100 %): U, 0.43 ± 0.01–38.8 ± 6.08 Bq g^{-1}, averaged at 8.03 ± 10.05 Bq g^{-1}; and Th^{232}, 0.0007 ± 0.0001–0.0790 ± 0.0306 Bq g^{-1}, averaged at 0.0163 ± 0.0189 Bq g^{-1}.

The results showed that the U content was low in nickel and antimony ores, but it was high in aluminum and tin ores. The Th content was low in copper ores and high in aluminum ores. The results are in agreement with reported data in the literature. For example, high radioactivities of U and Th were observed in tin mine area, ranging from 8.7 to 51 Bq g^{-1} for ^{238}U and from 16.8 to 98 Bq g^{-1} for ^{232}Th [13]. Chang et al. reported the natural radioactivity in industrial raw mineral commodities (domestic, 17 kinds; and imported, 18 kinds), and radioactivity for ^{232}Th (0.357 ± 0.059 Bq g^{-1}) in Bauxite was higher than other minerals [14].

Specific activity is calculated as follows:

$$N = N_0 e^{-\lambda . t}$$
$$-dN/dt = N_0 \lambda t = N_0 (\ln 2/t_{1/2}) t$$
$$= N_A/m (\ln 2/t_{1/2}) t = At.$$

So, specific activity $A = N_A/m$ (ln $2/t_{1/2}$), where m is the content of the isotope in question in this application.

A weak correlation was observed between Th and U in all samples ($R^2 = 0.6006$), indicating that U activities may be related to the presence of Th. other authors found similar weak correlations [15]. The specific activities of Th and U in raw minerals mainly depend on their geological sites of origin and their geochemical properties [16].

The guidelines related to the NORM have been introduced in many countries. Th activities in the 60 samples were much lower than the limits of EU and Canada (Table 3), while the U activities exceeded 10 Bq g^{-1} in four minerals and 5 Bq g^{-1} in eight samples. The 12 samples include three samples each of the tin and aluminum ores and

Table 1 Comparison of the analytical results of CRMs with the certified values (in μg g^{-1})

CRMs	U		Th	
	Standard values	Our results	Standard values	Our results
GBW 07430 (soil)	5.9 ± 0.3	6.1 ± 0.5	28 ± 2	27.6 ± 0.3
GBW 07114 (dolomite)	0.16 ± 0.06	0.15 ± 0.01	16.6 ± 0.8	16.7 ± 0.4

Table 2 Average contents (mean ± SD) of uranium and thorium in mine ores (dry)

Samples	*n*	Provinces	U		Th	
			μg g^{-1}	Bq g^{-1}[a]	μg g^{-1}	Bq g^{-1}[a]
Tin ore	8	Yunnan	9.36 ± 7.76	23.8 ± 19.74	2.94 ± 3.35	0.0119 ± 0.0136
Zinc ore	4	Yunnan	2.46 ± 0.98	6.25 ± 2.49	2.62 ± 3.46	0.0106 ± 0.0140
Coal	2	Ningxia	1.25 ± 0.03	3.17 ± 0.08	2.92 ± 0.12	0.0118 ± 0.0005
Iron ore	2	Shandong	2.68 ± 0.07	6.81 ± 0.18	7.19 ± 0.52	0.0290 ± 0.0021
Tungsten ore	4	Hunan	3.12 ± 0.25	7.91 ± 0.63	4.47 ± 3.92	0.0181 ± 0.0159
Copper ore	4	Xinjiang	2.04 ± 0.04	5.18 ± 0.10	0.19 ± 0.04	0.0007 ± 0.0001
Coal	6	Ningxia	1.68 ± 1.97	4.28 ± 5.01	1.71 ± 0.53	0.0100 ± 0.0021
Gold ore	2	Shandong	0.84 ± 0.02	2.12 ± 0.05	1.11 ± 0.01	0.0045 ± 0.0001
Coal	2	Heilongjiang	3.94 ± 0.36	10.0 ± 0.91	5.23 ± 0.15	0.0211 ± 0.0006
Aluminum ore	6	Guizhou	15.3 ± 2.39	38.8 ± 6.08	19.60 ± 7.56	0.0790 ± 0.0306
Manganese ore	2	Guizhou	0.80 ± 0.36	2.03 ± 0.91	4.64 ± 0.04	0.0187 ± 0.0002
Antimony ore	2	Guizhou	0.17 ± 0.04	0.43 ± 0.10	0.71 ± 0.14	0.0029 ± 0.0006
Clay	2	Shandong	1.27 ± 0.38	3.23 ± 0.97	6.86 ± 10.77	0.0277 ± 0.0436
Nickel ore	8	Xinjiang	0.28 ± 0.48	0.710 ± 1.22	0.74 ± 0.11	0.0030 ± 0.0004
Coal	4	Xinjiang	0.82 ± 0.20	2.08 ± 0.51	1.63 ± 0.12	0.0066 ± 0.0005
Mercury ore	2	Hunan	4.66 ± 0.08	11.8 ± 0.20	1.95 ± 1.31	0.0079 ± 0.0053

[a] Calculated by natural abundance

Table 3 Unconditional derived release limits (DRL, in Bq g^{-1})—diffuse NORM sources

Nuclides	DRL	Organizations
^{238}U (^{238}U, ^{234}Th, ^{234m}Pa, ^{234}U)	10	Health Canada
^{232}Th	10	Health Canada
U nat[a]	5	European Commission
^{232}Th	5	European Commission

[a] ^{238}U and ^{235}U are in their fixed natural ratio (99.275 and 0.72 % atomic fraction)

one sample each of the zinc, iron, tungsten, copper, coal and mercury ores.

^{232}Th is an alpha-ray emitter with a long half-life and therefore low specific activity. Because of its radiation properties and the biokinetics of ^{232}Th following incorporation, it is one of the radioisotopes with the highest radiotoxicity. The previous studies have shown that the activity of ^{232}Th in monazite and zircon is 182.425 ± 9.870 and 1.195 ± 0.048 Bq g^{-1}, respectively (Table 4), whereas the other raw minerals show the low activities of Th with the similar ranges of determined activities in our minerals samples.

Table 4 Literature data for ^{232}Th (in Bq g^{-1})

Samples	Range	Mean ± SD	Refs.
Monazite	165.45–195.10	182.425 ± 9.870	[14]
Zircon	1.12–1.25	1.195 ± 0.048	
Clay	0.0609–0.118	0.0777 ± 0.0272	[13]
Anthracite coal	0.0274–0.0712	0.0486 ± 0.0180	
Iron ore	0.0034–0.0058	0.0046 ± 0.0017	
Ilmenite	0.0215–0.474	0.202 ± 0.221	
Bauxite	0.246–0.408	0.357 ± 0.059	
Magnesite	<0.0016–0.0017	0.0016 ± 0.0001	
Coal	0.013–0.215		[5]
Pumice samples	0.0123–0.2379	0.0874 ± 0.0614	[16]

Since the half-life of uranium is shorter than thorium, the natural radioactivity of uranium is much larger than the contribution of thorium if their contents were little different. It is difficult to analyze the radioactivity of ^{238}U by direct γ-ray measurements; instead, radioactivity of Ra is used [16]. The ^{238}U radioactivities in different mineral ores reported in the literature are given in Table 5. The high radioactivity for ^{238}U was observed in monazite. In other minerals, the

Table 5 Literature data for ^{238}U (in Bq g^{-1})

Samples	Range	Mean ± SD	Refs.
Calcite	0.026 ± 0.008–0.049 ± 0.009		[16]
Basalt	0.0074–0.0111		[5]
Mafic	0.0074–0.0111		
Salic	0.0481–0.0592		
Granite	0.0370		
Shale	0.0370		
Sandstone	0.0370		
Clean quartz	0.0074–0.0111		
Dirty quartz	0.0370		
Arkose	0.0111–0.0259		
Carbonate	0.0259		
Monazite		40.58 ± 1.37	[14]

radioactivity for ^{238}U was lower than 0.05 Bq g^{-1}. With the exception of monazite, our results indicate that the radioactivity content of ^{238}U is higher than the reported values.

4 Conclusions

Since the high activity levels of NORM increase risks to human health, particularly the long-lived radioactive elements, such as uranium, thorium and the radioactive decay products in minerals, receive more concern for the potential dangerous exposure to employees overall the country [17, 18]. The radioactivity content of U and Th in a total of 60 mineral samples collected from seven provinces was analyzed. The results demonstrate that the radioactivity content of U in at least 12 minerals samples is beyond the limited values of European commission and suggest that further evaluation of dangerous exposure of U to employee should be taken into account.

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