

Unique Polycomponent Mineralization in Breccia Bodies at the Pavlovsk Brown Coal Deposit

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The Pavlovsk deposit is located at the margin of the Khankai Massif near the Voznesensk ore district, which is known for fluorite, tin, and tungsten deposits associated with the Paleozoic granitoid magmatism (Fig. 1). The Cenozoic stage of ore formation in this region was related to rifting. Since the Eocene–Oligocene period, this region was characterized by the formation of numerous grabens followed by basic–alkaline basic volcanism and hydrothermal activity. Consequently, the Pavlovsk deposit area was marked by the formation of a unique Spetsugli germanium–coal deposit and several ore occurrences with unusual rare earth and gold–PGE mineralizations in coal-bearing sediments and argillized rocks of the basement [1–3]. The present paper reports the first data on a new ore occurrence of the Cenozoic age. Ores of this occurrence are characterized by unique chemical and mineral compositions.

The ore occurrence was discovered in the Vostochnyi open pit of the Pavlovsk coal deposit within a small trough-shaped depression. The coal-bearing sediments are underlain by Early Cambrian shales with limestone lenses and interlayers. The shales are intruded by Paleozoic granitoids that host vein and stockwork tin mineralization with quartz and tourmaline. Rocks of the basement are underlain by sedimentation breccia (1–27 m thick) with fine cassiterite dissemination. According to P.I. Ostashchenko and A.F. Kramchanin, the ore-bearing sediments represent a deluvial (slightly dislocated) placer known as the Ozernoe placer deposit. In metalliferous units underlying coal seams, the Sn concentration varies from 0.1 to 2.2% and the cassiterite reserve is as much as 35 000 t [4]. In coals locally subjected to intense sulfidation, the Sn concentration (400 ppm) is several hundreds of times higher than the normal Sn concentration for such rocks.

The Vostochnyi ore occurrence includes breccia bodies (0.4–2 m thick) that intrude the Cenozoic volcanosedimentary sequence (private communication of M.G. Tsovbnun, 2005). The breccia is composed of fragments of green porous sandstone-type rocks cemented by brown iron oxyhydroxides. Dissemination of ore minerals is abundant in the fragments and cement. Fine (2–5 mm) crusts of iron oxyhydroxides are developed at the contact of breccias. Host rocks are also ferruginated at the contact with breccia.

The breccias have an extraordinary chemical composition (table). They are characterized by a very high Fe concentration. At the same time, they are enriched in siderophile (Cr), lithophile (Sn, W), chalcophile (Pb, Cu, Zn), and precious (Au, Ag) elements. In addition, they are enriched in As, Sb, Hg, Se, Te, and Bi, which are typically associated with the metals mentioned above. The concentrations of many metals reach commercial values, while the concentrations of Sn and Au significantly exceed the commercial values. In general, the breccias can be qualified as very high-grade gold–tin ores with high concentrations of W, Pb, Cr, As, and Hg. Owing to the polycomponent composition, these ores are very attractive for complex processing with the simultaneous extraction of several valuable metals. Analogues of such ores have not been described in the geological literature.

The breccias are mainly composed of ore minerals (cassiterite, scheelite, wolframite, chromite, rutile, pyrite, pyrrhotite, galena, sphalerite, chalcopyrite, covellite, cinnabar, calomel, native mercury, native gold, silver sulfosalts, and bismuth tellurides). The cement is composed of iron oxides and sulfates with traces of As. The minerals were identified with a JSM 5610LV electron microscope equipped with JED 2300 (Japan). Gangue minerals (quartz and feldspars) are subordinate. This is reflected in the extremely low concentrations of Si and Al in the bulk composition of breccias. In some places, the cement of breccias has a typical porous structure (Fig. 2a), suggesting a high gas content in the metalliferous fluid. However, iron oxides and

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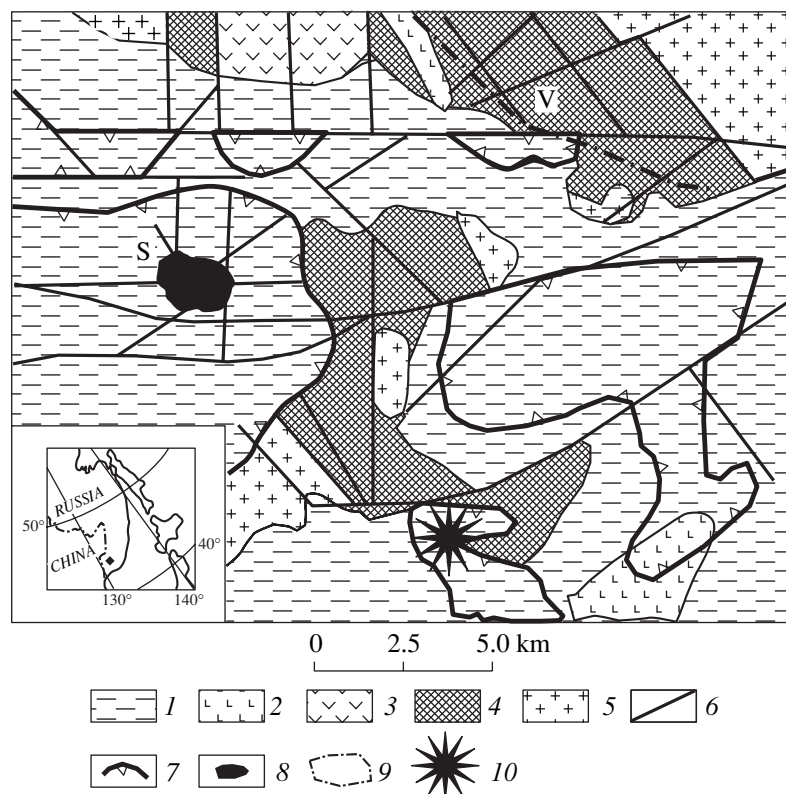


Fig. 1. Geological scheme of the Pavlovsk brown coal deposit. (1) Middle Paleogene–Miocene coal-bearing strata and overlying Quaternary sediments; (2) Late Neogene–Early Quaternary basalts; (3) Middle Paleozoic andesites, dacites, and rhyolites; (4) Early Cambrian carbonaceous–siliceous schists; (5) Paleozoic granites; (6) faults; (7) boundaries of the coal-bearing basins; (8) Ge-bearing coals; (9) boundary of the Voznesensk ore district; (10) ore-bearing breccia field. (S) Spetsugli germanium deposit, (V) Voznesensk ore district.

sulfates in rims around pores are also represented by fragments in the majority of polished sections studied (Fig. 2b), probably suggesting the relict nature of the

Chemical composition of the ore-bearing breccia

Element, oxide	Content	Element, oxide	Content
SiO ₂ , %	8.44	Pb, %	1.72
TiO ₂ , %	1.31	W, %	1.2
Al ₂ O ₃ , %	2.02	Hg, %	0.57
Fe ₂ O ₃ , %	65.11	Cr, %	0.46
MnO, %	0.46	Cu, %	0.14
MgO, %	0.13	Zn, %	0.09
CaO, %	0.89	Au, ppm*	150.5
Na ₂ O, %	0.25	Sb, ppm*	104.3
K ₂ O, %	0.15	Ag, ppm*	72.2
P ₂ O ₅ , %	0.079	Bi, ppm*	30
S, %	3.05	Te, ppm*	25
Sn, %	12.4	Se, ppm*	9.8
As, %	3.19		

Note: Contents were determined by the neutron activation (*) and X-ray fluorescence analyses in laboratories of the Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry (A.L. Kerzin and A.I. Yakushev, analysts).

porous cement and its crushing during the input of younger portions of metalliferous fluids. Disintegration of the cement was responsible for the weak lithification and fragility of breccias, which are readily disintegrated and transformed into a friable sandstone-type mass under the influence of atmospheric precipitation.

Ore minerals have different shapes. Cassiterite, the major mineral, primarily occurs as massive fragments (up to 1–2 mm in size) with the surface complicated by leaching pits in some places. Some detrital cassiterite grains are brecciated. The breccias also include rare crystals of tin wood that are slightly deformed and presumably related to the leaching and redeposition of the detrital cassiterite. High Sn concentrations (up to *n*%) are recorded in the Fe–As cement.

The clastic shape is also typical of chromite, scheelite, and wolframite. The much more frequent occurrence of scheelite suggests that this mineral is likely to be the major carrier of tungsten. Chromium occurs not only as detrital chromite, but also as intermetallide FeCr and as admixture in As-bearing iron sulfates confined to pores in the breccia cement. The distribution of Cr can also be related to the leaching of the detrital chromite and redeposition of Cr during the

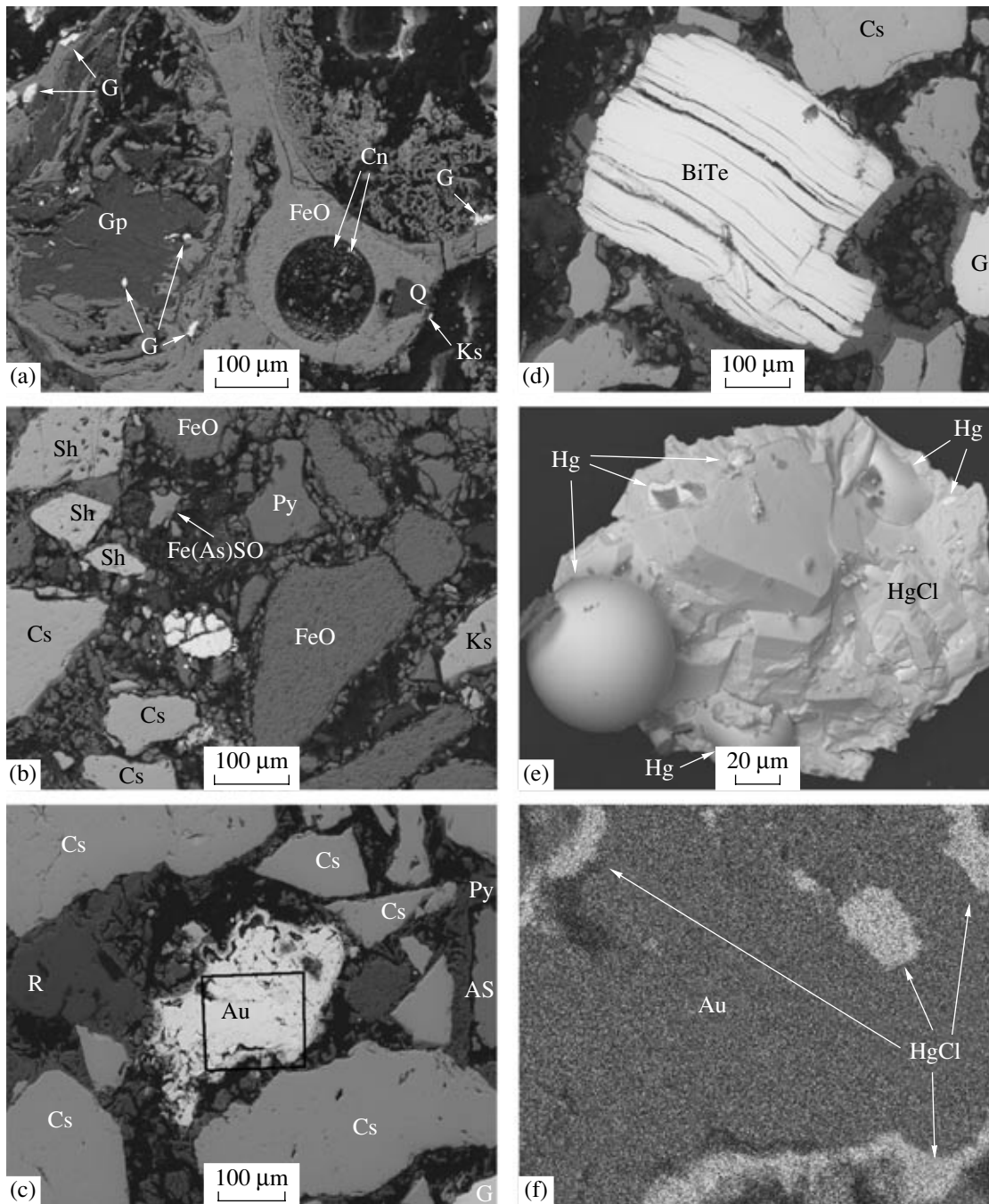


Fig. 2. Ore minerals in the metalliferous breccia. (a) Breccia-bearing sector with relict porous cement and ore mineral inclusions; (b) sector with crushed cement and ore minerals (white patch at the center is cinnabar); (c) brecciated gold surrounded by cassiterite grains; (d) bismuth telluride crystal; (e) spherical native mercury on calomel crystal; (f) fringes and inclusions of mercury chlorides in brecciated gold grain (characteristic radiation image of grain in Fig. 2c). (Cs) Cassiterite; (Sh) scheelite; (G) galena; (Cn) cinnabar; (Py) pyrite; (R) rutile; (FeO) iron oxyhydroxides; (Fe(As)SO) sulfates of arsenic gold; (Gp) gypsum; (Q) quartz.

input of new portions of S-, Fe-, and As-rich aggressive fluids into the breccia bodies.

Sulfides of chalcophile elements are appreciably oxidized and sufficiently large (1–2 mm) in some places. Generally, they are characterized by regular crystalline forms and localized in the breccia cement.

Some galena and chalcopyrite crystals are crushed. Pores in the cement include crystals and spherules of chalcopyrite.

Gold occurs as irregular brecciated segregations in the pores (Fig. 2c). The breccias contain not only pure gold, but also micrometer-scale Hg- and Ag-rich gold.

Gold is also present in the Sb- and Hg-rich silver sulfosalts. Sulfosalts grains are characterized by intergrowths with galena, localization in pores of the breccia cement, and lack of deformation signs.

Bismuth telluride, typical of many gold deposits, was recorded as a large (0.4×0.6 mm) undeformed crystal that probably formed at the latest stages of the evolution of ore-bearing breccias (Fig. 2d).

Mercury demonstrates the greatest compositional diversity among the minerals associated with Au. This element occurs in the breccias as native metal, Au–Ag alloy, sulfides, and chlorides. Mercury chlorides are found as intergrowths with spherules of native mercury (Fig. 2e), rims around the brecciated gold grains, and inclusions in the gold grains (Fig. 2f). The Au–Ag amalgams have a porous structure in some places. In contrast to these minerals, cinnabar grains are often crushed (Fig. 2b).

The mineralogy and geochemistry of ores in the study region suggest the polygenous and polychronous nature of mineralization in breccia bodies. The tin–tungsten and chromite mineralization, which is represented by fragments of ore minerals, can probably be considered as xenogenous. These metals were transported by gaseous fluid flows from rocks underlying the coal seams. The breccias are characterized by very high concentrations of Sn and low concentrations of Si and Al. Hence, we can suppose the existence of not only stockwork and placer tin mineralization, but also massive tin orebodies beneath the Vostochnyi open pit of the Pavlovsk deposit. The cassiterite–scheelite association suggests that the ores are confined to carbonate rocks (lenses and interlayers of limestones and dolomites) in Early Cambrian shales. The source of chromite fragments in the breccias is unknown. However, the presence of chromite and high Cr concentrations indicate that gas jets also penetrated the deep-seated chromite ores. Other ore minerals in the breccias were crystallized directly from the metalliferous fluid. The initial stages of crystallization were marked by the extensive precipitation of sulfides. Sulfosalts, chlorides, intermetallics, and native metals precipitated at the final stages. Gold precipitated at both the initial stage and the final stage of the hydrothermal process.

Thus, the breccia bodies considered here represent unique natural objects. Their closest analogues have been encountered in boreholes drilled at sites of recent ore formation. Materials recovered from these boreholes bear information on both the recent hydrothermal mineralization and the metal potential of deep horizons related to older processes.

Such analogies and previous data [2] indicate that the gold–tin mineralization in ore-bearing breccias of the Vostochnyi open pit of the Pavlovsk deposit can also accommodate other types of ore mineralization. We suppose the existence of a high-grade tin–tungsten mineralization of the skarn type in basement rocks beneath the operational coal open mine. This mineralization served as the source of cassiterite and scheelite fragments found in the ore-bearing breccias. The coal-bearing sediments with the typical superimposed sulfidation (coal seams) and hematitization (sedimentary cover) can incorporate stratiform gold mineralization related to the lateral percolation of Cenozoic metalliferous fluids along permeable zones in volcanosedimentary rocks. Study of these rocks and their exploitation is an urgent issue, because coal reserves of the Vostochnyi open pit are virtually exhausted and the entire ore-bearing area will be recultivated in the near future.

Thus, the data presented in this paper support our concept of the anomalous metal potential of Cenozoic depressions in Primorye. These depressions should be developed not only as a source of coal, but also as ore-bearing structures with a high potential of precious and rare metals as byproducts [2, 3].

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