

# Native Metals in Far Eastern Brown Coal (Russian Federation)

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## Research

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# Abstract

Metal-bearing brown coal and coal ash can have a practical importance as the alternate sources of metals. Brown coal of Sutarsk and Ushumunsk deposits, as well as other coal deposits of the Far East, contain rare and rare-earth, precious and ferrous metals. At a comprehensive approach they can be sequentially extracted from ashes of coals in a production string. The possibility of metal extraction heavily depends on mode of their occurrence and grain size. In coals and coal ash of the researched deposits metals are localized in various mineral phases: oxides, sulfides, carbonates, phosphates, in a native mode of occurrence and as a part of intermetallic compounds. Particles are usually fine (1-30 microns). Gold, silver, copper, bismuth, iron, titanium, tungsten, zinc, barium, alloy of rare earths (cerium - lanthanum - neodymium) are found in native mode of occurrence. The interesting fact is that mode of occurrence of metals typical both for the reduction and oxidizing conditions are observed in one sample. It is necessary to account for the processing and extraction of metals from coal ashes that the most mineral particles are small and characterized by various morphology and composition.

## 1 Introduction

Metalliferous coals have attracted much attention because the concentrations of rare metals in the ashes of some coals are equal to or higher than those found in conventional types of rare metal ores (Seredin and Finkelman 2008; Seredin and Dai 2012). Anomalously high Au and PGE contents ( $\approx 0.2$  ppm in the ash), which could be extracted as by-products from sufficiently large resources, have been found at almost 100 coal deposits and mines worldwide. Au and Au-PGE ores in carbonaceous rocks have been exploited for a long time in many countries, whereas similar mineralization in the coal-bearing sequences is still regarded as exotic, with unclear prospects. Meanwhile, growing information on anomalous Au and PGE concentrations and/or finding of Au and PGE minerals in coal deposits and ash-slag waste of power stations indicates that precious metal mineralization is also abundant in coal-bearing sequences and has economic potential (Seredin 2007).

Rare metals, including Ge, Ga, rare earth elements and Y (REY, or REE if Y is not included), Li, Sc, Se, Zr, Hf, Nb, Ta, platinum group elements, Au, Ag, Re, and U, as well as the base metal Al, are enriched not only in the coals but also, in some cases, in the roof and/or floor rock of the coal bed, and in non-coal bands (partings) within the coal seams (Seredin and Finkelman 2008; Dai et al. 2010, 2014; Seredin et al. 2013; Zhao et al. 2013, Dai et al. 2015).

Ketris and Yudovich (2009) report that the average content of precious metals and PGE in world coals are: 0.095 ppm Ag, 3.7 ppb Au and 0.035 ppm Pt (total); higher concentrations are considered to be anomalous. The average concentrations of Au for world low-rank and hard coals are 3.0 and 4.4 ppb, respectively (Ketris and Yudovich 2009). These researchers put special attention on inorganic matter of coal (IOM) (Yudovich and Ketris 2016).

According data derived by V.V. Seredin (Seredin and Shpirt 1995) high concentrations of several valuable trace elements were found in a number of Siberian and Russian Far East deposits. South China and South Primorye of Russia are considered to be the world's largest coal-hosted ore districts (Dai et al. 2015).

The chalcophile trace elements are associated with pyrite and other sulfides in coal, but those of lithophile participate in carbonates or clay minerals (Swaine and Goodarzi 1994; Huggins 2002).

Pb, Li, Mo, and Cu are probably associated with organic matter in coal. The chalcophile elements such as As, Cd, and Co are bound in sulfide minerals. The majority of elements such as Si, Al, Ca, Mg, and Cd show a higher degree of removal, while Mo, Li, Pb, and Cu because of their affinity to organic matter and As, Co and Fe because of their affinity to syngenetic pyrite (Rajabzadeh et al. 2016).

Volatile elements such as As, B, Hg, Cl, Cr, Se and most prominently S, condense on the surface of the fly ash particles (Kukier 2003).

As, B, Hg, Cl, Cr, Se, S, and Cd, Cu, Mo, Sb, V and Zn are also preferentially enriched on the surface, whereas Ba, Co, Cr, Mn, Ni and Pb tend to be more evenly distributed between the surface and the matrix (Jones 1995).

Precious metals concentrations (Au and Ag) up to commercial grade were found in Russian coals (e.g. Arbuzov and Mashen'kin 2007; Bakulin and Cherepanov 2003; Seredin 2007). Coal containing only about 50 ppb Au and PGE can be considered as precious metal ores (Bakulin and Cherepanov 2003). Au can also be accumulated in fly ash. In this case, by analogy with Ag and Ge, we can expect that precious metal concentrations in fly ash, particularly in its finest fraction, are at about ten times higher than in the initial solid fuel. In addition to native gold, whose fineness is strongly variable, coal-bearing sequences can contain kuestelite, as well as Cu- and Hg-bearing gold (Seredin and Finkelman 2008). It was demonstrated, for example, that Au extraction from wastes of the Reftinsk power station, Urals, is profitable at its average contents in coal combustion products of 0.1–0.2 ppm (Leonov et al. 1998).

Minerals with notable Os and Ir contents are found in Khurmulin'sk coal deposit (Russian Far East, Amur river region); they contain 89–90 % Os, 10–12 % Ir, 0.5–15 % Pt and 20–25 % Os, 50 % Ir, 15–25 % Pt, and 1–3 % Fe (Bakulin and Cherepanov 2003). Large positive Ce anomalies have been observed in high-REY Fe-Mn oxyhydroxide ores in the Cenozoic coal-bearing sequences of the Pavlovka deposit of Far East Russia (Seredin and Dai 2012; Dai et al. 2016).

The possibility of utilization of major elements such as Al, Si, Fe and Ti, and trace elements such as V, Ga, Ge, Se, Li, Mo, U, Au, Ag, Pt groups and rare earth elements (REEs) and other beneficial products such as magnetic materials, cenospheres, and unburned carbon from coal fly ash attracts the increasing attention of the scientists and businessmen who are engaged in processing of anthropogenic raw material (Sahoo et al. 2016).

Many reports and studies indicate that some Russian Far Eastern coals are enriched by valuable metals and we would like to represent the results of research of metal bearing potential of Sutarsk and Ushumunsk deposits. Current paper is devoted to a research of the native elements located in brown coal, coal ash and the clay minerals of the Ushumunsk and Sutarsk deposits (Far East, Russian Federation). The fact that metals in coal and coal ash are at the same time in several modes of occurrence (such as a native form, oxides, sulfides, carbonates, phosphates, silicates or related to organic matter) can be the complicating moment of technology of extraction of metals from ash coal.

## **2 Samples**

The Ushumunsk and Sutarsk brown coal deposits are located in the South of the Far East of Russian Federation, in the Jewish Autonomous Region. The samples were collected from 5 prospecting wells located on the area about 2 sq.km (Sutarsk deposit) and on a vertical profile of operating coal mine of the Ushumunsk deposit.

## **3 Analytical Procedures**

The element composition of coal was defined by spectral, chemical-spectral, X-ray fluorescence and ICP-MS methods of the analysis.

### **3.1 Scanning electron microscopy**

Samples of coals, coal ash and clay minerals were powdering for electronic-microscope researches. The electronic and microscopic research of samples was conducted on the raster electronic microscope "EVO 40HV" (Karl Zeiss, Germany) equipped with the power dispersion analyzer "INCA-ENERGY 350". The most often applied accelerating voltage is 20 kV, cathode-ray current ~ 200 picoamperes.

The detector of back dispelled electrons (QBS detector) was used in the process of analysis. By means of the QBS-detector, phases with higher average atomic number are reflected more brightly in comparison with phases with smaller atomic number. As the difference of atomic weights of a matrix and inclusions is great, we have got more contrast images, allowing visual revealing of metal inclusions. The structure of a matrix and the inclusions was compared. Despite of inaccuracies of definition of carbon and hydrogen, micro-mineral phases of metals are defined with feasible accuracy. The power dispersion analyzer "INCA-ENERGY 350" was used to carry out a local quantitative chemical analysis of a sample. Sensitivity of a method makes ~ 0.1 % (wt.). Width of an electron beam is ~ 20–30 nanometers. Depth of its penetration is ~ 1 micron.

## **4 Geological Setting**

### **4.1 Ushumunsk deposit**

*Ushumunsk deposit* of brown coals is located 30 km to the southeast of Birobidzhan. Sedimentary, effusive and intrusive rocks of Paleozoic, Mesozoic and Cainozoic age are presented in a geological structure of the area. The deposit is represented by the erosive and tectonic mould structure which is a constituent of complex-structured Birofeldsk graben located in a South-West part of the Middle-Amur valley. Cainozoic and Mesozoic components compose the base and frames of the deposit.

Chernorechensk and Ushumunsk suites are coal-bearing. The industrial-scale Ushumunsk suite (N1 u š) lies down on Birofeldsk suite. It consists of tuff-genic formations, siltstones, argillites, thin layers and lenses of fine-grained sandstones, gravelite, conglomerates, carbonaceous argillites, numerous coal interlayers and layers. Three coal layers of Ushumunsk suite are investigated; thickness of seams is 3.5; 0.7 and 0.5 m.

## 4.2 Sutarsk deposit

*Sutarsk deposit* of brown coal is located at the highest levels of Sutarsk ferromanganese deposit which is stretched for 14 km with a width up to 3 km in the northeast direction in the Valley of Sutara River and bond with the western iron-ore strip of Small Hingan.

Cambrian metamorphosed rocks of the iron-ore deposit are blocked by friable carboniferous Paleogene-Neogene sediments with 30–310 m thickness (Mukhinsk and Buzulinsk suites  $\square_3 mch-N_1 bz$ ). The section of carboniferous series is presented by the complex alternation of the aleurite- and carbon-containing clays with lenses and layers of brown coals, siltstones, sands with impurity of pebbles and gravel. Thickness of brown coal interlayers is from 1 to 13 m. Montmorillonite clay are found in some sections. The clay component has hydro-micaceous structure; siltstone fraction is presented by quartz and single grains of feldspar and augite.

Macromineral inclusions in coal is presented by kaolin clay 3–10 %, quartz, gypsum, feldspar, magnetite (1–5 %), single grains of pyrite, marcasite, manganese minerals, zircon, pomegranate, titanite, leucoxene.

## 5 Results And Discussion

### 5.1 Trace elements content

By the results of researches (Lavrik et al. 2011; Rasskazova et al. 2013) brown coal ash (produced by laboratory coal combustion,  $t = 800\text{ }^{\circ}\text{C}$ ) of the Ushumunsk deposit contain on average: Au 0.4 ppm, Pt 0.11 ppm; Ag 0.25 ppm, W 124 ppm; Sb 33 ppm; Nb 14 ppm; Ge 2 ppm; Ga 32 ppm; Y 235 ppm; Yb 6 ppm; Zr 273 ppm; Sc 36 ppm; Rb 127 ppm; V 145 ppm; Sr 848 ppm; Cu 278 ppm; Cr 102 ppm; Ba 2211 ppm; Co 193 ppm; Hg 21 ppm, Fe 4.6 % (in limits of an operating coal pit).

Coal ash of Sutarsk deposit contain by results of the spectral and X-ray fluorescence analysis (on average): Au 0.37 ppm; Pt 0.084 ppm; Pd 0.03 ppm; Ag 1.1 ppm; Ti 3953 ppm; V 76 ppm; Cr 90 ppm; Mn 745 ppm; Co 49 ppm; Ni 26 ppm; Cu 180 ppm; Zn 47 ppm; As 36 ppm; Rb 136 ppm; Sr 1107 ppm; Zr 339

ppm; Sn 10 ppm; Sb 15 ppm; Ba 863 ppm; W 76 ppm; Hg 42 ppm; Pb 48 ppm; Bi 0.7 ppm; Li 14 ppm; Ge 6 ppm, Fe 4.2 % (Lavrik et al., 2011; Rasskazova et al., 2013).

Some rare-earth metals (Ce, La, Nd, Y, Gd, Dy, etc.) are found in coals and coal ash of the researched deposits. Their summary content in coal ash makes about 300 ppm for each of deposits by results of ICP-MS.

The highest contents of metals can be found with low-ash coals, with high-ash coals and contact zones of coals and clay interlayers. However, detection of native elements does not depend on concentration of metal in the sample and its location inside the section.

## 5.2 Mineral associations in coal ash

Native mode of occurrence of iron, nickel, tungsten, zinc, silver, barium (?), intermetallic compounds (Cr-Fe, Fe-Ti, Al-Cu-Ag) and Nd-La-Ce-Si-P alloys are found in Ushumunsk brown coal deposit. Native mode of occurrence of iron, gold, silver, titanium, zinc, bismuth, intermetallic compounds (Fe-Cr-Cu, Cu-Zn) are found in coal and coal ash of Sutarsk deposit.

### 5.2.1 Iron (Fe)

Iron in fly ash is mainly present as magnetite mixed in various proportions with hematite, although a minor proportion can be assimilated in the glassy matrix (Kukier et al. 2003). Spinel structures are highly stable and resistant to weathering, and therefore Fe, and any isomorphously substituted elements, are not easily released to the environment. Iron oxyhydroxides are also present in fly ash (Dudas 1981).

Native iron is found in all sampling points of an open-cast: in coal, coal ash and clay minerals from coal interlayers. The size of detected grains varies from submicrons to 15–20 microns. Morphology of iron grains and composition of impurities are various even inside the same sample. Native iron is detected in the form of almost ideal microspheres; prismatic-shaped short crystals with flat and the arched basis (we can suppose that the crystal was formed in the moving process) (Fig. 1); prismatic long spear-shaped crystals; flocculent grains characterized by the intergrowth with potassium feldspars, with cryolite, etc.; in the form of the improper lumpy grains. Silicon (Si) and clay substance can be found as an impurity in native iron.

The grains of native iron found in brown coals of Sutarsk deposit have the irregular shape in most cases: smooth drop-shaped, angular fibrous, arched lamellar with a porous surface, lumpy spongy. Spongy grains have the non-uniform composition in their different parts: from clear iron to chrome - ferruginous compound. Inside the pore aluminosilicates are detected.

Besides native iron the intermetallic chrome-ferruginous compounds are detected in material of brown coal deposits. The ratio of Cr:Fe is 1:7 or 1:8 in these compounds. Grain size is from 5–7 microns to 50 microns. Morphology of chrome-ferruginous grains is various: lamellar aggregates with jagged edges; lumpy irregular-shaped grains; fibrous and rod-shaped grains with hackly edges; lumpy-crystal aggregate

(10 microns) with the incipient crystal of a cubic shape. Grains of intermetallic compounds Cr-Fe are found in coals, coal ashes and in coal clay minerals.

Native iron with various grain morphology makes up to 50% of all found grains of minerals in sample. Intermetallic compounds (Cr-Fe, Ti-Cr-Fe) are observed in association with iron, they are in the intergrowth with olivine, cryolite, barite; native nickel, microspheres of FeO (wustite); sphalerite with Fe, Hg impurities; marcasite with Nb; chalcopyrite with Hg; arsenopyrite, cotunnite  $\text{PbCl}_2$ ; anglesite  $\text{PbSO}_4$ ; delafossite  $\text{CuFeO}_2$ ; barite; witherite with impurities of iron and a tungsten, strontium;  $\text{TiO}$  titanium dioxides; turnerite; rare mineral bismoclite ( $\text{BiOCl}$ ), native tungsten, horny  $\text{WO}_2$  grains with Co; mendipite ( $\text{PbCl}_2 \cdot \text{PbO}$ ),  $\text{ZrSiO}_4$  zircon. Native titanium is found together with grains of native iron in coal samples of Sutarsk deposit.

## 5.2.2 Nickel (Ni)

Huggins with co-authors (1999) stated that the mode of occurrence of Co, Ni and Mn in ash is more dependent on similarities in the ionic radii than on the chalcophilic or lithophilic nature of the elements. Such similarities would favour their crystallization from the melt into Fe oxides. These elements are primary associated with Fe-bearing species (e.g. spinel-like structures). D. Misch et al. (2016) reports that direct evidence for the modes of occurrence of Ni is lacking, although Dale et al. (1999) reported that Ni may be either organically bound or associated with sulfides.

We have found a grain of native nickel (with iron impurity up to 5%) in one coal sample of Ushumunsk deposit. Aggregates about 5 microns are drop-shaped with hackly edges. Intermetallic compound ( $\text{CrFe}_8$ ) in association with native nickel is found in the sample; arsenopyrite, marcasite with Nb impurity, anglesite  $\text{PbSO}_4$  and delafossite  $\text{CuFeO}_2$ , pyrite with impurity of a cobalt and nickel. Rare Ni minerals are noted in coals and clay interlayers. They are violarite  $(\text{Ni, Fe, Co})_3\text{S}_4$ , copper silicide with nickel  $(\text{Cu, Ni})_2\text{Si}$ .

## 5.2.3 Tungsten (W).

Tungsten is relatively non-volatile, and its hexavalent state is thermodynamically very stable in ash (Cornelis et al. 2008). Scheelite ( $\text{CaWO}_4$ ) has been detected in coal fly ash (Vassilev and Vassileva 1996). A native tungsten is rarely mentioned in scientific literature. According to Dai et al. (2014), tungsten, similar to and closely associated with Ge, occurs in secondary minerals (mainly as complex oxides and seldom as carbides) and as an impurity in the glass of the Ge-rich ashes. Tungsten-bearing minerals, if not admixed with Ge, are members of an isomorphic series  $\text{CaWO}_4$ ,  $\text{FeWO}_4$  with various Ca/Fe ratios.

Tungsten is found in the form of single grains (3 microns) with triangular section and the laced friable congestions consisting from the tabular crystals (Fig. 2). Grains are triangle-shaped with slightly concaved sides and the truncated top with small spherical barnacles nearby. Other micromineral associations of a tungsten found in Ushumunsk deposit coals and clay minerals also have unusual composition: tungsten oxide  $\text{WO}_2$  with Co impurity, tungsten oxide  $\text{WO}$  with impurities of a cobalt and chlorine, tungsten oxide  $\text{WO}$  with impurity of a cobalt and copper, tungstenite  $\text{WS}_2$ . Ratio of a tungsten and cobalt varies.

## 5.2.4 Zinc (Zn)

The findings of Querol et al. (1996) underline the fact that the mode of occurrence in coal plays a critical role in the behaviour of Zn in ash. Querol et al. (1996) attributed high Zn mobilities in ash to the fact that much of the Zn was in sulphide association in the parent coal. Despite the well known affinity for sulphur during combustion, Zn would appear to have an important glass association (50–60 %) in UK fly ash (Spears 2004). Kim and Kazonich (2004) an even distribution of Zn between the silicate and non-silicate fractions.

Native zinc is found in coal ash (Fig. 3) and in coal clay minerals. A zinc grain has an irregular oblong lamellar shape with rough surface (it consists of interlocked square or rectangular plates). The size of association is about 30 microns. Native zinc grain (5 microns) has the lumpy form in the clay. We guess that it is composed by intergrow of cubic crystals. Chemical composition of grains is close, Zn content is about 89 % (weight) with Fe impurity and clay substance.

Sphalerite as single crystals and various joints of isomeric and irregular form prevails as other mineral formations of zinc in coals and clay. Native zinc is associated with ilmenite, barite, pyrite, celsian, sphalerite, pyrotine, iron oxide FeO (wustite) and turnerite in samples.

## 5.2.5 Rare-earth metals (Ce, La, Nd)

One isomeric grain (a rounded dipyrmaid) of unusual structure – natural Ce-La-Nd alloy (?) with phosphorus, silicon, aluminum and thorium (their distribution in a crystal is nonuniform) is found in coal of Ushumunsk deposit (Fig. 4). Content of rare-earth metals makes up to 83% (weight). Usually all rare-earth metals are localized in coals and clay minerals of Ushumunsk deposit as a part of a turnerite as single grains and accumulations of 1–8 microns. The structure of turnerite is changeable. Silicates like cerite and a thalenite are less often found in a form of the tabular and lamellar joints.

Marcasite, melanterite, barite, intermetallic Cr-Fe compound, zircon, a turnerite, native Zn, iron oxides – wustite and hematite are found in association with natural alloy of rare-earth metals in the sample.

## 5.2.6 Titanium (Ti)

Titanium commonly replaces Si in clays. Since clay minerals in coal give rise to the glassy matrix of fly ash during combustion, Ti is assimilated and retained within the aluminosilicate glassy matrix along with silicon. The findings of Warren and Dudas (1988) pointed to an almost exclusive partitioning of Ti into the internal matrix of ash particles.

Single grain of a native titanium is found in coal of Sutarsk deposit (Fig. 5). Coal ash content is 25.9 %. Coal contain clay lumps and plant residues. Native titanium grain (about 6 microns) has the detrital tabular form of presumably square section. Grain surface is irregular, porous (?) with silicate inclusions.

Native iron, pyrotine, complex Fe, Sr, Mn, Ca and W carbonates; bismite with Pb together with native titanium are noted in the sample. Native zinc (Zn) is also noted in coal ash of this sample. Titanium

mode of occurrence is most often rutile, ilmenite, titaniferous magnetite and columbite and xenotime as impurities in coals of Sutarsk deposit.

## 5.2.7 Silver (Ag)

Native silver is found only in 3 coal samples and coal clay. Copper impurities are observed in all cases with Ag:Cu = 10:1 atomic ratio. Native silver is observed in the form of cubic or lamellar crystals in intergrowth with anorthoclase in clay. In coals native silver is located in the form of rounded ribbed grain (3 microns) and oblong prismatic (or barrel-shaped) grains with uneven surface. The structure of the latter association is more complex; it also contains aluminum except copper. The atomic ratio of metals is Ag (10): Al (5): Cu (1). Silver grains are apparently covered with cerargyrite (AgCl) as a surface coating. Barium sulfide and barite with strontium and arsenopyrite impurities are noted in association with native silver in samples.

## 5.2.8 Gold (Au)

Fine-grained (from submicrons up to 3–5 microns) native gold is found in coal and coal ash in the form of single spherical and irregular-shaped grains, friable aggregations. Similar forms are characteristic also for gold macro-formations. Gold contains Ag and Fe impurities. In certain cases, gold is found in the coal ash lumps of the complex composition (Fe-Zr-Cr-W-Ti) of nano-size. Turnerite, fibrous grains of Cr-Fe intermetallic compound; barite (in coal), sphalerite, zincite, strontianite, xenotime, titaniferous magnetite, bismite are noted in coal ash together with native gold in samples.

## 5.2.9 Copper (Cu)

According experimental data derived by Kukier et. al. (2003) Cu is associated both the magnetic and non-magnetic fraction of fly ash samples.

Most authors, suggest that Cu to be mainly bound to chalcopyrite and other sulfides (Goodarzi 1987; Hower et al. 2000; Querol et al. 2001; Zhuang et al. 2012). However, additional modes of occurrence where reported by Dai et al. (2015), who found Cu to be associated with rare Cu-bearing minerals like krutaite (CuSe<sub>2</sub>) and eskebornite (CuFeSe<sub>2</sub>) in U-rich coals of the Yili Basin (northwestern China).

In current research macroscopic associations of native copper are found in several samples. Oblong grains (up to 5 microns) of native copper with zinc impurity up to 30% (native brass) with uneven clastic edges are found in micromineral mode of occurrence in coal ashes. Strontianite with impurities of W, Zr, Se (in the form of the complex globular associations and single grains), turnerite, globular witherite with Sr impurity are noted in the sample together with native copper. Other minerals of copper and zinc (copper-glance, zincite, sphalerite, zinc spar) are also noted along with native mode of occurrence.

Native bismuth occurs in the form of single irregular-shaped grains and aggregates (3–6 microns) and native barium, forming a coating on the barite surface, is also found in coal of Sutarsk deposit.

## 6 Conclusions

Native elements (Fe, Ti, Ni, Bi, W, Zn, Cu, Au, Ag, Ba) and intermetallic compounds or alloys (Fe-Cr, Fe-Cr-Cu, Fe-Ti, Cu-Zn, Ce-La-Nd-P-Si) are found in micromineral mode in coal, coal ashes and the clay minerals of Ushumunsk and Sutarsk deposits. The native mode of occurrence of noble metals in coal and coal ashes was noted by V. V. Seredin (Seredin and Finkelman 2008) in deposits of Primorye Territory and by V. I. Rozhdestvina (Rozhdestvina and Sorokin 2010) in deposits of the Amur Region. A set of native elements and intermetallic compounds is various for different deposits. However, there is something common for all deposits. Four types of native elements are located in coal, coal ash and clay minerals: 1) typical native elements - Au, Ag, PGE; 2) metals with a noticeable tendency to a presence in native mode of occurrence - Bi, Cu, Pb; 3) metals which native mode of occurrence is very rare and connected with specific reduction conditions – Fe, Ni, Co, Sn, W, Zn; 4) elements which native mode of occurrence appear only in an exclusive situation – Si, Ti, Al, Be, La, Ba, Sr, etc. Presence of metals simultaneously in several conventionally incompatible micromineral phases is characteristic of all coals deposits. These phases are oxides, sulfides, silicates, phosphates, carbonates, haloids, and rare compounds. The morphology of grains and a fine-dispersed condition of the substance are characteristic too (from submicrometer up to tens of microns). Micromineral compounds are found in a crystal and detrital forms, in the form of the irregular, lumpy, lace, lamellar, cloudy, spongy grains and agglomerations in coal. Globular and spherical shapes of native elements are often observed. All this is bound to features, specificity of formation of metal-bearing coals, to a variety, complexity and duration of the processes, defining a terminating metal content of coals and the bearing strata. In the process of consideration of a paragenesis of all found microminerals, including native ones, we can conclude that there are mineral compounds of all possible genetic types, including meteoric and volcano emissions in coals in an equilibrium position.

Localization of many metals in a fine-grained native mode of occurrence in coal is not the unique phenomenon. The modern technical capabilities and interest in a microcosm allowed findings of native lead and zinc in rocks of the Kuznetsk Alatau granitoid massif (Novgorodova 1983). Native mode of occurrence of Au, Sn, Cd, Fe and Ce-La-Nd in the form of flake, irregular and spherical shapes, numerous native elements and intermetallic compounds in a form of nano-films and impurities are found on the surface of diamonds (Belikova and Salikhov 2008; Lyutoyev and Filippov 2005) in rocks of the Kola superdeep well. Native elements are known in meteorites and lunar rocks, in sedimentary rocks, in the basalt of traprock, in kimberlites, in post-magmatic hydrothermal rocks, in the black-shale strata (Medvedev 2012) and in naphthoid, vein aggregates and bearing strata of oil and gas basins (Fe, Cr, Ni, Ti, Ag, Pb, Zn, Sn, In, Ag-Cd) (Lukin 2007). Native elements and various intermetallic compounds are found in the ash and in high-temperature gas jets of Kamchatka volcanoes (Fe, Au, Ag, Pt, Cu, Pb, Zn, Bi, Ti, Al, Si, W, etc. up to 50 elements) in the form of the irregular-shaped, lamellar and spherical particles (Karpov et al. 2012).

Therefore, not only alluvial minerals can be a source of metals in coal. We suppose they are also volcanic ash, the deep fluids which took part in formation of coal layers.

According to Seredin (2012), it is obvious that coal deposits should be investigated from the point of view of valuable elements content. The author considers that it is extremely important to conduct full

geochemical analysis of coals, not limited only to toxic or technologically important elements for coal power production, as tends to be the case. It is necessary to consider in the processing and extraction of metals from coal ashes that mineral associations are fine, have a various morphology and structure.

## Declarations

**Availability of data and materials** The experimental data presented in this study are available on request from the corresponding author.

**Competing interests** The authors declare no conflict of interest.

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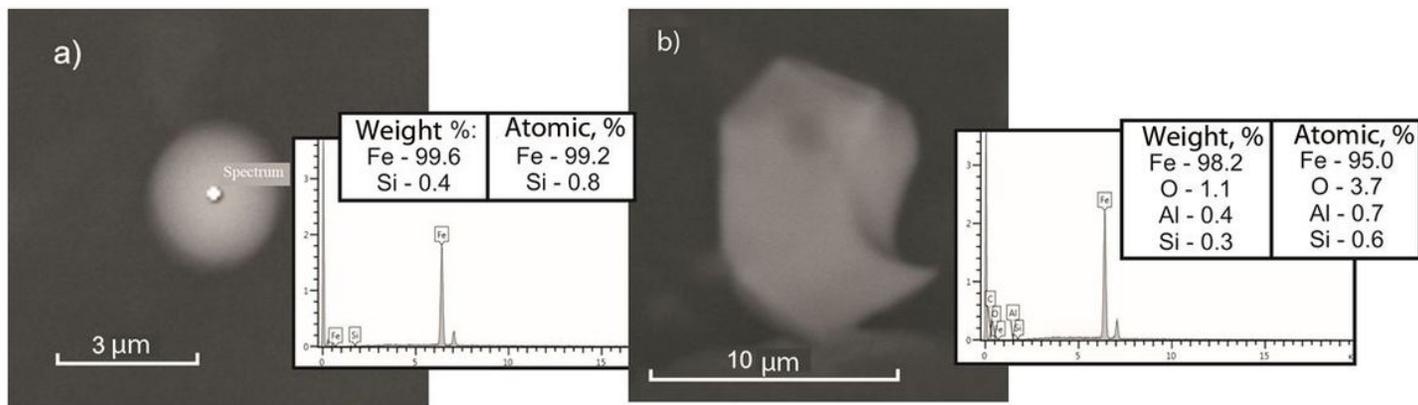
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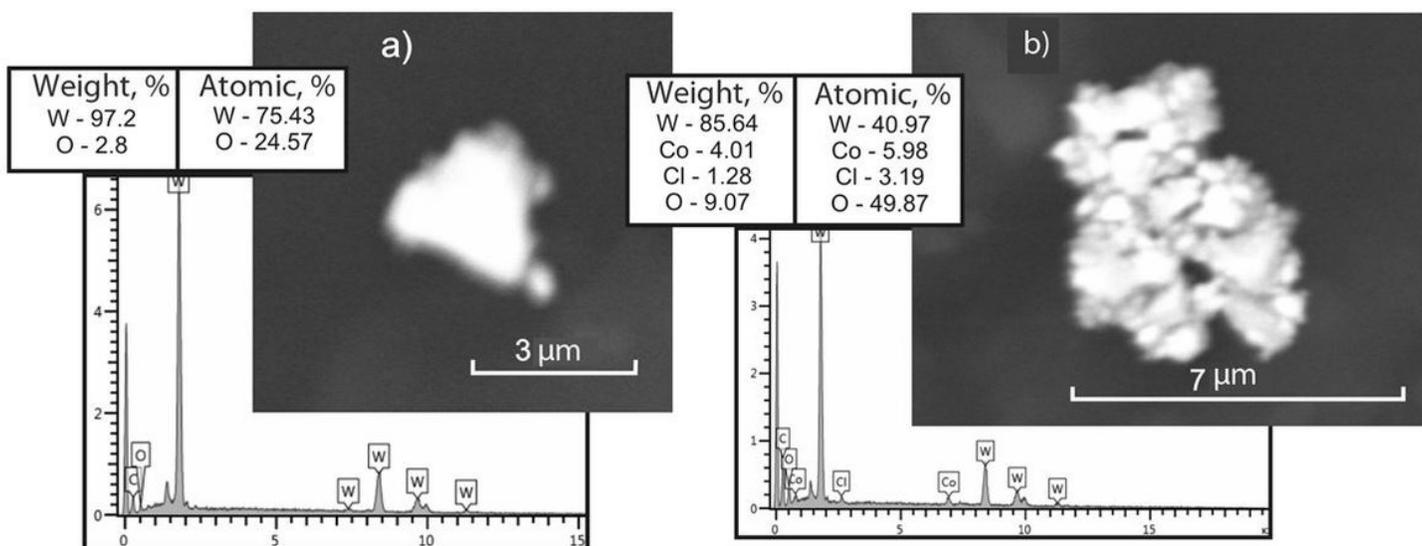
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## Figures



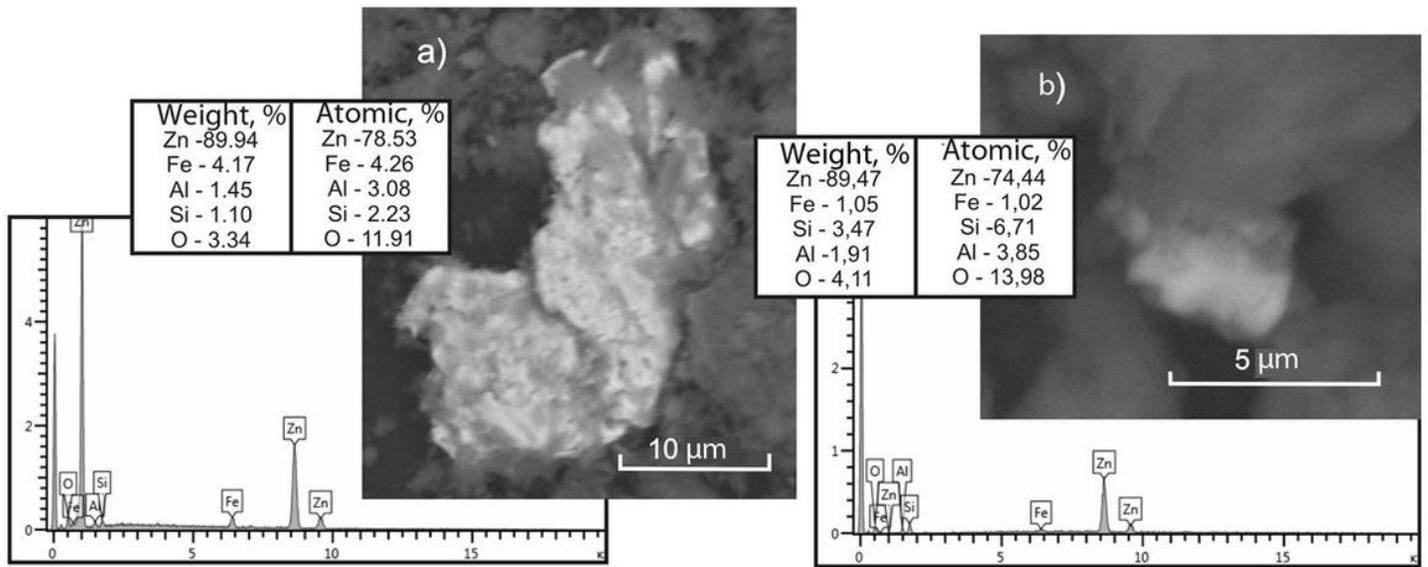
**Figure 1**

Micrograins of native iron of various morphology in brown coals of the Ushumunsk deposit: a) microsphere, b) arched crystal



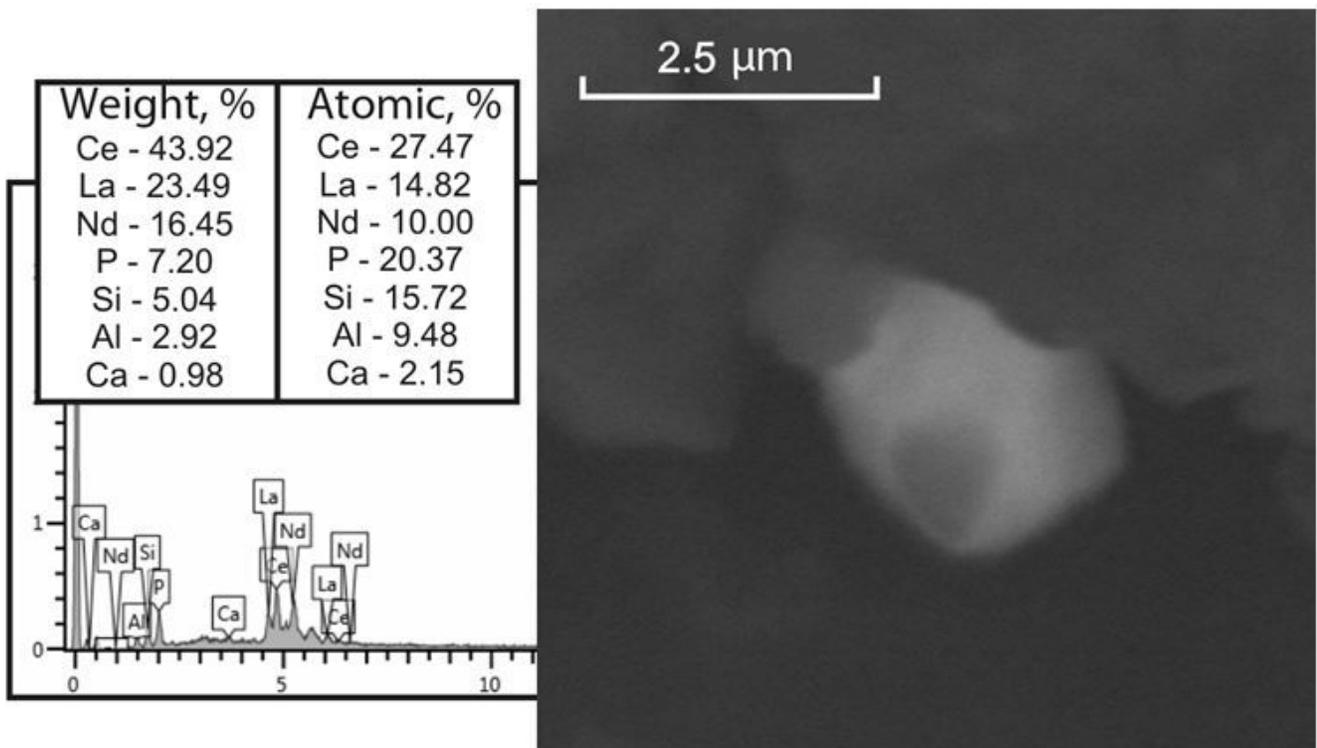
**Figure 2**

Associations of a tungsten in brown coal of Ushumunsk deposit: a) single crystal of a native tungsten; b) lace accumulation of tungsten oxide crystals with impurity of cobalt, chlorine and copper



**Figure 3**

Native zinc in Ushumunsk deposit coal: a) lamellar form grain in coal ashes; b) lumpy grain from clay of coals interlayers



**Figure 4**

Isomeric (dipyramidal) grain of natural alloy (?) Nd-La-Ce-P-Si with a non-uniform distribution of impurities in brown coals of Ushumunsk deposit

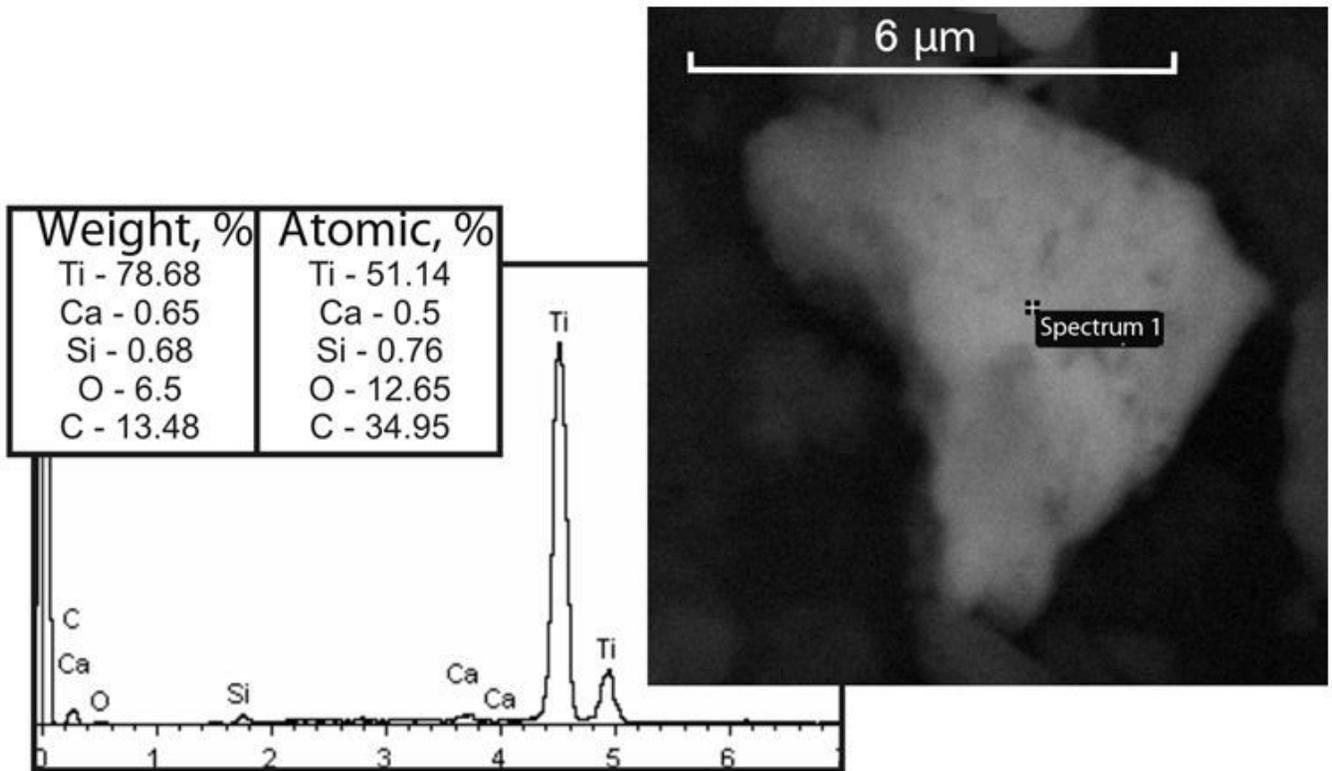


Figure 5

Detrital tabular grain of a native titanium in brown coal of Sutarsk deposit