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GEOCHEMISTRY

Noble Metals in Triassic Carbonaceous Cherts of the Sikhote-Alin*

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The sedimentary carbonaceous rocks gi ve rise to a special interest of geologists as a source of h ydrocarbons of the most oil and g as deposits and accumulator of some rare and noble metals. A researcher's attention is mainly attracted to Proterozoic and P aleozoic metamorphozed terrigenous formations that include noble metals in commercial significant amounts and concen trations [1–4]. At the Sikhote-Alin region gold and platinum group elements (PGE) were found in Early Cretaceous carbonaceous metasomatites and mang anoan rocks occurring in the Triassic metamorphosed cherts [5, 6]. Recognition of the role of or ganic matter and causes of metal accumulation in these units are rather difficult for deciphering. In this relation generall unmetamorphosed Triassic carbonaceous silicites of the Sikhote-Alin could arouse interest in the light of our recent findings of the noble metals mineralization. Carbonaceous silicites in the Early Mesozoic sequence s of the Sikhote-Alin were firstly disc vered at the 1970th beginning [7]. Until this time they have being regarded by geologists as ordinary black siltstone or even coal.

Table 1. Average content of chemical elements in carbonaceous cherts, (Co to Ag in ppm) (Au, Pt, and Pd in ppb)

Element	Gornaya River	Ogorodnaya River		Dalnegorsk town		Shirokaya Pad Creek		Koreiskaya River	SK
	CPh (6)	Ph (24)	CPh (40)	Ph (12)	CPh (9)	Ph (5)	CPh (3)	CPh (7)	
Co	8	3	1	18	5.2	13	n.d.	**50**	11
Ni	37	21	24	43	37	47	11	**150**	63
V	379	166	351	248	**409**	267	273	**492**	250
Cu	103	63	94	**153**	70	81	45	**184**	100
Zn	113	28	41	143	88	194	52	**491**	160
Pb	21	11	23	34	**41**	**158**	31	16	17
As	n.d.	18	17	52	47	31	n.d.	12	30
Sb	″	2	1.7	4.5	4.1	16.5	″	2.4	8.8
Ag	0.4	1.0	1.1	1.2	0.6	2.0	0.2	**3.6**	1.0
Au*	22	**67**	**45**	n.d.	28	23	27	**45**	8.5
Pt*	2	**26**	1.3	″	1	1.2	2.4	4	
Pd*	5	1.5	<1	»	12	4.4	7.5	23	

Note: Ph, phtanite; CPh, clayey phtanite; SK, the clark of element in carbonaceous cherty type of rock [4]. Figures in brackets are a number of samples analysed. n.d., not determined. Bold numbers are anomalous concentrations of elements. *, results of fire assay analyses with atomic-absorption finish [9]

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Table 2. Concentration of Au, Pt, and Pd in carbonaceous cherts of the Ogorodnaya River section

Sample	Concentration in the rock, ppb			Metal amount in DOM contained in 1 metric ton of rock, ppb			Metal proportion in DOM from total amount in the rock, wt %		
	Au	Pt	Pd	Au	Pt	Pd	Au	Pt	Pd
Og-2	17.6	11.1	5.1	13.2	7.8	2.5	75.0	70.3	49.0
Og-13	10.9	16.7	5.9	8.0	13.4	1.8	73.4	80.2	30.5
Og-18	52.6	5.2	4.9	47.0	3.1	2.2	89.4	59.6	44.9
Og-24	12.4	12.1	3.4	9.2	6.3	0.4	74.2	52.1	11.8
Og-28	15.6	12.8	4.7	8.9	7.7	s.l.	57.1	60.2	–
Og-32	11.7	13.3	6.8	7.4	9.8	0.2	63.2	73.7	3.0
Og-42	76.6	164.3	11.9	62.0	75.9	5.50	80.9	46.2	46.2
Og-43	23.5	14.3	11.3	6.7	9.4	5.2	28.5	65.7	46.0
Og-43a	33.0	185.6	4.7	22.0	40.0	3.30	66.7	21.6	51.6
Og-44	15.6	90.5	6.4	4.0	43.9	3.00	25.7	48.5	46.9
Og-45	27.6	39.3	1.6	17.0	22.1	1.60	61.6	56.2	100
Og-50	44.0	65.1	3.2	33.0	50.9	2.80	75.0	78.2	87.5
Og-51	38.2	168.2	3.1	23.0	144.6	1.50	60.0	86.0	48.4
Og-51a	11.6	8.4	6.6	5.9	4.9	0.2	50.9	58.3	3.0
Og-52	25.0	191.0	4.9	10.0	175.2	4.90	40.0	91.7	100
Og-52a	14.4	8.5	6.5	8.9	5.4	0.8	61.8	63.5	12.3
Og-53	13.8	65.9	4.9	2.0	32.1	4.90	14.5	48.7	100
Og-54	49.8	87.5	4.5	33.0	64.3	3.10	66.3	73.5	68.9
Og-55	198.8	38.5	9.9	170.0	22.7	5.90	85.5	59.0	59.6
Og-56	75.4	35.3	2.6	64.0	22.5	2.60	84.9	63.7	100
Og-57	30.6	47.1	290	17.0	36.1	95.4	55.6	76.7	32.9
Og-58	61.6	73.5	9.7	47.0	43.7	4.10	76.3	59.5	42.3
Og-59	12.0	149.4	5.2	–	84.8	1.80	0	56.8	34.6
Og-60	49.8	38.9	49.9	38.0	26.9	49.9	76.3	69.2	100
Og-61	36.0	389.6	19.3	25.0	348.6	11.9	69.5	89.5	61.7
Og-61a	10.5	9.1	7.1	9.0	5.7	1.5	85.7	62.6	21.1
Og-62	34.0	81.7	8.9	15.0	52.3	4.90	44.1	64.0	55.1
Og-63	41.4	22.3	3.4	26.0	10.5	2.40	62.8	47.1	70.6
Og-64	37.3	375.7	17.3	21.4	69.5	15.1	57.4	18.5	87.3
Og-65	91.4	59.9	4.2	69.0	36.3	2.80	75.5	60.6	66.7
Mean	39.1	82.7	17.6	27.4	49.2	8.1	70.1	59.5	45.9

Note: AAS using the extraction of metals in alkylaniline. Analysts: Zh.A. Shcheka and V.F. Zanina (FEGI).

At the Sikhote-Alin folded belt beds of carbonaceous silicites were concentrated near the base of the Triassic siliceous formation, in the Late Olenekian—Middle Anisian unit of rocks (4–20 m) named "the Phtanitic member" [8]. The member comprises light-gray or greenish-gray low-carbonaceous chert and clayey chert alternating with black phtanite or clayey phtanite (15–30%, rarely up to 50% of member volume). Phtanite and clayey ptanite are mostly radiolarian and sponge-spicule—radiolarian sediments transformed to cherts enriched in dispersed organic matter (DOM). The C_{org} content varies from 0.3 to 8.5 wt %. An average C_{org} in phtanite is 1.06% and in clayey phtanite as high as 2.26%. The estimated DOM value in the Middle Anisian clayey phtanite reaches 12 wt % [8]. C_{carb} concentration is extremely low (0–0.05 wt %). Total sulfure content varies from 0.004 to 0.7 wt % with a mean of 0.14 wt %. Sulfide sulfur dominates (~83% over sulfate one. A porosity of phtanites and clayey phtanites of some beds reaches 7–10%. A majority of pores and fractures (80–90%) are filled in organic mat-

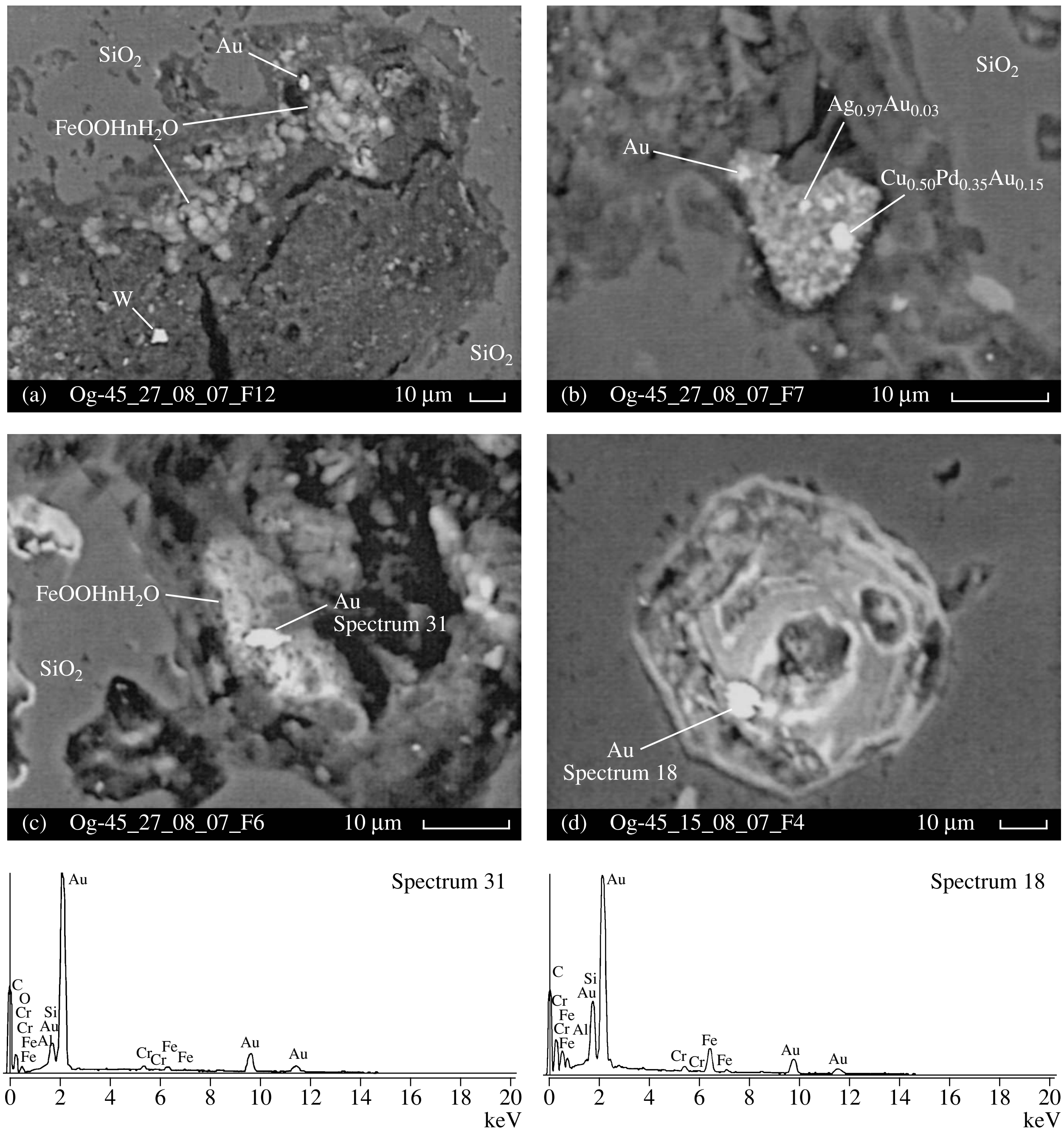

Fig. 1. Gold in carbonaceous cherts of Ogorodnaya River section. (a) Native gold and tungsten in the pore filled in carbonaceous clayey-quartzose mass and in globular hydrogoethite; (b) gold, goldish silver and goldish-palladium copper particles included in a lump of ferrous hydroxides (20 × 15 μm) in the fissure filled in carbonaceous-siliceous matter; (c) gold in ydrogoethite covering walls of the pore filled in carbonaceous-siliceous matter; (d) a particle of gold in diagenetic yrite replaced with jarosite and ferric hydroxides.

ter, quartz, illite, and ferric minerals (goethite and hydrogoethite).

The organic matter of phtanite is metamorphozed in different grade. Near Cretaceous granitic bodies, within the hornfels aureoles, it might be graphite fine scattere in the rock. But DOM of the phtanitic member rocks of the majority sections consists of X-ray amorphous k erogen and bitumen [9]. Bitumen content is 0.0*n*–0.*n* wt % in of carbonaceous silicites, and 1.2–6.3 wt % (rarely up to 27%) in DOM. Chloroform bitumen contains oils and resins of the petroleum-ether fraction and asphaltogenic acids dominated in ethanol fraction. The content of humin acids varies from 0 to 0.28 wt % [9]. According to UV- and IR-spectroscopy the humates from carbonaceous cherts are characteristic of the organic mat-

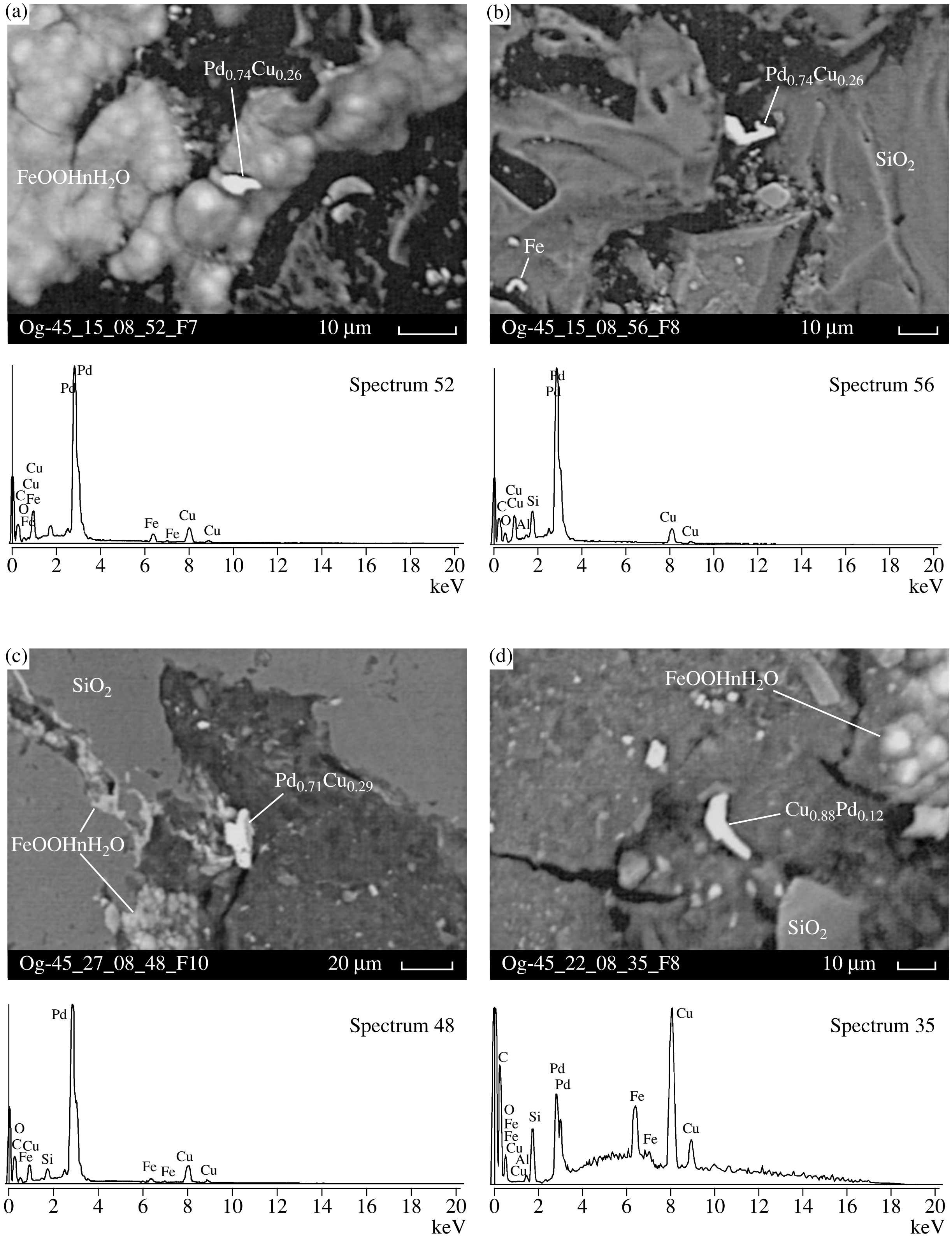

Fig. 2. Mineral forms of palladium in clayey phtanites of the Ogorodnaya R. Section. (a) Cupriferous palladium (Pd$_3$Cu) in globular hydrogoethite covering walls of pores; (b) cupriferous palladium (Pd$_3$Cu) in a carbonaceous infilling of a fracture; (c) cupriferou palladium (Pd$_7$Cu$_3$) in carbonaceous-quartzose-hydrogoethite fillings of the pore; (d) palladium copper (C $_9$Pd) in carbonaceous-clayey-quartzose infilling of the pore

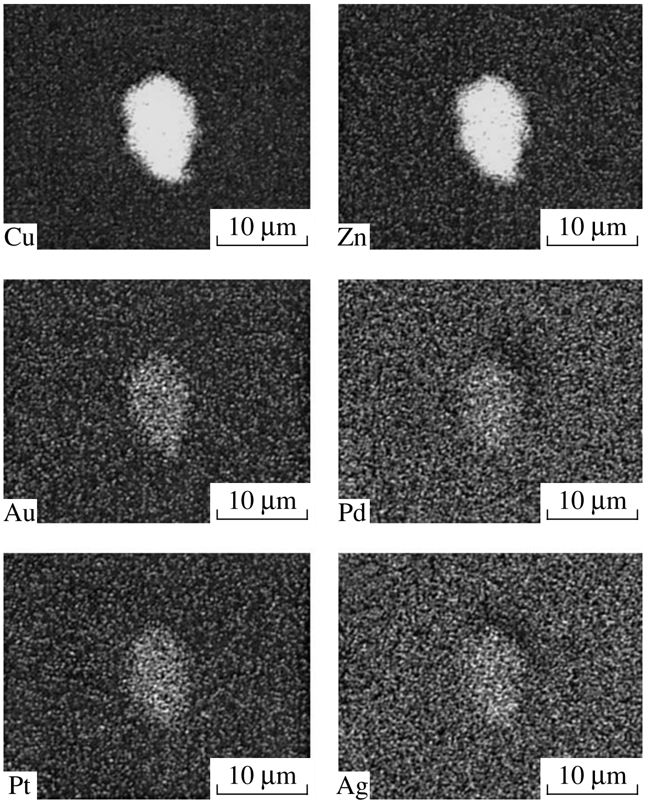

Fig. 3. A grain of intermetallic compound Cu_5Zn_3 in clayey phtanite from the Ogorodnaya R. section: Cu, Zn, Au, Pt, Pd, and Ag X-ray images.

ter of low-grade oxidation. They include quinones, methyl and methylene groups, ethers and organic sulfides (i.e. sulfonique acids, thiophenol and others). The $\delta^{13}C$ of organics of the phtanites and clayey phtanites varies within –30.2...–27.3 ‰ PDB that is identical to those of many bitumen and oils. DOM composition indicates the marine sapropelic origin of organic matter and its transformation is not more than at the middle of mesocatagenesis [9].

Average (Table 1) and modal (0.02–0.03 ppm) content of gold are essentially higher than clarke values at rocks of the same type [4]. Gold content in phtanite and clayey phtanite of Ogorodnaya River (right tributary of Ussuri R.) section is considerably higher (the mode is 0.035 ppm) than in other phtanitic member sections and reaches an anomalous concentration. Here, gold was detected in 50% of carbonaceous and in 60% of low carbonaceous beds of the member (ICP-MS). The average content of Au in phtanite is 4–5 times, and in clayey phtanite 8 times higher than those in "siliceous lithotype of black shale" (Table 1). This represents a strong anomaly by the opinion of Ya.E. Yudovitch and M.P. Ketris [4]. The carbonaceous cherts from this section are enriched in noble metals: Au up 7.5 ppm (fir assay analyses) or 18 ppm (ICP-MS); Pt and Pd reaches 3.3 and 8.3 ppm, respectively (ICP-MS). Low-carbonaceous silicites from the same section are also enriched in Au (up 0.68 ppm). According to AAS using alkylaniline extraction technique, as much as about 70% of Au, 60% of Pt, and 46% of Pd in carbonaceous cherts are related to DOM (Table 2). In the DOM of carbonaceous cherts, bitumen (mainly asphaltene and asphaltogenic acids) are the main concentrators of iron and trace elements: Cu, Ni, Zn, Pb, Co, and W as well as the gold (up 40 ppm) [9].

Native Au, Ag, and Pd were found with microprobe JXA-8100 in polished sections of carbonaceous cherts. Size of the grains and their aggregates of gold and palladium reaches 20–26 µm. Noble metals (Au, Ag) and other native elements (Cu, Pb, Ni, W, Se), and intermetallic compounds like Pd_3Cu, Pd_7Cu, CuAu, Cu_3Zn_2, Cu_5Zn_3, $(Cu,Ni)_5Zn_4$, Ni_4Cd, Fe_nNi were determined into pores and fissures filled in slilica-carbonaceous matter and hydroxides of Fe (hydrogoethite) (Figs. 1, 2). Gold was also recognized in crystals of diagenetic pyrite replaced by jarosite and iron hydroxides (Fig. 1) as well as in intermetallides Cu_5Zn_3 (Fig. 3). According to microprobe analysis, the native brass contains 1.34% of Au and 1.77% of Pt. It is remarkable that the majority of native elements, intermetallides and sulfides like galena, sphalerite, chalcopyrite, argentite, arsenopyrite and others have being also enriching bitumen fractions in DOM [9].

Thus, a major part of gold and PGE in the Triassic carbonaceous cherts is associated with dispersed organic matter of the rock. DOM of these rocks, having likely noble metals in metallo-organic, atomic or colloidal states, could be a source for microscopic grains of native gold and PGE. It could also be a source of gold and PGE determined in authigenic sulfides and intermetallides. Anomalous Au content in some low-carbonaceous silicites of the "phtanitic member" is likely the result of its input with bitumen fraction from adjacent carbonaceous layers. Second source of gold is authigenic pyrite that includes noble metals in colloidal or cluster forms. A hypergene disintegration of pyrite, its replacing with iron hydroxide or sulfate minerals (jarosite) has promoted a formation of bigger particles of native gold. The Au in rocks of some sections of the "phtanitic member" reaches anomalous values close to industrial concentrations in placers. After tectonic reworking and metamorphism, similar formations may be a source of gold for lode deposits and placers.

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