



## Review

## Coal deposits as promising sources of rare metals for alternative power and energy-efficient technologies

Vladimir V. Seredin<sup>a,\*</sup>, Shifeng Dai<sup>b</sup>, Yuzhuang Sun<sup>c</sup>, Igor Yu. Chekryzhov<sup>d</sup><sup>a</sup> Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry, Russian Academy of Sciences, Moscow 119017, Russia<sup>b</sup> State Key Laboratory of Coal Resources and Safe Mining, China University of Mining and Technology, Beijing 100083, China<sup>c</sup> Key Laboratory of Resource Exploration Research of Hebei Province, Hebei University of Engineering, Handan 056038, China<sup>d</sup> Far East Geological Institute, Far East Branch, Russian Academy of Sciences, Vladivostok 690022, Russia

## ARTICLE INFO

## Article history:

Received 4 August 2012

Accepted 5 January 2013

Available online 23 January 2013

Editorial handling by A. Kolker

## ABSTRACT

This paper presents data on widespread abnormal accumulations in coal deposits of some rare metal(loid)s (Ge, Ga, Se, Li and REE + Y), which play a key role in energy-efficient technologies and alternative power development. It is shown that enrichment of these metal(loid)s may occur in coal seams in host- and basement-rocks of coal basins at comparable concentrations to those in conventional ores. Genesis of high concentrations of the rare metal(loid)s and their modes of occurrence in coal basins are reviewed. Moreover, utilization prospects of these metal(loid)s as byproduct coal deposits are evaluated. The extraction of these metal(loid) resources during coal exploitation and utilization would not only increase beneficial use of coal deposits themselves but also promote humanity's further movement on the "green road".

© 2013 Elsevier Ltd. All rights reserved.

## Contents

|                                                                           |   |
|---------------------------------------------------------------------------|---|
| 1. Introduction .....                                                     | 2 |
| 2. Genetic types of rare metal(loid) accumulations in coal deposits. .... | 2 |
| 3. Rare elements for clean energy in coal basins .....                    | 2 |
| 3.1. Germanium .....                                                      | 2 |
| 3.1.1. Role in clean energy .....                                         | 2 |
| 3.1.2. Raw material sources .....                                         | 2 |
| 3.1.3. High-Ge coal deposits. ....                                        | 3 |
| 3.1.4. Mode of Ge occurrence .....                                        | 3 |
| 3.1.5. Origin of high-Ge accumulations .....                              | 4 |
| 3.1.6. Utilization prospects .....                                        | 4 |
| 3.2. Gallium .....                                                        | 4 |
| 3.2.1. Role in clean energy .....                                         | 4 |
| 3.2.2. Raw material sources .....                                         | 4 |
| 3.2.3. High-Ga coal deposits. ....                                        | 4 |
| 3.2.4. Modes of Ga occurrence .....                                       | 4 |
| 3.2.5. Origin of high-Ga accumulations .....                              | 5 |
| 3.2.6. Utilization prospects .....                                        | 5 |
| 3.3. Selenium .....                                                       | 5 |
| 3.3.1. Role in clean energy .....                                         | 5 |
| 3.3.2. Raw material sources .....                                         | 5 |
| 3.3.3. High-Se coal deposits .....                                        | 5 |
| 3.3.4. Modes of occurrence .....                                          | 5 |
| 3.3.5. Origin of high-Se accumulations .....                              | 5 |
| 3.3.6. Utilization prospects .....                                        | 7 |
| 3.4. Lithium .....                                                        | 7 |
| 3.4.1. Role in clean energy .....                                         | 7 |

\* Corresponding author.

E-mail address: [vlseredin@gmail.com](mailto:vlseredin@gmail.com) (V.V. Seredin).

|        |                                              |    |
|--------|----------------------------------------------|----|
| 3.4.2. | Raw material sources . . . . .               | 7  |
| 3.4.3. | High-Li coal deposits . . . . .              | 7  |
| 3.4.4. | Modes of Li occurrence . . . . .             | 8  |
| 3.4.5. | Origin of high-Li accumulations . . . . .    | 8  |
| 3.4.6. | Utilization prospects. . . . .               | 8  |
| 3.5.   | Rare earth elements and yttrium . . . . .    | 8  |
| 3.5.1. | Role in clean energy . . . . .               | 8  |
| 3.5.2. | Raw material sources . . . . .               | 8  |
| 3.5.3. | High-REE + Y coal deposits . . . . .         | 8  |
| 3.5.4. | Modes of REY occurrence . . . . .            | 8  |
| 3.5.5. | Origin of high-REE+Y accumulations . . . . . | 9  |
| 3.5.6. | Utilization prospects. . . . .               | 9  |
| 4.     | Conclusions . . . . .                        | 10 |
|        | Acknowledgments . . . . .                    | 10 |
|        | References . . . . .                         | 10 |

## 1. Introduction

Coal represents the oldest type (after wood) of hydrocarbon fuel used by people for energy production. Coal resources are significantly more abundant than oil and gas, and can meet world energy requirements for hundreds of years. Nevertheless, coal utilization for power generation has been steadily reduced in many countries because of its serious impact on the environment as a result of both coal mining and coal combustion in thermal power plants. On the other hand, humanity cannot completely deny the role of coal in the global energy matrix because of the low cost of coal energy, comparative abundance of coal resources, and a fairly uniform distribution of coal deposits on the surface of the planet. Coal will remain the dominant power fuel for many countries which have limited oil and gas resources, and consequently, may limit the extent to which humankind can reduce the overall C footprint and move towards a “greener” and more sustainable future. The governments and scientists of many countries have already tried to solve this issue by various methods.

Traditional methods to decrease the negative impacts of coal power on the environment include the introduction of modern methods of mining, upgrading and burning of solid fuel, as well as in the processing of coal into gaseous and liquid fuels. However, there is another way of softening the negative environmental impacts associated with coal power: extraction of some rare metals, from coal deposits and coal combustion wastes, that are necessary for “clean” energy, based on both alternative energy sources and energy-efficient technologies.

This paper summarizes the authors’ previous analyses and the wider literature on coal deposits containing high concentrations of Ge, Ga, Se, Li and REE + Y. All these rare metal(loid)s are crucial for clean energy development and are used in the production of solar cells, wind turbines, energy saving lighting and electric vehicles. The data were obtained mainly during a Russian–Chinese cooperative investigation into the distribution and origin of metalliferous coal deposits in both countries.

## 2. Genetic types of rare metal(loid) accumulations in coal deposits

Rare metal(loid) (RM)-rich coals are formed under various geological conditions at different stages in the evolution of coal basins and by various ore-forming processes (Seredin, 2004; Seredin and Finkelman, 2008). Four genetic types of RM accumulation in coal can be identified (Table 1):

- (1) Terrigenous type, with RM input in ionic and colloidal forms from surface waters.
- (2) Tuffaceous type, connected with the fall of felsic and alkaline volcanic ash enriched in RM.

(3) Infiltration or meteoric ground water driven type.

(4) Exfiltration type, connected with ascending flows of thermal and cold gas-saturated mineral waters and deep fluids of various origins.

The first two types of RM mineralization in coal basins are formed at the sedimentary stage, the infiltration type is mainly epigenetic, and the exfiltration type may be formed at any stage of coal basin development.

In some cases, both the high-RM coals and RM mineralization in adjacent geological units may have a polygenetic and multistage origin (Seredin and Finkelman, 2008; Dai et al., 2008b; Seredin and Chekryzhov, 2011). For example, some REE + Y-rich tuffaceous layers in coal basins from southwestern China and the Russian Far East were subjected to hydrothermal alteration, and as a result of the process, these pyroclastic rocks were transformed into kaolinite clays, the initial magmatic RM-bearing minerals were destroyed, and the RM were re-distributed either as secondary mineral phases or as ionic species adsorbed onto the clay matrix (Dai et al., 2010; Seredin and Dai, 2012). Therefore, such mineralization may be attributed to a mixed tuffaceous-hydrothermal type (Seredin et al., 2012).

Since the same rare metal(loid)s may accumulate in coal basins by different geological processes (Table 1), the identification of genetic types of high RM concentration is important from the technological point of view, for prediction of the inferred resources and mining conditions.

## 3. Rare elements for clean energy in coal basins

### 3.1. Germanium

#### 3.1.1. Role in clean energy

Germanium substrates have been used extensively in space-based solar cells and other solar power arrays for many years. At present, there is an increasing interest in developing the use of Ge in terrestrial-based solar concentrator systems, because of its excellent photoelectric conversion efficiency. Mass production of Ge-based solar cells with sunlight to electricity conversion efficiencies as great as 38.5% began in the USA in late 2010 (Guberman, 2012). Germanium is also used in the manufacture of energy saving light-emitting diodes.

#### 3.1.2. Raw material sources

Germanium is the only rare element that has already been successfully extracted from coal for more than 50 a. Other raw material sources of Ge are some Zn-, Cu-, and Pb–Zn–Cu sulfide ores enriched in Ge (usually up to 100–200 ppm).

World Ge production was approximately 120 t in 2010–2011, of which about 40 t was produced from recycled materials (Guber-

**Table 1**

The main genetic types of high Ge, Ga, Se, Li, and REE + Y accumulations in coal deposits.

| Type         | Rare metal(loid) content range in coal ash <sup>a</sup> (%)                                                                  | Examples                                                                                                                                                                                                                                                                                                                                                                                                                                           | Rare metal(loid) content range in partings, host and basement rocks (%)                   | Examples                                                                                                                                                                                                                                                                                                                           |
|--------------|------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Terrigenous  | Ga – 0.005–0.04<br>REY <sub>2</sub> O <sub>3</sub> – 0.1–0.16<br>Li <sub>2</sub> O – 0.1–0.8                                 | Jungar deposit, China (Dai et al., 2006, 2008a, 2012b; Sun et al., 2012)                                                                                                                                                                                                                                                                                                                                                                           | Ga – 0.005–0.01<br>Li <sub>2</sub> O – 0.05–0.2                                           | Partings and host rocks of Jungar deposit, China (Sun et al., 2012)                                                                                                                                                                                                                                                                |
| Tuffaceous   | Ga – 0.005–0.03<br>REY <sub>2</sub> O <sub>3</sub> – 0.1–0.3                                                                 | Fire Clay (Dean) seam, USA (Hower et al., 1999; Mardon and Hower, 2004)                                                                                                                                                                                                                                                                                                                                                                            | Ga – 0.005–0.03<br>REY <sub>2</sub> O <sub>3</sub> – 0.1–0.6                              | Alkaline and felsic tuffs in the basement of Yunnan and RFE coal basins (Dai et al., 2010; Seredin et al., 2011, 2012)                                                                                                                                                                                                             |
| Infiltration | Ge – 0.02–0.07<br>Se – 0.03–0.5<br>REY <sub>2</sub> O <sub>3</sub> – 0.2–0.4                                                 | Kol'dzhatsk deposit, Kazakhstan (Kislyakov and Shchetochkin, 2000) Aduunchulun deposit, Mongolia (Arbuzov and Mashen'kin, 2007; Seredin and Dai, 2012)                                                                                                                                                                                                                                                                                             | Se – 0.03–0.3                                                                             | Sand layers of Kol'dzhatsk deposit, Kazakhstan (Kislyakov and Shchetochkin, 2000)                                                                                                                                                                                                                                                  |
| Exfiltration | Ge – 0.1–1.0<br>Ga – 0.01–0.06<br>Se – 0.01–0.03<br>Li <sub>2</sub> O – 0.1–0.8<br>REY <sub>2</sub> O <sub>3</sub> – 0.1–1.0 | Wulantuga (Zhuang et al., 2006; Qi et al., 2007; Du et al., 2009; Dai et al., 2012a) and Lincang deposits, China (Hu et al., 2009; Dai et al., unpublished data); Spetzugli and Rakovka deposits, RFE (Seredin, 2004; Seredin and Finkelman, 2008) Yanshan deposit, China (Dai et al., 2008b) Jungar deposit, China (Dai et al., 2012b) Pavlovka and Rettikhovka deposits, RFE (Seredin, 1996; Seredin and Finkelman, 2008; Seredin and Dai, 2012) | Ge – 0.004–0.1<br>Li <sub>2</sub> O – 0.1–2.1<br>REY <sub>2</sub> O <sub>3</sub> – 0.1–13 | Quartz-carbonate metasomatites of Lincang deposit (Hu et al., 2009; Dai et al., unpublished data) Sand and clay layers of Krylovka and Verhne-Bikinsk deposits, Argillized basaltic sills of Partizansk basin, RFE (Seredin and Tomson, 2008) REY ores in host and basement rocks of Pavlovka deposit, RFE (Seredin and Dai, 2012) |

<sup>a</sup> Rare metal content is given in high-temperature (600–850 °C) laboratorial ash. These concentrations may be much higher for volatile RM (Ge, Se and in some cases Ga) in the fly ash of power plants. RFE – Russian Far East.

man, 2012). For comparison, the designed Ge capacity of the three high-Ge (240–850 ppm) coal deposits from which Ge is currently being extracted as a byproduct is 150–170 t of Ge/a. Moreover, some coals with relatively low Ge content (about 10 ppm) can also be the sources for Ge recovery when the coals are used for coking or gasification (Ivanov et al., 1984; Shpirt et al., 1990; Yudovich and Ketris, 2004). Thus, Ge-bearing coals can be considered as the main source for Ge for world industry at present and for the foreseeable future (Seredin, 2006; Höll et al., 2007).

### 3.1.3. High-Ge coal deposits

The average Ge concentration in world coals is 2.2 ppm, and 15 ppm in world coal ash (Ketris and Yudovich, 2009). The Ge concentration in high-Ge lignites and subbituminous coals is two orders of magnitude higher than the global average Ge concentration (Table 2). The fly ashes from industrial combustion of Ge-rich coals contain 1.5–3.9% Ge (Dai et al., unpublished data).

Globally, the known coal-hosted high-Ge deposits are located in China and the Russian Far East (RFE) (Fig. 1). Three of these (Lincang, Wulantuga, China and Spetzugli, Russia) serve as the base for production of various Ge compounds, including high-purity metallic Ge for domestic and world industries (Fig. 2). Total Ge reserves of all these coal deposits are more than 10,000 t (Seredin and Finkelman, 2008). In the three coal-hosted high-Ge deposits, Ge is extracted from coal combustion products (fly ash), although the combustion conditions among them are different.

### 3.1.4. Mode of Ge occurrence

The main mode of Ge occurrence in high-Ge lignites is an organo-ic association, typically in complex humates (75–96% of total Ge)

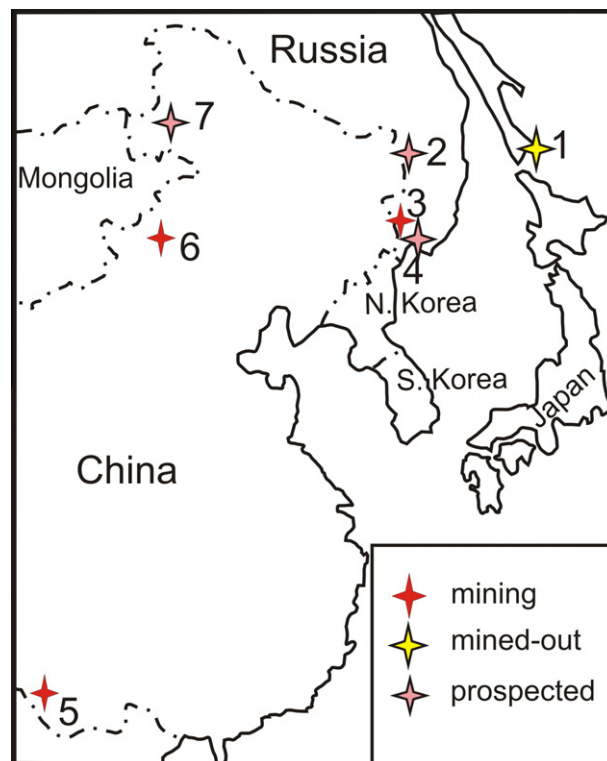


**Fig. 1.** Locations of the largest coal-hosted Ge deposits (modified from Seredin and Finkelman, 2008). 1 – Novikovsk; 2 – Bikinsk; 3 – Spetzugli; 4 – Shkotovo; 5 – Lincang; 6 – Wulantuga; 7 – Wumuchang.

**Table 2**

The Ge concentration and reserves in the largest coal-hosted Ge deposits of the world (modified from Seredin and Finkelman, 2008).

| Deposit                  | Novikovsk | Bikinsk | Spetzugli | Shkotovo | Lincang | Wulantuga | Wumuchang |
|--------------------------|-----------|---------|-----------|----------|---------|-----------|-----------|
| Ge content (ppm in coal) | 700       | 300     | 450       | 1040     | 850     | 240       | 30–50     |
| Ge reserve (t)           | 1665      | 2600    | 1015      | 880      | 1060    | 1700      | 4000      |



Fig. 2. High-pure metallic germanium (99.99999%), produced by Xilinguol Tongli Ge Refinery Co., Ltd. from Ge-bearing coal of the Wulantuga deposit.

(Shpirt et al., 1990). The role of mineral carriers for Ge in coals is insignificant. Fine-grained Ge oxides (oxalates-?) have been found in high-Ge coals of the Wulantuga deposit (Zhuang et al., 2006). It is cannot ruled out that these Ge-bearing minerals have a secondary origin, formed as a result of transformation from organically-bound Ge due to oxidation of the coal seam.

### 3.1.5. Origin of high-Ge accumulations

All of the known large Ge-bearing deposits exist in low-rank coals (lignite and subbituminous coal). However, the maceral groups present in different Ge-bearing coal deposits vary significantly, for example, huminite-group macerals amount to more than 90% (Dai et al., unpublished data) in Licnag lignite but inertinite-group macerals are >50% in Wulantuga lignite (Dai et al., 2012a). All of the large Ge-bearing deposits were formed as a result of circulating high-Ge low-temperature hydrothermal solutions in the basins during the peat accumulation and/or humification–gelification stages of organic matter transformation. The geological, geochemical, and mineralogical evidence for this process is reported by Kostin and Meitov (1972), Seredin (2004, 2006), Seredin and Tomson (2008), Zhuang et al. (2006), Qi et al. (2007), Seredin and Finkelman (2008), Du et al. (2009), Hu et al. (2009), and Dai et al. (2012a). For example, cell-filling quartz and pyrite present in some Ge-enriched coals indicate that they were derived from multi-stage hydrothermal solutions (Dai et al., 2012a). Elevated concentrations of epithermally-associated elements including As, Sb, Cs, Hg and Tl, also suggest hydrothermal influences on the coals (Seredin, 2006; Seredin and Finkelman, 2008; Dai et al., 2012a).

The hydrothermal model may explain the occurrence of high-Ge contents in quartz and carbonate stratabound and cross-cutting rocks that are found in the Novikovsk, Russia (Ivanov et al., 1984) and Lincang, China (Qi et al., 2004; Hu et al., 2009) Ge-bearing coal deposits.

High Ge accumulations (up to 100 ppm) in some infiltration coal-hosted U deposits do not have economic value, due to the high radioactivity and small thickness (up to 0.5–1.0 m) of the Ge-bearing zones.

### 3.1.6. Utilization prospects

It is highly likely that the contribution of coal deposits to the world's Ge production will constantly increase in the future; Ge-rich sulfide ores have already been mined-out in many countries, and three giant high-Ge coal deposits (Bikinsk and Shkotovo, Russia and Wumuchang, China) are candidates for development.

In addition, some known coal-hosted Ge-occurrences in a number of countries could potentially be identified as containing significant resources of Ge after further prospecting (Seredin and Tomson, 2008).

## 3.2. Gallium

### 3.2.1. Role in clean energy

Gallium is used in new generations of thin-film photovoltaics, typically in compounds together with Cu, In, and Se – the so-called CIGS solar cells. Moreover, Ga has a special usage in the production of light-emitting diodes (LEDs), which are quickly superseding conventional bulbs (Vulcan, 2009). The metal might also play an important role in hydrogen storage for “clean” cars of the future as the hydrocarbon-like clusters in Ga hydride materials have significant implications for the discovery of hydrides for hydrogen storage (Fahlquist et al., 2011).

### 3.2.2. Raw material sources

Most Ga (about 90%) is produced as a byproduct of bauxite processing and the remainder is produced from Zn-processing residues. The Ga content of bauxite and Zn ores usually varies from 30 to 80 ppm (50 ppm on average). In 2011, the estimated world primary Ga production was 216 t (Jaskula, 2012a); another 100 t was recovered from scrap.

### 3.2.3. High-Ga coal deposits

The average Ga content of world coal is 5.8 ppm and that of world coal ash is 33 ppm (Ketris and Yudovich, 2009). However, there are many coal deposits with higher Ga concentrations: up to 20–40 ppm in coal and 100–600 ppm in ash (Kler et al., 1987; Seredin, 2004; Yudovich and Ketris, 2006 and references therein). The fly ashes derived from industrial combustion of some coals may contain as much as 0.1–0.5% Ga (Kler et al., 1987; Dai et al., unpublished results). Gallium-bearing terrigenous and tuffaceous clayey layers with 50–300 ppm Ga have also been found in the basement and host rocks of some coal basins in southwestern China (Dai et al., 2010).

The Jungar deposit (Ordos Basin, northern China) stands out amongst other Ga-bearing coal deposits due to the very high total Ga accumulation (Dai et al., 2006, 2008a, 2012b). The Ga-bearing No. 6 coal seam, which is the main seam of the Jungar deposit, covers a distance of 65 km and has been mined from several open and underground pits. The thickness of the No. 6 seam varies from 15 (Guanbanwusu mine) to 27–28 m (Heidaigou and Haerwusu mines). The enrichment of Ga occurs both in the relatively low rank ( $R_{o,ran} = 0.58\%$ , Heidaigou Mine;  $R_{o,ran} = 0.56\%$ , Guanbanwusu Mine) and relatively high rank ( $R_{o,ran} = 1.58$ ; Adaohai Mine) coals. The Ga content of coal ash is from 45 to 135 ppm (88 ppm on average). In addition to Ga, the No. 6 coal seam is also enriched in  $Al_2O_3$ : from 44% to 62% in ash (55.5% on average). Thus, the concentrations of  $Al_2O_3$  and Ga in combustion residues from the Jungar coal deposit are very similar to those in conventional bauxite deposits (30–55%  $Al_2O_3$  and 30–80 ppm Ga). The proven resources of the metals are 49,000 t of Ga and 150 million t of  $Al_2O_3$  in the Heidaigou mine (Seredin, 2012).

### 3.2.4. Modes of Ga occurrence

Gallium in high-Ga coal deposits may occur both in different minerals and in the organic compounds of the coal. For example, the basic Ga carrier in the No. 6 coal from the Heidaigou open pit is boehmite ( $AlOOH$ ) (Dai et al., 2006), but that from the Guanbanwusu mine is organically-bound (Dai et al., 2012b). In the coals from the Adaohai mine, Ga is concentrated in diasporite and kaolinite (Dai et al., 2012c). The diasporite was derived from gibbsite through breakdown of boehmite due to the dehydration by the

heat of igneous intrusions (Dai et al., 2012b). This is also the reason that diasporite occurs in high-rank Adaohai coal but boehmite occurs in the relatively low-rank coals of Heidaigou, Haerwusu, and Guanbanwusu (Dai et al., 2006, 2012b). These data have confirmed the suggestion that Ga in coal may be present both in mineral and in organic matter and the partitioning between these forms may vary (Eskenazy, 1969; Ratynskiy and Zharov, 1980; Yudovich and Ketris, 2006).

### 3.2.5. Origin of high-Ga accumulations

High-Ga rocks in coal deposits may have various origins (Table 1). Significant Ga accumulation in the No. 6 coal in the Jungar deposit is attributed to the breakdown of adjacent bauxite deposits, which supplied Ga to the peat bog during the Late Paleozoic (Dai et al., 2006, 2008a). The Ga enrichment in the Fire Clay (Dean) coal seam (Kentucky, USA) is attributed to the input of felsic pyroclastics (Hower et al., 1999; Mardon and Hower, 2004). The origin of the Ga-bearing tuff layers in coal deposits of southern China was alkaline volcanic activity during the Late Permian (Dai et al., 2010). The high-Ga (30–100 ppm) Cenozoic coals of the Rakovka deposit, Russian Far East probably have a hydrothermal origin, as Ga enrichment accompanies high accumulation of Ge, Sb and other elements of epithermal association (Seregin, 2004).

### 3.2.6. Utilization prospects

The first pilot plant to produce Ga and  $\text{Al}_2\text{O}_3$  from fly ash, with an annual processing capacity of approximately 150 t Ga and 800,000 t  $\text{Al}_2\text{O}_3$ , was built by Shenhua Group Zhungeer Energy Corporation Limited (SHZECL) near the Heidaigou surface mine at the beginning of 2011. SHZECL plans to commence  $\text{Al}_2\text{O}_3$  and Ga production in 2012. According to SHZECL's development plans, an additional four plants for Al and Ga extraction with the same capacity will be built in the future. When (and if) this development plan is fully implemented, the annual metal production is expected to be in excess of 700 t Ga and 4 Mt  $\text{Al}_2\text{O}_3$  in 2015 (Seregin, 2012).

A spatial association of coal and bauxite has been found in a number of areas, for example, Arkansas in the USA (Maynard, 1983), South Timansk and some other coal basins in Russia (Yudovich and Ketris, 2002), and in several other countries (Kalaitzidis et al., 2010). Therefore, it may be possible to develop additional coal seams suitable for extraction of Ga and Al. Moreover, Ga recovery may be very effective through processing of some Ge-bearing fly ashes (Lincang and Rakovka deposits), as well as through processing to recover other RMs (Zr, Nb, REE + Y) from coal and host rocks with tuffaceous mineralization. If such a prognosis is correct, Ga production could increase markedly during the next decade, with costs of production significantly decreased. Such a scenario will inevitably lead to wider application of this rare metal

in high-tech industries, including new clean energy technologies (Fahlquist et al., 2011) that are limited now by the high cost of Ga.

## 3.3. Selenium

### 3.3.1. Role in clean energy

Because of its photovoltaic properties, Se is an ideal material for new generation thin-film voltaics, especially in compounds with Cu, In and Ga (CIGS solar cells) or with just Cu and In (CIS solar cells) (George, 2012).

### 3.3.2. Raw material sources

All Se is produced as a byproduct from the mining and processing of base metals (Cu, Pb and Ni). Nearly 90% of the world Se is derived from Cu refining, extracted from the anode or tank house slimes. Such extraction processes, however, are relatively complex, requiring a number of different treatments. World Se production was estimated to be 2000 t in 2011 (George, 2012).

### 3.3.3. High-Se coal deposits

Selenium has a low abundance in world coals (1.3 ppm) and in world coal ash (8.8 ppm) (Ketris and Yudovich, 2009). However, these figures are much higher than the average Se concentration in the Upper Earth Crust (0.09 ppm; Rudnick and Gao, 2003). Some coals, as well as host-rocks of some coal deposits, may contain up to several kg/t of Se (Table 1). Such high Se concentrations have been reported only in U-bearing coal deposits (Kislyakov and Shchetochkin, 2000). Additionally, abnormal but lesser Se concentrations (10–100 ppm) are reported in some coals that are enriched in sulfide minerals (Dai et al., 2008b). Due to the high volatility of Se and its capture from the gas phase on ash particles, its concentration in fly ash may be 20–100 times higher than that in the raw feed coals.

### 3.3.4. Modes of occurrence

The modes of Se occurrence in high-Se coal deposits vary considerably. They include fine-grained Se (native Se), clausthalite ( $\text{PbSe}$ ), ferroselite ( $\text{FeSe}_2$ ), and sulfide minerals containing Se as an isomorphic admixture (pyrite, arsenopyrite, chalcopyrite, galena, etc.) (Finkelman, 1980; Hower and Robertson, 2003; Maksimova and Shmarovich, 1993; Kislyakov and Shchetochkin, 2000) (Fig. 3). Sometimes Se is mainly distributed in marcasite though both pyrite and marcasite contemporarily occurs in the same coal (Dai et al., 2013). A portion of the Se may occur in the organic matter of high-Se coals (Yudovich and Ketris, 2005).

### 3.3.5. Origin of high-Se accumulations

High Se accumulations in coal basins may be of two genetic types (Table 1). The first is connected with infiltration of

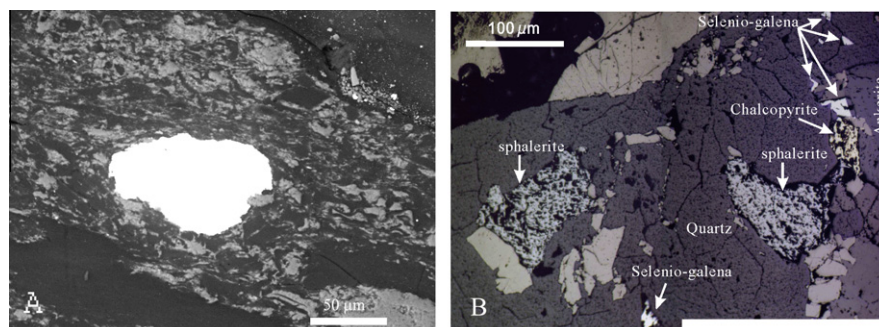


**Fig. 3.** Se-bearing galena (white) in coals of Jungar deposit (A) and in quartz veinlet in coal of Dafang deposit, China in association with chalcopyrite and sphalerite (B). A – SEM, back-scattered electron image; B – photograph in reflected light.

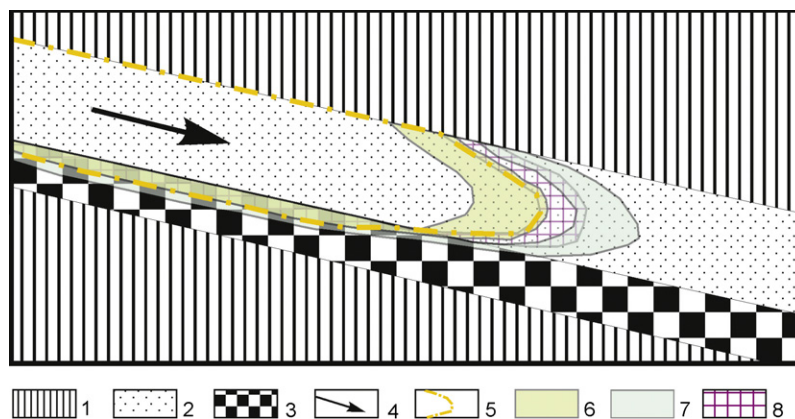


**Fig. 4.** Position of Se mineralization in U ore bodies of coal basins (modified from Danchev, 1977). 1 – clay; 2 – sand; 3 – coal; 4 – direction of O<sub>2</sub>-rich underground water moving; 5 – border of oxidized rocks; 6–8 – ore mineralization: 6 – Se, 7 – Mo, 8 – U.

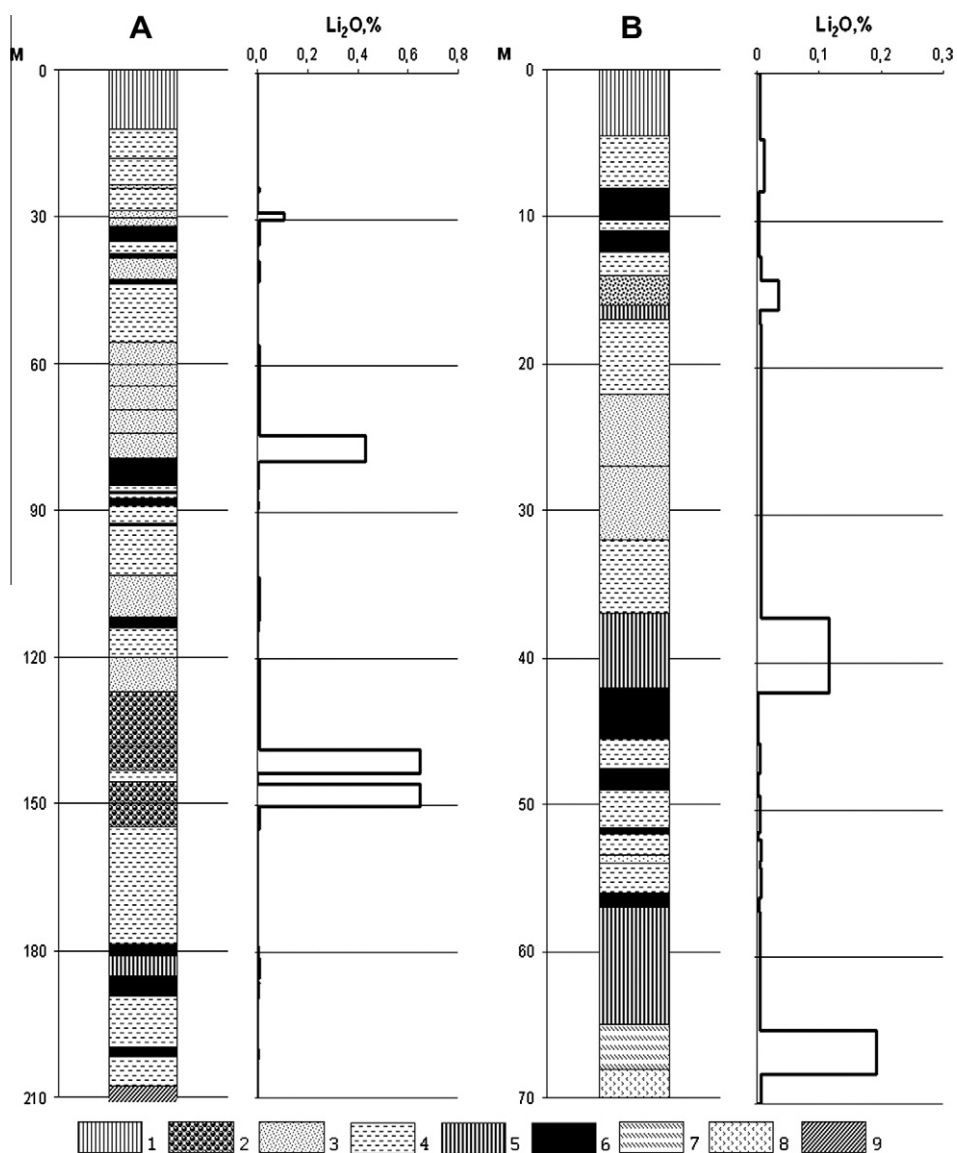


**Fig. 5.** Li anomalies in Cenozoic coal-bearing strata of Krylovsk (A) and Verkhne-Bikinsk (B) coal basins. Unpublished data of I.G. Sharova, M.P. Mel'tsaev, and I.V. Burjanov were used for construction of the figure. 1 – clay; 2 – conglomerate; 3 – sandstone; 4 – siltstone; 5 – coaly argillite; 6 – coal; 7 – argillized andesite; 8 – fresh andesite; 9 – shale.

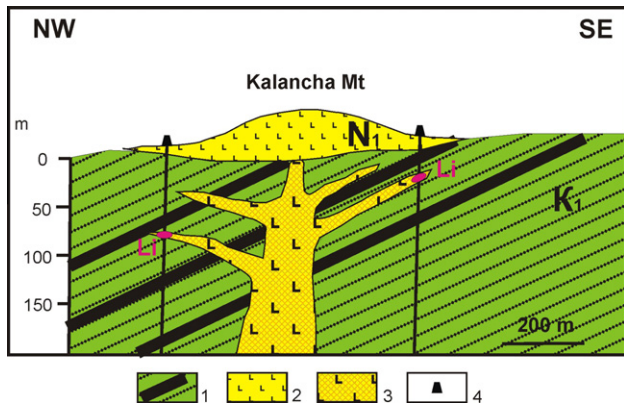


**Fig. 6.** Geological setting of Li mineralization in Partizansk coal basin, Russian Far East. 1 – coal-bearing strata; 2 – fresh basalt; 3 – argillized basalt; 4 – drill hole.

descending lateral flows of  $O_2$ -rich ground water in the coal-bearing strata. Selenium is concentrated in oxidized parts of the coal seams together with U, Mo and Re. In coarse-grained host rocks, high Se contents may occur in the limonitized rear zone of crescent-shaped ore bodies (rolls) with relatively low U and other associated element concentrations (Fig. 4).

The second type of Se enrichment is connected with penetration of ascending flows of thermal mineral waters with high  $SO_4$  content in the coal basins (Dai et al., 2008b). This kind of Se enrichment occurs in the coals preserved within marine carbonate successions and characterized by very high organic S (4–11%). The Se enrichment is generally accompanied by high levels of V, Mo, and U.

### 3.3.6. Utilization prospects

Coal deposits with high Se contents could be potential sources of this element, especially in those countries that do not have enough Se resources for solar power development and other applications. Uranium-bearing coal deposits, where the mineralization is developed not only in coals but in host-rocks, are the most interesting; in such cases Se may be extracted from coarse-grained sediments by *in situ* leaching selectively from U (Laverov, 1998).

## 3.4. Lithium

### 3.4.1. Role in clean energy

Lithium is a fuel for future power generation – thermonuclear Tokamak-reactors. However, it has already played an important role in clean energy, through mass production of rechargeable Li-ion batteries used in electric and hybrid electric vehicles.

### 3.4.2. Raw material sources

There are currently two main Li sources for world industry: surface and subsurface brines (0.02–0.14% Li) and spodumene-bearing pegmatites (0.6–1.6% Li) (Gruber et al., 2011). Lithium-bearing greisens and low-temperature hydrothermal clays have not yet been used as a source for Li production, in spite of their high Li content (0.1–0.5%). Subsurface brines have become the dominant raw material for Li production worldwide in the last decade, due to relatively low production cost compared to the cost of the mining and processing mineral-based ores. Worldwide Li production has grown from 28,100 t in 2010 to 34,000 t in 2011 (Jaskula, 2012b).

### 3.4.3. High-Li coal deposits

The average Li content is 12 ppm for world coal and 66 ppm for world coal ash (Ketris and Yudovich, 2009); this is much higher than those of Ge, Ga, and Se. However, unlike these elements, Li has not, until recently, been considered as a possible byproduct from coal mining and coal combustion.

The first data regarding high Li concentrations (up to 0.1–0.3% Li or 0.22–0.65%  $Li_2O$ ) in coal deposits were reported by Russian geologists in the 1980s when Li-bearing layers were identified in the Krylovsk and Verkhne-Bikinsk coal basins in the Russian Far East (Seredin, 2004; Seredin and Tomson, 2008). Despite the considerable distance between these two basins (about 350 km), it seems that the geological positions of the Li anomalies are similar; both occur in Cenozoic host- and basement-rocks outside the coal seams (Fig. 5). In the coarse-grained sediments of these deposits, Li is concentrated in the clay cement of the host rocks.

Over the years, high Li contents (up to 1%) have been identified in the Partizansk coal basin of the Russian Far East (Fig. 6). As in the previous cases, Li is concentrated outside the coal seams in argillized basaltic sills (Seredin and Tomson, 2008).

In the Jungar coal deposit, high Li accumulations were discovered not only in the host-rocks but also in the coals (Dai et al.,

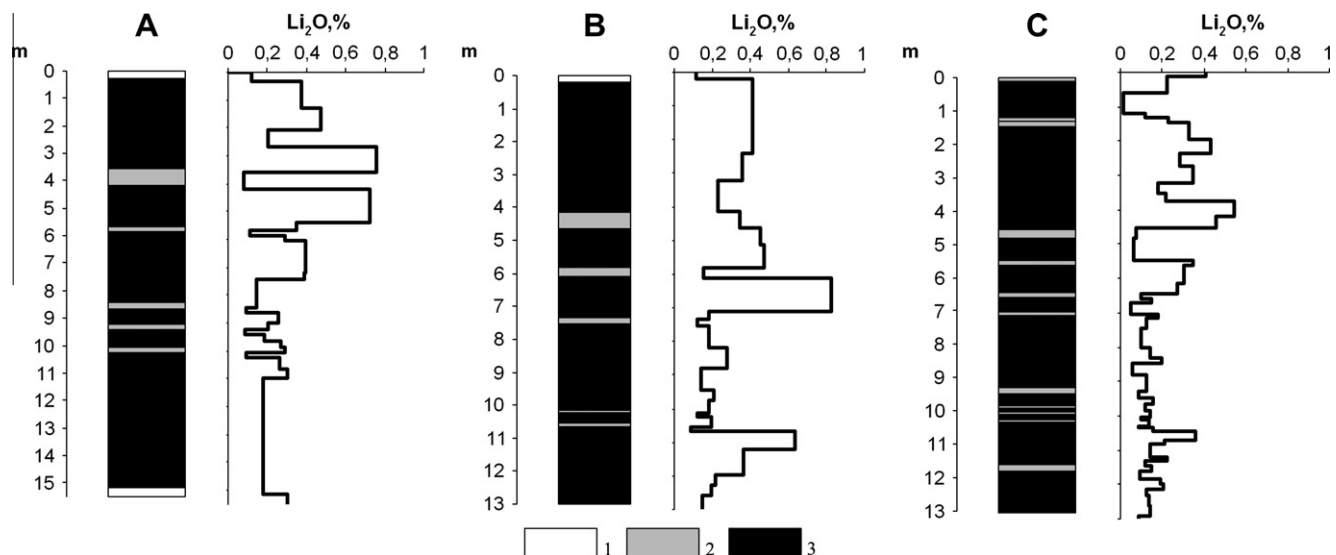


**Fig. 7.**  $Li_2O$  distribution in the studied sections of Li-rich No. 6 Coal, Guanbanwusu mine, Jungar deposit, northern China. Data from Sun et al. (2012) (A and B) and Dai et al. (2012b) (C) were used for construction of the figures.  $Li_2O$  content is given on a coal ash basis. 1 – host-rock clay; 2 – parting clay; 3 – coal bench.

2008a, 2012b; Sun et al., 2010, 2012). The weighted average  $\text{Li}_2\text{O}$  contents in the No. 6 Coal of the Guanbanwusu mine in the deposit are 0.26 (section A), 0.32 (section B), and 0.21% (section C) on a coal ash basis (Fig. 7). These are higher than the industrial grade for the Li-bearing pegmatite deposits of China:  $\text{Li}_2\text{O}$ –0.2% (DZ/T 0203–2002, 2003). Concentrations of  $\text{Li}_2\text{O}$  are up to 0.72–0.83% in the ashes of some Li-rich coal benches. The clayey rocks of the partings, roof and bottom of the coal seam in the coal deposit are also strongly enriched in  $\text{Li}_2\text{O}$  (up to 0.34–0.41%). The *in situ* inventory of this metal in the Guanbanwusu mine is estimated to be 52,000 t of  $\text{Li}_2\text{O}$  (Sun et al., 2012).

#### 3.4.4. Modes of Li occurrence

The main Li carriers in the above coal deposits are Li-bearing clay minerals: Li tosylite ( $\text{Na}_{0.5}(\text{Li}, \text{Al}, \text{Mg})_6(\text{Si}, \text{Al})_8\text{O}_{18}) (\text{OH})_{12} \cdot 5\text{H}_2\text{O}$ ) in the Russian Far East deposits (Seredin and Tomson, 2008) and a chlorite with composition intermediate between cookeite ( $\text{LiAl}_4 (\text{AlSi}_3\text{O}_{10}) (\text{OH})_8$ ) and chamosite in the coal from the Guanbanwusu mine (Dai et al., 2012b). Further evidence is needed for the presence of high-temperature detrital Li-minerals in some Chinese Li-rich coals (Sun et al., 2010).

#### 3.4.5. Origin of high-Li accumulations

The high Li contents in the Russian Far East coal deposits most likely have an epigenetic hydrothermal origin (Seredin and Tomson, 2008). These Li accumulations are similar to hydrothermal clayey ores of some volcanogenic Li deposits (Hector, and McDermitt, USA, Shavazsay, Uzbekistan) with respect to their mineralogical and geochemical relationships (high Be, Zn, Pb, and Ag contents).

The Li anomalies in the No. 6 Coal of the Guanbanwusu mine are probably more complicated in genesis. In this case, Li accumulation may have occurred during the peat bog stage, along with surface water from Li-bearing bauxites and with basin brines (Sun et al., 2012). However, epigenetic hydrothermal Li supply is another possible carrier of Li, rather than detrital material of terrigenous origin, as Li-bearing chlorite occurs as cell-fillings in the coal (Dai et al., 2012b).

#### 3.4.6. Utilization prospects

World Li consumption will increase with the inevitable growth in production of hybrid and electric vehicles using rechargeable Li-ion batteries. According to some estimates, the Li demand from 2010 to 2100 will be between 12 and 20 Mt (Gruber et al., 2011). Therefore, high-Li coals and clays could be used by the industry as byproducts of coal mining and combustion, especially in those countries where there are no other Li sources.

### 3.5. Rare earth elements and yttrium

#### 3.5.1. Role in clean energy

Lanthanides and Y play a special role in the development of alternative power and energy-efficient technologies. Rare Earth Elements (Nd, Pr, Sm, Dy, Tb) are one of the important components for super-power permanent magnets, which are irreplaceable in industrial generators because they can effectively transform any kind of energy (wind, tidal, geothermal, etc.) into electricity. Additionally, REE + Y have been widely used in hybrid and electric vehicles. Yttrium-, Eu-, and Tb-phosphors are the components of CFLs and LEDs. Moreover, Y is one of the basic components of superconducting electric power lines. Thus, REE + Y have now become a “corner stone” for alternative power and energy saving applications (Lifton, 2009; U.S. Department of Energy, 2011).

#### 3.5.2. Raw material sources

There are two main sources of REE + Y at present, carbonatites and weathered crust elution-deposited (ion-adsorbed) ores, both of which are almost exclusively mined in China and have been supplying world industry for many years. The carbonatite deposits, which have abundant bastnaesite and monazite, usually have high REE + Y contents (1–10%) and large reserves (from one Mt to tens of Mt), but are typically sources of only Light REE (La–Sm). The weathered crust elution-deposited ore deposits with ion-exchangeable REE + Y are sources for all these metals and are characterized by low total REE + Y contents (0.03–0.25%) and small (3–12 kt) reserves (Bao and Zhao, 2008; Chi and Tian, 2008). In spite of this, the ores have been mined successfully because of the simple techniques used for REE + Y extraction and the high proportion of crucial REE + Y available for clean energy (Eu, Tb, Dy, Y). Unfortunately, the resources of these weathered crust elution-deposited ore deposits are being exhausted. Estimates have shown that these metal resources will suffice only for 15–20 a (Chegwidden and Kingsnorth, 2011).

REE + Y consumption has shown an exponential growth in the 21st century and no doubt will continue to grow in the foreseeable future. For example, annual world REE + Y production was 91,000 t in 2000 and 130,000 t in 2011. According to some forecasts, the REE + Y demand will continue to grow, to approximately double in 2020 (220,000–300,000 t/a) (Chegwidden and Kingsnorth, 2011). However, the issue of how to meet the rapid growth in demand and how to provide such a huge amount of REE + Y raw materials is not clear. In essence, global industry has entered a long period of rare-earth raw material crisis in many respects, connected with the new technologies of clean energy development.

#### 3.5.3. High-REE + Y coal deposits

The average sum REE + Y contents, based on calculation of average individual lanthanide and Y content, are 68.5 ppm for world coals and 404 ppm for world coal ash (Ketris and Yudovich, 2009). The sum REE + Y oxides ( $\text{REY}_2\text{O}_3$ ), which is generally used to estimate the abundance of the metals in ores, is 483 ppm in ash, after recalculation from the concentration of the single elements. This figure is similar to the REE + Y cut-of-grade in the clayey ores of ion-adsorbed deposits.

The REE + Y content of coal ash for many coal deposits worldwide is much higher (0.1–1.0%  $\text{REY}_2\text{O}_3$ ) than the above mentioned average value for world average coal ash. Recent data on coals with  $\text{REY}_2\text{O}_3$  content  $\geq 0.1\%$  are summarized by Seredin and Dai (2012 and references therein). Moreover, high-REE + Y contents (up to 11%) have been found in host- and basement-rocks of several coal basins. The majority of REE + Y anomalies discovered in the coal deposits are characterized by a high proportion of those REE + Y that play a key role in clean energy development (e.g. Nd, Eu, Dy, Tb, Y) (U.S. Department of Energy, 2011).

#### 3.5.4. Modes of REY occurrence

Various REE + Y authigenic minerals (hydrous phosphates and Al phosphates as well as carbonates and fluorocarbonates) and organically-bound REE + Y are typically found in the high-REE + Y coals (Seredin and Dai, 2012). In some cases, such coals may contain abundant impregnations of fine-grained REE + Y minerals (Fig. 8A and B). In appearance these coals are very similar to REE + Y disseminated ores of more conventional type.

The same minerals are typical for REE + Y-rich sedimentary, tuffaceous (Fig. 8C and D), and hydrothermal (Fig. 8E and F) rocks in coal basins. In addition, REE + Y-bearing oxides (cerianite ( $\text{CeO}_2$ ), fergusonite ( $\text{YNbO}_4$ )), fluorosulfates, and titanates have been found in the REE + Y-rich rocks associated with coal seams (Seredin et al., 2012). Ion-exchangeable REE + Y adsorbed by clay particles and Fe–Mn oxyhydroxides may also occur in some of these rocks (Dai et al., 2010; Seredin and Dai, 2012).

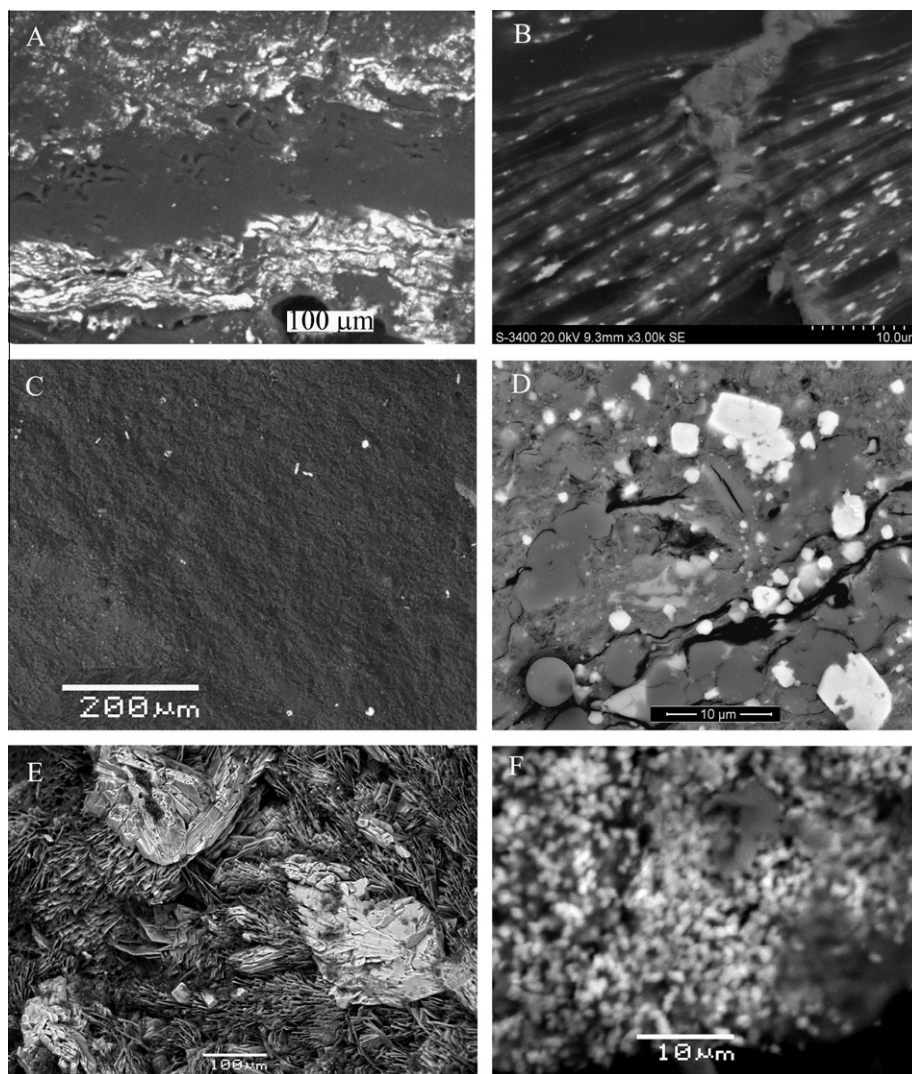


**Fig. 8.** Fine-grained REE + Y mineral disseminations in various REE + Y-rich rocks of coal basins: A and B – coals, C and D – tuffaceous clays, E and F – cross-cutting hydrothermal ores in basement rocks (SEM, back-scattered electron images). A – REE-bearing Al phosphates (white), Pavlovka Coalfield, Russian Far East (Seredin, 2004); B – rhabdophanes (white), Sichuan Basin, Changhe mine, China (Wang, 2009); C – bastnaesite and synchysite grains (white), Nanchuan Coalfield, Chongqing, China; D – REE-bearing Al phosphates (white), eastern Yunnan, China; E – kimuraite (gray lamellar minerals) with inclusions of Nd-lanthanite (white), Pavlovka Coalfield, Abramovka REE + Y occurrence, Russian Far East; and F – rhabdophane (white), Pavlovka Coalfield, Boikov REE + Y occurrence, Russian Far East.

### 3.5.5. Origin of high-REE+Y accumulations

The origin of REE + Y mineralization in coal deposits may vary significantly (Table 1). Terrigenous and infiltration REE + Y anomalies only occur in coal seams, but tuffaceous and exfiltration enrichment types may occur both in coals, host and basement rocks. In most cases, the high REE + Y accumulations in coal basins are stratabound. However, exfiltration REE + Y ores and, in particular, hydrothermal ores may be both stratabound and cross-cutting. The latter have been identified in the basement of some coal basins and may have extraordinarily high REE + Y contents (up to 4–11%) (Seredin et al., 2009).

### 3.5.6. Utilization prospects

REE + Y recovery as a byproduct from coal deposits may be considered as a promising way for obtaining these critical metals to meet the expected global supply/demand situation (Seredin and Dai, 2012).

This point of view is supported by the following data:

- (1) High-REE + Y concentrations ( $\geq 0.1\%$  in ash) have been found in several tens of coal deposits worldwide. Undoubtedly, the

number of such REE + Y-rich deposits will increase with further data collection.

- (2) Inferred REE + Y resources in coal basins are comparable with those of typical conventional REE + Y deposits. These reserves are present on a scale of  $n^*$  Mt in coals with terrigenous REE + Y enrichment (Jungar, northern China) and in the tuffaceous clays (southwestern China);  $n^*$  100 kt in coals with tuffaceous REE + Y (Fire Clay (Dean) bed, USA); and  $n^*$  10 kt in deposits with infiltration and exfiltration REE + Y (Russian Far East coal basins).
- (3) Many REE + Y ores in coal basins are characterized by carbonate and ion-exchangeable modes of REE + Y occurrence, of particular interest to the industry from the technological point of view.
- (4) Most of the REE + Y ores in coal basins are enriched in medium REY (e.g. Eu, Dy, Tb, Y), which are especially in short supply at present.
- (5) Some technological problems of REE + Y extraction from combustion residues derived from REE + Y-rich coals have already been solved on a laboratory scale (Seredin, 2004) (Fig. 9).



**Fig. 9.** View of Pavlovka coal deposit, Russian Far East and pure REE + Y oxides extracted from the high-REE + Y coal ash (0.4% REY<sub>2</sub>O<sub>3</sub>) of the deposit (test-tube is 100 mm long).

For these reasons the authors' believe that REE + Y could be the next metals (after Ge and Ga) for successful recovery as a byproduct from coal deposits to address the present-day raw material crisis.

#### 4. Conclusions

For the resolution of current supply problems of rare metal(loid)s required for the development of alternative power and energy-efficient technologies, it would be useful to focus on certain types of coal deposits that are currently being mined worldwide. Some metalliferous coal deposits may be sources for several metals used to produce clean energy: the Jungar deposit, China – Ga, REE + Y, and Li (Dai et al., 2012b); the Rakovka deposit, Russian Far East – Ge, Ga, and REE + Y (Seredin, 2004); the Aduunchulun, Mongolia – REE + Y (Arbuzov and Mashen'kin, 2007) and Se. The data presented in this paper demonstrate how important it is to conduct full geochemical analysis of coals and host-rocks, not limited to potentially toxic elements or technologically important elements for coal power production.

The benefits of rare metal extraction as a byproduct from coal deposits also include the relatively low cost of the necessary infrastructure and mining. Moreover, rare metal recovery from coal combustion residues can reduce adverse environmental effects. For example, extraction of Ga (together with Al, and Si) from the Jungar coal combustion residues will sharply reduce the quantity of stored fly ash. If the project proceeds as expected, more than 90% of the combustion residues will be processed in the metal recovery plant and, thus, the atmospheric pollution from dust carried by wind will be significantly reduced (Seredin, 2012).

Thus development of rare metal resources for clean energy development during coal exploitation and coal utilization will not only increase beneficial use of coal deposits themselves but will also promote humanity's further movement on the "green road".

#### Acknowledgments

This research was supported by the National Natural Science Foundation of China (Nos. 40725008 and 40930420), the Russian Foundation for Basic Research (No. 10-05-91160), and the Presidium of the Russian Academy of Sciences (No. 23-24). Special thanks are given to Prof. Deyi Ren for his great support in this study, Mr. Benjamin Stoikovich for editing of the manuscript. We would like

to thank two anomalous reviewers, the associated editor Dr. Allan Kolker, and the executive editor Prof. Ron Fuge for their careful and constructive comments that greatly improved the manuscript.

#### References

- Arbuzov, S.I., Mashen'kin, V.S., 2007. Oxidation zone of coalfields as a promising source of noble and rare metals: a case of a coalfield in central Asia. In: Problems and Outlook of Development of Mineral Resources and Fuel – Energetic Enterprises of Siberia. Tomsk Polytechnic Univ., Tomsk, pp. 26–31 (in Russian).
- Bao, Z., Zhao, Z., 2008. Geochemistry of mineralization with exchangeable REY in the weathering crusts of granitic rocks in south China. *Ore Geol. Rev.* 33, 519–535.
- Chegwidden, J., Kingsnorth, D.J., 2011. Rare Earths – An Evaluation of Current and Future Supply. <[http://www.tremcenter.org/index.php?option=com\\_attachments&task=download&id=41](http://www.tremcenter.org/index.php?option=com_attachments&task=download&id=41)>.
- Chi, R., Tian, J., 2008. Weathered Crust Elution-deposited Rare Earth Ores. Nova Science Publishers, New York.
- Dai, S., Jiang, Y., Ward, C.R., Gu, L., Seredin, V.V., Liu, H., Zhou, D., Wang, X., Sun, Y., Zou, J., Ren, D., 2012b. Mineralogical and geochemical compositions of the coal in the Guanbanwusu mine, Inner Mongolia, China: further evidence for the existence of an Al (Ga and REE) ore deposit in the Jungar coalfield. *Int. J. Coal Geol.* 98, 10–40.
- Dai, S., Li, D., Chou, C.-L., Zhang, Y., Ren, D., Ma, Y., Sun, Y., 2008a. Mineralogy and geochemistry of boehmite-rich coals: new insights from the Haerwusu surface mine, Jungar coalfield, Inner Mongolia, China. *Int. J. Coal Geol.* 74, 185–202.
- Dai, S., Ren, D., Li, S., 2006. Discovery of the superlarge gallium ore deposit in Jungar, Inner Mongolia, north China. *Chin. Sci. Bull.* 51, 2243–2252.
- Dai, S., Ren, D., Zhou, Y., Chou, C.-L., Wang, X., Zhao, L., Zhu, X., 2008b. Mineralogy and geochemistry of a superhigh-organic-sulfur coal, Yanshan coalfield, Yunnan, China: evidence for a volcanic ash component and influence by submarine exhalation. *Chem. Geol.* 255, 182–194.
- Dai, S., Wang, X., Seredin, V.V., Hower, J.C., Ward, C.R., O'Keefe, J.M.K., Huang, W., Li, T., Li, X., Liu, H., Xue, W., Zhao, L., 2012a. Petrology, mineralogy, and geochemistry of the Ge-rich coal from the Wulantuga Ge ore deposit, Inner Mongolia, China: new data and genetic implications. *Int. J. Coal Geol.* 90–91, 72–99.
- Dai, S., Zhang, W., Ward, C.R., Seredin, V.V., Hower, J.C., Li, X., Song, W., Kang, H., Zheng, L., Zhou, D., 2013. Mineralogical and geochemical anomalies of late Permian coals from the Fusui coalfield, Guangxi province, southern China: influences of terrigenous materials and hydrothermal fluids. *Int. J. Coal Geol.* 105, 60–84.
- Dai, S., Zhou, Y., Zhang, M., Wang, X., Wang, J., Song, X., Jiang, Y., Luo, Y., Song, Z., Yang, Z., Ren, D., 2010. A new type of Nb (Ta)-Zr(Hf)-REE-Ga polymetallic deposit in the late Permian coal-bearing strata, eastern Yunnan, southwestern China: possible economic significance and genetic implications. *Int. J. Coal Geol.* 83, 55–63.
- Dai, S., Zou, J., Jiang, Y., Ward, C.R., Wang, X., Li, T., Xue, W., Liu, S., Tian, H., Sun, X., Zhou, D., 2012c. Mineralogical and geochemical compositions of the Pennsylvanian coal in the Adaohai mine, Daqingshan coalfield, Inner Mongolia, China: modes of occurrence and origin of diasporite, gorceixite, and ammonian illite. *Int. J. Coal Geol.* 94, 250–270.
- Danchev, V.I., 1977. Textures and Structures of Uranium Ores of Exogenous Deposits. Atomizdat, Moscow (in Russian).

- Du, G., Zhuang, X., Querol, X., Izquierdo, M., Alastuey, A., Moreno, T., Font, O., 2009. Ge distribution in the Wulantuga high-germanium coal deposit in the Shengli coalfield, Inner Mongolia, northeastern China. *Int. J. Coal Geol.* 78, 16–26.
- DZ/T 0203–2002, 2003. *Geology and Ore Deposit Standard Specifications for Rare Metal Mineral Exploration of the People's Republic of China*. Geological Publishing, Beijing. ISBN 978-7-116-03802-8 (in Chinese).
- Eskenazy, G.M., 1969. On gallium geochemistry in coal-forming process. *Godishn. Sofiisk. Univ.* 61, 321–348 (in Russian).
- Fahlquist, H., Noreus, D., Callear, S., David, W.I.F., Hauback, B.C., 2011. Two new cluster ions,  $\text{Ga}(\text{GaH}_3)_4^{5-}$  with a neopentane structure in  $\text{Rb}_8\text{Ga}_5\text{H}_{15}$  and  $[\text{GaH}_2]_n^{n-}$  with a polyethylene structure in  $\text{Rb}_n(\text{GaH}_2)_n$ , represent a new class of compounds with direct Ga–Ga bonds mimicking common hydrocarbons. *J. Am. Chem. Soc.* 133, 14574–14577.
- Finkelman, R.B., 1980. *Modes of Occurrence of Trace Elements in Coal*. Ph. D. Dissertation. Dept. Chem., Univ. Maryland, College Park.
- George, M.W., 2012. Selenium. U.S. Geological Survey, Mineral Commodity Summaries. <<http://minerals.usgs.gov/minerals/pubs/commodity/selenium/mcs-2012-selen.pdf>>.
- Gruber, P.W., Medina, P.A., Keoleian, G.A., Kesler, S.E., Everson, M.P., Wallington, T.J., 2011. Global lithium availability: a constraint for electric vehicles? *J. Ind. Ecol.* 15, 755–760.
- Guberman, D.E., 2012. Germanium. U.S. Geological Survey, Mineral Commodity Summaries. <<http://minerals.usgs.gov/minerals/pubs/commodity/germanium/mcs-2012-germa.pdf>>.
- Hower, J.C., Robertson, J.D., 2003. Clausthalite in coal. *Int. J. Coal Geol.* 53, 219–225.
- Hower, J.C., Ruppert, L.F., Eble, C.F., 1999. Lanthanide, yttrium, and zirconium anomalies in the fire clay coal bed, eastern Kentucky. *Int. J. Coal Geol.* 39, 141–153.
- Höll, R., Kling, M., Schroll, E., 2007. Metallogenesis of germanium – a review. *Ore Geol. Rev.* 30, 145–180.
- Hu, R., Qi, H., Zhou, M., Su, W., Bi, X., Peng, J., Zhong, H., 2009. Geological and geochemical constraints on the origin of the giant Lincang coal seam-hosted germanium deposit, Yunnan, SW China: a review. *Ore Geol. Rev.* 36, 221–234.
- Ivanov, V.V., Katz, A.Ya., Kostin, Yu.P., Meitov, E.S., Solov'ev, E.B., 1984. *Economic Types of Natural Germanium Concentrations*. Nedra, Moscow (in Russian).
- Jaskula, B.W., 2012a. Gallium. U.S. Geological Survey, Mineral Commodity Summaries. <<http://minerals.usgs.gov/minerals/pubs/commodity/gallium/mcs-2012-galli.pdf>>.
- Jaskula, B.W., 2012b. Lithium. U.S. Geological Survey, Mineral Commodity Summaries. <<http://minerals.usgs.gov/minerals/pubs/commodity/lithium/mcs-2012-lithi.pdf>>.
- Kalaitzidis, S., Siavalas, G., Araujo, C.V., Christanis, K., 2010. Late Cretaceous coal overlying karstic bauxite deposits in the Parnassus–Ghiona unit, central Greece: coal characteristics and depositional environment. *Int. J. Coal Geol.* 81, 211–226.
- Ketris, M.P., Yudovich, Ya.E., 2009. Estimations of clarkes for carbonaceous biolithes: world average for trace element contents in black shales and coals. *Int. J. Coal Geol.* 78, 135–148.
- Kislyakov, Ya.M., Shchetochkin, V.N., 2000. *Hydrogenic Ore Formation*. Geoinformmark, Moscow (in Russian).
- Kler, V.R., Volkova, G.A., Gurevich, E.M., Dvornikov, A.G., Zharov, Yu.N., Kler, D.V., Nenakhova, V.F., Saprykin, F.Ya., Shpirt, M.Ya., 1987. *Metallogeny and Geochemistry of Coal-bearing and Pyroschist-bearing Sequences*. Geochemistry of Elements. Nauka, Moscow (in Russian).
- Kostin, Yu.P., Meitov, E.S., 1972. About genesis of high-germanium coal deposits and criteria of their exploration. *Izvestia Acad. Nauk of USSR, Geology* 1, 112–119 (in Russian).
- Laverov, N.P. (Ed.), 1998. *In-situ Leaching of Polyelemental Ores*. Academy of Mining Sciences Publishing House, Moscow (in Russian).
- Lifton, J., 2009. <<http://www.jackliftonreport.com/2009/11/the-rare-earth-crisis-of-2009.html>>.
- Maksimova, M.F., Shmariovich, E.M., 1993. *Bedded-infiltrational Ore Formation*. Nedra, Moscow (in Russian).
- Mardon, S.M., Hower, J.C., 2004. Impact of coal properties on coal combustion byproduct quality: examples from a Kentucky power plant. *Int. J. Coal Geol.* 59, 153–169.
- Maynard, J.B., 1983. *Geochemistry of Sedimentary Ore Deposits*. Springer Verlag, Heidelberg.
- Qi, H., Hu, R., Su, W., Qi, L., Feng, J., 2004. Continental hydrothermal sedimentary siliceous rock and genesis of superlarge germanium (Ge) deposit hosted in coal: a study from the Lincang Ge deposits, Yunnan, China. *Sci. China Ser. D Earth Sci.* 47, 973–984.
- Qi, H., Hu, R., Zhang, Q., 2007. Concentration and distribution of trace elements in lignite from the Shengli coalfield, Inner Mongolia, China: implications on origin of the associated Wulantuga germanium deposit. *Int. J. Coal Geol.* 71, 129–152.
- Ratynskiy, V.M., Zharov, Yu.N., 1980. About gallium in coals. *Lithol. Min. Resour.* 5, 38–48 (in Russian).
- Rudnick, R.L., Gao, S., 2003. Composition of the continental crust. In: Rudnick, R.L. (Ed.), *The Crust Treatise on Geochemistry*, vol. 3 (Holland, D., Turekian, K.K., Exec. Eds.). Elsevier, Amsterdam, pp. 1–64.
- Seredin, V.V., 1996. REE-bearing coals from Russian Far East deposits. *Int. J. Coal Geol.* 30, 101–129.
- Seredin, V.V., 2004. Metalliferous coals: formation conditions and outlooks for development. In: Cherepovskiy, V.F. (Ed.), *Coal Resources of Russia*, vol. VI. Geoinformmark, Moscow, pp. 452–519.
- Seredin, V.V., 2006. Germanium deposits. In: Laverov, N.P., Rundkvist, D.V. (Eds.), *Large and Superlarge Ore Deposits*, vol. 3. IREM RAS, Moscow, pp. 707–736 (in Russian).
- Seredin, V.V., 2012. From coal science to metal production and environmental protection: a new story of success. *Int. J. Coal Geol.* 90–91, 1–3.
- Seredin, V.V., Chekryzhov, I.Yu., 2011. Ore potentiality of the Vanchin Graben, Primorye, Russia. *Geol. Ore Deposits* 53, 202–220.
- Seredin, V.V., Dai, S., 2012. Coal deposits as potential alternative sources for lanthanides and yttrium. *Int. J. Coal Geol.* 94, 67–93.
- Seredin, V.V., Finkelman, R.B., 2008. Metalliferous coals: a review of the main genetic and geochemical types. *Int. J. Coal Geol.* 76, 253–289.
- Seredin, V.V., Tomson, I.N., 2008. Metallogeny of Primorski Krai connected with Cenozoic rifting processes. In: Khanchuk, V.I. (Ed.), *The Pacific Ore Belt: Data of New Investigations*. Dalnauka, Vladivostok, pp. 192–209.
- Seredin, V.V., Chekryzhov, I.Yu., Popov, V.K., 2011. Rare metal-bearing tuffs of Cenozoic coal basins of Primorye generated by transform interaction of lithosphere plates. In: Khanchuk, A.I. (Ed.), *Geological Processes in Subduction, Collision, and Transform Environments of Lithosphere Plates Interaction*. Dal'nauka, Vladivostok, pp. 375–377.
- Seredin, V.V., Dai, S., Chekryzhov, I.Yu., 2012. Rare metal mineralization in tuffaceous strata of the Russian and Chinese coal basins. In: Yudovich, Ya.E. (Ed.), *Diagnostics of Volcanogenic Rocks in Sedimentary Strata*. Geoprint, Syktyvkar, pp. 165–167 (in Russian).
- Seredin, V.V., Kremetskii, A.A., Trach, G.N., Tomson, I.N., 2009. New data on the REY hydrothermal ores with extraordinarily high concentrations of rare earth elements. *Dokl. Earth Sci.* 425, 403–408.
- Shpirt, M.Ya., Kler, V.R., Perticikov, I.Z., 1990. *Nonorganic Components of Solid Fuels*. Chemistry, Moscow (in Russian).
- Sun, Y.Z., Li, Y.H., Zhao, C.L., Lin, M.Y., Wang, J.X., Qin, S.J., 2010. Concentrations of lithium in Chinese coals. *Energy Explor. Exploit.* 28, 97–104.
- Sun, Y., Zhao, C., Li, Y., Wang, J., Liu, S., 2012. Li distribution and mode of occurrences in Li-bearing coal seam # 6 from the Guanbanwusu mine, Inner Mongolia, northern China. *Energy Explor. Exploit.* 30, 109–130.
- U.S. Department of Energy: Critical Materials Strategy, 2011. <[http://energy.gov/sites/prod/files/DOE\\_CMS2011\\_Final\\_Full.pdf](http://energy.gov/sites/prod/files/DOE_CMS2011_Final_Full.pdf)>.
- Vulcan, T., 2009. Gallium: A Slippery Metal. <<http://www.hardassetsinvestor.com/features-and-interviews/>>.
- Wang, X., 2009. Geochemistry of Late Triassic coals in the Changhe Mine, Sichuan basin, southwestern China: evidence for authigenic lanthanide enrichment. *Int. J. Coal Geol.* 80, 167–174.
- Yudovich, Ya.E., Ketris, M.P., 2002. *Inorganic Matter of Coal*. UrB RAS, Ekaterinburg (in Russian).
- Yudovich, Ya.E., Ketris, M.P., 2004. *Germanium in Coals*. Komi Science Centre, Syktyvkar (in Russian).
- Yudovich, Ya.E., Ketris, M.P., 2005. *Toxic Trace Elements in Coal*. UrB RAS, Ekaterinburg (in Russian).
- Yudovich, Ya.E., Ketris, M.P., 2006. *Valuable Trace Elements in Coal*. UrB RAS, Ekaterinburg (in Russian).
- Zhuang, X., Querol, X., Alastuey, A., Juan, R., Plana, F., Lopez-Soler, A., Du, G., Martynov, V.V., 2006. Geochemistry and mineralogy of the cretaceous Wulantuga high-germanium coal deposit in Shengli coal field, Inner Mongolia, northeastern China. *Int. J. Coal Geol.* 66, 119–136.