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Distribution, occurrence, and enrichment of gallium in the Middle Jurassic coals of the Muli Coalfield, Qinghai, China

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A R T I C L E I N F O

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A B S T R A C T

Gallium (Ga) is known as the backbone of the electronics industry, but its independent mineralization is rarely found in nature. The discovery of large Ga-bearing coal deposits suggests that the coal-bearing series can be used as the main source for the future development and utilization of Ga, and the organic matter of coal may play an important role in the aggregation of Ga. Based on the analysis of geological prospecting and study of coal samples, this paper discussed the distribution, occurrence, and enrichment of Ga in the Middle Jurassic coals of the Muli coalfield. The results demonstrate that coals from eastern mines are enriched in Ga, where the Ga concentration reaches the propositional cut-off grade (30 μg/g). The Ga concentration increases along with an increasing distance from the sediment source; the areas with the highest Ga concentration are the deposit-center and the location with the highest content of mudstone. Sediments were derived from the acid and intermediate magmatic rocks of the Tuolai Mountain in the northeastern Muli coalfield, partly from the crust weathering of the Upper Triassic formation. Ga was first transported in the form of colloids or solutions and finally deposited in authigenic kaolinite. In addition, the positive correlation between the Ga concentration and the inertinite constituents of coal indicates that fibrous tissue might be the dominant component absorbing Ga and that organic matter had a positive impact on the migration of Ga to peat swamps. Ga is prone to deposition in partially oxidized, acidic coal-forming environments with strong hydrodynamic forces. Hydrothermal activity might also stimulate the enrichment of Ga in coal.

1. Introduction

Gallium (Ga), as the backbone of the worldwide electronics sector, has widely been used in optoelectronics, telecommunication, aerospace, and many commercial and household items such as alloys, computers and DVD's (Moskalyk, 2003). However, Ga is a scare resource because it is a kind of dispersed elements and difficult to form ore deposits (Tu et al., 2004). In recent years, gallium as the coal-associated deposit has been found in several Chinese Permo-Carboniferous coalfields, where gallium distributes widely enough to reach the ore-forming scale with commercial value (Dai et al., 2006, 2006; Zhao et al., 2009; Sun et al., 2013). A super-large gallium ore deposit in Jungar, Inner Mongolia has been reported (Dai et al., 2006, 2006). Moreover, Ga has a high enrichment factor in coal ash (Conzemius et al., 1984), especially in fly ash (Fang and Gesser, 1996; Dai et al., 2006) and a few methods have been successfully designed to recover Ga from the coal fly ash (Tsuboi et al., 1991; Fang and Gesser, 1996; Gutierrez et al., 1997; Font et al., 2007; Arroyo et al., 2014).The first pilot plant to produce Ga and Al_2O_3 from fly ash, with an annual capacity of approximately 150 t Ga and 800,000 t Al_2O_3, was built by Shenhua Group Zhungeer Energy Corporation Limited (SHZECL) at the beginning of 2011 (Seredin et al., 2013). These indicated that coal deposits could act as a promising alternative source for Ga.

The crustal abundance of Ga is approximately 15 μg/g (Liu, 1984) and its average contents in coal in China and around the world are 6.6 and 5.8 μg/g, respectively (Dai et al., 2012; Ketris and Yudovich, 2009). Previous studies showed the Permo-Carboniferous coals are rich in Ga in some coalfields in China (Table 1). Besides the Permo-Carboniferous coals, Qin et al. (2015) also found that the Ga concentrations range from 12 to 249 μg/g, with an average of 71 μg/g, in Jurassic coals in

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Table 1
Distribution of Ga of Permo-Carboniferous coals in the in main coalfields in China.

Coalfields	Mines	Location	Sample number	Ga (μg/g)		References
				Range	Mean	
Jiyu	Dagaozhuang	N39°46′,E117°35′	200	8–24	20.1	Zhang (2001)
Tengxian	Jiangzhuang	N34°59′,E117°02′	633	6.6–171	15.33	Huang and Zhao (2012)
Dengfeng	Haiyan	N34°22′,E112°58′	314	3–37	17	Yang and Zhu (1993)
Heshan	Suhe	N23°49′,E108°52′	12	7.2–23.1	11.07	Shao et al. (2006)
Kaili	Yudong	N26°41′,E107°53′	9	19–44	31.74	Yi et al. (2007)
Gujiao	Xingjiashe	N37°47′,E112°10′	80	0.8–40.8	15.87	Liu et al. (2009)
Datong	Sitaigou	N40°0′,E113°08′	56	6.0–57	18.3	Wang et al. (2010)
Hedong	Guanjiaya	N38°30′,E111°10′	270	0.88–36	14.52	Gao and Guo (2012)
Xingtai	Gequan	N36°56′,E114°20′	20	3.81–46.43	21.18	Zhao et al. (2009)
Ningwu	Pingshuo	N39°26′,E112°21′	840	8.27–68.22	35.91	Sun et al. (2013)
Daqingshan	Adaohai	N40°36′,E110°27′	48	5.7–38	16.3	Dai et al. (2012)
Jungar	Guanbanwusu	N39°52′,E111°14′	50	3.4–59	18	Dai et al. (2012)
	Haerwusu	N39°51′,E111°13′	39	7.4–54	18	Dai et al. (2008)
	Heidaigou	N39°43′,E111°16′	7	62.2–178	89.2	Dai et al. (2006)

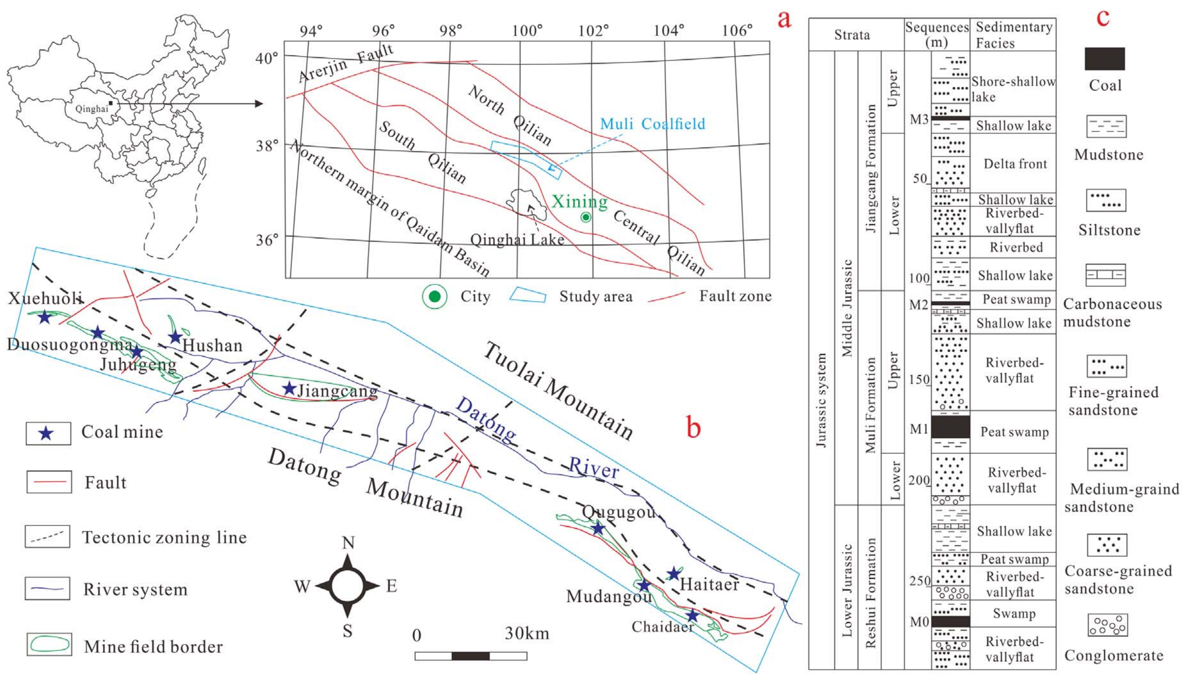

Fig. 1. (a) Location and regional structure of the Muli coalfield, (b) distribution of coal mines (Sun et al., 2009a) and (c) comprehensive stratigraphic column of the Muli coalfield (Chen et al., 2010).

Huanglong coalfield in Shanxi province, China. Moreover, in the Lower-Middle Jurassic coals in the Kunlun coal-bearing zone, the Ga concentration varied from 24.5 to 32.3 μg/g (Qiao et al., 2016), which indicates that Jurassic coals could also concentrate Ga under certain conditions. However, a further study might be needed to confirm this indication.

A few studies have demonstrated that Ga mainly exists in inorganic components in coal, such as, boehmite (Dai et al., 2006, 2006, 2012; Sun et al., 2013; Wang et al., 2011), diaspore (Dai et al., 2012) and kaolinite (Dai et al., 2012; Sun et al., 2013; Yi et al., 2007; Liu et al., 2014; Wang et al., 2011). Therefore, Ga enrichment may be affected by the sediment source. Dai et al. (2006) discovered a super-large Ga deposit in the Jungar coalfield, where sediment source is the bauxite of the Benxi Formation and the K-feldspar granite of the Yinshan Oldland. Sun et al. (2013) also reported that Ningwu coals were rich in Li, Ga, and Al, which were derived from the Yinshan Oldland or the bauxite of the Benxi Formation. On the other hand, some researchers thought that Ga has a close affinity to the organic fraction in coal. Bonnett and Czechowski (1980) first reported Ga porphyrins in bituminous coal, which is indicative of a possibly active role for organic matter during the accumulation of Ga in coal. In their later studies, it was proposed that Ga ions could be adsorbed and enriched effectively by humic acids and peats, and Ga was found to mainly exist in the gelatinous components in coal (Bonnett and Cousins, 1987; Bonnett, 1996). Lyons et al. (1990) found that the concentration of Ga exceeded those of Al, Ti, Fe, and V in the vitrinite after conducting a laser microprobe mass analysis on a bituminous coal. Mastalerz and Drobniak (2012) even suggested that the Ga in Indiana coal comes from organisms. The experiments were performed by a few researchers and demonstrated that plants contain small amounts of Ga, which could be resulted from absorption of organism (Zhang et al., 1993; Miao et al., 2008). Here, we found that Ga has a close affinity with both inorganic and organic components in the Muli coals. Based on the above discussion, it seems that the knowledge of Ga accumulation mechanisms in coal is still deficient.

In this paper, we analyze the distribution characteristics and modes of occurrence of Ga in the Middle Jurassic coals from the Muli coalfield, Qinghai, China, with an aim to study its enrichment mechanism. This study should be helpful in providing new evidence and ideas in order to