Content of Microelements in Brown Coals of Transbaikal Region

G P Sidorova¹, A AYakimov¹, N V Ovcharenko¹
¹Mining faculty, Transbaikal State University, St. Alexander-Zavodskaya, d. 30, Chita, 672039, Russia

E-mail: yaa76@yandex.ru

Abstract. The coal deposits containing a complex of the major valuable microelements which have various degree of study are disclosed in Transbaikal territory. The analysis of geological material on coal deposits of Transbaikal region demonstrates great prospect for search and surveying of germanium-bearing coals in this territory. Gallium and beryllium at infrequent elements’ group is expedient to consider which are contained in local coals in the increased concentration connected among themselves. Content of these elements in coals it is caused by space exposure of coal and rare-metal deposits. The last include the production reserves of beryllium and they are a part of the Transbaikal region beryllium-bearing province in Russia. It is noted that some coal deposits of Transbaikal region have the increased content of rare-earth elements. Noble metals in the increased concentration are established in many assay of coal of various deposits that is caused by constant aurum content within the Transbaikal metallogenic province. There are data on content of valuable ore elements in coal deposits of the Transbaikal region, regularities of their placement depending on geochemical features of metallogenic provinces, conditions of accumulation and to form into various components of coals and also information about ore elements’ localization and their associations. The analysis of these data gives geological and technological characteristic to metal-bearing coals as to perspective complex of mineral raw materials. There are considered infrequent and diffuse elements, non-ferrous, noble, rare-earth and radioactive metals with concentration less than 0.1% as microelements in coals. According to the International Organization for Standardization 84 elements are detected in coals which belong to various groups of a periodic system of elements. 35-40 elements are found stably in coals of deposits of Russia in detection limits of mass analyses.

1. Introduction

The analysis of extensive material shows the concentration of the most of microelements in coals and their waste is at the level of percent abundance. At the same time it is identified that microelements’ distribution in coals extremely uneven. The microelements content vary widely within the deposit and even one coal-bed and coal-bed crossing, reaching on certain local sites very high concentrations having the production value [9, 10].

Now coals are the main source of germanium in the world. Uranium is recovered from coals and carbonaceous rock on an industrial scale. Gallium and molybdenum is recovered from coals it is also profitable. It is possible to utilize beryllium, scandium, boron, lead, zinc at the contents established now. There are premises for identification in the coals of concentration of selenium, vanadium, silver, aurum, rhenium and other elements which are of the production interest [7, 8, 12].
### Table 1. Minimum, average and limiting content of microelements in coals.

| Elements     | Average content of elements in coals g/t | Average content of elements on the enriched sites, g/t | Limiting content of elements, % | Minimum content of elements for assessment of its use in the industry, g/t |
|--------------|------------------------------------------|-----------------------------------------------------|---------------------------------|------------------------------------------------------------------|
|              | Brown coals | Black coals | Ash of brown coals | Ash of black coals | In coals | In ash of coals | In coals | In ash of coals | In coals | In ash of coals |
| Beryllium    | 2.4         | 2.0         | 11             | 21             | 20-25    | 0.02         | 0.2       | 5             | 20       |
| Borum        | 85          | 55          | 560            | 680            | 10000    | 0.2          | 1.2       | 2000          | 10000    |
| Vanadium     | 23          | 31          | 120            | 180            | 200-1000 | 0.2          | >1        | 100           | 500      |
| Tungsten     | 2-6         | 2.6         | 20-40          | -              | 25-100   | 0.15         | 1         | 30            | 150      |
| Gallium      | 7           | 7           | 36             | 51             | 20-40    | 0.05         | 0.55      | 20            | 100      |
| Hafnium      | 0.1-0.3     | 0.1-0.3     | 1-3            | -              | -        | -            | -         | 5             | 25       |
| Germanium    | 1.5         | 2.9         | 9              | 20             | 30-300   | 0.5          | >1        | 3.5-15        | 75       |
| Auran        | 0.001-0.003 | 0.001-0.003 | 0.02          | -              | >1       | 0.003        | -         | 0.02          | 0.1      |
| Indium       | 0.02        | 0.02        | 0.08           | -              | -        | -            | -         | 0.2           | 1        |
| Yttrium      | 7           | 6           | 37             | 47             | -        | 0.02         | 0.15      | 15            | 75       |
| Ytterbium    | 0.9         | 0.8         | 5              | 7              | -        | 0.002        | 0.02      | 1.5           | 7.5      |
| Cadmium      | 0.3         | 0.6         | 3              | 6.5            | -        | -            | -         | 1             | 5        |
| Cobalt       | 3.4         | 5.2         | 20             | 34             | 20-70    | 0.1          | 0.2       | 20            | 100      |
| Lanthanum    | 1.5         | 1.5         | 3-80           | 3-80           | -        | 0.02         | 0.1       | 150           | 750      |
| Lithium      | 20          | 25          | 80             | 150            | -        | -            | -         | 35            | 175      |
| Copper       | 7.5         | 18.5        | 48             | 80             | 200      | >1           | >10       | 100           | 500      |
| Molybdenum   | 2.4         | 3.0         | 13             | 25             | 10-150   | 0.3          | 0.6       | 6             | 30       |
| Nickel       | 8           | 16          | 51             | 90             | 100-200  | 0.1          | 0.1       | 100           | 500      |
| Niobium      | 1           | 1.8         | 5              | 12             | 100      | 0.02         | 0.74      | 10            | 50       |
| Stannium     | 1           | 1           | 4.1            | 7.5            | -        | -            | -         | 20            | 100      |
| Palladium    | 0.001       | 0.001       | 0.01           | 0.01           | -        | -            | -         | 0.005         | 0.025    |
| Platinum     | 0.001       | 0.001       | 0.01           | 0.01           | -        | -            | -         | 0.005         | 0.025    |
| Rhenium      | 0.001-0.01  | 0.001-0.01  | 0.1-1         | -              | >1       | >0.0001      | -         | 0.1           | 0.5      |
| Selenium     | tb1         | tb1         | -              | -              | -        | -            | -         | 1             | 5        |
| Argentum     | 0.3         | 0.4         | 1              | 2.5            | ~5       | 0.001        | 0.02      | 1             | 5        |
| Plumbum      | 2.5         | 25          | 53             | 170            | 100-500  | 0.3          | 3         | 240           | 1200     |
| Scandium     | 2           | 3           | 15             | 20             | 60-80    | 0.01         | 0.02      | 10            | 50       |
| Strontium    | 130         | 76          | 1100           | 460            | -        | -            | -         | 400           | 2000     |
| Antimony     | 0.5-2       | 0.5-2       | 5              | 10             | -        | -            | -         | 30            | 150      |
| Thallium     | 0.1         | 0.1         | -              | -              | -        | -            | -         | 1             | 5        |
| Tantalum     | 0.3         | 0.3         | -              | -              | -        | 0.005        | -         | 1             | 5        |
| Titanium     | 500         | 500         | 2600           | 4600           | ~10000   | >1           | 10        | 1500          | 7500     |
| Uranium      | 1-3         | 1-3         | -7             | -              | 3000     | ~1           | -         | 100           | 10000    |
| Chromium     | 12          | 16          | 70             | 86             | 10000    | ~1           | -         | 1400          | 7000     |
| Caesium      | 0.4-2       | -           | -              | -              | -        | 0.01         | 0.07      | 30            | 150      |
| Zincum       | 18          | 22          | 100            | 150            | 100-750  | 0.03         | >1        | 400           | 2000     |
| Zirconium    | 30          | 41          | 160            | 250            | 300-800  | 0.07         | 0.7       | 120           | 150      |
In general microelements in coals are studied insufficiently. Now no more than 5-10% of elements from all complexes are estimated and only 2-3% develops. Their slow use can be explained with weak geological and geochemical studying of coals and poor volume of technological researches. Therefore many microelements are not used and are lost forever doing environment contamination.

In the territory of Transbaikal region the coal deposits containing a complex of valuable microelements having various degree of study are indicated as a result of the analysis of materials of geological reports on exploration. Germanium-bearing coals deposits are held special position among them [1, 2].

2. Germanium-bearing coals
Brown coals in Transbaikal region are characterized by the increased and high content of germanium. Tarbagatai germanium-coal deposit is the industrial installation on mining of germanium raw materials.

The analysis of geological material on coal deposits of Transbaikal region demonstrates great prospect for search and surveying of germanium-bearing coals in this territory [23, 24, 25].

Inferred reserves and expected resources of germanium in coals in this region are distributed as follows:
1) The germanium reserves adopted by State Commission on Mineral Reserves - 380 tones;
2) Reserves are counted but were not adopted - 420 tones;
3) Expected resources - 650 tones.

Total reserves and expected resources of germanium in coals are now 1450 tones. They have very great density in relation to the active reserves of germanium in Russia and provide to Transbaikal region the leading position.

The coals containing germanium in the territory of the region are propagated widely. The strip of germanium-bearing coals from the East on the West is stretched on 700 km, and from the South on the North on 600 km forming the extensive area about 20 thousand sq.km.

The high and increased content of germanium in coals, a wide propagation of deposits in the territory of the region, larger prospects on opening of new local sites, blocks and beds allow to allocate the largest Transbaikal germanium-coal metallogenic province in Russia [1, 2, 11].

3. Infrequent and diffuse elements
Gallium and beryllium at infrequent elements’ group is expedient to consider which are contained in local coals in the increased concentration.

The average background content of gallium in coals is 10 g/t, local-high is 30 g/t and the limiting is 500 g /t of coal. The percent abundance of gallium in clay rocks is 30 g/t. Background coefficient of concentration to percent abundance is 0,3 g/t. Gallium can be considered as potentially valuable element in coal. It is the constant companion of germanium. Properties of germanium and gallium are very close. The minimum content of gallium is accepted 20 g/t counting on dry coal and in ash of coals is accepted 100 g/t for assessment of its use in the industry. Gallium it is propagate in coals extremely nonuniformly, on certain sites forming the local increased concentration also as other ore elements [13, 15, 16].

Region’s coals contain the increased concentration of gallium connected with a germanium. The average content of gallium in ashes of germanium-bearing coals is 77 g/t and in not germanium-bearing coals is 22,8 g/t. The largest content of gallium in coals belongs to the richest Tarbagatai germanium-coal deposit. It is established that the average ratio germanium-gallium to germanium-bearing coals is 1:0,2 and in not germanium-bearing coals is 1:3,5. Gallium differs in wide propagation in coals. The coefficient of occurrence is equal to 80-100% [1, 10, 18].

Brown coals of Transbaikal region have the increased content of beryllium. Presence of the last in coals isn't casual and caused by space exposure of coal and rare-metal deposits. The last include the production reserves of beryllium and they are a part of the Transbaikal beryllium-bearing province in Russia.

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Concentration of beryllium has practical value. Content of beryllium in ashes of germanium-bearing coals of the Tarbagatai and Mordoysky deposits is equal to 28 and 50 g/t. Content of beryllium in ashes of coals of certain local sites and beds of following deposits - Krasnochikovsky is 27 g/t, Zashulansky is 31-45 g/t, Pogranichny is 25-64 g/t, Badinsky is 38 g/t, Burtuysky is 21 g/t. High contents of beryllium are noted in coals of the Chitkandinsky deposit 300 g/t [25].

Uranium mineralization is typical for the Transbaikal metallogenic province. Industrial deposits and uranium manifestation are known in limits of the Transbaikal metallogenic province.

As some large uranium deposits are closely connected with coals (the USA, Germany, Sweden, etc.), it is possible also in the Transbaikal region presence of high concentration of uranium in coal deposits. Urtuysky coal deposit located near Streletsovsky uranium unit includes coal reserves with the increased high content of germanium. The province has prospect for the uranium-coal deposits which are especially close industrial uranium deposits [14].

The increased high content of niobium, strontium, borus is noted on certain local sites of coal deposits in the region. However it is possible to draw any conclusions on their using only after conducting special researches because of low study of their distribution in coals, forms of stay and lack of technology solutions on extraction of these elements [3, 14, 20].

4. Rare-earth elements
As a rule the average background content of rare-earth elements in coals, is less than their percent abundance in clay rocks. Background coefficient of concentration of the main rare-earth elements to percent abundance for scandium is 0.3 g/t for lanthanum is 0.04 g/t for yttrium is 0.3 g/t and for ytterbium is 0.3 g/t.

Rare-earth elements are propagated widely in coals despite insignificant contents. Some coal deposits of Transbaikal region have the increased contents of rare-earth elements. Kharanorskoye and Urtuyskoye of brown coals deposits especially differ on the content of the basic rare-earth elements. The high contents of rare-earth elements are noted in ashes of coals of the Nerchugansky deposit and the sum of rare-earth elements is 800 g/t.

It should be noted that rare-earth and other rare elements are still not revealed on many coal deposits. One of the reasons is the use not enough precise and sensible methods of the analysis [17,19].

5. Noble metals
Au, Ag and platinoids are established in coals in group of noble metals. Data on determination their concentration and placement aren’t enough and. The available analyses on noble metals confirm their propagation in coals extremely nonuniformly. It complicates identification of regularities of their placement, formation and the decision on the prospects of their use. The average background content of Au in coals is 0.01 g/t, local-high is 1-5 g/t and the limiting is 40 g/t of coal. The percent abundance of Au in clay rocks is 0.008 g/t., background coefficient of concentration to percent abundance is 0.3 g/t, Au can be considered as potentially valuable element in coal. Conditions for quantitative studying of aurum’s propagation arise at his content in coals at 0,02 g/t and at 0,1 g/t in ashes of coals.

The raised aurum-bearing is established in many assay of coal of various deposits that is caused by constant aurum content within the Transbaikal metallogenic province. 48 from 104 ore units have accurate geochemical specialization on Au. In Mordoysky deposit Au was defined by an assay method in 48 tests, in 37 tests (coefficient of aurum’s occurrence in tests is 75%) and aurum content in ashes of coals is revealed from 0,04 to 0,6 g/t. On the Ureysky deposit aurum content in ashes of coals is revealed from 0,04 to 0,15 g/t in 52 tests from 96.

It is revealed visible Au in samples from core a borehole in Tigninsky coal-bed on the southern flanks of the Tarbagatai deposit.
To determine Au and Ag in coals of the region they selected tests of 10 coal deposits. In total it have been taken 28 samples which have shown the content from traces of Au and Ag is up to 34 g/t in ashes of coals and only two tests were ore-free from them.

Neutron-activation and assay analyses have established high (0,1-0,85 g/t) concentration of Au in the integrated tests of coals which is associated with the increased content of rare elements of the Kharanosky deposits. Here aurum’s concentration is 10-86 times higher than average background values for coals of Transbaikal region. The average of argentum’s content in coals of Kharanosky deposit low also makes 0,03 g/t. Level of concentration and propagation of Au in coals nomintates Transbaikal region as an object for carrying out check-auditing works to Au for the purpose of identification of the local enriched sites and their assessment for passing mining [2,5,6].

6. Conclusion
The analysis of the data about content of valuable ore elements in coal deposits of the Transbaikal region, regularities of their placement depending on geochemical features of metallogenic provinces, conditions of accumulation and to form into various components of coals and also information about ore elements’ localization and their associations gives geological and technological characteristic to metal-bearing coals as to perspective complex of mineral raw materials.

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