

Minerals in the Triassic Carbonaceous Silicites of Sikhote Alin

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Abstract—Over 60 minerals, including native elements, intermetallic compounds, haloids, sulfides, sulfates, arsenides, oxides and hydroxides, silicates, borosilicates, wolframates, phosphates and REE phosphates, were established in Triassic siliceous rocks of Sikhote Alin. Allothigenic and authigenic minerals in the carbonaceous silicites were formed over a long period through several stages. Judging from morphology, chemical composition, and structural position, K-feldspar (K-Fsp), illite, kaolinite, metahalloysite, monazite, xenotime, zircon, rutile, or its polymorphs are the disintegration products of sialic rocks of continental crust. Authigenic sulfides are dominated by diagenetic pyrite (fine-crystalline, microglobular, framboidal, as well as those developed after biogenic siliceous and carbonate fragments), which has been formed prior to precipitation of siliceous cement and lithification of siliceous rocks. Most of other sulfides (sphalerite, galena, chalcocopyrite, pyrrhotite, argentite, pentlandite, antimonite, ulmanite, and bravoite), arsenides and sulfoarsenides (arsenopyrite, nickeline, skutterudite, cobaltite, glaucodot, and gersdorffite), wolframates (scheelite and wolframite), intermetallides (Cu_2Zn , Cu_3Zn_2 , Cu_3Zn , Cu_4Zn , CuSn , Cu_4Sn , Cu_8Sn , $\text{Cu}_4\text{Zn}_2\text{Ni}$, $\text{Ni}_2\text{Cu}_2\text{Zn}$, Ni_4Cd), and native elements (Au, Pd, Ag, Cu, Fe, W, Ni, Se) were crystallized later (during catagenesis after the lithification and brecciation of siliceous beds) from metals involved in the easily mobile fractions of bitumens. Supergene mineral formation was mainly expressed in the sulfide oxidation and replacement of diagenetic pyrite by jarosite and iron hydroxides.

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INTRODUCTION

Sedimentary rocks with the elevated content of organic carbon (Corg) could serve as source of hydrocarbons for oil and gas fields and as accumulators of trace and noble metals of practical significance. The elevated contents of metals in carbonaceous sequences are thought to be related to their sorption by organic matter (OM) during sedimentogenesis or diagenesis (resource function of black shales) or later accumulation on geochemical barriers formed by OM along filtration pathways of metalliferous solutions (barrier function of black shales) (Kovalev and Michurin, 2005; Laverov et al., 2000; Nemerov et al., 2005; Yudovich and Ketris, 1988, 1994; Yudovich, 2009).

Triassic carbonaceous silicites (phtanites and clayey phtanites) in Sikhote Alin were described for the first time in the Bol'shaya Ussurka River basin (Dal'nyaya River mouth) (Volokhin, 1980; Mikhailov and Volokhin, 1980). Later stratigraphic studies (Volokhin et al., 1989, 1990, 2003; Filippov et al., 2001) revealed their wide regional distribution among sediments of the Triassic formation (Fig. 1). The carbonaceous silicites are characterized by extremely high concentrations of some trace and noble metals (Volokhin, 1985, 1988, 2013; Volokhin and Ivanov,

2007). The speciation of chemical elements in sedimentary rocks, composition of mineral-carriers, and their structural position bear genetic information, which helps in deciphering geochemical correlations, as well as factors, stages, and conditions of metal accumulations. The main components of carbonaceous silicites (quartz and chalcedony of skeletal remains of radiolarian and sponge spicules, as well as siliceous cement) are devoid of ore elements, thus diluting their concentrations. Virtually, the geochemical specifics of carbonaceous silicites are determined by the mineral admixture represented mainly by the clastic fine-silt fraction, clay minerals, authigenic sulfides, and organic matter. This paper is aimed at studying the finely dispersed minerals in the Triassic carbonaceous silicites of Sikhote Alin.

METHODS

Rocks were classified using the microscopic and chemical study (Volokhin, 2013). The clayey admixture in silicites was studied by the X-ray diffraction and electron microscopy (Volokhin, 1980, 1985, 2013). The composition of dispersed organic matter (DOM) in the Triassic silicites was analyzed by the bitumino-

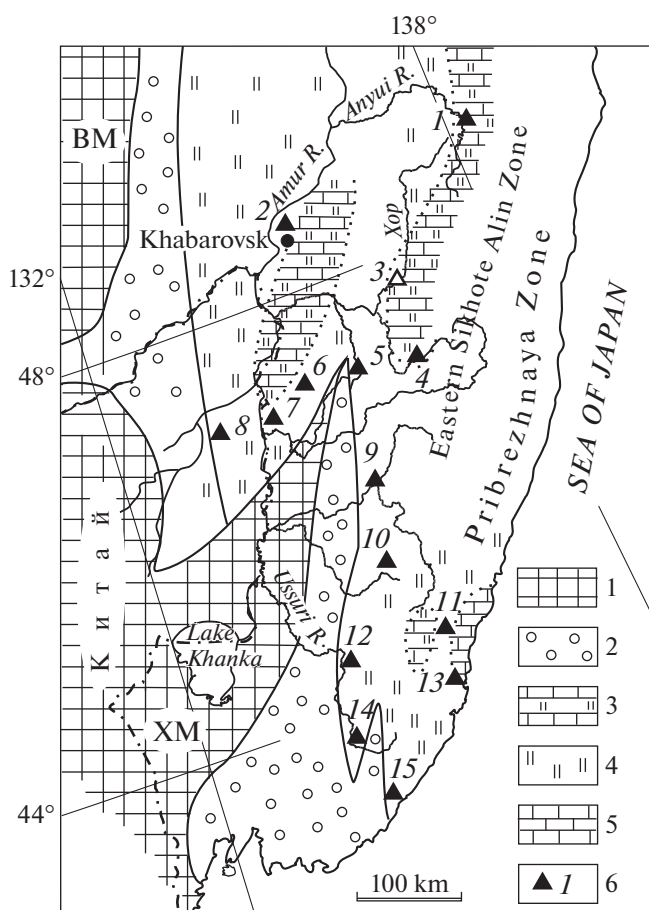


Fig. 1. Schematic distribution of the Triassic facies in Sikhote Alin.

(1) Areas of erosion and development of the kaolin weathering crusts after crystalline massifs: (BM) Bureya and (KhM) Khanka massifs; (2) Triassic terrigenous shelf sediments in foredeeps; (3–5) facies of Triassic siliceous formation: (3) carbonate-siliceous, (4) siliceous, (5) reef limestone; (6) “phtanite member”: (1) Anyui River, (2) Khabarovsk, (3) Khor River (4) Katen River, (5) Matai River, (6) Bol’shaya Ulitka River, (7) Bikin, (8) Si Chang Settlement (China), (9) Dal’nyaya River, (10) Gornaya River, (11) Dal’negorsk, (12) Ogorodnaya River, (13) Shirokaya Pad Creek, (14) Nizhnyaya Breevka Settlement, (15) Koreiskaya River.

logical method using technique (Korchagin and Chetverikova, 1976], UV and IR spectroscopy, as well as by atomic absorption and spectral analyses of chemical elements in DOM fractions extracted by the bituminological method (Volokhin et al., 2005; Volokhin and Ivanov, 2007). The finely dispersed minerals in carbonaceous silicites were determined by the microprobe analysis of mineral phases in polished sections (more than 2000 EDS spectra of 35 polished sections). Minerals in the polished sections were analyzed at the Analytical Center of the Far East Geological Institute (Far East Branch, Russian Academy of Sciences) on a JXA8100 microprobe equipped with three wave (JEOL, Japan) and EDS INCAx-sight (OXFORD

Instruments, England) spectrometers. Samples were sputtered with carbon. Chemical elements (Si, Al, and others) entrapped from the quartz-silicate matrix during the analysis of relatively small grains were omitted during calculation of the chemical formula of analyzed mineral.

GEOLOGICAL POSITION AND BRIEF CHARACTERISTICS OF THE TRIASSIC CARBONACEOUS SILICITES

In the reconstructed section of the Triassic siliceous formation of Sikhote Alin, silicites with the elevated content of organic matter (phtanites and clayey phtanites) form “phtanite member” (4–20 m thick) near the base of the formation (Volokhin et al., 2003). This unit rests on the greenish gray clayey cherts and siliceous mudstones and underlies platy cherts. It is characterized by almost equal proportions of silicites and clayey silicites. The lower and upper boundaries of the phtanite member are diachronous. The age of the member varies from the late Olenekian–Middle Anisian in the Dal’negorsk and Khabarovsk sections (*Neospathodus homeri*–*N. kockeli* conodont zones) to the Middle–Late Anisian (*N. kockeli* zone and the lowermost portions of the *Paragondolella excelsa* zone) in most other sequences (Burii, 1989; Volokhin et al., 1989, 1990, 2003).

The member is made up of alternating light gray and greenish gray low-carbon and black carbonaceous cherts and clayey cherts. The beds of carbonaceous silicites account for from 15 to 30%, locally reaching up to 50 vol %.

The carbonaceous silicites are mainly radiolarian and spicule-radiolarian cherts with variable content of authigenic silica of microfossils and quartz cement of the rock, clayey and finely clastic silt-sized admixture, authigenic sulfides (mainly pyrite), and DOM. The C_{org} content in the rocks varies from 0.3 to 8.5%, averaging 1.06–1.09% in phtanites, and 2.26–2.29% in clayey phtanites (Volokhin, 1985, 2013). Its maximum contents in rocks of the phtanite member from different sequences are as follows: 5.57% in Voronezh-2 hole (the margin of Khabarovsk, near the summer camp), 6.35% on the right bank of the Ussuri River near the Ogorodnaya River mouth, 6.04% in the Dal’nyaya River mouth, 7.4% in the Bol’nichnyi Spring (Dal’negorsk River), and 8.54% in the Koreiskaya River. The DOM content estimated from the C_{org} content in rocks of the member may reach 12 wt % (Volokhin and Ivanov, 2007). Rocks of the member are virtually devoid of carbonate carbon ($C_{carb} < 0.05\%$). The sulfur content in them varies from 0.004 to 0.7%, (average 0.14% in the Ogorodnaya River sequence), with the predominance of the sulfide form (~83% of total sulfur).

Main reservoir properties of Triassic rocks are related to the fracturing of brittle beds of cherts and

phtanites. These beds are intersected by a network of thin (0.1–0.5 mm, rarely up to 2 mm) fractures, which usually are not traced into the adjacent clay interbeds of siliceous mudstones. The rock porosity reaches 7–10%. Most of the pores and fractures (80–90%) are filled with fine detrital quartz, clayey and carbonaceous matter, as well as iron minerals (goethite and hydrogoethite) (Volokhin, 2013).

COMPOSITION OF DISPERSED ORGANIC MATTER IN THE CARBONACEOUS SILICITES

Organic matter of the rocks was metamorphosed to variable extent. It is represented by the finely dispersed graphite in hornfelsed zones near the Cretaceous granitic intrusions (Kazachenko and Sapin, 1990). However, in most of the studied sections of the phtanite member located beyond the zone of contact metamorphism, carbonaceous matter is represented by X-ray amorphous kerogen and bitumen (Volokhin and Ivanov, 2007). Contents of the neutral and acid bitumens, which vary from 0.0n–0.n% in the carbonaceous silicites to 1.2–6.3% (occasionally up to 27%) in the DOM, are presumably underestimated. The content of humic fraction in the rocks varies from 0% to 0.28% (Volokhin and Ivanov, 2007). The content of chloroform bitumens (CBA) in the carbonaceous silicites varies from 0.015 to 0.044%, which corresponds to the source rocks with the moderate bitumen content (Vassoevich, 1973). The CBA is dominated by petroleum–ether (oil and resin) and alcohol (asphaltogenic acids) fractions. According to UV and IR spectrometry, the weakly oxidized humic matter of the carbonaceous silicites contains quinine, methyl, ether groups and organic sulfides (sulfonic acids, thiophenols, and others). The carbon isotopic composition of the carbonaceous silicites varies within a narrow range from –30.2‰ to –27.3‰ PDB (Volokhin et al., 2005; Volokhin and Ivanov, 2007). Fractional and isotope compositions of the organic matter serve as arguments in support of the marine sapropel nature of organic matter in the carbonaceous silicites. In most Triassic sequences of Sikhote Alin, rocks of the phtanite member experienced catagenetic transformations no higher than the stage of middle mesocatagenesis (Volokhin and Ivanov, 2007).

DETRITAL AND CLAY MINERALS IN THE CARBONACEOUS SILICITES OF THE PHTANITE UNIT

Allothigenic detrital admixture. The silt-sized clastic fraction in the carbonaceous silicites is mainly represented by quartz and K–Na feldspars. The carbonaceous silicites show traces of microerosion of the non-lithified siliceous mud and accumulation of steady heavy minerals (monazite, rutile or its polymorphic modifications, and zircon) in individual interbeds (Fig. 2c). There are fragments (up to 0.5 mm, rarely

coarser) of the eroded underlying rocks: cherts, phtanites, silty mudstones, and chloritized basalts (Fig. 2d).

Potassium-feldspar (K-Fsp) frequently intergrown with chlorite and hydrogoethite (Table 1, Fig. 2) and the less common albite (Table 1, sample Og-43) were established in the clayey–siliceous interbeds among the Upper Olenekian and Middle–Upper Anisian carbonaceous silicites from sequences along the Rudnaya River (Dal’negorsk), Koreiskaya River, and the right bank of the Ussuri River (Ogorodnaya River). The content of K-Fsp grains usually increases from the siliceous central part of the beds to their clayey margins. Some coarse K-Fsp grains (sequences along the Rudnaya River) are oval. They were likely initially rounded, but corroded during catagenesis at the contact with the quartz cement (Fig. 2a). In terms of the chemical composition, K-Fsp differs in the low content of Na (0.3–0.6 at %) and almost complete absence of Ca (Table 1). Such composition may be inherited from the source (for instance, granite pegmatites) or caused by the removal of Ca during weathering, diagenesis, or catagenesis. Grains of the moderate- and high-Ca plagioclases were not found. The source of detrital components was likely represented by the felsic and alkaline magmatic and metamorphic rocks of the sialic basement of the adjacent land. The contribution of the previously accumulated sediments and basaltic edifices in the basin was lower.

Composition of the clay fraction. The clay fraction of the carbonaceous silicites of the phtanite member is dominated by illite. Other minerals are chlorite, kaolinite, and metahalloysite, and, locally, insignificant admixture of smectite (Table 2). The content of illite in the clayey phtanite fraction (<1 µm) of the phtanite member sometimes reaches 100%. Illite also is the main clay mineral in the light gray opoka-type clayey cherts alternating with phtanites and clayey phtanites. Illite is mainly dominated by 2M₁ polytype dioctahedral mica ($b = 9.02–9.04$ Å), with the subordinate 1M illite. The maximum values of parameter b (9.04–9.05 Å) were found in illites from the clayey cherts underlying the phtanite member. The chemical and component compositions of illites indicate predominance of the muscovite component (Table 3). The maximum content of chlorite in the clay fraction was established in rocks of the phtanite member in the section along the Rudnaya River (Dal’negorsk district) (Volokhin et al., 2003). Chlorite occurs as tabular ingrowths in K-Fsp grains representing the replacement products of biotite (Fig. 2a), develops after volcanic glasses in the pyroclastic or volcanoclastic rocks (Fig. 2d), or fills fractures and pores in the rocks. In terms of composition, chlorites are more magnesian and less ferruginous ($MgO/FeO = 0.43–0.46$) in the Olenekian portion of the siliceous sequence along the Rudnaya River and have higher Fe composition ($MgO/FeO = 0.21–0.27$) in its Norian–Raethian part (Tuchkova et al., 2004). The composition and mor-

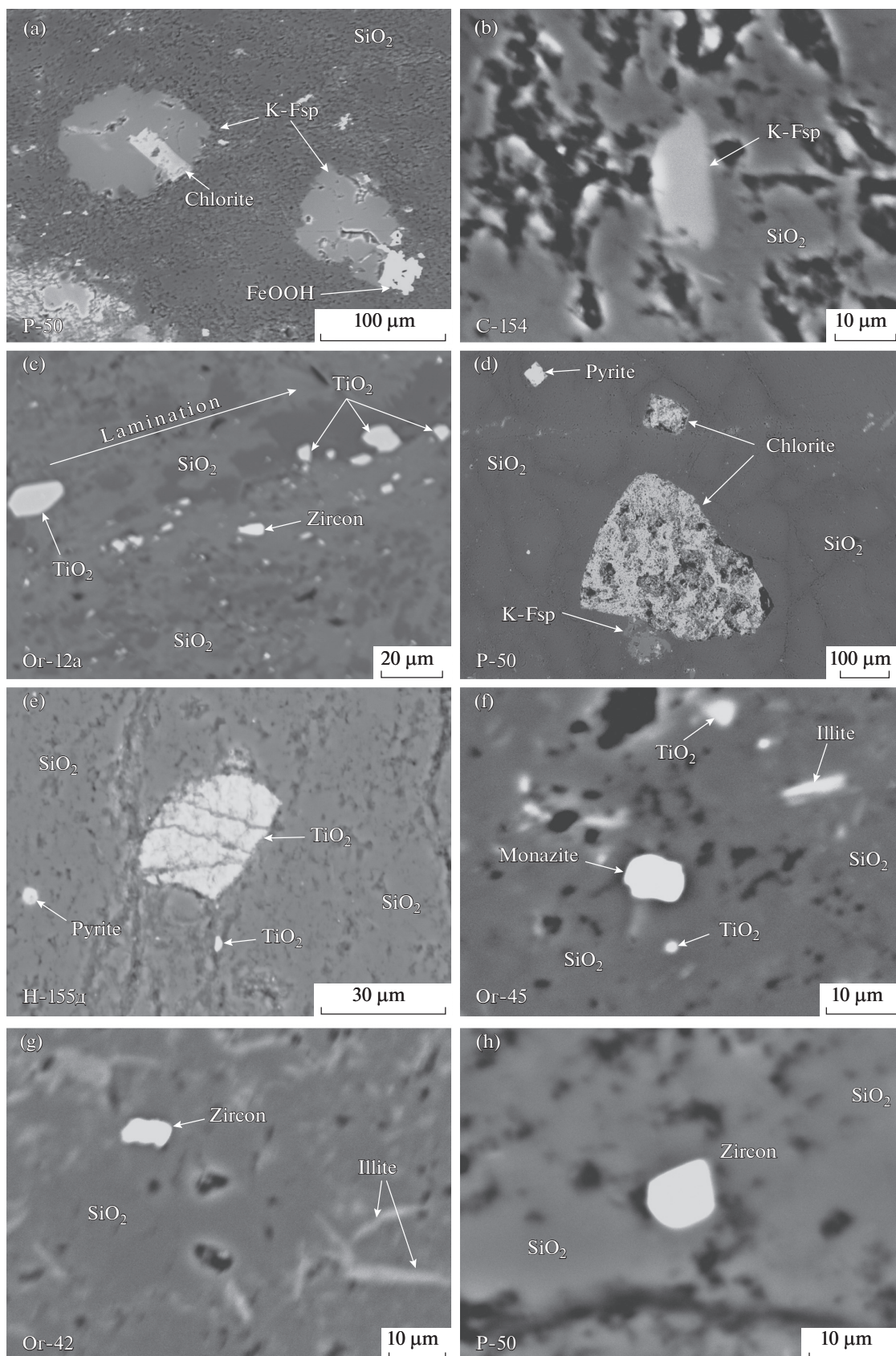


Fig. 2. Detrital and clay minerals in the Lower–Middle Triassic rocks of Sikhote Alin.

(a, b) K-feldspar in the quartz cement of phtanite (polished section R-50, Rudnaya River, T_{1ol_2} – T_{2an_1}) and clayey phtanites (polished section S-154, Koreiskaya River, T_{2an_3}); (c) rutile (brookite?) and zircon (polished section Og-12a, Ussuri River, Ogorodnaya River mouth, T_{2an_2}); (d) fragments of chloritized basalts in phtanite (polished section R-50, Rudnaya River); (e, f) rutile and monazite in the quartz cement of phtanites (polished sections N-155d and Og-45, Ogorodnaya River, T_{2an_2}); (g, h) zircon in the quartz cement of clayey phtanites (polished section Og-42, Ogorodnaya River, T_{2an_2}) and radiolarian phtanites (polished sections R-50, Rudnaya River, T_{1ol_2} – T_{2an_1}).

Table 1. Chemical composition of feldspars from Triassic carbonaceous cherts of Sikhote Alin

Sample	%	O	Na	Mg	Al	Si	K	Ca	Ti	Fe	Cu	Ba	Total
Og-42	wt	44.01	—	—	9.77	30.85	14.38	—	—	—	—	—	99.0
13_8_25	at	60.07	—	—	7.91	23.99	8.03	—	—	—	—	—	
Og-43	wt	45.28	6.61	0.35	9.8	30.59	1.53	0.51	0.59	0.63	—	—	96.29
8_8_39	at	60.61	6.16	0.31	7.78	23.32	1.06	0.27	0.26	0.24	—	—	
R-50	wt	45.9	0.42	—	9.93	30.09	13.18	—	—	—	—	—	99.52
3_7_4	at	61.52	0.40	—	7.89	22.97	7.22	—	—	—	—	—	
R-50	wt	46.93	0.46	—	10.02	31.04	13.43	—	—	—	—	—	101.87
3_7_7	at	61.45	0.42	—	7.78	23.15	7.19	—	—	—	—	—	
R-50	wt	45.38	—	—	9.98	30.94	13.99	—	—	0.31	0.54	—	100.44
3_7_15	at	60.93	—	—	7.94	23.13	7.69	—	—	0.12	0.18	—	
R-50	wt	43.73	0.32	—	9.77	29.98	13.17	—	—	—	—	—	96.97
3_7_20	at	60.56	0.31	—	8.02	23.65	7.46	—	—	—	—	—	
R-50	wt	44.59	0.4	—	9.8	29.93	13.18	—	—	—	—	—	97.91
3_7_25	at	60.98	0.38	—	7.95	23.32	7.38	—	—	—	—	—	
R-50	wt	43.23	0.37	—	9.44	29.87	12.81	—	—	—	—	1.02	96.75
4_7_13	at	60.49	0.36	—	7.84	23.81	7.33	—	—	—	—	0.17	
R-50	wt	45.18	0.49	—	9.98	30.00	13.02	—	—	—	—	—	98.68
4_7_38	at	61.17	0.46	—	8.02	23.14	7.21	—	—	—	—	—	
R-50	wt	44.27	—	—	9.64	30.02	14.2	—	—	—	—	—	98.13
11_7_3	at	60.73	—	—	7.84	23.46	7.97	—	—	—	—	—	
R-50	wt	44.50	0.29	—	9.66	29.55	13.27	—	—	—	—	—	97.27
11_7_12	at	61.22	0.28	—	7.88	23.16	7.47	—	—	—	—	—	
R-50	wt	45.56	0.49	—	9.51	28.92	11.96	—	—	—	—	—	96.43
17_7_12	at	62.49	0.47	—	7.73	22.6	6.71	—	—	—	—	—	
R-50	wt	44.97	0.48	—	9.62	29.63	12.98	—	—	—	—	—	97.68
18_7_14	at	61.43	0.46	—	7.79	23.06	7.26	—	—	—	—	—	
R-50	wt	44.99	0.40	—	9.62	29.63	12.7	—	—	—	—	—	97.35
18_7_26	at	61.59	0.38	—	7.81	23.11	7.11	—	—	—	—	—	
R-50	wt	43.18	0.55	—	9.77	28.65	11.94	—	—	—	—	1.76	95.86
18_7_29	at	61.02	0.54	—	8.19	23.06	6.90	—	—	—	—	0.29	
R-50	wt	43.68	0.40	—	9.57	29.34	13.11	0.09	—	—	—	—	96.19
18_7_39	at	60.88	0.39	—	7.91	23.29	7.47	0.05	—	—	—	—	

Polished sections Og-42 and Og-43 are taken from the right bank of the Ussuri River near the Ogorodnaya River mouth (Middle Anisian), (R-50) Rudnaya River, near the southeastern margin of Dal'negorsk (Upper Olenekian–Middle Anisian). (—) Below the detection limit.

Table 2. Composition of clay fraction in rocks of the “phtanite member” of the Triassic siliceous formation

Sample	Rock	Fraction	Sm	Chl–Sm	Chl	I	K + Mh
Amur River, above Voronezh-2 Settlement (T_{1ol_2} – T_{2an_2}), fraction $<1\ \mu\text{m}$							
Kh-28	CC	$<1\ \mu\text{m}$	—	—	10	90	—
Kh -29	CPh	$<1\ \mu\text{m}$	—	—	—	100	—
Kh -30	CC	$<1\ \mu\text{m}$	—	—	8	92	—
Ussuri River, near the Ogorodnaya River mouth (T_{2an_2}), fraction $<1\ \mu\text{m}$							
N-152	CC	$<1\ \mu\text{m}$	—	—	—	100	—
N-153	CPh	$<1\ \mu\text{m}$	—	—	—	100	—
N-154	CC	$<1\ \mu\text{m}$	—	—	—	100	—
N-155	Ph	$<1\ \mu\text{m}$	—	—	—	100	—
Ussuri River, near the Ogorodnaya River mouth (T_{2an_2}), fraction $<2\ \mu\text{m}$							
N-620	CC	$<2\ \mu\text{m}$	—	—	—	92	8
N-621a	CC	$<2\ \mu\text{m}$	—	1	—	94	5
N-621b	KM	$<2\ \mu\text{m}$	—	3	—	91	6
N-622	Ph	$<2\ \mu\text{m}$	—	Tr	—	100	—
Og-15	CPh	$<2\ \mu\text{m}$	—	—	—	96	4
Rudnaya River, Dal’negorsk district (T_{1ol_2} – T_{2an_2}), fraction $<2\ \mu\text{m}$							
R-171	CC	$<2\ \mu\text{m}$	—	—	15	85	—
R-101	Ch	$<2\ \mu\text{m}$	—	—	32	68	—
R-104	CPh	$<2\ \mu\text{m}$	—	—	11	89	—
R-237	Ch	$<2\ \mu\text{m}$	—	—	19	89	—
R-238	Ph	$<2\ \mu\text{m}$	3	—	—	97	—
R-176	Ch	$<2\ \mu\text{m}$	—	—	22	78	—
Kholodnyi Creek, tributary of the Koreiskaya River (T_{2an_3})							
S-154	CPh	$<2\ \mu\text{m}$	Tr	—	16	84	—

(Ch) chert, (CC) clayey chert, (Ph) phtanite, (CPh) clayey phtanite, (SM) siliceous mudstone. (Sm) smectite, (Chl–Sm) chlorite–smectite, (Chl) chlorite, (I) illite, (K) kaolinite, (MH) metahalloysite. Quantitative proportions of clay minerals were calculated using method (Kutsykovich and D’yakonov, 1971) in fraction $<1\ \mu\text{m}$ and using method (Biscaye, 1965) in fraction $<2\ \mu\text{m}$. (Tr) trace amounts of mineral. (—) Below the detection limit.

phology of clay particles indicate mainly terrigenous detrital origin of illite, kaolinite, halloysite, and, partially chlorite, which presumably were delivered to the sedimentation basin during erosion of the continental weathering crusts (Volokhin, 1980, 1985). Some chlorites could be derived from the Upper Permian volcanic edifices in the region. It could partially be formed in the course of alteration of the basic volcanic glasses during diagenesis and catagenesis.

ACCESSORY MINERALS IN THE CARBONACEOUS SILICITES OF THE PHTANITE MEMBER

Electron-microscopic and microprobe studies revealed more than 60 minerals, including native elements, intermetallic compounds, haloids, sulfides, sulfates, arsenides, oxides, hydroxides, silicates, borosilicates, wolframates, phosphates, and REE phosphates (Volokhin, 2013).

Sulfides are mainly represented by the monocrystalline, globular, and framboidal pyrite (Table 4; Figs. 3a, 3b). Pyrite frequently replaces organic remains (Table 4; Figs. 3g–3i). In addition to the common pyrite devoid of admixture of other elements, some pyrite grains in the carbonaceous silicites contain Mn, Cu, Zn, and As (Volokhin, 2013). Sulfides also occur as sphalerite, galena, chalcopyrite, pyrrhotite, and, more rarely, argentite (Figs. 3e, 3f, 4). There are also bornite, covellite, pentlandite, antimonite, ulmanite, bravoite, and sulfides with Se admixture (Volokhin, 2013). Arsenides and sulfoarsenides are represented by arsenopyrite, skutterudite, cobaltite, glaucodot, and gersdorffite, as well as single grains of clausthalite (Table 4).

Native metals are represented by Au, Pd, Ag, Cu, Fe, W, Ni, and Se (Fig. 5). Intermetallides are mainly represented by Cu–Zn and less common Cu–Sn compounds (Cu_2Zn , Cu_3Zn_2 , Cu_3Zn , Cu_4Zn , CuSn , Cu_4Sn , Cu_8Sn). There are also Ni–Cu and Zn–Cd

Table 3. Chemical composition of illites from the Middle Triassic carbonaceous clay cherts on the basis of microprobe analysis

Sample	Spectrum	%	O	Na	Mg	Al	Si	K	Ti	Fe	Σ	Chemical formula and end member composition of illites
Og-45	Sp. 25	wt	45.42	0.31	0.80	15.72	23.82	7.59	—	0.86	94.51	$(K_{0.82}Na_{0.06})(Mg_{0.14}Fe_{0.07})_{0.21}Al_{2.05}[(Al_{0.41}Si_{3.59})O_{10}](OH)_2$
		at	62.72	0.30	0.73	12.87	18.74	4.29	—	0.34		Mus. 84.0%, Par. 6.8%, Phlog. 6.1%, Annite 3.1%
Og-58	Sp. 8	wt	50.03	0.45	0.63	14.68	26.57	7.25	—	0.68	100.03	$(K_{0.72}Na_{0.08})Al_{1.80}(Mg_{0.10}Fe_{0.05})[(Al_{0.33}Si_{3.67})O_{10}](OH)_2 \cdot H_2O$
		at	65.83	0.41	0.51	10.8	18.6	3.63	—	0.24		Mus. 81.3%, Par. 9.6%, Phlog. 6.2%, Annite 2.9%
	Sp. 9	wt	48.13	0.25	1.01	13.03	26.78	6.82	—	0.70	96.72	$(K_{0.70}Na_{0.05})Al_{1.80}(Mg_{0.17}Fe_{0.05})[(Al_{0.16}Si_{3.84})O_{10}](OH)_2 \cdot H_2O$
		at	65.77	0.23	0.85	9.93	19.43	3.54	—	0.25		Mus. 81.8%, Par. 6.1%, Phlog. 9.3%, Annite 2.8%
	Sp. 3	wt	48.54	—	1.16	12.05	27.81	6.15	0.31	1.48	97.49	$K_{0.62}Al_{1.70}(Mg_{0.19}Fe_{0.10}Ti_{0.03})[(Al_{0.08}Si_{3.92})O_{10}](OH)_2 \cdot H_2O$
		at	66.18	—	0.97	9.08	19.96	3.16	0.13	0.53		Mus. 81.4%, Phlog. 11.5%, Annite 7.1%
Og-63	Sp. 7	wt	49.63	—	1.00	14.58	24.41	9.27	—	3.39	102.28	$K_{0.92}Al_{1.45}(Mg_{0.16}Fe_{0.23})[(Al_{0.64}Si_{3.36})O_{10}](OH)_2$
		at	63.95	—	0.85	11.14	17.92	4.89	—	1.25		Mus. 78.8%, Phlog. 8.7%, Annite 12.5%
	Sp. 25	wt	48.56	—	0.84	15.76	22.94	8.15	0.29	2.02	98.56	$K_{0.83}Al_{1.54}(Mg_{0.14}Fe_{0.14}Ti_{0.02})[(Al_{0.77}Si_{3.23})O_{10}](OH)_2$
		at	64.29	—	0.73	12.37	17.3	4.42	0.13	0.77		Mus. 84.6%, Phlog. 7.7%, Annite 7.7%
	Sp. 4	wt	53.24	0.51	0.56	13.04	28.14	6.34	0.19	1.95	103.97	$(K_{0.63}Na_{0.09})(Al_{1.80}Fe_{0.14}Mg_{0.09}Ti_{0.02})[(Al_{0.09}Si_{3.91})O_{10}](OH)_2 \cdot H_2O$
		at	65.78	0.44	0.46	9.55	19.8	3.20	0.08	0.69		Mus. 74.7%, Par. 12.1%, Phlog. 5.0%, Annite 8.2%
S-149	Sp. 25	wt	51.07	—	0.92	10.83	29.09	6.12	—	1.66	99.97	$K_{0.59}(Mg_{0.14}Fe_{0.11})Al_{1.40}[Al_{0.11}Si_{3.89}O_{12}] \cdot (OH)_2$
		at	65.69	—	0.78	8.26	21.31	3.22	—	0.61		Mus. 84.8%, Phlog. 8.5%, Annite 6.7%
Gl-8	Sp. 21	wt	44.33	—	0.80	12.41	27.56	7.14	0.27	2.78	95.29	$K_{0.97}(Mg_{0.18}Fe_{0.27}Ti_{0.03})_{0.48}Al_{2.3}[(Al_{0.16}Si_{3.84})O_{10}] \cdot (OH)_2 + SiO_2$
		at	61.81	—	0.74	10.26	21.89	4.04	0.13	1.11		Mus. 83.6%, Phlog. 5.9%, Annite 10.5%
Kh-1k	Sp. 17	wt	50.14	—	0.76	5.29	37.98	2.66	0.17	1.06	98.33	$K_{0.51}(Mg_{0.24}Fe_{0.12}Ti_{0.03})Al_{1.37}[(Al_{0.13}Si_{3.87})O_{10}](OH)_2 \cdot H_2O + SiO_2$
		at	66.91	—	0.63	3.88	26.66	1.33	0.07	0.37		Mus. 72.7%, Phlog. 17.4%, Annite 9.8%

Compositions of illites from clayey phanites: (Og-45, Og-58, Og-63) right bank of the Ussuri River (Ogorodnaya River mouth); (S-149) Koreiskaya River, (Gl-8) right bank of the Dal'naya River near the Glubinoe Settlement, (Kh-1k) illite-pyrite-siliceous nodule from the clayey phanites of the Voronezh Formation (Khabarovsk). Excess silica in the quartz cement. (—) Below the detection limit.

Table 4. Ore minerals in carbonaceous silicites from the sequence on the right side of the Ussuri River (Ogorodnaya River mouth)

Mineral	Total amount of grains	Structural position of grains in the rock			
		quartz matrix	carbonaceous veinlet	primary (relict) pores	secondary leaching pores
Pyrite FeS ₂	251	234	2	12	3
Monazite (Ce,La...)PO ₄	83	70	10	2	1
Rutile (brookite?, anatase?) TiO ₂	50	31	16	3	—
Zircon ZrSiO ₄	36	28	5	3	—
Goethite FeOOH	23	17	—	2	4
Apatite Ca ₅ [PO ₄] ₃ F	28	16	12	—	—
Hematite (Fe ₂ O ₃)	14	8	2	4	—
Xenotime (Y, Dy...)PO ₄	8	7	1	—	—
Magnetite	11	6	3	2	—
Ti-magnetite	3	—	3	—	—
Ni-magnetite	1	—	1	—	—
Romanechite BaMnMn ₈ O ₁₆ [OH] ₄	6	5	1	—	—
Cryptomelane K ₂ O · MnO · 15MnO ₂ · nH ₂ O	9	6	3	—	—
Ferrosilite Fe ₂ Si ₂ O ₆	2	2	—	—	—
(Fe, Cr) ₂ SiO ₄	1	1	—	—	—
Chromite? (<i>semidecomposed</i>)	2	2	—	—	—
Hydrogoethite FeOOH · nH ₂ O	56	23	17	12	4
FeOOH · nH ₂ O (with admixture of V, Cr, Co, Cu, P, Mn, S)	27	14	7	4	2
Barite BaSO ₄	44	16	10	9	9
Jarosite KFe ₃ [SO ₄] ₂ (OH) ₆	38	12	6	3	17
Sphalerite (Zn,Fe)S	18	5	4	6	3
Cassiterite SnO ₂	19	7	4	6	2
Galena PbS	50	4	26	17	3
Fe	34	1	10	19	4
Fe (with admixture of Cr, Mn, Ni)	5	—	1	4	—
Ag	25	3	11	11	—
Argentite (<i>acanthite</i> ?) Ag ₂ S	17	2	6	9	—
AgOH	3	—	3	—	—
Cu ₂ Zn, Cu ₃ Zn, Cu ₄ Zn	21	6	4	10	1
Cu ₉ Sn	1	—	—	1	—
Scheelite CaWO ₄	18	—	14	4	—
Au	15	1	5	8	1
AuPd	2	—	1	1	—
Ni	11	—	6	5	—
Ni ₄ Cd	6	—	4	2	—
Wolframite (Fe,Mn)WO ₄	10	—	3	6	1
Pd ₃ Cu	9	—	5	4	—
Sylvite KCl	9	2	—	2	5
Titanite CaTiSiO ₅	7	1	6	—	—
Chalcopyrite CuFeS ₂	5	1	2	2	—
Covellite CuS	5	—	1	4	—

Table 4. (Contd.)

Mineral	Total amount of grains	Structural position of grains in the rock			
		quartz matrix	carbonaceous veinlet	primary (relict) pores	secondary leaching pores
Cerianite CeO_2	4	2	—	1	1
Palladium copper	4	—	1	3	—
Copper	1	—	—	1	—
Ilmenite FeTiO_3	3	2	1	—	—
Ce_2O_3	3	1	—	2	—
W	3	—	2	1	—
Pyrrhotite FeS	2	—	—	—	2
Arsenopyrite FeAsS	2	—	1	1	—
Gersdorffite NiAsS	2	—	—	2	—
Skutterudite $(\text{Co}, \text{Fe})\text{As}_3$	2	—	—	2	—
Stibiconite $\text{Sb}_3\text{O}_6[\text{OH}]$	2	—	—	2	—
PbCuSnO	2	—	—	2	—
Glauco-dot $(\text{Co}, \text{Ni}, \text{Fe})\text{AsS}$	1	1	—	—	—
Cobaltite CoAsS	1	1	—	—	—
Antimonite Sb_2S_3	1	—	1	—	—
Ulmanite $(\text{Ni}, \text{Co})\text{SbS}$	1	1	—	—	—
Nickeline NiAs	1	—	1	—	—
Synchysite $\text{Ca}(\text{Ce}, \text{La} \dots)[\text{CO}_3]_2\text{F}$	1	—	1	—	—
Vivianite $\text{Fe}_2[\text{PO}_4]_2 \cdot 8\text{H}_2\text{O}$	1	1	—	—	—
PbSn	1	1	—	—	—
Bismite?, sillenite? Bi_2O_3	1	—	—	—	1
clausthalite PbSe	1	—	1	—	—
Anhydrite CaSO_4	1	—	—	1	—
Celestite SrSO_4	1	—	1	—	—
Se	1	—	1	—	—

Polished sections Og-58, Og-63, Og-44, Og-43, and Og-43-2. (—) Not established.

compounds ($\text{Cu}_4\text{Zn}_2\text{Ni}$, $\text{Ni}_2\text{Cu}_2\text{Zn}$, Ni_4Cd). Phtanites from sequences along the Ogorodnaya and Bol'shaya Ulitka rivers contain native gold, as well as palladium, auricupride, Cu-palladium, Au-copper, and Pd-copper (Volokhin and Karabtsov, 2009).

The most abundant accessory silicate is zircon (Table 5). Titanite, thuringite, chamosite, and ferrosilite are less common (Volokhin, 2013). Small tabular borosilicates chemically close to datolite and danburite were found in the clayey phtanites of the Dal'nyaya River basin (Glubinnoe Settlement area) (Table 5). Carbonates are usually represented by calcite, with the less common dolomite, ankerite, and siderite. Wolframates are scheelite and the more occasional wolframite (Fig. 4).

The most abundant sulfates are jarosite and barite. Some sequences (Ogorodnaya River) also contain celestite and anhydrite (Table 4). Haloids were found

in the carbonaceous veinlets and pores. They are represented by the euhedral crystals of sylvite (Fig. 5), halite, and K–Na chlorides. In the Koreiskaya River basin, the clayey phtanites contain iodates $(\text{Cu}, \text{Fe}, \text{Cr})_3(\text{S}, \text{I})_4$. The most widespread oxides are TiO_2 (rutile?, brookite?), hematite, and magnetite, with the subordinate ilmenite. The studied samples are enriched in goethite and hydrogoethite (FeOOH and $\text{FeOOH} \cdot n\text{H}_2\text{O}$) or their polymorphic modifications, which cover or fill primary (relict) pores in the rock and represent the oxidation and replacement products of pyrite. Other oxides are cerianite, uraninite, and bismuth oxides (bismite or sillenite?) (Bol'shaya Ulitka River).

Phosphate minerals are represented by three groups. The first group includes the ubiquitous apatite of conodonts and other organisms with the phosphate test, as well as grains of detrital and diagenetic apatite

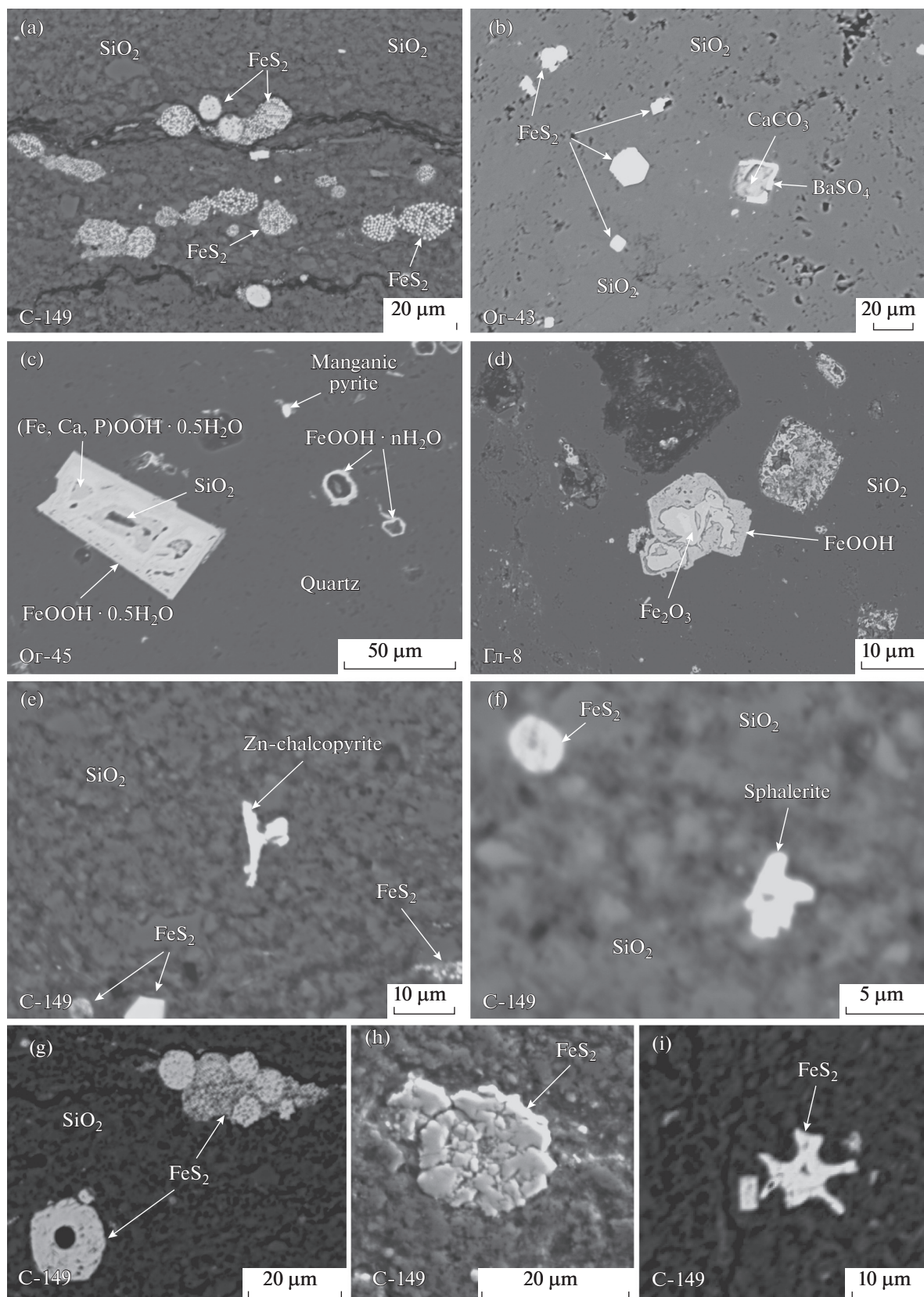


Fig. 3. Diagenetic sulfides, sulfates, and hydroxides in carbonaceous silicites.

- (a) Globular and framboidal pyrite in clayey phtanite (polished section S-149, Koreiskaya River, T_{2an3});
 (b) barite rim around diagenetic calcite;
 (c) zoned euhedral hydrogoethite with silica inclusion in the central part (polished section Og-45, Ogorodnaya River, T_{2an2});
 (d) hematite replaced by goethite in margins, embedded in the quartz cement of clayey phtanite. Secondary leaching pores of diagenetic carbonates filled with the siliceous and carbonaceous matter (polished section G1-8, Dal'naya River, T_{2an}) are shown in the left top corner;
 (e, f) diagenetic chalcopyrite and sphalerite replacing small bone fragments (e) and skeletal fragments of nanofossils (f);
 (g–i) pyrite pseudomorphs after foraminiferal shells and remains of calcareous nanofossils.

enclosed in the quartz cement. The second group includes the crystalline, possibly catagenetic carbonate–fluorapatite, which is localized in quartz or quartz–carbonaceous veinlets of the microbrecciated phtanites and phtanite–quartzites. The third group includes REE phosphates mainly represented by monazite (Fig. 2f) and occasional xenotime (Tables 4, 6). The clayey phtanites of the Koreiskaya River basin contain goyazite (Sr, Ba, Ce, Nd) Al₃[PO₄]₂ · (OH)₅ · H₂O.

MINERALS CONTAINING RARE EARTH ELEMENTS

In (Tuchkova et al., 2004), first data on the content of eight rare earth elements (REE) in eight samples of the Triassic cherts of Sikhote Alin (Rudnaya River) are presented as C1-chondrite and PAAS (post-Archean Australian shale)-normalized REE distribution patterns. According to the cited authors, the REE distribution pattern indicates derivation of the silicate fraction of silicites from the continental sial. Figure 6 demonstrates the normalized REE distribution patterns for 14 samples of phtanites, clay phtanites, clay cherts, and phtanite–quartzites of the phtanite member obtained by ICP-MS (Volokhin, 2013). As compared to clays derived from the continental platforms and Pacific pelagic sediments, the silicites are characterized by much lower (up to ten times) REE contents. This appears to be related to the dilution of REE-carrier minerals by the biogenic silica (Volokhin, 2013). As the carbonate tests of planktonic organisms, the silica virtually does not contain REE (Dubinin, 2006). Similarity of the carbonaceous silicites with the platform clays is expressed in the prominent negative Eu anomaly in the chondrite-normalized REE patterns, which is presumably related to the absence of main Eu carrier (Ca-plagioclase) in the rocks. The latter may indicate a relatively high maturity of weathering crusts in the continental provenances. Most of the Triassic carbonaceous silicites of Sikhote Alin also exhibit small negative Ce anomaly typical of the hydrogenic sediments, which inherit REE from seawater, in particular, diagenetic phosphates (*Rare Earth ...*, 1984, Dubinin, 2006). However, statistical calculations presented in Table 4 and the chemical composition of REE carriers (Table 6) suggest that the main LREE carrier in rocks of the “phtanite member” is monazite, while MREE and HREE are accumulated in xenotime representing the detrital fraction. Much lower REE

amounts are accumulated in some apatites, REE oxides (cerianite?), and rare Y–Ti-rich zircon (Volokhin, 2013). The total REE content in the high-silica phtanites is always lower than in the clayey phtanites, which is consistent with the lower content of the allochthonous terrigenous admixture.

NOBLE METALS IN THE CARBONACEOUS SILICITES

Native elements are usually localized in the pores and microfractures filled with the carbonaceous–siliceous material and iron hydroxides (Fig. 5). Microprobe studies revealed gold in the sequences of the phtanite member of the Polisaevsky Spring, the tributary of the Bol'shaya Ulitka River, and on the right bank of the Ussuri River near the Ogorodnaya River mouth (Table 7). The size of gold crystals and polycrystalline aggregates varies from 0.3 to 5 μm, locally reaching 26 and 60 μm, respectively. The largest particles of native gold, auricupride, and palladium were found in the microbrecciated carbonaceous silicites that were recrystallized under the thermal effect of the Late Jurassic–Early Cretaceous pyroxenite sill 3.5 m thick. The size of auricupride particles Cu_{0.69}Au_{0.19}Ag_{0.08}Pd_{0.03} in it reaches 100 μm.

The total Au and Pt contents in the individual grains of Cu₃Zn₃ reaches 3% (Table 8). Around 70% Au, 60% Pt and 46% Pd of their total content in phtanites and clayey phtanites from the sequence in the Ogorodnaya River mouth is related to DOM (Volokhin and Karabtsov, 2009), in which these metals could occur as atomic and cluster forms or organometallic compounds. The Au content reaches 40 ppm in the bitumen fractions from the Triassic carbonaceous cherts of Sikhote Alin and 10 ppm in the kerosene that is insoluble in the low-boiling organic liquids (Volokhin and Ivanov, 2007). Mobile bitumen fractions could serve as the carrier of some metals and possible source of gold.

NATURE OF ACCESSORY MINERALS IN THE CARBONACEOUS SILICITES

The structural position of ore minerals in the carbonaceous cherts, morphology of grains, and composition of minerals bear information on their origin. Many researchers believe that the consistence of matter (loose, solid) is one of the main features, which

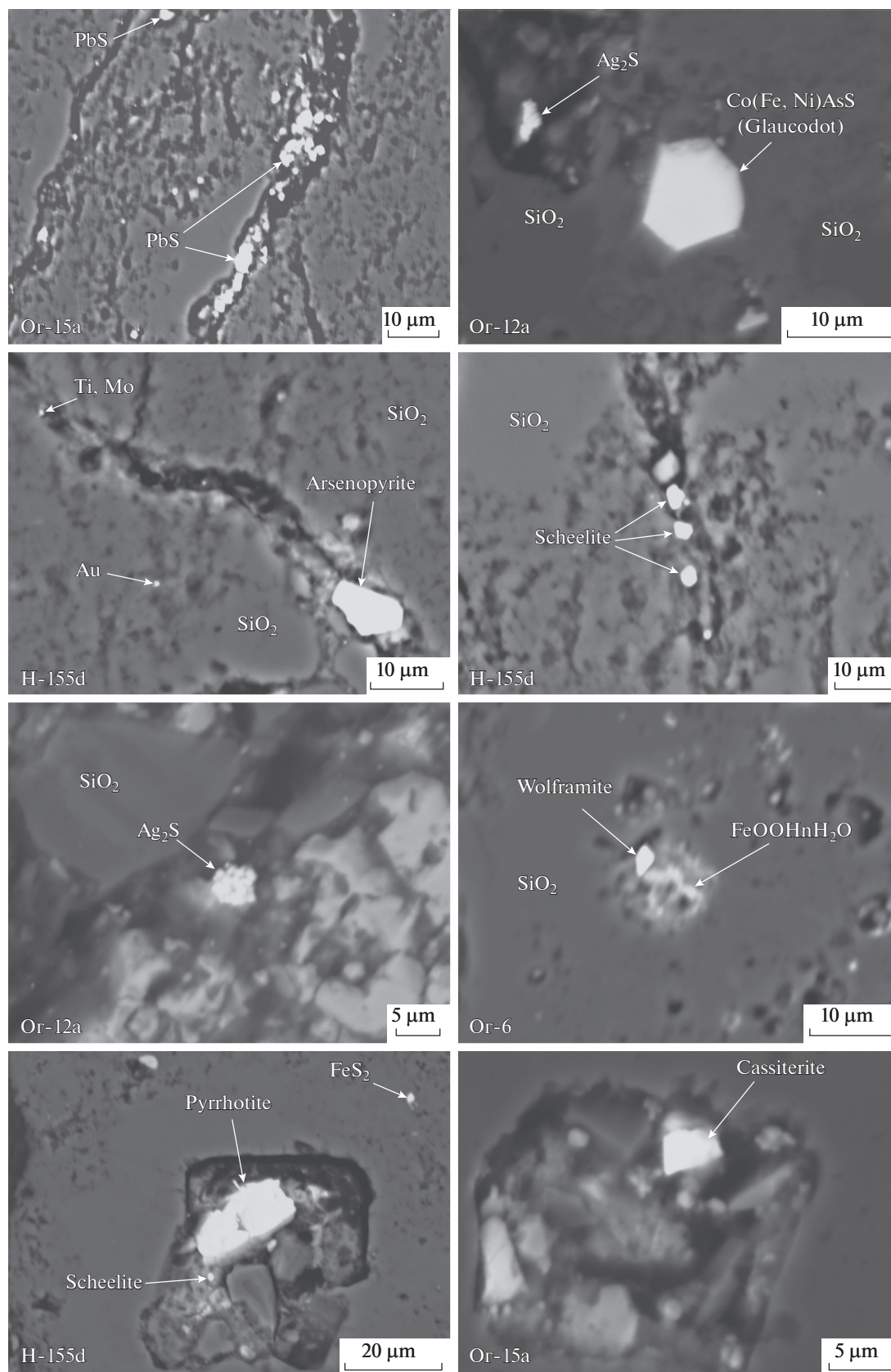


Fig. 4. Ore minerals in the fracture–pore space of the carbonaceous silicites (right bank of the Ussuri River, near the Ogorodnaya River mouth).

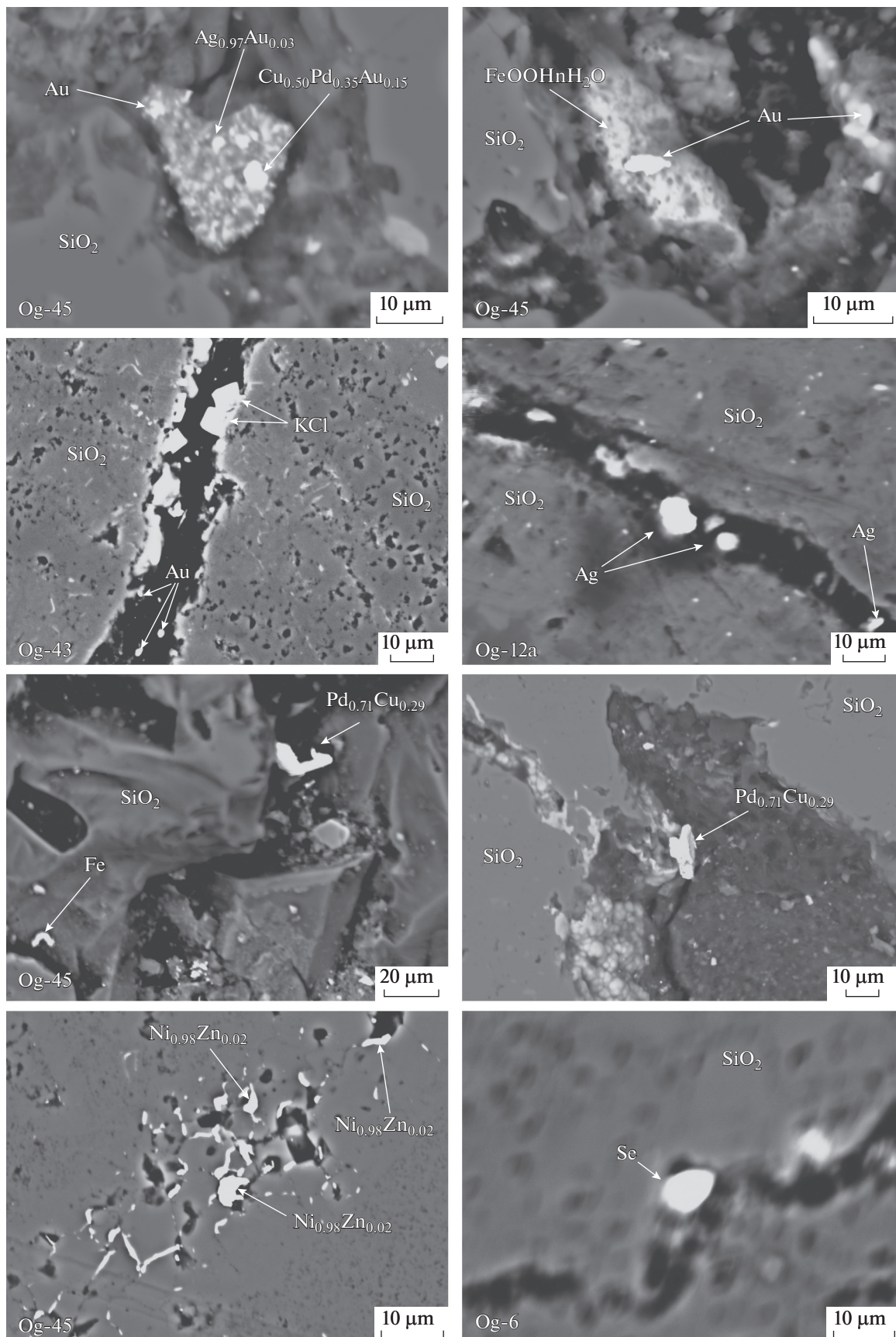


Fig. 5. Native elements and intermetallics in the carbonaceous silicites of the Ogorodnaya River sequence.

Table 5. Chemical composition of zircon and borosilicates from the carbonaceous silicites of the phtanite member

Sample no.	%	B	O	Mg	Al	Si	K	Ca	Sc	Mn	Fe	Zr	Nb	Hf	W	U	Total
N-155d	wt	—	34.05	—	—	14.93	—	—	—	—	—	49.04	1.77	—	—	—	99.78
29/17	at	—	66.17	—	—	16.52	—	—	—	—	—	16.72	0.59	—	—	—	
Og-44	wt	—	38.38	—	—	15.80	—	—	—	—	—	44.71	—	1.16	—	—	100.00
22/32	at	—	71.11	—	—	15.48	—	—	—	—	—	13.23	—	0.18	—	—	
T-50	wt	—	33.25	—	—	14.82	—	—	—	—	—	47.81	1.62	1.44	0.32	—	99.26
11/31	at	—	65.83	—	—	16.71	—	—	—	—	—	16.60	0.56	0.26	0.06	—	
S-149	wt	—	36.68	—	—	14.72	—	—	—	—	—	42.88	—	1.55	—	—	95.82
22/11	at	—	69.57	—	—	15.91	—	—	—	—	—	14.26	—	0.26	—	—	
S-153	wt	—	42.53	—	1.23	16.36	0.35	0.27	0.32	—	0.43	30.46	—	0.89	—	4.82	97.66
3/15	at	—	72.32	—	1.24	15.85	0.24	0.19	0.19	—	0.21	9.08	—	0.14	—	0.56	
S-153	wt	—	45.66	0.29	1.43	24.78	0.57	0.29	—	—	0.63	23.01	—	0.44	—	1.70	98.79
3/32	at	—	69.68	0.29	1.29	21.54	0.36	0.17	—	—	0.27	6.16	—	0.06	—	0.17	
Gл-36	wt	—	36.23	—	—	16.55	—	—	—	—	—	45.56	—	1.53	—	—	99.87
14/88	at	—	67.36	—	—	17.53	—	—	—	—	—	14.86	—	0.26	—	—	
Shch-111a	wt	—	36.61	—	—	18.46	—	—	—	—	—	44.12	—	—	—	—	99.19
6/56	at	—	66.73	—	—	19.17	—	—	—	—	—	14.11	—	—	—	—	
Gл-8	wt	8.73	45.58	—	—	16.59	—	25.31	—	0.43	0.67	—	—	—	—	—	97.31
18/11	at	16.48	58.16	—	—	12.06	—	12.89	—	0.16	0.25	—	—	—	—	—	
Gл-8	wt	11.52	47.53	0.26	—	29.26	—	14.49	—	0.39	0.56	—	—	—	—	—	104.00
18/18	at	19.49	54.34	0.19	—	19.05	—	6.61	—	0.13	0.18	—	—	—	—	—	
Gл-8	wt	6.76	48.95	0.21	—	23.02	—	20.59	—	0.53	0.77	—	—	—	—	—	100.82
18/32	at	12.37	60.59	0.17	—	16.23	—	10.17	—	0.19	0.27	—	—	—	—	—	
Gл-8	wt	6.81	47.87	0.21	—	10.12	—	30.51	—	0.47	0.94	—	—	—	—	—	96.94
18/29	at	13.18	62.63	0.18	—	7.54	—	15.93	—	0.18	0.35	—	—	—	—	—	
Gл-8	wt	8.17	48.03	0.41	—	9.30	—	30.64	—	0.85	0.98	—	—	—	—	—	98.38
18/39	at	15.41	61.22	0.35	—	6.75	—	15.59	—	0.31	0.36	—	—	—	—	—	

Samples from sections of the phtanite unit. (N-155d, Og-44) Ogorodnaya River; (R-50) Rudnaya River; (S-149, S-153) Koreiskaya River, (Gл-8, Gл-36, Shch-111a) Dal'nyaya River. (—) Below the detection limit.

determine the boundary between sediment and rock (Frolov, 1992). Biosiliceous muds are transformed into cristobalite or opal—cristobalite—tridymite rocks (porcelanites, opal cherts) at the boundary between diagenesis and initial catagenesis, while the subsequent transformation of opal—cristobalite—tridymite into chalcedony—quartz rocks occurs at the initial—deep catagenesis transition (Yapaskurt, 2005).

Minerals are involved in the siliceous (quartz) cement are mainly allochthonous or diagenetic. Other minerals localized in fractures were formed much later, already after the cementation and fracturing of beds in response to fault and fold deformations of beds and sequences. The latter may be arbitrarily regarded as catagenetic. Some of the allochthonous and diage-

netic minerals could be introduced into fractures during their formation, which partially disturbs the initial temporal mineral relations. Results of modal calculations in the nonmetamorphosed carbonaceous silicites from the sequence of the Ogorodnaya River yield somewhat lower pyrite content (Table 4). At the same time, the assessment of mineral position in the rock seems to be useful for deciphering the temporal relations of accessory minerals.

Four groups of accessory minerals are distinguished in terms of their position in the rock: (1) located in the quartz cement of rock, (2) localized in fractures filled with the carbonaceous and quartz—hydroxide—ferruginous material, (3) found in the residual (relict) pores, and (4) developed after the

Table 6. Chemical composition of REE-bearing minerals from the Middle Triassic carbonaceous silicites of Sikhote Alin

Sample no.	%	O	F	Al	Si	P	K	Ca	Fe	Ni	La	Ce	Pr	Nd	Sm	Eu	Gd	Th	W	U	Total	
Og6-13/11	wt	23.69	—	—	1.31	13.03	—	—	—	—	13.46	27.09	2.67	10.59	2.27	0.81	1.45	1.73	—	—	98.1	
	at	62.54	—	—	1.97	17.76	—	—	—	—	4.09	8.16	0.80	3.10	0.64	0.23	0.39	0.32	—	—	—	
Og43/2-21	wt	26.55	—	—	0.70	13.39	—	0.34	—	—	11.74	25.37	2.78	11.14	1.39	—	—	1.77	—	—	95.16	
	at	68.19	—	—	0.93	15.99	—	0.32	—	—	3.15	6.75	0.74	2.88	0.34	—	—	0.28	—	—	—	
Og44-31	wt	31.57	1.53	0.41	4.23	11.29	—	1.31	0.49	—	12.52	24.12	1.76	6.65	—	—	—	6.96	—	—	102.8	
	at	67.11	4.06	0.48	4.75	11.30	—	1.03	0.28	—	2.81	5.38	0.39	1.44	—	—	—	0.93	—	—	—	
N155d-30/6	wt	25.76	—	—	1.04	12.84	—	1.40	—	—	10.86	22.37	—	9.10	1.29	—	1.06	8.90	—	1.21	95.83	
	at	65.54	—	—	1.51	16.88	—	1.42	—	—	3.18	6.50	—	2.57	0.35	—	0.27	1.56	—	0.21	—	
S149-15/26	wt	33.54	—	0.46	5.90	12.08	—	—	—	—	11.40	22.31	2.33	8.80	—	—	1.01	2.10	—	—	99.67	
	at	68.82	—	0.56	6.90	12.80	—	—	—	—	2.63	5.23	0.54	2.00	—	—	0.21	0.30	—	—	—	
S149-24/22	wt	26.66	—	—	0.84	12.76	—	0.48	—	—	11.74	23.87	3.04	9.46	0.71	—	1.11	2.91	—	0.75	94.33	
	at	66.92	—	—	1.20	16.56	—	0.49	—	—	3.39	6.84	0.87	2.63	0.19	—	0.28	0.50	—	0.13	—	
Gl8-25/3	wt	26.38	—	2.14	2.58	—	—	0.44	0.45	—	21.65	36.73	3.60	8.00	—	—	—	—	—	—	101.97	
	at	70.52	—	3.39	3.93	—	—	0.47	0.35	—	6.66	11.21	1.09	2.37	—	—	—	—	—	—	—	
Gl36-7-54	wt	30.18	—	1.03	4.05	12.15	0.36	—	—	—	12.98	24.69	2.80	10.37	—	—	—	—	—	—	98.62	
	at	66.62	—	1.35	5.10	13.85	0.32	—	—	—	3.30	6.22	0.70	2.54	—	—	—	—	—	—	—	
Gl36-14-24	wt	29.47	—	—	5.97	11.95	—	—	—	—	13.46	25.56	—	10.61	—	—	—	—	—	—	97.02	
	at	65.94	—	—	7.61	13.82	—	—	—	—	3.47	6.53	—	2.63	—	—	—	—	—	—	—	
Shch-111a 30/13	wt	33.10	—	—	1.10	13.49	—	—	—	—	13.54	26.69	—	10.39	—	—	—	—	10.39	—	99.01	
	at	71.15	—	—	1.35	14.98	—	—	—	—	3.35	6.55	—	2.48	—	—	—	—	2.48	—	—	
Shch-111a 30/32	wt	27.03	0.37	0.54	1.29	12.50	—	—	—	—	18.16	26.71	2.39	8.53	—	—	—	—	—	—	97.52	
	at	62.68	0.75	0.78	1.79	15.67	—	—	—	—	5.07	7.40	0.66	2.29	—	—	—	—	—	—	—	
Shch-111a 6/4	wt	29.01	—	0.62	1.39	13.02	—	0.21	—	—	17.32	27.09	2.90	8.84	—	—	—	—	—	—	100.39	
	at	66.89	—	0.84	1.82	15.50	—	0.19	—	—	4.60	7.13	0.76	2.26	—	—	—	—	—	—	—	
Shch-111a 6/35	wt	28.70	0.24	0.60	1.55	12.79	0.26	—	—	0.18	20.32	24.55	2.28	6.56	—	—	—	0.34	—	—	98.36	
	at	66.66	0.48	0.82	2.05	15.35	0.25	—	—	0.11	5.43	6.51	0.60	1.69	—	—	—	0.05	—	—	—	
Sample no.	%	O	Al	Si	P	K	Ca	Fe	Co	As	Br	Y	Gd	Tb	Dy	Ho	Er	Tm	Yb	Ta	U	Total
Og6-20/7	wt	34.03	—	4.67	14.91	—	—	—	—	—	—	30.84	2.32	0.67	5.6	—	3.12	—	2.83	—	0.33	99.32
	at	66.23	—	5.17	14.99	—	—	—	—	—	—	10.8	0.46	0.13	1.07	—	0.58	—	0.51	—	0.04	—
Og15a-23/50	wt	41.28	—	10.39	12.24	—	—	—	—	—	—	26.4	2.03	0.65	4.35	—	2.32	—	2.5	—	—	102.14
	at	69.47	—	9.96	10.64	—	—	—	—	—	—	7.99	0.35	0.11	0.72	—	0.37	—	0.39	—	—	—
Og43/2-10	wt	31.2	—	—	16.12	—	—	—	0.12	0.46	—	28.54	4.93	1.06	7.21	1.35	2.33	0.3	2.04	0.2	—	95.85
	at	68.92	—	—	16.68	—	—	—	0.07	0.2	—	10.29	1.01	0.22	1.43	0.26	0.45	0.06	0.38	0.04	—	—
S153-3/16	wt	41.81	—	16.57	9.27	0.55	0.24	0.48	0.64	—	—	20.22	—	—	2.09	—	—	—	2.94	—	—	94.81
	at	68.78	—	15.53	7.88	0.37	0.16	0.23	0.29	—	—	5.99	—	—	0.34	—	—	—	0.45	—	—	—
Gl8-25/42	wt	37.42	1.91	4.64	10.26	0.75	—	11.12	—	—	—	23.77	1.87	—	3.58	—	2.11	—	—	—	—	97.44
	at	68.02	2.06	4.81	9.64	0.56	—	5.79	—	—	—	7.78	0.35	—	0.64	—	0.37	—	—	—	—	—
Og43-2/18	wt	41.5	—	0.65	7.24	—	—	34.67	—	—	0.65	12.11	0.6	—	1.75	—	—	—	—	—	—	100.17
	at	73.75	—	0.59	5.9	—	—	15.75	—	—	0.21	3.44	0.1	—	0.27	—	—	—	—	—	—	—

Samples Og6, Og15a, N155d are taken from the Ogorodnaya River mouth; (S149, S153) Koreiskaya River, (Gl8, Gl36, Shch-111a) Dal'naya River; (Gl8-25/3) cerianite; (Og43-2/18) Fe-Y phosphate (Fe, Y) (Fe,P)O₄. Compositions of other minerals correspond to monazite (Ce, La,...)PO₄ and xenotime (Y, Dy, Gd,...)PO₄. Excess Si and Al are related to beam excitation of not only analyzed mineral, but also quartz-silicate matrix of the rock. (—) Below the detection limit.

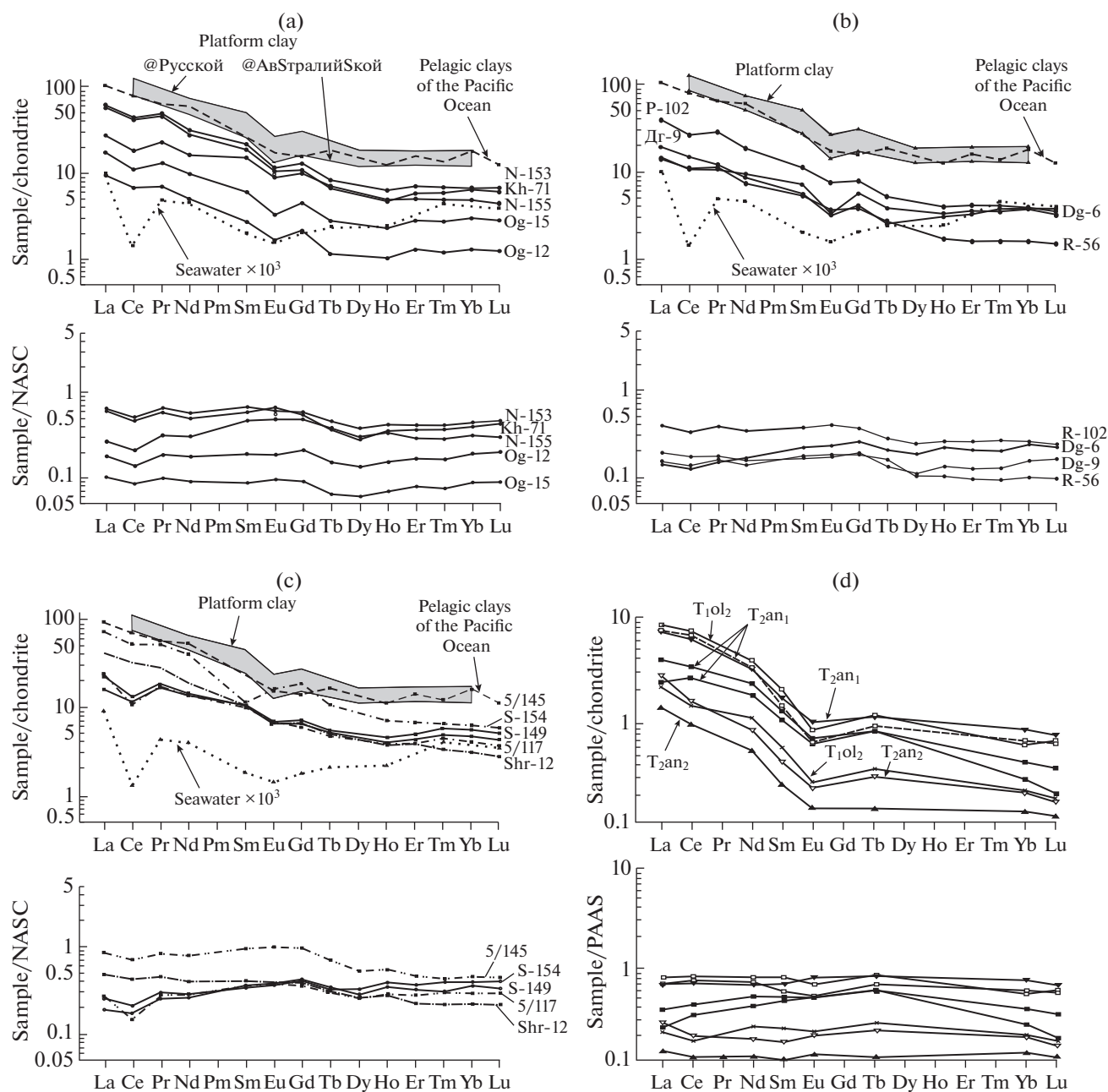


Fig. 6. Chondrite- and PAAS-normalized REE distribution patterns for the carbonaceous silicites of the phtanite member. (a–c) Phtanites and clayey phtanites: (a) Ogorodnaya River (samples N-153d, N-153d1, Og-12, Og-15), Khabarovsk (sample Kh-71); (b) Dal'negorsk (samples R-56, R-102, Dg-2, Dg-6); (c) Koreiskaya River (samples S-149, S-154), Shirokaya Pad Creek (sample Shr-12), Bol'shaya Ulitka River (samples 5/117, 5/145); (d) cherts (T1–T2, Dal'negorsk) (Tuchkova et al., 2004). (NASC) North American Shale Composite (Haskin et al., 1968; Rollinson, 1995).

diagenetic sulfides and carbonates or crystallized in the secondary leaching pores (Table 4). The main minerals of the first group are pyrite, monazite, rutile (or other polymorphic modifications of TiO_2), zircon, xenotime, goethite, magnetite, and hematite. Most minerals of this group are the heavy-fraction detrital minerals resistant to weathering, which are typical of many marine placers. These are allothigenic minerals

that were delivered to sediment at the stage of radiolarian mud precipitation. It is known that monazite, zircon, rutile, and xenotime are widespread in the metamorphic and vein rocks and, as accessory minerals, in granites, syenites, and carbonatites. In the Triassic carbonaceous cherts of Sikhote Alin, their grains are disseminated in the quartz cement or accumulated in individual interbeds (Fig. 2c), which is caused by the

Table 7. Chemical composition of noble metals in the Middle Triassic phanites

No Ordinal no.	No Spectrum	%	O	Mg	Al	Si	S	Cl	Cr	Mn	Fe	Cu	Zn	Sr	Ag	Pd	Au	Te	Total
1	15_08_18	wt at	19.10 60.23	—	0.49 0.90	6.99 12.01	—	—	1.80 1.62	—	11.96 9.76	—	—	—	—	—	64.74 15.49	—	105.08
2	15_08_19	wt at	11.27 39.23	—	0.43 0.86	17.26 32.57	—	—	—	—	16.54 14.83	—	—	—	—	—	47.58 12.50	—	93.08
3	15_08_20	wt at	12.94 46.27	—	0.45 0.92	11.22 21.78	—	—	0.92 0.94	—	16.40 15.12	—	—	—	—	—	55.44 14.97	—	97.37
4	27_08_31	wt at	6.31 44.32	—	0.24 1.00	2.16 8.63	—	—	1.21 2.61	—	1.74 3.51	—	—	—	—	—	69.98 39.91	—	81.64
5	15_08_52	wt at	10.01 36.21	—	—	1.88 3.88	—	—	—	—	4.73 4.90	15.88 14.49	—	—	—	74.52 40.54	—	—	107.02
6	15_08_55	wt at	17.53 52.51	—	0.54 0.93	4.01 6.57	—	—	—	—	—	14.99 10.53	—	—	—	70.25 29.45	—	—	107.32
7	22_08_26	wt at	13.28 45.59	—	0.50 1.02	1.38 2.69	0.20 0.35	—	—	—	3.59 3.53	15.52 13.41	—	—	—	64.74 33.41	—	—	99.22
8	22_08_28	wt at	11.04 41.70	—	0.68 1.51	1.36 2.93	—	—	—	—	3.09 3.34	15.62 14.85	—	—	—	62.81 35.66	—	—	94.6
9	27_08_19	wt at	17.40 53.70	—	1.63 2.97	2.70 4.75	—	—	0.38 0.36	—	3.37 2.98	14.28 11.10	—	—	—	52.02 24.14	—	—	91.79
10	27_08_48	wt at	9.82 39.65	—	—	1.41 3.23	—	—	—	—	1.54 1.78	16.02 16.29	—	—	—	64.35 39.06	—	—	93.14
11	22_08_19	wt at	—	—	—	—	—	—	—	—	—	2.32 4.26	—	—	88.69 95.74	—	—	—	91.02
12	22_08_20	wt at	—	0.32 1.35	—	—	0.27 0.87	0.29 0.83	—	—	—	2.67 4.32	2.13 3.35	0.57 0.67	92.23 88.01	—	—	0.73 0.59	99.2
13	22_08_21	wt at	7.69 39.05	—	—	—	0.26 0.66	—	—	—	—	2.39 3.06	1.59 1.98	—	73.35 55.25	—	—	—	85.29
14	22_08_23	wt at	6.95 32.79	—	—	—	—	—	—	—	—	2.19 2.61	2.00 2.31	—	89.09 62.3	—	—	—	100.24
15	22_08_33	wt at	12.28 47.43	0.30 0.76	0.84 1.93	4.00 8.81	0.20 0.39	—	—	—	1.50 1.66	—	—	—	67.61 38.72	—	—	0.63 0.31	87.38
16	5-50_22	wt at	11.88 50.79	—	—	—	—	—	—	1.21 1.51	1.73 2.12	23.65 22.04	—	—	6.43 4.08	—	55.99 19.45	—	100.9

(1–15) Ogorodnaya River; (16) Bol'shaya Ulitka River. Si and Al belong to opal, quartz, and clay minerals, while Fe is involved in iron oxyhydroxides of the siliceous–carbonaceous infill of pores and fractures, with microparticles of native gold. (–) Not found.

Table 8. Composition of intermetallide Cu_5Zn_3 (polished section Og-6)

Element	% (wt)	Square deviation	at %	Line	Calculated composition of intermetallide (at %)
O	5.94	0.39	20.63	K_series	0
Si	1.25	0.1	2.47	K_series	0
Fe	0.68	0.1	0.68	K_series	0.884
Cu	52.3	0.54	45.76	K_series	59.488
Zn	33.97	0.53	28.89	K_series	37.557
Pt	1.77	0.83	0.5	L_series	0.65
Au	1.34	0.86	0.38	L_series	0.494
Pb	2.3	0.34	0.62	M_series	0.806
Total	99.66				

washing of light mineral fraction by the submarine currents from yet nonlithified ooze or the enrichment of interbeds in heavy minerals due to underwater separation. Allothigenic minerals also include apatite of biogenic fragments, which enrich individual interbeds, and some part of cassiterite.

The fine-crystalline, microglobular, and frambooidal pyrite, as well as pyrite developed after biogenic siliceous and carbonate fragments (Fig. 3), represent diagenetic mineral in most cases. In addition to pyrite, diagenetic minerals also presumably include some part of goethite and hydrogoethite, barite, romanechite, and cryptomelane. This group also comprises some chalcopyrite and sphalerite, which represent pseudomorphs after plant remains or skeletal fragments (Figs. 3e, 3f).

Most of other ore minerals (sphalerite, galena, chalcopyrite, as well as manganic, arsenic, and cupriforous pyrites, pentlandite, chalcocite, cobaltite, arsenopyrite, argentite, scheelite, wolframite, stibiconite, skutterudite, zirkelite, ulmanite, and celestite) are localized in fractures filled with the carbonaceous matter (Table 4). They were crystallized already after the lithification (cementation) of siliceous beds during catagenesis.

Rare earth elements (REE) are frequently used to identify sedimentation settings of definite sedimentary rocks, in particular, silicites (Shimizu and Masuda, 1977; Murray et al., 1990; Murray, 1994; Karl et al., 1992; Rollinson, 1995). In the carbonaceous silicites of Sikhote Alin, REE-bearing minerals represent the fine-clastic mixture delivered mainly from land with the suspended particulate matter of rivers (including those sorbed on clay particles). This is consistent with data on the modern river runoff. For instance, the majority (80%) of REE, especially LREE, in the modern river runoff in the Sea of Japan are restricted to the suspended particulate matter (Chudaeva and Chudaev 2011). The real content of REE in the terrigenous material of river runoff is possibly higher, taking into account the arbitrary assignment of REE passing through 0.45-mm filters to the soluble species. Thus,

in addition to geochemical data, it is required to determine the nature and amount of main REE carriers to reconstruct the sedimentation setting in the silica accumulation basin.

Native elements (gold, silver, copper, lead, iron, nickel iron, tungsten, selenium) and intermetallides (Pd_3Cu , Pd_7Cu_3 , CuAu , Cu_3Zn_2 , Cu_5Zn_3 , $(\text{Cu},\text{Ni})_5\text{Zn}_4$, Ni_4Cd) are also mainly enclosed in the carbonaceous–siliceous matter and iron hydroxides, which fill pores and fractures in the rocks (Tables 4, Fig. 5). Their crystallization occurred after the lithification (cementation by silica) of rocks and appears to be related to the catagenetic transformation of DOM and release of metals from it. The source and carrier of ore elements were possibly bitumen fractions, which are characterized by high (with respect to the whole rock) contents of Fe, Mn, Pb, Zn, Ni, Co, As, Ag, and Au (Volokhin and Ivanov, 2007). The humic fraction of DOM enriched in these elements also could play significant role in the accumulation and transfer of Sn, Mo, Cr, and V (Volokhin, 2013). The presence of halite, sylvite, and K–Na chlorides in the carbonaceous veinlets indicates the possible participation of chloride solutions in the transfer of some elements. The primary source of gold is seawater, where the AuCl_2 content can reach 44 $\mu\text{g/L}$ (Yudovich, 2009). The fine rhythmic structure of the phtanite member suggests repeated alternation of the anoxic (H_2S -contaminated) and oxic settings in the near-bottom and mud waters. This change provided the influx of fresh marine waters to O/ H_2S chemocline, which facilitated the influx of dissolved gold in mud waters (Yudovich, 2009). The low degree of oxidation of DOM devoid of carboxyl groups indicates the long-term preservation of reducing conditions during the diagenetic and catagenetic mineral formation.

This was followed by the oxidation of sulfides (pyrite, chalcopyrite) and the formation of sulfates (jarosite, anhydrite, and, partially, barite), Fe–Cu oxides and hydroxides, and REE oxides in the oxic water infiltration zone. The formation of jarosite,

anhydrite, and other sulfates in the sulfide-bearing black shales is widespread in nature and usually thought to be related to the sulfuric acid weathering (Yudovich and Ketris, 2008).

CONCLUSIONS

The finely dispersed trace minerals were formed in the Triassic carbonaceous silicites of Sikhote Alin for a long time through several stages. Their association depends on many factors, including the composition of provenances, conditions, settings, and regime of accumulation of the autochthonous organic matter, which predetermined the environment and conditions of diagenesis, as well as catagenetic transformation of mineral matters. Most of detrital and clay minerals (quartz, K-Fsp, illite, kaolinite, and metahalloysite) are allochthonous formations that represent erosion products of the continental weathering crusts. Thus, the main "diluent" of biogenic silica in silicites of the phtanite member was the terrigenous material supplied by the erosion of continental rocks. This is consistent with the structure of the Triassic siliceous sequence of Sikhote Alin: the phtanite member (T_{1ol_2} – T_{2an}), as well as the underlying clayey cherts (T_1 – T_{2an_2}) and siliceous mudstones, mark the initial transgressive stage of its accumulation (Volokhin et al., 2003). The terrigenous components also include some accessories: zircon, monazite, and xenotime as the main REE carriers and rutile or its polymorphic modifications.

The autochthonous material (organic matter, colloids and Fe-Mn solutions derived from different sources, as well as phosphate, carbonate, and other skeletal fragments of organisms) and the marine mud water with dissolved salts and gases played significant role in the diagenetic and catagenetic mineral formation. A significant part of ore minerals, including noble metals and intermetallides, is postdiagenetic. It is assumed that they were formed at the catagenetic stage due to destruction of the autochthonous organic matter and during the formation of easily mobile bitumens—main accumulators and carriers of ore elements in the carbonaceous sedimentary sequences. However, other sources of metals are also possible. Elision and hydrothermal processes provoked by subsidence of the sequence and tectonomagmatic activation in the Middle–Late Jurassic, Early Cretaceous, and Late Cretaceous–Paleogene time also stimulated the catagenetic mineral formation. They served as additional factor of mineral transformations of the autochthonous material, thus determining significant differences of the mineral and chemical composition of rocks of the phtanite member.

The reducing environment of mineral formation existed in the carbonaceous sequences for a long time and facilitated the preservation of most metals in the sulfide, sulfoarsenide, native, and intermetallic min-

eral forms. Significant regional and geochemical differences in the carbonaceous silicites of the phtanite member (Volokhin and Ivanov, 2007) accumulated within a relatively narrow time range are caused by the long-term evolution and different conditions of the authigenic mineral formation in different regions of the Sikhote Alin basin.

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