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Geology, geochemistry, mineralogy and genesis of the Spetsugli high-germanium coal deposit in the Pavlovsk coalfield, Russian Far East

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ABSTRACT

The geology, mineralogy, and geochemistry of the Spetsugli high-germanium coal deposit in the Pavlovsk coalfield were studied. The deposit is characterized by the complex polyelemental composition of the ores and can be evaluated as a complex rare metal-coal deposit. The metal-bearing coals of the deposit are characterized by abnormally high, tens or even hundreds of times greater than the mean contents for brown coals of the world, for Ge, Sb, Hg, W, Li, Be, Cs, and As. Somewhat less anomalous are the levels of accumulation of U, Mo, Y, Rb, medium and heavy lanthanides, Zn, and Ga. Detailed mineralogical and geochemical characteristics of the germanium mineralization and associated anomalous concentrations of W, Sb, Hg, As Li, Be, Cs, U, Mo, Y, Rb, and HREE are described in the paper. The variations in concentrations were studied in vertical profiles and laterally. Complex mineralogical-geochemical and geological-structural analysis of the composition and structural features of the Spetsugli Ge-coal deposit allow us to revise the accepted hydrothermal model of the Ge mineralization formation in coals and substantiate the previously proposed hypergenic model for deposits of this type. The new data are in good agreement with the hydrogenic hypergenic model of the formation of complex Ge coal deposits where the source of metals is the basement rocks or the coal-bearing depression margins. The formation of the Ge and associated mineralization in the Spetsugli deposit was controlled by the weathering crust formation on hydrothermally altered rare metal granites of the Voznesenk Complex, broken through by the Late Permian dikes. The isotopic ages of the granites (448.2 Ma) and dikes (263.6 Ma) were determined and also the rhyolitic tuffs (25.1 Ma) which overlie the Eocene-Oligocene coal- bearing sediments in the basin. The isotopic age of the granites (448.2 Ma), dikes (263.6 Ma), and rhyolite tuffs overlapping the carbonaceous deposits (25.1 Ma) was determined. The rare metal mineralization is related to the basement protrusion in the centre of the deposit, forming a concentric-zone halo of Ge and associated elements around it. The basement protrusion granites were hydrothermally altered to form quartz-albite-microcline metasomatites and greisen containing the W-Mo and Hg-Sb-As mineralization. The metasomatically altered granites and dikes were transformed into a kaolin weathering crust as a result of late hypergenic alterations, with destruction of primary endogenous mineralization and removal of major elements to the surrounding paleopeatlands. Both types of endogenous mineralization in granites and dikes have anomalous accumulation of W, Mo, Sb, Hg, As, Li, Rb, Cs, Be, U, Y, lanthanides, Zn and Ga in the germanium-bearing coals during the Eocene- Oligocene time.

1. Introduction

Germanium is the main by-product element in coal, the extraction of which has been developed by industry. The Spetsugli germanium coal deposit, discovered in the mid 1960 s, is currently one of the largest deposits in the world and the only one of this kind in Russia. Similar deposits are known and exploited in China (Zhuang et al., 1998a, b; Zhuang et al., 2006; Du et al., 2009; Hu et al., 2009; Dai et al., 2012; Dai et al., 2015a; Dai et al., 2015b). Their main common feature is the complex nature of the ores, which include tungsten, beryllium, antimony and other valuable trace elements in addition to germanium.

Despite more than half a century of research on the Spetsugli germanium deposit and the commercial exploitation of most of it, the discussions about its nature are ongoing. The main unresolved issue so

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far is the nature of the source of the germanium and other associated elements. According to some authors the ores are products of the weathering (crust) of the basin's surroundings and the basement rocks, whereas other authors have attributed the source to hydrothermal solutions. The first model, suggested early in the study of the deposit, was called the hypergenic model (Saprykin and Bogdanov, 1967, Saprykin, 1978; Vyalov et al., 2012; Vyalov et al., 2020). The second model was proposed a few years later and has been variously termed the hydrothermal-sedimentary, exhalation-sedimentary or exfiltration model (Kostin and Meitov, 1972; Kostin et al, 1973; Ivanov et al., 1984; Levitsky et al., 1994 ; Seredin and Danilcheva, 2001; Sedykh, 1999; Seredin, 2003a; Seredin, 2003b; Seredin, 2006; Seredin and Finkelman, 2008; Dai et al., 2015b; etc.). This second model was originally based on a study of peats with high germanium concentrations in the Nalychevsk depression of the Kamchatka Peninsula, which is in a zone of thermal springs (Kostin and Meitov, 1972). The attractiveness of this model is the similarity of geochemical associations of the majority of germanium-coal deposits of the world, explained by the input of these elements by hydrotherms synchronous to the coal accumulation.

At present, the Spetsugli deposit is being mined for the germanium-bearing coals by an open-pit method. The deposit has been exploited to its full depth, including the basement, that allows us not only to model the deposit structure but also to visually observe and study it and to map the traces of various geological processes that took place there in different geological periods. This current paper is devoted to the analysis of new geological and geochemical data obtained in the last decade in order to compare two basic hypotheses on the origin of the deposit and to develop a geological and geochemical model of its formation. The solution of this issue is not only of great scientific importance, but is also extremely important in the exploration of similar mineralization in other areas.

2. Geological location of the deposit

The Spetsugli germanium deposit is located within the Voznesenk terrain, which is part of the Khankiysk superterrain. The latter region is in close proximity to the Voznesenk ore district, known for its W, Sn, and fluorite deposits associated with Paleozoic granitoid magmatism (Fig. 1) (Khanchuk, 2006). The deposit is located within the Usuriysk-Voznesensk Mn-Fe-rare metal- fluorite metallogenic zone. The metallogeny of the zone is very complex (State geological map of the Russian Federation, 2011). The main ore-forming epochs were in the the Proterozoic and Early Paleozoic with several stages of ore genesis. In addition, the complexity of the structure was increased by the overlapping subsequent, Paleozoic-Mesozoic stages of tectonic-magmatic activation. Graphite and Fe-Mn mineralization is connected with

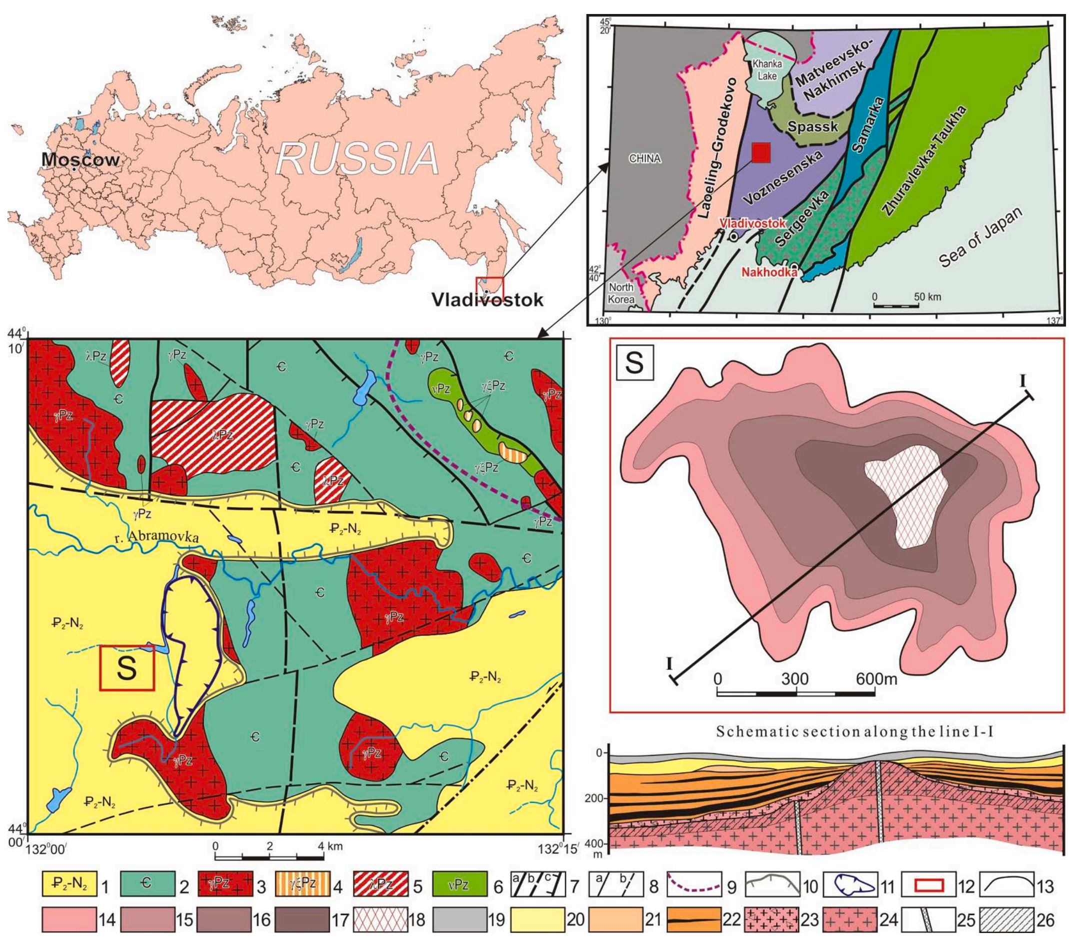

Fig. 1. Location and geological map of the studied area (by State geological map of the Russian Federation, 2016) with changes and supplements of the authors), scheme of the Ge distribution and geological cross-section of the Spetsugli deposit. Legend: 1 - Paleogene-Neogene sandy-pebble (Neogene) and coal-bearing sediments (sandstones, siltstones, claystones and coals) (Paleogene); 2 - Cambrian sediments (sericite, quartz-sericite and carbonaceous slates, siltstones, limestone lenses); Paleozoic magmatic rocks: 3 - granites; 4 - granosyenite; 5 - rhyolite; 6 - gabbro and gabbro-diorite; 7 - major faults: a- proven, b-predicted, c- overthrusts; 8 - secondary faults: a- determined, b- predicted; 9 - Voznesenky ore district; 10 - boundary of coal-bearing deposits of the Pavlovsk coal field; 11 - Pavlovsky-2 working area; 12 - contour of the Spetsugli deposit area (C); 13 - contour of the industrial mineralization with the Ge content in coals (ppm): 14 - greater than50; 15 - greater than200; 16 - greater than400; 17-greater than1000; 18 - basement outcrop; Deposits: 19 - modern soft sediments; 20 - Neogene slightly lithified sediments; 21 - tuff and tuffite lenses; 22 - Paleogene carbonaceous sediments; 23 - redeposited weathering crust; 24 - intrusive rocks (granites); 25 - dikes; 26 – Pg weathering crust.

ancient stages of the Riphean and Early Cambrian ore genesis. The fluorite, rare metal mineralization confined to the fracture structures of active zones of the lithium-fluorine granites of the Voznesenk complex is connected with the early Paleozoic stages. The Spetsugli germanium deposit is confined to the Voznesenk ore district. Fluorite is the essential mineral of the area, but tin, tungsten, zinc, lead–zinc, and rare metal (Ta, Nb, Li, Rb, Cs, Be) mineralization also widely occurs (Kononets et al., 2008; State geological map of the Russian Federation, 2011). Ordovician granites of the Voznesenk complex, represented by two varieties (porphyraceous biotite tourmaline-bearing granites and leucocratic biotite-protolothionite granites), have primary significance in ore-formation (Ryazantseva et al., 2003; Kononets et al., 2008). Vein tin deposits with tungsten and vein cassiterite-silicate-sulfide deposits are associated with the former. The latter ones are accompanied by intense boron metasomatosis and minor beryllium-fluorite mineralization. Tantalum (with niobium) commercial mineralization is genetically associated with the rare metal Voznesenk granites (State geological map of the Russian Federation, 2011).

The deposit is located in the eastern part of the Pavlovsk depression (Fig. 1), one of the depressions that make up the Pavlovsk coalfield (Pavlyutkin et al., 2005). The general features of the geological structure of the Spetsugli germanium coal deposit within the Pavlovsk brown-coal deposit have been described in detail in numerous works (Seredin, 2003a, 2006; Sedykh, 2008; Vyalov et al., 2012; Kuzevanova, 2014; Arbuzov et al., 2021a).

The deposit is located 2–3-km from the eastern side of the largest Pavlovsk depression, part of the Pavlovsk group of depressions which unite overlapping Cenozoic depressions formed by Cenozoic sediments with commercial coal deposits. The germanium bearing strata of the depression frame a protrusion in the basement composed of Paleozoic granites. The basement rocks were weathered and formed a well-developed, thick kaolin weathering crust. Paleozoic granitoids and Cambrian sericites, quartz-sericites, carbonaceous slates, and siltstones with limestone lenses dominate in this part of the depression.

3. Research methods

The study included investigation of the open-cut sections in the central part of the germanium coal deposit, sampling of the coal seams, coal-bearing rocks, basement rocks, groundwater, and surface water and their study by modern analytical methods.

In 2018–2021 detailed mapping of the open pit was carried out and several sections were sampled. In each section three to five coal samples were taken from each available coal, as well as the samples of the coal-bearing rocks and thin rock layers in coal seam. At the basement, stripped in the process of the deposit exploitation, the structure of the deposit was studied and samples were taken of the weathering crust of the granites, andesite dikes, and the remnant of the greisenized granite. Eighty samples of coal and coal-bearing rocks were collected in total. In addition, surface and drainage waters from the coal seams and from the settling pond directly within the open pit were sampled (10 samples). The sampling diagram of the section is shown in Fig. 2.

For comparative purposes a small number of samples (27) were taken from the coal seams adjacent to the granitic basement and the basement itself at the Pavlovsky-2 site located 1.5–2.0 km north-east of the Spetsugli germanium deposit (Fig. 1).

The study of the matter composition was carried out using a complex of modern analytical methods. The composition of trace elements was studied by inductively coupled plasma mass spectrometry on the spectrometer Agilent 7700x (Agilent Techn., USA) at the Laboratory of Analytical Chemistry of the Center for Collective Use in Far-East Geological Institute (FEB RAS, Vladivostok, Russia). The element contents in the coals were determined using two methods of the sample preparation: with preliminary ashing and without ashing with chemical decomposition (Zarubina et al., 2021). Direct element determination in the coals without pre-ashling allows high quality detection of Ge, As, Sb,

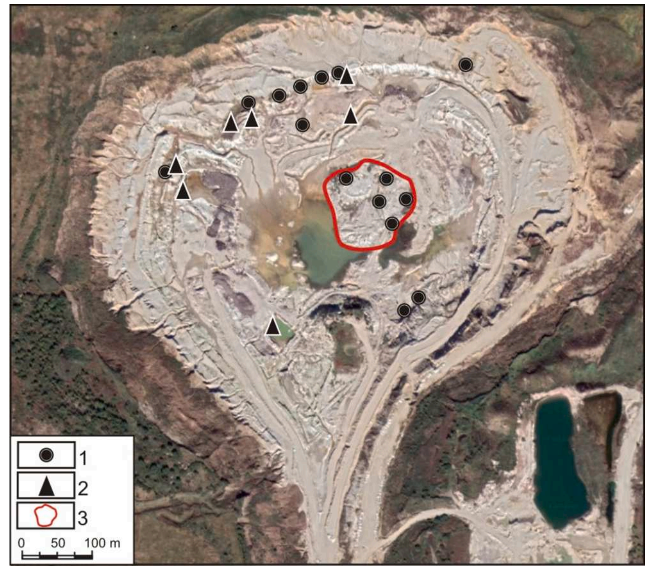

Fig. 2. Scheme of the sampling, host rocks and water in the coal mine. (Photo source - Google maps) 1 – coal sampling areas, coal-bearing rocks and basement rocks; 2 - water sampling areas; 3 - surface contour of the granite protrusion.

Tl, and other volatile elements. The contents of 29 elements were also parallelly evaluated by INAA method. The analysis was performed at the Nuclear Geochemical Laboratory of the International Research Scientific Educational Center (IRSEC) "Uranium Geology" at Tomsk Polytechnic Universtity (Tomsk, Russia).

The mercury content was determined by atomic absorption analysis on the spectrometer RA-915 + using RA915P software package (PND F 16.1:2.23–2000) at the IRSEC "Uranium Geology". The samples were analyzed using the PIRO-915 pyrolytic attachment (pyrolysis method).

The isotopic age of granites and andesite dikes of the basement as well as tuffs in the coal sequence was determined by U-Pb method on zircons on SIMS SHRIMP-II (Secondary Ion Mass-Spectrometry by Sensitive High-Resolution Ion Micro Probe) at the Isotopic Research Center of Federal State Enterprise "VSEGEI" (St. Petersburg, Russia).

The mineral composition of the coals and rocks was studied by optical microscopy and X-ray phase analysis at the IRSEC "Uranium Geology" (Tomsk, Russia). X-ray phase analysis was performed on the X-ray diffractometer Bruker D2 Phaser with Bregg-Brentano geometry imaging. The standard imaging parameters were: Cu (copper) anode, 30 kV X-ray tube voltage and 10 mA current. The measurement angles 2θ for bulk sample composition analysis were 3° to 140°, rotation – 10 rpm, exposure time – 1.5 s per point, and 0.02° step. The minimum volume fraction of the mineral to be determined was 1%. Eva and TOPAS software packages based on X-ray powder diffractometry PDF2 databases of the International Center for Diffraction Data (ICDD, Denver, USA) were used for the interpretation of the X-ray diffractograms.

The micromineral phases were investigated at the IRSEC "Uranium Geology" on the scanning electron microscope "Hitachi S-3400 N" with the attachment for quantitative elemental analysis "Bruker". This technique allows to identify and photograph mineral forms of micron and nanometre dimensions, to determine their elemental composition.

The correlation analysis was made by Spearman rank correlation method.

The chosen set of analytical methods enables a comprehensive study to be made of the components of the coal and mineral material composition of coals and rocks.

4. Features of the geological structure of the deposit

Basement. The basement of the Pavlovsk Depression is heterogeneous. It is represented by the Cambrian sedimentary-volcanogenic strata of the Grigorievsk series composed of quartz-sericite, sericite-chlorite, coal-graphite schists, sandstones, siltstones, tuffs, tuffites, felsic lavo-breccias and, rarely, interlayers of limestone (State geological map of the Russian Federation, 2016). Magmatic rocks, predominantly Paleozoic granitoids, also play an important role in the basement structure (Fig. 1).

The composition of the basement in the Spetsugli area is more homogeneous. It is represented by medium-grained granites with single dikes of presumably basite composition and a well-developed kaolin weathering crust. The weathering crust thickness reaches 40–50 m (Levitsky et al., 1994). The granites are biotitic and greisenized. In connection with this complex, outside of the uncovered part of the basement, skarn bodies distributed in the contact zone of granitoids and carbonate rocks were also described by Levitsky et al. (1994). The relief of the basement in the depression is highly differentiated. The difference in the paleorelief between uplands and lowlands in some 40–80 m. Consequently, the thickness of the Cenozoic sediments in the area varies from 42 to 200 m (Levitsky et al., 1994). Five areas of high relief in the basement have been identified within and in the vicinity of the deposit area, one of which is located in the centre of the Spetsugli germanium deposit. The distribution of the areas of high relief in the basement allows us to consider them as relicts of the watershed of the river net that existed before the formation of the Pavlovsk Depression. The absence of *syn*-depositional and post-depositional faulting and folding in the basement and overlying sediments does not provide grounds for attributing these uplifts to syndepositional uplands, as previously suggested (Ivanov et al., 1984).

Currently the basement within the central protrusion has been uncovered by coal extraction. Eluvial weathering crust on the granites has been well preserved in this area. The structure of the granite is well preserved and there is no evidence of tectonic disturbance such as brecciation, cataclasis, and mylonitization zones. Vertical zoning of the weathering crust, expressed in the replacement of the disintegration zone by hydromica-kaolinite and kaolinite zone is observed. The relict structure of the granite is preserved through the whole section. In the centre of the protrusion, under the weathering crust, there is a remnant of slightly weathered greisenized granite. The granite, according to the TAS classification, belongs to the group of normal-alkaline to moderately alkaline leucogranites. The alkali content is 6.9–8.6 %, the silica content is 73–76% (Table 1).

Within the boundaries of the granite body in the open cut, there is also an outcrop of a dike of presumably andesite composition with well-preserved fine-grained relict structure. No traces of tectonic activity after the formation of the weathering crust with the formation of disintegration zones attributable to thermal solution migration pathways were identified. Hydrothermal-metasomatic zoning caused by hydrothermal processes after the formation of the weathering crust within the basement rocks was also not identified. The unweathered granites studied in the open pit are subject to albitization, microclinization and superimposed greisenization. The greisenization is weak, mainly in the form of muscovite development on feldspar, biotite chloritization and formation of specific accessory mineralization. Early albite-microcline metasomatic transformations are also accompanied by the formation of secondary green biotite. Diverse mineralization, represented by sulphides (molybdenite, arsenic pyrite, galena), as well as cassiterite, phosphates and fluorine carbonates of rare-earth elements, was identified in the greisenized granites.

The age of the granites from the central protrusion determined by the U-Pb method (SHRIMP-II, AC VSEGEI) is 448.2 ± 4.1 million years (Fig. 3).

The results of the isotopic age analysis along with the geochemical features of the granites allow us to refer them to the Voznesenk complex of rare metal protolithionite granites (Rub & Rub, 1994, 2006). The studied granites are characterized by anomalous radioactivity with the thorium content ranging from 38.8 to 118 ppm and the uranium content from 10 to 37.6 ppm (Table 2).

The studied samples of the double-mica granite are also characterised by abnormally high contents of a large group of rare elements (REE, Y, Be, Rb, Cs, Nb, Se, Hf), W, Sn, and chalcophile elements (Mo, Pb, Sb, Ag, As, Co).

The age of the dike in the granites determined by U-Pb method (SHRIMP-II, AC VSEGEI) is 263 ± 1.6 Ma, which corresponds to the Late Permian period (Fig. 4). Earlier these dikes were considered to be Late Cretaceous (Levitsky et al., 1994) and even Cenozoic (Seredin, 1998). They were associated with hydrothermal rare metal mineralization in the Pavlovsk depression margin and in the coal-bearing sediments in the Spetsugli area (Seredin, 1998, 2006). It follows from the new data that the formation of the dikes is significantly separated in time from the coal formation period.

No large tectonic faults were identified within the Cenozoic sedimentary cover near the deposit (State geological map of the Russian Federation, 2016). There is also no evidence of any in the basement within this area of the coal-bearing depression. However, some tectonic activity was noted in the study area, not only by the presence of the Late Paleozoic dikes, but also by the general inclination of coal-bearing sediments from 2 to 12° in the western direction towards the centre of

Table 1
Chemical composition of the weakly altered granites from the basement of the Spetsugli deposit, %

Components	SU-81-19A	SU −81-19B	SU-81-19C	SU −55-18
SiO_2	73.01	76.17	75.31	74.56
TiO_2	0.52	0.14	0.34	0.27
Al_2O_3	11.11	11.60	11.82	13.63
Fe_2O_3	6.10	2.69	3.21	1.22
MnO	0.13	0.03	0.05	0.03
CaO	0.49	0.16	0.56	0.25
MgO	0.48	0.12	0.19	0.13
K_2O	4.05	6.17	3.85	5.13
Na_2O	2.85	2.46	3.44	3.06
P_2O_5	0.09	0.05	0.10	0.08
H_2O-	0.04	0.07	0.17	0.28
LOI	1.05	0.27	0.53	1.04
Sum	99.91	99.92	99.57	99.68
$K_2O + Na_2O$	6.90	8.63	7.29	8.19

Note: LOI – losses of ignition.

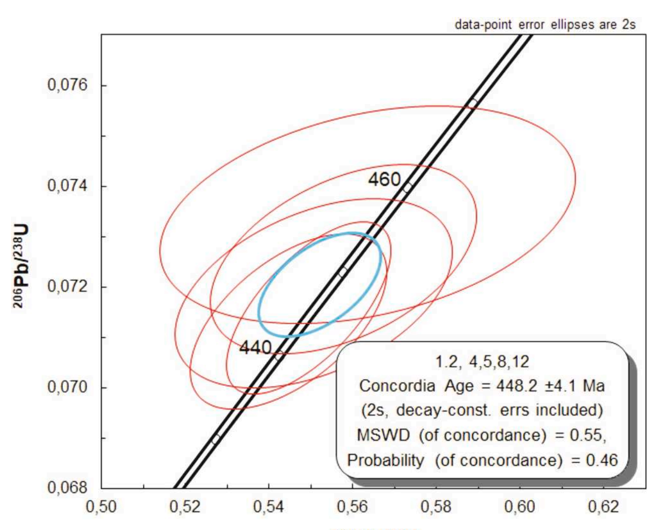

Fig. 3. U-Pb data for zircon grains (n = 6) of the sample SU-1–18 Concordia diagram. Age, MSWD and probability are for the concordant grains with discordance of less than 10 %. N is for the number of filtered zircon analyses from which concordia age was calculated (shown by red ellipses). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 2
Contents of trace elements in the granites of the basement, ppm.

Element	SU-63–19	SU–81-19A	SU-81-19B	SU-81-19C	SU-55–18	SU-62–19	Granite*
Li	52.4	92.6	27.0	36.7	28.1	45.5	37.0
Be	6.7	6.1	3.2	8.3	3.9	6.0	3.6
Sc	14.1	18.2	5.9	8.9	8.1	8.0	6.5
V	19.1	32.1	13.8	16.0	6.8	18.0	38.0
Cr	7.1	8.5	7.6	3.1	6.2	4.2	5.6
Co	55.6	34.2	15.1	60.0	14.3	1.2	1.0
Ni	4.5	4.3	4.1	5.6	0.4	1.2	3.5
Cu	5.8	11.4	10.0	21.0	4.0	3.7	10.0
Zn	69.7	100.1	37.9	59.9	49.6	56.0	39.0
Ga	30.0	30.6	24.2	34.6	36.3	36.7	18.0
Ge	3.0	2.4	1.9	2.7	25.7	3.2	2.8
As	35.2	3.5	3.1	9.5	72.8	2.6	1.6
Se	8.9	6.0	1.6	12.8	47.5	4.9	0.07
Rb	396	386	593	327	311	357	180
Sr	101	80	89	98	82	49.3	150
Y	378	270	101	156	467	154	50
Zr	130	230	100	94	193	219	180
Nb	35.9	76.3	29.8	51.6	38.4	57.7	21
Mo	3.7	5.0	7.4	4.7	1.8	0.48	1.5
Ag	0.46	0.48	0.26	0.18	0.21	0.27	0.038
Cd	0.75	0.42	0.58	0.29	0.27	0.14	0.17
Sn	9.4	14.6	4.9	8.9	6.0	11.9	3.0
Sb	4.9	1.7	1.0	2.7	7.4	1.2	0.2
Cs	7.0	8.1	5.5	6.0	7.1	11.2	5.0
Ba	397	314	463	294	406	242	750
La	414	261	196	652	1063	207	48
Ce	1124	609	338	1193	991	95.3	72
Pr	79.1	62.8	44.7	128	250	55.6	7.4
Nd	221	250	173	484	808	196	31
Sm	54.3	61.9	40.0	107	187	36.3	7.5
Eu	2.6	2.5	1.9	4.2	8.4	2.1	1.4
Gd	52.7	51.3	31.8	78.4	118	33.7	6.8
Tb	9.5	9.0	4.8	11.1	17.4	4.5	1.1
Dy	54.0	56.0	27.9	54.7	88.0	26.2	5.0
Ho	10.5	9.4	4.3	7.1	12.8	5.0	1.3
Er	30.9	31.0	12.4	18.6	32.4	15.7	3.1
Tm	4.1	4.3	1.7	2.1	4.6	2.4	0.3
Yb	28.5	32.1	11.8	13.5	26.5	16.0	4.0
Lu	3.9	3.9	1.5	1.5	3.1	2.4	0.9
Hf	4.3	9.1	4.2	4.1	5.4	8.5	3.9
Ta	2.9	7.2	2.0	3.5	2.1	4.3	3.6
W	17.4	11.1	5.9	11.4	15.3	20.8	2.2
Tl	3.5	2.5	3.5	2.6	n.o	1.9	1.9
Pb	35.1	44.6	41.1	39.6	94.5	105	18
Th	38.8	60.2	67.4	118	52.6	64.1	18
U	10.5	19.5	13.1	10.0	37.6	25.9	3.9
∑REE	2089	1444	890	2755	3610	698	190

Note: * granite averages for the World, according to (Grigoriev, 2003).

the coal-bearing depression, as well as the inclination of the basement in the same direction. Tectonic activity, expressed in the formation of cataclase and mylonitization zones in the Paleozoic granitoids and Cambrian shales, is also evident in the mountain-faulted margin of the Pavlovsk depression. In this connection, a hydrothermal (?) REE mineralization is known in dikes and associated mudstones to the east of the Pavlovsky- 2 section of the Pavlovsk brown coal deposit (Seredin, 1998). Tectonic active zones of post- coal shear origin were identified within the same area 2-km north-west of the Spetsugli germanium deposit as well as in the Yuzhny area (Sedykh, 2008).

Coal-bearing sediments. The coal-bearing strata of the Eocene-Oligocene age are composed of grey, greenish-grey mudstones, siltstones, and sandstones. In addition, the section contains thick horizons of white quartz sands and isolated lenses of conglomerates. A horizon of ash tuffs of rhyolitic composition is present in the strata at the boundary of the coal-bearing and overlying sediments. Its age determined by U-Pb method (SHRIMP-II, AC VSEGEI) is late Oligocene (25 ± 0.2 Ma) (Fig. 5). The isotopic age of the tuffs corresponds well with modern paleontological data (Pavlyutkin et al., 2005).

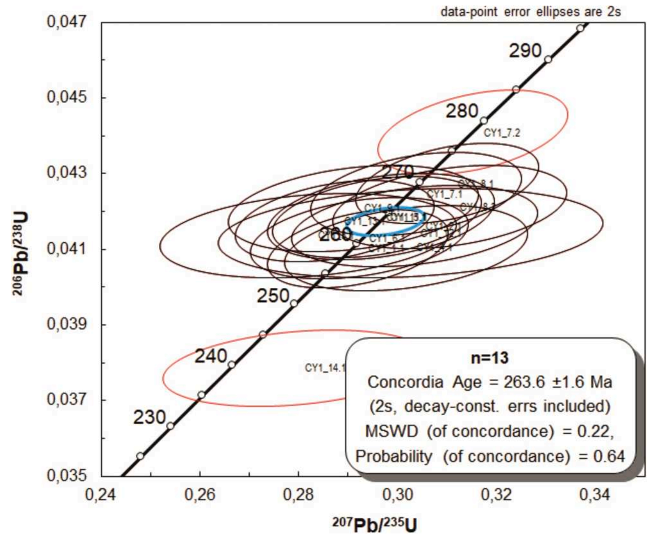

Fig. 4. U-Pb data for zircon grains (n = 13) of the sample SU-2–18 Concordia diagram. Age, MSWD and probability are for the concordant grains with discordance of less than 10 %. N is for the number of filtered zircon analyses from which concordia age was calculated (shown by brown ellipses).

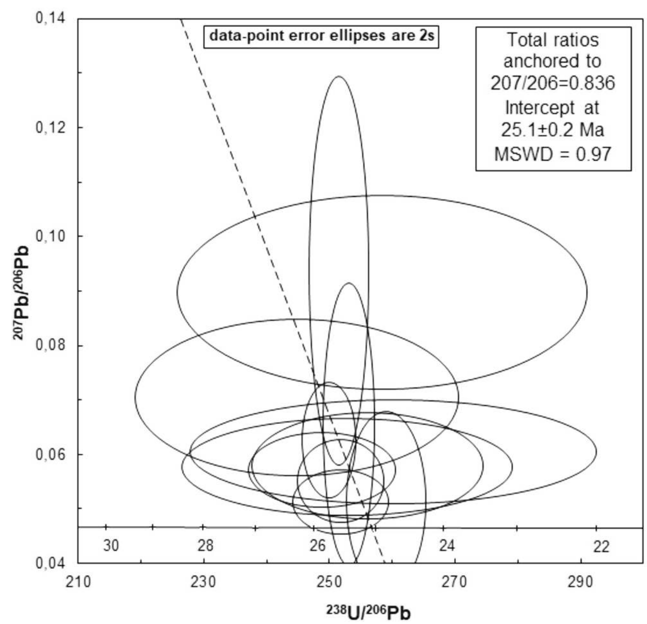

Fig. 5. U-Pb data for zircon grains of the sample Su-21–18 Concordia diagram. Age, MSWD and probability are for the concordant grains with discordance of less than 10 %. N is for the number of filtered zircon analyses from which concordia age was calculated (shown by black ellipses).

Four to seven coal seams are distinguished in the deposit as follows: First Lower (Il), First Upper (Iu), Second Lower (IIl), Second Upper (IIu), Third Lower (IIIl), Third Upper (IIIu), and Fourth (IV). The coal seams in the upper part of the section are thin and mostly simple in structure (Fig. 6). The seam I is continuous for most of the deposit but it splits into two parts in the northeastern part. The lower seam is common only in the northeastern part and pinches out in the central protrusion area.

The deposit exploitation has shown that all of the metal-bearing coal seams in the central protrusion area of the Spetsugli germanium coal deposit have “erosion windows”. In fact, it was an elevated area of land in a paleobog-paleolake deposit during the period of the coal-bearing sediment accumulation with progressive onlap of the younger

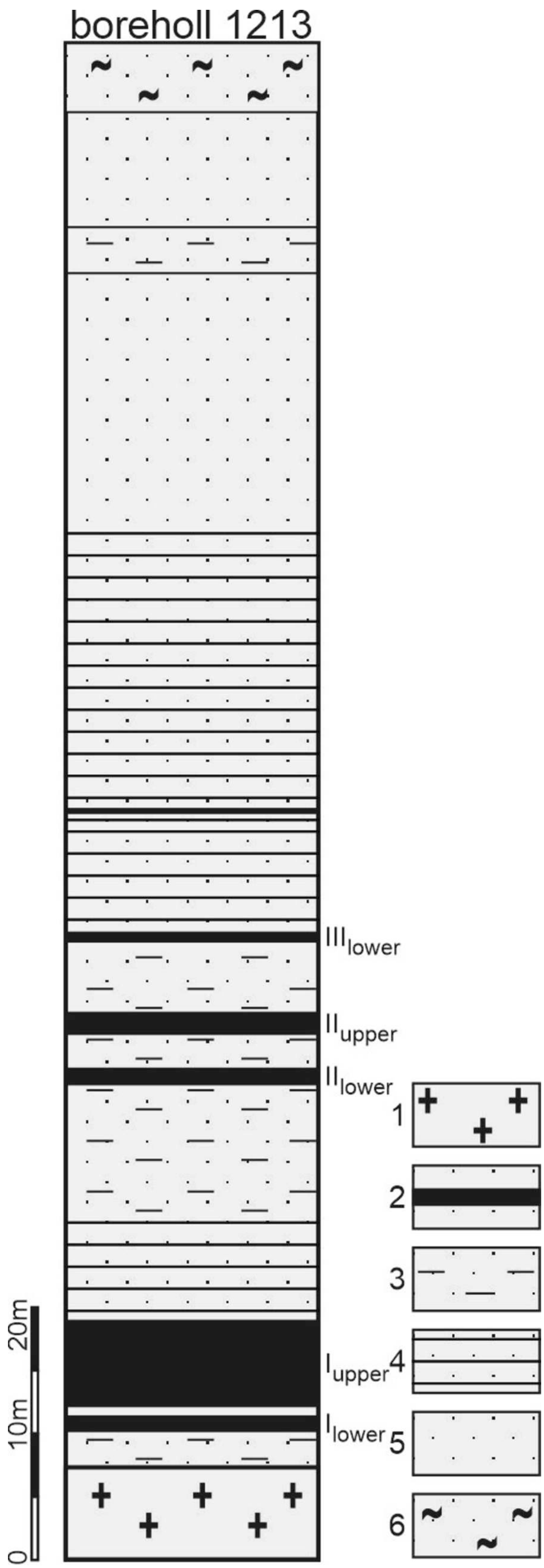

Fig. 6. Geological section of the coal-bearing deposits in the borehole 1213 in the Spetsugli deposit (according to Levitsky and Ivanov, 1969) 1 - granites, 2 - coal seams, 3 - siltstones, 4 - sandstones, 5 - sand, 6 - clay.

sediments. According to the results of exploratory drilling, the lower seam has several such "windows" attached to other smaller protrusion (Levitsky and Ivanov, 1969).

The coals of the deposit are represented by brown humic subbituminous C coals (Vyalov et al., 2006). The coals are dense, brownish-black, matte, semi-matt, or, less often, semi-glossy. The average vitrinite reflectance is 0.39%. The coals of the deposit have medium ash yield (Ad = 20%), with high volatile matter yield (59%), low sulfur (0.4%), medium calorific value (27.1 MJ/kg). The maximum moisture content by strata cross-sections ranges from 23 to 48%. Humic acid content in the dry ash-free mass ranges from 9 to 70%, with an average of 28% (Coal base of Russia, 1997).

The maceral composition of the coals is characterized by high content of vitrinite of 80 to 99%, represented mainly by attrite and fragments of structural and weakly structured vitrinite, relics of wood, leaf parenchyma, and bark tissue. Inertinite and liptinite are respectively 1–16% (7–8% on average) and 1–20% (3–6% on average). According to these characteristics they are very similar to the germanium-rich coals of the Lincang deposit, consisting of more than 88.5% huminite (Dai et al., 2015b) and differ significantly from the germanium-rich coals of the Wulantuga deposit, consisting of 52.5% huminite and 46.8% inertinite (Dai et al., 2012; Wei et al., 2017).

5. Geochemical features of the germanium-bearing coals and coal-bearing rocks

In the Spetsugli germanium deposit, as in the majority of known germanium-rich coal deposits, along with Ge, abnormally high contents of W and Be were recorded (Kostin et al., 1973). Later, information on the As and Sb enrichment of the coals appeared (Ivanov et al., 1984). However, the earliest papers did not report specific data on the content and distribution of these elements in the coal deposits, and the conclusions were based on the results of approximate quantitative analysis. More recently, comprehensive sampling and analyses have demonstrated anomalous contents of Rb, Cs, U, Th and REE (Seredin, 2003b; Seredin, 2005; Seredin, 2006), as well as In, Sr, Ga, Zn, Cu, Ag, Tl and Mo (Vyalov et al., 2021).

To learn more about the geochemistry of the deposit, and particularly the element associations and nature of accumulation, a detailed sampling of the upper germanium-bearing coal seams (IIl, IIuc and IIIl) was carried out in several sections in the stripped part of the open pit. As can be seen from Table 3, all coal seams are characterized by similar spectrum of main trace elements.

In general, the metal-bearing coals of the deposit are characterized by abnormally high, tens- or even hundreds-times exceeding the mean contents for brown coals of the world for Ge, Sb, Hg, W, Li, Be, Cs, and As. Somewhat less anomalous are the levels of accumulation of U, Mo, Y, Rb, medium and heavy lanthanides, Zn and Ga.

Germanium. The studied sections of the studied area of the deposit are characterized by extremely high Ge contents, exceeding the mean values for the seams from exploration work and more recent assessments from a limited number of samples (Vyalov et al., 2012, 2020; Sedykh, 1999). In general they are close to the published single-section mean value (Seredin, 2003a; Seredin, 2003b). The trend expressed in decreasing mean content in the seams from bottom to top of the section was confirmed by Vyalov et al. (2020). It should be noted that this trend is not so obvious. However, other data shows the content increases from bottom to top (Sedykh, 1999; Seredin, 2003a). We should also take into account that we did not test the seam I which lies in the lower part of the section. Nevertheless, considering all the available data, there is no clear, consistent depth related trend

Correlation analysis carried out by Spearman's rank correlation method for 45 coal samples showed significant positive association of Ge with the group of satellite elements. The highest correlation coefficients of Ge are with Sb ($r = 0.91$), Hg ($r = 0.72$), As ($r = 0.61$), Mo ($r = 0.62$), W ($r = 0.64$), U ($r = 0.67$), Tl ($r = 0.59$), and Na ($r = 0.79$). Positive

Table 3
Average contents of main trace elements in germanium-bearing coal seams of the Spetsugli deposit, ppm.

Element	Seam III	IIu	IIIl	Average for the section	Mean for the coals of the world*
Li	27.9	113	172	105	10 ± 1
Be	50.2	55.6	57.0	54.4	1.2 ± 0.1
Sc	5.1	6.6	3.5	5.3	4.1 ± 0.2
V	40.6	63.4	22.7	45.3	22 ± 2
Cr	19.7	24.4	11.6	19.4	15 ± 1
Co	7.6	12.9	8.0	10.0	4.2 ± 0.3
Ni	11.8	22.7	12.8	16.8	9.0 ± 0.9
Cu	12.6	35.7	12.5	22.4	15 ± 1
Zn	17.0	99.9	57.9	64.2	18 ± 1
Ga	27.3	10.2	8.1	14.5	5.5 ± 0.3
Ge	1676	1016	1173	1249	2.0 ± 0.1
As	26.6	189	238	157	7.6 ± 1.3
Se	1.7	2.6	3.5	2.6	1.0 ± 0.15
Rb	71.6	31.7	30.7	42.8	10 ± 0.9
Sr	116	79.2	103	96.5	120 ± 10
Y	81.1	55.1	108.7	77.8	8.6 ± 0.4
Zr	98.5	70.7	55.1	74.2	35 ± 2
Nb	6.4	5.2	4.1	5.2	3.3 ± 0.3
Mo	5.9	7.8	6.2	6.8	2.2 ± 0.2
Ag	0.08	0.19	0.08	0.13	0.09 ± 0.02
Cd	0.26	0.97	0.25	0.56	0.24 ± 0.04
Sn	1.4	1.4	1.1	1.3	0.79 ± 0.09
Sb	698	164	148	312	0.84 ± 0.09
Cs	72.7	26.0	18.2	37.1	0.98 ± 0.1
Ba	281	183	175	209	150 ± 20
La	14.0	24.0	17.2	19.2	10 ± 0.5
Ce	26.8	45.3	41.8	39.0	22 ± 1
Pr	3.4	5.5	6.1	5.1	3.5 ± 0.3
Nd	13.9	21.6	29.4	21.7	11 ± 1
Sm	3.9	4.8	9.7	5.9	1.9 ± 0.1
Eu	0.9	0.9	2.0	1.2	0.50 ± 0.02
Gd	7.0	6.2	12.6	8.3	2.6 ± 0.2
Tb	1.3	1.1	2.2	1.5	0.32 ± 0.03
Dy	10.1	7.2	15.2	10.3	2.0 ± 0.1
Ho	2.3	1.6	3.5	2.3	0.50 ± 0.05
Er	6.8	4.4	11.1	7.0	0.85 ± 0.08
Tm	1.0	0.6	1.8	1.1	0.31 ± 0.02
Yb	5.8	3.6	11.0	6.4	1.0 ± 0.05
Lu	0.9	0.5	1.8	1.0	0.19 ± 0.02
Hf	2.4	1.8	1.5	1.9	1.2 ± 0.1
Ta	0.4	0.3	0.3	0.35	0.26 ± 0.03
W	276	239	246	252	1.2 ± 0.2
Hg	0.78	3.01	3.37	2.47	0.10 ± 0.01
Tl	0.6	0.6	0.5	0.5	0.68 ± 0.07
Pb	7.0	17.6	8.3	11.9	6.6 ± 0.4
Th	4.8	9.5	6.6	7.3	3.3 ± 0.2
U	15.8	11.7	10.3	12.5	2.9 ± 0.3
∑REE	98.1	127.3	165.4	130.0	56.7
A^d,%	39.9	28.5	25.3	30.8	

Note: * - according to (Ketris and Yudovich, 2009); A^d –ash yield.

correlation, not high but significant, above critical value ($p = 0.05$) is determined for Li ($r = 0.39$), Be ($r = 0.50$), Cs ($r = 0.39$), Ga ($r = 0.46$), Y ($r = 0.37$), and heavy lanthanides ($r = 0.39$–0.40). Most of these elements (Sb, Hg, U, Tl, Li, Cs, Ga, HREE, Na) have a positive correlation with the ash yield. This fact connects Ge with a source of supply of these elements to the coal seam, which in this case is represented by greisenized granite. Negative correlation with the ash yield was marked only for W and absence of correlation (insignificant relation) was determined for Ge, As, Se, Be, Y, Mo, and medium lanthanides (MREE). This indicates a predominantly aquagenic inflow of these elements into the coal seam.

Distribution of germanium in the deposit. Assessment of standard reserves of Ge performed in the late 1960 s showed that 75.3% of them are concentrated in the thickest seam I with the average Ge content of 348 ppm of coal (Levitsky and Ivanov, 1969). This indicates that the main input of the metal took place at an early stage in the accumulation of the coal bearing sequence, or the discharge of germanium-bearing waters took place predominantly in the lower part of the coal-bearing section.

Another important feature of the Ge distribution over the area is the subisometric shape of the ore bodies. The paleorelief of the basement over the area of the deposit is highly variable; the thickness of the overlying sediments varies from 42 to 320 m. In the centre of the metal-bearing area is the highest paleorelief, forming what has been referred to as an “erosion window” in the coal seams, but is actually an area of non-deposition. The areal distribution of Ge in the coal seams has sub-isometric concentric-zonal shape around this protrusion of the granite basement (Levitsky and Ivanov, 1969; Ivanov et al., 1984; Ivanov et al., 1989; Vyalov et al., 2012; Vyalov et al., 2020). The pattern of the Ge distribution over the area within each seam is such that it strongly suggests area-wide inflow of the metal into the coal seams associated with the granite protrusion in the basement (Fig. 1). The shapes of the ore bodies and the Ge halos in the coal seams within the deposit allow us to conclude that the source of Ge, W, Sb and other satellite elements was located within the dome-shaped granite protrusion. It is also noteworthy that the apparent source area for the mineralization is not linear, which would have been anticipated if tectonic structures such as faults had any involvement in the mineralization. There are no linear discharge zones, which could be associated with tectonic disturbance subsidence zones in the studied area (Kostin and Meitov, 1972; Ivanov et al., 1984; Sedykh, 1999; Seredin, 2006). In addition, they cannot provide this form of the ore bodies. The degree of contrasting mineralization in the coals within the ore body varies, which may be due to both the irregular distribution of the metals in the source and the irregular transport of matter by waters in local areas.

Commercial germanium-bearing seams have close spatial distribution contours. The metal-bearing zones in the seams are located on top of each other, creating a stepped structure of the deposit **(**Fig. 7**).** The areal dimensions of the metal-bearing zones of the seams decrease from bottom to top from 550,000 m^2 for the seam I to 250,000 m^2 for the seam IIIl (Levitsky and Ivanov, 1969; Seredin and Finkelman, 2008). All metal-bearing coals are clearly centred on the area in the basement with the greatest paleorelief. At the same time, there are several independent halos within the deposit area, confined to other protrusion, but not of commercial significance because of the relatively low Ge content. The presence of “erosion windows”, represented by eluvial weathering crust of greisenized granites, is characteristic of all layers with commercial mineralization, up to seam IIIl. The seams within the deposit without such “windows” have no commercial mineralization, although they are distinguished by the increased Ge content (15 ppm for IIIu and 11 ppm for IV).

An important characteristic of the ore-bearing area is also more significant enrichment of the coal-bearing rocks in the interlayers compared to the rocks outside the deposit. While the Ge content outside the deposit in mudstones, siltstones, and sandstones varies between 1 and 3 ppm, it ranges from 4 ppm to 156 ppm within the deposit. The minimum concentrations occur in coarser-grained sediments.

In the vertical profile of the coal seam, Ge is distributed non-uniformly. In areas with low content (less than50 ppm), its distribution either follows the “Zilbermints law” with enrichment of the near-contact zones of the seam (Yudovich, 2003b), or, more often, its content decreases consistently from the near- bottom zone to the roof. In the metal-bearing coals, enrichment of the central zone of the seam has been previously determined (Vyalov et al., 2012; Kuzevanova, 2014).

For the coal ash, negative correlation of the Ge content with ash yield is clearly seen within separate sections. This indicates an aqueous mechanism of the germanium influx into the coal seam and is in good agreement with its predominantly organic form in the coals (Yakushevich et al., 2013; Arbuzov et al., 2021b). If the clastogenic mechanism of the germanium accumulation prevailed, its content in the ash would depend on suspension composition and would be approximately uniform throughout the entire coal seam (Yudovich and Ketris, 2002).

A similar pattern of the germanium distribution, but with multiple enrichment zones, was observed for the thicker coal seams of the

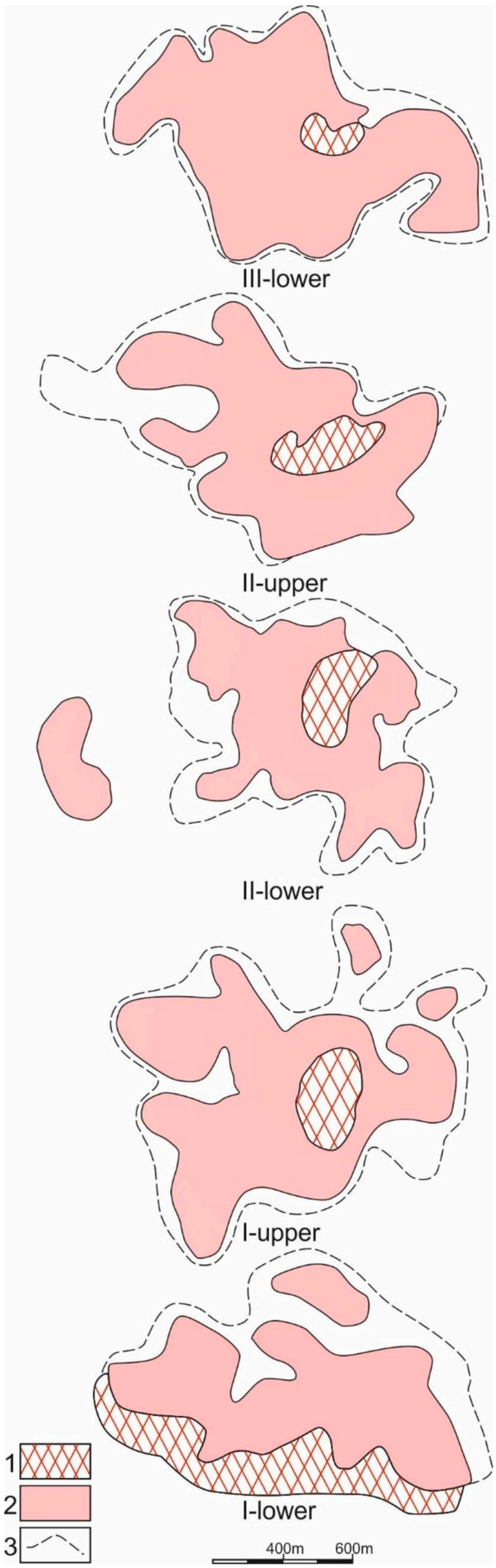

Fig. 7. Distribution of Ge in the seams of the Spetsugli deposit (according to Levitsky and Ivanov, 1969 with the athors' supplements) 1 – protrusion of the basement depression ; 2 – Ge content greater than 400 ppm; 3 – orebody boundaries (greater than50 ppm).

Lincang deposit (Dai et al., 2015b) and Wulantuga deposit (Du et al., 2009; Jiu et al, 2021b).

6. Satellite elements associated with the Ge mineralization

As is demonstrated by the averages (Table 3), the germanium-bearing coals of the deposit are characterized by anomalous contents of Ge, Li, Be, Cs, As, Sb, Hg and W, by factors of tens- and even hundreds-times greater than the mean content for the brown coals of the world. The concentrations of U, Mo, Y, Rb, medium and heavy lanthanides, Zn, and Ga are somewhat less anomalous. The spectrum of associated elements is quite extensive and includes associations which in endogenous conditions can only be caused by different processes. Endogenous mineralization of this type must be polygenic-polychronous. At the same time, accumulation of these elements in hypergenesis may be determined by a single process. In the coal-bearing sequence in the basin there is a sequential decrease of the contents of Ge, Ga, Rb, Cs, Nb, Ta, Zr, Hf, Sn, Sb, Ba, W, Tl, U, and Th from the lower to the upper seams accompanied by a decrease in ash yield. Upwards, the contents of Li, Be, As, Se, Hg, and medium and heavy lanthanides clearly increases. For the coal ash, the trends are slightly different. There is a distinct upward increase of Li, Be, As, Se, Sr, Y, W, Hg, Tl, and lanthanides contents. The contents of Ga, Sb, and Cs distinctly decrease. Trends of other elements in the section are ambiguous.

Rare alkalis (Li, Rb, Cs). The enrichment of the germanium-bearing coals of the Spetsugli deposit by rare alkalis (Rb and Cs) was studied in detail in one borehole section by Seredin (2003b). The same anomalous accumulation of lithium can be added to these data (Table 3). The correlation analysis (45 coal samples) showed high ($r = 0{,}76$–$0{,}87$) correlation of the contents of these elements in the coal with the ash yield. On the other hand, they are also connected by high correlations with each other and with the basic rock-forming alkaline elements K and Na. The correlation with potassium is particularly high. For Rb, the rank correlation coefficient with K_2O is 0.98, for Cs − 0.88, and for Li − 0.64. The high correlation coefficients ($r = 0.7$–0.9) were determined for these elements with SiO_2 and Al_2O_3. This fact allows us to consider mica and microcline, which are widely distributed in the greisenized granites of the Voznesenk complex, as the main source of Li, Rb and Cs. This is confirmed by the results of the analysis of monofraction "biotite", selected from the remnant of the greisenized granite in the Spetsugli germanium deposit (Table 4**).**

The name of the monofraction is conditional as it represents both biotite proper and newly formed mineral phases developed on it: chlorite, muscovite, etc. As is clear from these data, the mica aggregate is extremely rich in Rb (0.22%), substantially enriched with Li (483 ppm) and Cs (104 ppm) and may be well considered as the main source of the rare alkalis in the germanium-bearing coals. In addition, however, a

Table 4
Trace element composition of the "biotite" monofraction, ppm.

Element	Content	Element	Content	Element	Content
Li	483	Zr	1089	Gd	503
Be	14.0	Nb	460	Tb	84.9
Sc	147	Mo	14.6	Dy	430
V	125	Ag	2,0	Ho	78.8
Cr	21.0	Cd	1,6	Er	214
Co	131	Sn	86.0	Yb	201
Ni	21.8	Sb	96.1	Lu	31.1
Cu	15.3	Te	0.14	Hf	40.8
Zn	662	Cs	104	Ta	20.2
Ga	162	Ba	311	W	493
Ge	12.8	La	4111	Re	0.023
As	385	Ce	7253	Tl	45.8
Se	77.5	Pr	937	Pb	758
Rb	2189	Nd	2992	Th	203
Sr	94.9	Sm	695	U	670
Y	2568	Eu	32.9	∑РЗЭ	17,564

significant portion of these elements may be associated with feldspars and albite (Seredin, 2003b). Complete or substantial decomposition of these minerals saturates solutions with rare alkalis and could be the source of sorption accumulation of Rb, Cs and Li in the organic matter of the coal and on clays.

The modes of occurrence study shows that 62–66% of Rb and Li are bound to the mineral matter of the coal and about 1/3 is bound to the organic matter or sorbed on the clay matter (Seredin, 2003b; Arbuzov et al., 2021a). For Cs, the proportion of the mineral phase is somewhat less, and the organic phase is more, but still with distinct predominance of mineral-associated Cs (Seredin, 2003b; Arbuzov et al., 2021a). The secondary importance of water-soluble forms in enrichment of the coals with the rare alkalis is also confirmed by the fact of their low content in coal inclusions (Table 5).

At the same time carbonaceous wood inclusions in the sandstones near the basement outcrop are slightly enriched with Li and Cs as compared with their counterparts at a distance from it. This confirms the important role of the granite protrusion in the accumulation of not only germanium, but also other accompanying elements in the coal. Coal-bearing rocks near the granitic protrusion in the Spetsugli germanium deposit are significantly richer in Rb and Cs as compared with those in the coal mine “Pavlovsky-2″ located 1.5–2.0-km from it. This indicates, first of all, the specific composition of the area of erosion and formation of these deposits. As has been noted, the eroded basement area in the Spetsugli deposit is represented by feldspathised and greisened granites. The seam IIIl, in addition, is anomalously enriched with Li along with Y and lanthanides. The nature of this enrichment may be related to modern acidic sulphate waters draining through this seam (Table 6). These waters are anomalously enriched with Li, Y, REE, Ge, Co, Ni, Zn, Rb, Cs, Sr, U, Al, Fe, and Mn. The formation of a similar type of acidic sulphate waters anomalously enriched with rare alkalis is shown by the example of the destruction of greisenic W-Mo ores in Transbaikalia in the present-day hypergenesis zone (Chechel, 2020).

Lanthanides and yttrium. The germanium-bearing seams are significantly enriched with REE. They are especially anomalous with Y, the concentration of which in the coal ash exceeds 250 ppm on average in the studied section, and in the IIIl seam it is 430 ppm. As a source, as for the group of rare alkaline elements (Li, Rb, Cs), the greisenized granites of the basement anomalously enriched with Y may also be considered (Table 2). In the monofraction “biotite” from these granites, the Y content exceeds 0.25% (Table 4). They can be considered as a source of lanthanides in the coals. A similar conclusion was made by Seredin (2005) studied the REE distribution in two boreholes, which opened the entire coal section in the Spetsugli germanium deposit. He assumed that the clastogenic nature of background accumulation of REE

Table 5
Trace element composition of the carbonised wood, ppm.

Element	SU-9*	SU −80*	SU −22**	Element	SU −9*	SU −80*	SU −22**
Li	4.6	6.5	3.6	Cs	4.9	4.5	0.9
Be	10.0	10.0	1.6	Ba	467	344	70
Sc	1.70	0.69	3.1	La	3.3	2.2	6.7
V	200	174	14.1	Ce	6.8	4.8	15.2
Cr	27.4	25.5	42.1	Pr	0.86	0.63	1.66
Co	2.5	2.2	25.8	Nd	3.7	2.9	6.0
Ni	2.4	2.4	16.2	Sm	1.2	1.0	1.3
Cu	3.8	0.27	12.5	Eu	0.26	0.24	0.26
Zn	5.5	11.3	31.8	Gd	1.9	1.8	1.4
Ga	11.1	9.1	2.6	Tb	0.40	0.40	0.20
Ge	5306	7210	32	Dy	3.3	3.4	1.3
As	52	49	65	Ho	0.81	0.85	0.28
Se	0.7	0.4	1.1	Er	2.51	2.86	0.78
Rb	8.5	4.6	7.6	Tm	0.44	0.42	0.12
Sr	135	152	19	Yb	3.2	3.4	0.77
Y	18.5	15.3	7.8	Lu	0.47	0.52	0.11
Zr	144	129	108	Hf	1.18	0.85	1.17
Nb	42.3	39.9	4.1	Ta	0.08	0.04	0.18
Mo	90.1	99.2	28.1	W	489	724	3.1
Ag	0.23	0.05	0.26	Tl	4.2	6.1	0.09
Cd	0.16	0.27	0.29	Pb	4.4	5.2	7.0
Sn	0.57	0.15	1.5	Th	4.0	4.6	3.1
Sb	2714	3269	30.0	U	26.5	38.0	1.1

Note: *- samples in the sandstones of the coal–bearing sediments near the basement; **-samples in the sandstones above the coal-bearing sediments.

Table 6
Composition of the drainage waters in the Spetsugli deposit, μg/l.

Element	SU-67–19	SU-66–19	SU-70–19	SU-77–19	Average*
Li	26.4	52.8	37.8	5.86	13.0
Be	2.8	27.9	2.3	0.015	0.19
B	53.1	156	45.8	37.9	77.9
Al	89.6	727	721	16.2	226
Si	21,900	23,830	25,930	18,170	17,900
P	4,1	8,6	6,8	4,1	58,0
SO_4^{2-}, mg/l	521	775	725	72.5	70.7
Sc	0.12	0.32	1.05	0.079	0.07
Ti	0.11	0.14	0.13	1.3	17.4
V	0.0076	0.0060	0.0068	0.11	1.31
Cr	0,10	0,21	0,19	0,094	2.70
Mn	3099	5950	4320	628.6	54.5
Fe	3871	690	4079	17.1	481
Co	17.2	69.0	103	22.6	0.39
Ni	11.2	73.4	68.3	16.8	3.38
Cu	0.93	3.2	5.6	0.45	5.38
Zn	85.3	280.3	129.9	9.7	38.4
Ga	0.049	0.15	0.10	0.015	0.37
Ge	25.9	56.7	4.8	0.59	0.62
As	1.2	2.7	1.0	0.61	1.46
Se	0.14	0.49	0.39	0.037	0.74
Rb	29.7	52.9	32.5	10.4	1.86
Sr	1186	1974	1650	188.5	183
Y	1.76	11.3	7.80	0.055	0.096**
Zr	0.021	0.034	0.057	0.24	1.20
Nb	0.0003	0.0008	0.0007	0.0094	0.45
Mo	0.017	0.028	0.021	0.60	1.75
Ag	0.011	0.011	0.0065	0.0035	0.26
Cd	0.52	1.69	0.52	0.054	0.24
Sn	0.0093	0.018	0.012	0.010	0.39
Sb	0.12	0.37	0.033	0.68	0.68
Cs	14.6	18.2	8.1	2.7	0.26
Ba	33.4	19.6	60.3	51.2	18.3
La	0.65	5.9	4.3	0.038	0.079**
Ce	1.20	12.4	9.8	0.073	0.060**
Pr	0.15	1.14	1.06	0.0082	0.022**
Nd	0.68	4,7	4.4	0.034	0.093**
Sm	0.17	1.06	0.98	0.0079	0.022**
Eu	0.038	0.25	0.25	0.0056	0.014**
Gd	0.22	1.56	1,17	0.0092	0.025**
Tb	0.036	0.25	0,19	0.0011	0.004**
Dy	0.,26	1.73	1.30	0.0080	0.016**
Ho	0.059	0.35	0.28	0.0017	0.004**
Er	0.20	1.09	0.95	0.0069	0.011**
Tm	0.028	0.13	0.13	0.0009	0.002**
Yb	0.20	0.85	0.95	0.0065	0.009**
Lu	0.032	0.12	0.15	0.0012	0.003**
Hf	0.0018	0.0053	0.0058	0.0029	n.d.
Ta	0.0003	0.0009	0.0008	0.0007	n.d.
W	0.0022	0.011	0.0096	0.051	n.d.
Hg	less than0.010	less than0.010	less than0.010	0.23	0.041
Tl	0.18	0.30	0.20	0.12	n.d.
Pb	2.9	3.1	15.9	0.048	2.65
Bi	0.0018	0.0022	0.0012	0.0012	0.15
Th	0.094	0.039	1.55	0.015	0.24
U	0.54	0.67	4.5	0.37	1.31
M, Мг/л	1260	1228	1199	237	469
pH	4.17	4.17	3.91	7.36	6.9

Notes: - SU-66–19, SU −67–19, SU −70–19 - drainage waters from the seam III-l; SU −77–19 – waters from the tuff horizon above the coal-bearing sequence; * - Groundwaters of the supergene zone (Shvartsev, 2008); **- underground water from the supergene zone of Primorye (Chudaev et al., 2017); M – total dissolved solids; n.d. – no data.

in the coals of the deposit and epigenetic concentration of heavy REE and Y was due to the late Pliocene-Quaternary hydrothermal process.

As the present studies have shown, the role of water solutions in the accumulation of both heavy and light REE is quite large. The character of normalized plots (Fig. 9) is regular and does not carry traces of two or more equivalent but not interrelated processes. Moreover, the dikes associated with hydrothermal activity after the coal seams formation (Seredin, 2005) are not of the Neogene-Quaternary age, but of the Late Permian age, which is much earlier than the age of the coal accumulation. The feature of the normalized plots does not detract from the importance of the granites in the accumulation of both heavy and light lanthanides in the coals. The granites in the basement subjected to quartz-feldspar metasomatism and greisenization, which can be regarded as the main source of REE in the coals, are distinguished by abnormally high sum contents of the lanthanide (from 0.07 to 0.36%) and Y (from 101 to 467 ppm) (Table 2). The weathering crusts developed over them are distinguished by 2–15-times lower REE contents (Table 7). Lanthanides and yttrium leached in the process of the granite weathering can be considered as a source of their accumulation in the coals. In this case, metasomatically altered basement granites within the Spetsugli germanium deposit are significantly enriched with REE compared with those at a distance from it.

The modern water solutions draining germanium-bearing coal seams are also anomalous in terms of REE content (table 6). Even more anomalous REE concentrations were found in modern acidic sulphate waters of the hypergenesis zone to the east of the study area (Chekryzhov et al., 2019). One of the features of modern waters draining the coal seams in the deposit is the presence of negative Eu anomaly (Eu/Eu*=0.6–0.7), indicating the connection of these water solutions with acidic igneous rocks (Fig. 8, **E**).

Vertical sections of the coal seams were studied within the ore-bearing area with anomalously high Ge content and outside this area

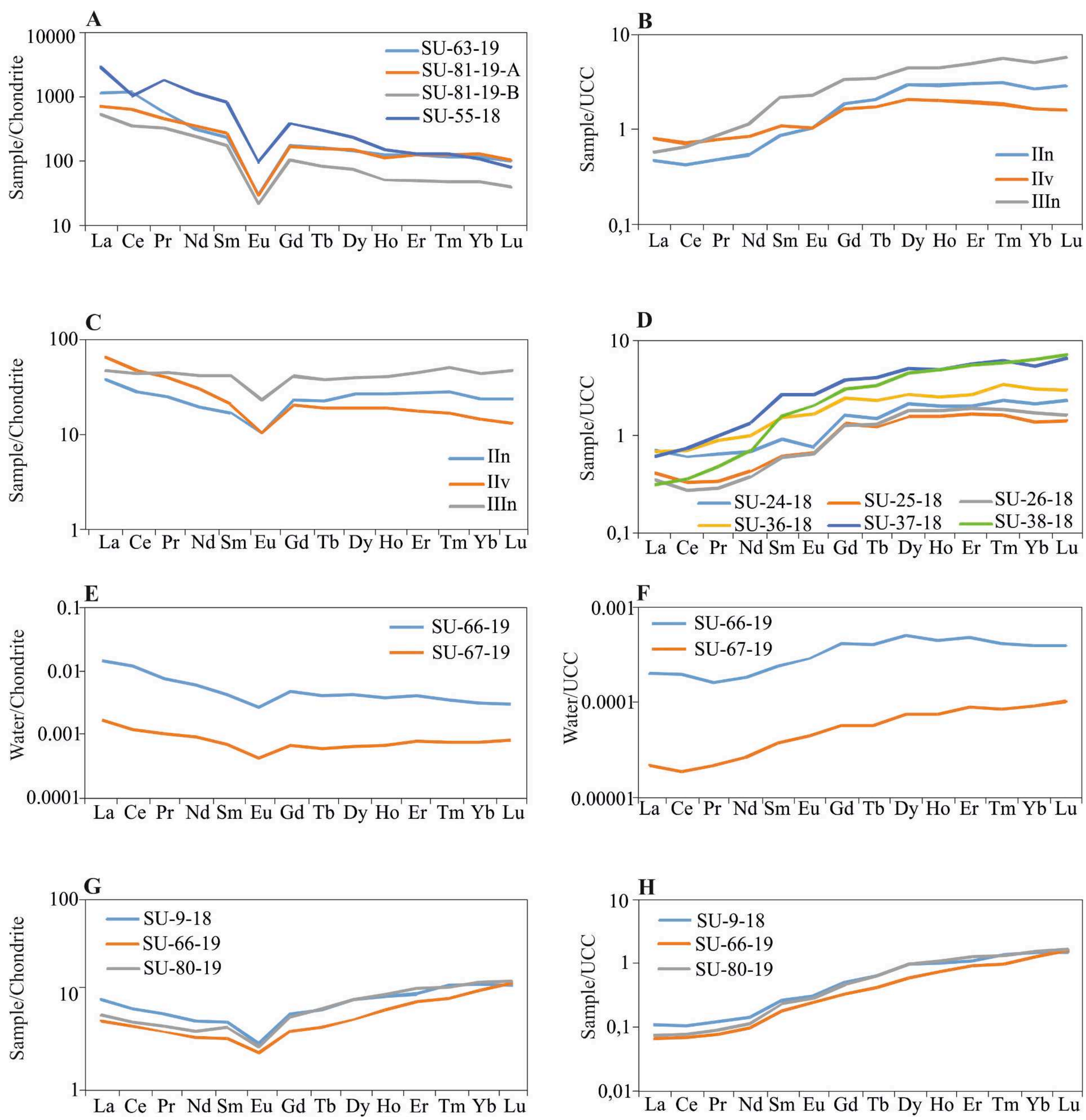

Fig. 8. Normalized graphs of the REE distribution in the granites of the basement (A), coal seams (B, C), coal seam IIII (D), drainage water (E, F) and carbonized wood (G, H) of the Spetsugli deposit. Note:* - normalized for chondrite according to (Taylor & McLennan, 1985); ** - normalized for the content in the upper continental crust according to (Taylor & McLennan, 1985).

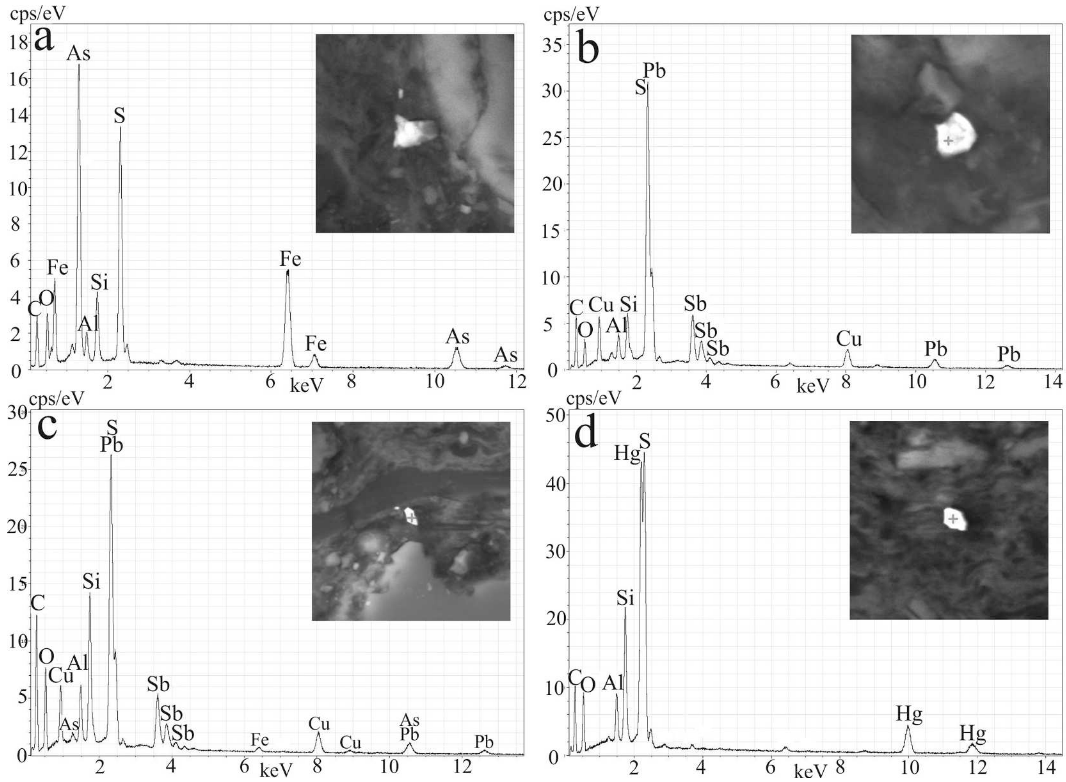

Fig. 9. Electron-microscopic pictures of Sb, Hg and As minerals in the coal and their EDS spectrums. Fragments of arsenopyrite (a), bournonite (b, c) and cinnabar (d).

Table 7
Lanthanide and yttrium contents in the weathering crust samples from the granites and andesite dikes.

Element	SU-1–18*	SU −3–20*	SU −4–20**	SU −2–18*	SU −16–20**
	гранит			андезит	
Y	178.0	48.0	17.7	236.0	43.0
La	31.8	130.5	16.0	191.5	36.6
Ce	61.9	40.7	42.8	125.6	26.4
Pr	7.64	31.0	3.75	44.2	10.2
Nd	25.6	117.1	14.0	157.4	37.4
Sm	5.77	23.3	2.93	37.1	8.19
Eu	0.32	1.02	0.33	2.55	0.41
Gd	8.63	17.94	2.46	32.8	7.11
Tb	1.61	2.59	0.36	5.49	1.03
Dy	17.9	12.23	2.30	34.4	5.99
Ho	4.59	2.14	0.53	6.70	1.27
Er	16.5	5.91	1.88	19.3	3.79
Tm	2.87	0.84	0.33	2.75	0.49
Yb	17.3	5.5	2.48	19.8	2.60
Lu	2.90	0.8	0.39	2.32	0.65
∑РЗЭ	208.3	391.4	90.6	681.8	141.9
La/Yb	1.8	23.7	6.5	9.7	14.1

Note: * - samples from the Spetsugli area; ** - samples from the Pavlovsky-2 area, 1.5–2-km north-west.

where contents are close to the mean values of Worlds coals (Ketris and Yudovich, 2009). In the germanium-bearing coals, the REE content is 1.5–2-times higher. However, because of high ash yield in the metal-bearing coals, the ashes of mineralized and non-metalliferous varieties are comparable in lanthanide and yttrium contents. However, because of high ash yield in the metal-bearing coals, the ashes of mineralized and non-metalliferous varieties are comparable in lanthanide and yttrium contents. The lanthanum- yttterbium ratio also does not differ significantly: on average 3.0 for germanium-bearing coals and 4.5 for coals with the ordinary Ge content near the ore block. This suggests a single source of the REE accumulation in the coals within the investigated area. That is, probably, hydrothermally altered rare metal granite of the basement protrusion. In this case, the leading role belongs not to granites proper, but to hydrothermally metasomatic changes associated, apparently, with the intrusion of the dikes of the Permian age and subsequent weathering. The role of these processes can be seen in the coals from the Pavlovsky-2 coal mine section 1.5–2-km northeast of the Spetsugli site (Fig. 1). There, in the coals directly overlapping the weathering crust of the basement granites and enriched with Ge (13–144 ppm), the content of the lanthanide sum is 44–50 ppm and Y – 20–22 ppm. Immediately near and above the weathered dike, the content of the sum of lanthanides in the overlying coals is 61–214 ppm, Y is 46–361 ppm. The contents of Ge (27–125 ppm), Hg (up to 1.5 ppm), Mo (up to 68 ppm) and W (22–63 ppm) are also anomalous there. The relationship of the REE accumulation levels in the coals with the dike complex is visible. The weathering crust on the similar dike in the Spetsugli germanium deposit is also richer with REE than that on granites at a distance from it (Table 7). The Y content in the weathering crust of the dike and granites is 236 ppm and 178 ppm, respectively, and the sum of lanthanides is 682 and 208 ppm. The difference in the REE content in hydrothermally altered granites and in the weathering crust on them is very large, which suggests an important role of these rocks as a source of lanthanides and Y in the Spetsugli germanium deposit. Such a large decrease in their content in the eluvial weathering crust in comparison with the original granite indicates a relatively mobile form of REEs in the granite and their leaching with the participation of water solutions.

The feature of the normalized graphs of the lanthanide distribution in the coals indicates the REE inflow to the coal seams from the weathering crust of the granites (Fig. 8 B – 8C). Both normalising to chondrite (Fig. 8 C) and normalising to the average composition of the upper continental crust (Fig. 8 B) clearly show the Eu anomaly (Eu/Eu*=0.50–0.60), typical for rocks related to granitoids. Simultaneously, there is a weak Ce anomaly, which is typical for the weathering zone because of the Ce oxidation to valence 4 + and its removal in the process of the lanthanide migration. Both positive and negative Ce anomaly appeared because of the granite weathering (Fig. 8, A).

The character of the graphs also indicates the predominantly hydrogenic nature of the REE accumulation in the coals (Fig. 8 B – 8 D). H-type distribution of REE is characteristic there, indicating aqueous mechanism of their accumulation in the coal seam (Seredin & Dai, 2012). Yttrium lanthanides are more mobile in water solutions, which led not only to the specific feature of the normalized graphs, but also to lower La/Yb ratio in comparison with the granitoids of the basement. Whereas for the granites and greizens it varies from 8.1 to 48.3 and for coals from 1.6 to 6.7 (3.0 on average). For commercially germanium-bearing coals within the boundaries of the ore body and the coals outside it, the shapes of the graphs are similar. The ore areas are generally characterized by a steeper slope of the graph, which is probably due to more significant contribution of REE carried with solutions.

The seam IIIl is illustrative in this respect. Modern acid sulphate waters draining from the coal are enriched in Ge, REE and rare alkaline elements (table 6). As follows from Table 3, the coals of the seam are significantly enriched with REE compared with the other seams, especially significantly with heavy lanthanides and yttrium. In the area of the germanium-bearing coals, the ratio of light and heavy lanthanides is considerably changed to heavier ones (Fig. 8, D, samples SU 36–18, SU 37–18, SU 38–18) in comparison with coals outside the ore body (Fig. 8, D, samples SU 24–18, SU 25–18, SU 26–18). Apparently, there is an additional inflow with modern waters of the hypergenesis zone and concentration of Ge and REE in the coals.

The importance of aqueous transport of the REE is clearly demonstrated by the example of carbonaceous wood extracted from sandstones within the boundaries of the ore block (Fig. 8 G to 8H). In fossil wood, any significant REE contents can only accumulate from solutions. According to the data obtained the accumulation of all lanthanides with clear predominance of heavy ones is observed in the wood. Lanthanum-ytterbium ratio in this case is less than 1 (Table 5). Negative Eu anomaly of Eu/Eu*=0.54–0.56 is also preserved there.

The low but still significant association of Ge with heavy and medium lanthanides and Y at r = 0.39–0.40 allows us to relate them to a single primary matter source, as well as W.

Tungsten. Tungsten is considered as one of the main Ge-associated elements in germanium-coal deposits (Kostin and Meitov, 1972; Kostin et al., 1973; Seredin, 2006; Seredin and Finkelman, 2008, Dai et al., 2016, etc.). The W content in the coals in the studied sections (Table 3) exceeds more than 200-times the average estimates for coals of the world. Moreover, the halo of the W distribution in the coal seams is much wider than the halo of Ge. The same anomalous content of W in the area of high germanium contents (contour of the germanium mineralization) is observed in the coals with the ordinary Ge content near the deposit, but outside the ore body. In the neighbouring section "Pavlovsky-2″, 1.5–2-km from the Spetsugli deposit, the W content is generally low. The presence of W (63 ppm) and Mo (68 ppm) anomalies was registered only in the area of the basement uplift near the andesite dike. The Hg (up to 1.5 ppm) and Ge (up to 125 ppm) contents are also high in that area

The W content in the coal seams is directly related to its presence in the source area of the coal accumulation basin. In a study of tungsten-bearing coals of Transbaikalia and Mongolia it was noted that whatever way W was deposited in the coals, its sources were the ore occurrences and deposits framing the coal-bearing depressions (Osokin, 1993). In the Pavlovsk deposit tungsten is abundant in coals in contact with tungsten-bearing metasomatically altered granites. Negative correlation of the W content with the ash yield and its predominantly organic form (Arbuzov et al., 2021b) suggests a hydrogenous mechanism of its accumulation in the coals. A hydrogenic mechanism for the W anomalies implies that the source was situated at a relatively short distance from the place of its deposition, as the halos of its dispersion in hypergenesis does not usually exceed several hundred meters in extent (Kraynov et al., 1965). Rare inclusions of tungsten mineral phases found near the granite protrusion (Arbuzov et al., 2021b) indicate a possible role of greisenized granites as a source of W in the coals of the Spetsugli germanium deposit. The possibility of coal enrichment with W due to metasomatically altered granite is confirmed by an anomalously enriched "biotite" fraction obtained from the greisenized granite (Table 4). The basement granites themselves are also 5–10-times enriched with W compared with the average estimates for similar rocks (Table 2). It should be taken into account that in this case only the preserved base of the greisenization zone and ore body is represented. Not high, although significant, correlation of the W and Ge contents is explained by difference of conditions of their migration in water solutions during transportation from the weathering crust to the coal seam (Kraynov, 1973).

Antimony, mercury and arsenic. Antimony is characterized by anomalously high content in the coals of the deposit. Its concentrations on average for the studied seams exceeds 370 times the mean value for coals of the world, and for the seam II-lower it is more than 800 times. The Sb content distinctly decreases upwards through the section, similar to the changes of the Ge content, which provides their high correlation (r = 0.90). These data differ from previously published data on the Sb distribution across the deposit seams obtained on the basis of single-borehole studies (Seredin, 2003a).

The modes of occurrence of antimony in the coals are different. In addition to the predominant concentration in the organic matter of the coal, finely dispersed fragments of fahlores and bournonite were found in the coal seams near the basement protrusion (Fig. 9 **b, c)**. The shapes of these clasts and their position in the organic matrix indicate their formation as a result of mechanical destruction of primary minerals. In addition, antimony in the coals occurs together with arsenic and germanium in Fe-Mn "crusts" and Fe sulphates (Arbuzov et al., 2021b).

The mercury content in the germanium-bearing coals of the Spetsugli deposit is also anomalous (Table 4), on average 25 times higher than the mean content in coals of the world and more than 30 times higher than in the seam III-lower. In contrast to Sb, the Hg content increases upwards through the section from 0.78 ppm in the seam IIl to 3.35 ppm in the seam III-lower. In general, steam coals of the Pavlovsk deposit are characterized by low concentrations of Hg in the range of 0.10 – 0.20 ppm. At the same time, in the areas of the coal seams related to metasomatically altered granites, its concentration increases by one order. In the metasomatically altered granites the content of mercury exceeds 1 ppm. Mercury, as well as antimony, shows high correlation with Ge (r = 0.72). At the same time Hg shows low but significant correlation with the ash yield (r = 0.34). Apparently, the organic form of Hg predominates, but its mineral phases are also present. In particular, some micron-sized fragments of cinnabar in the coals near the contact of the coal seam with the granite weathering crust were observed (Fig. 9 d).

There is an excess of As in the metal-bearing coals Spetsugli deposit over the other coals by about an order, up to 20-times the mean concentration for coals of the world. The As content, as well as the Hg content, increases from the lower to the upper seams (Table 3). Arsenic shows significant (above the critical level) relations with the main group of satellite elements of Ge, although the correlation coefficients are lower than those for Sb and Hg. The highest rank correlation coefficient is for As with Hg (r = 0.77), Ge, Mo, Sb, Tl (r = 0.53). The correlation of As with the ash yield is insignificant, that confirms its preferential connection with the organic matter. At the same time, arsenopyrite fragments were recorded in the coals, mainly near the protrusion (Fig. 9 d). The coals also contain arsenic pyrite, hydroxides, and iron sulphates enriched with As.

The accumulation of Sb, As and Hg in the coals probably occurs predominantly from water solutions. Direct evidence for this is the enrichment of these elements in coal inclusions in the coal-bearing sandstones (Table 5). The As enrichment of inclusions is much lower than that for Sb and Hg. At the same time, only the coals and the coal inclusions within the boundaries of the ore block are enriched with all these elements. The steam coals outside the ore block show no enrichment.

Antimony and arsenic, along with W, Li, F, Be, Mo, Sn, Co, Cu, Zn, Pb, and Ag, are the most characteristic elements for the W-Sn-greisen type of endogenous mineralization in Primorye region (Shashorin et al., 2019). This association with characteristic zoning is used as a geochemical criterion in the search for such mineralization. The source of antimony in the coals could be the fahlores described earlier in the Voznesensk deposit. Such rare antimony-containing sulfosalts as ouyheeite, franckeite, and diaphorite were also identified there (Androsov and Ratkin, 1990). Among all trace elements, Sb is most closely bound with Ge in the Spetsugli deposit ($r = 0.91$).

Radioactive elements (U, Th). Germanium-bearing coals are 3–5 times richer with U and 2–3 times richer with Th relative to the mean content in the world coals (Table 3). The thorium-uranium ratio is less than 1, indicating a selective accumulation of U associated with its hydrogenic input into the coal seam (Arbuzov et al., 2011). The U accumulation in the coals of the deposit is clearly associated with the presence of the basement protrusion, represented by highly radioactive granites, during the formation of the coal-bearing sediments (Table 2). The coals sampled at a distance from the central protrusion are distinguished by significantly lower U content whereas the Th content in both cases is comparable. This conforms well with the established concept of mainly hydrogenous mechanism of the U accumulation and detrital Th accumulation. Uranium forms a single association with Ge, Sb, Hg, As, Li, Rb, Cs, Be, Se, and several others, mainly chalcophile elements. The fact of its significant accumulation in the carbonaceous wood also indicates the aquagenic nature of U in the coal seam (Yudovich, 2003a; Hower et al., 2016). Coal inclusions in sandstones from the coal seam are enriched with U by an order more than the inclusions from the overlying sediments (Table 5). At the same time, a weaker, but significant (above critical value) relationship with Zr, Hf, Nb, and REE ($r = 0.3–0.4$) is noted. There is also positive relationship with the ash yield ($r = 0.54$). This indicates dual nature of the U accumulation in the coals of the deposit with the predominance of the hydrogenous mechanism.

According to exploration data, another important fact to mention is the presence of the U hydrogenous mineralization at the bottom of the coal-bearing sediments (Levitsky and Ivanov, 1969). The ore bodies are located either at the boundary of the weathering crust and overlying carbonaceous siltstones or directly in the carbonaceous siltstones. The siltstones are also commercially germanium-bearing, although Ge concentrations are lower than in the the overlying coal seams. This fact is consistent with significantly higher mobility of U during the weathering under oxidizing conditions than Ge. According to numerous studies, the loss of U, mainly the "mobile" form, occurs in the early stages of the weathering crust formation. As some studies have shown, even relatively "fresh" granites can lose up to 70% or more of U with minor weathering (Smellie & Stuckless, 1985; Stuckless et al., 1977; Stuckless & Nkomo, 1978, 1980). Due to the fact that the migration capacity of Th in the hypergenesis zone is much less than that of U, this leads to the increase of thorium-uranium ratio in the altered part of the granites and allows us to trace the formation of the weathering crust (Titaeva, 2005). Formation of the U mineralization occurs at the earliest stages of the basement granite transformation. This may explain the exceptional association of the U mineralization with the lowest, i.e., the earliest sediments of the Pavlovsk depression. Subsequent weathering of granites in humid climate was not accompanied by any significant input of U in paleobogs. The residual U is represented there mainly in the form of accessory minerals and entered the coal seam mainly as mechanical admixture. This explains not only its relatively low content in the coal seams in comparison with what would be expected based on the anomalous radioactivity of the granites, but also the increased thorium-uranium ratio. Where there is weathering of granites in contemporary conditions, modern hypergenic U anomalies are formed. However, such anomalies in coals can form only near the source area because the reducing environment in the coal seam sharply limits the migration of U in waters of the hypergenesis zone. The position of the Spetsugli germanium deposit at a distance from the Pavlovsk depression margins is not favorable for the U accumulation in the coal-bearing sediments after the coal seam formation and overlapping the granite basement protrusion by sediments. In the neighboring open-pit "Pavlovsky-2″ near the boundary with the margins formed by the same granitoids of the Voznesenk complex, the U anomaly of 0.23% was detected in the coals. With the ash yield of the sample of 32.5% it would be 0.70% of U in coal ash. The uranium anomaly is accompanied by the accumulation of Mo (127 ppm), W (118 ppm) and As (114 ppm). In addition, based on the fact that there is no radioactive equilibrium in the decay series of 238U in the studied sample, we can conclude that the age of the U anomaly is less than 1.7 Ma (Titaeva, 2005).

Beryllium is one of the typical elements of the Ge mineralization in coals. It was one of the first noted as a satellite of Ge in germanium-coal deposits (Kostin et al., 1973). The Be content of 54.4 ppm in the germanium-bearing coals of the Spetsugli deposit, relatively consistent across the section , which is more than 40-times higher than its mean content in coals of the world. The coals outside the ore body are also significantly enriched with Be, but the enrichment factor is half as much. The Be halo, as well as the W halo, is wider than the Ge halo. The steam coals from the Pavlovsk deposit are significantly poorer with Be than the coals from the Spetsugli germanium deposit. The connection of the beryllium enrichment with the granite protrusion is clearly seen.

However, some aspects of the Be enrichment in the coals is unclear. The sampled greisenised granite of the basement is enriched with Be, but not by a significant amount and yet the coal seams have anomalous Be contents. It is possible that the beryllium-bearing rock varieties were located in the upper part of the protrusion and were eroded. In the neighboring Voznesensk ore district, greisen ores with quartz-topaz-zinnwaldite and cassiterite-wolframite- berthrandite paregenesis are known (Kupriyanova and Shpanov, 1997). The absence of correlation with the ash yield suggests a hydrogenous mechanism for its accumulation in the coals. This is also indicated by the relative Be absence in the host sedimentary rocks. On the other hand, the coal inclusions in the sandstones are slightly enriched with Be (Table 5), although they are anomalous with respect to Ge and other satellite-elements. The study of its modes of occurrence in the coals showed that from 30 to 40 % of Be in the metal-bearing coals is still associated with the organic matter. Beryllium has significant correlation with Ge, Li, Cs, W, U, REE, Y, Hg, Sb, As, as well as Fe and Na.

7. Main regularities of the distribution of germanium and associated elements

Despite Ge and all associated elements of the Ge mineralization being related to the granite protrusion, their distribution features are different. The distribution of Ge in the deposit significantly differs from the distribution of W and Be (Sedykh, 2008). The halo of increased concentrations of W and Be is wider than the halo of Ge. Based on published data only in the central part of the deposit there are blocks where the Ge, W, and Be halos coincide to some extent (Sedykh, 2008). Such distribution of the elements, in the absence of strongly pronounced zonality, testifies to independent inflow of each of these elements into the coal seam. In the case of the inflow of the elements in one solution from a thermal source, there is usually a strongly pronounced zonality caused by different mobility of the elements and their relation to the zone of hydrotherm discharge (Grigoryan, 1987; Voroshilov, 2009) For example, this is shown for peats of the Nalychevskaya depression in Kamchatka, where the halos are clearly bound with the hydrothermal discharge zone (Kostin and Meitov, 1972). The attempt to relate the Ge, W, and Be distribution halos to tectonic disturbances, as in the schemes of Sedykh (2008), was unsuccessful. Also, significant tectonic faults, which could have acted as conduits for hydrothermal solutions, were not recorded in the exposed basement.

8. Results and discussion

The clarification of the source and conditions of the accumulation of Ge and associated elements in the coal and coal-bearing rocks of the Spetsugli deposit is of great scientific and practical importance, as this knowledge determines the development of criteria and markers to identify similar mineralization in other areas. At present there are two models for the formation of this mineralization: one hydrothermal and the other hypergenic. The hydrothermal model requires the discharge of hypothetical hydrotherms associated with major tectonic faults in the basement, with access to the coal-bearing sediments in the Oligocene-Miocene time. It has gained the greatest acceptance among geologists since the end of the twentieth century. Its attractiveness is determined by the automatic solution of the Ge source problem in the deposit. In this interpretation, the hypothetical source is fluids bringing Ge and characteristic satellite elements in connection with volcanogenic-hydrothermal processes in the subsurface (Kostin et al., 1973; Ivanov et al., 1984; Levitsky et al., 1994; Sedykh, 1999; Seredin and Danilcheva, 2001; Qi et al., 2004, 2007; Dai et al., 2015a; Dai et al., 2015b; Dai et al., 2018). The conductors of such fluids are large tectonic faults in the basement that appeared or were refreshed during the period of the peat and coal accumulation. Exploitation of the Spetsugli germanium deposit has uncovered a significant area of basement where there is no evidence of hydrothermal activity in the post-weathering crustal formation period on the basement rocks of the Pavlovsk depression. Traces of hydrothermal activity were only identified in connection with the formation of the granite massif of the Voznesenk complex that composes the basement and in the later period in connection with the formation of the Late Permian dike complex. In both cases, the time gap between the formation of hydrothermally altered rocks (quartz-feldspar metasomatites and greisen), associated rare metal mineralization, and the formation of germanium-coal mineralization is more than 200 million years. One small post-coal tectonic disturbance, a localised minor fault, has been identified in the deposit, but no trace of hydrothermal activity has been identified in connection with it. There are no traces of cataclasis and mylonitization and no tectonic breccias have been identified. The content of Ge and its satellites in the disturbance zone is not elevated relative to other parts of the seam. No traces of volcanic activity synchronous or subsynchronous to coal accumulation (Eocene-Oligocene) have been detected either within the Pavlovsk Depression or in its margins. The ash tuffs whose lenses were identified above the coal-bearing sequence are airborne pyroclastic material and zircons from them record the age of explosive eruptions at a distance from the depression. Thus, the absence of any trace of hydrothermal activity within the uncovered part of the deposit does not support the hydrothermal model.

Previous evidence of the hydrothermal nature of this type of germanium mineralization has been limited to the specific geochemical association of Ge with W, Be, Sb, and As. It was noted that the characteristic set of associated elements cannot be realized with the participation of a single carbonaceous-nitrogen fluid due to different properties of the elements forming the association (Dai et al., 2015b). It was suggested that the formation of Ge - W and As - Hg – Sb element associations could occur from different hydrothermal sources at different stages of ore formation (Seredin, 2006; Dai et al., 2015b). However, in the Spetsugli deposit the closest relationship is found between Ge and Sb ($r = 0.91$), which suggests their joint deposition. In addition, the multi-stage hydrothermal ore formation implies not only clear occurence of metasomatic zoning, but also repeated refreshing of tectonic zones for the penetration of metal- bearing fluid into the upper horizons of the coal sequence. No supporting evidence for this has been detected. The coal-bearing sediments are virtually unaffected by tectonic deformation and contain no traces of hydrothermal activity.

Some papers have referred to the presence of carbonate, chalcedony, and chlorite microstreaks in some horizons of coal-bearing siltstones (Seredin, 2003a, 2006). However, the formation of such mineral phases is also common where there is no connection with thermal waters (Yurgenson et al., 2004). As one of the criteria of hydrothermal water involvement, an increased value of $\delta^{18}O$ was noted in the Lincang deposit (China) (Hu et al., 2009). However, the exogenous nature of $\delta^{18}O$ and δD isotopic ratios in kaolinite developed on the granites of the Pavlovsk depression basement was demonstrated by Nechaev et al. (2018). As determined for Kuzbass, the long-term interaction of soda waters with coal and aluminosilicate rocks leads not only to increased mineralization, but also to a significant shift of isotopic ratios towards $\delta^{18}O$ weighting by 2-7‰ and $\delta^{13}C$ by 25.5–30.9‰ (Shvartsev et al., 2016; Lepokurova, 2018). Soda waters are the most common type of water in coal basins (Lepokurova, 2020). Highly significant correlation Na with Ge ($r = 0.79$), Sb ($r = 0.90$), Hg ($r = 0.73$), U ($r = 0.70$), As ($r = 0.62$) and other associated elements in the germanium mineralization and the formation of rare-earth carbonates (bastnesite) in the coal seams indicates a high probability of soda waters participation in the processes of element redistribution in the ore bodies. The hydrotherms in the Spetsugli germanium deposit were previously associated with basite dikes of the Cenozoic age (intrusive analogues of the Miocene age basalts), undercut by boreholes in the basement (Seredin, 2003, 2005). The dikes with the rare metal mineralization are of the Late Permian age, as shown by the present studies. They have the same weathering crust as the host granites. Probably, their composition is not basite either based on the chondrite normalized REE distribution which shows a Europium minimum (Fig. 10). The Europium minimum (Eu/Eu*=0.20), typical for rocks of felsic composition, is clearly seen. For the host granite dikes there is an even greater contrast (Eu/Eu*=0.13–0.16).

A number of studies recognise that the sources of Ge and associated elements in both the Spetsugli and Lincang deposits are the basement rocks below the coal sequence, but their inflow into the coal seams is caused by the involvement of hydrothermal solutions (Sedykh, 1999; Dai et al., 2015; Hu et al., 2009; Etschmann et al., 2017; Liu et al., 2021; Jiu et al., 2021b). The present authors suggest that the formation of siderite, calcite chlorite, and kaolinite is not particularly convincing evidence for hydrothermal activity as these minerals are also common in the hypergenic zone without hydrothermal involvement. The connection of rare metal mineralization of the germanium-rich Vulantuga coal deposit with coal-bearing rocks of granitoid composition was also proved with the use of strontium isotopes (Liu et al., 2021). The authors substantiated the hydrogenous model with participation of meteoric waters in the enrichment of coals with Ge and W at the stage of the peat accumulation. In another article on the same subject, the difference between the hydrothermal model proposed by the authors and the classical hypergene model is only participation of thermal waters in this process (Jiu et al., 2021b). It is known that in the absence of Ge-enriched lithological rock complexes, even in the presence of volcanism, the germanium-bearing hydrotherms are not formed (Kraynov, 1973). The participation of fluids in the ore-forming processes is always relatively easy to recognize by the presence of specific mineral associations, hydrothermal-metasomatic zoning and textural and structural features. None of this has been identified within the coal- bearing cover in the Spetsugli germanium deposit. Metasomatic processes are clearly shown

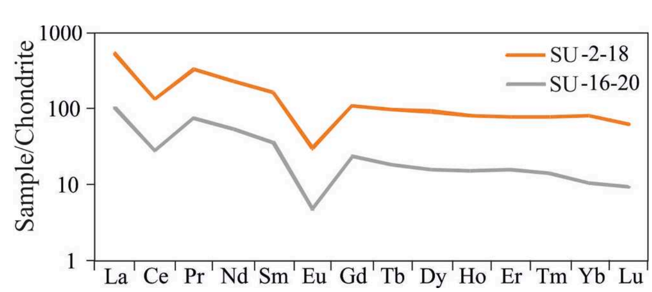

Fig. 10. Chondrite-normalized graphs of the REE distribution in the weathered basement dikes of the Spetsugli (SU-2–18) and «Pavlovsky-2» (SU-16–20) areas.

in the basement of the Pavlovsk depression, including in the Spetsugli area, where the formation of quartz-feldspar metasomatites and greisen is clearly identified, but all these hydrothermal- metasomatic alterations occurred in the period preceding the formation of the weathering crust in the basement and are pre-coal processes. No traces of hydrothermal alteration of the basement rocks after formation of the weathering crust have been identified in the outcropped part of the deposit.

The absence of direct evidence of the involvement of hydrothermal solutions in the formation of the germanium mineralization and the evidence of its clear relationship with the composition of the basement rocks and the coal-bearing depression margins led to the creation of a hybrid model for the Yimin deposit, where the role of hydrotherms is reduced only to the redistribution of metals accumulated during hypergenesis in the coal seams (Jiu et al., 2021a).

Kosterin et al. (1963) noted that the coals of the Chyhezsky (Pavlovsk) deposit are characterized by very contrasting negative cerium anomaly, which was interpreted as a consequence of the Ce oxidation to the tetravalent state and its loss either in the outcrop or in the process of migration. In either case, REE underwent an oxidation phase before entering the coal seam. This suggests the presence of the weathering crust over the rare metal granites and dikes as the most likely source of REE in the coals. The presence of a number of potentially commercial occurrences of the REE mineralization of this type was previously determined in the Pavlovsk depression margins (Seredin, 1998; Chekryzhov et al., 2018).

As noted in numerous papers, volcanogenic-hydrothermal processes are characterized by the specific behavior of europium. Hydrothermal fluids are usually enriched with Eu relative to trivalent REE (Haas et al., 1995; Gammons et al., 2005; Chudaeva and Chudaev, 2011; Karpov et al., 2013; Inguaggiato et al., 2017). On chondrite-normalized plots, they give clear positive anomalies. In some cases, there are weakly expressed negative anomalies of europium, which are attributed to the process of fluid interaction with liparites and dacites (Karpov et al., 2013). Modern hydrotherms do not have a cerium minimum. A weakly pronounced cerium anomaly was formed over time during the migration of hydrothermal fluids in the hypergenesis zone (Karpov et al., 2013; Inguaggiato et al., 2017). As can be seen from the data given for the Spetsugli germanium deposit (Fig. 4), in all cases, the presence of distinct Eu minimum is characteristic for the coals, carbonaceous wood from the interlayers, and waters draining in the germanium-bearing seams. If the waters associated with the Cenozoic basite magmatism had been involved in these processes, a positive Eu anomaly would have occurred. Negative cerium anomalies are weaker. According to some studies, the distribution of REE in authigenic chemogenic and biogenic minerals is inherited, reflecting their distribution in aquafacies (Holser, 1997). All this indicates the hypergenic nature of the REE accumulation in the coals of the deposit from their host rocks.

It is known from summarised data that waters in the hypergenesis zone of tungsten deposits contain a very wide range of rare and other elements - W, Mo, Zn, Cu, Li, Rb, F, Sn, Hg, Sb, As (Kraynov, 1973; Zamana et al, 2018). The range of these elements in the waters of specific deposits is determined by the mineral composition of the deposit ores and the general metal features of the region. Our new data obtained about the composition of the remnant of the greisenized granites in the basement indicate that these rocks can be considered as a source of most of elements from the main ore association. The “biotite” fraction extracted from these granites, abnormally enriched with rare alkalis (Li, Rb, Cs), is a rare metal concentrate (Table 4). The mineral matter of this fraction is also enriched with another group of trace elements and can be considered as a source of Zn, Ga, As, Y, Zr, Nb, Sn, Sb, lanthanides, Tl, U, and Th in the coals. The contribution of this fraction to the total balance of each element in the coals varies but is probably significant in most cases. It was determined that most of these elements are contained in it as their own micro-mineral phases or are part of the minerals in the form of impurities. High W concentrations are associated with this fraction. The studied fraction was extracted from the remnant of the slightly greisenized granite. Based on the zoning features of quartz-albite-microcline metasomatites and greisen, we can confidently interpret that the fully developed greisens were hypsometrically higher and, possibly, there were pegmatites typical to the Voznesenk complex (Kononets et al., 2008), now converted to the kaolin weathering crust. The greisens apparently contained W-Mo mineralization and caused the enrichment of the coals with W, Mo, Sn. This is indicated by the presence of molybdenite in the remnant of the greisenized granite and the presence of micron-sized scheelite fragments in the coals near the granite protrusion (Arbuzov et al., 2021b). In addition, in the mineral fraction of the coal seam IIIl in direct contact with the granite protrusion, muscovite (17–20%) and albite (7–13%) together with secondary anhydrite (52–58%), predominate

Significant positive correlations of germanium in the coals with W, Mo, rare alkalis, and Be indicates the rare metal greisens of the Voznesenk complex as the main source of Ge in the coals of the Spetsugli deposit. According to investigations of the metal-bearing greisen of the Voznesenk complex, topaz contents can be up to 20% (Rub & Rub, 2006), with germanium concentrations up to 200 ppm. Topazes are known to have anomalously high contents of Ge, up to 1500 ppm (Ivanov et al., 1989), and abnormally high Sb content. At the same time there is close correlation of Ge with Sb ($r = 0.91$) suggesting the presence of Ge-Sb mineral phases in the source. Such minerals include fahlores typical for greisen W deposits. The Ge content in tennantite can reach 0.5%. Other mineral phases (molybdenite, sphalerite, chalcopyrite, etc.) identified in the greisenized granites are also often carriers of anomalously high Ge (Ivanov et al., 1989; Bernstein, 1985). Sulfosalts containing Sb and As were identified in the greisenized granite from the basement protrusion in the Spetsugli germanium deposit. In addition, Ge is characterized by high correlation with As, Hg, Cd, Ga, Y, and heavy lanthanides. Probably, this range of elements reflects the formation in the basement rocks of hydrothermal REE and sulfide polymetallic mineralization, associated with the Late Permian dike complex. Large occurrences of such mineralization are the rare metal deposits of the Voznesenk ore district located to the northwest of the Spetsugli deposit (Ryazantseva et al., 2003; Khanchuk, 2006; Kononets et al., 2008; State geological map of the Russian Federation, 2011).

The hypergenic model of the Spetsugli germanium deposit ore formation on the basis of the currently available information seems to be the most reasonable. The composition of the coal in the coal- bearing seams includes fragments of cassiterite, arsenopyrite, topaz, fahlores, and cinnabar. The high content of muscovite and sericite, microcline, albite, topaz and other characteristic greisen mineral phases (cassitrite, scheelite) in the coal-bearing sandstones is good evidence for the molybdenum-tungsten greisens as a potential source of Ge and W. The presence of small clastogenic forms of these hydrothermal minerals in the coals indicates the weathering crust formation directly during the accumulation of the swamp. The stability of scheelite, wolframite, and molybdenite during weathering in humid climate is low, therefore, the preservation of the mineral phases is insignificant. But W is well sorbed by the organic substance of the peat, forming the most stable compounds with humic acids and with lignin. It is important to note that W is a typomorphic element of alkaline waters formed in crystalline rocks (Kraynov, 1973; Kraynov et al., 2012). In alkaline environment, it is easily leached from scheelite and somewhat less from wolframite. In acidic environments its mobility is lower. This is probably the reason for the presence of W-poor ferromanganese crusts directly in the weathering crust and those W-enriched in the coal seams near the weathering crust. In the first case, under oxidizing conditions, wolframite was easily destroyed, and the alkaline solution contributed to the removal of tungsten. In other conditions, partially decomposed wolframite with Fe and Mn hydroxide admixture was moved to acidic or near neutral reducing environment of the paleopeatland and was preserved in it. The same phases form Ge and Sb. Tungsten in the hypergenesis zone conditions is not highly mobile and, as a rule, migrates over small distances not exceeding several hundred meters (Kraynov et al., 1965; Kraynov, 1973; Chechel, 2020). Molybdenum, as a very mobile element in the hypergenesis zone, migrates more actively. Molybdenum traces were identified by Chekryzhov (unpublished data) at a distance of 1.5-km from the Spetsugli deposit at the bottom of the coal-bearing stratum of the "Pavlovsky-2″ open pit. A lenticular body was found there, represented by molybdenite and ilsemanite. Anomalous Mo contents were also noted in some samples in the ash from the lower seams of the deposit. Anomalous Mo was also detected in the coals in contact with the granite weathering crust within the Pavlovsk deposit 2-km north of the Spetsugli germanium deposit.

The formation of the weathering crust probably took place mainly during the formation of the coal-bearing sediments. According to paleobotanical, isotopic, and geochemical data (Pavlyutkin et al., 2020; Bechtel et al., 2020), the beginning of the coal formation in the Pavlovsk depression coincides with the end of the Eocene climatic optimum in the region that was favorable for the crust formation. The subsynchroneity of the crust formation and the beginning of the coal accumulation is also indicated by the presence of uranium mineralization in the coal-bearing mudstones at the bottom of the coal stratum (Levitsky and Ivanov, 1969). The ore reserves are insignificant, so it was considered as a cut-off grade ore. However, the presence of these ores in the underlying weakly permeable sediments is the evidence of the U input at the stage of their accumulation. Their relation to the protrusion of the basement testifies to their rather probable interrelation with the weathering granites. Since U has high mobility in the hypergenesis zone and can be eroded at the early stages of the granite weathering, very little is retained in the mature weathering crusts. At two different sites in the Pavlovsk deposit the U content does not exceed 2 ppm, whereas the relatively fresh granite uncovered at the bottom of the central protrusion in the Spetsugli area contains 10–38 ppm uranium. Uraninite was recorded in these granites. According to a radiogeochemical classification, such granites belong to the group of rare metal highly radioactive granites (Rikhvanov, 2003).

In summary, the studies reviewed in this work, indicate the hydrogenic mechanism of the formation of the complex rare metal mineralization of the Spetsugli germanium coal deposit in the process of the weathering crust formation on the greisenized granites of the Voznesenk complex without the participation of hydrothermal fluids, either synchronous with or post-coal formation. This is confirmed by the composition of mineralization, modes of occurrences of germanium and associated elements, shapes of the ore bodies, and mineral and geochemical zoning. The formation of the deposit was favoured by the presence of the granite basement protrusion in the centre of the deposit with specific rare metal mineralisation, the development of the kaolin weathering crust along it and a favourable hydroregime during the peat accumulation.

9. Conclusions

The Spetsugli germanium-coal deposit has a complex mineralogy. The metal-bearing coals are characterized by abnormally high contents of Ge, Sb, Hg, W, Li, Be, Cs, and As, which exceed the mean contents for world brown coals by factors from 10 to 100 s. Also concentrated, but not to the same degree, are U, Mo, Y, Rb, medium and heavy lanthanides, Zn, and Ga.

The mineralogical-geochemical and geological-structural analysis of the composition and structural features of the Spetsugli germanium-coal deposit leads to the conclusion that the model that best fits the data is the hydrogenic hypergenic model, rather than the generally accepted hydrothermal model.

The rare metal mineralization in the coals is related to a granite protusion in the basin, which was exposed at the time the coals were accumulating. Compelling evidence for the link is provided by the concentric concentration zones of germanium and associated elements in the coals around the granite protrusion. In addition, the wide range of elements concentrated in the coals is consistent with a hydrogenic hypergenic origin rather than hydrothermal. There is also a lack of field evidence for hydrothermal activity during and after coal formation.

The granites of the basement protrusion had been subjected to earlier hydrothermal-metasomatic alteration with the formation of quartz-albite-microcline metasomatites and greisens containing W-Mo and Hg-Sb-As mineralization. A phase of mineralization which is well documented in granites of this province. The metasomatically altered granites and dikes were then subjected to hypergenic alteration in the Eocene-Oligocene at the time of coal formation. This alteration led to the formation of kaolin weathering crust, the destruction of primary endogenous mineralization and the transfer of elements to the surrounding paleo-peatlands.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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