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Gold-Bearing Brown Coal Deposits of the Zeya–Bureya Sedimentary Basin (East Russia): Fundamental Model of Formation

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Abstract: The primary sources and the conditions for the formation of the Paleogene–Neogene coal-bearing deposits in the Zeya–Bureya sedimentary basin were identified and studied with the help of paleogeographic reconstructions and geochemical analyses. Based on the results obtained, we suggest a new basic model of element transfer into the coal, involving two mutually complementary processes to account for the introduction and concentration of gold and other trace elements in the sequences investigated. The first process reflects the system in which peatlands were concentrated along the basin's junction zone and the passive internal residual mountain ranges. The second reflects the junction's contrast-type (sharp-type) forms conditions along the external mobile mountain-fold frame. The eroded gold particles were transported over 10–20 km as complex compounds, colloids, dispersed particles, and nanoparticles, and remobilized into clastogenic and dissolved forms along the first few kilometers. The release of gold in the primary sources occurred due to weathering of gold-bearing ore zones, followed by transportation of gold by minor rivers to the areas of peat accumulation. This study considered the probability of the accumulation of high concentrations of gold and rare earth elements (REE) in coal due to the introduction of organic and inorganic materials during floods, with episodes of catastrophic events, and volcano–hydrothermal activities.

Keywords: brown coal; gold content; provenances analysis; gold mineralization; weathering; sedimentation model; metal transfer; REE distribution

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1. Introduction

In recent years, considerable information has been collected on gold-bearing brown coal basins in Russia, Uzbekistan, China, and Kazakhstan. Their depositional conditions were classified and reconstructed. The geochemistry and mineralogy of the coals were studied. In addition, issues regarding transportation, forms of transfer and localization of trace elements in peats, and physicochemical processes occurring during the interaction of metals with organic matter were examined [1–10]. Investigations are being actively pursued to refine the paleogeographic reconstruction of provenance to determine the primary composition of basin fill [11] and to study the mechanism of rock weathering [12,13]. Knowledge of the mechanisms of enrichment of coals with gold and other elements makes it possible to determine the scale of the prevalence of ore mineralization in coal seams and to propose technologies for extracting ore elements from coals and their combustion products [14].

Our previous studies dealt with the distribution of gold in coal-bearing deposits of the Zeya–Bureya basin and mountain massifs [15–18]. In the Late Cretaceous and Paleogene, gold deposits were subjected to intense weathering processes and served as sources of gold and other ore components for coal-bearing deposits.

This study aimed to identify the conditions of the formation of gold-bearing coal deposits and to develop a basic model of their formation. The model developed in this study will make it possible to study the behavior of ore elements in the process of their release from the primary sources, transportation, and concentration in the peatlands.

2. Geological Setting

2.1. Zeya–Bureya Sedimentary Basin

The Zeya–Bureya Basin, where the majority of the fieldwork was conducted, is bound within four orogenic structures: Yankan–Tukuringra–Dzhagdy to the north, Turan (Bureya) to the east, Bol'shekhingan to the west, and Malokhingan to the south. The Gonzhinsky, Oktyabrsky, and Shimanovsky inner mountain ranges divide the Zeya–Bureya basin into Middle Zeya, Amur-Zeya, Ushmyn, and Lower Zeya second-order basins, respectively. As shown in Figure 1, the foreland basins are situated along the outer periphery of the basin.

The structural evolution of the Zeya–Bureya basin occurred in two stages, riftogenic (Cretaceous) and neotectonic (Paleogene–Neogene). The riftogenic stage is associated with the formation of the Priamursky, Ushmynsky, Zeisko–Selemdzhinsky, Yekaterinoslavsky, and Arkharinsky grabens. In the Late Cretaceous, they were transformed into zones of steady downwarping of crust drained by the Amur, Zeya, Selemdzha, Tom, and Arkhara paleorivers [17,19]. The riftogenic stage culminated with the formation of denudational plains along the inner mountain ranges with weathered rocks.

The neotectonic stage (Paleogene–Neogene) in the development of the Zeya–Bureya sedimentary basin took place during the activation of the Malokhingansky and Turan (Bureya) ranges. This led to the formation of Srednezeya, Amur–Zeya, Ushmyn, and Lower Zeya second-order basins [20]. These processes proceeded under conditions of growing activity with ascending types of movement of the outer mountain frame and oscillatory modes in areas of sedimentation. These conditions of growing activity were accompanied by volcanic activity within the Turan (Bureya) massif in the flanking orogenic belt.

2.2. Paleogene-Neogene Coal Accumulation Zones of the Zeya-Bureya Basin

The brown coals of the Zeya–Bureya Basin are predominantly Paleocene and Early–Middle Miocene in age. The Tyndinskoe, Sianchik, Mukhinskoe, Svobodnoe, and Sergeevskoe deposits, comprising the four major coal depositional areas on the northwestern flank of the basin, are located on the denudational plains along the inner mountain ranges in the valleys of the Paleo–Amur and Paleo–Zeya tributaries (Figure 1). Paleocene coals of the Tygdinskoe, Ushumunskoe, and Svobodnoe deposits, represented by seams of thicknesses 2–14.9 m, are overlain by Lower–Middle Miocene coal sequences 20.1 m thick, with fluctuations in seams thickness from 0.7–10.4 m.

Coal-bearing sequences, located in the eastern half of the Lower Zeya basin (Figure 1) are represented by four coal accumulation zones (6, 7, 8, and 9). The Paleocene coal-bearing sediments prevail in the western part of the coal-bearing zones, while the Lower–Middle Miocene coal-bearing sediments dominate the eastern zones. Sediments in the western part comprise deposits with thicknesses in a range of 5–9 m, which are split into two to three layers between the transition zones and the areas of enhanced subsidence. In contrast, the eastern zone sediments form up to five deposits 13.2 m thick, which tend to be thin and pinched out at the boundary with the mobile Turan (Bureya) massif.

The Gonzhinsky, Oktyabrsky, Shimanovsky, and Turan (Bureya) massifs were the main sources of sediments for the Zeya–Bureya basin during the Cenozoic. The resource potential of these structures is due to the ore deposits and ore occurrences of noble, rare metals, rare earth elements, and gold placers.

The Umlekan–Ogodzhinskaya zone is located within the Gonzhinsky and Oktyabrsky massifs and is bordered by the Zapadnoturanskaya and Niman–Mel'ginskaya zones of the Turan (Bureya) massif in the east [21]. These ore structures form an amphitheater with complex deposits flanked by Paleogene–Neogene gold placers.

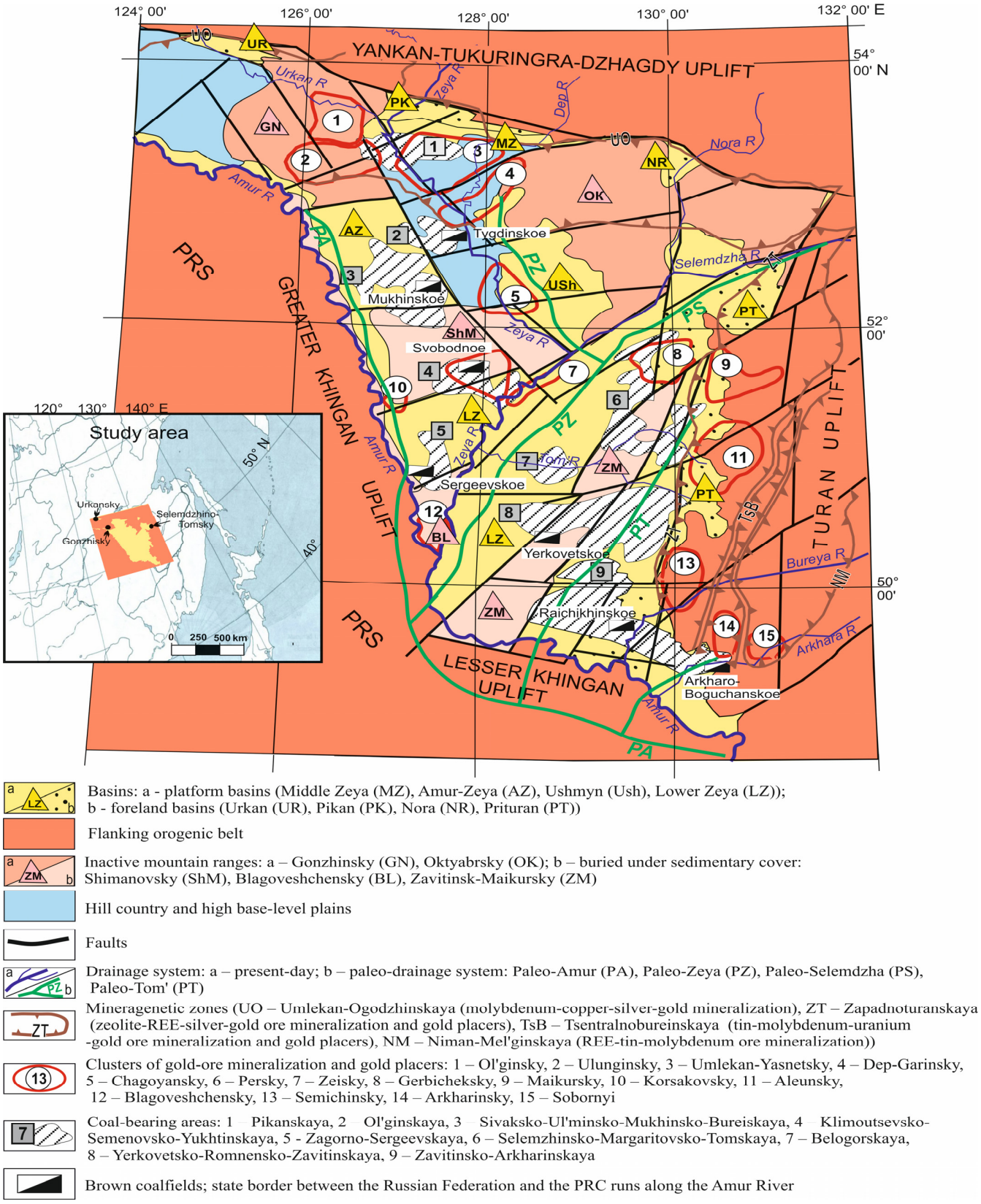


Figure 1. Schematic tectonostructural map of the Zeya–Bureya sedimentary basin [20].

The gold placers are spatially associated with coal-bearing areas of the same age along the residual mountain massifs, whereas along the periphery of the eastern mountain-fold frame, they are separated by zones of predominantly alluvial–proluvial sedimentations.

This determined the choice of two types of systems as objects of study. The first type is a basin bordering on the internal leveled mountain ranges. The second type is a pool—mobile ranges of the external frame.

2.3. Analytical Investigations

2.3.1. Sampling, Technical, Elemental, and Petrographic Research Methods

We collected coal samples from the Yerkovetskoe, Raichikhinskoe, Arkharo–Boguchanskoe, and Sergeevskoe deposits. Samples weighing 5–6 kg were collected using point sampling. Channel sampling of coal weighing 6 and 12 kg was conducted in a 0.5–0.7 m section [22–25]. In 2018, studies on coal and ash deposits were conducted at the Federal Research Center for Coal and Coal Chemistry, Siberian Branch of the Russian Academy of Sciences (FITSUiU SB RAS), Kemerovo. Determination of the technical characteristics of coal, and elemental and chemical compositions, were carried out according to the interstate technical standards (GOSTs) adopted by the Russian Federation: moisture—GOST 33503-2015, ash content—GOST R 55661-2013, volatile-matter output—GOST R 55660-2013, sulfur—GOST 8606-2015 (Eschka method), carbon and hydrogen—GOST 2408.1-95 (ISO 625: 1996), nitrogen—GOST 28743-93 (Kjeldahl method).

The sulfur content in the coal was determined by sintering it with a mixture of magnesium oxide and anhydrous sodium carbonate (Eschka mixture) in an oxidizing atmosphere with free air access at a temperature of 1073.15 $\pm$ 25 K to form sodium and magnesium sulfates. The sulfates were dissolved in hot water or hydrochloric acid. In solution, sulfate ions were determined by gravimetric method with precipitation in a hydrochloric acid medium with barium chloride in the form of barium sulfate. The mass fraction of total sulfur in the weighed portions of the solid fuel samples was calculated based on the mass of barium sulfate sediments.

Petrographic analyses of the samples were performed in oil immersion using a SIAMS-620 (SIAM, VUHIN, Russia, Sverdlovsk Oblast, Yekaterinburg) automated coal petrographic analyzer. Macerals were determined in the oil immersion by their reflectance index, color, morphology, microrelief, structure and texture, degree of destruction, and size. Manual counting of accessory and ore minerals was performed in reflected light at a magnification of 300×.

The chemical composition of coal samples was determined in accordance with the GOST P 54237-2010, "Solid mineral fuel. Determination of the chemical composition of ash by atomic emission spectrometry with inductively coupled plasma". The sample preparation procedure of these samples was identical to that of the standard samples. Standard samples SGD-2A (GSO 8670-2005), ZUK-1 (GSO 7125-94), SG-1A (GSO 520-84P), and SG-3 (GSO 3333-85), prepared at the Vinogradov Institute of Geochemistry (Irkutsk), were used as reference samples. The chemical composition of the ash residues was determined by atomic emission spectroscopy using an iCAP 6500 Duo LA (Thermo Fisher Scientific, Carlsbad, CA, USA) inductively coupled plasma spectrometer (Thermo Scientific).

Thermal analyses were carried out using a Netzsch STA 409 (Netzsch, Selb, Bavaria, Germany) thermal analyzer with Aeolos (Netzsch, Selb, Bavaria, Germany) mass spectrometric attachment under the following conditions: a sample weighing 40 mg was heated at 1273.15 K in a platinum–iridium crucible at a rate of 283.15 K/min in a helium environment. Weight loss and the rate of weight loss were recorded during the analyses. Thermogravimetric data were processed using NETZSCH Proteus software (v. 5.2.1.). To characterize the thermal decomposition, the following indicators were used: V_{max}—temperature of the maximum decomposition rate, and V_{max}—decomposition rate. Weight loss was calculated for the temperature ranges of the most intensive sample decompositions. Mass spectra of the products of thermal destruction were recorded on an Aelos (Netzsch, Selb, Bavaria, Germany) mass spectrometric attachment with electron impact ionization energy of 70 eV in the scanning range of 1–300 u.

2.3.2. Methods for Obtaining Separate Fractions of Coal Combustion Products

The separation of the coal combustion products (CCPs) was carried out at the "Amur" Experimental Technological Complex (ETC), as per procedures given by Sorokin et al. [18,26].

The experiments included the combustion of large-volume coal samples from the Erkovetskiy (251 kg) and Arkharo–Boguchanskiy (270 kg) deposits at temperatures of 1073.15–1273.15 K, with the forced transfer of the air–gas mixture from the combustion chamber to the afterburner of the ash catcher at a temperature of 873.15–1073.15 K, wet cleaning of flue gases with a reduction in temperature up to 473.15–773.15 K, and obtaining purified gases that were carried out into the atmosphere. The liquid phase entered the filtered block for further purification. The experiments were carried out in the process of burning large-volume coal samples weighing 240–270 kg from the Erkovetskoye, Raichikhinskoye, and Arkharo–Boguchanskoye deposits along with the production of furnace slag, fly ash, and sludge [18,26].

The resulting combustion products of brown coal underwent a sequential beneficiation procedure. The slag was ground with a JC-80-150 jaw crusher (Amurskiy Metallist, Amur Oblast, Blagoveshchensk, Russia) through a 1 mm fraction. To isolate and separate underburned and light particles, a slightly inclined sluice of the rectangular cross section was used, on the bottom of which the dredge mats were laid, which made it possible to create a turbulent flow in the bottom layers and keep heavy particles settled at the bottom. The crushed heavy fraction of the sluice was passed through a WMS-0.1 wet magnetic separator (ITOMAK, Novosibirsk Oblast, Novosibirsk, Russia). The non-magnetic fraction of the table was fed to a CT-0.5 concentration table (Sibir-complect, Novosibirsk Oblast, Novosibirsk, Russia), on which the final products of concentration, concentrate and tailings, were obtained.

Fly ash was distributed on an A-50 sieve analyzer (VIBROTECHNIK, Saint Petersburg, Russia) according to size classes classified as fractions from +0.5 to −0.04 mm. Magnetic and non-magnetic fractions were separated on a WMS-0.1wet magnetic separator (ITOMAK, Novosibirsk Oblast, Novosibirsk, Russia), following which the non-magnetic fraction was enriched on a CT-0.5 concentration table (Sibir-complect, Novosibirsk Oblast, Novosibirsk, Russia). The sludge obtained from the purification of technogenic water on a coarse filter was washed in bromoform and separated into magnetic, electromagnetic, non-magnetic heavy, and non-magnetic light fractions.

2.3.3. Methods for the Determination of Gold from Coals and Their Combustion Products

The coal samples were also analyzed for gold, using the assay method, in the experimental and analytical laboratory of the Amur Scientific Center (AmurSC) and the Institute of Geology and Nature Management, Far East Branch of the Russian Academy of Sciences (IGiP FEB RAS). On this basis, a method was developed and adapted for coal and host rocks of the Far East deposits [16,27]. The method was first tested in 2009 at the experimental and analytical assay laboratory of the Amur Scientific Center of the Far East Branch of the Russian Academy of Sciences (Blagoveshchensk), and then in the OAO Irgiredmet laboratory in Irkutsk.

The original channel samples, obtained by grab sampling, were crushed to <0.16 mm to obtain 50 g representative subsamples. Each 50 g representative subsample was further divided into twenty 2.5 g subsamples. Each 2.5 g subsample was separately mixed with chemically pure litharge, soda, borax, and other reagents to accelerate the oxidation of coal and subjected to Scherber smelting (pyro-metallurgical technique) in a fireclay–graphite crucible to obtain a 25 g lead bullion (verkbley). Cupellation was performed on standard cupels following the addition of silver to a lead alloy (inquartation). Lastly, the final beads were leached with nitric acid, washed, dried, and finally annealed by heating.

The gold–silver beads derived from cupellation were weighed, and the obtained values were used to calculate the gold content of the coal. For a rapid assessment of gold content in coals, 20 g subsamples were employed with the technological operations described in Table 1 below. Atomic absorption analyses were applied at the final stage if

the gold concentrations were low. As an internal control, chemically pure starch, instead of coal, was used as a reference sample. The experiments demonstrated the precision and accuracy of the measurements.

Table 1. Gold contents in coal samples of different weights based on assay data.

Deposit and Sample ID	Au, ppm	
	Primary Sample, 20 g	Primary Sample, 50 g
Yerkovetskoe		
Ye-6/3	n/f; 4.87; 4.18	2.76
Ye-7/5	6.4	4.72
Ye-10/1	n/f; 3.06	6.28
Ye-11/3	n/f; 0.36; 2.61	0.44
Pavlovskoe		
P-2/1	3.73	3.16
P-2/3	3.30; 2.16; 10.10	5.04
Raichikhinskoe		
R-1/7	1.6	1.4
R-1/12	1.5	5.08
Darmakanskoe		
D-1/1	11.28; 2.29	8.0
D-3/2	tg	3.6

Abbreviations: n/f—not found; tg—trace gold.

The CCPs in gold were analyzed following the gravity and magnetic concentration procedures. A combined concentrate was obtained from the slag and fly ash. Mineralogy of the noble metals, isolated from the concentrate, was examined at IGiP FEB RAS using microchemical reactions and immersion methods. The chemical composition of the particles was determined using a VEGA 3LMH scanning electron microscope (TESCAN, Brno, Czech Republic) equipped with an X-Max80 energy-dispersive X-ray microanalyzer (Oxford Instruments, High Wycombe, UK) at the Innovation-Analytical Center of the Institute of Tectonics and Geophysics (ITiG) FEB RAS (Khabarovsk). The gold fire assay was performed at the AmurSC FEB RAS.

2.3.4. Trace Element Analyses

The chemical compositions of the rocks were studied using inductively coupled plasma mass spectrometry (ICP-MS) (Cs, Ga, Rb, Sr, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y, Nb, Hf, Ta, Th, U, and Pb) at the Institute of Tectonics and Geophysics, Far East Branch of the Russian Academy of Sciences in Khabarovsk, Russia.

For ICP-MS analyses, acid dissolution of samples was performed in HCl, HNO_3, HF, and $HClO_4$. Measurements were taken in a standard regime on a Perkin Elmer Sciex Elan 6100 DRC ICP-MS system (Perkin Elmer, Waltham, MA, USA), the sensitivity of which over the whole mass scale was calibrated using standard reference solutions that contained all elements to be analyzed in the samples. The relative measurement error for the major and minor elements was 3–10%.

3. Research Results

3.1. Physical and Chemical Properties of Brown Coals

Technical and elemental analysis suggest that the coals from the analyzed deposits were low-sulfur (0.3–0.7%), and predominantly mid-ash (<20%) with an increased ash content (up to 24.2%). The coals of the Sergeevskoye Deposit could be distinguished by their lower chemical maturity compared to the Paleogene coals of the Yerkovetskoe and Arkharo–Boguchanskoe deposits. Lower–Middle Miocene coals were characterized by low degrees of coalification with minor (11–16%) amounts of micro components of inertinite, and displayed reflectance (R_o,r) up to 0.299%, indicating carbonization of coal.

The primary petrographic components of Paleogene coals were vitrinite (42–48%) and inertinite (41–44%), with low proportions (up to 11%) of semivitrinite. Moreover, these coals exhibited the highest vitrinite reflectance (R_o,r) values of 0.4%.

The ash remains in Paleogene coals had a high content of aluminum oxides (up to 30%) and silicon (up to 48.6%), allowing us to classify them as aluminosilicates, with clay components being represented by montmorillonite and hydromica. For the coals of the Sergeevskoe Deposit, the Al_2O_3/SiO_2 ratios were in the range of 1.41–3.3, which was associated with enrichment of coals with alumina supplied from the weathering rocks of the eroded areas. All coal samples had high content of CaO (up to 25.7%), indicating the presence of organo-mineral complexes in the form of humates. Coals of the Arkharo–Boguchanskoe and Yerkovetskoe deposits corresponded to sub-bituminous coal, and the Sergeevskoe Deposit to lignite. The burial depth of the former two was approximately 1000 m, while that of the latter was no more than 500 m [22].

3.2. The Release of Gold and Transport Away from the Primary Sources

The southern slope of the Gonzhinsky massif was chosen as a typical site for studying the junction zone between the basin and the internal residual mountain massifs. This zone covers the Tygda–Ulunginsky ore cluster containing numerous gold, ore, and placer deposits (Figure 2). Areal and linear weathering rocks of predominantly kaolinite–hydromica composition, averaging between 20 and 30 m in thickness, are widely developed within the ore fields of the base-level plain. According to N.I. Orlova et al. [28], the highest gold contents have been recorded from the upper horizons of the weathered rocks, increasing two- to fourfold compared to primary ores (Table 2).

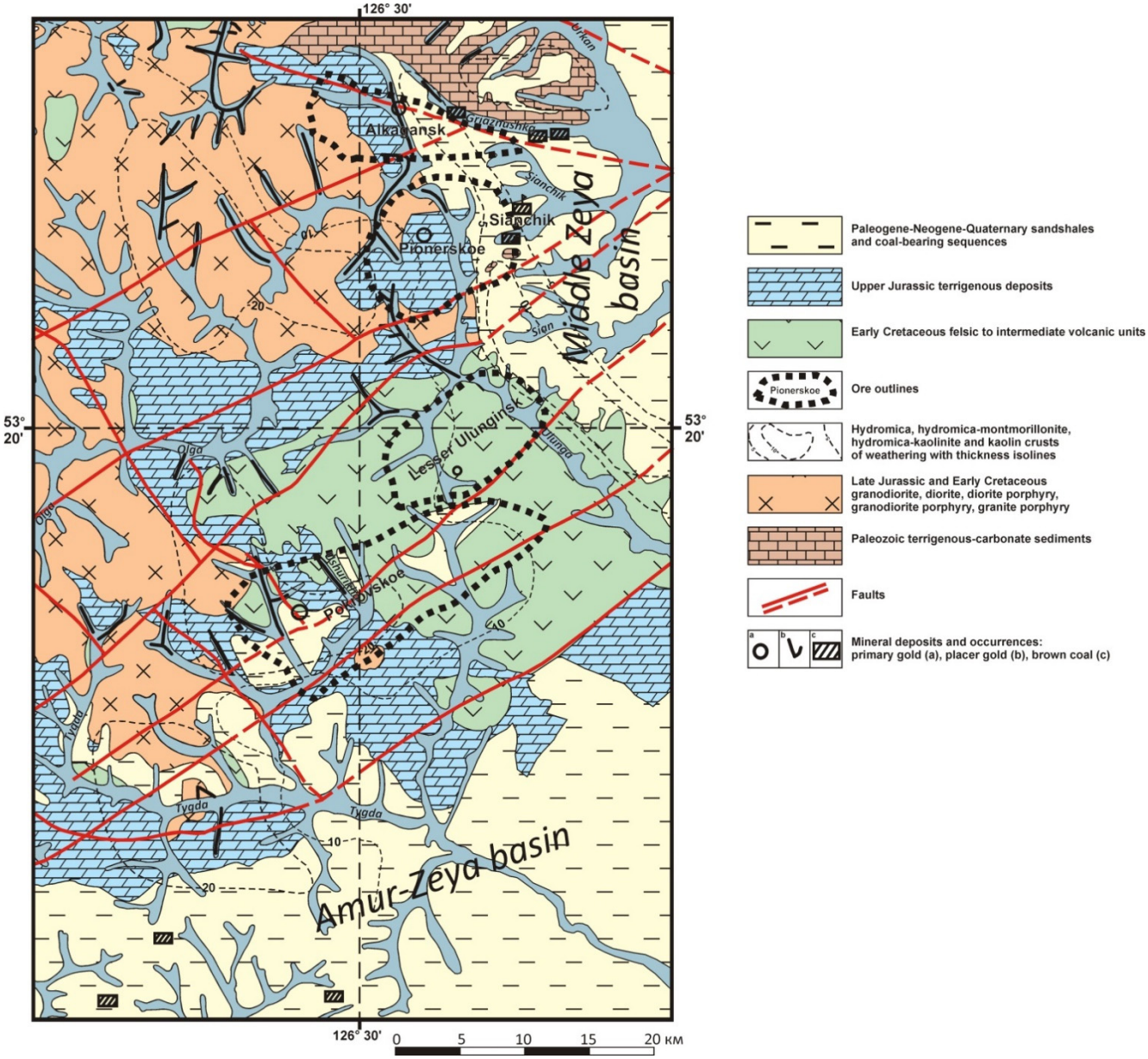


Figure 2. Zones of adjacent mineralized areas of the Tygda-Ulunginsky cluster and the Cenozoic basin [29], with additions by the authors.

The Tygda–Ulunginsky mountain cluster is drained by the Gryaznushka stream. Placer deposits in the Miocene sediments, with commercial gold grades, have been explored in the brook. The Au concentrations in well number 32 ranged from 1.96 to 2.03 ppm (Figure 3). The Sianchik brown coal deposit is located on the left bank of the Gryakhnushka brook. It was sampled at intervals of 0.5 m along the entire coal seam. Its gold content ranged from 1.64 to 4.68 ppm.

To the south of this site, on the gentle slopes of the Shimanovskiy and Blagoveshchenskiy internal massifs, are the Svobodnoye and Sergeevskoye coal-bearing deposits with an established gold content. Detailed investigations of the Lower–Middle Miocene layers from the Sergeevskoye Deposit, with a thickness of 0.7 and 6.8 m, were carried out along the central and southeastern margins, and in the junction zone with the Blagoveshchensky gold-bearing placer area. On the periphery of the deposit, brown coals and their host sediments are characterized by higher gold grades (up to 8.68 ppm) compared to those in center (up to 1.28 ppm).

Table 2. Gold contents in weathering rocks of gold deposits and occurrences in the Tygda–Ulunginsky cluster of the Gonzhinsky gold district, modified from [28] and [30].

Deposits, Occurrences	Weathering Rocks (WCs)						Gold Contents in Weathering Rocks, (ppm)
	Predominant Type	Profile	Age	Thickness, (m)	Host Rocks	Main Supergene Minerals	
Pokrovskoe	Linear–areal	Hydromica–kaolinite, gelite–kaolinite	Late Cretaceous–Eocene	Linear 150–250 or more	Contact between granitoids and effusive rocks	Hydrosericite, kaolinite, hydromica	Up to 99
Zheltunak		Kaolinite–hydromica		Areal 15–20	Dacites and metasomatic quartz breccias	Kaolinite, hydromica, hydrochlorite	Up to 5.1
Pioner		Kaolinite–hydromica		Areal 20–22	Granodiorites, dacites	Hydromica, kaolinite, mont-morillonite	0.1–0.9
Anatolyevskoye		Kaolinite–hydromica		Areal 15–20	Granodiorites	Hydromica, kaolinite	Up to 1–3
Rybinskoe		Hydromica–kaolinite		More than 10–15	Contact between plagiogranites and volcanic rocks	Limonite, kaolinite, leucoxene, hydromica, leucoxene	Up to 67.6
Kulikan		Kaolinite–limonite		Areal more than 1	Tectonic breccias	Kaolinite, hydrolimonite	Up to 68.3
Velikiye Luzhki		Kaolinite–hydromica with ferruginization		1–5	Sandstones, mud-stones	Sandstones	11–30
Sergeevskoe		Hydromica with ferruginization		More than 5	Tectonic breccias	Limonite	Up to 1–3
Dul'neiskoe		Kaolinite–hydromica		10–15	Andesidacites	Hydromica, kaolinite, limonite	Up to 10

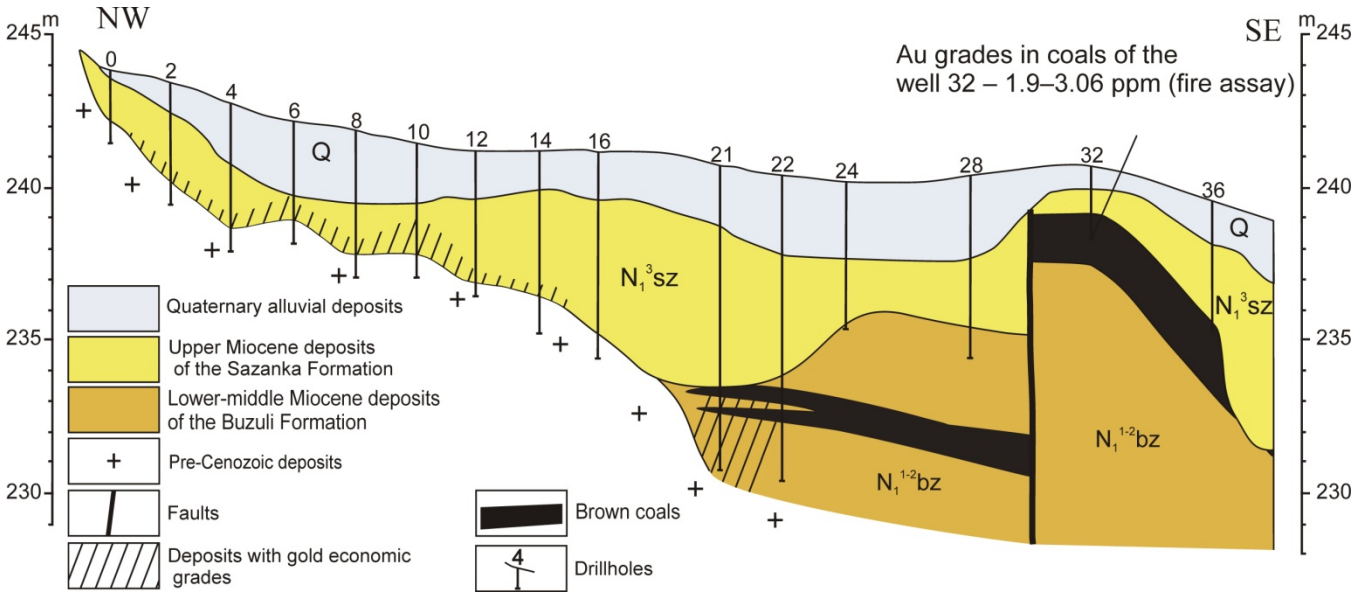


Figure 3. Geological section of gold placer in Gryaznushka Creek.

The study of gold-bearing coal deposits in the contrasting (sharp) junction zone of the mountain-fold frame and the area of accumulation was carried out in the Urkan basin and on the eastern edge of the Lower Zeya basin (Figure 1). Studies in the Urkansky basin are concerned with the Nagiminskaya gold placer located in the graben, 300–400 m wide and more than 1 km long. The placer is formed by gold-bearing alluvial–proluvial deposits with lenses of brown coal and carbonaceous clays (up to 1 m) overlying the mineralized granitoids outlined in Figure 4. The prevalence (from 36% to 91%) of fine, and fine and

dusty (0.25–0.12 mm) gold has been established in the weathering rocks and the redeposited sediments. Following elutriation and evaporation of the silty and clay fractions, the assay test of the obtained products yielded gold in grams per ton.

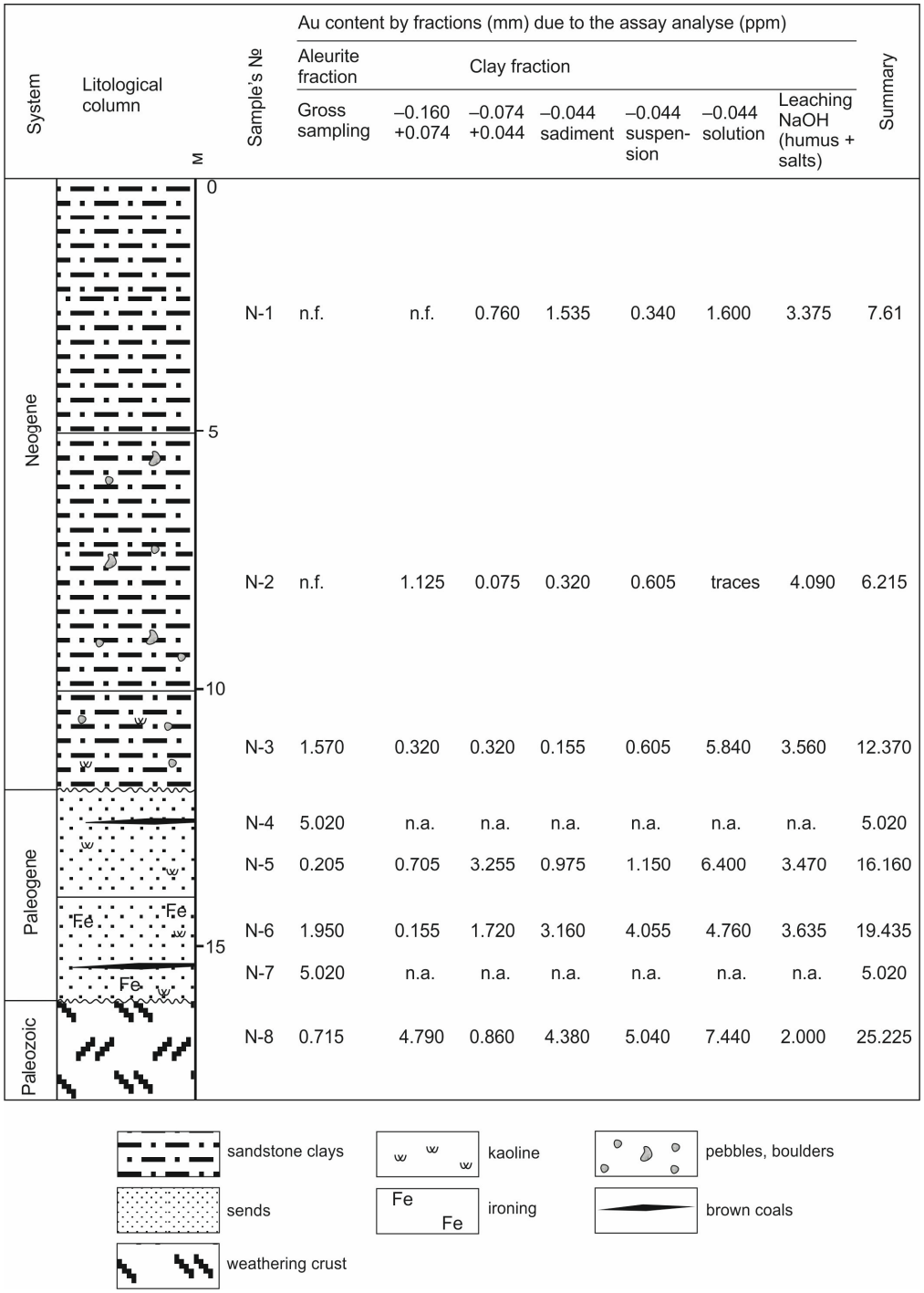


Figure 4. Gold distribution in the silty and clay fractions of the Nagiminskaya gold placer [23]. Abbreviations: n.f.—not found; n.a.—not analyzed; traces—trace gold.

Brown coals contained native gold, sulfides (pyrite, galena, argentite), and minerals with REE, Sc, and Y—bearing accessory minerals (monazite, xenotime, fergusonite). The aggregates of gold particles formed platy grains 10–20 μm in size, with a loose, spongy structure [16].

The second section on the periphery of the Lower Zeya basin and the Turan (Bureya) massif was investigated based on the evolution of the considered type of gold-bearing coal-bearing deposits [22]. Coal formation here took place on alluvial cones and in foothill troughs with a polyfacial structure of Paleogene–Neogene alluvial–proluvial and lacustrine–bog sediments [20]. On the western edge of the Turan (Bureya) massif, cinnabar, cassiterite, and wolframite are constantly present in heavy mineral aureoles. Monazite and fergusonite have also been observed on rare occasions. Copper, lead, zinc, bismuth, and silver plates were found in the Maykursky, Aleunsky, and Semichinsky gold placer clusters [20]. These nodes are located within the Selemdzha and Tom paleovalleys, which, during the Cenozoic, transported the above microcomponents to the Lower Zeya basin, including the areas of Erkovetsky and Raichikhinsky brown coal deposits (Table 3).

The elemental concentration data for sampled coals is given in Table 3; for most of the samples, the concentrations exceeded their Clarke values (up to 2×–3× in the cases of Zn, Sn, Pb, Li, Be, Zr, La, Ce, and Y).

The convergence of the composition of trace elements on the periphery of the Turan (Bureya) massif and in the coals of the Erkovetsky, Raichikhinsky, and Arkharo–Boguchansky deposits suggest that their removal from the peat accumulation area was carried out by the river network, mainly in the form of complex compounds and mineral dispersed particles suspended in water flows.

Table 3. Distribution of trace elements in Paleogene coals of the Erkovetsky, Raichikhinsky, and Arkharo–Boguchansky deposits (ppm).

Elements	Brown Coal Deposits			Clarke *
	Erkovetsky	Raichikhinsky	Arkharo–Boguchansky	
Li	19.35	6.40	14.97	10
Be	2.14	1.89	3.96	1.2
Sc	3.20	3.68	5.20	4.1
V	25.61	40.02	33.92	22
Cr	36.04	30.39	17.89	15
Co	9.11	5.45	7.14	4.2
Ni	19.14	48.57	17.52	9
Cu	12.47	19.86	17.53	15
Zn	62.24	44.97	36.78	18
Ga	10.97	12.15	11.09	5.5
Ge	0.96	3.42	1.61	2
Rb	35.34	18.64	35.06	10
Sr	156.69	106.62	82.13	120
Y	20.89	14.23	19.45	8.6
Zr	38.23	59.35	70.76	35
Nb	4.95	8.56	6.56	3.3
Mo	0.82	1.10	2.45	2.2
Sn	2.51	1.85	1.63	0.79
Cs	3.84	2.60	3.94	0.98
Ba	498.85	312.61	268.15	150
La	17.16	13.90	21.87	10
Ce	30.22	28.57	53.88	22
Pr	3.15	3.06	5.39	3.5
Nd	12.40	11.74	19.71	11
Sm	2.37	2.33	3.67	1.9
Eu	0.44	0.46	0.64	0.5
Gd	2.63	2.72	3.89	2.6
Tb	0.38	0.37	0.63	0.32
Dy	2.42	2.18	3.32	2
Ho	0.53	0.45	0.65	0.5

Table 3. *Cont.*

Elements	Brown Coal Deposits			Clarke *
	Erkovetsky	Raichikhinsky	Arkharo–Boguchansky	
Er	1.59	1.40	2.06	0.85
Tm	0.20	0.20	0.31	0.31
Yb	1.27	1.35	2.09	1
Lu	0.20	0.21	0.29	0.19
Hf	1.12	1.42	2.10	1.2
Ta	0.45	0.41	0.54	0.26
W	1.12	0.91	1.56	1.2
Pb	12.00	14.53	18.37	6.6

* Clarke value by Ketris M.P. and Yudovich Ya.E. [5].

3.3. Gold Distribution in Coal Deposits, Coal Beds and Host Rocks

The past two decades have witnessed comprehensive studies on the content of gold in coals from the Amur region and in their combustion products. The results indicated that the gold contents in these deposits were in the range of 1–5 ppm, approximately half of that in the studied samples (Table 4).

Table 4. Relative abundance of gold in brown coals of Zeya–Bureya Basin [16].

Brown Coalfield	Number of Samples	Distribution of Gold (Rel. %) by Intervals (ppm)					
		<1 ppm	1–5	5–10	10–20	20–40	>40 ppm
Yerkovetskoe	133	8.3	48.1	25.6	2.2	9.1	6.7
Raichikhinskoe	40	15.0	35.0	22.5	10.0	15.0	2.5
Sergeevskoe	60	78.3	20	1.7	* n/f	n/f	n/f

* Abbreviation: n/f—not found.

The intervals with high gold grades at the Yerkovetskoe deposit can be seen established in the coal roof (1.01–2.96 and 0.81–2.31 ppm), the coal floor (1.43–3.87 ppm), and in the central part of the coal seam (0.84 and 0.81–1.94 ppm), which were separated by interlayers with low concentrations (0.2–0.4 ppm) (Figure 5). The coals of the Raichikhinskoe coal deposit had grades below the Erkovetsky deposits with distinct intervals and increased gold concentrations in the central part of the seam (0.78–1.24 and 1.48 ppm). The gold (0.78–1.24 and 1.48 ppm) and silver (0.10–0.35 ppm) concentrations were low in the rest of the reservoir. In the Arkharo–Boguchanskoe field, high-grade intervals occurred in the coal roof (4.88 ppm) of the Dvoinoy coal horizon and in the coal floor (1.88–2.94 ppm) of the Nizhny coal horizon.

The intervals with increased contents of REEs + Y + Sc (from 2 to 10 times the average content for the deposit) in the coals of the Yerkovetskoye Deposit are confined to the top of the seams and, in some cases, to the overlying sands and clays. In the Raichikhinskoe Deposit, an increase in the content of REE (from 15% to 40%), in relation to the average for the deposit, was noted in the top of the seams and in the soil (Figure 5). The next ones were also distinguished by the increased concentrations of REEs, which were also found in the tuffs in the top of the layers of the listed deposits.

Within the Sergeevskoe coal deposit, the upper coal was characterized by elevated gold grades in individual intervals of the coal roof (1.22–5.58 ppm), the central part (1.29–0.88 ppm), and the coal floor (1.11 ppm). The ground coal was enriched in gold (0.91, 1.87 ppm) in the coal floor. The samples of the Sianchik Deposit showed higher gold contents in the coal roof (2.27–4.68 ppm) and the coal floor (1.64–2.64 ppm); Figure 6 shows REE with Y and Sc groups mainly in the upper half of the coal deposit, accounting for 30% to 40% of the section.

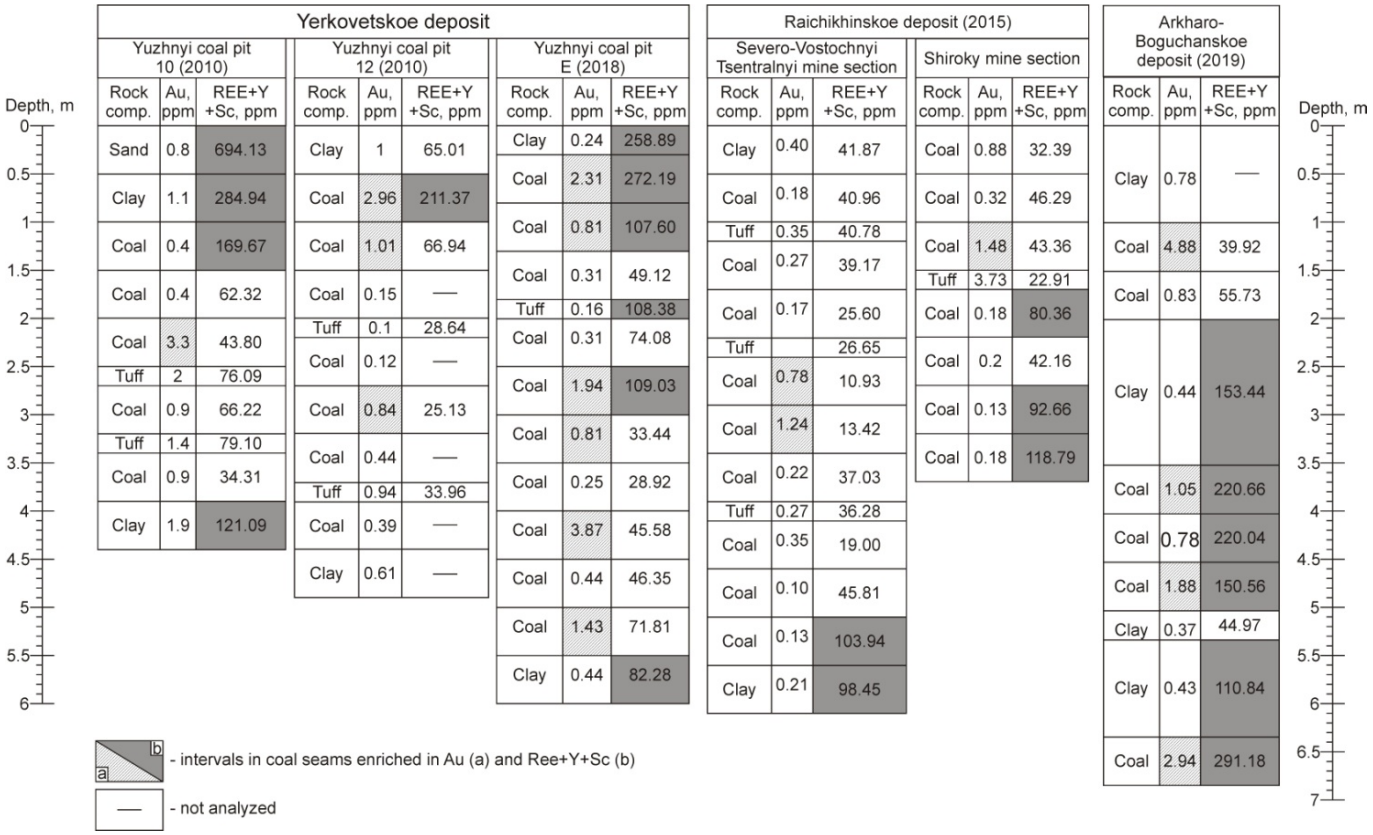


Figure 5. Distribution of Au and REE + Y + Sc in the Paleocene coals of the Yerkovetskoye, Raichikhinskoye, and Arkharo–Boguchanskoye coal deposits.

By analyzing the distribution of gold in coals we found that the Paleocene coals of the Yerkovetskoe and Arkharo–Boguchanskoe deposits, as against the Raichikhinskoe Deposit, exhibited generally higher concentrations of gold within pay intervals. Intervals with high gold concentrations in the Lower–Middle Miocene coals account for 31–40% of the total coal content. The intervals appear to form discrete interlayers and lenses.

Native gold is found in the combustion products of the Erkovetskiy brown coal deposit including, slag (0.50 ppm), fly ash (0.22 ppm), and sludge (0.26 ppm) (Figure 7).

Globular, aggregated, and spongy varieties were distinguished by analyzing the gold morphology. The globular was represented by rounded (balled) (Figure 7a,b,e,i) or lamellar (Figure 7j) forms, indicating its possible arrival from the Turan placers. This gold was of high fineness, with Ag, Fe, As, S, and Pb impurities. The aggregate (lumpy) composite types (Figure 7d,f–h) were unique, representing alloys with silver and inclusions of Fe, Sn, Cu, Pb, and Hg. They were probably formed as a result of carrier minerals "sintering" with organic material or aluminosilicates. Spongy gold (Figure 7c) with voids and caverns could be seen filled with organic substances. We propose that [25] they reflected the results of dissolved gold compounds penetrating into coals, infilling the cracks and pores at the initial stage of catagenesis. Gold remains in a dendritic form when the organics are burned. The high fineness of gold in slime should be noted, attributed to the burnout of low-temperature mineral inclusions.

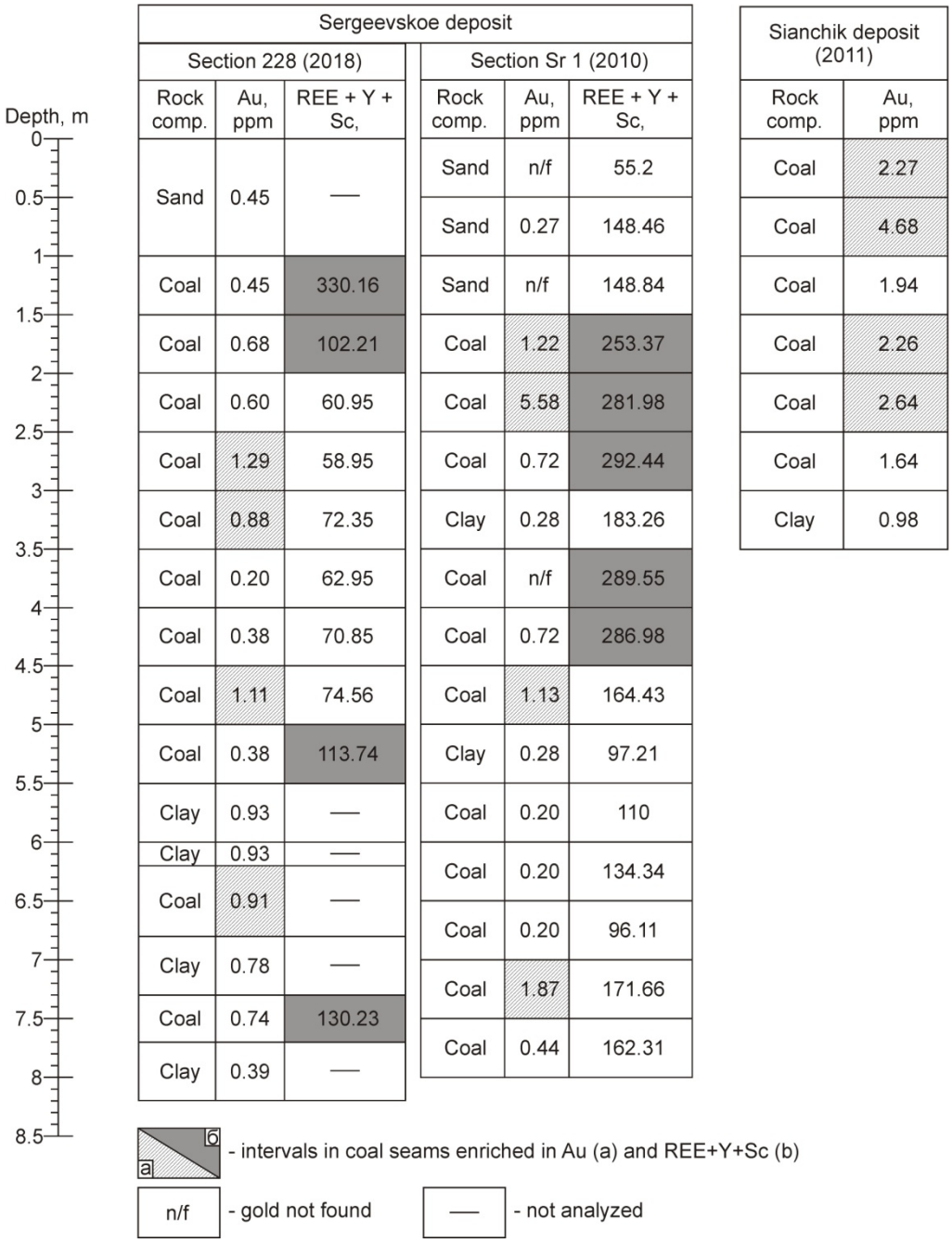


Figure 6. Distribution of Au & REE + Y + Sc in the Lower–Middle Miocene coals of the Sergeevskoe and Sianchik deposits.

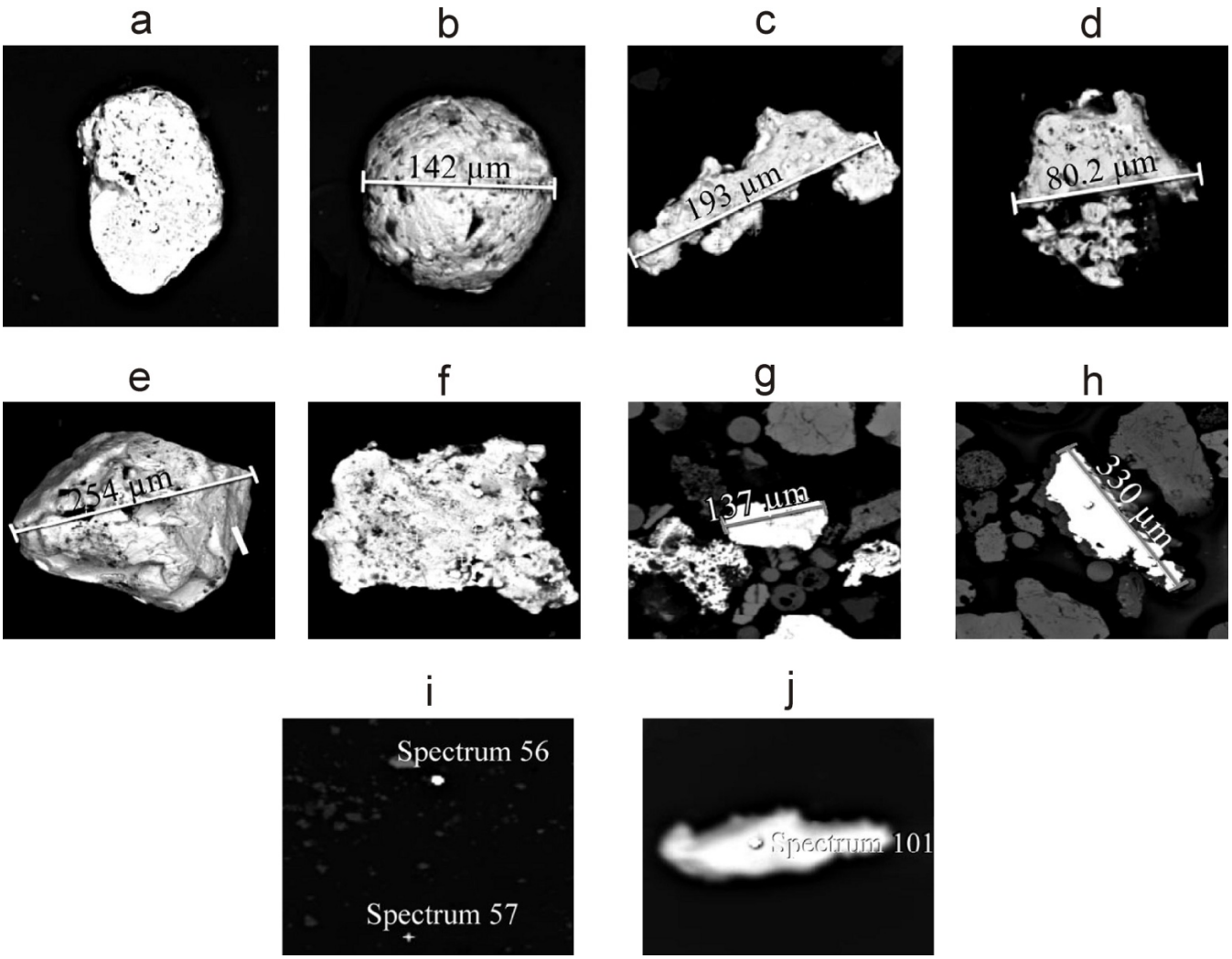


Figure 7. Native gold particles with mineral inclusions extracted from (**a**–**d**) slags, (**e**–**h**) fly ash, and (**i**–**j**) slime.

4. Discussion

Based on the analysis of the gold grade distribution in sections of coal sequences, we suggest two probable mechanisms for their accumulation. The first mechanism characterizes the evolution of the successive accumulation of metals with grades less than 1 ppm, under a stable hydrological regime. The second mechanism is associated with significant changes in environmental conditions (catastrophic floods, as well as processes with volcanic and hydrothermal activity), which caused the concentrations of gold in coals to increase manyfold. These changes were reflected in the composition and structure of the coal beds.

Up to four cycles corresponding to different conditions of coal formation with fluctuations from 1.0 to 1.5 m were identified in the coals of the Raichikhinsky and Erkovetsky deposits, associated with an increase in the haze of coals in the upward direction of the seams, a decrease in inertinite, and an increase in huminite [22]. In addition, the final stages of these cycles reflected the transition to more humid conditions and an increase in nutrient supply. Mineral-rich horizons were observed in the central part of the Yerkovetskoe coal section, which, to a certain extent, corresponded to the position of elevated gold concentrations in the coal seams (Figure 6).

The ratio of organic carbon (C) to total nitrogen (N) is another indicator of variability in the swamp development regime. The C/N ratio for the Yerkovetskoe and Arkharo–Boguchanskoe coals was in the range of 53–64 and 66–71, respectively. According to [31], values in the range of 20–100 suggest terrestrial organic matter constituting the main supply

for the accumulation of peats, whereas those below 20 suggest input of organic matter from the sea.

We believe that the deposition of intervals with coal-bearing seams of high gold concentrations is associated with the periodic supply of large terrestrial woody vegetation with soil, tree roots, and ore micro-components found in the combustion products of coals from the Erkovetsky and Arkharo–Boguchansky deposits. These events would have taken place during the flooding of the bogs, triggering a drastic rise in water levels of the Amur, Zeya, and Selemdzha paleorivers with huge drainage areas. Another contributing factor was the warm, humid climate in Danian age during the Early–Middle Miocene [20,32]. Such phenomena substantiate the research by [33], who reported data on the periodicity of large-scale Holocene and Late Pleistocene (1.04–19.24 thousand years) floods in the northern hemisphere. Similar events have been established in other regions during the deposition of Miocene coal [34].

The influence of paleovolcanic activity, manifested within the Malyi Khingan, can be considered as another example of the accumulation of elevated concentrations of micro-components in peats under extreme conditions [35]. It is associated with inputs of ash to the Zeya–Bureya Basin, which occurs in the form of tuff in the Paleogene coal seams. This pyroclastic material of subalkaline basaltoid composition was 2–4 cm thick and contained gold (Figure 5). Moreover, elevated concentrations of Zr (two- to threefold) in the coals of the Raichikhinskoe Deposit and high contents of REE + Y + Sc in the Yerkovetskoe coals were confined to tuffs.

5. Conclusions

1. The formation of metalliferous Paleogene–Neogene coal deposits took place under conditions of ascending movements of the Malokhingan and Turan (Bureya) massifs and low-amplitude movements within the Zeya–Bureya sedimentary basin.
2. Complicated nature of tectonic movements caused different types of conjugations between Zeya–Bureya Basin and drainage areas. Contrast-type (sharp-type) conjugations were located along the outer frame of the Zeya–Bureya Basin, while gentle-type conjugations were located along the Gonzhinsky, Shimanovsky, and other inner mountain ranges with levelled surfaces. Accordingly, these different types of conjugations were characterized by their own features of the release and transportation of metals from the primary sources.
3. Within the Gonzhinsky and Shimanovsky inner mountain ranges, the release of gold occurred from the chemical-weathered rocks. Then the gold, as dispersed particles, dissolved complexes of organic and inorganic compounds and colloids, and was transported by small rivers along gentle denudational plains, combined with the lacustrine and bog areas.
4. Along the Turan (Bureya) Massif, contrastingly (sharply) conjugated with the Zeya–Bureya sedimentary basin, the areas of lacustrine–bog accumulation were located at a long distance from the metal source provinces. The surface of this massif was practically not subjected to chemical weathering. The release of gold from the primary sources and its subsequent transportation was carried out by tributaries of the Zeya and Amur paleorivers, draining the Turan (Bureya) Massif.
5. Globular, aggregated, and spongy form types of gold were discovered in the brown coal of the Yerkovetskoe Deposit. The globular-type of gold was represented by rounded (bolled) or table particles, indicating its possible supply from the placers. Mostly, it was high-fineness gold with low impurities of Ag, Fe, As, S, and Pb. The aggregated-type of gold was represented by composite particles (alloys with silver), with impurities of Fe, Sn, Cu, Pb, and Hg. The spongy-type of gold was represented by particles with voids and cavities filled with organic matter, which indicated the penetration of dissolved gold compounds into the coals.
6. A model of the formation of metalliferous coal deposits in the Zeya–Bureya Basin is proposed. This model includes a complicated system of the release of gold, its

transportation, and its accumulation from the primary sources. These processes within the Zeya–Bureya Basin took place under the different conditions of the conjugations between this basin and drainage areas. The gold periodically entered the accumulation areas during catastrophic floods after being released from the primary sources. In this regard, the coal stratum in the Zeya–Bureya Basin contained layers enriched with gold and rare earth elements.

7. The authors are planning further research of the interaction between solutions and the organic environment, and the transformation of gold under early diagenesis condition.

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References

1. Varshal, G.M.; Velyukhanova, T.K.; Koshcheeva, I.Y.; Baranova, N.N.; Kozerenko, S.V.; Galuzinskaya, A.K.; Safronova, N.S.; Bannykh, L.N. Concentration of noble metals by carbonaceous substance of rocks. *Geochem* **1994**, *6*, 814–824. (In Russian)
2. Dai, S.; Ren, D.; Zhang, J.; Hou, X. Concentrations and origins of platinum group elements in Late Paleozoic coals of China. *Int. J. Coal Geol.* **2003**, *55*, 59–70. [CrossRef]
3. Dai, S.; Ren, D. Effects of magmatic intrusion on mineralogy and geochemistry of coals from the Fengfeng-Handan Coalfield, Hebei, China. *Energy Fuels* **2007**, *21*, 1663–1673. [CrossRef]
4. Seredin, V.V. Distribution and formation conditions of noble metal mineralization in coal-bearing basins. *Geol. Ore Depos.* **2007**, *49*, 1–30. [CrossRef]
5. Ketris, M.P.; Yudovich, Y.E. Estimations of Clarkes for Carbonaceous biolithes: World averages for trace element contents in black shales and coals. *Int. J. Coal Geol.* **2009**, *78*, 135–148. [CrossRef]
6. Keskin, S. Geochemistry of Çamardı formation sediments, Central Anatolia (Turkey): Implication of source area weathering, provenance, and tectonic setting. *Geosci. J.* **2011**, *15*, 185–195. [CrossRef]
7. Sun, Y.Z.; Zhao, C.L.; Zhang, J.Y.; Yang, J.J.; Zhang, Y.Z.; Yuan, Y.; Xu, J.; Duan, D.J. Concentrations of valuable elements of the coals from the Pingshuo Mining District, Ningwu Coalfield, northern China. *Energy Explor. Exploit.* **2013**, *31*, 727–744. [CrossRef]
8. Bai, Y.; Liu, Z.; Sun, P.; Liu, R.; Hu, X.; Zhao, H.; Xu, Y. Rare earth and major element geochemistry of Eocene fine-grained sediments in oil shale- and coal-bearing layers of the Meihe Basin, Northeast China. *J. Asian Earth Sci.* **2015**, *97*, 89–101. [CrossRef]
9. Vyalov, V.I.; Bogomolov, A.K.; Shishov, E.P.; Chernyshev, A.A. Coal deposits of the Far East Russia and resource potential of precious metals contained in them. *Georesources Spec. Issue* **2017**, *P2*, 256–262. [CrossRef]
10. Dai, S.; Bechtel, A.; Eble, C.F.; Flores, R.M.; French, D.; Graham, I.T.; Hood, M.M.; Hower, J.C.; Korasidis, V.A.; Moore, T.A.; et al. Recognition of peat depositional environments in coal: A review. *Int. J. Coal Geol.* **2020**, *219*, 103383. [CrossRef]
11. Liu, L.; Nechaev, V.P.; Dai, S.; Song, H.; Nechaeva, E.V.; Jiang, Y.; Graham, I.T.; French, D.; Yang, P.; Hower, G.C. Evidence for multiple sources for inorganic components in the Tucheng coal deposit, western Guizhou, China and the lack of critical-elements. *Int. J. Coal Geol.* **2020**, *223*, 103468. [CrossRef]
12. Holbrook, W.S.; Marcon, V.; Bacon, A.R.; Brantley, S.L.; Carr, B.J.; Flinchum, B.A.; Richter, D.D.; Riebe, C.S. Links between physical and chemical weathering inferred from a 65-m-deep borehole through Earth's critical zone. *Sci. Rep. UK.* **2019**, *9*, 4495. [CrossRef] [PubMed]
13. Zhmodik, S.M.; Kalinin, Y.A.; Roslyakov, N.A.; Mironov, A.G.; Mikhlin, Y.L.; Belyanin, D.K.; Nemirovskaya, N.A.; Spiridonov, A.M.; Nesterenko, G.V.; Airiyants, E.V.; et al. Nanoparticles of noble metals in the supergene zone. *Geol. Ore Depos.* **2012**, *54*, 141–154. [CrossRef]
14. Dai, S.; Finkelman, R.B. Coal as a promising source of critical elements: Progress and future prospects. *Int. J. Coal Geol.* **2018**, *186*, 155–164. [CrossRef]
15. 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]

16. 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]
17. Sorokin, A.P.; Konyushok, A.A.; Kuz'minykh, V.M.; Artyomenko, T.V.; Popov, A.A. Distribution of Cenozoic metalliferous coal deposition the Zeya-Bureya sedimentary basin (Eastern Siberia): Tectonic reconstruction and paleogeographical analysis. *Geotectonics* **2019**, *53*, 193–204. [CrossRef]
18. Sorokin, A.P.; Chanturiya, V.A.; Ageev, O.A.; Dugin, S.V. Morphological characteristics of noble metals in the combustion products of coals from the Arkhara-Boguchan Deposit (Amur River Region). *Solid Fuel Chem.* **2020**, *54*, 196–207. [CrossRef]
19. Sorokin, A.P.; Malyshev, Y.F.; Kaplun, V.B.; Sorokina, A.T.; Artemenko, T.V. Evolution and deep structure of the Zeya-Bureya and Songliao sedimentary basins (East Asia). *Russ. J. Pac. Geol.* **2013**, *7*, 77–91. [CrossRef]
20. Sorokin, A.P. *Young Platforms of Eastern Edge of Eurasia (Deep Structure, Conditions of Formation and Metallogeny)*; Dal'nauka: Vladivostok, Russia, 2013; p. 366. (In Russian)
21. Volkova, Y.R.; Schadrina, N.I.; Petruk, N.N. *Map of Mineral Resources 1:1 000000 Scale*; Eastern Series. Sheet M-52 (Blagoveshchensk); Far Map Factory VSEGEI: Saint Petersburg, Russia, 2012. (In Russian)
22. Crosdale, P.J.; Sorokin, A.P.; Woolfe, K.J.; Macdonald, D.I.M. Inertinite-rich Tertiary coals from the Zeya-Bureya Basin, Far Eastern Russia. *Int. J. Coal Geol.* **2002**, *51*, 215–235. [CrossRef]
23. Sorokin, A.P.; Belousov, V.I.; Kuz'minykh, V.M.; Artyomenko, T.V. Distribution of fine gold in the Paleogene-Neogene placers of the Upper Amur region. *GIAB* **2007**, *S16*, 123–130. (In Russian)
24. Sorokin, A.P.; Savchenko, I.F.; Noskova, L.P.; Kuz'minykh, V.M.; Konyushok, A.A.; Rimkevich, V.S.; Krapiventseva, V.V. Multi-purpose use of caustobioliths of carbonic series based on innovative coal chemistry technologies in the Far East of Russia. *J. Min. Sci.* **2018**, *54*, 147–157. [CrossRef]
25. Sorokin, A.P.; Konyushok, A.A.; Ageev, O.A.; Kuz'minykh, V.M. Mineralogical and geochemical features of native gold in combustion products of coal from the Erkovetsky deposit (Upper Amur Region). *J. Min. Sci.* **2019**, *55*, 643–651. [CrossRef]
26. Sorokin, A.P.; Konyushok, A.A.; Ageev, O.A.; Zarubina, N.V.; Ivanov, V.V.; Wang, J. Distribution of rare earth and selected trace elements in combustion products of Yerkovetskoe brown coal deposit (Amur Region, Russia). *Energy Explor. Exploit.* **2019**, *37*, 1721–1736. [CrossRef]
27. Kuz'minykh, V.M.; Chursina, L.A.; Sorokin, A.P. Technique for Gold Extraction from Gold-Bearing Raw Material. Patent N 2249053. 08.10.2003, MPK7 S 22 V 11/00, 3/12, 3/24. Bulletin N 9, 2005. (In Russian).
28. Orlova, N.I.; Vlasov, N.G.; Golitsyn, Y.A.; Kazantsev, A.E.; Ozhogin, D.O.; Sporykhina, L.V. Weathering crust and associated oxidation zones of gold deposits in the Amur Region. *Prospect Prot. Miner. Resour.* **2013**, *11*, 45–52. (In Russian)
29. Zakharov, A.P. The main features of Tygda-Ulunga ore node gold-bearing. *Prospect Prot. Miner. Resour.* **2013**, *11*, 11–16, (In Russian with English abstract).
30. Melnikov, A.V.; Melnikov, N.V.; Popov, A.B. Gold content of the weathering crusts of the Gonzhinsky gold-bearing region. In *Geology, Mineralogy, and Geochemistry of Precious Metal Deposits in the East of Russia. New Technologies for Processing Noble Raw Materials*, 2nd ed.; Moiseenko, V.G., Sorokin, A.P., Eds.; Institute of Geology and Nature Management, Amur Scientific Center, Far Eastern Branch of RAS: Blagoveshchensk, Russia, 2005; pp. 169–174. (In Russian)
31. Sajnović, A.; Stojanović, K.; Pevneva, G.S.; Golovko, A.K.; Jovančičević, B. Origin, organic geochemistry, and estimation of the generation potential of Neogene lacustrine sediments from the Valjevo-Mionica Basin, Serbia. *Geochem. Int.* **2010**, *48*, 678–694. [CrossRef]
32. Leusova, N.Y. Phytolites in brown coals of the Sergeevskoe deposit. In: Eurasia in the Cenozoic. *Stratigr. Paleoecol. Cult.* **2019**, *8*, 92–97, (In Russian with English Abstract).
33. Levi, K.G. Floods, hydrospheric disasters and related phenomena of the Northern Hemisphere. In *Radiocarbon Chronology of Natural and Social Phenomena in the Northern Hemisphere*, 2nd ed.; Levi, K., Zadonina, N., Yazev, S., Eds.; IrGU: Irkutsk, Russia, 2010; Volume 1. (In Russian)
34. Oskay, R.G.; Christanis, K.; Inaner, H.; Salman, M.; Taka, M. Palaeoenvironmental reconstruction of the eastern part of the Karapınar-Ayrancı coal deposit (Central Turkey). *Int. J. Coal Geol.* **2016**, *163*, 100–111. [CrossRef]
35. Rasskazov, S.V.; Chuvashova, I.S.; Yasnygina, T.A.; Fefelov, N.N.; Saranina, E.V. *The Cenozoic Potassic and Potassic Sodic Volcanic Series of Asia*; Academic Publishing House "GEO": Novosibirsk, Russia, 2012; p. 310. (In Russian)