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A cut-off grade for gold and gallium in coal

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HIGHLIGHTS

- We studied the Au and Ga contents in coal and ash by INAA.
- The average contents of Au and Ga in Guizhou coal are 6.92 ng/g and10.65 μg/g.
- Gallium is enriched in the residues more easily than Au during the coal ashing process.
- The cut-off grades of Au and Ga in coal are considered to be 200 ng/g and 60 μg/g.

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ABSTRACT

The contents of Au, Ga, As, Sb and other elements in two hundred and thirty-four samples of coal, partings, roof and floor collected from Guizhou Province, China were analyzed by Instrumental Neutron-Activation Analysis (INAA). In order to discuss the relationship between Au, Ga in coal and in coal ash, the contents of Au and Ga in 815 °C coal ash were also determined by INAA and partial Ga by Inductively Coupled Plasma Mass Spectrometry (ICP-MS). The analysis results showed that: (1) the average contents of Au and Ga in upper Permian coal from Guizhou are 6.92 ng/g and 10.65 μg/g, respectively, far higher than that in Chinese coal and world coal; the average contents of Au (59.73 ng/g) and Ga (19.16 μg/g) in partings, roof and floor are higher than that in the coal and the Clarke value of sedimentary rock (especially for Au); (2) during the coal ashing process, Ga is enriched in the residues more easily than Au, which is mainly because of the difference in the mode of occurrence of the two elements. Gallium mainly occurs as the substitute of Al in the form of isomorph, which makes it hard to volatize; while Au shows a high association with organic matter, sulfide, and carbonates, and some may be nano-gold, which is easily volatile during coal combustion. Only Au occurred in the aluminosilicate is easily left in the residues; (3) we collected data on the Au and Ga contents in coal and coal ash from China and then conducted correlation analysis by combining data from coals and coal ashes worldwide; the cut-off grades of Au and Ga in coal are considered to be 200 ng/g and 60 μg/g, respectively. This method could also be used to determine the cut-off grade of other valuable elements in coal.

1. Introduction

China is the largest coal production and consumption country in the world. By 2013, coal production in China has exceeded 3.6 billion tons per year. Generally, every 4 tons of coal combustion will produce 1 ton of coal ash [1], but the low rate of comprehensive utilization of coal ash in China not only leads to great environmental problems but also wastes a large amount of mineral resources and industrial valuable elements in the ash. In the 1990s, joint efforts were taken by USA and Canada to study Ga in coal ash, and Ga was successfully extracted from coal ash [2]. In Ordos, China, a pilot plant with an annual processing capacity of approximately 150 t Ga was built at the beginning of 2011 [3]. Gold was also extracted from wastes of the Reftinsk power station, Russian [4]. Although there has been a lot of research work done on extraction of trace elements from coal ash [5], the industrial cut-off grade of metals in coal has rarely been reported.

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The precious metal minerals in coal basins can be extracted as by-products during secondary treatment of the coal or as the products of coal combustion [6]. Recently, more and more researchers have found valuable trace elements enriched in coal [5,7–10]. Thus, the minimum mining grade of trace elements is of vital importance to the combined exploration of trace elements and coal, which could reduce the exploration budget and promote the exploitation of metals in coal ash. Unfortunately, there are only a few related researches. Sun et al. [11] suggested that the minimum mining grades of Li, U, Th and REE should be 120, 40, 150 and 300 μg/g, respectively. Their work is foresighted to some extent, however, the conclusion was drawn based on the 17% average ash yield in Chinese coal. Moreover, they might not have considered the occurrence mode of trace elements in coal and the combustion mode, therefore, their conclusion may not be applied to other elements in coal.

In order to explore the relationship between the Au and Ga contents in coal and in coal ash, and further determine their cut-off grade in coal, we conduct an analysis of the Au and Ga contents in 234 coal and 75 coal ash samples.

2. Sampling and analytical method

Samples were collected from working coal mines in Guizhou Province, China, 234 pieces in total, including 44 partings, roof and floor samples, and 190 coal samples. All of the coal samples are mixed and ply samples of upper Permian coal seam and feed of 4 power plants.

Proximate analysis (total moisture, volatile matter, and ash yield) was conducted using ISO recommendations (ISO-11722 [12], ISO-562 [13], and ISO-1171 [14]). The total sulfur and forms of sulfur were determined following ISO-351 [15] and ISO-157 [16], respectively. All samples were ashed in a muffle oven at 815 °C to constant value of weight (ISO-1171). X-ray fluorescence spectrometry was used to determine the oxides of major elements for these ash samples. Some trace elements such as As, Au, Ga and Sb in solid samples, and Au in 34 ash samples and Ga in 25 ash samples were determined using Instrumental Neutron Activation Analysis (INAA). Inductively Coupled Plasma Mass Spectrometry (ICP-MS), in a pulse counting mode (three points per peak), was used to determine Ga in the other 50 ash samples.

3. Results and analysis

3.1. The Au and Ga contents in Guizhou coal and coal ash

The contents of Au and Ga in Guizhou coal range from 1.16 to 313 ng/g and from 2.54 to 30.7 μg/g, averaged at 9.53 ng/g and 11.25 μg/g, respectively, which are far higher than the average contents in Chinese coal and world coal (Table 1), implicating their significant enrichment in Guizhou coal. However, the average contents of Au (especially Au, 59.73 ng/g) and Ga (19.16 μg/g) in partings, roof and floor are significantly higher than that in coal and the Clarke value of sedimentary rock, respectively. Moreover, the average Au content in coal is even higher than the Clarke value of sedimentary rock (6 ng/g), but the Au content in ash (15.52 ng/g) is lower than that in world coal ash (22 ng/g). On the contrary, the average Ga content in Guizhou coal (11.25 μg/g) is lower than the Clarke value in sedimentary rock (12 μg/g), but in Guizhou coal ash, the Ga content (35.31 μg/g) is higher than the average content in world coal ash (33 μg/g). The results showed that compared with world coal, Au in Guizhou coal is easily volatile during coal combustion and only partial Au is left in the residue while Ga shows opposite behavior.

Table 2 shows the contents of Au and Ga in some coal and coal ash samples. As Table 2 shows, the Au content in 7 out of 34 samples is significantly lower than that in raw coal samples, and the content in some coal and ash is approximately the same. By contrast, Ga in ash samples is higher than that in raw coal sample, which could indicate that Ga is enriched in the residues more easily during coal combustion. The different behavior of the two elements reflects their different modes of occurrence in coal.

3.2. The occurrence mode of Au and Ga in Guizhou coal

Generally, it is believed that Ga in coal mainly occurs as inorganic phase and replaces Al in aluminiferous minerals (mainly boehmite) in the form of isomorph [7]. Thus, Ga usually shows a positive correlation with ash yield, and this is also shown in Guizhou coal but with a weak relationship (Fig. 1a). Moreover, Ga in coal also shows a weak correlation with Al_2O_3 (Fig. 1b), while in coal ash, an obviously positive correlation is shown between Ga and Al_2O_3 (Fig. 1c). This phenomenon shows that although Ga mainly occurs in the inorganic matter of coal, not all Ga replace Al in aluminiferous minerals in the form of isomorph. According to the above correlation analysis, it seems that Ga in coal in the form of isomorph remains more in ash during coal combustion, while the other occurrences of Ga (organic phase) are easily volatile.

The occurrence mode of Au in coal is considerably complex. Seredin et al. [19] thought that there are four kinds of occurrences for Au in coal: dispersed native gold, associated with sulfide, absorbed by clay minerals, and organically bonded. Our previous research on the sequential chemical extraction of four pieces coal samples from Guizhou demonstrated that the occurrence mode of Au in the studied coal samples is complex [20]: Au occurs in coal bound to organic matter, as a sulfide, within clay minerals and as a carbonate (Table 3). Yang [21] conducted research on Puan coal samples from Guizhou with sequential chemical extraction method and the result also showed that the Au occurs mainly as a sulfide affinity while also associating with organic matter, silicate and carbonate. Our correlation analysis demonstrates that Au in coal has a weakly positive correlation with ash yield (Fig. 2a) but it is in association with a more positive correlation with pyrite, Sb and As (Fig. 2b–d), which might indicate that Au in coal mainly exists in pyrite, especially Sb/As-bearing pyrite. Iron in coal mainly exists in pyrite, and could also occur in aluminosilicate. During the coal ashing process, some Fe maybe escape with the decomposition of pyrite. As shown in Fig. 2e, Au in coal has a certainly positive correlation with Fe_2O_3, but less than the relationship between Au in

Table 1
The Au and Ga contents in upper Permian coal from Guizhou Province.

Elements	Coals			Coals ashes			Partings, roof and floor			Chinese coals	World		Clarke value of sedimentary rock
	Range	Total number of samples	Average	Range	Total number of samples	Average	Range	Total number of samples	Average		Coals	Coal ashes	
Au (ng/g)	1.16–313	190	6.92	2.4–190	34	15.74	1.41–1261	44	59.73	3	3.7	22	6
Ga (μg/g)	2.54–30.7	106	10.65	12.2–71.45	75	35.88	2.72–47.6	28	19.16	6.55	5.8	33	12

Chinese coals from Tang and Huang [17] and Dai et al. [9], world coal and Clarke value in sedimentary rock from Ketris and Yudovich [18].