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Ge-Bearing Coals of the Luzanovka Graben, Pavlovka Brown Coal Deposit, Southern Primorye

V. V. Seredin, Yu. A. Danilcheva, L. O. Magazina, and I. G. Sharova†

Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry, Russian Academy of Sciences, Staromonetnyi per. 35, Moscow, 119017 Russia

e-mail: seredin@igem.ru

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Abstract—Results of the study of a new Ge-bearing area of the Pavlovka brown coal deposit are presented. Ge is accumulated in bed III_2 lying at the bottom of the Late Paleogene–Early Neogene coal-bearing sequence adjacent to the Middle Paleozoic granite basement. The Ge content in coals and coal-bearing rocks varies in different sections from 10 to 200–250 ppm, reaching up to 500–600 ppm in the highest-grade lower part of the bed. The metalliferous area reveals a geochemical zoning: complex Ge–Mo–W anomalies subsequently grades along the depth and strike into Mo–W and W anomalies. Orebodies, like those at many Ge-bearing coal deposits, are concentric in plan and dome-shaped in cross-section. Coals in their central parts, in addition to Ge, W, and Mo, are enriched in U, As, Be, Ag, and Au. Distribution of Ge and other trace elements in the metalliferous sequence and products of gravity separation of Ge-bearing coals is studied. These data indicate that most elements (W, Mo, U, As, Be) concentrated like Ge in the Ge-bearing bed relative to background values are restricted to the organic matter of coals. The electron microscopic study shows that Ge-bearing coals contain native metals and intermetallic compounds in association with carbonates, sulfides, and halogenides. Coal inclusions in the metalliferous and barren areas of the molasse section strongly differ in contents of Ge and associated trace elements. Ge was accumulated in the coals in the course of the interaction of ascending metalliferous solutions with organic matter of the buried peat bogs in Late Miocene. The solutions were presumably represented by N_2-bearing thermal waters (contaminated by volcanogenic CO_2) that are typical of granite terranes.

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INTRODUCTION

The Pavlovka deposit, the second largest brown coal deposit in Primorye is characterized by not only enormous reserves of solid fuels (~400 Mt), but also anomalous metal contents (Seredin, 1996; Seredin, 2004a, 2004b). The Ge-bearing coals are best studied among diverse ore-bearing rocks of the Pavlovka deposit. The first area of Ge-bearing coals at the Pavlovka brown coal deposit, presently known as the Spetsugli germanium deposit, was discovered and explored more than 30 years ago. Geology and geochemistry of this giant deposit are considered in numerous publications (Kostin et al., 1973; Ivanov et al., 1984; Levitskii et al., 1994; Sedykh, 2002; Seredin, 2003a, 2004b).

This work presents data on a new Ge-bearing coal occurrence discovered in the southern part of the Luzanovka graben during geochemical study in the late 1990s (Seredin et al., 1999; Seredin and Danilcheva, 2001). This ore occurrence was the first object in Russia, where Ge-bearing coals were studied with modern analytical methods. Despite the relatively small amount of inferred Ge resources (30–50 t), the data obtained are of significant interest, because information on small germanium deposits and occurrences were not previously published. The absence of such data hampered the comparison of small and large germanium deposits in the coal-bearing sequences and ruled out the development of criteria for their discrimination at the early stages of study.

†Deceased.

OBJECTS AND METHODS

Geological Structure and Evolution of the Luzanovka Graben

The Pavlovka brown coal deposit located within the Voznesensk terrane of the Khankai Massif consists of several small Late Cenozoic coal-bearing basins (Fig. 1). These rift structures formed simultaneously with repeated outbursts of volcanic activity. This is evidenced by the presence of the following rocks: (1) argillized basaltic horizon (previously considered as sedimentary rocks) within the Miocene coal-bearing sequences 1 km east of the Spetsugli area; (2) tuffaceous material and interbeds of acid tuffs among Late Miocene silty–sandy sediments of the Ust-Suifun Formation that overlies coal-bearing sediments in some basins; (3) Late Pliocene–Early Quaternary basaltic and alkali basaltic lava flows and dikes.

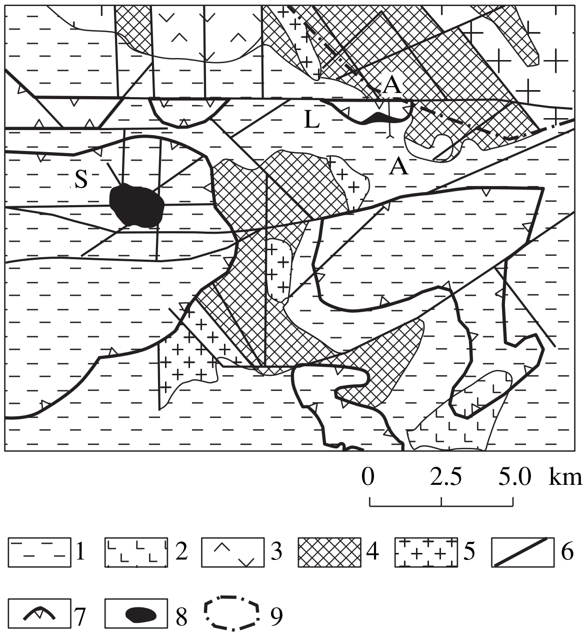

Fig. 1. Geological scheme of the Pavlovka brown coal deposit. (1) Early Neogene–Quaternary coal-bearing deposits and overlying sediments; (2) Late Neogene–Early Quaternary basalts; (3) Middle Paleozoic andesites, dacites, and rhyolites; (4) Early Cambrian carbonaceous–siliceous schists; (5) Paleozoic granites; (6) faults; (7) boundaries of the coal-bearing basins; (8) Ge-bearing coal fields: (S) Spetsugli, (L) Luzanovka; (9) boundary of the Voznesensk ore district. (AA) Section in Fig. 2.

The Luzanovka Basin, one of the coal-bearing structures of the Pavlovka deposit, is an asymmetric graben 5×0.7–1.2 km in size (Fig. 2) located near the southern boundary of the Voznesensk ore district. The ore district incorporates the largest fluorite deposits in Russia, as well as numerous Sn, W, Pb, Zn, Be, and Ta deposits and occurrences related to the Paleozoic granitoid magmatism.

The southern wall and basement of the studied basin area is composed of Late Paleozoic granites, while the northern wall is composed of the Early Cambrian low-grade quartz–sericite and carbonaceous schists with limestone lenses. The basement is cut by numerous basaltic dikes of the supposedly Cenozoic age.

The basin is filled with continental sediments of the Late Paleogene–Early Neogene Pavlovka Formation consisting of weakly cemented sandstones, siltstones, and mudstones with brown coal beds. The beds (1–2 to 10–12 m thick) have a complex structure. They consist of several coal units separated by partings (sandstones, mudstones, and siltstones with a variable amount of organic matter). Coals of the Luzanovka section correspond to slightly metamorphosed varieties (ranks B1 and B2 in the Russian coal geology approximately corresponding to the lignitic and subbituminous classes, respectively) and contain fossil wood inclusions.

The coal-bearing sequence is unconformably overlain by sandy–pebbly rocks of the Late Neogene Suifun Formation and Quaternary clays. The total thickness of the Cenozoic molasse in the Luzanovka graben varies from a few tens to 150–200 m.

The coal-bearing sediments dip gently (5–10°) northward. The thickness of the Pavlovka Formation and the number of coal beds gradually increase in the same direction. The coal beds and enclosing sediments in the northern part of the graben are deformed into recumbent folds, with brecciation of the underlying rocks and plastic deformations of the overlying beds. The plastic deformations are manifested as coal diapirs at the roof of the uppermost bed (III_3), which protrude pebbles and lower clay horizons of the Suifun Formation and lower horizons of Quaternary clays (Fig. 3). The occurrence of diapirism suggests plastic state of organic matter in the upper bed up to the Quaternary time and, hence, relatively recent cessation of coalification of the Miocene organic matter.

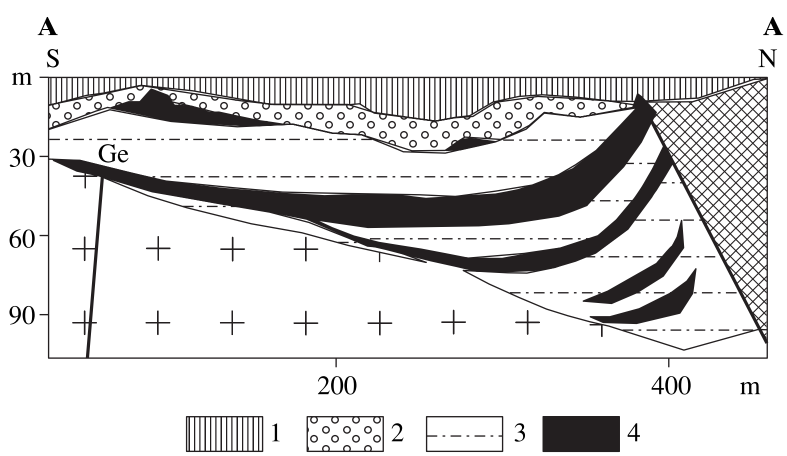

Fig. 2. Schematic geological section across the Luzanovka graben along line A–A (see Fig. 1). (1) Late Neogene–Quaternary clays; (2) sandstones and pebbles of the Late Neogene Suifun Formation; (3) silty sandstones, siltstones, and mudstones of the Early Neogene Pavlovka Formation; (4) brown coals; (Ge) Luzanovka Ge occurrence. Other symbols are as in Fig. 1.

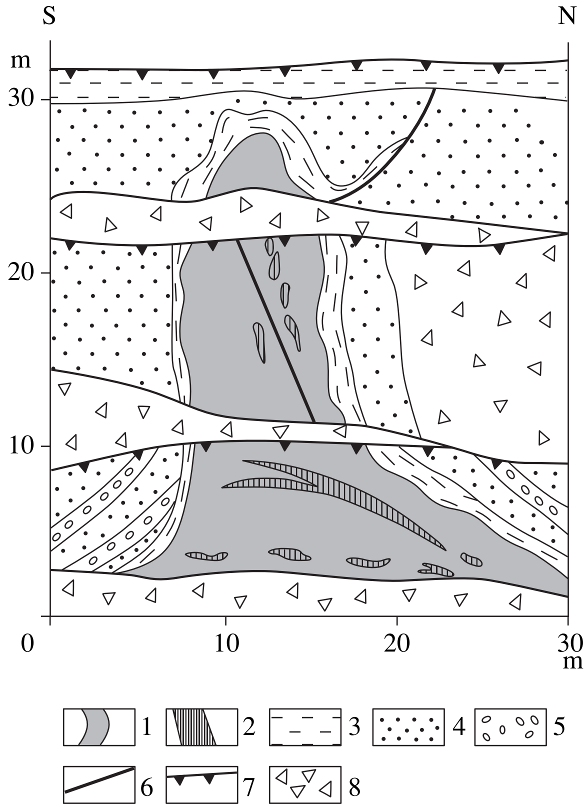

Fig. 3. Coal diapir in the roof of bed III_3 penetrating alluvial sediments of the Suifun Formation. Wall of the Luzanovka coal section, August 8, 1989 (sketch of V.V. Seredin). (1) Coal; (2) coal-bearing clays; (3) siltstones and mudstones; (4) sands; (5) pebbles; (6) faults; (7) margins of escarpments; (8) talus.

Based on the structure and composition of the Cenozoic molasse, evolution of the Luzanovka graben can be divided into three main stages: (1) Late Paleogene–Early Neogene subsidence; (2) Late Neogene inversion; and (3) Quaternary compression.

The first stage involved asymmetric subsidence of the graben floor and accumulation of the coal-bearing sequence with a characteristic splitting of coal beds toward the mobile fault-line border (Varnavskii and Kuznetsov, 1987). During the formation of lower beds (I, II) at the beginning of the stage, coal accumulated only near the northern wall in the maximal subsidence area. Then, the process of coal deposition occupied the entire graben area (bed III_2). The coal deposition area again reduced before inversion (bed III_3).

The second stage was marked by pulsating uplift of the area, which preceded the outburst of volcanic activity and the eruption of basaltic flows in the Pavlovka deposit area. At this time, the upper part of the coal-bearing sequence was rapidly eroded. Therefore, only fragments of bed III_3 are preserved. Then, eroded surface of the Pavlovka Formation was overlain by the Suifun pebbles that were also subsequently eroded.

At the final stage, the dominant extensional setting was replaced by compressional one, resulting in the transformation of normal faults around the basin into reverse faults, overthrusting of basement rocks onto the Cenozoic sediments, and intense fault-line deformations of the coal-bearing sequences along the northern wall of the Luzanovka graben.

Such an evolution scenario is typical of the fault-line asymmetric coal-bearing grabens in Primorye and other regions of the world (Varnavskii and Kuznetsov, 1987; Sedykh, 1997).

Methods

Geochemical investigations were performed in the western part of the Luzanovka coal-bearing basin in 1995–1997. By that time, its eastern part was already exhausted. Core material was taken from 49 boreholes and analyzed.

The coal beds were sampled according to requirements applied during prospecting and exploration of metalliferous coals (Kler et al., 1988). Assignment of samples to bed sections was controlled by methods of borehole geophysics.

All samples were dried, ground to 2-mm particles, quartered, and material for analysis was taken in this process. The material was powdered and ashed in an open muffle furnace at 550–600°C. Such ashing conditions make it possible to minimize the loss of most volatile trace elements (Kler et al., 1988). This was later confirmed by the comparison of Ge contents in ashed and primary coal samples.

The analytical work was carried out at three stages. At the first stage, approximately 2000 samples were analyzed by the semiquantitative spectral methods using evaporation of samples in the electrode channel in the Spectral laboratory of Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry (A.I. Galudzina and S.I. Gavrilova, analysts).

At the second stage, 105 Ge-rich samples were analyzed by the traditional chemical method (Russian standard GOST 10175-75) at the Institute of Fossil Fuels (M.Ya. Shpirt and N.P. Goryunova, analysts), the proton-induced X-ray emission (PIXE) method at the Eagle Peatcher Co. (United States), and the ICP-MS (S.A. Gorbacheva, analyst) and XRF (A.I. Yakushev, analyst) methods at the Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry. The chemical and ICP-MS methods included the procedure of sample ashing. The PIXE analysis was used to analyze primary samples, while the XRF method was applied to determine the Ge content in both coal and ash. Data on boreholes 7 (samples 723–730) and 45 (samples 396–402) show good agreement between results obtained by different methods and absence of significant Ge loss at the chosen ashing regime (Table 1).

At this stage, samples from boreholes 7 and 45 drilled at the center of different orebodies were also

Table 1. Ge contents (ppm) in coals and host rocks measured by different methods

Sample	Rock	A^d, %	Chem.(a)	PIXE(c)	ICP MS(a)	XRF(c)	XRF(a)	Average
723	1	10.3	111.0	125.0	126.3	–	–	120.8
724	1	9.7	146.0	154.0	179.5	–	–	159.8
725	1	17.2	139.0	131.0	139.0	–	–	136.3
726	1	46.2	116.0	120.0	171.9	–	–	136.0
727	1	14.6	211.0	224.0	233.6	–	–	222.9
728	2	61.1	122.0	111.0	105.7	–	–	112.9
729	1	17.5	564.0	610.0	504.9	588.0	–	566.7
730	2	55.0	231.0	212.0	208.5	–	–	217.2
396	1	25.0	163.0	113.7	105.5	–	117.5	124.9
397	1	32.7	–	189.5	159.9	183.1	186.4	179.7
398	1	37.1	193.0	179.3	156.9	186.4	181.8	179.5
399	2	60.5	–	302.4	255.3	285.1	272.3	278.8
400	2	59.0	443.7	463.9	426.6	476.1	531.0	468.3
401	3	91.2	–	31.9	26.4	37.3	–	31.9
402	4	95.7	–	8.5	3.3	–	–	5.9

Note: (c) Contents analyzed in the coal; (a) contents determined in ash and calculated on a whole coal basis; (–) not determined. (1) Coal, (2) coal-bearing siltstones and sandstones; (3) siltstones and mudstones, (4) sandstones.

studied by the INAA, ICP-MS, and ICP-AES methods. Thus, we obtained representative data on the abundance of many elements that were not previously determined in metalliferous coals of this type (REE, U, Th, and others) or determined only by the semiquantitative spectral analysis (W, Mo, Be, and others). The silicate composition of the Ge-bearing coal ash was analyzed in these samples by the XRF method. In addition, Hg contents were determined in samples from borehole 7. Eight samples of coals and coal-bearing rocks were analyzed by the cold vapor atomic absorption (CVAA) method in the US Geological Survey Laboratory.

At the third stage, we studied sample 389 taken from borehole 44 in the central part of the bed. The aim of these investigations was to determine modes of the occurrence of Ge and associated elements in the metalliferous coals. For these purposes, we analyzed the trace element distribution in the specific gravity fractions of coals and studied the coal mineralogy with SEM-EDX method.

Ge-bearing coals were fractionated in organic and heavy liquids in the Laboratory of Inorganic Components of Solid Fuels at the Institute of Fossil Fuels (N.P. Goryunova, analyst).

SEM-EDX study of metalliferous coals (L.O. Magazina, analyst) was performed at the Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry on a JSM-5300 microscope equipped with Link ISIS. Fresh chips of samples and mineral grains picked under a binocular microscope were analyzed. Pure materials and their natural compounds were used as standards.

RESULTS

Structure and Geochemical Zoning of the Ore Field

Zone of anomalous Ge concentrations in bed III_2 outlined by the Ge content of 10 ppm coal extends for 1.5 km along the southern wall of the Luzanovka graben at a width of 150–350 m (Fig. 4a). In this part of the structure, beds I and II are absent, while bed III_2 rests immediately on granites or near the basement. The Ge content in bed III_2 beyond the metalliferous zone is <1–3 ppm, which corresponds to the clarke value for brown coals (Yudovich et al., 1985). Similar distribution is typical of only Mo and W, the accumulation level of which is comparable with that of Ge and can be tens or hundreds of times higher than background values for brown coals (Figs. 4b, 4c).

The anomalous W-rich zone is wider than the Mo-rich zone, which, in turn, is wider than the Ge-rich zone. The Ge–Mo–W anomalies are successively replaced by the Mo–W and W anomalies from the south to north. The wider areal distribution of anomalous W contents, as compared to that of Ge, was previously noted at some deposits (Kler et al., 1987). In the Luzanovka occurrence, tungsten is also distributed far beyond the Ge mineralization in the vertical cross-section of metalliferous coal-bearing sequence. The preserved fragments of bed III_3 contain 110 ppm W per 3–5 m thickness. Narrow (0.1–0.2 m) intervals enriched

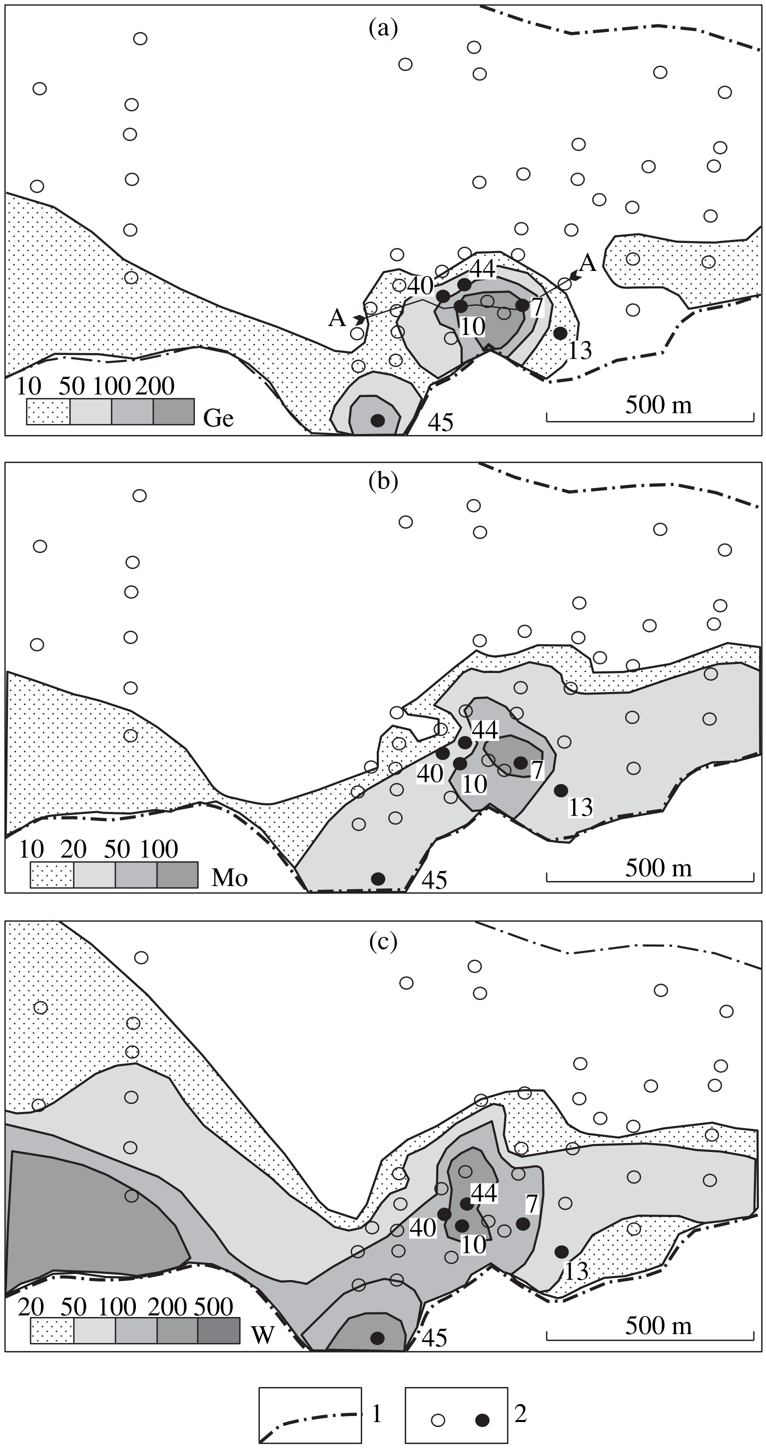

Fig. 4. Ge, Mo, and W distribution in bed III_2. (1) Boundaries of the bed; (2) boreholes (solid circles with numbers are boreholes mentioned in the text). (A–A) Section in Fig. 5.

in Ge (up to 70–75 ppm) and Mo (up to 20 ppm) are sporadically found at the bottom of the upper bed.

Concentration of metals in the southern rather than northern wall adjacent to the Voznesensk ore district contradicts concepts of the spatial and genetic relation of Cenozoic Ge mineralization of the Pavlovka deposit with the Paleozoic rare metal mineralization.

Geological Setting and Structure of Orebodies

The geochemical field of the Luzanovka area, like the geochemical fields of other similar deposits (Kostin and Meitov, 1972; Seredin, 2004b), shows irregular Ge distribution. Concentric anomalies recorded in the metalliferous zone can be considered as individual local

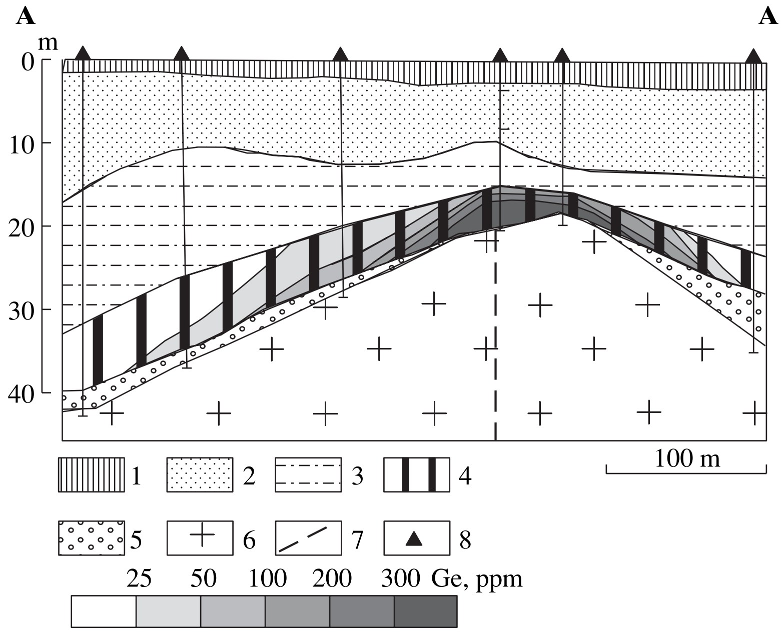

Fig. 5. Distribution of the Ge concentration in bed III_2, Northern orebody. (1) Quaternary clays; (2) Pliocene sandstones and pebbles; (3–5) Miocene coal-bearing sequence: (3) weakly lithified sandstones and siltstones; (4) coals, (5) conglomerates and breccia-conglomerates; (6) Middle Paleozoic granites; (7) fault; (8) boreholes. For location of the section, see Fig. 4.

orebodies (Fig. 4a). They are located at the intersection of sublatitudinal faults extending along the southern wall with faults of different orientations. The faults are traced by basaltic dikes and escarpments in the basement relief, as well as brecciation zones and flexures in coal beds. Two such orebodies (Northern and Southern) were recovered by boreholes. Structure of the geochemical field suggests the presence of additional two orebodies on the western and eastern sides.

The dome-shaped Northern orebody is located above a small basement uplift (Fig. 5). The highest Ge contents are found in the lower part of the bed. The thickness of the high-Ge zone (Ge > 100 ppm coal) is reduced from 4.5 (borehole 10) to 1 m or less. Brecciation of bed in the central part of the orebody is responsible for low core recovery in boreholes drilled here. Basement granites recovered by these boreholes are also brecciated. They experienced intense argillization (kaolinite and montmorillonite) and contain finely disseminated siderite and pyrite.

The Southern orebody is located above the slope of the basement uplift. Thickening of the Ge-rich interval from 0.6 at the periphery of the coal bed to 3 m in the central zone (borehole 45) suggests that this body is also characterized by a dome- or mantle-shaped morphology.

Ge Distribution across the Profile of the Bed

The Ge distribution across bed III_2 significantly differs in different parts of the Northern orebody (Fig. 6).

High Ge contents (>100 ppm) in boreholes in the central highest-grade part of the orebody are traced throughout the whole section (boreholes 10 and 7). Maximal contents (567 ppm in borehole 7 and 506 ppm in borehole 10) are restricted to the lowermost coal unit. The Ge contents gradually decrease toward the bed roof. Similar pattern is typical of the mineralized interbeds. Like the coal-bearing units, the lower partings are universally enriched in Ge than the upper ones. Such a parallel decrease of Ge content in the coals and partings from the bottom to top is distinctly observed in borehole 10. The Ge contents here vary as follows (from bottom to top): 506 ⟶ 384 ⟶ 318 ⟶ 143 ppm in the coal units and 238 ⟶ 102 ⟶ 40 ppm in the partings.

In the lowermost unit of the orebody, the Ge content varies from 150 to 256 ppm in boreholes 40 and 44, respectively, which is 2–3 times lower than those in boreholes 7 and 10. In the upper part of the bed, the Ge content decreases to 36 and 10 ppm, respectively. The Ge content in coals from borehole 44 decreases toward the bed roof (256 ⟶ 98 ⟶ 70 ⟶ 36 ppm), while the Ge content in borehole 40 shows a sharp (10 times) decrease of Ge content in the upper unit located above clay parting.

The typical Ge distribution in boreholes drilled in the marginal zone of orebody can be illustrated by borehole 13. High (80–190 ppm) Ge contents were found only in the 50-cm-thick interval near the bottom. Upward, they sharply drop to background values (1–3 ppm). It should be noted that the most contrasting Ge

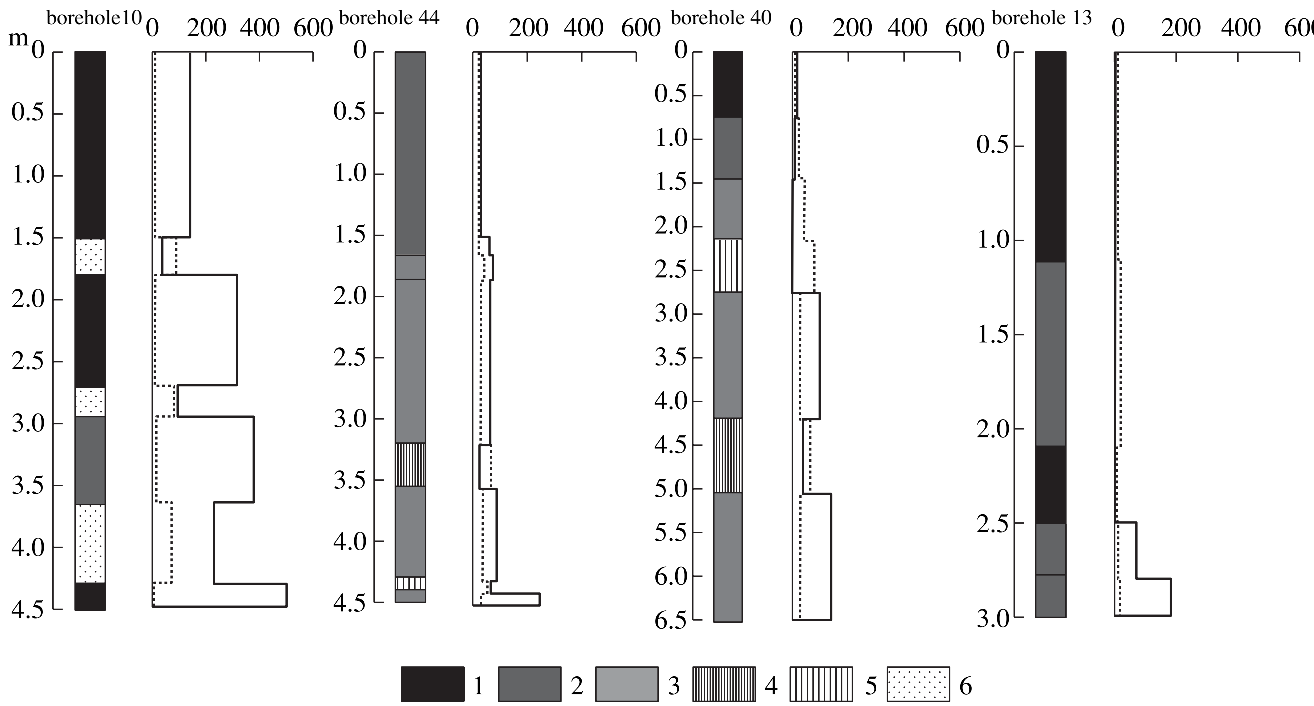

Fig. 6. Distribution of Ge (solid line) and ash (dashed line) contents across the Ge-bearing bed (Luzanovka occurrence) in the central (borehole 10), intermediate (boreholes 44 and 40) and peripheral parts (borehole 13) of the orebody. (1–3) Coals: (1) low-ash (A^d, <15%), (2) moderate-ash ($15 < A^d < 35\%$), (3) high-ash ($35 < A^d < 50\%$); (4) coaly siltstones; (5) clays; (6) silty sandstones.

distribution typical of this part of orebody is observed in the bed with a simple structure and is unrelated to the presence of clay partings.

Thus, all considered examples are characterized by decrease in the Ge content from bottom to roof of the bed. In each case, specifics of the manifestation of these trends are determined by the combination of two factors: position within orebody and structure of bed, i.e., number, thickness, and composition of mineral interbeds (partings). Since the Ge content in the partings is universally lower than in the adjacent coal horizons, the vertical Ge distribution in the Northern orebody has a saw-like shape. However, this statement is only valid for the adjacent intervals. If we compare the Ge contents in remote section samples from borehole 10, coal-free rocks from the lower parting turn out to be enriched in Ge relative to the low-ash coal of the roof.

Such a pattern of Ge distribution across metalliferous beds indicates its input with ascending high-pressure waters. In our case, the spreading dome-shaped structure typical of the present-day mineral veins in nonlithified sediments is complicated by heterogeneity of the medium (intercalating horizons of organic matter, sands, and clays with different degrees of permeability for metalliferous waters and sorption capacity for Ge).

Geochemistry of Ge-Bearing Coals and Coal Inclusions

Contents and levels of trace element accumulation in the Ge-bearing coals

In spite of the spatial proximity and insignificant differences in the average Ge contents in coal (154 ppm in borehole 45 and 228 ppm in borehole 7) and whole bed (180 and 202 ppm, respectively), the Northern and Southern orebodies show significant geochemical differences (Tables 2–4). As was shown in (Seredin, 2004b), with respect to the world background values, coals from the Southern orebody most the highest concentrations of the following elements (concentration coefficient, CC is shown in parentheses): W (272), U (177), Ge (64), Au (23), Mo (9.0), As, Be (5), and Ag (3). Coals from the Northern body predominantly accumulate Ge (95), W (82), Mo (32), Au (16), Ag, Be (5), and U (4). The Ge-bearing coals from the Southern orebody are 44.5 times enriched in U, 8.7 times enriched in As, 3.3 times enriched in W, 14 times depleted in Se, and 3.6 times depleted in Mo as compared to coals from the Northern orebody. Differences in abundances of other elements are less significant.

Se and Mo typically associate with U in sedimentary sequences at the majority of infiltration deposits, including coal-bearing uranium deposits (Kislyakov and Shchetochkin, 2000). Therefore, low Se and Mo contents in coals of the uraniferous Southern orebody

Table 2. Chemical composition of the coal ash and host rocks from boreholes 7 and 45

Sample no.	Thick-ness, m	A^d, %	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O_3	K_2O	P_2O_5	L.O.I.	Total
723	0.2	10.3	49.35	1.17	19.75	7.92	0.14	2.34	10.82	0.21	1.40	0.06	7.20	100.36
724	0.2	9.7	49.19	1.00	17.57	7.69	0.18	2.57	11.38	0.30	1.90	0.08	7.70	99.56
725	0.2	17.2	58.75	0.67	15.82	6.02	0.12	1.49	6.86	0.65	2.60	0.06	6.60	99.64
726	0.15	46.2	72.52	0.38	11.93	4.07	0.06	0.59	2.16	0.58	3.92	0.05	3.00	99.26
727	0.2	14.6	52.99	0.89	21.87	6.28	0.13	1.85	7.84	0.09	2.24	0.04	6.20	100.42
728	0.4	61.1	63.51	0.70	24.65	2.42	0.02	0.66	1.13	0.08	2.88	0.02	3.90	99.97
729	0.2	17.5	57.60	0.64	17.10	5.35	0.11	1.42	6.20	0.39	3.23	0.04	7.00	99.08
730	0.4	55.0	65.07	0.62	20.50	3.40	0.04	0.65	1.34	0.25	3.57	0.04	3.80	99.28
Coal (7)	1.15	18.1	60.51	0.68	16.14	5.64	0.10	1.41	6.13	0.43	2.91	0.05	6.28	100.30
396	1.05	25.0	56.41	0.87	18.68	11.50	0.11	1.32	6.08	0.30	1.80	0.10	4.23	101.40
397	0.45	32.7	55.10	0.71	23.25	14.02	0.07	0.88	2.83	0.21	1.33	0.07	3.55	102.02
398	1.0	37.1	56.20	0.64	23.18	12.18	0.06	0.81	2.43	0.27	1.44	0.13	3.20	100.54
399	0.15	60.5	61.94	0.68	29.95	4.00	0.04	0.63	1.18	0.12	1.76	0.07	1.10	101.47
400	0.15	59.0	59.14	0.61	30.93	3.53	0.03	0.51	1.18	0.10	1.90	0.13	0.93	98.99
401	0.1	91.2	62.16	0.58	28.20	2.75	0.02	0.30	0.37	0.13	2.87	0.07	0.15	97.60
Coal (45)	2.5	30.6	56.06	0.73	21.68	12.30	0.07	0.99	3.73	0.27	1.54	0.12	3.66	101.16

Note: Coal (7) and coal (45) are the weighted average contents of oxides in the coal ash from boreholes 7 and 45, respectively; (L.O.I.) loss on ignition. High L.O.I. values typical of coal ash are related to incomplete ashing of OM during heating at 550°C.

suggest that U was accumulated by a different mechanism.

Thus, both orebodies show high contents of Ge, W, Mo, Au, Ag, Be, and U. In terms of elements maximally accumulating in the coals, the Southern and Northern orebodies have W–U–Ge and Ge–W–Mo specializations, respectively.

Geochemical specifics of the orebodies are also expressed in the REE composition (Fig. 7). Normalized REE distribution in coals and coal-bearing rocks of both orebodies shows low La_N/Yb_N values (<1), indicating the H-type pattern (Seredin, 2001). However, REE patterns of coals and coal-bearing rocks from the Northern orebody exhibit sharp Eu minimum typical of coal beds from the basins with granite basement and framing, whereas those in the Southern orebody show less expressed anomaly up to its complete disappearance in the coal-bearing clays. Coals from the Southern orebody are generally enriched in LREE and, especially, in Eu (by 1.6 times) with respect to the Northern orebody. Similar (1.8 times) relative Eu enrichment is observed in the coal-bearing rocks of the Southern body (Fig. 7c).

The Ge-bearing coals from the Northern and Southern orebodies also sharply differ in the major element composition. Average Fe and P contents in coals from borehole 45 are almost four times higher than in borehole 7. Differences in the ash content (30.6% in borehole 45 and 18.1% in borehole 7) are insignificant to explain such enrichment by increase in the terrigenous admixture.

Variations in concentrations of the major elements depending on the ash content show that the distribution of Fe and Mn in samples from borehole 7 is similar to that of Si (element of the terrigenous component of coal). In samples from borehole 45, the distribution is similar to that of Ca that typically accumulates in the organic matter of brown coal (Fig. 8). Hence, U enrichment in coals of the Southern orebody correlates not only with high Fe and P contents, but also with Fe and Mn concentrations in the organic part of coal.

High contents of the majority of elements accumulating in coals are also typical of virtually organic-free sedimentary rocks. Mudstones underlying the coal bed have extremely anomalous contents of Ge (31.9 ppm), W (87.6 ppm), U (45.6 ppm), Ag (3.5 ppm), and Au (0.31 ppm), while sandstones are enriched in W (111 ppm), As (102.4 ppm), Ag (0.3 ppm), and Au (0.15 ppm).

Such a high level of trace element concentration in coal-free rocks is observed only near the central parts of orebodies. The majority of mudstone and siltstone samples beyond these areas show background values of trace elements. Hence, sporadic high contents of trace elements in the sedimentary rocks cannot be explained by the introduction of terrigenous suspension enriched in these metals into the coal accumulation basin.

Table 3. Contents (ppm) of trace elements in samples from borehole 45 and their concentration coefficients in the Ge-bearing coals relative to background values in the coals

	Sample no.							Coal (45)	Coal (b)	CC
	396	397	398	399	400	401	402			
Be	11.3	12.4	11.1	12.7	14.8	10.0	7.5	11.2	2.1	5.3
B	75.0	65.4	111.3	30.3	118.0	27.4	28.7	86.1	63.0	1.4
Sc	4.3	5.2	5.6	9.7	9.4	12.8	9.1	4.9	2.7	1.8
V	29.0	46.4	46.7	47.2	57.2	21.0	11.5	38.5	24.2	1.6
Cr	19.0	23.2	18.2	12.1	18.3	17.3	17.2	19.0	14.2	1.3
Co	3.5	2.9	3.2	3.8	2.7	3.0	6.0	3.2	4.5	0.7
Ni	8.5	7.0	6.6	8.5	5.6	9.3	8.4	7.3	10.2	0.7
Cu	30.0	42.5	37.1	21.8	62.5	34.7	135.9	34.4	11.8	2.9
Zn	25.0	39.2	55.7	60.5	106.2	36.5	114.8	39.0	27.8	1.4
Ga	8.3	12.4	13.0	32.1	36.0	45.6	31.6	10.7	6.5	1.6
Ge	124.9	179.7	179.5	278.8	468.3	31.9	5.9	153.5	2.4	64.0
As	39.0	153.4	116.9	58.1	116.2	10.0	102.4	89.0	19.1	4.7
Se	0.3	0.3	0.2	0.5	0.3	0.4	0.4	0.2	2.9	0.1
Rb	11.5	14.4	16.7	38.7	35.4	66.6	102.4	13.8	15.0	0.9
Sr	72.8	60.2	69.0	84.1	88.5	41.0	71.8	67.6	103.0	0.7
Y	12.8	13.4	14.8	22.4	15.3	12.8	24.9	13.4	7.5	1.8
Zr	34.0	44.8	43.8	83.5	98.5	179.7	194.3	39.1	37.0	1.1
Nb	3.3	4.3	4.1	7.9	8.9	14.6	17.2	3.7	2.2	1.7
Mo	20.0	24.5	23.0	7.9	11.8	3.7	1.5	21.6	2.4	9.0
Ag	0.11	0.18	0.19	0.32	0.25	3.47	0.32	0.15	0.05	3.0
Cd	0.3	0.4	0.4	0.7	0.9	0.5	0.3	0.3	0.4	0.9
Sb	0.3	3.0	0.5	0.6	0.8	2.7	1.1	0.9	1.2	0.7
Cs	2.1	3.6	4.1	10.3	8.3	11.9	9.6	3.1	1.2	2.6
Ba	125.0	179.9	222.6	151.3	206.5	182.4	287.1	170.5	129.8	1.3
Hf	1.3	1.6	1.8	3.3	3.5	8.5	10.1	1.5	1.2	1.2
Ta	0.4	0.4	0.5	0.9	1.1	1.8	2.1	0.4	0.27	1.5
W	625.0	758.6	667.8	439.8	460.8	87.6	111.0	653.1	2.4	272.1
Au	0.05	0.09	0.07	0.26	0.09	0.31	0.15	0.07	0.003	22.5
Tl	0.4	1.5	1.4	1.2	0.9	2.4	1.8	1.0	0.5	2.0
Pb	9.0	11.8	12.6	25.4	20.1	18.2	28.7	10.7	12.8	0.8
Bi	0.2	0.3	0.3	0.9	0.3	1.1	0.6	0.3	0.7	0.4
Th	8.3	8.8	8.9	19.4	17.7	19.2	18.2	8.4	3.8	2.2
U	106.5	635.8	594.3	194.8	128.6	45.6	8.4	389.1	2.2	176.9
La	13.3	18.2	19.3	25.0	12.9	27.9	15.0	16.2	12.0	1.4
Ce	24.9	33.0	34.5	47.3	21.6	48.8	36.8	29.6	21.0	1.4
Pr	2.8	3.8	4.1	5.3	2.8	5.9	3.3	3.5	2.4	1.4
Nd	10.9	13.7	14.9	20.2	10.5	21.5	12.1	12.8	9.5	1.3
Sm	2.0	2.6	3.0	4.1	2.0	3.5	2.3	2.4	1.7	1.4
Eu	0.45	0.40	0.48	0.98	0.56	0.37	0.64	0.44	0.4	1.1
Gd	2.3	2.9	3.1	4.7	2.2	3.3	2.7	2.7	1.8	1.5
Tb	0.3	0.4	0.4	0.7	0.4	0.4	0.7	0.4	0.3	1.2
Dy	1.9	2.3	2.3	4.0	2.5	2.6	3.1	2.1	1.9	1.1
Ho	0.4	0.5	0.5	0.8	0.6	0.5	0.8	0.4	0.35	1.3
Er	1.3	1.4	1.4	2.6	2.0	1.7	2.8	1.4	1.0	1.4
Tm	0.19	0.22	0.19	0.37	0.37	0.31	0.50	0.19	0.15	1.3
Yb	1.3	1.3	1.5	3.0	2.3	2.1	3.9	1.4	1.0	1.4
Lu	0.21	0.21	0.20	0.48	0.38	0.37	0.56	0.20	0.14	1.4

Note: Coal (b) is the background value for elements in the coal (Seredin, 2004b); (CC) is the coal (45)/coal (b) ratio. The ash content is listed in Table 2.

Table 4. Contents (ppm) of trace elements in samples from borehole 7 and their concentration coefficients in the Ge-bearing coal relative to the background value in coals

	Sample no.								Coal (7)	Coal (b)	CC
	723	724	725	726	727	728	729	730			
Be	7.9	7.4	8.1	8.8	11.5	6.7	16.3	6.6	10.1	2.1	4.8
B	61.8	67.9	68.8	46.2	73.0	122.2	87.5	137.5	68.5	63.0	1.1
Sc	2.8	2.2	2.7	3.0	2.6	7.3	3.1	5.9	2.7	2.7	1.0
V	16.7	18.6	29.6	48.5	28.0	65.4	15.7	55.0	25.2	24.2	1.0
Cr	6.3	7.9	9.5	22.2	8.6	40.3	11.7	34.1	10.5	14.2	0.7
Co	4.1	3.6	4.5	5.0	3.7	3.2	2.9	4.2	3.9	4.5	0.9
Ni	4.1	3.9	5.3	17.6	5.0	7.9	8.8	11.0	7.0	10.2	0.7
Cu	16.4	9.6	20.1	65.1	15.3	20.8	27.5	79.8	24.0	11.8	2.0
Zn	15.5	3.9	25.8	46.2	10.2	91.7	26.3	82.5	20.2	27.8	0.7
Ga	2.6	1.9	6.0	9.2	3.7	24.4	8.8	16.5	5.2	6.5	0.8
Ge	120.8	159.8	136.3	136.0	222.9	112.9	566.7	217.2	227.6	2.4	94.8
As	9.6	8.9	10.1	11.6	8.5	22.0	13.1	19.8	10.2	19.1	0.5
Se	5.8	2.0	1.9	2.8	2.0	2.6	6.3	1.5	3.5	2.9	1.2
Rb	6.7	6.0	12.6	8.8	11.5	63.5	14.3	58.3	10.0	15.0	0.7
Sr	61.8	47.4	55.9	90.6	62.1	66.0	60.7	68.2	61.9	103.0	0.6
Y	12.8	11.0	12.6	13.9	15.8	17.7	27.8	20.4	15.7	7.5	2.1
Zr	32.5	16.1	24.8	57.3	21.6	92.3	36.8	77.0	30.4	37.0	0.8
Nb	2.7	1.0	1.9	4.6	1.4	9.2	2.6	7.2	2.3	2.2	1.0
Mo	83.0	57.5	55.4	72.1	100.7	21.4	91.4	51.2	76.9	2.4	32.0
Ag	0.32	0.03	0.15	0.25	0.09	0.22	0.61	0.20	0.2	0.05	4.8
Cd	0.4	0.1	0.3	0.5	0.4	0.6	0.9	0.8	0.4	0.4	1.1
Sb	0.5	0.5	0.6	0.7	0.4	0.9	8.2	1.4	1.9	1.2	1.6
Cs	1.0	1.4	2.1	3.7	2.6	16.5	2.3	11.0	2.1	1.2	1.8
Ba	257.5	181.4	258.0	462.0	292.0	549.9	350.0	440.0	293.1	129.8	2.3
Hf	0.9	0.8	1.0	2.2	1.0	4.1	1.4	4.7	1.2	1.2	1.0
Ta	0.3	0.2	0.2	0.4	0.1	1.0	0.3	0.8	0.2	0.27	0.9
W	149.1	168.1	165.5	118.7	242.1	113.0	317.1	163.9	196.7	2.4	82.0
Au	0.173	0.015	0.007	0.046	0.035	0.061	0.019	0.055	0.049	0.003	16.4
Hg	0.04	<0.02	0.04	0.07	0.04	0.84	<0.02	0.08	<0.04	0.15	<0.02
Tl	0.2	0.2	0.5	1.3	0.2	2.4	0.2	1.9	0.4	0.5	0.8
Pb	4.1	5.9	8.1	20.3	8.9	28.1	6.5	35.8	8.5	12.8	0.7
Bi	0.4	0.1	0.4	0.5	0.2	0.8	2.0	0.7	0.6	0.7	0.9
Th	3.7	4.5	4.6	6.5	4.8	11.6	5.4	11.6	4.9	3.8	1.3
U	5.3	6.8	5.3	5.1	10.4	5.8	18.7	9.4	8.7	2.2	4.0
La	11.4	11.2	11.4	15.1	13.1	23.2	8.2	29.2	11.6	12.0	1.0
Ce	19.8	20.6	20.5	25.4	22.8	37.9	15.9	48.4	20.6	21.0	1.0
Pr	2.3	2.6	2.6	3.0	2.9	4.9	2.6	5.5	2.7	2.4	1.1
Nd	9.5	10.2	10.1	12.0	11.0	17.1	8.9	22.0	10.2	9.5	1.1
Sm	2.2	2.4	2.4	2.7	2.5	3.8	2.3	4.9	2.4	1.7	1.4
Eu	0.3	0.3	0.3	0.4	0.3	0.4	0.2	0.4	0.3	0.4	0.7
Gd	2.3	2.0	2.3	2.4	2.6	4.2	3.2	4.5	2.4	1.8	1.4
Tb	0.4	0.3	0.4	0.4	0.4	0.7	0.6	0.8	0.4	0.3	1.4
Dy	2.3	2.0	2.2	2.3	2.6	4.3	3.5	4.4	2.5	1.9	1.3
Ho	0.5	0.4	0.5	0.5	0.5	0.9	0.9	0.9	0.5	0.35	1.5
Er	1.3	1.2	1.4	1.4	1.5	2.7	2.5	2.8	1.5	1.0	1.5
Tm	0.2	0.2	0.2	0.2	0.2	0.4	0.4	0.4	0.2	0.15	1.4
Yb	1.3	1.1	1.3	1.5	1.3	2.7	2.5	2.8	1.5	1.0	1.6
Lu	0.2	0.2	0.2	0.2	0.2	0.4	0.4	0.4	0.2	0.14	1.6

Note: See notes for Table 3.

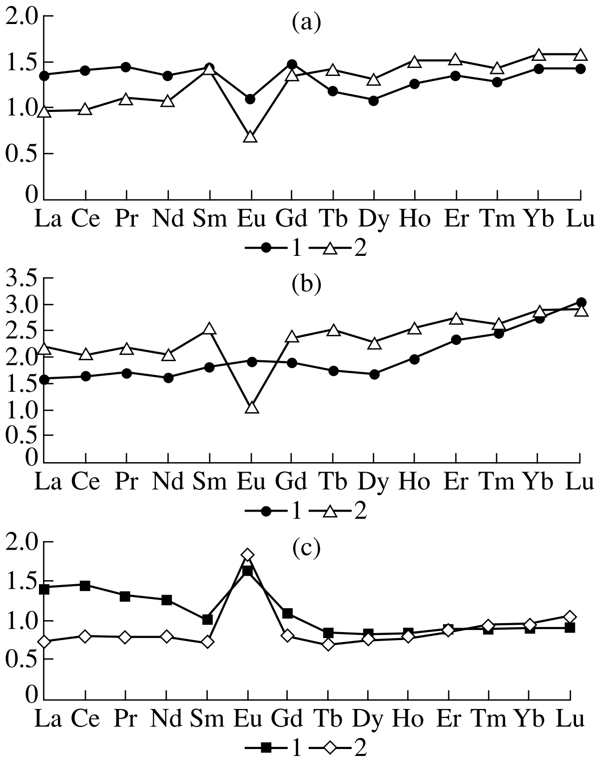

Fig. 7. REE distribution patterns in the coals and coal-bearing rocks from boreholes 7 and 45. (a) Coals: (1) borehole 45; (2) borehole 7. (b) Coal-bearing rocks: (1) borehole 45; (2) borehole 7. REE contents are normalized to the average REE contents in the USA coals (Finkelman, 1993). (c) Borehole 45/borehole 7: (1) coals; (2) coal-bearing rocks.

Trace element distribution across the bed

In terms of distribution pattern, all studied elements can be divided into several groups (Figs. 9, 10). The first group includes trace elements (Zr, Hf, Nb, Ta, Th, and others) and the major components (Si, Al, Ti, K and others) compose terrigenous minerals. Their vertical distribution is very similar to that of the ash content. Anomalous contents of these elements are unknown in the considered coals.

The second group includes most trace elements (Ge, W, Mo, U, and Be) that strongly enrich coals relative to background values. Their contents in the coal and coal-bearing rocks from borehole 45 are higher than in the coal-free siltstones and sandstones. In borehole 7, their contents in the coal units are higher than in partings, suggesting the predominance of organic compounds of these elements in the coals.

The distribution of As has positive correlation with its content in coals. In particular, As (39–153 ppm) behaves as a typical organophile element in borehole 45 and correlates with the ash content and elements of terrigenous component in borehole 7 (As 9–13 ppm).

The third group includes trace elements lacking any correlation with the ash content. These elements are often concentrated near the bed near contract zones of the bed. As seen in borehole 7, average contents of these elements in coals can correspond to background values (Sb, Bi, and Se) or strongly exceed them (Au and Ag). Local maximums of these elements at the coal bed roof, which is least enriched in Ge, indicate that an additional portion of Ag, Au, and some other elements

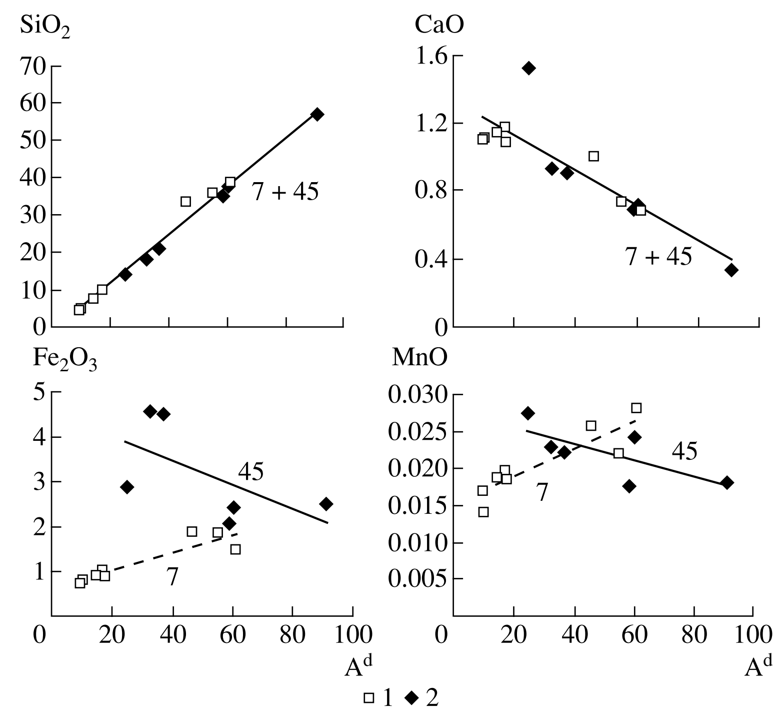

Fig. 8. Variations of SiO_2, CaO, Fe_2O_3, and MnO (%) vs. ash content. (1) Sample from borehole 7; (2) sample from borehole 45.

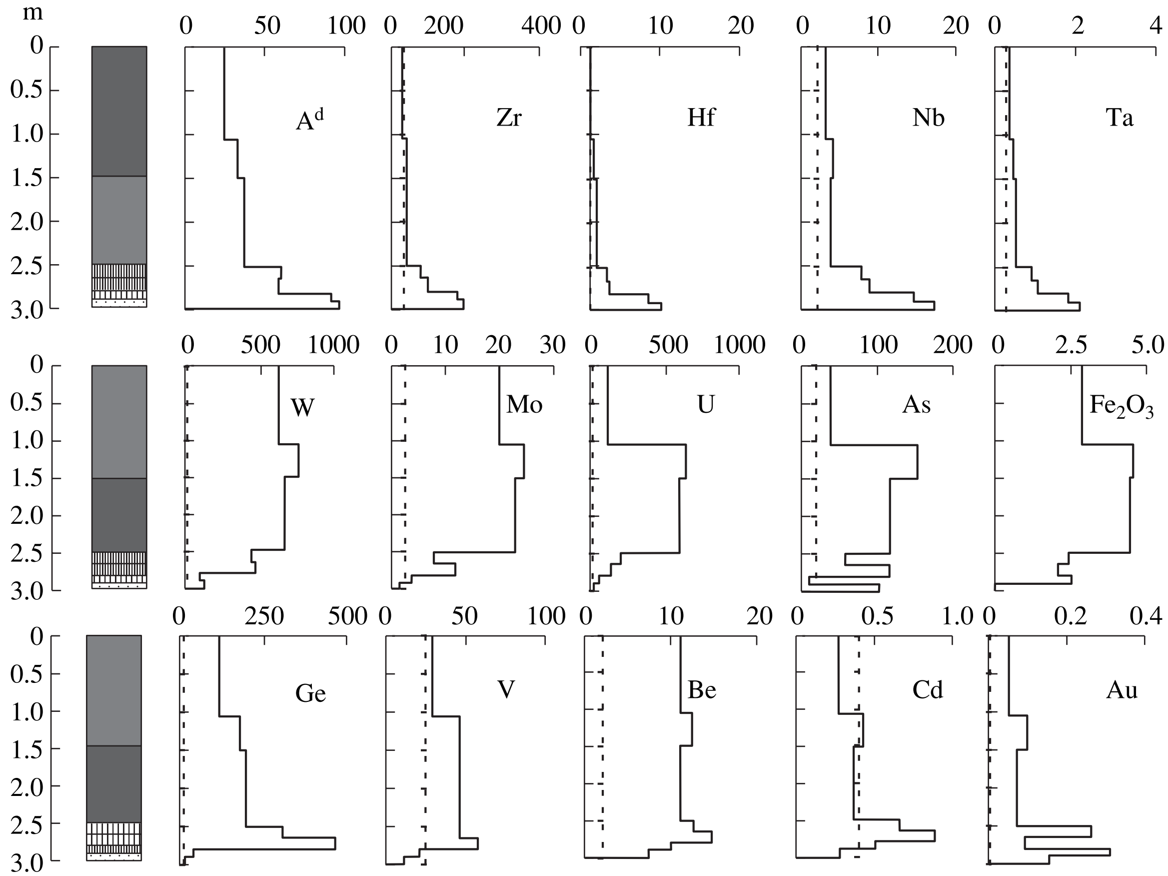

Fig. 9. Distribution of ash content and trace elements across the Ge-bearing bed III_2 (borehole 45). Fe_2O_3 and A^d are given in %, other elements, in ppm. Background contents of elements in the coals are shown by dashed line. Legend as in Fig. 6.

was introduced together with solutions circulating along the roof after the Ge mineralization.

Distribution of trace elements in specific gravity fractions of coals

The Ge distribution in different-density fractions of Ge-bearing coals has been discussed in (Ratynskii et al., 1966; Kler et al., 1988). However, the distribution of other elements in them remains poorly studied. Examples of five most frequent distribution patterns are shown in Fig. 11.

The majority of trace elements (Zr, Hf, Ta, Ba, Ga, Cs, Rb, Ti, Al, K, Na, Cu, Zn, Pb, Tl, Bi, Co, and Ni) show the first type of distribution. Their distribution in the fractions is generally consistent with the ash content distribution. Concentrations of these elements correlate with the density of fractions and the content of mineral particles in them.

The second pattern typical of Ca, W, and Mo is almost opposite to the first pattern. Contents of all these elements decrease from the light to heavy fractions, with a small peak in the fraction with a density of 1.45–1.53 g/cm^3. Such a distribution is commonly attributed to the organic mode of occurrence of trace elements in the coals. Some decrease of trace element concentrations in the lightest fraction can be related to the increased content of resin bodies, which are typically depleted in trace elements (Kler et al., 1988).

The third type with maximums in the moderate-density fraction is typical of Ge, U, and B. Such a distribution was previously noted for Ge in the Ge-bearing coals (Ratynskii et al., 1966; Shpirt et al., 1990), as well as for REE in the high-REE coals (Seredin, 1996). It was proposed that all these elements occur in coal as organic compounds. Relative Ge accumulation in the moderate-density fractions was found in coals from the Blue Gem seam (Kentucky, United States) (Hower et al., 1994). It was established that such a Ge distribution correlates with vitrinite distribution. Probably, a similar situation is observed in our case, since vitrinite is the main carrier of Ge in the Ge-bearing coals (Kler et al., 1988; Yudovich and Ketris, 2004).

The fourth distribution type with peak in fraction 1.64–1.8 g/cm^3 is typical of P, most REEs (except the heaviest species), Y, Nb, Ag, Sb, and Cd. Similar distribution of P and REE is quite natural, because phos-

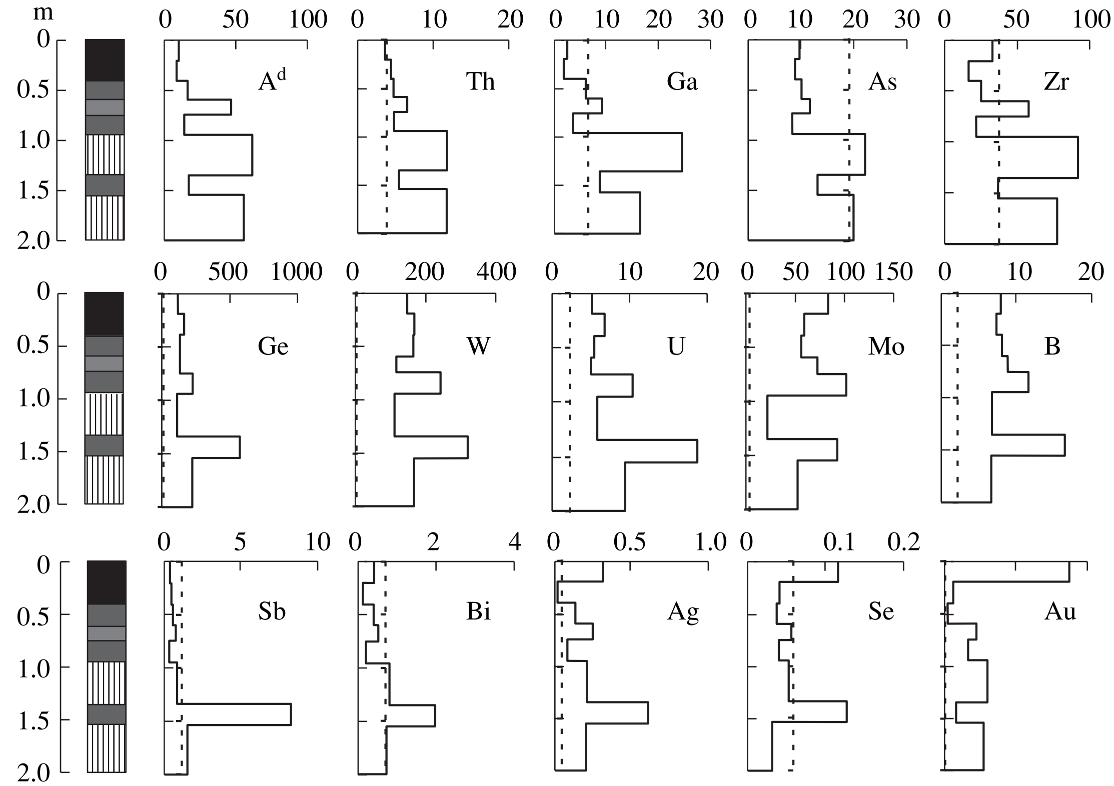

Fig. 10. Distribution of the ash (%) and trace element (ppm) contents in the profile across the Ge-bearing bed III_2 (borehole 7). Legend as in Fig. 9.

phates are the main carriers of REE and Y in the coals (Finkelman, 1993).

The fifth pattern observed in a large group of trace elements (V, Cr, Sc, As, Au, Fe, Mg, Sr, Sn, Th, Be, Tm, Yb, and Lu) is a combination of types 1 and 3. These elements show double peaks in the moderate and heaviest fractions, suggesting two different modes of their occurrence in the coals. These elements are transported by both organic matter and mineral particles.

The possible occurrence of trace elements in different modes is seen from REE distribution patterns. As seen in Fig. 12a, REE distribution patterns of three light and two heavy fractions are sharply different. These differences become sharper if one compares the weighted average REE contents in both groups and the values normalized to contents in the starting sample (Fig. 12b). The presented data distinctly indicate different modes of REE occurrence in the light and heavy fractions of the Ge-bearing coal sample. One can assume that REEs are mainly transported as organic matter in the light fractions and as mineral components (presumably, phosphates and clay particles) in the heavy fractions.

Thus, accumulation of elements (Ge, W, and Mo) characterized by anomalous concentration relative to the background value in the light and moderate fractions of the studied sample may indicate the predominance of their organic compounds. The subordinate trace elements (Ag, Au, and Be) in the coals demonstrate a mixed distribution type with peaks in the moderate and heaviest fractions, indicating the presence of both organic and mineral carriers.

Geochemistry of coal inclusions

The chemical composition of buried plant remains was determined in the following rocks: (1) Miocene silty sandstone interbeds in the Ge-bearing bed (Northern orebody, borehole 10, sample 1026); (2) Miocene sandstones located beyond the metalliferous zone (sample DP-97); (3) Pliocene gray sandy–pebbly sediments of the Suifun Formation, which overlay the eroded surface of coal-bearing sequence in the southern part of the Luzanovka graben (sample D-1).

Plant remains from mineral interbeds in the Ge-bearing bed are geochemically similar to the coals (Table 5). With respect to remains buried in coeval deposits of the barren zone, the plant remains are sharply enriched in the following elements (concentration coefficient is shown in parentheses): Mo (505), W (305), and Ge (210). They are less enriched in U (6), B (5), HREE (3–4), Y, and Be (3).

As compared to plant remains from Pliocene sands of the Suifun Formation, coal inclusions from partings

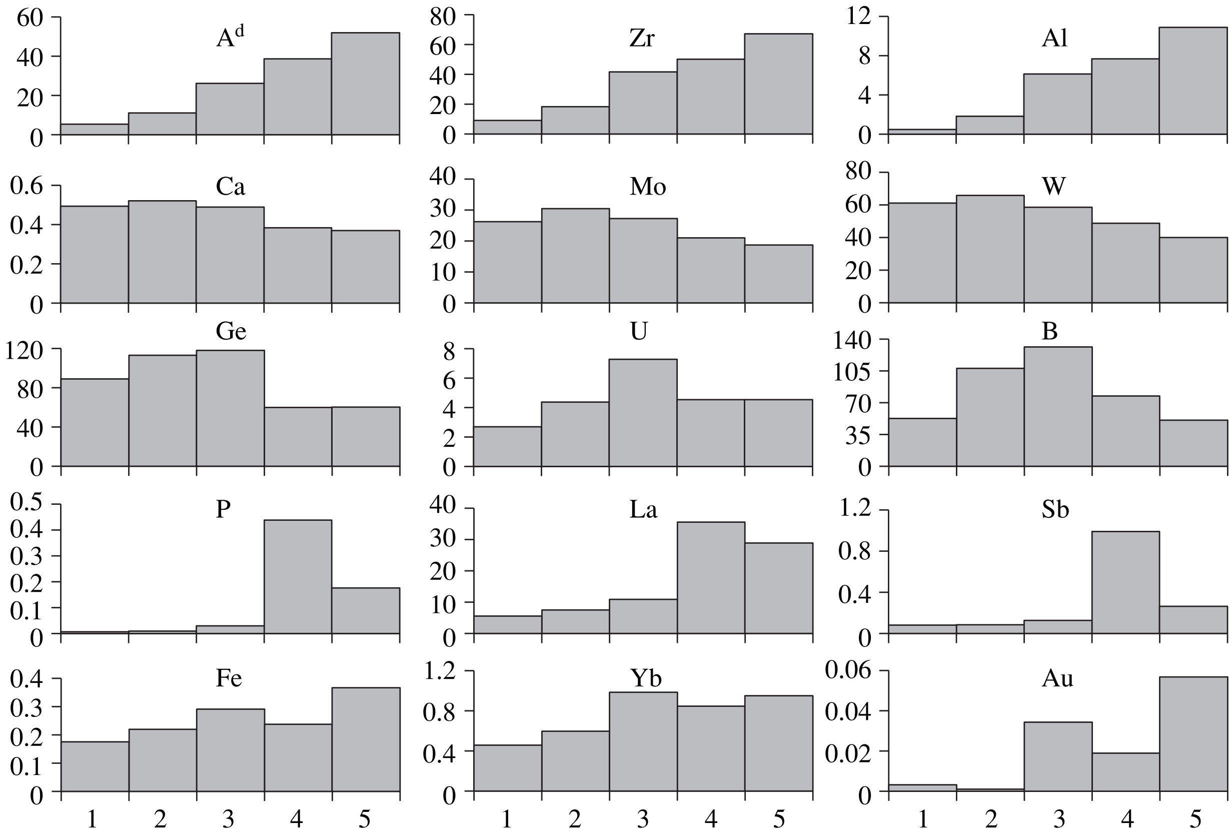

Fig. 11. Distribution of the ash and trace element contents in specific gravity fractions of the Ge-bearing coals. (1–5) Density fractions (g/cm^3): (1) <1.45; (2) 1.45–1.53; (3) 1.53–1.64; (4) 1.64–1.8; (5) >1.8. A^d, Al, Ca, P, Fe are given in %; other elements, in ppm.

of the Ge-bearing bed are enriched in W (183), Ge (53), B (51), Mo (10), Ta (8), and Be (8), but they are significantly (3–15 times) depleted in siderophile (V, Cr, Co, Ni) and some other elements.

As known, most trace elements are accumulated in the fossil wood debris after their extinction and burial through sorption and organic reduction of different ions from solutions circulating in the host rocks (Yudovich, 1972; Seredin and Magazina, 1999). Therefore, the data presented above primarily reflect significant differences in the chemical composition of groundwaters interacting with the plant remains.

Plant remains from silty–sandy partings of the Ge-bearing bed are enriched in Ge (530 ppm). However, these contents do not provide the bulk Ge contents (102–238 ppm) in the parental mineral interbeds, since the content of organic matter in these partings does not exceed 3–5%. This may indicate that clay particles of the partings can accumulate Ge if the content of organic sorbent is low.

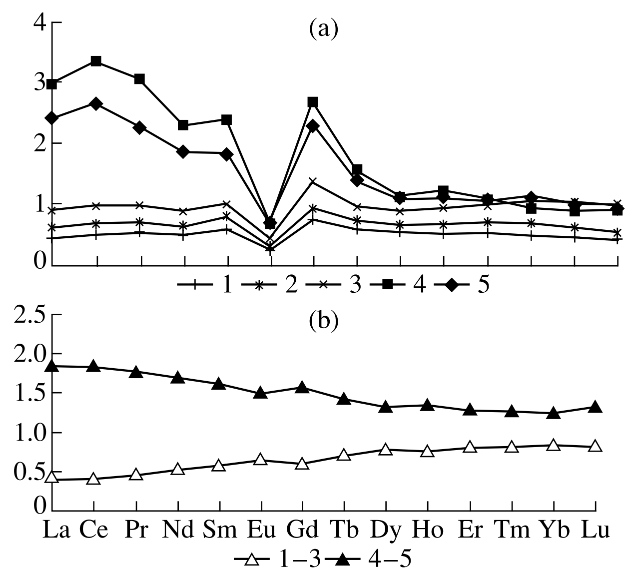

Fig. 12. REE distribution patterns for specific gravity fractions of the Ge-bearing coals. (a) REE contents in fractions normalized to their average contents in the USA coals (Finkelman, 1993). (1–5) Density fractions (see Fig. 11). (b) Total REE contents in the (1–3) light and (4–5) heavy fractions normalized to their contents in the starting sample.

Mineralogy of Ge-Bearing Coals

Study of sample 44-389 showed that Ge-bearing coals of the Northern orebody contain two independent

Table 5. Contents (ppm) and concentration coefficients (CC) of trace elements in coal inclusions

	1026	DP-97	D-1	CC1	CC2
A^d, %	10.6	16.8	10.5	0.6	1.0
Be	2.1	0.7	0.3	3.2	7.5
B	53.0	11.8	1.1	4.5	50.5
Sc	1.0	1.7	11.1	0.6	0.1
V	10.6	37.5	89.6	0.3	0.1
Cr	3.6	16.8	57.8	0.2	0.06
Mn	212.0	52.1	63.8	4.1	3.3
Co	1.1	4.2	5.6	0.3	0.2
Ni	3.2	6.7	11.6	0.5	0.3
Cu	5.3	4.0	59.9	1.3	0.1
Zn	10.6	12.4	19.8	0.9	0.5
Ga	5.3	5.0	3.9	1.1	1.4
Ge	530.0	2.5	10.1	210.3	52.5
Sr	53.0	33.6	21.6	1.6	2.5
Y	5.3	1.7	3.7	3.1	1.4
Zr	31.8	19.8	72.1	1.6	0.4
Nb	2.1	1.5	2.9	1.4	0.7
Mo	212.0	0.4	21.7	504.8	9.8
Ag	0.21	0.09	0.72	2.5	0.3
Sn	0.7	1.0	0.8	0.7	0.9
Sb	0.3	0.7	2.6	0.4	0.1
Cs	0.8	3.9	1.3	0.2	0.6
Ba	74.2	50.4	30.1	1.5	2.5
Hf	1.43	0.55	1.11	2.6	1.3
Ta	0.33	0.29	0.04	1.2	8.0
W	138.5	0.5	0.8	305.4	183.3
Au	0.0392	0.011	0.0018	3.6	22.0
Pb	7.4	2.9	4.4	2.6	1.7
Th	3.3	1.0	3.6	3.3	0.9
U	1.9	0.3	5.0	6.3	0.4
La	6.5	2.3	7.4	2.8	0.9
Ce	12.0	6.0	26.4	2.0	0.5
Nd	5.4	2.1	9.5	2.6	0.6
Sm	1.2	0.4	2.0	2.8	0.6
Eu	0.10	0.08	0.51	1.4	0.2
Gd	1.1	0.3	1.3	3.2	0.8
Tb	0.2	0.1	0.2	3.4	1.0
Yb	0.6	0.1	0.6	4.4	1.2
Lu	0.10	0.02	0.08	4.4	1.2

Note: (CC1) 1026/DP-97; (CC2) 1026/D-1.

mineral assemblages: (a) terrigenous minerals introduced by water and atmospheric flows during peat accumulation (quartz, feldspars, zircons, and other minerals typical of coals); (b) authigenic minerals produced during coal formation.

The authigenic minerals, in addition to common pyrite (framboidal and fine-crystalline), siderite (micronodular) and barites, include different native metals (Al, Fe, Ni, Cu, Zn, Pb, Sn, Ag, and Au), intermetallic compounds (Fe–Si, Fe–Cr, Fe–Cr–Ni, Cu–Ni, Cu–Zn, Cu–Ag, Pb–Sn, Pb–Sn–Bi, Sn–Fe–Pb, Pb–Sn–Au, and Au–Ag), sulfides (Zn–S, Cu–Zn–S, and Fe–Zn–S), as well as halogenides, carbonates, and halogen carbonates (Cu–Zn–Cl, Cu–I, Cu–Co, and Pb–Cl–CO). Such an association of sulfides, halogenides, and carbonates with native metals and intermetallic com-

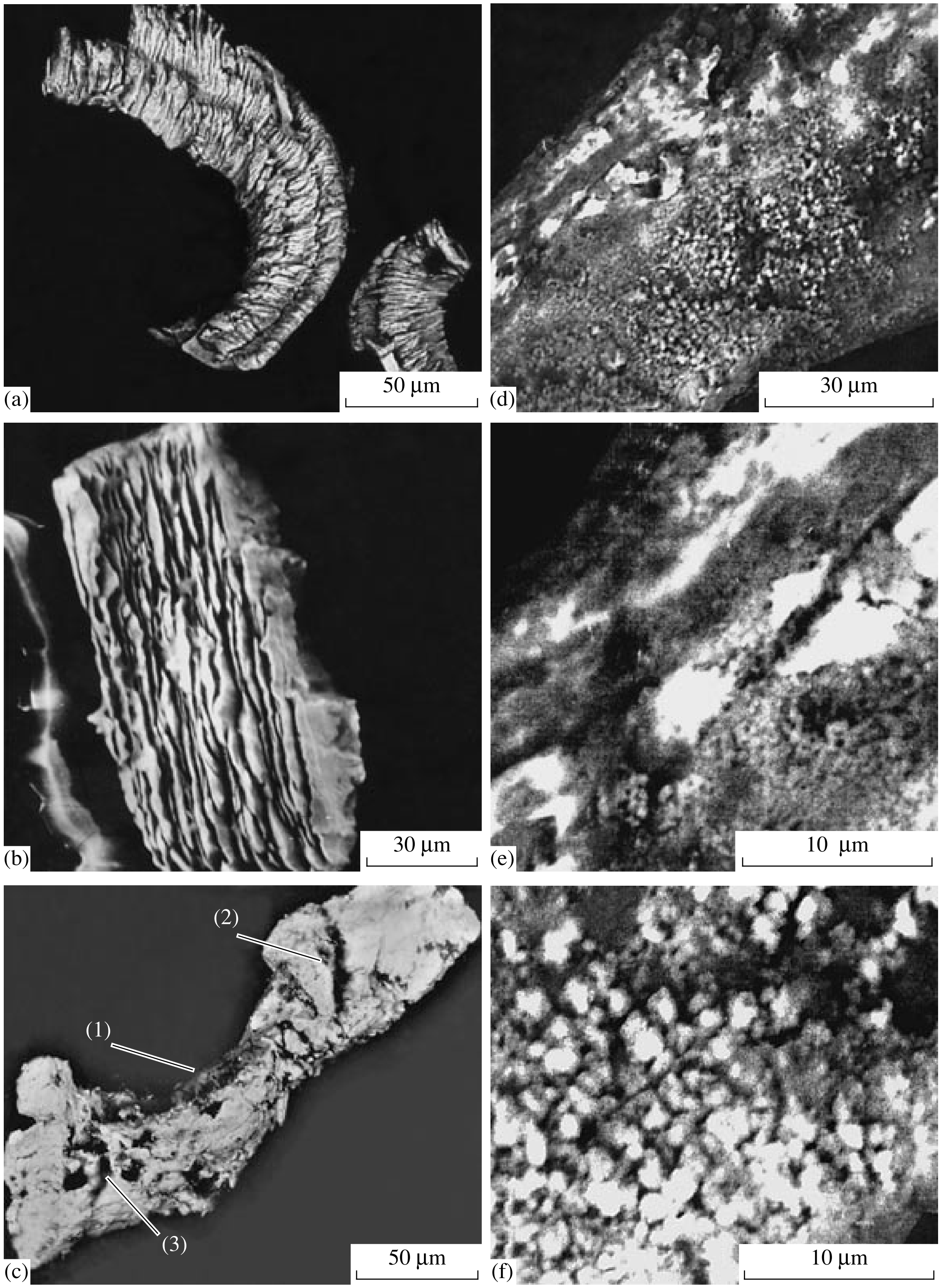

Fig. 13. Authigenic minerals of the Ge-bearing coals. (a, b) Lamellar aggregates: (a) Zn-bearing copper; (b) gold; (c) cupriferous Au with (1) copper carbonates at the surface, (2) veinlet of Cr-ferrite and (3) inclusions of Ca-aluminosilicates (supposedly, zeolites); (d–f) Ni-bearing Cu plate with inclusions of Pb–Sn intermetallic compounds (white) and overgrowths of fine crystals of Cu sulfoiodides: (d) general plan, (e, f) closeup of inclusions and overgrowths. Back-scattered electron images.

pounds suggest the contribution of CO_2-bearing chloride–sulfate solutions in the formation of metalliferous coals (Seredin, 1997). Native metals can form by the organic reduction of metal ions (Baranger et al., 1991) owing to the decomposition of heterorganic compounds (Buslaeva and Novgorodova, 1989) and during the fractionation of metal–halogenide complexes (Marakushev, 1995). It should be noted that native metals (Zn and Au) and intermetallic compounds (Sn–Sb) occur at the Angren Ge-bearing coal deposit in Uzbekistan (*Mineraly…*, 1975; Klimanov, 2002).

Minerals of this assemblage are unevenly dispersed in the coaly organic matrix. In some samples, their high contents were found in vitrinite lenses and microfissures. The minerals in vitrinite lenses likely predated, while the minerals in microfissures postdated the coalification of organic matter. The majority of gold minerals were found in microfissures. This fact indicates their epigenetic formation suggested by anomalous Au contents at the roof of ore bed in borehole 7 (Fig. 10).

Particles of native metals and intermetallic compounds vary from n to $100n$ μm in size. They form plates, regular crystals, needles, and dendrites. Lamellae and multilayer packages are the most widespread morphologies for almost all native metals and intermetallic compounds mentioned above (Figs. 13a, 13b). One can also see intergrowths of native metals with barite (e.g., Al) and clay minerals (Pb–Sn and Au), as well as overgrowths of native metals on pyrite (Pb–Sn and Au). Some grains represent large (up to 0.5 mm) intergrowths of minerals of different compositions (Figs. 13c–13f).

Elements characterized by the highest concentration in Ge-bearing coals (e.g., Ge, W, and Mo) were not found as minerals in the studied sample. This fact is consistent with their distribution across the bed and in the products of gravity separation indicating mainly organic mode of occurrence. However, spectral analysis of pyrite extract from coal revealed high contents of Mo (up to 500 ppm) and Ge (up to 50 ppm), suggesting that a part of these metals can occur as isomorphic impurity in the pyrite. Ge-bearing coals can also contain W in the mineral form, because some scheelite and wolframite grains, as well as native tungsten grains 5–8 μm in size, were found in coals of the Luzanovka graben beyond the Ge mineralization zone and at the adjacent Spetsugli deposit (Seredin, 2004b).

DISCUSSION

Formation Conditions of Ge-Bearing Coals in the Luzanovka Graben

Timing of ore deposition

Anomalous accumulations of Ge and associated elements (W and Mo) in beds III_2 and III_3 unambiguously indicates that metalliferous solutions circulated in the coal-bearing molasse after the deposition of organic matter of the uppermost bed. Hence, organic matter of the underlying ore-bearing bed was already buried beneath the Pavlovka Formation at that time and subjected to common diagenetic transformations (gelification and humification). The upper age limit of ore formation is constrained by the absence of significant W and Ge contents in the fossil wood from Pliocene alluvium, which overlays the eroded surface of the metalliferous coal-bearing sediments. The available data on protrusion of coal diapirs into Pliocene sediments (Fig. 3) suggest that Ge mineralization was formed after the accumulation of Late Miocene coal-bearing sediments, but before organic matter coalification and the deposition of the Pliocene alluvium of the Suifun Formation.

The late ore stage related to the intense Pliocene–Quaternary volcanism is recorded at both the Luzanovka occurrence and the adjacent Spetsugli germanium deposit (Seredin, 2004a, 2004b). The late ore stage was characterized by a different (mainly, noble metal) specialization, resulting in the epigenetic Au enrichment of the roof of the Ge-bearing bed (borehole 7) and the deposition of auriferous minerals in microfissures in the central part of the ore bed (borehole 44).

Character of circulation and types of metalliferous solutions

Morphology of the orebody (concentric in plan and dome-shaped in cross-section) and decrease in the Ge content from the bottom to top indicate ascending circulation of flows of the metalliferous solutions. Since bed III_2 overlies granites in places, these solutions were presumably delivered to the buried peatbog along the basement faults and centrifugally transported from discharge zones to form spreading domes. Judging from significant thickness of metalliferous beds in the central parts of orebodies (up to 4–5 m), these flows penetrated the entire organomineral mass of the future bed III_2, presumably, under high pressure. By analogy with the Ge-bearing peatbog in Kamchatka (Ivanov et al., 1984) with similar Ge distribution, high pressures of metalliferous solutions were presumably caused by their high gas saturation.

Thus, in terms of Russian uranium geology, Ge mineralization in the metalliferous bed of the Luzanovka graben is an exfiltrational ore deposited around vents of high-pressure mineral springs, which operated during the diagenesis of organic matter at the base of coal-bearing deposits.

Hundreds of times higher Ge contents, relative to those in river and sea waters (0.05 μg/l), were found in mineral springs of different geochemical and genetic types with pH = 3.8 to 9.5 and T = 9.5–96°C (Table 7): (1) cold waters of CO_2-bearing mineral springs; (2) chloride and chloride–sulfate hydrothermal solutions in the volcanically active regions; (3) N_2-bearing hydrothermal waters of nonvolcanic regions related to

Table 6. Contents of trace elements in the products of gravity separation of the Ge-bearing coal

	Fraction, g/cm^3					Total
	<1.45	1.45–1.53	1.53–1.64	1.64–1.8	>1.8	
Output, %	28.90	17.10	12.90	19.20	21.90	100.0
A^d	5.30	10.90	26.20	38.60	51.70	25.51
Al	0.48	1.86	6.16	7.72	10.96	5.13
Ca	0.49	0.51	0.48	0.38	0.36	0.44
Na	0.06	0.09	0.14	0.27	0.43	0.20
K	0.03	0.10	0.24	0.78	0.95	0.41
Mg	0.17	0.19	0.25	0.23	0.28	0.22
Ti	0.03	0.06	0.13	0.14	0.17	0.10
P	0.01	0.01	0.03	0.43	0.18	0.13
Fe	0.18	0.22	0.29	0.24	0.37	0.25
Be, ppm	5.9	5.5	8.4	7.7	8.3	7.02
B	53.0	109.0	131.0	77.2	51.7	77.0
Sc	2.7	3.5	6.3	6.2	7.8	5.07
V	9.0	17.3	31.4	29.7	44.5	25.1
Cr	13.9	20.5	46.6	29.0	92.0	39.3
Mn	95.9	93.4	107.9	111.2	130.3	107.5
Co	1.7	1.9	2.1	2.2	2.6	2.1
Ni	2.4	2.6	3.1	3.7	5.7	3.5
Cu	5.7	7.6	8.1	10.8	11.4	8.6
Zn	3.0	9.8	21.2	49.8	54.3	26.7
Ga	4.2	8.3	18.1	18.5	23.8	13.7
Ge	58.3	71.7	100.9	59.1	60.0	66.6
As	2.8	4.3	10.5	8.5	10.9	6.9
Se	3.1	6.2	10.2	11.6	17.1	9.2
Rb	1.7	6.0	17.3	32.0	50.7	21.0
Sr	35.1	38.5	41.7	39.4	39.8	38.4
Y	6.2	8.3	12.1	13.9	13.4	10.4
Zr	9.3	18.3	41.7	50.6	67.2	35.6
Nb	0.5	1.4	5.0	5.8	5.7	3.4
Mo	26.4	30.8	27.5	21.2	18.6	24.6
Ag	0.14	0.32	0.26	1.24	0.43	0.46
Cd	0.08	0.09	0.14	0.39	0.32	0.20
Sn	0.5	1.3	2.9	2.6	3.4	2.0
Sb	0.08	0.09	0.13	1.00	0.26	0.3
Cs	0.3	1.6	6.0	6.2	9.8	4.5
Ba	39.4	49.6	97.5	79.5	106.0	70.9
Hf	0.2	0.4	1.0	1.5	1.6	0.9
Ta	0.03	0.07	0.29	0.34	0.57	0.25
W	122.0	131.0	117.4	99.6	79.6	109.4
Au	0.003	0.001	0.034	0.019	0.057	0.022
Tl	0.004	0.071	0.254	0.297	0.383	0.19
Pb	1.4	6.5	12.3	16.6	46.5	16.5
Bi	0.004	0.024	0.118	0.158	0.243	0.104
Th	2.5	4.5	8.9	7.7	8.3	5.9
U	2.7	4.4	7.3	4.6	4.6	4.4
La	5.5	7.5	11.0	35.7	29.0	17.5
Ce	10.7	14.6	20.7	70.4	55.8	34.0
Pr	1.3	1.7	2.4	7.3	5.4	3.6
Nd	4.8	6.0	8.4	21.8	17.6	11.5
Sm	1.0	1.4	1.7	4.1	3.1	2.2
Eu	0.10	0.13	0.18	0.29	0.28	0.19
Gd	1.4	1.7	2.5	4.8	4.1	2.8
Tb	0.18	0.22	0.29	0.46	0.41	0.31
Dy	1.0	1.3	1.7	2.1	2.1	1.6
Ho	0.18	0.23	0.33	0.42	0.39	0.3
Er	0.5	0.7	1.0	1.1	1.1	0.8
Tm	0.07	0.10	0.16	0.14	0.17	0.12
Yb	0.45	0.60	0.98	0.85	0.96	0.7
Lu	0.06	0.08	0.14	0.13	0.14	0.1

Table 7. Concentrations (μg/l) of trace elements (accumulated in the Ge-bearing coal of the Pavlovka deposit) in the waters of mineral springs in Kamchatka and Bulgaria as compared to their average contents in the river and ground waters

Water type	Spring	*T*, °C	pH	Ge	W	Mo	U	As	Sb	Cs	Be
R				0.05	0.03	5.0	0.04	4.0	<0.1	0.03	0.1
G				–	–	1.16	0.56	1.34	0.64	0.18	0.16
I	1	9.5	6.6	33.0	–	4.4	1.4	–	6.8	41.0	9.9
II*	2	96.1	3.8	39.3	–	96.0	0.4	–	239.0	211.0	6.1
II*	3	73.0	5.8	32.8	–	10.3	–	–	290.3	486.0	18.9
II*	4	92.5	8.2	32.1	–	44.4	–	–	88.3	305.1	6.0
III	5	96.0	9.4	25.0	100.0	20.0	<.007	0.7	0.3	50.0	0.02
III	6	43.0	9.5	38.0	41.0	3.6	<.004	<0.2	<0.02	14.0	<0.03
IV	7	56.0	8.4	24.0	30.0	1.0	0.01	<0.5	0.2	73.0	<0.2
IV	8	73.0	6.8	40.0	27.0	7.2	0.2	2.6	<0.5	210.0	6.9
IV	9	34.5	7.3	26.0	8.5	0.5	0.29	<0.2	0.4	19.0	0.3
IV**	10	55.0	8.4	6.5	11.0	8.6	44.0	6.0	2.7	39.0	<0.16
IV**	11	42.0	8.2	2.3	8.6	9.2	73.0	1.0	0.16	24.0	0.05

Note: Water types: (R) river water (Reimann and de Caritat, 1998); (G) groundwater of the supergene zone without the consideration of provinces of continental salinization (Shvartsev, 1998); (I) cold CO_2-bearing water; (II) volcanogenic-hydrothermal chloride and sulfate-chloride waters; (III) alkaline N_2-bearing waters; (IV) N_2–CO_2 waters. (1–4) Mineral springs of Kamchatka (Chudaev et al., 2000): (1) Malka CO_2-rich springs (borehole 15, average from two determinations), (2) Mutnov geothermal system (Dachnyi area, Active group spring), (3) Uzon-Geyser geothermal system (Uzon caldera, Central spring), (4) Uzon-Geyser geothermal system (Geyser Valley, Velikan-Dvoinik spring); (5–11) mineral springs of southern Bulgaria (Pentcheva et al., 1997): Sapareva-Blagoevgrad basin (Sapareva banja), (6) Southern Srednegorsk basin (Poibrene spring), (7) Sapareva-Blagoevgrad basin (Blagoevgrad spring), (8) Mikhalkovo basin (Bedensky Banja spring), (9) Simitli-Sandan basin (Petrich spring), (10) Chepino Basin (borehole 21), (11) southern Srednegorks basin (Momina Salsa spring), (12) Karlovo basin (borehole). * Springs enriched in As, Ag, and Au (Karpov, 1988); ** U-bearing springs; (–) no data.

deep (>1 km) circulation of meteoric waters along fault zones in the sialic basement; and (4) hybrid N_2–CO_2 waters formed during the contamination of meteoric N_2-bearing waters by volcanic or deep-seated CO_2.

Association of Ge with W and Mo found at the Luzanovka occurrence is typical of the alkaline N_2-bearing amagmatic hydrothermal waters (Krainov, 1973). According to isotope data, Ge-bearing thermal N_2-bearing waters (acratotherms) are generated by the deep (up to several kilometers) and long-term (up to several million years) circulation of meteoric waters in the tectonically active regions, including zones of continental rifting. The constant high concentration of Ge, W, and Mo in the meteoric waters circulating in granites and gneisses is related to their selective leaching from these rocks. The waters are characterized by sodium sulfate composition, high Si content, and low gas saturation (Krainov, 1973; Krainov and Shvets, 1992; Pentcheva et al., 1995; 1997; Chudaeva et al., 1999). The low gas saturation and typical low contents of U, Be, and As, which are abundant in the Luzanovka coals, suggest that the classical acratotherms could not serve as metalliferous solutions that generated Ge mineralization of the Luzanovka graben.

Mineralogy and geochemistry of the Ge-bearing coals indicate that mineralization of the Luzanovka graben was not produced by purely N_2-bearing mineral springs, but was related to the activity of N_2–CO_2 waters formed by the mixing of N_2-bearing alkaline hydrothermal solutions with the volcanogenic fluid.

The reality of such a process is confirmed by investigations near the Quaternary volcano in Bulgaria (Pentcheva et al., 1995, 1997). It was found that the contamination of alkaline N_2-bearing thermal waters by the volcanogenic fluid leads to their saturation in CO_2 and sharp increase in reactivity of water relative to the host rocks. Consequently, the waters with high contents of Ge (25–40 μg/l), W (up to 150 μg/l), and Mo (up to 62 μg/l) are enriched not only in trace elements presumably derived from the magma chamber (As, Sb, Ag, Au), but also in elements additionally leached from the host granites (Be and P). The N_2–CO_2 mineral springs differ from the N_2-bearing acratotherms by significantly higher contents of gas and halogenides and lower (often, near-neutral) pH values.

Geochemistry of such hybrid waters best agrees with the data on geochemistry and mineralogy of the Ge-bearing coals of the Luzanovka graben (the presence of sulfides, halogenides, and halogen carbonates; an irregular distribution of As, Sb, Au, Ag, Be, U, and P; and the presence of siderite and pyrite dissemination in argillized granites of the basement).

The study of mineral springs of Bulgaria revealed a trend in the variation of geochemical indicators (in particular, Sr/Ba and W/Mo) with the increase of volcanogenic CO_2 content in the N_2-bearing waters. This process is also accompanied by the increase in contents (and change in transfer forms) of Fe and Mn, which are mainly transported as suspension in N_2-bearing waters and as dissolved species in the N_2–CO_2 waters (Pentcheva et al., 1995, 1997).

These indicators can be used to explain significant geochemical differences between Southern and Northern orebodies. The relative enrichment of the Southern orebody in U, P, and As correlates with a twofold increase of Sr/Ba (from 0.2 to 0.4) and almost 12 times increase of the W/Mo ratio (from 2.6 to 30.2). In addition, as was shown above (Fig. 8), Fe and Mn in the Northern orebody are mainly confined to the mineral component, whereas these elements behave like Ge in coals of the Southern orebody and are bound with the organic matter, indicating the enrichment of metalliferous waters in dissolved compounds of the elements.

Thus, by analogy with modern mineral springs, one can assume that the N_2–CO_2 spring functioning beneath the central part of the Southern orebody was enriched in volcanogenic CO_2 as compared to the spring beneath the Northern orebody. According to such assumption, high concentration of U in coals of the Southern orebody can be related to its more intense leaching from the underlying granites and the more favorable transportation conditions. This is suggested by the mainly carbonate mode of U transfer in the hydrothermal solutions (Naumov, 1998). High reactivity of N_2–CO_2 thermal waters of the Southern orebody to underlying granites is also indirectly supported by the Eu enrichment of coals and coal-bearing rocks of the Southern orebody relative to the Northern orebody. Eu is intensely concentrated in the K-feldspar. Therefore, intense leaching of this major rock-forming mineral of the subalkaline basement granites by hydrothermal solutions leads to the growth of Eu content in the solutions. Such a mechanism of Eu enrichment was established, in particular, for vapor hydrothermal waters of the Yellowstone Park (Levis et al., 1995).

Comparison of Ge-bearing coals from the Luzanovka graben and Spetsugli deposit

The Ge mineralization was simultaneous in coals of the Luzanovka graben and Spetsugli deposit. However, relative to the Luzanovka occurrence, the Spetsugli deposit is distinguished by tens of times larger Ge reserves and significantly higher Ge concentrations (average 400–500 ppm, maximum 4–5 kppm). Ge-bearing coals of this deposit are sharply enriched in Be, Cs, and Sb as compared to their counterparts in the Luzanovka graben. Table 7 shows that average contents of these elements are significantly higher in boreholes drilled in the central parts of orebodies of the Spetsugli deposit (6–7, 9–12, and 60–120 times, respectively). Their concentrations are several times higher in the highest-grade intervals of the beds. In particular, the Sb content at the Spetsugli deposit reaches 1175 ppm (Seredin, 2003a).

Table 8. Contents of trace-elements (ppm) in the Ge-bearing coal of the Spetsugli deposit and Luzanovka occurrence

	Luzanovka		Spetsugli
Borehole	7	45	4
Bed	III_2	III_2	I
Thickness, m	1	2.5	1.05
Number of samples	5	3	3
A^d, %	13.9	31.2	38.4
Ge	227.6	153.5	920.6
Be	10.1	11.2	73.6
As	10.2	89.0	78.2
Mo	76.9	21.6	17.0
Sb	1.9	0.9	110.8
Cs	2.1	3.1	26.4
W	196.7	653.1	199.2
U	8.7	389.1	3.1

Note: Contents were calculated on a whole coal basis of the bed without the consideration of the Ge-bearing coaly-clayey and clayey rocks of partings and near-contact zones of the beds.

High concentrations of these elements in the Ge-bearing coals of the Spetsugli deposit indicate that Ge was presumably transported together with the volcanogenic chloride–sulfate vapor hydrothermal waters, which are characterized by such geochemical specialization (Table 8). The formation of Ge mineralization in four beds above each other and the presence of ore shoots across them indicate a higher pressure of hydrothermal solutions at this deposit relative to the Luzanovka occurrence, where Ge is accumulated only in the lowermost bed adjacent to the basement.

Thus, discrepancies in the scale and geochemical specialization of Ge mineralization are presumably related to different shares of volcanogenic fluid in the composition of groundwaters circulating in these areas at the end of Miocene. We suppose that the concentration and pressure of juvenile fluid in the ascending metalliferous solutions were significantly higher at the Spetsugli deposit relative to the Luzanovka graben. By analogy with modern hydrothermal systems, where chloride–sulfate vapor hydrothermal waters in the central part give way to N_2–CO_2 waters at the periphery, the discrepancies discussed above were presumably determined by different depths of the location of peripheral magma chambers. Hence, the Spetsugli deposit can be ascribed to the proximal type (location above the magma chamber), whereas the Luzanovka occurrence is a distal type. Germanium occurrences of the distal type can be found in the Pavlovka deposit and other coal-bearing basins, as indicated by high W concentration in coal-bearing beds of the Poiskovyi area.

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