

Geochemistry and Metal Potential of Triassic Carbonaceous Silicites in Sikhote Alin

Yu. G. Volokhin and V. V. Ivanov

*Far East Geological Institute, Far East Division, Russian Academy of Sciences,
pr. Stoletiya Vladivostoka 159, Vladivostok, 690022 Russia*

e-mail: yvolokhin@mail.ru

Received June 13, 2006

Abstract—In the Triassic siliceous formation of Sikhote Alin, carbonaceous silicites occur in the late Olenekian–middle Anisian member (4–20 m) of alternating cherts and clayey cherts (“phtanite member”) near the section base. The silicites are represented by radiolarian and spicule–radiolarian cherts alternating with clayey cherts. They contain up to 8.5% C_{org} . In the majority of sections, the rocks underwent structural and mineral transformation at the mesocatagenetic stage. The slightly oxidized organic (primarily, marine sapropelic) matter contains quinones, methyl, methylene, and ether groups. The content of neutral bitumens in rocks shows a wide variation range. The carbon isotopic composition in phtanites and clayey phtanites ($\delta^{13}C$ from -27.3 to -30.2‰) is identical to that in many Paleozoic–Mesozoic bitumens and oils. As compared with other Mesozoic sedimentary rocks of Sikhote Alin, the carbonaceous silicites are enriched in V, B, Mo, Ni, Cu, and Ag. Anomalous high concentrations of Ba are recorded in phtanite rock sections at the Gornaya and Khor rivers and in the vicinity of Khabarovsk. Modal value of the Au content in phtanites and clayey phtanites is three or four times higher than the Clarke value in carbonaceous silicites and reaches anomalous values in some sections (e.g., Ogorodnaya River section). Carbonaceous silicites of this section are also enriched in Pt. Positive Au– C_{org} correlation is recorded in clayey phtanites of the Ogorodnaya River section containing more than 0.5% C_{org} . In organic fractions, Au and Ag are concentrated in alcohol and alcohol–benzene bitumens, asphalt acids, and asphaltenes. Migration of bitumens from high-carbonaceous clayey phtanites to the pore-fissure space of cherts and phtanites also fostered the concentration of these metals in some low-carbonaceous layers of the member.

DOI: 10.1134/S0024490207040049

“Black shales” is a general term for genetically and compositionally different sedimentary (sandy–silty, clayey, siliceous, carbonate, or mixed) rocks with a high content of carbonaceous material (more than 1% C_{org}). They are of great interest as a source of hydrocarbons (oil source rocks) and concentrators of various metals (V, U, Re, Mo, Pb, Zn, Cu, and Ni). Contents of these metals in the carbonaceous member are higher than their Clarke values in the low-carbonaceous varieties. In some places, their concentrations can reach the ore grade (Ankinovich and Ankinovich, 1968; Coveney et al., 1987; Gorzhevskiy, 1987; Holland, 1979; Kesler et al., 1986; Kholodov, 1973; Lewan and Maynard, 1982; McKelvey et al., 1986; Petrov, 1976; Poplavko et al., 1974, 1978; Sheldon, 1959; Yudovich and Ketris, 1988, 1994). Interest to black shales was also heightened by the discovery of large gold and platinum deposits in them (Arifulov, 2005; Buryak, 1987, 2000; Chernyshov, 1999; Coveney and Pasava, 2005; Gurskaya et al., 1999; Ermolaev and Sozinov, 1986; Ermolaev et al., 1999; Jiang et al., 2005; Korobeinikov, 2002; Korobeinikov et al., 1999; Kovalev and Michurin, 2005; Laverov et al., 1997; Nekrasov et al., 2001; Ne-

merov et al., 2005; Orberger et al., 2005; Plyusnina and Kuz'mina, 1999; Razvozhayeva et al., 2002; Sidorov and Tomson, 2000; Sidorov and Volkov, 2001; Vud and Popov, 2006; Zhang et al., 2005; and others).

Enrichment of carbonaceous members with metals is related to the primary concentration of organic matter (OM) and chalcogenides during sedimentogenesis (resource function of black shales) and their secondary concentration at the redox geochemical barrier created by the carbonaceous material along the filtration pathway of metalliferous solutions (Kovalev and Michurin, 2005; Laverov et al., 2000; Nemerov et al., 2005; Yudovich and Ketris, 1994). In Sikhote Alin, extraction of metals from the underlying carbonaceous members by high-mobile bitumen fractions and the subsequent redistribution of metals could produce manganese, beryllium, gold, and other mineralizations of the vein-stringer, disseminated, and other morphological types in the overlying volcanosedimentary members (Ivanov et al., 1997; Kazachenko and Sapin, 1990; Kazachenko et al., 2005; Zin'kov et al., 1993). Fractured Early Cretaceous black shales (carbonaceous metasomatites) of the Dal'negorsk ore district are enriched in Au, Ag, Mo, Re, Bi, Zn, Ni, and Co concentrated as sulfides, native

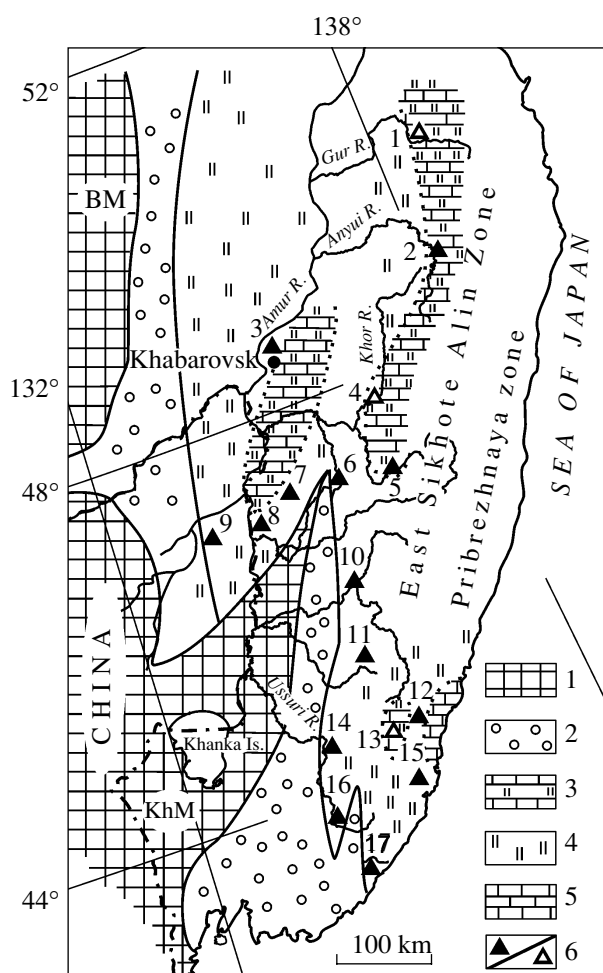


Fig. 1. Locations of Triassic sections and exposures of the phtanite member (in the schematic map of Triassic facies of Sikhote Alin). (1) Zones of erosion and formation of the kaolin weathering crust: crystalline massifs: (BM) Bureya, (KhM) Khankai; (2) Triassic terrigenous shelf sediments in marginal troughs; (3–5) facies of the Triassic siliceous formation: (3) carbonate–chert; (4) chert, (5) reefal limestone; (6) locations of Triassic sections and exposures (filled triangles) of the phtanite member. Numeral designations: (1) Gur River; (2) Anyui River; (3) Khabarovsk; (4) Khor River; (5) Katen River; (6) Matai River; (7) Bol'shaya Ulitka River; (8) Bikin; (9) Shichang Settlement (China); (10) Dal'nyaya River; (11) Gornaya River; (12) Dal'negorsk; (13) Balagannyi Spring; (14) Ogorodnaya River; (15) Shirokaya Pad Creek; (16) Breevka Settlement; (17) Koreiskaya River.

metals, intermetallides, carbides, and organometallic compounds owing to the endogenic transport and mantle origin of carbon and metals (Tomson et al., 1993, 2001, 2003, 2006).

The well-known geochemical data are mainly related to noble metal deposits in Paleozoic and Precambrian sedimentary carbonaceous members subjected to intense catagenetic and metamorphic alterations. Data on the metal potential of Mesozoic black shales are scanty (Yudovich and Ketris, 1994).

Mineralogy and geochemistry of carbonaceous silicites discovered in Triassic rocks of Sikhote Alin (Mikhailov and Volokhin, 1980) are insufficiently studied. Geochemistry of the carbonaceous members and associated rocks is based on determinations of the major elements by methods of wet chemistry and X-ray fluorescence analysis. Distribution of Sn, Ni, Co, Pb, Zn, Cu, Cr, V, Mo, B, Ga, and Ag was investigated by the emission spectrometry (Volokhin, 1985, 1988). Recently, application of new high-precision analytical methods has made it possible to obtain more accurate results and expand significantly the range of analyzed chemical elements. First data on the composition of dispersed organic matter (DOM) in the rocks have been reported in (Volokhin et al., 2005). We have established the nearly universal distribution of carbonaceous silicites in Triassic members of the Sikhote Alin foldbelt (Fig. 1) and refined the age of the silicite-enclosing unit (Volokhin et al., 1990, 2000, 2003; and others). The aim of the present communication is to characterize the geological setting, structure, composition, and metal potential of carbonaceous silicites in the study region based on all materials available to date.

FACIES AFFILIATION AND STRATIGRAPHIC POSITION OF TRIASSIC CARBONACEOUS SILICITES

Figure 2 demonstrates reconstruction of the Triassic siliceous formation of Sikhote Alin (Volokhin et al., 2003) based on the stratigraphic correlation of sections. The siliceous formation is a large (regional-scale) poly-facies and polycyclic geological body (macro-cyclothem) from a few tens of meters to 500 m thick. The body was deformed by submarine sediment sliding, folding, and fractures in the Middle–Late Jurassic and Early Cretaceous. The macrocyclothem includes upper Olenekian–Rhaetian conodonts and radiolarians that mainly represent planktonic siliceous and carbonate formations (Bragin, 1991, 2000; Burii, 1989; Volokhin et al., 1987, 1990, 2000, 2003).

The carbonaceous silicites (phtanites and clayey phtanites) in the triassic formation are mainly confined to the siliceous facies. However, they occur also in the margins sectors of the more pelagic (carbonate–siliceous) facies (Fig. 1). Layers with the highest DOM content make up the 4- to 20-m-thick “phtanite member” (Volokhin et al., 2003) near the base of the triassic formation. The member is composed of intercalation of light gray and greenish gray, low-carbonaceous and black carbonaceous cherts and clayey cherts. Layers of carbonaceous silicites (1–30 cm thick) account for 15–30% of the member (up to 50% in some places). The phtanite member characterized by nearly equal proportions of silicites and clayey silicites overlies the greenish gray clayey cherts and siliceous mudstones. This member is overlain by a member of platy cherts. The lower and upper boundaries of the phtanite member are diachronous. Its age varies from the late Olenekian–

middle Anisian (*Neospathodus homeri*–*N. kockeli* conodont zones) in the Dal'negorsk and Khabarovsk sections to the middle–late Anisian (*N. kockeli* zone and lower part of the *Paragondolella excelsa* zone) in the majority of the remaining sections (Burii, 1989; Volokhin et al., 2003).

METHODS

Mineralogy of rocks was studied by various methods (optical microscopy, microprobe analysis of mineral phases in polished sections, and electron microscopic and X-ray diffraction analyses of the clay fraction). The major elements were determined by the wet chemistry and X-ray fluorescence analysis (RFA) with a VRA-30 spectrometer (Carl Zeiss, Jena). Microelements in rocks were determined by the X-ray spectrophotometry (S4 Pioneer, BRUKER Company, Germany), the inductively coupled plasma-atomic emission spectroscopy (ICP-AES) using a Plasmaquant 110 spectrometer (Analytik Company, Jena), and the inductively coupled plasma mass spectroscopy (ICP-PM) using an Agilent 7500c mass spectrometer (Agilent Technologies Inc.). Gold, platinum, and palladium were determined by the ICP-MS and AAS methods with the flame and electrothermic atomization in an AA-6200 (SHIMADZU) atomic absorption spectrophotometer. Preliminary concentration of noble metals was accomplished by methods of chemical extraction or fire assay.

The content of organic carbon C_{org} in rocks was determined by the gasometric method according to the technique (Kitaev and Likht, 1971). The DOM composition was studied by the standard bituminological analysis (Korchagina and Chetverikova, 1976). Rocks were ground to 0.25–0.5 mm fraction. Free bitumens sequentially extracted from these fractions in a Soxhlet apparatus are divided into the following varieties: bitumens dissolved in chloroform (CB), bitumens dissolved in alcohol–benzene (ABB 1 : 2), and bonded alcohol–benzene bitumens (BAB) extracted after the decomposition of carbonates and saltlike bituminous components with the 10% HCl solution. Humic substances were extracted from the rock with the 0.1 N NaOH solution. The insoluble residue (IR) includes the material left after the twofold treatment of the debituminized rock with concentrated (HF + HCl) acids and the separation of accessory minerals. Contents of metals in organic fractions were determined by the approximate quantitative spectral analysis and atomic absorption methods. The group composition of chloroform bitumens was estimated by the Markuson–Sakhanov method (Korchagina and Chetverikova, 1976).

Organic matter from 10 samples of carbonaceous silicites was extracted by the simplified aqueous alkaline method at the Far East Institute of Bioorganic Chemistry. Sample (1 g) placed in a flask (10 ml) was treated with 2 ml of 0.1 NaOH solution, sealed with a cork, and stirred at room temperature for 3 days. The

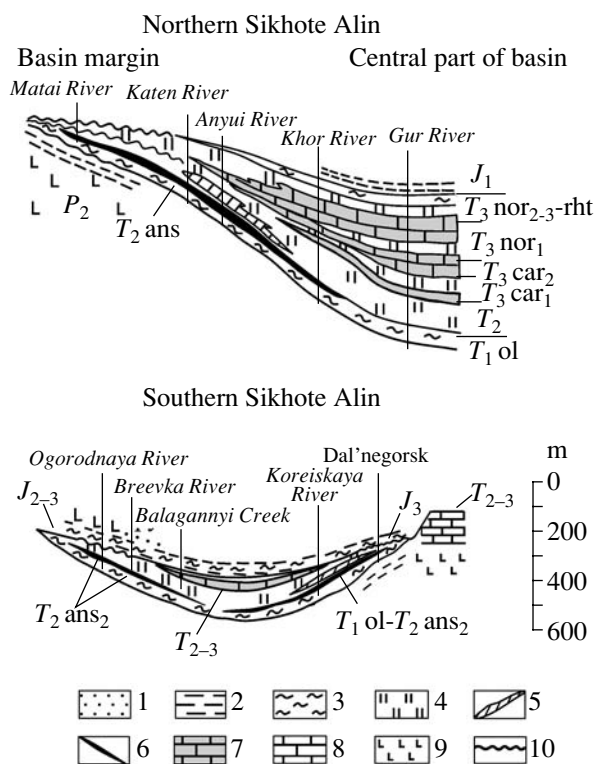


Fig. 2. Position of the phtanite member in the Triassic chert section of Sikhote Alin (Volokhin et al., 2003). (1) Sandstones; (2) siltstones and mudstones; (3) clayey cherts; (4) cherts; (5) jaspers; (6) carbonaceous silicites; (7) pelagic limestones; (8) reefal limestones; (9) basalts and their tuffs; (10) hiatus.

supernatant was carefully separated. The precipitate was washed three times with water and then centrifuged. The combined supernatant sample (total volume 8 ml) was separated into 2-ml portions and lyophilized. The yield of dissolved matter was determined by weighing. Ultraviolet spectra of the aqueous alkaline extracts were recorded with a Cecil CE 7200 UV spectrometer (Cambridge, Great Britain). Infrared spectra of samples of carbonaceous rocks and their aqueous alkaline extracts in the KBr solution were recorded by the IR spectrometer equipped with a Vektor-22 Fourier-transform (BRUKER, Germany).

COMPONENT AND MINERAL COMPOSITIONS OF SILICITES

The carbonaceous silicites are mainly composed of the authigenic silica (as quartz and chalcedony of fossilized skeletons and skeletal fragments of radiolarians, sponge spicules, and rock cement), clay minerals, and carbonaceous matter dispersed in the rock. The silicites also contain clastogenic admixture of quartz, feldspars, and rare basaltoids, cherts, phtanites, siltstones, and mudstones.

Table 1. Contents of DOM fractions in carbonaceous silicites of the phtanite member

Sample no.	Rock	C _{org} , %	DOM fraction, %				IR	β _{CB}	CB/ABB
			CB	ABB	BAB	HA			
Khabarovsk (T ₁ ol ₂ ?)									
Kh-70/78	CPh	4.51	0.118	0.014	0.021	0.028	5.0	2.6	8.4
Kh-73	CPh	2.61	0.040	0.014	0.114	0.000	3.4	1.5	2.9
Ogorodnaya River (T ₂ an ₂)									
N-170d	CPh	0.90	0.030	0.003	0.036	0.044	4.7	3.3	10
N-153d	CPh	2.11	0.030	0.010	0.036	0.043	5.8	1.4	3
Rudnaya River (T ₁ ol ₂ -T ₂ an ₂)									
R-50	Ph	0.18	0.018	0.047	0.014	0.081	1.1	10.0	0.4
R-54	CPh	0.34	0.008	0.083	0.028	n.d.	4.6	2.4	0.1
R-56	CPh	0.13	0.002	0.037	0.015	0.095	1.0	1.5	0.05
R-102	CPh	1.42	0.014	0.283	0.020	0.280	5.9	1.0	0.05
Dal'negorsk, Central quarry (T ₂ an)									
R-145	Ph	0.26	0.025	0.009	0.218	n.d.	0.7	9.6	2.8
R-120	CPh	5.85	0.041	0.016	0.016	0.024	6.3	0.7	2.6
Dal'negorsk, Bol'nichnyi Spring (T ₂ an)									
R-263	Ph	0.72	0.006	0.002	0.013	n.d.	1.7	0.8	3.0

Note: (CP) Clayey phtanite; (P) phtanite; (DOM) dispersed organic matter; (C_{org}) content of organic carbon in rock. Bitumens: (CB) chloroform bitumens, (ABB) additionally extracted alcohol–benzene bitumens, (BAB) bonded alcohol–benzene bitumens additionally extracted after the dissolution of salts and carbonate minerals in 10% HCl; (HA) humic acids; (IR) insoluble residue; (n.d.) not determined; (β_{CB}) coefficient of bituminosity ($\beta_{CB} = CB \times 100/C_{org}$).

The clay fraction is dominated by the 2M₁ dioctahedral illite ($b = 9.04 \text{ \AA}$) and the subordinate 1M illite (Volokhin, 1980, 1985). Illite is also the sole clay mineral in light gray clayey cherts associated with carbonaceous rocks of the phtanite member.

Authigenic sulfides are mostly represented by pyrite. Pyrrhotite, As-pyrite, arsenopyrite, chalcopyrite, galena, sphalerite, and pentlandite, argentite, and native silver are the subordinate components. We found rare flakes of gold (0.01–0.005 mm) in the insoluble (in HF) residue of samples from the Koreiskaya, Anyui, and Breevka sections. Carbonaceous silicites from a quarry of the Dal'negorsk borosilicate deposit contain abundant secondary copper minerals (chalcocite, bornite, azurite, and malachite).

The carbonaceous matter of phtanites and clayey phtanites is differently metamorphosed. It is represented by the fine-dispersed graphite (Kazachenko and Sapin, 1990) in hornfelsized sectors near the Cretaceous granitoid intrusions (Shirokaya Pad River). However, it is represented by the X-ray amorphous kerogen and bitumens in the majority of areas located beyond the contact metamorphism zone (Table 1). The DOM (C_{org}) content in the middle Anisian clayey phtanites is as much as 12 wt % in the Koreiskaya River section.

The insoluble residue (IR) of the dispersed organic matter is mainly composed of kerogen, which is insoluble in the low-boiling organic solvents. The IR content

shown in Table 1 is probably overestimated because of the admixture of fine-dispersed sulfides, which cannot be removed completely from the sample (Martikhaeva, 2000), as well as oxides, silicates (rutile and zircon), and native elements, which are insoluble in HCl and HF. Contents of neutral and acid bitumens vary from 0.0n–0.n% in the carbonaceous cherts to 1.2–6.3% (27% in rare cases) in the DOM. These contents are presumably underestimated. The CB content in the carbonaceous silicites shows a wide variation range (in general, 0.015–0.044%). According to Vassoevich's classification (1973), they can be qualified as rocks with medium contents of neutral bitumens (Table 1). The group composition of bitumens (Table 2) is dominated by oils and resins (petrol etheric fraction) and asphalt acids (alcohol fraction). In the vicinity of Dal'negorsk, the lowest CB content and CB/ABB ratio are recorded for carbonaceous silicites taken from the second nappe exposed along the Rudnaya River (Table 1). The silicites underwent thermal impact of the Cretaceous basalt sill (Baskina et al., 2004; Volokhin et al., 2003). The maximal bitumen content (0.83 wt %) is recorded in the clayey phtanite layer (C_{org} 7.4%) exposed at the Bol'nichnyi Spring near the Dal'negorsk borosilicate deposit (Table 2, sample Ya-730). The total content of oils and resins in this sample is 0.75% in the rock and 90.6% in the DOM, suggesting a parautochthonous origin of bitumens in this phtanite layer. The

Table 2. Content of fractions and group composition of bitumens in carbonaceous silicites of the Dal'negorsk district

Sample no.	Rock	Content of fractions in rock, g/kg			Ratio of bitumens in the DOM, %		
		PE	A	AB	O	AA	APh
R-50	Ph	0.049	0.033	0.014	51.2	34.0	14.8
R-54	CPh	0.018	0.023	0.005	38.1	50.6	11.4
R-56	CPh	0.028	0.021	0.010	47.3	35.1	17.6
R-102	CPh	0.011	0.049	0.029	12.0	55.4	32.6
R-120	CPh	0.030	0.027	0.007	47.3	42.0	10.6
R-145	Ph	0.116	0.035	0.017	69.1	20.9	10.0
Ya-730	CPh	3.158	0.383	0.391	90.6 (59.6)*	4.6	4.7

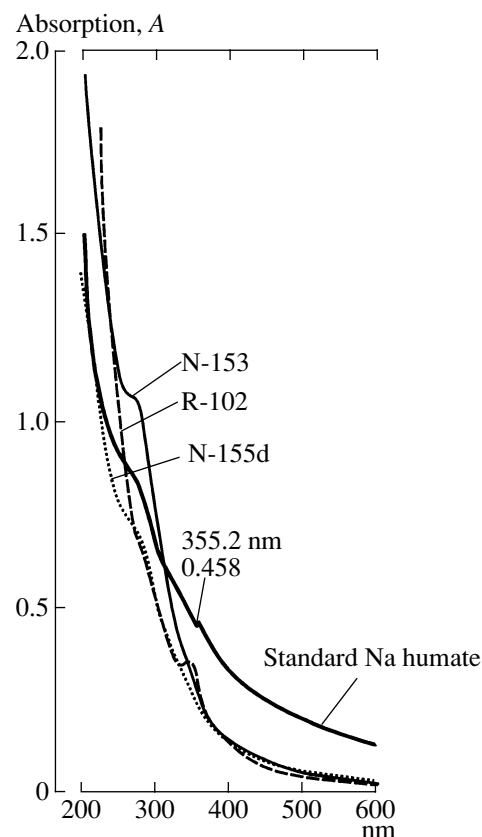
Note: Extracted fractions: (PE) petrol etheric, (A) alcoholic, (AB) alcohol-benzene; group composition of bitumens: (O) oils and petrol etheric resins, (AA) asphalt acid, (APh) asphaltenes; (*) content of oil (hexane) fraction in maltha.

coefficient of bituminosity (β_{CB}) of carbonaceous silicites varies from 0.7 to 10. According to (Medvedeva et al., 2003), this range is typical of Upper Jurassic and Lower Cretaceous bituminous mudstones in Sikhote Alin ($\beta_{CB} = 0.6\text{--}11.2$).

The UV spectra of aqueous alkaline extracts of the DOM show a weak but characteristic absorption at 270 nm (aromatic structures) and 340–350 nm (quinones), which are also observed in the standard sodium salt of humic acid (HA) extracted from brown coal of the Pavlov deposit (Fig. 3). The IR spectra (Fig. 4) show the characteristic absorption bands of quinoid ($1625\text{--}1690\text{ cm}^{-1}$), as well as methyl ($-\text{CH}_3$) and methylene ($>\text{CH}_2$) groups ($2923\text{--}2928\text{ cm}^{-1}$). Absorption bands at other intervals of IR spectra support the presence of aromatic, aliphatic, or naphthene structures: $3080\text{--}3100\text{ cm}^{-1}$ (aromatic HC), $1925\text{--}1930$, $1447\text{--}1460$, and 1385 cm^{-1} (deformation oscillations of $-\text{CH}_3$ and $>\text{CH}_2$) (Korchagina and Chetverikova, 1976; *Prikladnaya...*, 1970; Galimov and Kodina, 1982). Absorption band at 834 cm^{-1} is present in all IR spectrograms of clayey phtanites. This band is recorded in spectra of humid acids of coals if the substitution rate of their aromatic rings is 1.4 (Ibarra and Juan, 1985). The organic matter of carbonaceous silicites is distinguished from the standard HA by a lesser degree of oxidation. This is suggested by the absence of absorption band of the carboxyl (COO^-) group at $1610\text{--}1550\text{ cm}^{-1}$ (Fig. 4). Absorption (rather intense in some samples) at $1117\text{--}1152\text{ cm}^{-1}$ typical of oscillations of C–OH bonds in etheric groups and alcohols is present in IR spectra of the OM of carbonaceous silicites and is absent in the spectrogram of the standard sodium humate. The organic matter of phtanites and clayey phtanites differs significantly from the OM of the humid acid by the higher content of hydrocarbons (more intense absorption bands at $2923\text{--}2928\text{ cm}^{-1}$). IR spectra of the OM of carbonaceous silicites also contain an intense absorption band at $2500\text{--}2700\text{ cm}^{-1}$, which is missing in the standard sodium humate. Absorption in this segment of

the spectrum is probably related to valence oscillations of S–H thiophenols, organic sulfides, or sulfonic acids (Bellami, 1963). Absorption bands of hydrocarbon groups ($>\text{CH}_2$ and $-\text{CH}_3$) at $2922\text{--}2927\text{ cm}^{-1}$ are also observed in the IR spectra of some carbonaceous silicite samples.

Distinctive features of the humic standard (high contents of methyl, methylene, and etheric groups; low

**Fig. 3.** UV spectra of aqueous alkaline extracts of organic matter in carbonaceous silicites.

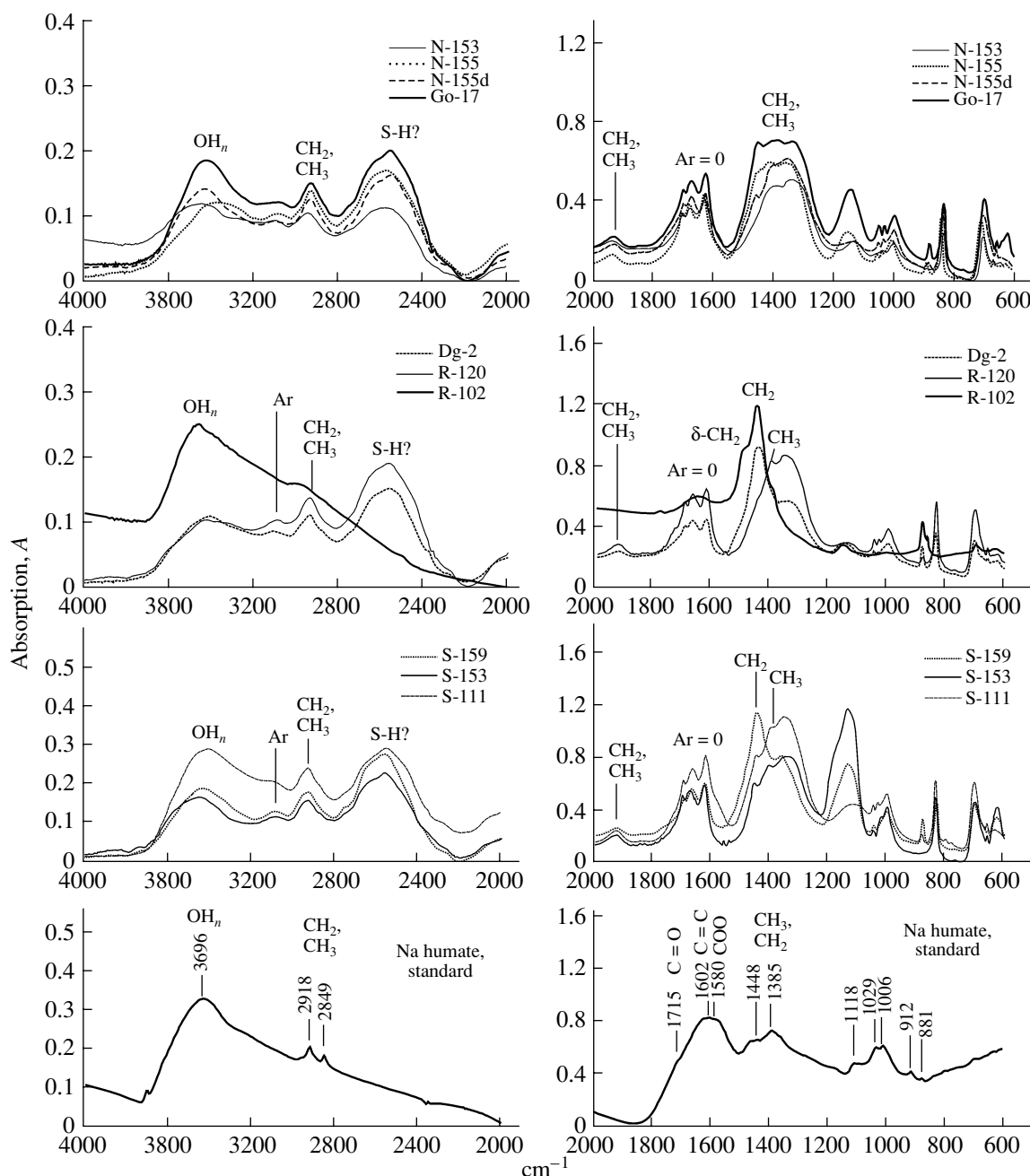


Fig. 4. IR spectra of aqueous alkaline extracts of organic matter in carbonaceous silicites.

oxidation degree of OM) testify to the preferential sapropelic and autochthonous (marine) origin of the organic matter of carbonaceous silicites (Pentina, 1973; Korchagina and Chetverikova, 1976). Lower frequency of the occurrence of respective fractions in the DOM estimated empirically based on the maximal rock subsidence depth is 2.5 km for humic acids, 3 km for humins, 1.8 km for sapropelic acids, and 2.3 km for saproins (Korchagina and Chetverikova, 1976). The sapropelic acids are not commonly retained in rocks subjected to transformations higher than the initial

mesocatagenesis stage. Taking into consideration other geological and lithological features—rock texture, porosity of carbonaceous silicites, and composition of the clay fraction (Volokhin, 1980, 1985; Volokhin et al., 2003)—we can assume that transformations of the studied rocks do not exceed the middle mesocatagenesis stage.

Study of slides with a scanning electron microscope revealed that rocks of the phtanite member can serve as pore-fissure reservoirs. Some pores can be primary (incompletely filled) cavities of microfossils. At the

same time, the majority of pores are secondary formations developed after the removal of bitumens from the intergrain space and the leaching of diagenetic calcite and dolomite. Porosity is as much as 7–10% in some rock strata. The reservoir property of Triassic rocks is mainly related to their fracturing caused by the brittleness of chert and phtanite layers. Such layers are cross-cut by fine (0.1–0.5 mm, up to 2 mm in rare cases) cracks, which are not usually traced in the adjacent (more clayey) layers of siliceous mudstones or bituminous siliceous mudstones. The majority of cracks (80–90%) are filled with the carbonaceous (presumably, bitumoid) matter.

ORE-FORMING ELEMENTS AND THEIR ASSOCIATION IN CARBONACEOUS SILICITES

The C_{org} content is 0.01–0.34% in ordinary (gray, dark gray, and olive green) Triassic cherts and 0.2–8.54% in carbonaceous beds of the phtanite member, whereas the average content is 1.06–1.09% in phtanites and 2.26–2.29% in clayey phtanites (Volokhin, 1985). Carbonaceous silicites of the phtanite member virtually do not contain carbonate carbon ($C_{car} < 0.05\%$). The content of total sulfur in them varies from 0.004 to 0.7% (average 0.14%), and the sulfide sulfur accounts for 83% of the total sulfur in the Ogorodnaya River section.

Relative to siliceous rocks in Sikhote Alin with a lower content of carbonaceous matter but a similar content of authigenic silica, carbonaceous silicites contain 2–3 times more V and 20–50 times more Mo and Ag (Volokhin, 1985, 1988). Maximal V concentrations are recorded in the Koreiskaya River section (810 ppm) and the Dal'negorsk section (1300 ppm). Contents of rare metals are characterized by significant regional variations in carbonaceous rocks of phtanite member (Table 3). Contents of other chemical elements in the carbonaceous layers of these sections are as follows (ppm): Zn up to 890, Cu up to 490, Ni up to 350, Mo up to 180, and Ag up to 10. Contents of elements in carbonaceous silicites of the phtanite member are as follows (ppm): Li 14–86, Rb 36–138, Cs 4–13, Tl 0.28–1.16, Sr 21–159, Ba 189–6315, Be 0.3–3.7, Sc 3–15, Y 1–30, La 4–21, Ce 9–38, Ge 0.7–11, Ga 6–147, Zr 3–125, Nb 4–27, Th 1.48–5.43, U 0.53–9.14, V 57–1300, Cr 10–120, Co 0.2–180, Ni 35–350, Cu 25–950, Zn 30–2800, Pb 5–300, Cd 0–6, Sn 0–30, Hg 0.01–0.15, Se 0.3–3, In 0.01–0.05, Bi 0.07–0.37, As 2–96 (up to 200 in rare cases), and Sb (0.01–30).

Regional variations of Ba are most significant in rocks of the phtanite member: from the background value of 127–379 ppm (Ogorodnaya River section) to 4000 ppm (Khor River section) and 6300 ppm (Gornaya River section). The average Ba content is 2990 ppm in the Anisian silicite of the Khor River section. The Ba content corresponds to strong anomaly in rocks of phtanite sections exposed in Khabarovsk and

to very strong (ore-grade) anomaly in sections at the Gornaya and Khor rivers (Yudovich and Ketris, 1994). The Ba anomaly is recorded in these sections in both carbonaceous and alternating low-carbonaceous silicites of the phtanite member. In the remaining sections, the Ba content is close to or even lower than its background value in carbonaceous cherts (Table 3).

Associations of elements in rocks based on the matrix of partial pair coefficients of correlation (without the consideration of SiO_2) are shown as structural schemes (Fig. 5) proposed by Tkachev and Yudovich (1975). Negative correlations between some elements are skipped for the sake of clearness.

In *clayey phtanites*, the terrigenous associations are represented by elements incorporated in structures of illite (Al–Mg–K) and feldspars (Ca–Na). Probably, the Ti–Pb group, which has strong relations with these two groups, also represents a terrigenous association in most cases. The majority of elements are combined into two slightly antagonistic groups: P–Cu–Cr–V–B–Mo–Ag and Fe^{2+} –Mn–Sn–Zn–Ni–Co. The first group, which includes phosphorus and elements more concentrated in carbonaceous silicites than in low-carbonaceous rocks, is formed as early as the sedimentation stage. The second group includes elements preferentially absorbed by manganese and iron hydroxides that are usually concentrated in authigenic sulfides in the reducing setting of diagenesis. Acid bitumens and humic acids are enriched in the same elements.

In *phtanites*, the Al–B pair (often with Ca) belongs to the silicate (mainly, terrigenous) association. Group Sn–Cr–Zn–Ni–Co–Ag includes some chalcophile elements of authigenic sulfides. Origin of groups Fe^{3+} –Ti–P and Cu–V is probably dualistic. They have strong correlation with both the terrigenous Al–B (illite) and authigenic sulfide associations. Group Fe^{2+} –Mg–Mn includes elements presumably related to the femic silicate admixture. This group shows negative correlation with other groups. The majority of microelements commonly concentrated in carbonaceous rocks lack correlation with C_{org} . Only Mo and, probably, Pb, which are associated with K and Na, show preferential correlation with carbon. Strong positive correlation of K and Na with C_{org} is almost always related to the illitic composition of the clay fraction and the positive correlation between contents of the DOM and clayey admixture in the silicites.

Associations of microelements in carbonaceous silicites reflect their preferential occurrence in mineral phases related to stages of diagenesis and catagenesis. Primary relations of these elements with the organic matter can appreciably be distorted notably by processes of the decomposition of organic matter, the partial decay of metalloorganic complexes, and the evacuation of highly mobile fractions of bitumens.

Table 3. Average contents of chemical elements in carbonaceous silicites of the phtanite member, ppm

Element	Bol'shaya Ulitka River	Gornaya River	Ogorodnaya River		Dal'negorsk		Shirokaya Pad Creek		Korei- skaya River	Khaba- rovsk	SCI
	PhQ (38)	CPh (6)	Ph (24)	CPh (40)	Ph (12)	CPh (9)	Ph (5)	CPh (3)	CPh (7)	CPh (15)	
Li	59	n.d.	25	27	29	52	33	n.d.	50	43	19
Rb	51	100	35	68	43	101	84	n.d.	46	50	47
Sr	19	84	25	38	29	47	27	n.d.	50	60.6	140
Ba	177	5100	176	241	392	393	600	n.d.	255	1040	740
Be	1.5	2.2	1.3	1.7	1.3	1.5	2.4	2.0	1.6	n.d.	2.2
B	21	71	68	154	41	49	155	237	47	113	87
Ga	21	21	11	12	5	18	33	30	8	14	14
Zr	n.d.	101	52	79	32	68	n.d.	130	n.d.	n.d.	120
Nb	9	18	14	16	9	12	18	19	17	8	17
Th	3.7	n.d.	1.9	3.8	2.0	3.2	4.5	n.d.	3.3	5.4	5
U	3.7	n.d.	2.7	4.3	0.6	5.5	0.7	n.d.	6.1	4.6	13
V	93	379	166	351	248	409	267	273	492	180	250
Cr	19	47	33	62	27	44	65	56	33	39	86
Co	50	8	3	1	18	5.2	13	n.d.	50	3.7	11
Ni	158	37	21	24	43	37	47	11	150	30	63
Cu	111	103	63	94	153	70	81	45	184	59	100
Zn	447	113	28	41	143	88	194	52	491	45	160
Pb	15	21	11	23	34	41	158	31	16	23	17
Mo	18	8	18	37	13	42	14	56	51	20	29
Sn	2.4	3.8	2.9	3.4	1.6	3.2	14	4.7	2.1	3.6	4.0
As	8	n.d.	18	17	52	47	31	n.d.	12	16	30
Sb	1.7	n.d.	2	1.7	4.5	4.1	16.5	n.d.	2.4	2	8.8
Ag	0.3	0.4	1.0	1.1	1.2	0.6	2.0	0.2	3.6	1.1	1.0
Au	n.d.	22	67	45	n.d.	28	23	27	45	n.d.	8.5
Pt	n.d.	2	26	1.3	n.d.	1	1.2	2.4	4	n.d.	n.d.
Pd	n.d.	5	1.5	<1	n.d.	12	4.4	7.5	23	n.d.	n.d.

Note: (Ph) Phtanite, (CPh) clayey phtanite, (PhQ) phtanite-quartzite, (SCI) subclarke value in carbonaceous siliceous rocks (Yudovich and Ketris, 1994); (n.d.) no data. The number of analyses is given in parentheses. Concentrations of elements corresponding to strong anomalies are shown in bold face. Concentrations of Au, Pt, and Pd are given in mppm.

DISTRIBUTION OF GOLD, PLATINUM, AND PALLADIUM IN ROCKS

Distribution of Au in Middle Triassic carbonaceous silicites of the phtanite member in the majority of sections does not differ from that in Lower-Middle Jurassic black siltstones of the same regions. In both cases, the modal Au content varies from 0.02 to 0.03 ppm (Fig. 6). The Au content is 1.5 times higher (0.03–0.04 ppm) in carbonaceous silicites of the Ogorodnaya River section.

In the Ogorodnaya River section, Au was detected by the ICP-MS method in 50% of carbonaceous and 60% of noncarbonaceous layers of the phtanite member. The maximal Au content in the carbonaceous silicites reaches 7.5 ppm (based on the fire assay analysis)

and 10 ppm (based on the ICP-MS method). In the non-carbonaceous silicites, the Au content is 0.68 ppm (ICP-MS method). Relative to the subclarke Au value in the siliceous lithotype of black shales (Table 3), the average Au concentration is 4–5 times higher in phtanites and 8 times higher in clayey phtanites. Such concentrations of Au represent a strong anomaly (Yudovich and Ketris, 1994).

The whole set of analyses of cherts from the phtanite member of the Ogorodnaya River section lack any significant correlation of Au with C_{org} and S. However, silicites containing more than 0.5% C_{org} show positive Au– C_{org} correlation (Fig. 7). Concentration of Au in some low-carbonaceous (and high-siliceous) layers of

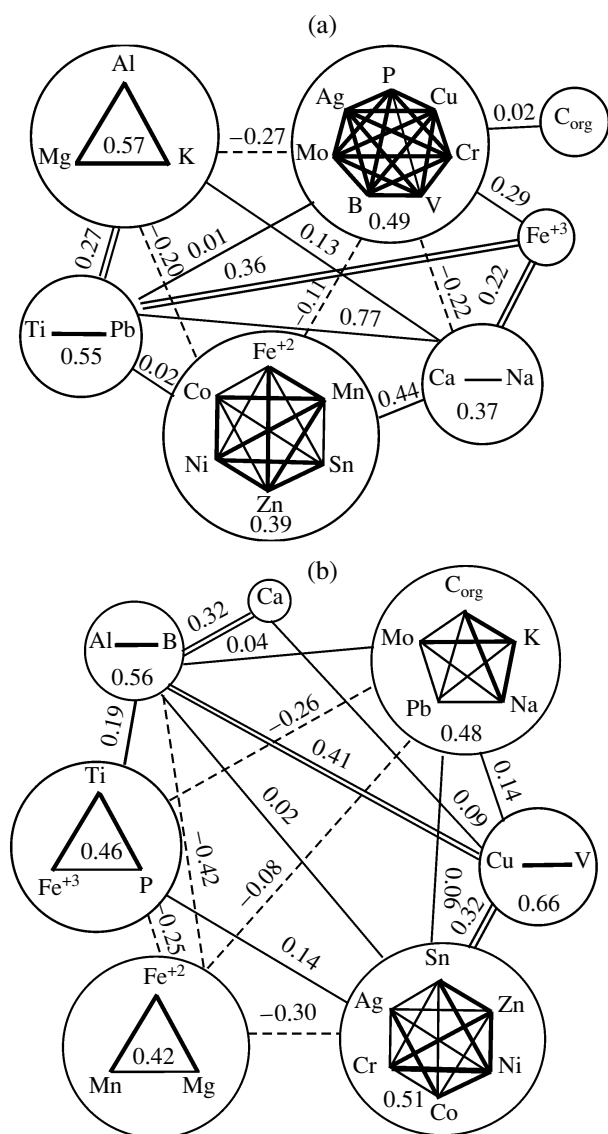


Fig. 5. Association of chemical elements in carbonaceous silicites of Sikhote Alin (Volokhin, 1998). (a) Clayey phthanites; (b) phthanites. Bold lines show positive correlation with the 95% confidence limit; dashed lines show negative correlation between antagonistic groups of elements.

the phthanite member can be related to its transport and redistribution by bitumens migrating along microfissures.

High concentrations of Pt were detected in some phthanite samples from the Ogorodnaya River section (Table 3). Based on the flame-atomic absorption method, contents of Pt and Pd are 0.13 and 0.014 ppm, respectively. Based on the ICP-MS method, which uses small weighed portions, contents of Pt and Pd are up to 3.3 and 8.3 ppm, respectively. Such discrepancies can be related to the loss of a significant amount of platinum group elements during the fire assay analysis, the diversity of their compounds, and the complex matrix

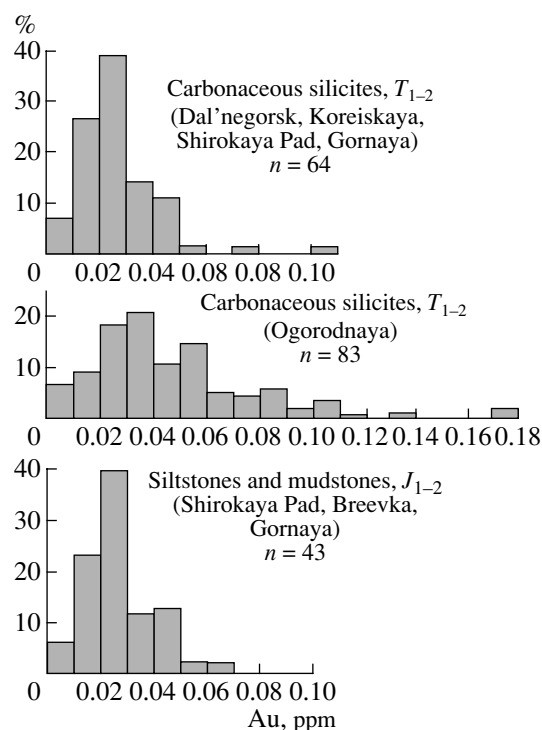


Fig. 6. Distribution of Au in Triassic and Jurassic carbonaceous rocks of Sikhote Alin (based on fire assay-atomic absorption analyses).

composition of carbonaceous rocks (Distler et al., 1996; Ermolaev et al., 1999; Kurskii and Mitkin, 2003; Mitkin et al., 2000; Razvozzhaeva et al., 2002; Varshal et al., 1994). Despite the significant discrepancy of results yielded by these methods, we believe that rocks of the phthanite member in the Ogorodnaya River area can include ore-grade concentrations of both Au and platinum group elements.

DISTRIBUTION OF METALS IN FRACTIONS OF THE DISSEMINATED ORGANIC MATTER

In clayey phthanites of the Voronezh-2 section (Khabarovsk area), neutral (chloroform) bitumens are enriched in Mn, Ni, and Co, while acid (alcohol-benzene) bitumens are enriched in Mn, Ni, Co, Pb, and Zn (Table 4). The total content of these metals in the bitumen fraction is higher than in the rocks. Sn and Mo are absent in the bitumoids and concentrated in the humic fraction. This fraction is also enriched in V, Cr, and Ag. Au is absent in both rocks and their organic fractions.

In samples from the Ogorodnaya River section (N-170d, N-153d, and N-155d₁), bitumen fractions are enriched (relative to the rocks) in Mn, Cu, Ni, Co, Pb, and Zn (Table 5). The bitumen fractions lack any correlation with V, Cr, Mo, and Ag. The humic fraction shows anomalously high contents of Sn (samples N-170d and N-153d), V, Cr, and Mo (sample N-170d). Au is concentrated in the bonded alcohol-benzene (BAB) bitu-

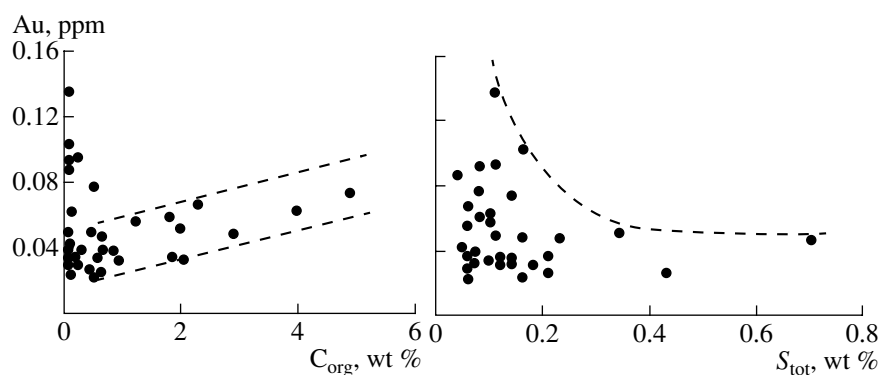


Fig. 7. Au vs. C_{org} and S concentrations in carbonaceous silicites of the Ogorodnaya River section.

mens and the insoluble residue of the DOM. In the free alcohol–benzene bitumens of sample N-155d₁, the As content is 10 times higher than its bulk content in rocks.

Table 6 shows that bitumen fractions from carbonaceous silicites in the vicinity of Dal'negorsk are significantly enriched in Mn, Ni, Co, Zn, Cu, and Ag, as well as V and Mo in some samples. Maximum contents of metals in the free alcohol–benzene bitumens are as follows (%): Pb 0.02, Zn and Ni 0.3, and Cu 1–3. Relative to the rocks, chloroform bitumens are enriched in Sn, Pb, Zn, Cu, and Ni. At the same time, they are depleted in V and Co. Ag and Au concentrations are usually increased in the alcohol and alcohol–benzene extracts of chloroform bitumens. The insoluble residue of the DOM is usually characterized by low concentrations of metals. Elevated concentrations of Cu, Ni, and Co in the insoluble residue of samples R-54 and R-145 are probably related to abundance of the fine sulfide

fraction, which is difficult to separate from the insoluble residue of the DOM. Concentration of Pb, Zn, Cu, Ni, and Cu in bitumens of these carbonaceous silicites is consistent with the common metallogenic specialization of the Dal'negorsk ore district.

ISOTOPIC CHARACTERISTICS OF CARBON IN PHTANITES

The carbon isotopic composition is commonly used to determine the marine or continental origin of the DOM in sediments and rocks. The carbon isotopic composition in the OM of the phtanite member varies from –27.3 to –30.2‰ PDB (Table 7). These values are identical to those for Paleozoic bitumens and oil, as well as the continental plant at middle and tropical latitudes (Deines, 1980; Galimov, 1973; *Organicheskaya...*, 1974). Carbon of marine plankton in waters at low and middle latitudes is enriched in the

Table 4. Contents of microelements in rocks and DOM fractions of the clayey phtanite in the Voronezh-2 Settlement section (vicinity of Khabarovsk), ppm

Element	Sample Kh-70/78						Sample Kh-73					
	Rock	CB	ABB	BAB	HA	IR	Rock	CB	ABB	BAB	HA	IR
Fe, %	3.35	–	≤0.1	2.5	–	n.d.	0.90	–	≤0.1	5.0	–	n.d.
Mn	200	6000	1000	2000	80	50	100	6000	–	1000	80	30
Sn	3	–	–	–	10	–	4	–	–	–	30	–
Pb	20	–	120	–	10	10	30	48	194	–	20	20
Zn	100	–	70	130	–	–	100	–	60	70	–	–
Cu	40	–	4	–	60	10	40	–	5	–	100	10
Ni	50	123	366	316	70	–	60	140	399	325	60	20
Co	–	6	109	72	–	–	–	74	139	69	–	–
Cr	100	–	39	–	100	40	200	–	49	–	500	10
V	400	n.d.	n.d.	n.d.	400	20	~600	n.d.	n.d.	n.d.	200	30
Mo	60	–	–	–	1000	5	80	–	–	–	200	5
Ag	0.3	–	–	tr.	0.2	0.3	0.3	–	tr.	–	0.7	0.1

Note: (–) Below the detection limit; (n.d.) no data; (tr.) traces. See Table 1 for designations of fractions.

Table 5. Contents of chemical elements in rocks and organic matter of carbonaceous silicites in the Ogorodnaya River section, ppm

Element	Sample N-170d						Sample N-153d			Sample N-155d ₁			Sample N-153d/ N-155d ₁	
	Rock	CB	ABB	BAB	HA	IR	Rock	BAB	HA	Rock	BAB	HA	ABB	IR
Fe, %	1.36	0.4	1.3	2.3	–	0.6	4.6	1.0	0.01	2.1	1.1	1.0	1.0	0.1
Ti	5000	–	–	n.d.	–	6000	3060	1	4	3480	1	3	5	200
Mn	80	4000	3000	300	80	50	49	700	2	53	30	2	700	10
Sn	3	–	–	–	30	–	2	4	500	3	3	–	10	–
Pb	18	–	420	–	20	30	7	10	–	17	3	–	20	4
Zn	20	–	220	30	100	–	20	70	3	3.2	30	–	100	50
Cu	29	–	100	50	20	20	104	300	5	105	100	3	300	4
Ni	33	164	163	401	60	20	19	50	–	5	4	–	30	–
Co	1	530	132	80	–	–	3	20	–	0.8	–	–	2	–
Cr	65	–	250	–	500	10	86	20	–	81	5	–	10	–
V	350	–	120	310	500	20	355	300	95	255	300	–	10	45
Mo	76	–	–	–	300	5	30	20	–	12	5	–	1	–
Gd	–	0.45	1	–	–	–	4	4	1	3	5	–	1	–
Zr	30	n.d.	n.d.	n.d.	40	–	20	–	5	40	4	–	3	–
Be	1.4	n.d.	n.d.	n.d.	4	–	5	1	–	7	3	–	1	–
As	n.d.	n.d.	n.d.	n.d.	n.d.	–	32	–	–	30	–	–	300	–
Ag	1.4	–	–	–	0.3	0.3	0.72	1	–	0.97	0.3	–	0.6	1
Au	–	–	–	–	–	–	–	1	–	1	–	–	–	10

Note: Column N-153d/N-155d₁ presents compositions of combined fractions of samples N-153d and N-155d₁; chloroform bitumens in samples N-153d and N-155d₁ contains a small amount of Fe, Cd, Zn, Ni, and Cr; (–) below the detection limit.

heavy isotope ^{13}C ($\delta^{13}\text{C}$ more than -24‰) as compared to carbon of the continental OM (Calvert and Fontugne, 1987; Fontugne and Duplessy, 1978; Simoneit, 1986). Plankton dwelling in cold waters (approximately 0°C) of high-latitude zones in the South Atlantic has a lower $\delta^{13}\text{C}$ value (-27.9‰) because of a higher solubility of atmospheric carbon dioxide in cold waters (Galimov, 1973). Late Holocene sapropelic sediments of the Black Sea and lipids of modern sediments on the insular slope of Japan have similar but generally higher $\delta^{13}\text{C}$ values ranging from -23 to -29‰ (Calvert and Fontugne, 1987; Shirinskii et al., 1974). Dia- and catagenetic alterations of organic matter decrease the $\delta^{13}\text{C}$ value in lipids due to the partial loss of carbon connected with heteroatoms, in particular, ^{13}C of carboxyl groups (Galimov, 1973; Galimov and Kodina, 1982).

Among carbonaceous rocks of the phtanite member, the highest $\delta^{13}\text{C}$ value (-27.3‰) is recorded in the OM of clayey phtanites from Dal'negorsk (Table 7) characterized by the low coefficient of bituminosity. Concentration of ^{13}C in these rocks can be caused by the loss of a part of highly mobile neutral bitumens owing to the thermal impact of basaltic sill in the section. In bitumen fractions, minimal $\delta^{13}\text{C}$ values are typical of hydrocarbons and low-polar resins concentrated in the CB frac-

tion, while asphaltenes and polar resins are commonly depleted in the light isotope ^{12}C (Galimov and Kodina, 1982).

PALEOGEOGRAPHIC FACTORS OF METAL CONCENTRATION IN THE PHTANITE MEMBER

In the modern World Ocean, facies most favorable for the OM accumulation are represented by the terrigenous, siliceous, and carbonate sediments mainly confined to highly bioproductive continental-margin and intracontinental basins, submarine margins of continents, and some deep-sea trenches (Pelet, 1985; Romankevich, 1977). The amount of organic carbon accumulated in marginal and intracontinental seas accounts for approximately 20–30% the total reserve of organic carbon in modern sediments of the World Ocean. Accumulation of metals in sapropelic sediments is promoted by the anoxic condition and hydrosulfuric contamination of waters. Such environment can appear and exist for a long time in basins of two basically different paleogeographic settings (Arthur and Schlanger, 1979; Dean et al., 1986; Degens and Stoffers, 1976; Graciansky et al., 1986; Pratt et al., 1986; Schlanger and Jenkyns, 1976; Simoneit, 1983, 1986).

Table 6. Contents of chemical elements (ppm) in carbonaceous silicites and organic fractions (vicinity of Dal'negorsk)

Sample R-50		Sample R-54											
Element	Rock	CB		ABB	BAB	IR	Rock	CB			ABB	BAB	IR
		PE	AB					PE	A	AB			
Fe, %	1.03*	~1.3	~0.6	>1.3	>1.3	~1.0	1.2*	~0.3	~0.3	~1.2	>6	>6	>6
Mn	230	9000	2000	2500	9000	30	470	4000	800	4000	5000	10000	400
Ti	100	500	500	200	600	80	240	500	500	600	100	300	450
Zr	30	30	40	10	45	30	100	40	30	100	20	30	300
V	350	20	20	450	—	—	250	—	10	40	450	5	5
Ni	80	10	80	200	750	20	60	10	30	200	700	1500	100
Co	10	—	—	450	30	30	3	—	—	3	1000	150	150
Cu	100	100	200	3000	500	30	40	80	100	300	3000	400	70
Pb	20	10	100	30	—	—	10	20	30	60	100	50	50
Zn	—	450	200	300	—	—	—	100	100	300	1200	—	—
Sn	5	20	100	5	60	—	5	10	60	70	—	60	—
Mo	3	1	2	1	1	1	10	2	1	3	3	150	150
W	—	—	60	—	—	—	—	—	60	—	—	—	—
Ag	0.4	0.3	4	0.6	0.4	0.5	0.2	0.1	2	2	0.6	0.3	0.8
Au	—	—	10	—	—	—	—	—	10	<10	—	—	—

Table 6. (Contd.)

Sample R-102																
Element	Rock	CB				ABB	BAB	IR	Rock	CB				ABB	BAB	IR
		PE	A	AB	PE					A	AB					
Fe, %	0.94*	~0.9	~0.3	~4	>5	>5	>5	>5	1.3*	≥6	~0.3	~0.3	>6	>6	>6	0.6
Mn	500	4000	800	4000	>10000	>10000	300	300	300	4000	1000	3000	600	10000	10000	—
Ti	80	600	100	600	10	300	300	1000	500	300	300	500	60	500	300	300
Zr	60	60	40	60	80	30	80	80	50	40	40	30	—	20	60	60
V	600	20	20	50	100	5	5	150	—	—	10	10	100	—	5	5
Ni	20	150	40	200	700	3000	50	30	100	30	30	60	200	450	40	40
Co	6	3	—	3	450	10	10	3	4	—	—	—	6	—	—	—
Cu	40	300	100	300	8000	400	60	40	200	100	100	200	10000	500	5	5
Pb	5	30	80	200	50	5	5	10	30	40	40	200	—	—	—	—
Zn	—	100	50	800	1000	—	—	—	300	2000	500	500	1000	—	—	—
Sn	—	40	80	50	—	40	10	5	60	60	60	40	5	30	—	—
Mo	2	1	2	3	—	2	2	5	3	2	2	2	—	—	—	—
W	—	—	100	60	—	—	—	—	60	—	—	60	—	—	—	—
Ag	—	0.2	2	1	10	0.3	0.3	0.2	0.4	5	5	5	5	0.1	—	—
Au	—	<10	—	10	—	—	—	—	—	—	40	10	—	—	—	—

Table 6. (Contd.)

Element	Sample R-120						Sample R-145							
	Rock	CB			ABB	BAB	IR	Rock	CB			ABB	BAB	IR
		PE	A	AB					PE	A	AB			
Fe, %	5.52*	~10	~0.5	~0.5	>10	>10	~1	1.85*	~1.5	~0.8	~0.4	~2	~2	~2
Mn	4600	10000	2000	500	10000	10000	–	500	2000	500	800	10000	10000	700
Ti	2940	600	300	500	30000	30000	80	60	600	400	500	30000	300	450
Zr	200	30	40	40	40	40	10	100	60	40	40	30	30	300
V	400	15	10	–	30	30	–	80	20	30	10	400	20	20
Ni	200	5	50	40	400	400	5	100	60	100	80	600	1000	200
Co	–	5	–	–	75	75	–	–	2	3	–	500	30	300
Cu	80	200	100	100	30000	30000	5	60	100	200	100	30000	500	100
Pb	20	20	30	50	–	–	–	60	20	60	100	200	40	40
Zn	100	300	200	400	–	–	–	100	100	300	700	1000	100	100
Sn	–	5	3	30	15	15	–	5	50	50	30	40	40	–
Mo	4	1	–	–	–	–	–	40	3	3	2	20	150	150
W	–	–	–	–	–	–	–	–	–	–	60	–	–	–
Ag	0.6	3	1–3	3	2	2	0.2	0.4	0.2	4	5	0.2	0.3	10
Au	–	–	–	–	–	–	–	–	<10	10	–	–	–	–

Note: Chloroform bitumen (CB) fractions: (PE) petrol etheric, (A) alcohol, (AB) alcohol–benzene (1 : 1); (ABB) additionally extracted free alcohol–benzene (1 : 2) fraction; (BAB) additionally extracted bonded alcohol–benzene (1 : 2) fraction; (IR) insoluble residue; (–) below the detection limit. Based on approximate quantitative spectral analysis performed at the Far East Geological Institute, Vladivostok (T.V. Sverkunova and V.I. Sechenskaya, analysts). *Chemical analysis data.

Table 7. Contents of silica and organic carbon and the isotopic composition of carbon in Lower–Middle Triassic carbonaceous silicites of Sikhote Alin

Sample no.	Section location	Rock	SiO ₂ , %	C _{org} , %	δ ¹³ C _{PDB} , ‰
I-15	Mouth of the Dal'nyaya River	Ph	90.15	2.96	–30.2
I-16	The same	Ph	85.48	6.04	–30.0
I-17	"	CPh	88.12	3.95	–27.6
Go-17	Upper reaches of the Gornaya River	CPh	72.94	1.32	–30.1
N-153	Right bank of the Ussuri River near the mouth of the Ogorodnaya River	CPh	78.18	2.21	–27.7
N-155	The same	Ph	88.25	1.59	–27.9
N-169	"	Ph	87.45	1.99	–27.7
R-102	Rudnaya River (Dal'negorsk)	CPh	87.10	1.42	–27.3
R-120	The same	CPh	68.60	5.85	–27.3
S-156	Middle course of the Koreiskaya River	CPh	74.46	8.54	–29.0
S-159	The same	CPh	78.01	5.58	–27.9

Note: (Ph) Phthanite; (CPh) clayey phthanite.

The first paleogeographic environment is represented by isolated (Tanganyika, Bogoria, and other lakes) and semiisolated (Black Sea) stagnating basins with prominent density stratification of water. Anoxia in them is caused by the intense blooming of plankton and bacterial decay of OM in sediments. This process is accompanied by the reduction of sulfates, the removal of H₂S from interstitial waters, and its dispersion owing to the slow convection of water (Kholodov, 2002; Strakhov, 1976). These basins are divided into structures with stable and instable H₂S contamination. The stable type is represented by the Black Sea and the Cariaco Basin (Caribbean Sea). The unstable type is represented by the Gotland, Bornholm, and Landsort basins (Baltic Sea), Saanich Inlet (British Columbia), and several estuaries and fiords with different thicknesses and volumes of the contaminated watermass (Kholodov, 2002).

The second paleogeographic environment is related to highly-productive zones of oceanic upwellings, where anoxic conditions are created by waters of the oxygen minimum zone that embraces the outer shelf, continental slope, or slopes of topographic rises (Arthur and Schlanger, 1979; Schopf, 1984; Simoneit, 1983, 1986). Anoxic basins (~0.5 × 10⁶ km²) and upwelling zones (~0.14% of the World Ocean area) occupy approximately equal areas, but the amount of OM accumulated in sediments of the upwelling zones is 20 times more relative to the anoxic basins (Baturin, 1983).

It has been established that anoxic conditions embraced large areas in some geological epochs (e.g., the Cenomanian/Turonian boundary). This fact promoted the concept of global anoxic events (Brumsack, 1986; Graciansky et al., 1986). A prolonged (~10-Ma-long) "superanoxia" of ocean responsible for the extinction of a large group of marine organisms (50–

57% of families and 70% of genera of invertebrates) is assumed at the Permian/Triassic boundary (Isozaki, 1994, 1997; Hallam, 1994). According to (Bragin, 2000), this global anoxia was responsible for the deposition of carbonaceous sediments of the phthanite member.

Reconstruction of paleographic settings of the phthanite member formation would make it possible to more accurately forecast the distribution of organic matter in the rock member and its productivity in terms of rare and noble metals. Small semiisolated marine basins and lakes are characterized by the centripetal distribution of OM with the thickening of carbonaceous layers and increase in the OM concentration toward depocenters of basins (Huc, 1988). Concentrations of C_{org} and metals in sapropel of anoxic basins are fostered by lower sedimentation rate relative to upwelling zones (Brumsack, 1986; Mangini and Dominik, 1979). Other conditions being equal, anoxic basins can play a more significant role than upwelling zones as accumulators of several chemical elements. Large basins of the Black Sea type with the hydrosulfuric contamination of large volumes of water can retain huge masses of dissolved metals that can be equal to their reserves in giant ore deposits (Kholodov, 2002; Strakhov, 1976). Concentrations of Si, Fe, Mn, P, Ni, Co, N, and other elements in the H₂S-contaminated waters can be tens to tens of thousand times higher than their clarke values in the aerated seawater (Kholodov, 2002).

In the Triassic siliceous formation, the phthanite member is not universally developed but mainly confined to the siliceous facies and adjacent areas with the carbonate–siliceous facies (Fig. 2). This pattern is more consistent with the upwelling model of the carbonaceous member formation. Age of the carbonaceous member in the studied section is estimated as the upper

Olenekian–middle Anisian (more often, middle Anisian); i.e., this member is appreciably younger than its counterparts in Japan, where the section is dominated by Lower Triassic carbonaceous shales and the anoxia lasted from the Longtanian age of Late Permian to the Anisian age of the Middle Triassic (Isozaki, 1994). However, a significant part of the carbonate–siliceous facies deposited in bathypelagic setting of the marginal sea can be buried under the Jurassic–Early Cretaceous member (Volkhin et al., 2003). Data on the structure of deep-sea facies of the Triassic formation are obviously insufficient. Therefore, we do not rule out the possibility of phtanite member formation in an anoxic basin. The Sikhote Alin Basin in the Triassic incorporated several wedge-shaped troughs widening in the northeastern direction (Likht, 1993). The basin could hardly be more than 1.5–2 times wider than the present-day fold zone. The maximal width could be 300–360 km in the southern area extending from the Arsen'ev fault to the Pribrezhnaya zone (Volkhin et al., 2003). The presence of barrier marked by Late Paleozoic and Triassic calcareous reefs of the Pribrezhnaya zone uplift suggests the existence of a semiisolated anoxic basin. The paleogeographic setting of the studied region shows certain similarities with Paleozoic seas with vanadiferous shales. For example, Cambrian basins in Karatau and Ulutau represented narrow but extended straits separated from the open sea by archipelagos or submarine barriers (Kholodov, 1972). Model of the deposition of sediments in narrow troughs separated from the open sea by barriers suggests the universal development of phtanite member (Fig. 1), its thickening, and enrichment with organic matter under Jurassic–Lower Cretaceous members of the East Sikhote Alin zone.

The phtanite member formation coincides with the initial phase of the global sealevel rise designated as megacycle Upper Absaroka A in (Haq et al., 1987) and the initial phase of transgression. The confinement of bituminous facies to the onset of transgressive cycles was previously reported for Cretaceous, Jurassic, and Triassic members of some epicontinental seas (Hallam, 1981, 1994; Naidin et al., 1986). The flooding of reservoirs is commonly followed by vigorous blooming of plankton owing to the transfer of biogenic elements from the soil to water. According to Lisitsyn et al. (1980), this process could be developed in a global scale during the Cretaceous transgression.

Average contents of Ni, Co, Zn, Ba, Cr, and Mo in Triassic carbonaceous cherts are similar to those in Holocene sapropel sediments of the Gulf of California (Brumsack, 1986). The Sr content is considerably lower, whereas contents of V, Cu, and Ag are appreciably higher than in sapropel sediments of this gulf. In Cenomanian/Turonian black shales of Morocco, the Sr content is similar to that carbonaceous silicites of northern Sikhote Alin (Khabarovsk area section), while the V content is analogous to that in phtanites of southern Sikhote Alin (Koreiskaya River section). According

to (Brumsack, 1986), the Zn content in sapropel sediments of anoxic basins (Holocene of the Black Sea; Cenomanian–Turonian of the Cape Verde basin, Atlantic Ocean) is usually as much as 0.1%. This value is higher than the Zn content in carbonaceous silicites of Sikhote Alin. The Ag content is analogous in these regions. In Precambrian and Paleozoic black shales from different regions, concentrations of Zn, V, U, Mo, Cu, and Ag are often one order of magnitude higher than those in Triassic carbonaceous silicites of Sikhote Alin (Kholodov, 1973; Martikhaeva, 2000; McKelvey et al., 1986; *Metallogeniya*..., 1978; Yudovich and Ketris, 1994). The modern erosion level probably shows only marginal parts of the phtanite member with carbonaceous siliceous rocks characterized by moderate concentrations of C, Mn, U, Pb, Zn, Ni, and Mo. The deeper-water sediments of the phtanite member hidden beneath Upper Triassic and Jurassic–Early Cretaceous rocks of the eastern Sikhote Alin flysch zone could more serve as generators of hydrocarbons and reserves of metals (Sn, Pb, Zn, Ag, and Au) in endogenous ores formed at the late (Cretaceous–Paleogene) tectonomagmatic stage of evolution of the study region.

CONCLUSIONS

Study of Triassic carbonaceous silicites of Sikhote Alin fills the gap in geological and mineralogical–geochemical data on unmetamorphosed Early Mesozoic black shales of the Russian Far East. We obtained first data on the composition and nature of OM in carbonaceous silicites of the phtanite member, concentrations of Au and Pt in these rocks, and contents of metals in the DOM fractions.

In Triassic carbonaceous silicites of Sikhote Alin, concentrations of OM and ore elements are strongly variable and generally low. Such concentrations could appear at stages of sedimentation and diagenesis. They are comparable with concentrations in sapropel sediments in the present-day upwelling zones, such as the Gulf of California. Anomalously high concentrations of chemical elements are recorded both in rocks subjected to the local thermal metamorphism and recrystallization (e.g., Zn, Ni, and Co in the Bol'shaya Ulitka River area; Sn, Pb, and B in the Shirokaya Pad Creek area) and in silicites not subjected to appreciable thermal impact, e.g., V, Co, Ni, Cu, Zn, Ag, and Au in the Koreiskaya River section. Barium anomaly is recorded in rocks of the phtanite member in the Gornaya River, Khabarovsk, and Khor River sections. In other sections of the phtanite member, the Ba content is similar to the Clarke value in carbonaceous silicites and the Ba content in sapropel sediments of modern upwelling zones (e.g., sediments of the Gulf of California).

In zones located beyond the thermal impact of granitoids, organic matter of carbonaceous silicites includes humic substance and is characterized by moderate contents of chloroform bitumens. It contains quinones and differs from the brown coal standard humic acid by

higher contents of hydrocarbons, ether compounds, and organic sulfides. The carbon isotopic composition is identical to that of bitumens and Paleozoic oils in many regions of the world. The OM composition in carbonaceous silicites in the majority of phtanite sections matches the composition in the primary (marine) sapropel matter subjected to alteration not higher than the stage of middle mesocatagenesis. In organic fractions, the major part of metals (Fe, Mn, Cu, Ni, Co, Zn, Ag, and Au) is concentrated in acid bitumoids (mainly in asphaltenes and asphaltene acids). Other metals (V, Sn, Cr, and Mo) are accumulated in the humic fraction. Anomalous concentrations of Ag and Au in some low-carbonaceous rocks of the phtanite member are presumably related to the redistribution of metals or their additional input in the course of catagenesis.

According to fire assay with AAS completion, the Au content in carbonaceous silicites of the phtanite member is higher than the Clarke value in black shales. Contents of Au and Pt in the Ogorodnaya River section are anomalously high. Therefore, the Au and Pt potential of phtanite member in this region should be studied in detail. We should also investigate the possibility of Au and Pt concentration in low-carbonaceous silicites adjacent to the phtanite member.

ACKNOWLEDGMENTS

The authors thank L.I. Azarova, T.K. Babova, I.V. Borovik, A.S. Bukatin, V.N. Zalevskaya, T.A. Ivanova, V.I. Kiselev, L.A. Kozlova, E.A. Nozdachev, V.V. Sattarova, and V.I. Sechenskaya (Analytical Center of the Far East Geological Institute, Vladivostok) for the RFA, ICP-AES, ICP-MS, and assay-atomic absorption analyses; T.I. Velivetskaya and V.M. Avchenko (isotopic analyses); and S.P. Slavkina (determinations of C_{org} and S). We are grateful to O.A. Kiseleva for the extraction of bitumen fractions; V.F. Zanina (Far East Geological Institute) for the determination of metals in the bitumen fractions; A.V. Kurike and V.P. Glazunova (Pacific Institute of Bioorganic Chemistry, Far East Division, Russian Academy of Sciences) for the determination of UV and IR spectra of aqueous-alkaline spectra of OM; and O.V. Chudaev and Akihito Kuno (Tokyo University) for the replicate ICP-MS determinations of 30 chemical elements in 15 samples of carbonaceous rocks. We are also grateful to S.A. Schcheka and L.P. Plyusnina for methodical recommendations and critical remarks during the preparation of manuscript.

This work was supported by the Russian Foundation for Basic Research (project no. 04-05-65269) and the Far East Division of the Russian Academy of Sciences in collaboration with the Russian Foundation for Basic Research (project no. 06-05-96106).

REFERENCES

- Ankinovich, S.G. and Ankinovich, E.A., Conditions of the Deposition and Formation of Lower Paleozoic Metalliferous Shales in Southern Kazakhstan, in *Geokhimiya osadochnykh porod i rud* (Geochemistry of Sedimentary Rocks and Ores), Moscow: Nauka, 1968, pp. 356–375.
- Applied Infrared Spectroscopy*, Kendall, D., Ed., New York: Chapman and Hall, 1966. Translated under the title *Prikladnaya infrakrasnaya spektroskopiya*, Moscow: Mir, 1970, pp. 172–189.
- Arifulov, Ch.Kh., Gold Deposits in Black Shales in Various Geological Settings, *Rudy Metally*, 2005, no. 2, pp. 9–19.
- Arthur, M.A. and Schlanger, S.O., Middle Cretaceous “Oceanic Anoxic Events” as Causal Factors in Development of Reef-Reservoired Giant Oil Fields, *Am. Assoc. Petrol. Geol.*, 1979, vol. 63, pp. 870–885.
- Baskina, V.A., Tomson, I.N., and Arakelyants, M.M., Early Cretaceous Alkaline Basic Rocks and Carbonaceous Metasomatites of Primorye, *Dokl. Akad. Nauk*, 2004, vol. 398, no. 5, pp. 652–655 [*Dokl. Earth Sci.* (Engl. Transl.), 2004, vol. 399, no. 8, pp. 1051–1054].
- Baturin, G.N., Some Unique Sedimentological and Geochemical Features of Deposits in Coastal Upwelling Regions, in *Coastal Upwelling: Its Sediment Records: Part B. NATO Conference Series IV*, Thiede, J. and Suess, E., Eds., New York, London: Plenum Press, 1983, pp. 11–27.
- Bellamy, L.J., *The IR Spectra of Complicated Molecules*, London, 1958. Translated under the title *Infrakrasnye spektry slozhnykh molekul*, Moscow: Inostran. Literat., 1963.
- Bragin, N.Yu., *Radiolyarii i nizhnemezozoiskie tolshchi Vostoka SSSR* (Radiolarians and Lower Mesozoic Sequences of the Eastern USSR), Moscow: Nauka, 1991.
- Bragin, N.Yu., The Permian–Triassic Crisis of Biosphere as Manifested in the Paleo-Pacific Deep-Water Sequences, *Stratigr. Geol. Korrelyatsiya*, 2000, vol. 8, no. 3, pp. 93–99 [*Stratigr. Geol. Correlation* (Engl. Transl.), 2000, vol. 8, no. 3, pp. 232–242].
- Brumsack, H.-J., Trace Metal Accumulation in Black Shales from the Cenomanian/Turonian Boundary Event, in *Lecture Notes in Earth Sciences: Vol. 8. Global Bio-Events*, Walliser, O., Ed., Berlin, Heidelberg: Springer, 1986, pp. 337–343.
- Burii, G.I., *Konodonty i stratigrafiya triasa Sikhote-Alinya* (Conodonts and Triassic Stratigraphy of the Sikhote Alin Region), Vladivostok: Dalnevost. Otd. Akad. Nauk SSSR, 1989.
- Buryak, V.A., Formation of Gold Mineralization in Carbonaceous Sequences, *Izv. Akad. Nauk SSSR, Ser. Geol.*, 1987, no. 12, pp. 94–105.
- Buryak, V.A., Problem of the Genesis of Black Shale Sequences and Gold Mineralization in Them, *Tikhookean. Geol.*, 2000, vol. 19, no. 1, pp. 118–129.
- Calvert, S.E. and Fontugne, M.R., Stable Carbon Isotopic Evidence for the Marine Origin of the Organic Matter in the Holocene Black Sea Sapropel, *Chem. Geol.*, 1987, no. 66, pp. 315–322.
- Chernyshov, N.M., Gold–PGM Mineralization in Precambrian Black Shale Sequences and Metasomatic Rocks of the Voronezh Crystalline Massif as the Basis for the Development of Noble Metal Resource Base in Central Russia in XXI Century, in *Platina Rossii* (Platinum of Russia), Moscow: ZAO Geoinformmark, 1999, vol. 3, book 2, pp. 226–241.

- Coveney, R.M. and Pašava, J., Origins of Au–Pt–Pd–Bearing Ni–Mo–As–(Zn) Deposits Hosted by Chinese Black Shales, in *Mineral Deposit Research: Meeting the Global Challenge (Proc. 8th Biennial SGA Meeting, Beijing, 2005)*, Berlin: Springer, 2005, pp. 101–102.
- Coveney, R.M., Leventhal, J.S., Glascock, M.D., et al., Origins of Metals and Organic Matter in the Mecca Quarry Shale Member and Stratigraphically Equivalent Beds across the Midwest, *Econ. Geol.*, 1987, vol. 82, pp. 915–933.
- Dean, W.E., Arthur, M.A., and Claypool, G.E., Depletion of ^{13}C in Cretaceous Marine Organic Matter: Source, Diagenetic, or Environmental Signal?, *Mar. Geol.*, 1986, no. 70, pp. 119–157.
- Degens, E.T and Stoffers, P., Stratified Waters as a Key to the Past, *Nature*, 1976, no. 263, pp. 22–27.
- Deines, P., The Isotopic Composition of Reduced Organic Carbon, in *Handbook of Environmental Isotope Geochemistry: Vol. I, The Terrestrial Environment*, Fritz, P. and Fontes, J.Ch., Eds., Amsterdam: Elsevier, 1980, pp. 329–406.
- Distler, V.V., Mitrofanov, G.L., Nemerov, V.K., et al., Modes of Occurrence of the Platinum Group Elements and Their Origin in the Sukhoi Log Gold Deposit (Russia), *Geol. Rudn. Mestorozhd.*, 1996, vol. 38, no. 6, pp. 467–484 [*Geol. Ore Deposits* (Engl. Transl.)], 1996, vol. 38, no. 6, pp. 413–428].
- Ermolaev, N.P. and Sozinov, N.A., *Stratiformnoe rudoobrazovanie v chernykh slantsakh* (Stratiform Ore Formation in Black Shales), Moscow: Nauka, 1986.
- Ermolaev, N.P., Sozinov, N.A., Chinenov, V.A., et al., Metalliferous Black Shales as a New Prospective Source of Platinum Group Elements, in *Platina Rossii. Problemy razvitiya MSB platinovykh metallov v XXI veke* (Platinum of Russia: Development of the Mineral Resource Base of Platinum Group Elements in XXI Century), Moscow: ZAO Geoinformmark, 1999, vol. 3, book 2, pp. 212–215.
- Fontugne, M.R. and Duplessy, J.C., Carbon Isotopic Ratio of Marine Plankton Related to Water Masses, *Earth Planet. Sci. Lett.*, 1978, vol. 41, pp. 365–371.
- Galimov, E.M., *Izotopy ugleroda v neftegazovoi geologii* (Carbon Isotopes in Oil and Gas Geology), Moscow: Nedra, 1973.
- Galimov, E.M. and Kodina, L.A., *Issledovanie organicheskogo veshchestva i gazov v osadochnykh tolshchakh Mirovogo okeana* (Study of Organic Matter and Gases in Sedimentary Sequences of the World Ocean), Moscow: Nauka, 1982.
- Gorzhhevskiy, D.I., On Role of Organic Matter in Ore Formation, *Int. Geol. Rev.*, 1987, vol. 29, no. 2, pp. 207–217.
- Graciansky, P.C., Deroo, G., Herbin, J.P., et al., Ocean-Wide Stagnation Episodes in the Late Cretaceous, *Geol. Rundsch.*, 1986, vol. 75/1, pp. 17–41.
- Gurskaya, L.I., Makar'ev, L.B., Savitskii, A.V., et al., Perspectives of Commercial Platinum Mineralization in Black Shale Sequences (in Connection with the Creation of a New Mineral Resource Base of Platinum Minerals in Russia), in *Platina Rossii. Problemy razvitiya MSB platinovykh metallov v XXI veke* (Platinum of Russia: Problems of the Development of Mineral Resource Base of Platinum Metals in XXI Century), Moscow: ZAO Geoinformmark, 1999, vol. 3, book 2, pp. 216–226.
- Hallam, A., *Facies Interpretation and the Stratigraphic Record*, Oxford: Freeman and Company, 1981. Translated under the title *Interpretatsiya fatsii i stratigraficheskaya posledovatel'nost'*, Moscow: Mir, 1983.
- Hallam, A., The Earliest Triassic as an Anoxic Event, and Its Relationship to the End-Palaeozoic Mass Extinction, in *Pangea: Global Environments and Resources*, Can. Soc. Petrol. Geol., 1994, Memoir 17, pp. 794–804.
- Haq, B.Y., Hardebol, J., and Vail, P.R., Chronology of Fluctuation Sea Levels Since the Triassic, *Science*, 1987, vol. 235, pp. 1156–1167.
- Holland, H.D., Metals in Black Shales—A Reassessment, *Econ. Geol.*, 1979, vol. 74, pp. 1676–1680.
- Huc, A.Y., Aspects of Depositional Processes of Organic Matter in Sedimentary Basins, *Org. Geochem.*, 1988, vol. 13, nos. 1–3, pp. 263–272.
- Ibarra, J.V. and Juan, R., Structural Changes in Humic Acids during the Coalification Process, *Fuel*, 1985, vol. 64, pp. 650–656.
- Isozaki, Y., Superanoxia across the Permo-Triassic Boundary: Record in Accreted Deep-Sea Pelagic Chert in Japan, in *Pangea: Global Environments and Resources*, Can. Sci. Petrol. Geol., 1994, Memoir 17, pp. 805–812.
- Isozaki, Y., Permo-Triassic Boundary: Superanoxia and Stratified Superocean: Records from Lost Deep Sea, *Science*, 1997, vol. 276, pp. 235–238.
- Ivanov, V.V., Shelekhov, A.E., Molchanova, G.B., et al., Specific Features of Gold Mineralization in Carbonaceous Sequences of the Central Sikhote Alin and Southern Verkhoyansk Region, Abstract of Papers, *Mezhd. konf. "Sovremennyye problemy geologii, poiskov i otsenki mestorozhdenii poleznykh iskopaemykh"* (Int. Conf. "Modern Problems of Geology, Exploration, and Estimation of Mineral Resources") Moscow: PAIMS, 1997, pp. 38–39.
- Jiang, S.-Y., Chen, Y.-Q., Ling, H.-F., et al., Platinum Group Elements as Useful Genetic Tracers for the Origin of Polymetallic Ni–Mo–PGE–Au Sulfide Ores in Lower Cambrian Black Shales, Yangtze Platform, South China, in *Mineral Deposit Research: Meeting the Global Challenge (Proc. 8th Biennial SGA Meeting, Beijing, 2005)*, Berlin: Springer, 2005, pp. 765–767.
- Kazachenko, V.T. and Sapin, V.I., *Mineralogiya i genezis zhelezomargantseвого orudneniya Pribrezhnoi zony Primor'ya* (Mineralogy and Genesis of Ferromanganese Mineralization in the Pribrezhnaya Zone of Primorye), Vladivostok: Dalnevost. Otd. Akad. Nauk SSSR, 1990.
- Kazachenko, V.T., Chubarov, V.M., Solyanik, V.A., et al., Berilium-Bearing Manganese Rocks of the Central Sikhote Alin Region, *Dokl. Akad. Nauk*, 2005, vol. 400, no. 6, pp. 785–788 [*Dokl. Earth Sci.* (Engl. Transl.)], 2005, vol. 401, no. 2, pp. 232–235].
- Kerndorff, H. and Schnitzer, M., Sorption of Metals on Humic Acid, *Geochim. Cosmochim. Acta*, 1980, vol. 44, no. 11, pp. 1701–1708.
- Kesler, S.E., Kettler, R.M., Meyers, P.A., et al., Relation between Organic Material and Precious Metal Mineralization in the Moore Ore Body, Pueblo Viejo, Dominican Republic, in *Organic and Ore Deposits*, Denver Explor. Geol. Soc., 1986, pp. 86–92.
- Kholodov, V.N., Facies–Paleogeographic Formation Conditions of Vanadium and Phosphorus Ores in Karatau, *Litol. Polezn. Iskop.*, 1972, vol. 7, no. 6, pp. 80–94.
- Kholodov, V.N., *Osadochnyy rudogenez i metallogeniya vanadiya* (Sedimentary Ore Genesis and Metallogeny of Vanadium), Moscow: Nauka, 1973.

- Kholodov, V.N., The Role of H₂S-Contaminated Basin in Sedimentary Ore Formation, *Litol. Polezn. Iskop.*, 2002, vol. 37, no. 5, pp. 451–473 [*Lithol. Miner. Res.* (Engl. Transl.), 2002, vol. 37, no. 5, pp. 393–411].
- Kitaev, I.V. and Likht, F.R., Determination of Contents of Carbonates and Organic Carbon in Rocks by the Gasometric Method, in *Voprosy litologii i geokhimii vulkanogenno-osadochnykh obrazovaniy yuga Dal'nego Vostoka* (Problems of Lithology and Geochemistry of Volcanosedimentary Rocks in the Southern Far East), Vladivostok, 1971, pp. 238–244.
- Korchagina, Yu.I. and Chetverikova, O.P., *Metody issledovaniya rasseyannogo organicheskogo veshchestva osadochnykh porod* (Methods for the Investigation of Dispersed Organic Matter in Sedimentary Rocks), Moscow: Nedra, 1976.
- Korobeinikov, A.F., Conditions of the Formation and Distribution of the Gold–Platinum–Rare Metal Deposits, in *Geologiya, genezis i voprosy osvoeniya kompleksnykh mestorozhdenii blagorodnykh metallov* (Geology, Genesis, and Problems of the Development of Complex Deposits of Noble Metals), Moscow: OOO SVYaZ'-PRINT, 2002, pp. 39–42.
- Korobeinikov, A.F., Mitrofanov, G.L., Kolpakova, N.A., et al., Platinum Potential of Gold Deposits and Perspectives for the Discovery of Commercial Types of Gold–Platinum Objects in Siberia, *Platina Rossii. Problemy razvitiya MSB platinovykh metallov v XXI veke* (Platinum of Russia: Problems of Development of the Mineral Resource Base of Platinum Metals in XXI Century), Moscow: ZAO Geoinformmark, 1999, vol. 3, part 2, pp. 260–274.
- Kovalev, S.G. and Michurin, S.V., Geochemical Features of Carbonaceous Rocks on the Western Slope of the Southern Urals, *Litol. Polezn. Iskop.*, 2005, vol. 40, no. 3, pp. 281–291 [*Lithol. Miner. Resour.* (Engl. Transl.), 2005, vol. 40, no. 3, pp. 245–253].
- Kurskii, A.N. and Mit'kin, V.N., Sample Decomposition. Assay Smelting, in *Analiticheskaya khimiya metallov platinovoi gruppy* (Analytical Chemistry of Platinum Group Metals), Zolotov, Yu.A., Varshal, G.M., and Ivanova, V.M., Eds., Moscow: UIK, 2003, pp. 111–139.
- Laverov, N.P., Distler, V.V., Mitrofanov, G.L., et al., Platinum and Other Native Metals in Ores of the Sukhoi Log Deposit, *Dokl. Akad. Nauk*, 1997, vol. 355, no. 5, pp. 664–668 [*Dokl. Earth Sci.* (Engl. Transl.), 1997, vol. 355A, no. 6, pp. 904–907].
- Laverov, N.P., Prokof'ev, V.Yu., Distler, V.V., et al., New Data on Conditions of Ore Deposition and Composition of Ore-Forming Fluids of the Sukhoi Log Gold–Platinum Deposit, *Dokl. Akad. Nauk*, 2000, vol. 371, no. 1, pp. 88–92 [*Dokl. Earth Sci.* (Engl. Transl.), 2000, vol. 371, no. 2, pp. 357–361].
- Lewan, M.D. and Maynard, J.B., Factors Controlling Enrichment of Vanadium and Nickel in the Bitumen of Organic Sedimentary Rocks, *Geochim. Cosmochim. Acta*, 1982, vol. 46, no. 12, pp. 2547–2560.
- Likht, F.R., Sedimentation in Modern and Ancient Epicontinental Basins of Asia, *Tikhookean. Geol.*, 1993, no. 4, pp. 20–33.
- Lisitsyn, A.P., Bogdanov, Yu.A., Levitan, M.A., et al., History of Mesozoic–Cenozoic Sedimentation in the World Ocean, in *Geologicheskaya istoriya okeana (geologiya okeana)* (Geological History of Ocean: Geology of Ocean), Moscow: Nauka, 1980, pp. 407–427.
- Mangini, A. and Dominik, J., Late Quaternary Sapropel on the Mediterranean Ridge: U-Budget and Evidence for Low Sedimentation Rates, *Sediment. Geol.*, 1979, no. 23, pp. 113–125.
- Martikhaeva, D.Kh., Study of Carbonaceous Matter in Metamorphic and Hydrothermal Rocks (Siberian Craton and Baikal Region), *PhD (Geol.-Miner.) Dissertation*, Irkutsk: Inst. Geokhim., 2000.
- McKelvey, V.E., Strobell, J.D., and Slaughter, A.L., The Vanadiferous Zone of the Phosphoria Formation in Western Wyoming and Southeastern Idaho, *US Geol. Surv. Prof. Pap.*, 1986, no. 1465, pp. 1–27.
- Medvedeva, S.A., Kirillova, G.L., Ryazanova, T.A., et al., Some Results of Bituminous Analysis of Rocks of Lower Mesozoic Sedimentary Complex of the Amur River Region, Abstracts of Papers, *XII godichnoe sobranie Severo-Vostochnoy otdeleniya VMO po geodinamike, magmatizmu i minerologii kontinental'nykh okrain severa Patsifiki* (XII Annual Meeting of the Northeastern Division of the All-Russian Mineralogical Society Devoted to Geodynamics, Magmatism, and Mineralization at Continental Margins of the North Pacific Region, Magadan, June 3–6, 2003), Magadan, 2003, vol. 2, pp. 71–72.
- Metallogeniya Kazakhstana. Rudnye formatsii. Mestorozhdeniya rud khroma, titana, vanadiya, silikatnogo nikelya i kobal'ta, boksitov* (Metallogeny of Kazakhstan. Ore Formations. Ore Deposits: Chromium, Titanium, Vanadium, Silicate Nickel and Cobalt, Bauxite), Abdulin, A.A., Kayupov, A.K., Li, V.G., et al., Eds., Alma-Ata: Nauka KazSSR, 1978.
- Mikhailov, M.A. and Volokhin, Yu.G., Geochemistry of Carbonaceous Siliceous Rocks of the Far East, in *Geokhimiya i petrokimiya osadochnykh kompleksov Dal'nego Vostoka* (Geochemistry and Petrochemistry of Sedimentary Complexes of the Far East), Vladivostok: Dalnevost. Nauchn. Tsentr Akad. Nauk SSSR, 1980, pp. 3–16.
- Mitkin, V.N., Galizsky, A.A., and Korda, T.M., Some Observations on the Determination of Gold and Platinum-Group Elements in Black Shales, *Geostand. Newslett.*, 2000, vol. 24, no. 2, pp. 227–240.
- Naidin, D.P., Pokhialainen, V.P., Kats, Yu.I., and Krasilov, V.A., *Melovoi period. Paleogeografiya i paleoceanologiya* (The Cretaceous Period: Paleogeography and Paleocyanology), Moscow: Nauka, 1986.
- Nekrasov, I.Ya., Likhovidov, G.G., Plyusnina, L.P., and Kuz'mina, T.V., Specific Features of Geology, Geochemistry, and Genesis of the Ulakhan-Sissk, Kular, and Kharaulakh Gold Ore Nodes in the Verkhoyansk Fold Zone, *Tikhookean. Geol.*, 2001, vol. 20, no. 3, pp. 79–86.
- Nemerov, V.K., Spiridonov, A.M., Razvozzhaeva, E.A., et al., Major Factors of Ontogenesis of Noble Metal Deposits of the Sukhoi Log Type, *Otech. Geol.*, 2005, no. 3, pp. 17–24.
- Orberger, B., Wagner, C., Vymazalova, A., et al., Rare Metal and Mobility in Mineralized Black Shales from the Zunyi Region, South China, in *Mineral Deposit Research: Meeting the Global Challenge (Proc. 8th Biennial SGA Meeting, Beijing, 2005)*, Berlin: Springer, 2005, pp. 167–170.
- Organic Geochemistry: Methods and Results*, Eglinton, J. and Merphy, M.T.J., Eds., Berlin: Springer, 1969. Translated under the title *Organicheskaya geokhimiya*, Leningrad: Nedra, 1974.
- Pelet, R., Sédimentation et evolution géologique de la Matière Organique, *Bull. Soc. Geol. Fr.*, 1985, vol. 1, no. 7, pp. 1075–1086.

- Pentina, T.Yu., Humic Acids in Sedimentary Rocks, *PhD (Geol.-Miner.) Dissertation*, Moscow: Vses. Nauchno-Issled. Geol. Neft. Inst., 1973.
- Petrov, V.G., *Zoloto v opornykh razrezakh verkhnego dokembriya zapadnoi okrainy Sibirskoi platformy* (Gold in Upper Precambrian Reference Sections at the Western Margin of the Siberian Craton), Novosibirsk: Nauka, 1976.
- Plyusnina, L.P. and Kuz'mina, T.V., Experimental Investigation of Platinum Concentration by Bitumens at 200–400°C and 1 kbar, *Geokhimiya*, 1999, vol. 37, no. 5, pp. 506–515 [*Geochem. Int.* (Engl. Transl.), 1999, vol. 37, no. 5, pp. 441–449].
- Poplavko, E.M., Ivanov, V.V., Loginova, L.G., et al., Rhenium Concentration in Oils, Oil Bitumen, and Oil Shales, *Geokhimiya*, 1974, vol. 12, no. 9, pp. 1339–1402.
- Poplavko, E.M., Ivanov, V.V., Orekhov, V.S., et al., Specific Features of Metal Concentration in Oil Shales and Some Suppositions of Their Origin, *Geokhimiya*, 1978, vol. 16, no. 9, pp. 1411–1418.
- Pratt, L.M., Claypool, G.E., and King, J.D., Geochemical Imprint of Depositional Conditions on Organic Matter in Laminated-Bioturbated Interbeds from Fine-Grained Marine Sequences, *Mar. Geol.*, 1986, no. 70, pp. 67–84.
- Razvozhayeva, E.A., Spiridonov, V.D., Tsykhanskii, I.E., et al., Platinum in Carbonaceous Matter from Ores of the Sukhoi Log Deposit, *Geol. Geofiz.*, 2002, vol. 43, no. 3, pp. 286–296.
- Romankevich, E.A., *Geokhimiya organicheskogo veshchestva v okeane* (Geochemistry of Organic Matter in Ocean), Moscow: Nauka, 1977.
- Schlanger, S.O. and Jenkyns, H.S., Cretaceous Oceanic Anoxic Events: Causes and Consequences, *Geol. Mijnbouw*, 1976, vol. 55, pp. 179–184.
- Schopf, T.J.M., Paleozoic Black Shales in Relation to Continental Margin Upwelling, in *Coastal Upwelling: Its Sediment Record: Part B. Sedimentary Records of Ancient Coastal Upwelling*, Suess, E., Ed., Washington: U.S. Gov. Printing Office, 1984, pp. 579–596.
- Sheldon, R.P., Geochemistry of Uranium in Phosphorites and Black Shales of the Phosphoria Formation, *US Geol. Surv. Bull.*, 1959, no. 1084-D.
- Shirinskii, V.G., Romankevich, E.A., and Belyaeva, A.N., Carbon Isotopic Composition of Lipids in Bottom Sediments as Indicator of the Degree of Organic Matter Transformation, in *Organicheskoe veshchestvo v sovremennykh i iskopaemykh osadkakh* (Organic Matter in Modern and Fossil Sediments), Moscow: Mosk. Gos. Univ., 1974, pp. 40–41.
- Sidorov, A.A. and Tomson, I.N., Depositional Environment of Sulfidized Black Shale Sequences and Their Metallogenic Significance, *Tikhookean. Geol.*, 2000, vol. 19, no. 1, pp. 37–49.
- Sidorov, A.A. and Volkov, A.V., Sources of Ore Materials and Formation Condition of Gold Deposits in Northeastern Russia, *Dokl. Akad. Nauk*, 2001, vol. 376, no. 5, pp. 658–661 [*Dokl. Earth Sci.* (Engl. Transl.), 2001, vol. 377, no. 2, pp. 143–146].
- Simoneit, B.R.T., Organic Geochemistry of Laminated Sediments from the Gulf of California, in *Coastal Upwelling: Its Sediment Records: Part A. Responses of the Sedimentary Regime to Present Coastal Upwelling*, NATO Conference Series IV, Suess, E. and Thiede, J., Eds., New York: Plenum Press, 1983, pp. 527–543.
- Simoneit, B.R.T., Organic Geochemistry of Black Shales from the Deep Sea Drilling Project, a Summary of Occurrences from the Pleistocene to the Jurassic, in *SCOPE/UNEP Sonderband, Heft 60*, Hamburg: Mitt. Geol.-Palaeont. Inst. Univ. Hamburg, 1986, pp. 275–309.
- Strakhov, N.M., *Problemy geokhimii okeanskogo litogeneza* (Problems of the Geochemistry of Oceanic Lithogenesis), Moscow: Nauka, 1976.
- Tkachev, Yu.A. and Yudovich, Ya.E., *Statisticheskaya obrabotka geokhimicheskikh dannykh: metody i problemy* (Statistical Analysis of Geochemical Data: Methods and Problems), Leningrad: Nauka, 1975.
- Tomson, I.N., Polyakova, O.P., Polokhov, V.P., et al., Conditions of the Formation of Endogenic Black Shales in Primorye, *Geol. Rudn. Mestorozhd.*, 1993, vol. 35, no. 4, pp. 344–351.
- Tomson, I.N., Chernyshev, I.V., Gol'dtsman, Yu.V., et al., First Isotope Data on the Age of Metalliferous Carbonaceous Metasomatites of the Primorye Region, *Dokl. Akad. Nauk*, 2001, vol. 376, no. 5, pp. 668–670 [*Dokl. Earth Sci.* (Engl. Transl.), 2001, vol. 377, no. 2, pp. 178–180].
- Tomson, I.N., Polyakova, O.P., and Alekseev, V.Yu., On the Rhenium Accumulation in the Carbonaceous–Ilmenitic Metasomatic Rocks at Primorye, *Geol. Rudn. Mestorozhd.*, 2003, vol. 45, no. 3, pp. 250–252 [*Geol. Ore. Deposits* (Engl. Transl.), 2003, vol. 45, no. 3, pp. 222–224].
- Tomson, I.N., Polyakova, O.P., Alekseev, V.Yu., et al., On Two Types of Carbonaceous Metalliferous Rocks, *Geol. Rudn. Mestorozhd.*, 2006, vol. 48, no. 1, pp. 86–88 [*Geol. Ore. Deposits* (Engl. Transl.), 2006, vol. 48, no. 1, pp. 74–84].
- Varshal, G.M., Velyukhanova, T.K., Koshcheeva, I.Ya., et al., Concentration of Noble Metals by the Carbonaceous Substance of Rocks, *Geokhimiya*, 1994, vol. 32, no. 6, pp. 814–824.
- Vassoevich, N.B., Major Features of Organic Matter in Modern and Fossil Sediments, in *Priroda organicheskogo veshchestva sovremennykh i iskopaemykh osadkov* (Nature of Organic Matter in Modern and Fossil Sediments), Moscow: Nauka, 1973, pp. 11–59.
- Volokhin, Yu.G., Clay Minerals in Paleozoic and Mesozoic Geosynclinal Sileaceous Rocks in Southern Far East, in *Geokhimiya i petrokhimiya osadochnykh kompleksov Dal'nego Vostoka* (Geochemistry and Petrochemistry of Sedimentary Complexes on Far East), Vladivostok: Dalnevost. Nauchn. Tsentr Akad. Nauk SSSR, 1980, pp. 76–99.
- Volokhin, Yu.G., *Kremnevye porody Sikhote-Alinya i problema proiskhozhdeniya geosinklinal'nykh kremnevyykh tolshch* (Sileaceous Rocks of Sikhote Alin and the Genesis of Geosynclinal Sileaceous Sequences), Vladivostok: Dalnevost. Nauchn. Tsentr Akad. Nauk SSSR, 1985.
- Volokhin, Yu.G., Geochemical Criteria for the Correlation of Sileaceous Sequences and Paleogeographic Reconstructions, *Litol. Polezn. Iskop.*, 1988, vol. 23, no. 3, pp. 64–81.
- Volokhin, Yu.G., Burii, G.I., Filippov, A.N., and Mikhailik, E.V., Carbonate-Sileaceous Facies in the Geosynclinal Triassic of the Sikhote Alin Region, in *Geosinklinal'nye osadochno-vulkanogennye formatsii sovetskogo Dal'nego Vostoka* (Geosynclinal Volcanosedimentary Formations of the Soviet Far East), Vladivostok: Dalnevost. Otd. Akad. Nauk SSSR, 1987, pp. 70–91.

Volokhin, Yu.G., Burii, G.I., Rudenko, V.S., and Filipov, A.N., Triassic Sileaceous Formation of the Southern Sikhote Alin Region, *Izv. Akad. Nauk SSSR, Ser. Geol.*, 1990, no. 4, pp. 45–57.

Volokhin, Yu.G., Mikhailik, E.V., and Burii, G.I., Triassic Sileaceous Formation in Anyui River Basin (Sikhote Alin), *Tikhookean. Geol.*, 2000, vol. 19, no. 3, pp. 18–29.

Volokhin, Yu.G., Mikhailik, E.V., and Burii, G.I., *Triasovaya kremnevaya foermatsiya v basseine r. Anyui (Sikhote-Alin)* (Triassic Sileaceous Formation of the Sikhote Alin Region), Vladivostok: Dal'nauka, 2003.

Volokhin, Yu.G., Khanchuk, A.I., Ivanov, V.V., et al., Geochemistry and Gold Content of the Triassic Carbonaceous Cherts of the Sikhote Alin, Russia, in *Mineral Deposit Research: Meeting the Global Challenge (Proc. 8th Biennial SGA Meeting, Beijing, 2005)*, Berlin: Springer, 2005, pp. 187–190.

Vud, B.L. and Popov, N.P., The Sukhoi Log Giant Deposit, *Geol. Geofiz.*, 2006, vol. 47, pp. 315–341.

Yudovich, Ya.E. and Ketris, M.P., *Geokhimiya chernykh slantsev* (Geochemistry of Black Shales), Leningrad: Nauka, 1988.

Yudovich, Ya.E. and Ketris, M.P., *Elementy-primesy v chernykh slantsakh* (Trace Elements in Black Shales), Yekaterinburg: Nauka, 1994.

Zhang, G., Li, J., Xiong, Q., et al., Platinum-Group Elements in Cambrian Black Shale in Southern China: Differential Enrichment of Platinum and Palladium, in *Mineral Deposit Research: Meeting the Global Challenge (Proc. 8th Biennial SGA Meeting, Beijing, 2005)*, Berlin: Springer, 2005, pp. 219–222.

Zin'kov, A.V., Ivanov, V.V., Khomich, V.G., et al., Epigenetically Altered Auriferous Coal-Bearing Rocks of the Central Primorye Region, in *Problemy geologii, razvedki i razrabotki mestorozhdenii poleznykh iskopaemykh Dal'nego Vostoka* (Problems of Geology, Exploration, and Development of Mineral Resources in the Russian Far East), Vladivostok: Dalnevost. Tekhnich. Gos. Univ., 1993, no. 3, ser. 4, pp. 24–27.