

## Article

# Morphostructural, Chemical and Genetic Features of Native Gold in Brown Coals from the Yerkovetsky Deposit, Far East Russia

Veronika I. Rozhdestvina <sup>1,\*</sup>  and Galina A. Palyanova <sup>2,\*</sup> <sup>1</sup> Institute of Geology and Nature Management, FEB of RAS, Riolochniy Ln., 1, 675000 Blagoveshchensk, Russia<sup>2</sup> Sobolev Institute of Geology and Mineralogy, SB of RAS, Akademika Koptyuga Pr., 3, 630090 Novosibirsk, Russia

\* Correspondence: veronika@ascnet.ru (V.I.R.); palyan@igm.nsc.ru (G.A.P.)

**Abstract:** We studied the morphostructural features and chemical composition of micron and submicron particles of native gold from brown coals and overcoal sediments of the Yerkovetsky deposit (Zeya-Bureya sedimentary basin, Far East Russia). The samples of coal and host rocks in the form of thin sections, as well as coal particles and grains of native gold obtained during the process of dispersion and the fractionation of loose and crushed samples divided according to size and density, were analyzed using scanning electron microscopy in combination with X-ray microanalysis, involving various visualization modes. It was revealed that native gold is syngenetic with the mineralization of brown coals, and microphases dispersed in the minerals of overcoal loose and sandy-clay sediments were the source of native gold. In coal, gold is accumulated at the stages of formation (alluvial and eolian, including terrigenous and ionogenic subtypes) and the diagenesis of coal deposits (ground-infiltration subtype). A significant part of the mineralization process of coals and the formation of microparticles of native gold was contributed to by the descending water infiltration of polycomponent colloid solutions. During the dehydration of hydroxysiliconized iron-based hydrogels, mineral phases have an unstable composition and floccular structure and contain submicron gold particles. The coatings of all gold microparticles have identical origin and composition. Coal beds that border host rocks are an open system with a constant inflow of the substance, which leads to the gradual formation of polycomponent aggregated particles in micro cavities. Part of the gold in coals occurs as sulfur-bearing complexes dissolved in pore water. The key factor in the migration and deposition of gold in coals is the inorganic substances involved in the processes of coal mineralization. Organic substances play a more passive role and have medium-forming, fractionating (colloid, molecular, and ionic sieves), and accumulation functions.

**Keywords:** native gold; coal; typomorphism; colloidal transfer; hydrogels

**Citation:** Rozhdestvina, V.I.; Palyanova, G.A. Morphostructural, Chemical and Genetic Features of Native Gold in Brown Coals from the Yerkovetsky Deposit, Far East Russia. *Minerals* **2024**, *14*, 503. <https://doi.org/10.3390/min14050503>

Academic Editor: Huan Li

Received: 12 April 2024

Revised: 3 May 2024

Accepted: 8 May 2024

Published: 10 May 2024



**Copyright:** © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

## 1. Introduction

The geochemical uniqueness of fossil coals, which were formed through the long-term biokos interaction in the system of caustobololiths of coal series ↔ host rocks, is determined by the combination of biogenic, physicochemical, and mechanical migration. Modern concepts about the genetic sources of the inorganic substance of coals are based on the stage-by-stage character and multifactorial nature of the process involving ingress and transformation. The accumulation of trace elements is attributed to the concentration function of coal-forming plants, the barrier function of peat and coal substances, their medium-forming and transport functions as well as the physicochemical conditions of the transformation of organomineral materials in multiscale spatially localized and conjugated zones in the deposit body. The current state and the history of this problem were discussed in review papers [1–5], in which the authors analyzed the genetic types, and geochemical processes that formed metal-bearing coal worldwide. The genetic classification is based on the relationships between the stages of ore and coal formation in combination with the

forms of ingress of chemical elements into coal-bearing series (mineral particles and ions) and transportation agents (air flows, surface and groundwaters).

Close attention has been paid to the noble metal mineralization of coals [6–12]. These studies are mainly aimed at determining the concentration of noble metals in coals, solving scientific and methodological problems of the reproducibility of the results of determinations, analysis of possible sources of ingress and forms of speciation of noble metals, and the development of methods and technologies of extraction with due account for the specifics of the host organomineral matrix. Au in coals is characterized by the strongest natural variance of the distribution, which is responsible for the lack of reproducibility of its concentration. The trace and anomalously high values of gold are attributed to the absence or presence of particles of native gold in the light coal matrix.

In accordance with theoretical concepts [1–3], gold in coals occurs in the following different forms:

1. A nonmineral sorbed form is able to exchange ions; probable sorbents are coal organic substances (OS) and inorganic substances (IOS), such as clay minerals, sulfides, etc.;
2. A nonmineral form associated with coal OS includes complex compounds of the humate and chelate type;
3. A micro mineral form connected with coal OS refers to micro minerals redistributed in coal OS, which remain in light organic fractions during the gravitational enrichment of coals;
4. The macro mineral form is composed of allothigenic and authigenic minerals, some of which are no less than 10  $\mu\text{m}$  in size.

The presence of nonmineral forms of gold is proven by indirect analytical methods [5]. Mineral forms can be observed using direct methods, the most informative and presentable of which are a complex of scanning electron microscopy and energy-dispersive X-ray spectroscopy (SEM-EDX).

However, despite the wide application of these procedures for solving the problem of the forms of occurrence of noble metals in coals, the main aim of the published micrograph is only to confirm the presence of native gold in coals from different deposits [2–10]. Moreover, gold particles extracted from ash and slag wastes that undergo uncontrolled high-temperature transformations are often detected [8,11,12]. The unobservability of most processes of phase formation of noble metal minerals and the difficulty of determining the forms of transfer and features of geochemical behavior show that these substances require ontogenetic methods of research based on the detailed analysis of morphostructural characteristics of noble metal particles owing to genetic processes and conditions of formation and transformation of particular mineral-forming systems. The mineralogy of coal is important to assess the extraction technology and behavior during combustion.

The aim of this study is the ontogenetic analysis of morphostructural features of mineral forms of gold in brown coals and superimposed sediments from the Yerkovetsky deposit (Far East Russia) and the establishment of structurally determined relationships between different modes of gold occurrence in coals during the processes of their structural transformation.

## 2. Geological Setting

The Yerkovetsky brown coal deposit is situated in the southwestern part of the Zeya–Bureya sedimentary basin (Far East Russia) and is composed of loose and poorly compacted varieties of Cretaceous, Paleogene, and Neogene sediments. The coals were found to contain hurricane concentrations of noble metals and the following mineral native forms: gold, silver, platinum, and palladium [6–10]. The gold content in coal samples changes from trace amounts to hurricane concentrations of more than 40 ppm at average values of 3–7 ppm [7,10]. The presence of samples with high gold concentrations suggests that coal contains grains of native gold.

The deposit has a simple geologic structure where the flat, shallow bedding of coal seams inundated by surface and underground waters lacks any visible connection with

synchronous or superimposed endogenic processes and is located at a significant distance from the regions of the possible source rock (more than 100 km).

Sandy-clay overcoal deposits and deposits of the Kivda formation, including overcoal, undercoal, impermeable benches of coal and aleurites, coal seams, and undercoal water-bearing horizons, are a single exchange system with a considerable difference in the acid–alkaline properties of the water solutions circulating in them. Overcoal sediments from 7.4 to 58.0 m in thickness, including a series of water-bearing horizons with a high permeability of rocks and quite favorable conditions of recharge, are composed of inequigranular quartz-feldspar sands with hydromica kaolin clay. At the Yuzhnyi site, their water abundance is unevenly distributed, water transmissibility averages 2000 m<sup>2</sup>/day, and the filtration coefficient is 30 to 200 m/day. In chemical composition, the waters are hydrocarbonate with a mixed cationic composition rather fresh with mineralization of 0.07–0.17 g/L, neutral (pH = 6.93–7.51), with a high content of total iron (to 20–30 mg/L), and contain carbonic acid from 7.7 to 31.9 mg/L [13].

Productive aleurite-clay sequence hosting coal seams are characterized by low water abundance owing to the filtration properties of coal. Filtration coefficients range from 0.03 to 0.16 m/day, and water transmissibility is 0.15–0.82 m<sup>2</sup>/day. Coal waters are acidic (pH = 4.04–4.94). The undercoal water-bearing horizon is separated from the coal seam by impermeable illite-montmorillonite clays and aleurites with uneven thicknesses from 2 to 30 m. The waters of the horizon are hydrocarbonate, magnesium–calcium–sodium, rather fresh with mineralization up to 0.2 g/L, with iron content from 0.01 to 20.0 mg/L, and the content of carbonic acid at 7.5 mg/L [13].

Paleogene coals of the deposit are of medium degree for carbonization (grade B2) and, to a sufficient degree, are lithified from lignite to subbituminous coals. The porosity of dense coals is high and amounts to 32% [13]. Among the mineral impurities, whose content is 2–23%, clay substance is predominant, whereas quartz, carbonate, and iron sulfides occur in small quantities. The coals are medium ash, low sulfur, low phosphorus and are characterized by the following average parameters (in %): moisture content is 35–37, ash content is 17.0–17.9, the yield of volatiles is 43–45, sulfur content is 0.28–0.41, phosphorus is 0.09–0.16, and density is 1.66 g/cm<sup>3</sup> [14].

In material and petrographic composition, the coals belong to the class of helitolites and fusenolites of the humolite group and are subdivided into the following four types: fusinite-hoelinite, fusinite-hoelite, hoelite, and hoelite-fusitite [7]. They are characterized by a high content of inertinite, the reflectivity (mattness) of which decreases upward of this section, indicating cyclicity in the process of organic matter accumulation [15]. In the middle part of the coal seam, there are 1–2 interlayers of coal clay and, less frequently, clay and aleurite with uneven thicknesses from 0.01 to 0.7 m and rough contacts with the host coals, which divide the seam into 2–3 persistent bands. In the present work, for ontogenetic analysis of processes and mechanisms of formation of native gold in brown coals, we studied the parts of the seam with one mineralized interlayer.

### 3. Materials and Methods

We studied coal samples in the form of polished sections and polished bricks, as well as particles obtained in the process of the dispersion and fractionation of loose and crushed samples by size and density. The material for making coal samples was obtained by trenching Paleogene coals and sampling host rocks at the exploited Yerkovetsky brown coal deposit (Yuzhny site) as part of geochemical studies, the results of which are published in [6–10]. Lumpy and loose samples were placed in individual polyethylene bags during sampling in order to preserve their natural state.

A water-dispersed sample was taken with a pipette from different depths and applied on a prepared slide; then, the sample was dried to an air-dry condition and transferred by the imprinting method with special conductive tape of the stage for electron-microscopic observation of samples. The precipitate remaining at the bottom of the beaker, after separating the aqueous dispersed substance, was dried. Thereafter, it was separated into an

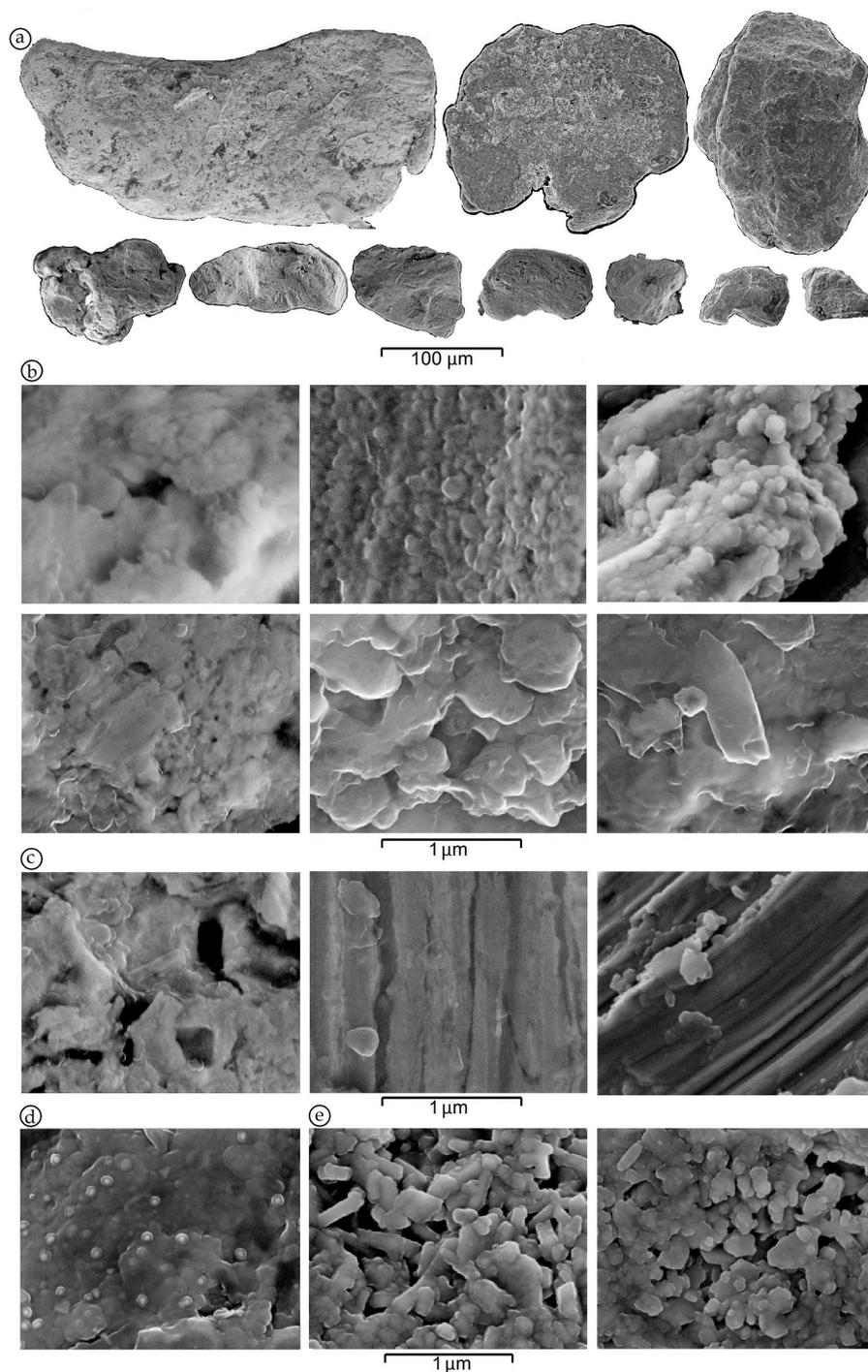
organic liquid with a density of  $1.9 \text{ g/cm}^3$  (a mixture of benzene and carbon tetrachloride). The surface and bottom fractions, after washing in ethyl alcohol and drying, were also used to prepare the samples for study. The samples of host rocks and the fraction that settled at the bottom after the separation of dispersed coals in organic liquid were subjected to mineralogical separation into fractions (magnetic, electromagnetic, and non-magnetic heavy and light) by the heavy concentrate method with the use of microchemical reactions and the separation of native gold particles from them (mineralogist E.N. Voropaeva IGNM FEB RAS).

The research was carried out using the scientific–analytical basis of the Laboratory of Microscopy and Structural-Molecular Studies Amur Centre of Mineral-Geochemistry Investigation in the Institute of Geology and Nature Management: a complex array of scanning electron microscopes (SEM), equipped with the systems of energy dispersive X-ray microanalysis (EDX), LEO (Zeiss, Jena, Germany); JSM-6390LV JEOL, equipped with a joint microanalysis system of INCA Energy 350; and INCA Wave (Oxford Instruments Ltd., Abingdon, UK), SIGMA (Zeiss, Jena, Germany), equipped with a microanalysis system Aztec X-Max 80 were used (Oxford Instruments Ltd.) (research analyst V.I. Rozhdestvina). Modes of imaging (accelerating voltages of 5 and 10–20 keV (at working distances and signal detection) and processing were chosen depending on the task and features of the samples. Microimages were obtained in the modes of the secondary (SEI) (contrast due to topography), reflected (BEI) (compositional contrast due to the differences in the average atomic number of phases), and mixing of signals from secondary and reflected electron sensors. X-ray spectral determinations of the chemical composition of phases were performed by points, scanning areas in the form of maps on the distribution of characteristic X-ray emissions of particular wavelength intervals, taking into account the effect of the superposition of peaks from different elements by scanning areas and profiles. To control the probe current and energy shift of the registered spectrum, calibrations on metallic cobalt were used. The results were processed using the XPP method in Software INCA 4.12, INCA 5.04Energy and Aztec 2.0. To prove the presence of micro-impurity elements, or in the case of overlapping peaks, we used a joint system of microanalysis INCA Energy 350 and INCA Wave (Oxford Instruments Ltd.), SIGMA (Zeiss).

## 4. Results

### 4.1. *Ontogenetic Features of Macro Particles of Native Gold Separated during the Gravitational Enrichment of Loose Rocks of Overcoal Sediments of Yerkovetsky Brown Coal Deposit*

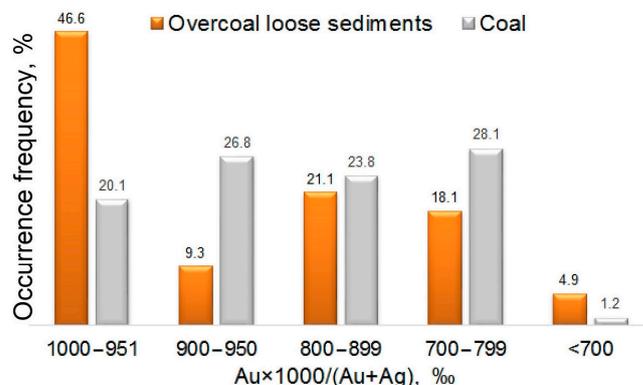
Overcoal sediments are made up of inequigranular quartz-feldspar sands (where the fraction of quartz is more than 70%) of gray shade. In the upper horizons, they are light gray medium-grained with gravel and pebbles, before changing to gray medium-grained (fraction  $< 0.5 \text{ mm}$  is  $\sim 90\%$ ), and closer to the top of the coal seam, the sands are yellowish-gray and fine-grained with hydrous mica-kaolinite clays and iron hydroxides scattered in them, mica (biotite and muscovite) and charcoal are also present. Data from the mineralogical analysis show that the fraction of accessory minerals in the samples of loose sediments are no more than 1% and consists (in the descending order of frequency of occurrence) of amphibole, epidote, ilmenite, siderite, sphene, garnet, tourmaline, zircon, andalusite, magnetite, leucoxene, pyrite, spinel, distene, apatite, corundum, rutile, anatase, staurolite, sillimanite, arsenopyrite, monazite, ortite, native gold and bismuth. In three samples of loose overcoal sediments, 25 particles of native gold were found in the form of golden-yellow irregularly flattened ( $\sim 50 \times 50\text{--}190 \times 420 \text{ }\mu\text{m}$ ) and lumpy ( $\sim 50 \times 50\text{--}250 \times 350 \text{ }\mu\text{m}$ ) grains with the low smoothed relief of the micro-rough surface (Figure 1a).



**Figure 1.** Morphological (a) and structural features of particles (b,c) of native gold extracted from loose overcoal sediments, and the surface nonmetallic phase: film (iron oxides with chlorine impurities) with the isolation of hexagonal plate-like higher-iron crystals (d) and ultradispersed aluminosilicates (clay) (e).

Figure 2 shows the histograms of fineness of native gold from the samples of overcoal loose sediments and brown coals, calculated as  $\text{Au} \times 1000 / (\text{Au} + \text{Ag})$ . The fineness of native gold extracted from the samples of overcoal sediments changed in a wide range from 648 to 997‰ (Figure 2). High-fineness gold occurred in more than 55% of cases, with the predominance of notably high-fineness varieties (more than 951‰) more than five times. This is most likely due to the effect of refining gold grains as a result of silver leaching [16]. The number of grains of medium-fineness (800‰–899‰) and relatively low-fineness gold

(less than 799‰) is comparable. The presence of Cu, Zn, and Ni as impurities in native gold was detected. The appearance of peaks of the characteristic radiation of Fe, Si, and O in some energy-dispersive spectra indicated the presence of microphases of oxides and hydroxides of iron and silicates distributed on the surface.



**Figure 2.** Distribution of the intervals of fineness of native gold extracted from overcoal loose sediments (25 grains 100 analysis points) and from brown coal (31 grains 150 analysis points).

High-fineness gold is characterized by floccular, fine ( $>0.1 \mu\text{m}$ ), and ultrafine ( $<0.1 \mu\text{m}$ ) globular (corpuscular) structures with different degrees of merging structural units and the formation of the quasi-amorphous surface layer (Figure 1b). That is, they are in the stage of capsulation of globular aggregate with the formation of a common grain coating [17,18]. With increasing silver content, substructural fragments have a denser structural organization and appear as lamellar-elongated, directed fibrous (fibrillar) forms (Figure 1c). The rough microrelief of native gold grains is unevenly filled with film and dispersed nonmetallic phases with local zones of recrystallization and the separation of more stable mineral phases of clay, silica, iron oxides, and other hydrogenic forms of authigenic minerals and mineraloids (Figure 1d,e).

The morphological and structural features of native gold particles from overcoal loose sediments are similar to native gold from weathering crusts or placer deposits [16,19,20].

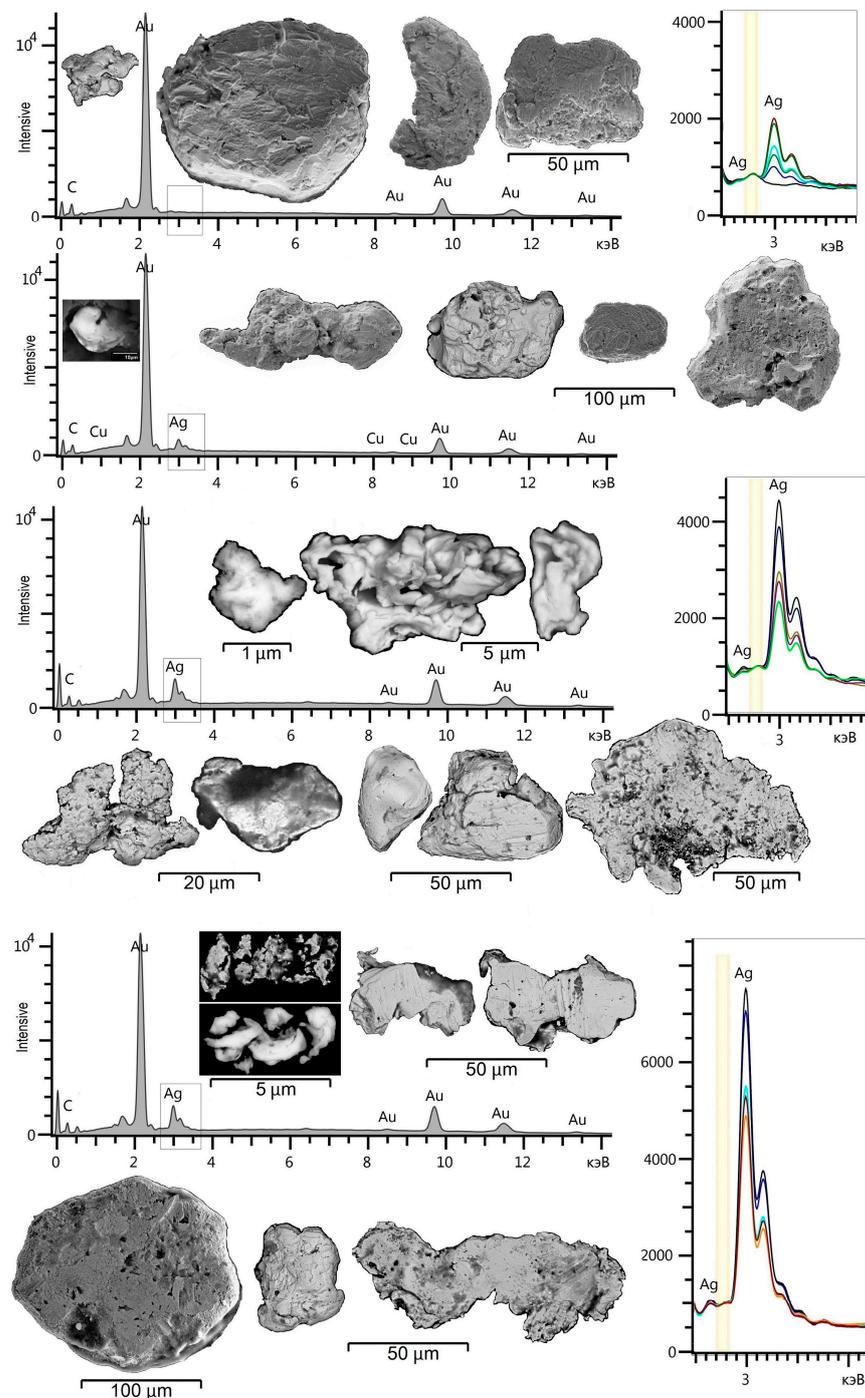
#### 4.2. Ontogenetic Features of Macroparticles of Gold Separated during the Gravitational Enrichment of Crushed Coal Samples from the Yerkovetsky Brown Coal Deposit

Methods of mineralogical analyses were used to separate accessory minerals from the fraction of averaged samples of coal from the upper and lower layers and a mineralized interlayer, which settled on the bottom during separation in the organic liquid. The mineralized interlayer is a thin carbonaceous clay layer separating the upper and lower coal layers. The coals of the upper layer were found to contain (in descending order of frequency of occurrence) the following: ilmenite, zircon, garnet, corundum, rutile, pyrite, arsenopyrite, amphibole, apatite, cassiterite, epidote, magnetite, chromite, sphene, tourmaline, monazite, spinel, galena, anatase, staurolite, sillimanite, distene, hydroxides and oxides of iron, and native gold (22 particles). The set of accessory minerals in the samples of interlayer and lower-layer coals is similar, but magnetite, hematite, and ilmenite dominate. The organomineral substance of the interlayer macroparticles contains native gold (9 particles), but in the coals of the lower layer, no macroparticles of native gold were found.

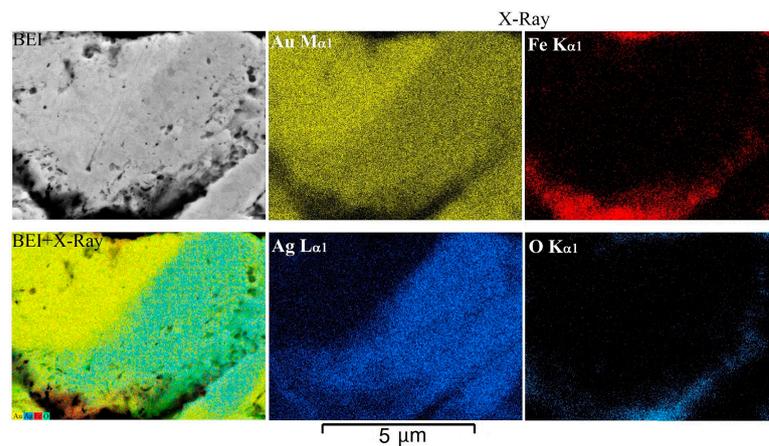
Macroparticles of gold ( $>10 \mu\text{m}$ ) from the coals of the upper layer and mineralized interlayer did not significantly differ from each other morphologically and did not have any distinct features. The native gold of golden-yellow color has a thin, uneven coating of nonmetallic phases, not rounded, with a rough surface, predominantly lamellar-like in shape. Lumpy, rod, elongated flat, and flake shapes are present.

Native gold is presented mainly by Au-Ag and Au-Ag-Hg varieties (Figures 2–5), frequently with Cu impurities. The gold fineness in coal varies in the range from 594 to

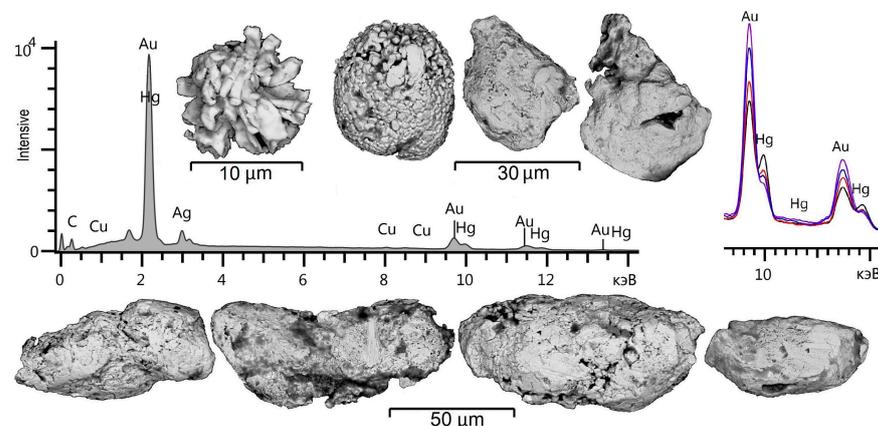
999‰ (Figures 2 and 3). Among Au-Ag phases, which is the same as in native gold from overcoal sediments, high-fineness varieties are predominant (more than 900‰), but their content in the coal is somewhat lower and accounts for 46.9%. The distribution between high-fineness intervals shifts to the region of predominance of phases with a fineness of 900‰–950‰ (Figure 2). Phases with medium (800‰–899‰) and relatively low (less than 799‰) fineness do not demonstrate significant fluctuations in the frequency of occurrence.



**Figure 3.** Morphological features of particles of native gold from coal of the upper layer and mineralized interlayer and typical energy-dispersive spectra in the resolution region of characteristic Ag  $L_{\alpha}$  X-ray lines reflecting the changes in the gold to silver ratio of native gold. Color shades show changes in Ag content in one group (high-fineness, medium-fineness, low-fineness) for different grains of native gold.



**Figure 4.** An image of the chemical heterogeneity of native gold (with contrast due to the average atomic number of BEI) showing the overlay of distribution maps of chemical elements (BEI + X-Ray) and distribution map of X-ray radiation in the regions Au  $M_{\alpha 1}$ , Ag  $L_{\alpha}$ , Fe  $K_{\alpha 1}$ , and O  $K_{\alpha 1}$ .



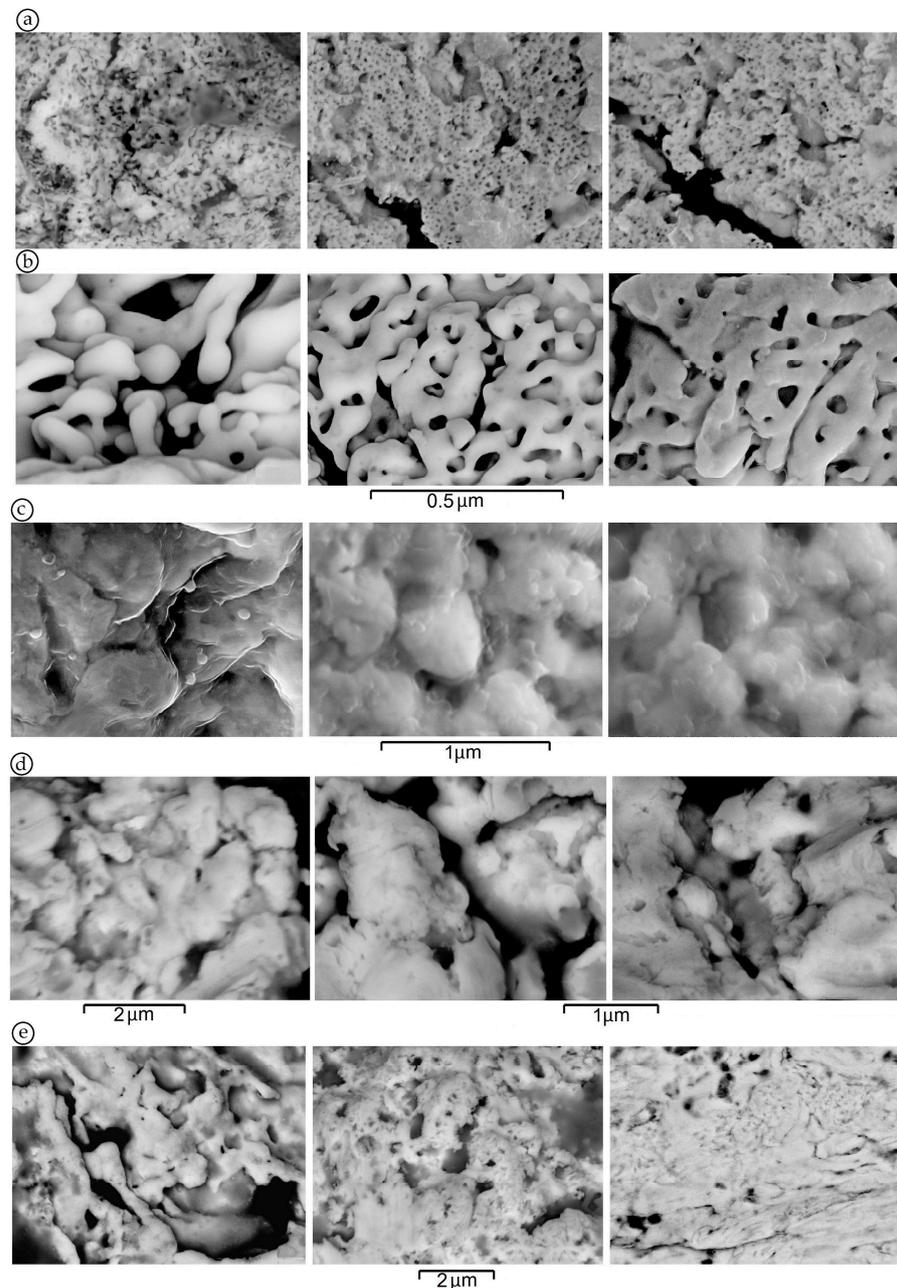
**Figure 5.** Morphostructural features of particles of mercury varieties of native gold from coal and energy dispersive spectra in the region of the resolution of characteristic X-ray lines Au  $L_{\alpha}$  and Hg  $L_{\alpha}$ .

Some subgrains in aggregated individuals of native gold have considerable differences in their concentrations of Au and Ag, and there are also subgrains with zonal heterogeneity and varying composition of Au and Ag (Figure 4), which occurs at different scale levels in the structural organization of grains. Particles of native gold, both individual (monograins) and subindividual, which is a constituent element of the aggregate, have coatings of varying thickness and the density of a ferruginous–siliceous composition (Figure 4).

Particles of mercurian high-fineness gold (to 5 wt.% Hg) are predominantly voluminous, with a relatively smooth surface (Figure 5) and a spongy fine porous structure at a submicron level (Figure 6a). Some individual particles with a significantly higher mercury content (Hg~25 and 12 wt.%) are aggregates of a thin platelet and globular structure with a low degree of intergrowth and compaction (Figure 5).

Individuals with high-fineness, with and without Hg, have a corpuscular sponge-like structure (Figure 6a,b). The morphostructural features of grain subindividuals can clearly be observed. There are individuals that have a globular structure with different degrees of merging grains, which gradually lose their individuality, forming lumpy, structurally unexpressed surfaces (Figure 6c). They form lumpy subgrains (Figure 6d) with the elements of contact intergrowth with each other, the mechanisms of which are described in [17]. The lumpy aggregates of native gold are polyphase. They are corpuscular sponge aggregates with relatively dense structures, unevenly covered with quasi-amorphous Au–Ag phases (Figure 6d). These grains are at the stage of the compaction and formation of the surface layer (encapsulation), which gradually hides the internal substructure of the organization

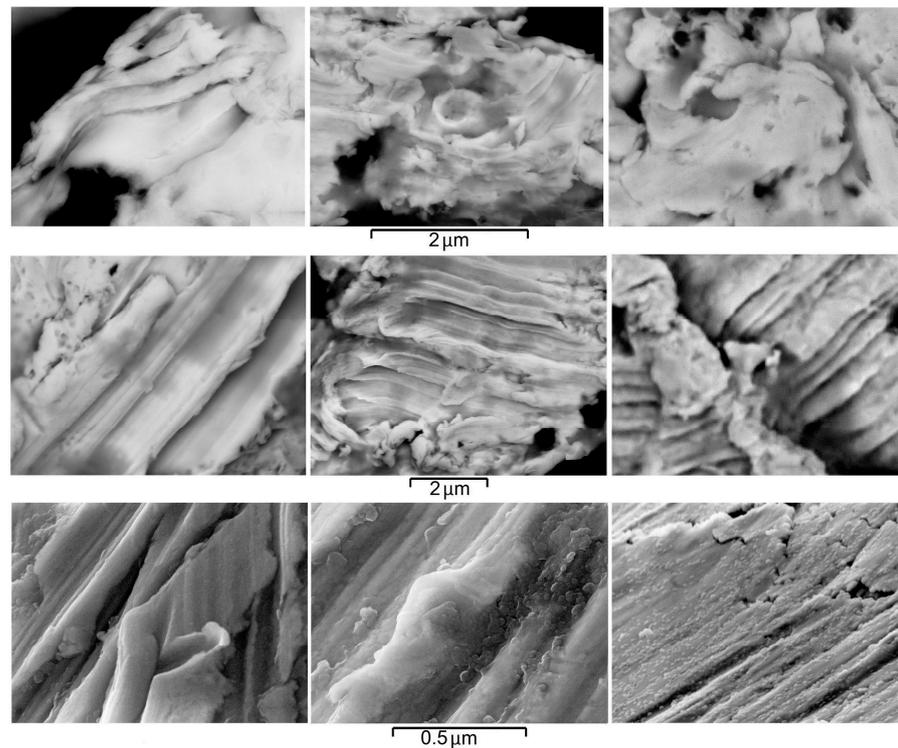
of native gold grains (Figure 6e). The corpuscular spongy structure of native gold grains suggests that a rather large specific surface develops in the pores while excessive surface energy leads to the effects of their solid-phase transformation, respectively [17,18].



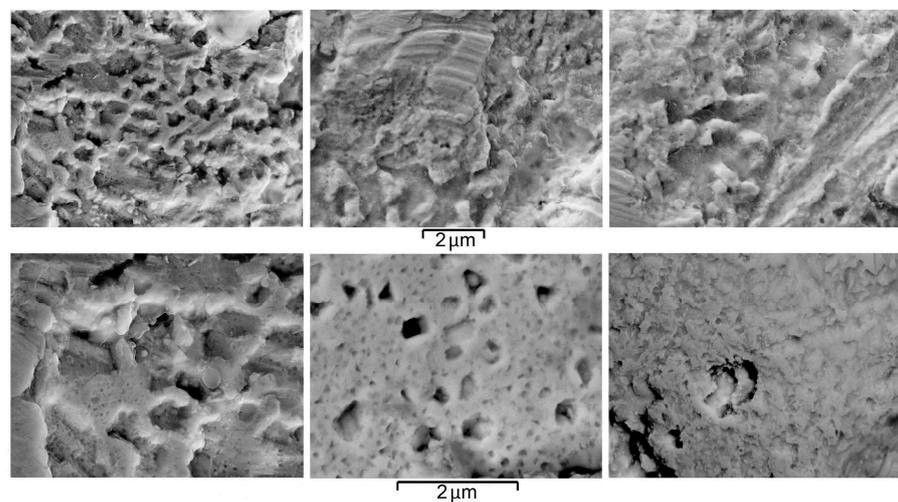
**Figure 6.** Globular and spongy substructure of high-fineness gold at different degrees of merging and compaction: spongy structures of Hg-bearing gold (a), corpuscular spongy structures of high-fineness gold (b), globular (c) and lumpy (d) structures of phases with different mutual contents of Au and Ag, and the formation of a surface layer (process of encapsulation of the individual formed as a result of the intergrowth of submicron particles) (e).

With the increase of silver content in native gold, a characteristic substructural element of which is fibrils (filiform substructural element), at the submicron level, filiform-elongated, tabular elements begin to appear in native gold (Figure 7). There are gold grains whose microsculpture at some surfaces reflects the imprinted pattern of the contact surface of OS (Figure 8). This may suggest the authigenic formation of these gold grains that were

deposited on the organic substance. This is especially related to the thin tabular individuals, which occur in the fractures of some coals.



**Figure 7.** Tabular–filiform substructure of native gold with medium (800‰–899‰) and low (<799‰) fineness of different degrees of merging and compaction.

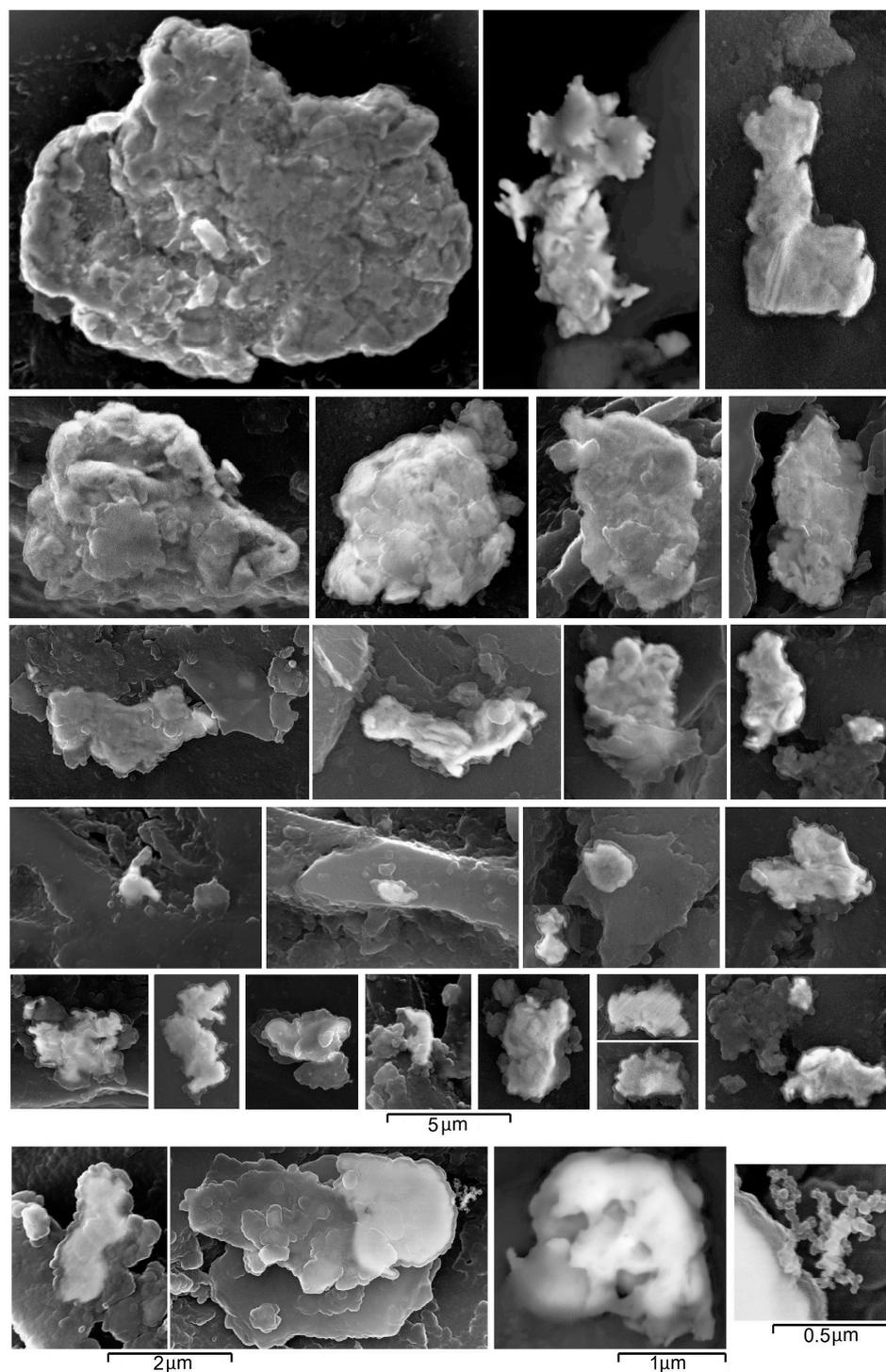


**Figure 8.** Induction surfaces of native gold particles formed at the boundary with host OS.

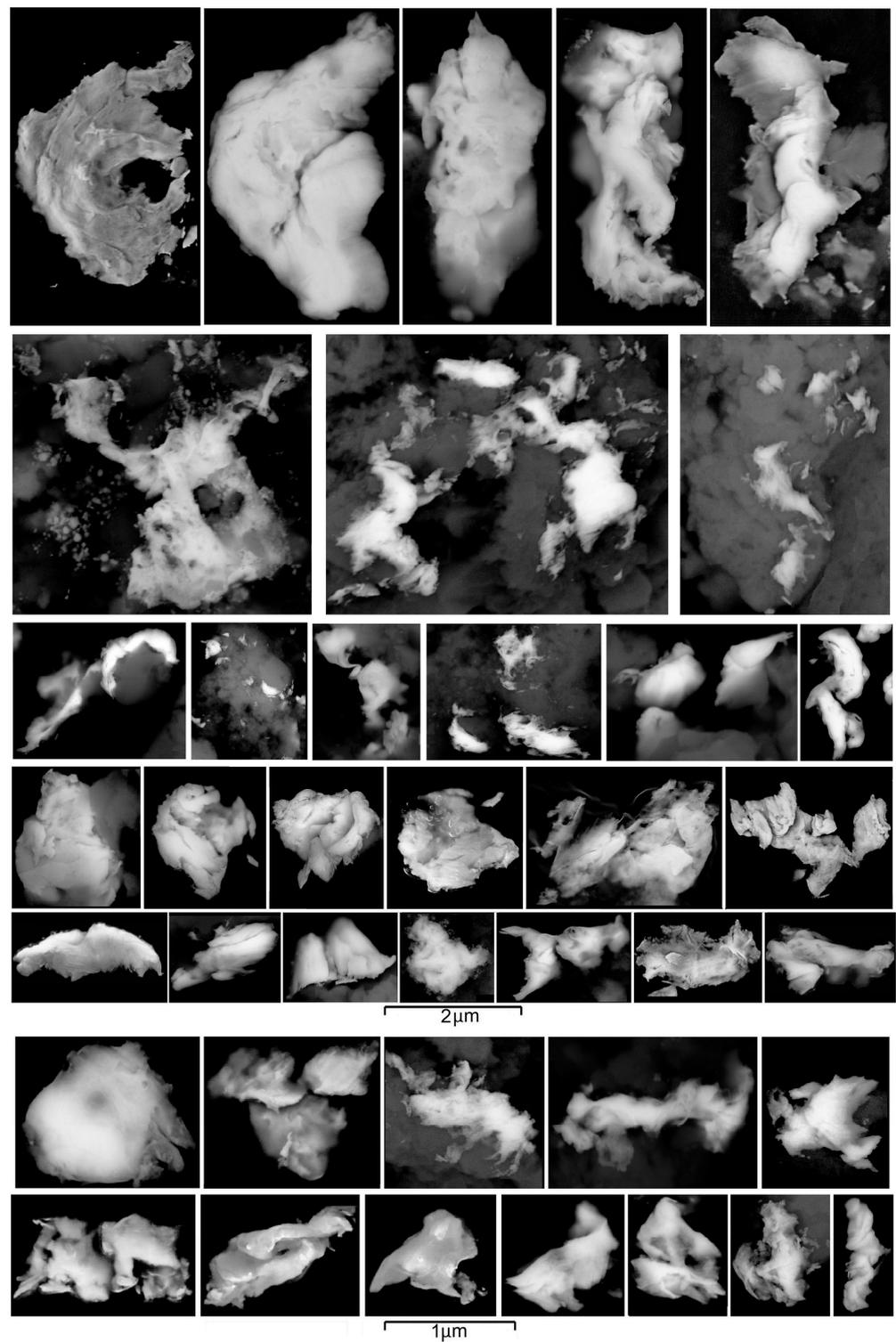
Thus, macroparticles of native gold extracted using isolated gravitational enrichment methods from crushed samples of the Yerkovetsky brown coal deposit have significant similarities in morphostructural organization and chemical composition with the native gold of overcoal deposits. Native gold grains of high fineness are represented by the aggregates of submicron particles of a globular-sponge structure, which are at identical stages of compaction and encapsulation with the formation of a surface layer, with gradual merging and smoothing of the boundaries of substructural components. Medium- and low-fineness varieties of native gold have a denser structural organization owing to the fibrillar-tabular structure of substructural elements inherited from silver.

#### 4.3. Ontogenetic Features of Microparticles of Native Gold That during Gravitational Enrichment Remain in Light Organic Fractions

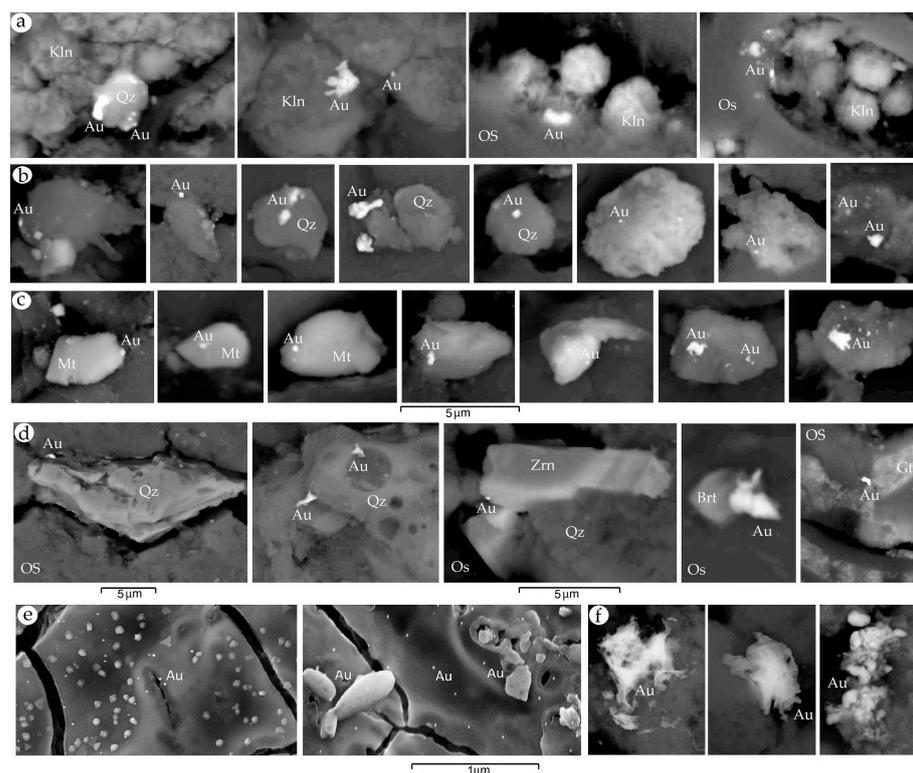
Electron-microscopic and X-ray spectral studies of the surface of coal-polished sections and dispersed coal particles show that the micromineral form of gold redistributed in OS and remaining in light organic fractions during the gravitational enrichment of Yerkovetsky brown coal deposits is a rather common phenomenon (Figures 9–11).



**Figure 9.** Morphostructural characteristics of native gold microparticles in association with the OS and IOS of coals. Micrographs of the surface fragments of polished sections and polished section bricks obtained in the mode of mixing SEI + BEI signals in their various combinations.



**Figure 10.** Morphostructural characteristics of native gold in association with the OS and IOS of coal. Micrographs of gold grains from dispersed coals obtained in the mode of mixing SEI + BEI in their various combinations.



**Figure 11.** Submicron particles of native gold (BEI is contrasted with the average atomic number of the phase, where gold is the lightest phases (a–f)) in association with the following inorganic phases: aluminosilicates (a), silicates (b), iron oxides (Mt) and hydroxides (c); quartz (Qz), zircon (Zrn); barite (Brt), goethite (Gt) (d); ferrous aluminosilicate films with the separation of nano-sized globules and submicron gold particles and ferrous particles of different geometries (e); and native gold with OS (f) (in the mode of mixing SEI + BEI signals).

Among the particles of native gold remaining in light organic forms, we identified coarse-dispersed ( $>1 \mu\text{m}$ ) (Figure 9), medium-dispersed ( $0.1\text{--}10 \mu\text{m}$ ) (Figures 9–11), and ultradispersed ( $<0.1 \mu\text{m}$ ) (Figure 11) particles. Native gold,  $1\text{--}10 \mu\text{m}$  in size, associated with both OS and IOS coals, has mainly irregular platy and lumpy shapes with irregular jagged and smoothed edges of the spongy microrelief surface and are most commonly aggregates of submicron tabular individuals of the above-described structure (Figures 9 and 10). High-fineness gold prevailed, while medium- and low-fineness gold was scarce (Figure 3). High-fineness gold occasionally exhibits zonal heterogeneity in silver content, resulting from the difference in the chemical composition of some intergrown platelets. Individual grains are either monoplatelets or intergrowths of submicronic plates with a varying degree of intergrowth and the smoothing of the surface, most of which have irregular edges with numerous outgrowths and pits (Figures 9 and 10). The borders with associated mineral phases are ragged and penetrating, and relatively discernible boundaries are formed only with well-crystallized minerals (quartz, feldspar, zircon).

Gold nanoparticles ( $<0.05 \mu\text{m}$ ) are deposited on the walls of structural niches of coals (Figure 11) that are partially filled with kaolinite oolites. Tabular submicron particles of irregular shape are localized directly on oolites and in interoolite space (Figure 11a). Gold nanoparticles are often found in silicified and aluminosilicified phases of variable composition (containing various amounts of Fe, Mn, Ti, Ca, Mg, K, Na, S, and rarely Cl) with a flocculent, flaky structure (Figure 11b), occasionally with compaction and recrystallization zones and chemical compositional stratification in ferruginous oxy-hydroxide phases (seldom with an admixture of S and Cl). Oxide and hydroxide iron phases of the flocculent loose structure often contain numerous gold nanoparticles unevenly distributed throughout the volume of the host matrix (Figure 11c). Gold nanoparticles are deposited on the surface of

quartz, zircon, native copper (with admixture of Ni and Fe), and barite (Figure 11d). Gold is deposited on the surface of IOS, encapsulated by flake-like ultradispersed matter and released in film phases in the form of ~20 nm spherical particles and on the surface of films in the form of bulk and plate-like individuals (Figure 11e) and is present in the relatively dense structureless mass of OS coals (Figure 11f).

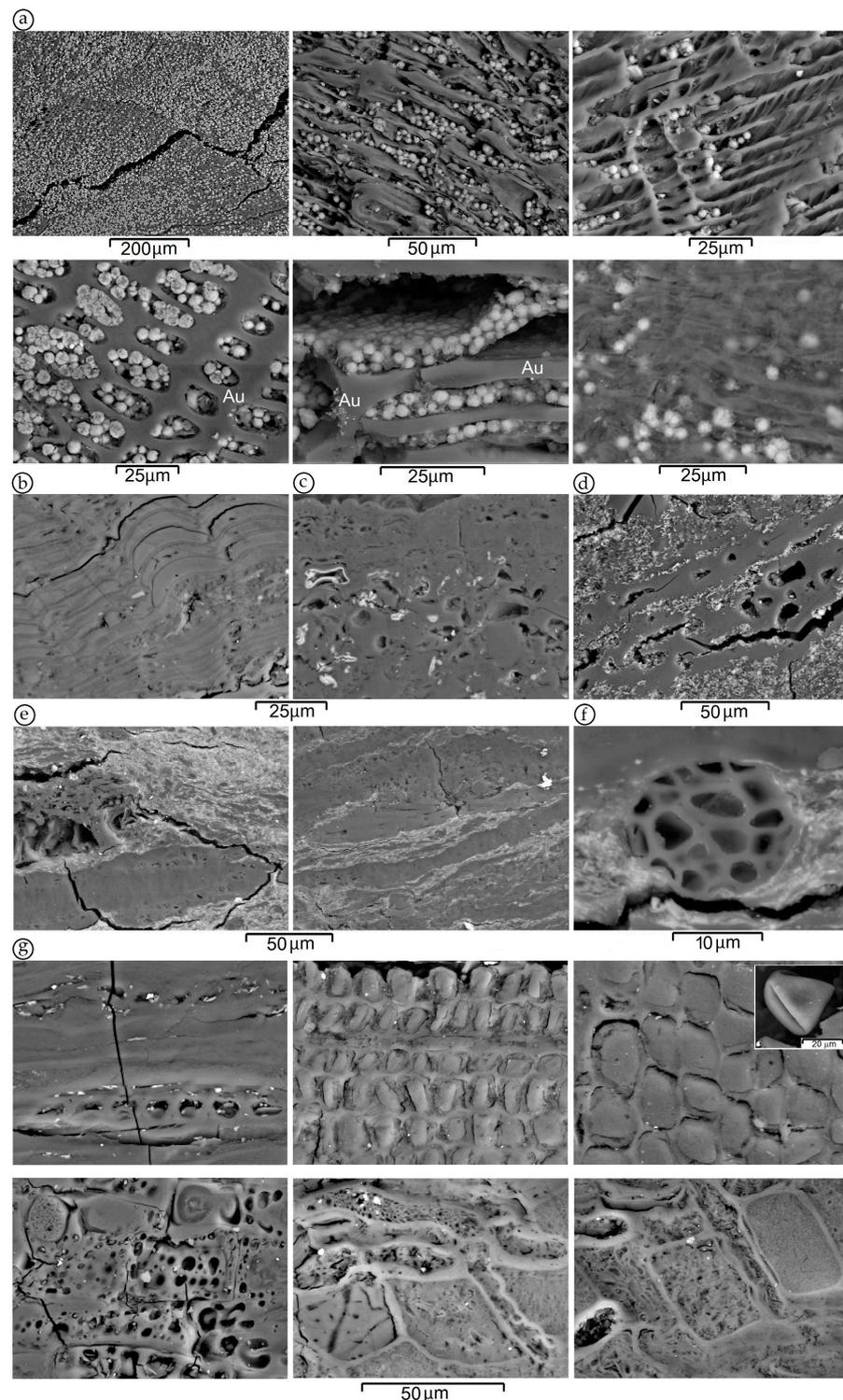
Submicron gold particles are of a fineness close to 1000‰, and the silver content is often below the detection limit of X-ray microanalysis. The peculiarities of the interaction of submicron gold particles with other mineral phases and OS suggest the following two mechanisms of their formation: the precipitation of dissolved forms on adsorbents of different compositions and the colloidal flocculation of the polycomponent substrate with the formation of polyphasic particles.

Gold particles are found in all selected coal samples, but their distribution in the samples along the coal seam is uneven. The coal samples above the interlayer are composed mainly of fusinite-helitites, which preserve a well-defined wooden structure represented mainly by conductive and mechanical fibers and frequently corky bark tissue; resin bodies and cuticles are also present (Figure 12a,b). The tissues of carbonized wood are mineralized to varying degrees (Figure 12a–d). Structured elements are cemented by the main gelified structureless heterogeneous mass composed of flakes, fibers, and fragments of fusenized tissues, sometimes with traces of cellular structure. The interlayer material has organomineral formations of stable carbonized plant residues with the main mass of structureless silicified and aluminosilicified coals (Figure 12e,f). The coals under the interlayer are composed of gelified structureless fibrous masses containing structured fragments corresponding to parenchyma leaf and stem tissues, and fragments with the structure of conducting tissues are rarely observed (Figure 12g). The most stable parts of higher plants are also present here as follows: spores, spore sheaths, cuticles, cork, and sclerenchyma tissues.

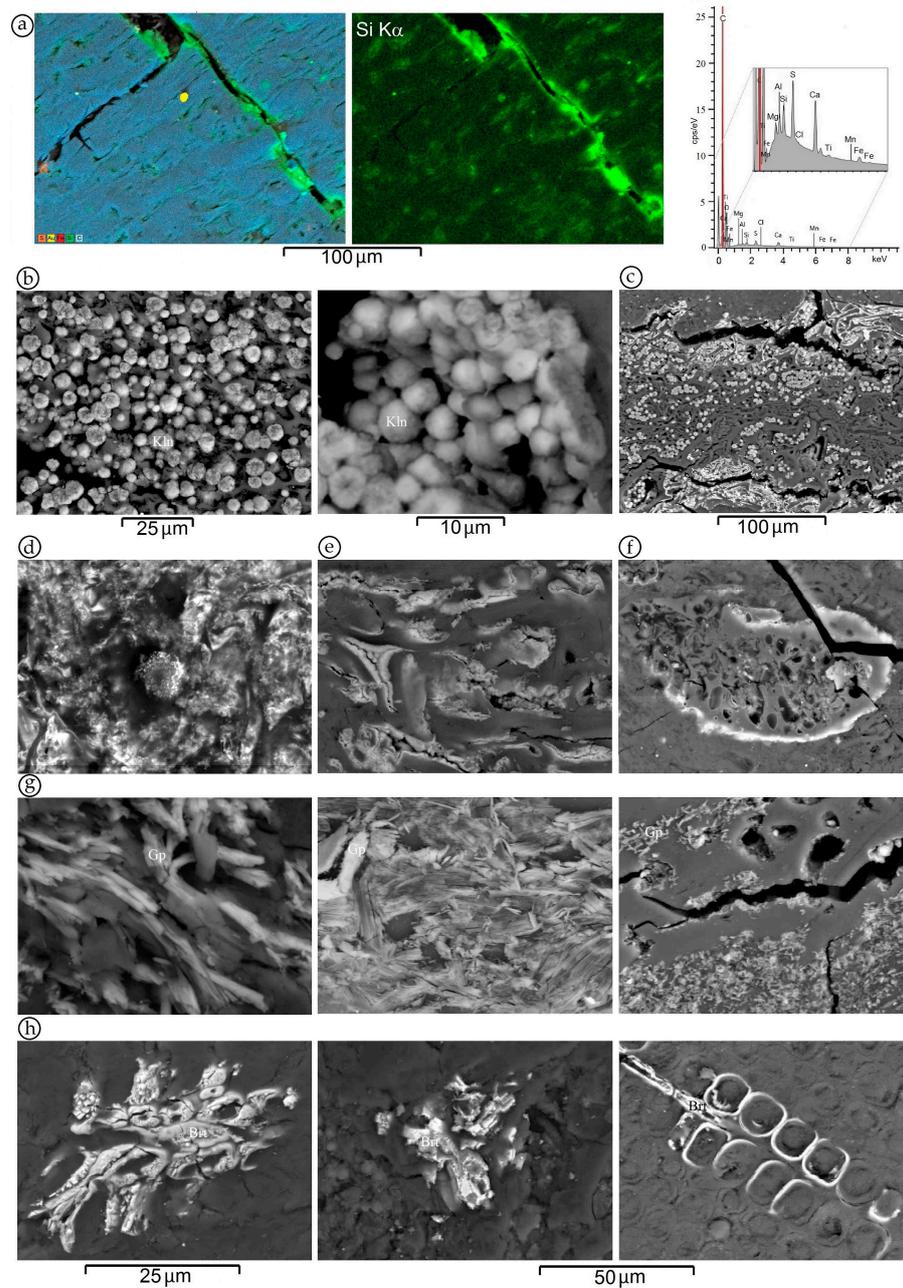
The main type of mineralization in the coal seam roof is determined by the infiltration processes of the migration of chemical elements with surface water penetrating from overcoal sediments into coal by the developed percolation system resulting from the preservation of the structure of carbonized wood and the fracture and interstructural elements of coal. The main mineralizing agent in the seam roof is silica hydrogels. Silica is deposited when infiltrating alkaline and neutral surface ground waters are replaced by acidic waters circulating in the coal seam. This results in the silicification of coal (Figure 13a). The evaporation or freezing of solutions containing silica causes precipitation in the form of powder, crusts, or gels. Silica hydrogels in the acidic medium of coal are consumed in the reactions of the resilication of hydroxides of aluminum and iron, favoring the processes of the hydrogen formation of clays and other mineral phases (Figures 12 and 13).

Aluminosilicates are the first to precipitate out of solutions to generate hydrogenic kaolinite in the form of micron oolites with a floccular structure, which fill natural structural niches of coal, forming a diffuse type of mineralization with a gradual decrease in the number of oolites below the section (Figures 12a and 13b,c). Together with kaolinite oolites, the natural structural niches of coal contain the following micromineral accumulations: native gold (Figures 11 and 12), solid solutions Zn-Cu and Pb-Sn-Cu, sulfosalts of Ag-Sb and Cu-Sn, sulfides of Fe, Pb, Zn, Sb, and Hg, oxides of Zn, Sn, Ti, Fe (occasionally in the form of ~5 μm spheres), and Fe(Mn), ironmagnesian and magnesian chromospinel with Ni admixture.

After the main reaction of aluminum hydroxide resilication and the increase in the acidity below the section (below the level of ~0.5 m from the seam roof), oxy-hydroxide and oxy-silicified iron mineral phases begin to precipitate from the hydrogels (Figure 13c). In the samples picked within the range of 1 m from the seam roof, 10 microparticles of gold ( $0.66 \times 1.57\text{--}4.1 \times 8.3 \mu\text{m}$ ) and 12 submicron (less than 0.1, ~0.12–0.5,  $0.3 \times 0.6 \mu\text{m}$ ) particles were found. Particles in the form of individual platelets with irregular edges and their aggregates were immersed in a structureless silicified mass with the stratification of compositions and separation of ferruginous, magnesian-ferruginous, and aluminosilicate phases in Fe(Mn) oxides and OS coals. Aggregated particles contain enrichment zones of Ag and occasionally Hg.



**Figure 12.** Microstructural organization of OS brown coals of the Yerkovetsky brown coal deposit characterized by the presence of widely developed remains of cover, stem, and parenchyma woody and swamp-grass plant tissues. Upper layer: (predominantly carbonized wood with a pronounced cellular structure of conductive and mechanical tissues and authigenic minerals (mainly micron oolites of kaolinite) are deposited in cell cavities (a), fragments of bark tissue (periderm) (b), zones with deposition of iron hydroxides (c), and sulfatization in coal bordering the mineralized interlayer (d). Clay-siltstone coal interlayer: substantially mineralized helictified plant tissue of fragmentary fibrous structure (e) and sclerenchyma tissue (f). Lower layer: predominantly helictified remains of parenchyma leaf and stem plant tissue with scattered fine mineralization (g) and a spore.



**Figure 13.** Types of dominant OS mineralization in the Yerkovetsky brown coal deposit: OS silicification and filling the parting with silica, most intensively exhibited in the roof of the coal seam (with the overlay image of characteristic X-ray distribution maps along C  $K_{\alpha}$ , Si  $K_{\alpha 1}$ , Au  $M_{\alpha 1}$ , Fe  $K_{\alpha 1}$ , and S  $K_{\alpha 1}$  lines and the energy-dispersive spectrum characterizing the chemical composition of the organic mass of coals with an increased fragment in the range of 0–8 keV) (a); hydrogenic aluminosilicate mineralization from filling structural niches of coal with kaolinite oolites (Kln) (b); the overlapping of ferruginous mineralization along partings of the structural zone, in which kaolinite was earlier formed (c); local infiltration types of the sulfate (d) and hydroxide (e); ferruginous mineralization with the zone of maximum concentration in the center of the seam and a gradual decrease in the frequency of occurrence toward the roof and bottom of the layer, with manifestation in the form of the encrustation of borders of stable fragments in the plant tissue (f); local zones of calcium sulfatization (gypsum Gp) exhibited in the contact zones of the upper and lower layers of coals with a mineralized interlayer (g); and local segregations of high-strontium barite (Brt) observed in the form of independent isolations at all levels of the coal section (h).

The frequency of occurrence of zones of ferruginous mineralization gradually increases and reaches a maximum in the middle part of the seam at the level of  $\sim 2/3$  from the top layer from the roof of the coal seam, then gradually decreases to the separating interlayer of clayey coals. With the increase in the zones of ferruginous mineralization, the frequency of occurrence of native gold microparticles also increases. In the zone of the maximum saturation of oxy-hydroxide ferruginous mineralization, the largest number of gold particles was found, with 20 microns and 45 submicrons among them. Gold microparticles, the size of which varies within 1–5  $\mu\text{m}$ , are represented by plate-like monoparticles or intergrowths of two particles. The larger particles are aggregates of tabular micron and submicron particles of various degrees of intergrowth and compaction. Four of them are more than 10  $\mu\text{m}$  in size ( $6.8 \times 10.5$ ,  $9.7 \times 10.2$ ,  $16.1 \times 29.1$ ,  $14.2 \times 17.8 \mu\text{m}$ ) and refer to macromineral forms (Figure 9). Submicron gold particles are associated with aluminosilicates, silica, Fe(Mn) oxides and hydroxides, and barite. Together with gold particles, there are microphases of sulfides of Ag and Au, Fe, Pb (with Ag impurities), Zn (with Fe and Sb impurities), oxides of Zn, Ti, Fe(Mn), magnesian chromospinels, as well as fluorapatite, scheelite and zircon. Gold sulfide ( $\text{Au}_2\text{S}$ ) was found in association with iron oxysilicide and in the organic matrix.

The coals of the upper and lower layers bordering the mineralized clayey coal interlayer ( $\uparrow\downarrow \sim 0.5 \text{ m}$ ) are characterized by a significant number of local zones of calcium sulfate mineralization (Figure 13d). This was due to the higher degree of metamorphism of coal in the contact zones. OS, under the influence of pressure and increased temperature, underwent compaction and dehydration, and chemical and biochemical transformations led to the loss of functional groups that retained the elements (Ca, Fe, S, O, etc.) associated with it. Phase-forming reactions are activated between the released elements in local zones. The frequency of occurrence of sulfate mineralization zones decreases with the distance from the contact zone. The zones of oxy-hydroxide ferruginous mineralization with areas of ferruginous sulfatization are also present (Figure 13c). However, despite the similarities in the basic type of mineralization of the coal from the contact zone of the upper and lower coal layers, resulting from the internal resource of the coals, there are some individual differences for the disseminated mineralization above and below the interlayer.

The mineral set of microphases of the bordering coal layer upward from the clayey coal interlayer is determined by its interaction with overlying coals. Above this section, with a decrease in calcium sulfatization zones, the number of zones with oxy-hydroxide ferruginous mineralization increases. The microparticles of magnetite (with Mn admixtures), magnesian chromospinels, rutile, zincite, quartz, feldspar, fluorapatite, talc, kaolinite, and ferruginous aluminosilicates of variable composition are present. Sulfides consist mainly of Fe and Pb (often with the admixture of Ag), scarce Zn (with admixture of Fe), and Sb, Cu, Cu-Fe, and As-Fe minerals. Four micron ( $1.3 \times 2.1$ ,  $2.1 \times 3.1$ ,  $2.9 \times 4.0$ ,  $4.2 \times 4.5 \mu\text{m}$ ) and two submicron (0.26 and 0.3  $\mu\text{m}$ ) high-fineness gold particles were found. The submicron gold particles are associated with oxy-silicified phases of dense and floccular structure, Fe(Mn) hydroxides with impurities of elements contained in various types of coals (Ca, Mg, S, and Cl), gypsum, and the OS of coals.

In the polished sections collected from the mineralized bordering layer of clayey coal, 16 microparticles of mainly irregular plate-like morphology ( $0.8 \times 1.16$ – $4.6 \times 7.6 \mu\text{m}$ ,  $\sim 0.2 \mu\text{m}$  thick, single plate measurement) were found. The relief surface was relatively smoothed, and the edges were irregular and rolled. Several particles were intergrowths of 2–3 plates, one intergrown with copper. High-fineness gold varieties were predominant, but medium-fineness Au-Ag varieties and Au-Ag-Cu solid solutions were also present, with the Hg admixture occurring rarely. Submicron gold particles (14 units) were identified in the Fe(Mn) oxides of the floccular structure, some of which contained impurities of Hg and Cl and ferruginous aluminosilicates of denser structure. Submicron gold particles deposited on feldspar grains were also detected. Microphases of native Ag, Bi, Ni(Fe), Fe sulfides (frequently with Ni impurities), and Pb (with Cu impurities) were found in clayey coal. Among the oxides, hematite, magnetite (with Mn admixtures), titanomagnetite, and

ilmenite were predominant; zincite, fluorapatite, scheelite, zircon, feldspar, quartz, and ferruginous aluminosilicates were also present.

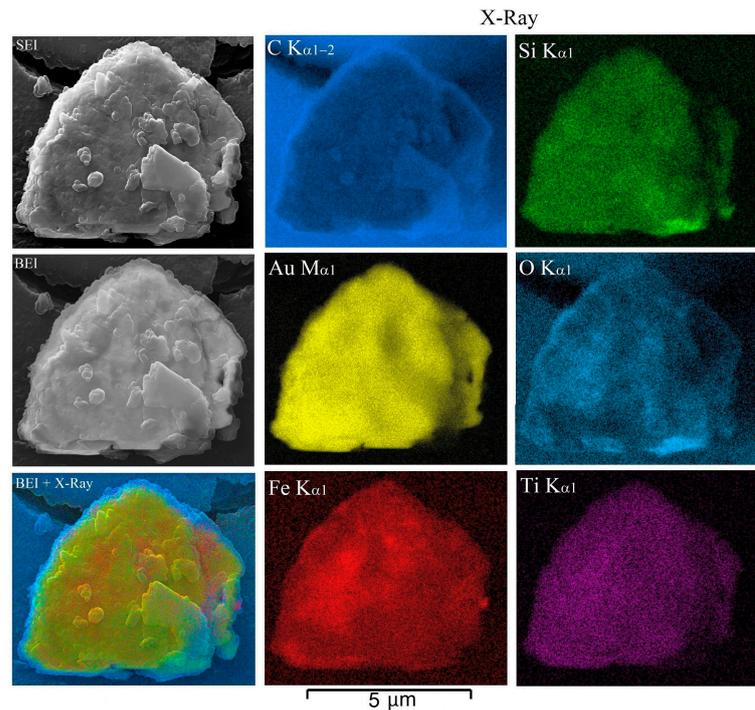
The bordering coal of the lower layer inherited the main mineral set of the overlying mineralized clayey coal interlayer. The number of gold particles relative to the clayey coal interlayer was less: 10 microns ( $0.95 \times 1.46\text{--}2.8 \times 5.8 \mu\text{m}$ ) and 8 submicrons ( $0.05\text{--}0.9 \mu\text{m}$ ). High- and medium-fineness gold varieties and a microparticle of native silver (with S and Cl impurities) were present. One microparticle of gold was intergrown with gypsum. Submicron gold particles were identified in the flake-like mass of Fe(Mn) oxides and ferruginous aluminosilicates of a denser structure. Hematite, magnetite (with Mn impurities), titanomagnetite, and ilmenite dominated among accessory minerals, and zincite, quartz, corundum, fluorapatite, feldspar, ferruginous aluminosilicates were present. Sulfides are represented mainly by Fe (often with Ni impurities) and Pb and rarely by Zn (with Fe impurities) and Sb minerals.

In the coals of the lower layer below the sulfatized zone and up to the bottom of the bed, one could observe scattered, dispersed forms of coal mineralization and rare isolations of ferruginous mineralization encrusting the boundaries of stable elements of plant tissue. The morphostructure of gold microparticles (8 units: elongate  $0.8 \times 1.3\text{--}4.1 \times 8.95 \mu\text{m}$ , rounded  $1.1 \times 1.3, 4.1 \times 5.3 \mu\text{m}$ ) is characterized by a smooth surface and edges, and substructural elements are poorly exhibited. Submicron gold particles (31 units  $0.08\text{--}0.56 \mu\text{m}$ ) are associated with aluminosilicate phases and ferrous oxides (with Hg and Cl impurities). Only one flat particle ( $6.26 \times 7.3 \mu\text{m}$ ) of high-fineness gold was found in the polished section of the sample selected from the bottom of the formation. The microphases of Cu-Zn and Cu-Sn intermetallides, Fe, Fe-Cu, Fe-As, Pb, Sb sulfides, hematite, magnetite (with Mn impurities), titanomagnetite, and ilmenite dominated among oxides, and rutile, zincite, cassiterite, sphene, magnesian chromospinels, quartz, corundum, talc, feldspars, ferruginous aluminosilicates, and barite (with impurities of Sr and Ca) were identified.

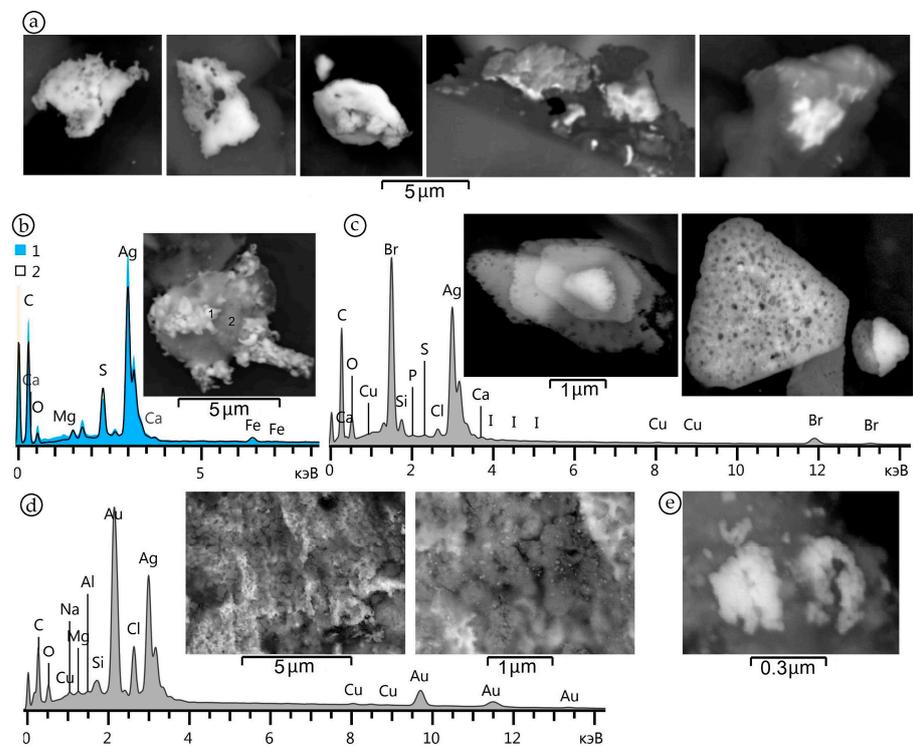
All the particles of native gold found in coals have a mineralized coating, the thickness of which increases with the decreasing particle size. The substance of the coating has a polycomponent composition based on the oxysilicized iron of a variable composition with a wide range of impurity elements (Ti, Mn, Ca, Mg, Al, S) and carbon (Figure 14).

Occasionally, in the local zones of coal, one can observe the co-occurrence of submicron Au- and Ag-bearing particles as independent mineral phases as follows: native, sulfide minerals, and ultradisperse structureless phases of silver chlorides on the surface of larger gold particles (Figure 15). Platy and porous native gold is deposited in polymineral hollow structures of coal partings (Figure 15a). Native silver contains an admixture of Cu, but more often, the energy dispersive spectra obtained from silver phases display additional peaks only from the elements that dominate in the system (C, O, Ca, Fe, Si, Al), the appearance of which is due to the small sizes and platy, porous structure of the particle.

Single particles of sulfides (Figure 15b), bromides (Figure 15c), and chlorides of silver (Figure 15e) were detected. The presence of acanthite among the segregations of native gold may suggest the migration of part of silver in the form of sulfide complexes [21]. The deposition of submicron particles of gold associated with silver halides is based on the exchange reaction of silver sulfide, which leads to the formation of gold sulfide that decomposes to release metallic gold. In the association under study, haloid elements mainly enter the composition of silver minerals. Cl is included in the compounds together with Ag. It was found both in native gold and its sulfides and sulfates. Br, together with Cl, I, and Ag, were included in the composition of the embolite.



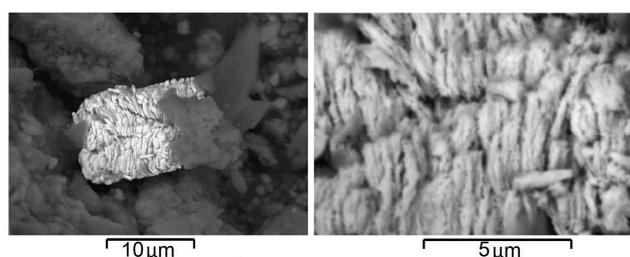
**Figure 14.** Native gold particles in association with the OS of coal in the mineralized coating (thin section) in the SEI and BEI overlay on a BEI image of the distribution of X-ray radiation and the distribution map of X-ray radiation of C  $K_{\alpha 1-2}$ , and Si  $K_{\alpha 1}$  (Al  $K_{\alpha 1}$  has an identical distribution pattern but lower signal intensity) and Au  $M_{\alpha 1}$ , O  $K_{\alpha 1}$ , Fe  $K_{\alpha 1}$ , and Ti  $K_{\alpha 1}$  (Mn  $K_{\alpha 1}$  has an identical distribution pattern with Mg  $K_{\alpha 1-2}$  and Ca  $K_{\alpha 1}$  as well but with a lower signal intensity, and Ca  $K_{\alpha 1}$  has local enrichment sites) over the area.



**Figure 15.** Silver-bearing phases from the coals: native silver (a); silver sulfide with the release of silver (b); silver bromide (embolite) in the OS of coal (c); precipitation of silver chloride on native gold (d); and the organo-mineral substrate (e).

It is worth noting that part of the gold in brown coals can be found in a dissolved state in pore water in the form of sulfur-bearing complexes of the following types,  $\text{AuSO}_3^-$ ,  $\text{Au}(\text{SO}_3)_2^{3-}$ ,  $\text{Au}(\text{S}_2\text{O}_3)_2^{3-}$ ,  $\text{Au}(\text{SO}_3)(\text{S}_2\text{O}_3)^{3-}$ ,  $\text{Au}(\text{SO}_3)\text{Cl}^{2-}$ ,  $\text{AuHS}$ ,  $\text{Au}(\text{HS})_2^-$ ,  $\text{AuS}^-$ ,  $\text{Au}(\text{SO}_4)_2^-$  etc. [21–25], which could have been formed as a result of the dissolution of ultradisperse forms of gold in the acidic sulfur-saturated medium of coals. The confirmation of this form of gold in brown coals is the appearance of gold nanoparticles along the boundaries of cracks formed on the surface of the coal-polished section during this study. In the energy dispersive spectra of these gold nanoparticles, a slightly increased intensity of the S  $K\alpha$  peak relative to the host matrix was observed. The reason for the appearance of cracks on the polished section of coal in a vacuum environment is the shrinkage of the substance due to the loss of the gas–liquid phase localized in the pore space of coal. Waters containing dissolved forms of gold, with the appearance of cracks, are released from the pore space and migrate to the surface of the polished section, and while decomposing, release gold deposited at the crack boundary.

A particle of high-fineness gold with the substructure imitating the plant tissue (pseudomorphoses) was identified (Figure 16). The formation of this particle is, most likely, related to the processes of saturation of the OS ultraporous structure with ionic Au solutions and their further mineralization. The ionic form of OS infiltration of this particle is more preferable since no gelified coating was observed on this grain.



**Figure 16.** Native gold particle with the substructure of plant tissue (pseudomorphoses).

## 5. Discussion

Ontogenetic analysis of native gold, accompanying phases, and the variability of the mineralogical–petrographic composition of brown coals and host rocks from the Yerkovetsky brown coal deposit supports the following statement:

- Loose sediments hosting coal seams have dispersed gold–silver mineralization, which is a genetic source of gold in coals;
- The coals of the lower layer were formed in the conditions of a stagnant peat bog. Dense impermeable illite-montmorillonitic clay occurred at the bottom of the seam, owing to which the role of the upward infiltration of the water flow as a genetic source of IOS in coals was insignificant;
- The formation of a highly mineralized coal–clay interlayer was related to the stages when the accumulation of OS slowed down. These could be periods of drought (aeolian type) or flood (alluvial type), when substantial masses of mineral matter were deposited from air or water-dispersed media, increasing the content of IOS in the caustobiolites of coal series at the stage of OS accumulation, which could be a source of the terrigenous component of gold in coals;
- The coals of the upper layer, composed predominantly of carbonized wood, were formed from the accumulation of woody material in the hydromorphologically conditioned lowland area of a flowing peat bog as the result of a large-scale extreme flood (double flood). Mineral suspension carried by water flows after the change in the dynamic water regime to stagnant underwent sedimentation, contributing to the formation of dispersed forms of IOS in the coal seam and was concentrated in the near-bottom zone of the highly mineralized OS layer.

The high water availability and water conductivity of overcoal sandy-clay sediments and the preservation of the structure of carbonized wood with a widely developed structure of percolation channels in the upper layer of coals determine the high significance of the downward infiltration of the water flow with a drastic change in the neutral-alkaline medium to acidic conditions, as a genetic source of IOS in coals.

Significant similarities in typomorphic features, including morphology, structural organization, the range of gold fineness native gold macroparticles ( $>10\ \mu\text{m}$ ), and a set of accessory minerals extracted from brown coals and overcoal sediments by gravity enrichment methods, can serve as evidence of the identity of their source. That is, macroparticles of native gold in coals are terrigenous and concentrated in coals at the stage of OS accumulation by water and air flow.

At the stage of diagenetic transformations, in accordance with the obtained data on the nature of changes in the mineralization of the coal seam, the dominant source of IOS input into coals is surface-water-saturated overcoal sediments. Water saturation and the permeability of rocks contribute to the processes of the chemical and mechanical destruction of minerals and cause the transition of passive forms of elements into mobile ones. Under these conditions, gold released from minerals remains inert. However, ground and surface waters are saturated with colloidal solutions of silicon, aluminum, and iron hydroxides, as well as their amorphous gels, which perform stabilizing and transport functions for low-stable metal sols, such as Au. The idea of the deposition of gold in the form of colloid was proposed by [16] and is still being developed to find more evidence in the study of the fine structure of gold-bearing mineral systems [26–29].

The porosity of coals, which is due to the high degree of preservation of structural organization inherited from the original tissue of woody plants, creates a developed water-permeable system providing the transport of chemical elements in ionic, colloidal, and suspension forms. Silica-rich liquids seep into the structureless mass of coal and penetrate through cracks and partings and vascular and pore spaces. Hydrogels containing silica and hydroxides of aluminum, iron, and carbonic acid, when changing neutral and alkaline waters to acidic that circulate in the coal deposit, can precipitate, participate in resilication processes, form hydrogenic minerals, and promote the deposition of other authigenic minerals.

The ontogenetic analysis of micromineral forms of native gold and mineral phases, which are released together, suggests that gold from overcoal sediments to coals migrates with downward infiltration waters, mainly in the form of dispersed suspension and colloids. Infiltration waters are polycomponent colloidal solutions dominated by silica gel and iron hydroxide, which protect Au sol from coagulation in the acidic environment of coals.

Gold migrating in the form of colloid is precipitated under the action of electrolytes or oppositely charged colloids, which in the conditions of the studied system primarily include iron hydroxide. The maximum content of the mineralization zones of iron hydroxide was found at the level of  $\sim 2/3$  upper layer from the roof of the coal seam in which the maximum number of gold particles was detected. Ferrous sulfate, which is also an active precipitant of gold, can appear in pore solutions at deeper horizons of the coal seam, as the roof of the seam is less acidic due to the constant inflow of water from overseam sediments. Therefore, it plays an active role in the zone of the stabilization of acidity. Colloidal gold is also extracted from solutions by kaolinite, quartz, barite, calcite, and other mineral phases.

Polycomponent colloidal solutions filling the structural cavities of coals during their interaction with the OS of coals are fractionated in the processes of seeping water into the thinner structural cavities of coals (function of molecular sieves), evaporation, cycles of freezing/thawing, undergoing dehydration and are transformed into concentrated hydrogels. As a result of dehydration, hydrogels are mineralized to form particles of a flocculent structure. The further stratification and crystallization of some phases form heterogeneous particles, the composition of which is determined by the local composition of inflowing colloidal solutions that fill the structural niches of coal. Owing to the coagulation of gold-

bearing gels, both sorption forms, typically nanoparticles and independent microparticles of native gold, are formed.

The mineral composition of the coating of gold microparticles is also determined by the composition of hydrogels in the local zones of their combined dehydration and mineralization. As infiltration waters are saturated with silica gel and iron hydroxide and concentrated together with gold in the structural niches of coal, the coating and particles of the floccular structure, containing nanosized globules and thin structures of mutual intergrowth with gold, mainly consist of phases of a variable composition on the basis of oxysilicized iron with a wide range of impurity elements (Ti, Mn, Ca, Mg, Al, S) and carbon. The coating protects the deposited gold particles from redissolution in the acidic coal medium saturated with aggressive acids and compounds. Aggregated particles were formed by the repeated processes of filling structural cavities, in which submicron gold particles were deposited earlier, with portions of gold-bearing hydrogels. Gold deposits on the surface formed thin interpenetrating structures with the mineralization phases of other components localized in the structural cavities of the coal. The submicron gold particles intergrew, forming aggregated larger particles of native gold, which gradually became compacted, and the surface and edges were smoothed [17,18].

Moreover, gold in the coals under study may occur in pore waters in the form of sulfur-bearing complexes. Pore waters containing dissolved forms of gold, with the appearance of cracks, were released from the pore space, migrated to the surface, and decomposed to form metallic gold precipitated at the crack boundary.

Thus, the main sources of IOS in brown coals of the Yerkovetsky brown coal deposit at the stage of accumulation of OS were the mineral particles transported by water and air flows to the zones of concentration of OS. At the stage of diagenetic transformations, IOS was supplied to the coals from the overcoal sediments in ionic, colloidal, and suspension forms during water infiltration, which played an important role in the deposition of gold.

## 6. Conclusions

Macromineral particles of native gold in the coals from the Yerkovetsky brown coal deposit are predominantly of terrigenous type, and they were transported by air currents (aeolian type) and surface water (alluvial type) at the stage of the concentration of OS. Native gold has a globular-spongy structure with different degrees of compaction and the encapsulation of grains. Micron and submicron gold particles in brown coals formed at the stage of diagenesis and belonged to the infiltration type. Gold transfer in the organo-mineral system “loose sediments coals” under the conditions of a downward infiltration flow is predominantly mechanical in its colloidal form. The main substance of transfer is polycomponent iron-silicified hydrogels, which, in the structural and crack spaces of coals in the process of dehydration, flocculate and form polyphase microparticles with a flake-like structural organization and the encapsulation of colloidal gold particles. These flocculated masses retain the quasi-amorphous structure or gradually recrystallize to form stable mineral phases. In the process of mineralization, hydrogels form a coating on gold particles, making them more stable in the acidic medium of coals. Sulfur-bearing complexes of gold dissolved in pore water, when released from pores, are deposited as nanoparticles of metallic gold. However, owing to the lack of a protective coating, they can redissolve in the aggressive medium of coals.

The determining role in the migration and deposition of gold in coals belongs to inorganic matter participating in the mineralization processes of coal. Organic matter fulfills medium-forming, fractionating (colloidal, molecular, and ionic sieves) and accumulating functions.

**Author Contributions:** Conceptualization, V.I.R. and G.A.P.; methodology, V.I.R.; investigation V.I.R.; resources, V.I.R.; data curation, V.I.R.; writing—original draft preparation, V.I.R.; writing—review and editing, V.I.R. and G.A.P.; visualization, V.I.R.; supervision, V.I.R.; project administration, V.I.R. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was carried out within the framework of the state assignment of the Institute of Geology and Nature Management of Far East Branch (Blagoveshchensk) (No. 224022000193-7) and the Sobolev Institute of Geology and Mineralogy of Siberian Branch (Novosibirsk) (No. 122041400237-8) of the Russian Academy of Sciences financed by the Ministry of Science and Higher Education of the Russian Federation.

**Data Availability Statement:** Data are contained within the article.

**Acknowledgments:** The authors are grateful to V.N. Borisov for their assistance in coal sampling and to E.N. Voropaeva (IGiP FEB of RAS) for the mineralogical separation of loose samples. We thank three anonymous reviewers for their comments and suggestions, which helped to improve the manuscript.

**Conflicts of Interest:** The authors declare no conflicts of interest.

## References

1. Yudovich, Y.E.; Ketris, M.P. *Inorganic Matter in Coal*; Ural Division of the Russian Academy of Science: Ekaterinburg, Russia, 2002; 422p. (In Russian)
2. Yudovich, Y.E.; Ketris, M.P. *Valuable Trace Elements in Coal*; Ural Division of the Russian Academy of Science: Ekaterinburg, Russia, 2006; 558p. (In Russian)
3. Seredin, V.V. Distribution and formation conditions of noble metal mineralization in coal-bearing basins. *Geol. Ore Depos.* **2007**, *49*, 1–30. [[CrossRef](#)]
4. Seredin, V.V.; Finkelman, R.B. Metalliferous coals: A review of the main genetic and geochemical types. *Int. J. Coal Geol.* **2008**, *76*, 253–289. [[CrossRef](#)]
5. Dai, S.; Finkelman, R.B.; French, D.; Hower, J.C.; Graham, I.T.; Zhao, Z. Modes of occurrence of elements in coal: A critical evaluation. *Earth-Sci. Rev.* **2021**, *222*, 103815. [[CrossRef](#)]
6. Sorokin, A.P.; Kuz'minykh, V.M.; Rozhdestvina, V.I. Gold in brown coals: Localization conditions, modes of occurrence, and methods of extracting. *Dokl. Earth Sci.* **2009**, *424*, 109–113. [[CrossRef](#)]
7. Rozhdestvina, V.I.; Sorokin, A.P. First finds of native palladium, platinum, gold, and silver in brown coals of the Yerkovetsky Field (Upper Amur Region). *Rus. J. Pac. Geol.* **2010**, *4*, 483–494. [[CrossRef](#)]
8. Rozhdestvina, V.I.; Sorokin, A.P.; Kuz'minykh, V.M.; Kiseleva, A.A. A gold content in brown coal and combustion products. *J. Min. Sci.* **2011**, *47*, 842–849. [[CrossRef](#)]
9. Sorokin, A.P.; Rozhdestvina, V.I.; Kuz'minykh, V.M.; Chanturiya, A.V.A.; Zhmodik, S.M. Nonconventional types of noble-, rare-metal, and rare-earth mineralization in coal-bearing basins in the Far East. *Dokl. Earth Sci.* **2012**, *446*, 1215–1219. [[CrossRef](#)]
10. Sorokin, A.P.; Rozhdestvina, V.I.; Kuz'minykh, V.M.; Zhmodik, S.M.; Anoshin, G.N.; Mitkin, V.N. The regularities of formation of noble- and rare-metal mineralization in cenozoic coaliferous deposits in the southern Far East. *Russ. Geol. Geophys.* **2013**, *54*, 671–684. [[CrossRef](#)]
11. Cherepanov, A.A. Noble metals in ash-cinder wastes of the Far East thermal power plants. *Russ. J. Pac. Geol.* **2008**, *27*, 110–121. [[CrossRef](#)]
12. Sorokin, A.P.; Konyushok, A.A.; Kuz'minykh, V.M.; Dugin, S.V. Gold-Bearing brown coal deposits of the Zeya–Bureya sedimentary basin (East Russia): Fundamental Model of Formation. *Minerals* **2021**, *11*, 682. [[CrossRef](#)]
13. *Russia's coal base. v.V. Book 1. Coal basins and deposits of the Far East (Khabarovsk Krai, Amur Oblast', Primorsky Krai, Jewish AO)*; CJSC «Geoinformmark»: Moscow, Russia, 1997; 371p. (In Russian)
14. Vasil'ev, I.A.; Kapanii, V.P.; Kovtonyuk, G.P.; Mel'nikov, V.D.; Luzhnov, V.L.; Danilov, A.P.; Sorokin, A.P. *Mineral–Raw Material Base of the Amur District on the Turn of Centuries*; Zeya: Blagoveshchensk, Russia, 2000; 168p. (In Russian)
15. Crosdale, P.J.; Sorokin, A.P.; Woolfe, K.J.; Macdonald, D.I.M. Inertinite-rich Tertiary coals from the ZeyaBureya Basin, Far Eastern Russia. *Intern. J. Coal Geol.* **2002**, *51*, 215–235. [[CrossRef](#)]
16. Petrovskaya, N.V. *Native Gold*; Nauka: Moscow, Russia, 1973; 348p. (In Russian)
17. Rozhdestvina, V.I. Solid Phase Evolution of Nanodispersed Palladium Powders. In *Synthesis Methods and Crystallization*; Open access peer-reviewed; IntechOpen: London, UK, 2020; 21p. [[CrossRef](#)]
18. Rozhdestvina, V.I. Solid-Phase Gold Transformation in Contact Interactions. In *XIII General Meeting of the Russian Mineralogical Society and the Fedorov Session*; GMRMS 2021; Springer Proceedings in Earth and Environmental Sciences; Marin, Y., Ed.; Springer: Cham, Switzerland, 2023; pp. 79–87. [[CrossRef](#)]
19. Kalinin, Y.A.; Palyanova, G.A.; Naumov, E.A.; Kovalev, K.R.; Pirajno, F. Supergene remobilization of Au in Au-bearing regolith related to orogenic deposits: A case study from Kazakhstan. *Ore Geol. Rev.* **2019**, *209*, 358–369. [[CrossRef](#)]
20. Nikiforova, Z.S.; Kalinin, Y.A.; Makarov, V.A. Evolution of native gold in exogenous conditions. *Russ. Geol. Geophys.* **2020**, *61*, 1244–1259. [[CrossRef](#)]
21. Webster, J.G. The solubility of gold and silver in the system Au–Ag–S–O<sub>2</sub>–H<sub>2</sub>O at 25 °C and 1 atm. *Geochim. Cosmochim. Acta* **1986**, *50*, 1837–1845. [[CrossRef](#)]

22. Mironov, I.V.; Kharlamova, V.Y. Gold(I) complexes in sulfite-thiosulfate aqueous solutions. *Russ. J. Inorg. Chem.* **2016**, *61*, 123–128. [[CrossRef](#)]
23. Mironov, I.V.; Kharlamova, V.Y. Properties of the gold(I) sulfite complex in acidic chloride solutions. *Rus. J. Inorg. Chem.* **2016**, *61*, 1047–1053. [[CrossRef](#)]
24. Williams-Jones, A.E.; Bowell, R.J.; Migdisov, A.A. Gold in Solution. *Elements* **2009**, *5*, 281–287. [[CrossRef](#)]
25. Zhang, N.; Kou, J.; Sun, C. Investigation on Gold–Ligand Interaction for Complexes from Gold Leaching: A DFT Study. *Molecules* **2023**, *28*, 1508. [[CrossRef](#)] [[PubMed](#)]
26. Saunders, J.A. Colloidal transport of gold and silica in epithermal precious-metal systems: Evidence from the Sleeper deposit, Nevada. *Geology* **1990**, *18*, 757–760. [[CrossRef](#)]
27. Saunders, J.A.; Burke, M. Formation and aggregation of gold (electrum) nanoparticles in epithermal ores. *Minerals* **2017**, *7*, 163. [[CrossRef](#)]
28. Petrella, L.; Thebaud, N.; Fougereuse, D.; Evans, K.; Quadir, Z.; Laflamme, C. Colloidal gold transport: A key to high-grade gold mineralization? *Miner. Depos.* **2020**, *55*, 1247–1254. [[CrossRef](#)]
29. Mcleish, D.F.; Williams-Jones, A.E.; Vasyukova, O.V.; Clark, J.R.; Board, W.S. Colloidal transport and flocculation are the cause of the hyperenrichment of gold in nature. *Proc. Natl. Acad. Sci. USA* **2021**, *118*, e2100689118. [[CrossRef](#)] [[PubMed](#)]

**Disclaimer/Publisher’s Note:** The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.