Geochemistry and gold content of the Triassic cabonaceous cherts of the Sikhote-Alin, Russia

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Abstract. Triassic carbonaceous cherts are widesp-read in the Sikhote-Alin fold belt. They occur in a 4 to 20 m-thick sequence of interbedded cherts, carbonaceous cherts, and argillites that ranges in age from Upper Olenekian to Upper Anisian. The carbonaceous cherts are marine radiolarian rocks that contain 0.3 to 8.5 wt. % C_{org}. The majority of these rocks have undergone textural and mineralogical changes to a middle stage of catagenesis. Their organic matter contains low-grade oxidized humic acids with quinone, >CH_2, –CH_3 hydrocarbon groups. The $\delta^{13}C$ values are between –27.3 and –32.5 ‰. Carbonaceous cherts are anomalously enriched in V, B, Cu, Ni, Mo, Ag, and locally Au.

Keywords. Carbonaceous chert, geochemistry, precious metals, Triassic, Sikhote-Alin, Russia

1 Introduction

Mikhailov and Volokhin (1980) were the first to describe the carbonaceous cherts of the Sikhote-Alin fold belt. Subsequent fieldwork combined with stratigraphic, sedimentologic, and structural studies have defined the stratigraphy and age of the carbonaceous chert (Volokhin et al. 2003). Previous geochemical study of the carbonaceous chert and associated rocks has included major and trace element (Sn, Pb, Zn, Cu, Ni, Co, Cr, B, Ag, Mo, and Ga) analyses (Mikhailov and Volokhin 1980; Volokhin 1988). Advances in analytical methods have allowed the analysis of a wide range of elements that have previously not been recognized in the carbonaceous cherts of the Sikhote-Alin fold belt.

2 Geological setting of carbonace-ous cherts

The Triassic sediments of the Sikhote-Alin fold belt represent a basinal sequence that is up to 500 m-thick and ranges in age from Upper Olenekian to Rhaetian. Sediments are composed of interbedded siliceous mudstones, cherts and carbonate sediments. The carbonaceous cherts occur at the base of the sequence in siliceous offshore facies, but also in carbonate-siliceous facies (Fig. 1). Carbonaceous cherts comprise a 4-20 m-thick unit that we have informally named the Phtanitic member (Volokhin et al. 2003). This member consists of alternating beds of light-gray chert, argillite, and carbonaceous chert (15 - 30%, rarely up to 50%). The Phtanitic member overlies olive-green clayey cherts or siliceous mudstones and is underlain by dark-gray bedded cherts (Fig. 2). The age of the Phtanitic member is diachronous and varies from the Late Olenekian - Middle Anisian (Dalnegorsk) to the Middle Anisian (other sites) (Volokhin et al. 2003).

3 Methods

The mineralogy of the Phtanitic member was studied using light, TEM, and SEM microscopy, and X-ray diffraction. Major oxides and trace elements were analyzed with wet chemistry, and X-ray fluorescence, ICP-AES, and ICP-MS. Au and Pt were determined with ICP-MS, fire assay and AAS. Ten samples of carbonaceous cherts were dissolved with 0.1N NaOH for 3 days at the room temperature to obtain organic matter extracts. UV spectra of

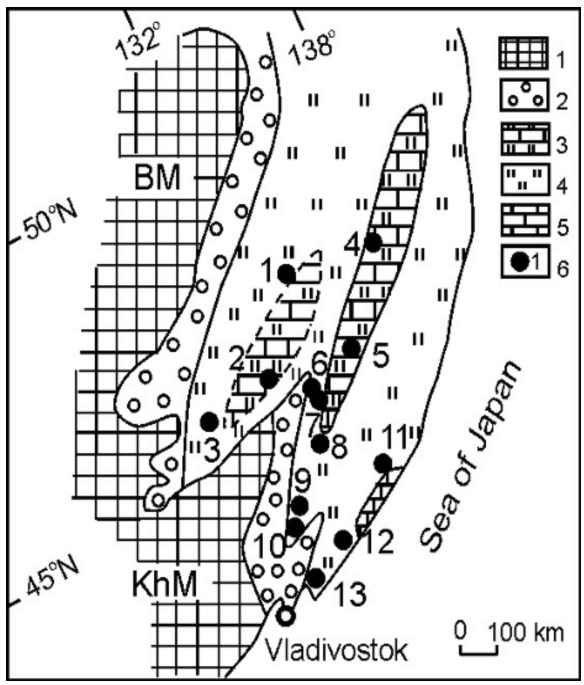

Figure 1: Locations of the Triassic carbonaceous cherts at the Sikhote-Alin folded belt. 1, ancient sialic massifs: BM – Bureya massif, KhM – Khanka massif; 2-5, types of the Triassic: 3, terrigenous shelf sediments; 3, bedded chert facies, 4, facies of bedded chert associated with micritic limestone, 5, reef limestone facies, 6, carbonaceous chert sections: 1, Khabarovsk; 2, Bikin; 3, Shichang; 4, Anuy; 5, Khor; 6, Matai; 7, Katen; 8, Dalnya; 9, Ogorodnaya; 10, Breyevka; 11, Dalnegorsk; 12, Olga; 13, Koreyskaya.

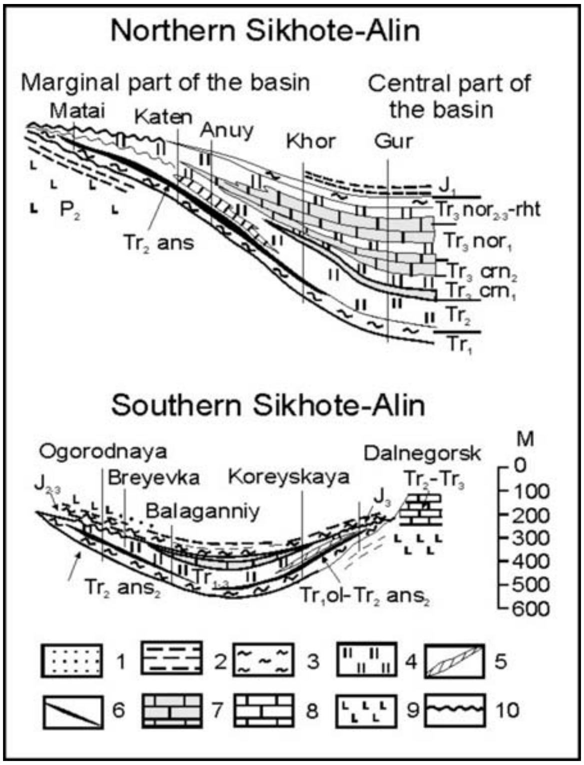

Figure 2: Position of the Phtanitic member in the Triassic siliceous formation (Volokhin et al. 2003).1, sandstone; 2, mudstone and siltstone; 3, siliceous shale and clayey chert; 4, gray and green chert; 5, red chert; 6, carbonaceous chert; 7, pelagic limestone; 8, reef limestone; 9, basalt and tuff; 10, stratigraphic hiatus.

the extracts were measured using a UV-spectrometer (Cecil CE 7200; Cambridge, England). IR-spectra of samples and their water-alkaline extracts in KBr were measured using IR-spectrometer with Fourier-transformation Vector-22 (Bruker, FRG).

4 Components and mineral composition

Carbonaceous cherts are primarily composed of recrystalized radiolarian skeletons, sponge spicules, quartz cements, clay minerals, and dispersed organic matter. They also contain grains of quartz and feldspar, and small clasts of basalt and claystone. The clay fraction of the carbonaceous cherts consists of dioctahedral (b=9.04 Å) $2M_1$ illite and minor amounts of 1M illite (Volokhin et al. 2003). Illite is also the dominant clay mineral in light-gray chert. Some thin dust-sized gold particles were found in residues of dissolved carbonaceous chert. Pyrite with minor chalcopyrite and pyrrhotite also occur in the carbonaceous chert. The maturity of carbonaceous matter in the cherts is variable. Regionally it consists of amorphous kerogen and bitumen, but it has been recrystalized to thin-dispersed graphite around magmatic bodies.

Table 1: UV- and IR-spectra of water-alkaline extracts from carbonaceous siliceous rocks

Sampe No.	IR-bands of humate ν_{max} (cm^{-1})	IR-bands of humate ν_{max} (cm^{-1})	UV-bands of humate ν_{mx} (cm^{-1})
Go-17	1084 Si-O	1670 Ar=O, 2924 CH_3, CH_2	n.d.
H-153	1089 Si-O	1672 Ar=O, 2927 CH_3, CH_2	270 Ar-H
H-155	1089 Si-O	1671 Ar=O, 2928 CH_3, CH_2	n.d.
H-155d	1092 Si-O	1670 Ar=O, 2926 CH_3, CH_2	270 Ar-H
R-102	1093 Si-O	1652 Ar=O	340 Ar=O
R-120	1087 Si-O 2922 CH_3, CH_2	1670 Ar=O, 2927 CH_3, CH_2	n.d.
Dg-2	1088 Si-O 2923 CH_3, CH_2	1670 Ar=O, 2923 CH_3, CH_2	n.d.
C-111	1090 Si-O 2927 CH_3, CH_2	1668 Ar=O, 2925 CH_3, CH_2	n.d.
C-153	1091 Si-O 2924 CH_3, CH_2	1672 Ar=O, 2925 CH_3, CH_2	n.d.
C-159	2090 Si-O 2924 CH_3, CH_2	1670 Ar=O, 2923 CH_3, CH_2	n.d.

Ar – aryl (phenyl, naphtyl etc.), *Alk* – alkyl (methyl, ethyl, etc.), *Ar=O*, quinone; *n.d.* – not determined.

Table 1: UV- and IR-spectra of water-alkaline extracts from carbonaceous siliceous rocks All water-alkaline extracts from carbonaceous rocks contain humate (Table 1). There are weak but characteristic absorption bands on UV-spectra at 270 nm (aromatic compounds) and 340-350 nm (quinone). This agrees with IR-spectroscopy results that show absorption bands at 1652-1672 cm^{-1} (quinone groups), and 2923-2928 cm^{-1} (methyl and methylene groups). The humate from carbonaceous cherts are low-grade oxidized. The preservation of hydrocarbon groups suggests a rather incomplete transformation of organic matter of the Triassic carbonaceous cherts.

5 Geochemistry of carbonaceous rocks

The carbonaceous rocks of the Phtanitic member contain C_{org} from 0.3 to 8.54 wt. %. An average C_{org} in carbonaceous clayey cherts (2.28 wt. %) is twice as high as carbonaceous cherts (1.08 wt. %). $C_{carbonate}$ is commonly less than 0.05 wt. %. $S_{tot.}$ varies from 0.004 to 0.7 wt. % with a mean of 0.14 wt. %. Sulfide sulfur dominates (~83%) over sulfate. The carbonaceous cherts are enriched 2-3 times V and 20-50 times in Mo and Ag above ordinary cherts. The elements content in places reach as much as 1300 ppm of V, 200 ppm of As, 890 ppm of Zn, 490 ppm of Cu, 350 ppm of Ni, 10 ppm of Ag, and 180 ppm of Mo. The most significant regional variation is found for Ba: 127-379

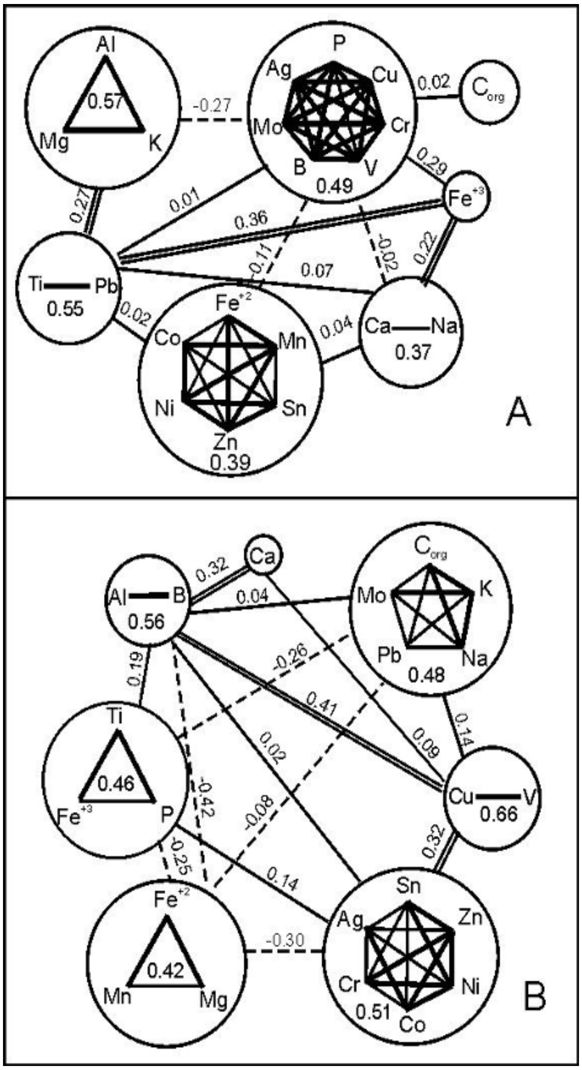

Figure 3: Element associations in carbonaceous siliceous rocks of the Sikhote-Alin. A, carbonaceous clayey chert; B, carbonaceous chert. Bold lines show correlations significant with 95% confident probability. Dashed lines connect antagonistic groups

ppm (Ogorodnaya) to 7000 ppm (Gornaya). Concentrations of other elements (ppm): Pb (5-300), Cu (25-950), Ni (35-350), Co (0,5-180), Cr (10-120), Cd (0,062-0,233), Hg (0,01-0,08), Tl (0,28-1,16), U (0,53-7,25), Th (1,48-5,43), Se (0,3-3), Rb (36-100), In (0,025-0,045), Cs (4-13), La (4-21), Ce (9-38), Bi (0,08-0,37), and Ge (4-8).

Element associations (Fig. 3) based on correlation coefficients (SiO_2 excluded) are shown on the structural schemes of Tkachev and Yudovitch (1975). In carbonaceous clayey cherts the associations of Al-Mg-K, Ca-Na, and Ti-Pb appears to be a terrigenous component. Trace elements associations separate into two distinct groupings. The assemblage of P-Cu-Cr-V-B-Mo-Ag suggests that these elements were dominantly accumulated by organics matter. The grouping of Fe^{+2}-Mn-Sn-Zn-Ni-Co (chalcophile elements) suggests they accumulated in sulfide minerals. Al, B, and Ca belong to of terrigenous silicate group as of Fe^{+3}-Ti-P.

In carbonaceous cherts there is a strong correlation of K and Na with C_{org}. The Sn-Zn-Ni-Co-Cr-Ag and Cu-V groups tend being connected with authigenic sulfides. However with the exception of Mo and Pb, the majority of elements generally accumulating in carbonaceous rocks show a poor correlation with C_{org}. The absence of a direct correlation might result from the oxidation and loss of organic compounds during post-sedimentation processes. The initial organic matter in sediments was likely 2-3-times that measured in the rocks.

The $\delta^{13}C$ of organic of the carbonaceous rocks vary within from –27, 3 to –32, 5‰ PDB (table 2). These values are close to those of Paleozoic bitumen and oil (Galimov 1973).

In recent sediments of the continental slope of Japan the close values of $\delta^{13}C$ (from –23 to -29‰) have lipid of marine organic matter (Shirinsky et al. 1974).

Table 2: Carbon isotope composition of carbonaceous cherts of the Phtanitic member

Sample No.	Section	SiO_2, %	C_{org}, %	$\delta^{13}C_{PDB}$, ‰
U-15	Big Ussurka	90,15	2,96	-30,2
U-16		85,48	6,04	-30,0
U-18		88,12	3,95	-27,6
Go-17	Gornaya	72,94	1,32	-30,1
H-153		78,18	2,21	-27,7
H-155		88,25	1,55	-27,9
H-169		87,45	1,99	-27,7
R-102	Dalnegorsk	87,10	1,42	-27,3
R-120		68,60	5,85	-27,3
C-156	Koreyskaya	74,46	8,54	-29,0
C-159		78,01	5,58	-27,9

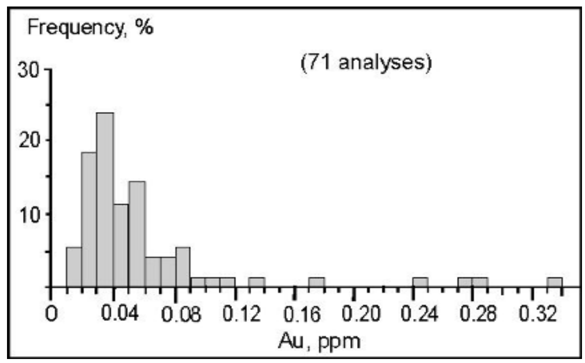

Figure 4: Frequency of Au distribution in carbonaceous cherts of the Ogorodnaya section

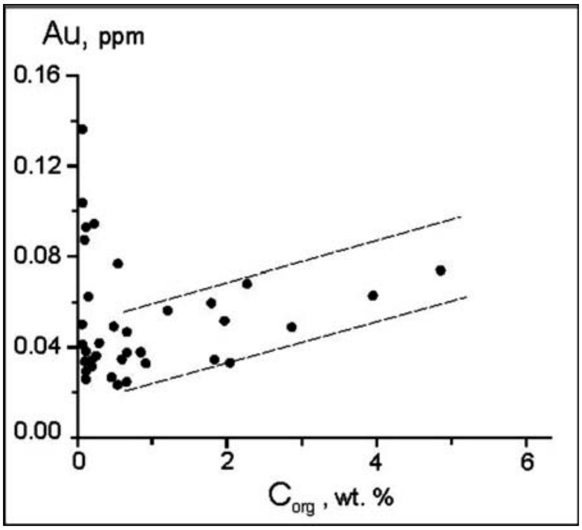

Figure 5: Au vs. C_{org} in rocks of the Phtanitic member.

6 Gold and platinum distribution

A detailed study of the gold distribution in the Phtanitic member reveals a heterogeneous distribution. Au was above detection in 50% of carbonaceous and in 60% of non-carbonaceous samples of the Ogorodnaya section (ICP-MS).

The maximum of Au was found in carbonaceous chert having the high SiO_2 content and relatively low C_{org} (0.3-0.5%). In non-carbonaceous cherts the Au concentration reaches 0.68 ppm (ICP-MS). An average Au content (anomalous samples excluded) is 0.017 ppm (ICP-MS) and 0.052 ppm (AAS). Fire assay with atomic-absorption finish gave Au lognormal distribution with mode 0.035-0.040 ppm (Fig. 4). This is 4 times higher than the clarke concentration in black shales (8-10 ppb, by Yudovitch and Ketris 1994). The positive correlation between Au and C_{org} in rocks containing >0.5% C_{org} (Fig. 5) suggests a genetic link between Au and organic matter.

The 7 samples with <0.5% C_{org} and high Au may indicate the redistribution or addition of Au during post-sedimentation processes. The Pt and Pd concentration was above their 0.001 ppm detection limit in 13 of 56 samples of carbonaceous cherts (fire assay with AAS finish). The maximum of Pt and Pd measured in Ogorodnaya carbonaceous rocks was 0.13 and 0.02 ppm, respectively.

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References

Galimov EM (1973) The carbon isotopes to the oil-gas geology (in Russian). Nedra, Moskow: 384

Mikhailov MA, Volokhin YG (1980) Geochemical peculiarities of carbonaceous siliceous rocks of the Far East. In Geochemistry and Petrochemistry of sedimentary complexes of the Far East. FESC Ac. Sci. of the USSR, Vladivostok: 3-16

Tkachev YA, Yudovitch JE (1975) Statistical processing of geochemical data: methods and problems (in Russian). Nauka, Leningrad: 233

Yudovitch JE, Ketris MP (1994) Admixture elements in black shale (in Russian). Nauka, Ural publ. firm, Ekaterinburg: 304

Volokhin YG (1988) Geochemical criteria for correlation of chert units and paleogeographic reconstruction (in Russian). Lithology and Mineral Resources 3: 64-81

Volokhin YG, Mikhailik EV, Buryi GI (2003) Triassic siliceous formation of the Sikhote-Alin (in Russian). FEB RAS, Vladivostok: 252