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GEOLOGY

Nature of Carbonaceous Rocks in Shear Zones in the Dal'negorsk District, Primorye: Black Shales or Mantle-Related Ilmenite–Graphite Metasomatites?

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Carbonaceous mineralization with associated metals in the sulfide or native form has been reported from various geological settings. However, the source of metals remains an open issue. The superimposed character of mineralization is evident in areas with the deposition of carbon in contrasting environments, such as fissures, cavities, exfoliation zones in granites, granitic pegmatites, and marbles [1]. In such cases, the carbon isotopic composition also matches the endogenic composition. It is more difficult to elucidate the nature of carbon-bearing rocks in crush zones if the rocks are similar to carbonaceous units in sedimentary sections of the region in terms of age and composition. The problem is complicated by the fact that the carbon isotopic composition also matches the sedimentary type in all cases. Elaboration of criteria of the endogenic carbonization in sedimentary rocks (siltstones, mudstones, and siliceous shales) is a pressing issue.

We report for the first time results of the comparison of carbonaceous rocks from tectonic crush zones in Mesozoic sedimentary blocks of the central Dal'negorsk ore district with their counterparts in regional sedimentary sections.

Carbonaceous rocks are widespread in Triassic, Jurassic, and Early Cretaceous marine siliceous and siliceous–terrigenous sediments of Primorye [2, 3]. Like rocks of the black shale association in other regions, the carbonaceous rocks are characterized by concentrations of a wide range of rare and ore elements [4–7]. In addition, ore districts of the southern Primorye region include carbonaceous rocks in crush, shear, and foliation zones. In [8, 9], the carbonaceous rocks are described as titanium–carbon and ilmenite–graphite metasomatites related to the input of carbon by mantle fluids with high reducing properties. However, rocks of the Dal'negorsk ore district lack the isotopic–geochemical attributes of the titanium–carbon metasomatism.

In Primorye, carbonaceous sequences in Late Jurassic–Early Cretaceous rocks retained elasticity. Therefore, the surfaces of tectonic and submarine landslide displacements are confined to such sequences [3]. Mesozoic sediments are involved in nappe dislocations, separated into blocks, displaced along differently oriented faults, and overlain by Cretaceous–Paleogene volcanic rocks. In Mesozoic sedimentary sections, carbonaceous siliceous and clayey–siliceous siltstones and phtanites alternate with deep red jaspers, light gray siliceous cherts, and mudstones. Interlayers of carbon-bearing rocks are from 2–20 cm to 4–25 m thick. Their chemical composition is presented in Table 1. They are characterized by high contents of alumina (up to 18%) and significant domination of K over Na. The TiO_2 content varies from 0.2 to 0.76%. The K_2O content is as much as 3.9%. According to [10], the C_{org} content is up to 8.5%. The maximal contents of trace elements are as follows (ppm): V 1300, Mo 180, Ag 10, Zn 890, Cu 490, Ni 350, and As 200. The maximal Au content in carbonaceous silicites varies from 7.5 g/t (based on assay analysis) to 35 g/t (based on atomic absorption analysis). High concentrations of metals, in particular Au, Ag, PGM, and others, in the Triassic cherty association of Sikhote Alin, as well as findings of native Ag, Au, Pb, Fe, and Ni in them, were also reported in [6, 7]. The carbon isotopic composition varies from –27.3 to –30.2‰ PDB. These values match the isotopic composition of marine sapropel matter, oils, and bitumens [10].

Numerous tectonite zones occur among cherts, siltstones, and limestones at the borosilicate deposit in the central Dal'negorsk district (44°36′ N, 135°35′ E). In the cherts and siltstones, the tectonite zones are observed as gray to black sectors of intense fracturing, shearing, and foliation previously described as zones of titanium–carbon or ilmenite–graphite metasomatism [8, 9]. Such zones have the following properties: aver-

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Table 1. Compositions of typical carbonaceous silicites in Mesozoic sedimentary sequences of Primorye [3]

Component	1	2	3	4	5	6	7	8
SiO_2	78.90	82.10	68.60	85.30	85.10	91.60	86.70	69.30
TiO_2	0.42	0.30	0.50	0.17	0.24	0.10	0.20	0.60
Al_2O_3	9.60	6.70	8.20	5.20	5.50	2.60	6.60	12.20
Fe_2O_3	1.40	1.00	4.80	0.00	0.70	1.00	0.40	4.60
FeO	2.90	1.80	2.80	3.00	2.18	1.80	1.50	1.60
MnO	0.05	0.10	0.60	0.05	0.08	0.03	0.05	0.03
MgO	1.60	1.20	1.30	1.20	1.00	0.70	0.80	1.90
CaO	0.20	0.46	0.50	0.13	0.40	0.00	0.00	0.70
Na_2é	0.1	0.14	0.00	0.20	0.15	0.06	0.06	1.10
K_2O	1.60	1.20	0.95	1.30	1.00	0.57	1.60	3.20
P_2O_5	0.03	0.13	0.43	0.04	0.11	0.04	0.05	0.13
L.O.I.	2.70	4.30	5.20	3.20	3.10	1.10	1.90	4.60
C_{org}		1.75	5.90	0.18		0.48	1.05	
Total	99.53	101.18	99.78	99.97	99.56	100.08	100.91	99.96
Component	9	10	11	12	13	14	15	16
SiO_2	61.70	83.10	73.70	79.60	70.50	75.40	64.80	60.80
TiO_2	0.74	0.46	0.65	0.55	0.76	0.51	0.68	0.75
Al_2O_3	17.30	7.00	12.60	10.20	14.60	8.20	15.70	17.90
Fe_2O_3	2.50	1.50	2.00	1.91	1.80	4.10	1.50	2.80
FeO	3.40	0.60	0.60	0.42	1.70	1.20	4.30	3.90
MnO	0.20	0.03	0.03	0.11	0.04	0.13	0.40	0.30
MgO	2.50	0.70	1.10	0.70	1.20	1.00	2.20	2.60
CaO	0.80	0.04	0.20	0.10	0.20	2.10	0.90	0.70
Na_2é	1.60	0.09	0.12	0.20	1.50	0.11	1.50	1.50
K_2O	3.30	1.80	3.10	2.90	3.90	3.20	3.00	3.40
P_2O_5	0.16	0.40	0.20	0.04	0.10	0.40	0.12	0.20
L.O.I.	5.30	3.80	3.10	3.90	3.80	3.00	4.00	3.90
C_{org}	n.d.	0.45	0.67	0.15	0.15	1.60		
Total	99.50	99.97	98.07	100.78	100.25	100.95	99.10	98.75

Note: (1–7) Central part of the Dal'negorsk ore node: (1) siliceous shale, Mt. Rudnaya (near Dal'negorsk); (2) clayey phtanite, the same locality; (3) clayey phtanite, Bor quarry, road to the Central sector; (4) carbonaceous siliceous shale, Mt. Rudnaya; (5) cherts, Mt. Rudnaya; (6) phtanite, Mt. Rudnaya; (7) clayey phtanite, Sadovyi sector; (8–10) Triassic chert, Ussuri River; (11, 12) clayey phtanite, near Khabarovsk; (13) siliceous mudstone, Dzhaur River; (14) clayey phtanite, Anyui River; (14, 15) siliceous mudstone, Kolumbe River; (16) clayey phtanite, Ussuri River.

age thickness from 0.1–0.3 to 0.4–0.8 m (up to 20 m in rare cases), strike azimuth 20°–40°, and steep dip angle 80°–85°. The powdery pelitic material includes fine (<1 mm) quartz–sulfide veinlets. Crush zones in limestones are commonly represented by a dark gray folded and foliated silty material that cements limestone fragments. The thickness of such zones varies from 0.3 to 3 m in swells. Finely crushed limestone is absent in such siltstone zones (Table 2, analysis 19).

We determined the contents of the major and accessory elements in samples of the most carbonized rocks taken from the crush zones (Table 2). Samples from collections of V.P. Polokhov and N.T. Mityushkin were also used. The TiO_2 content is 0.2–0.7% in black schistosed siltstones. This value matches the content in carbon-bearing sedimentary rocks. Thus, the siltstones lack any signs of Ti accumulation owing to the inferred infiltrational titanium metasomatism. The C_{org} content varies from 0.2 to 7.7% in tectonite zones (determinations by A.Kh. Galuzinskaya, L.V. Krigman, and N.V. Budarina at the Vernadsky Institute of Geochemistry and Analytical Chemistry, Moscow). A correlation between C_{org} and Ti is absent (Fig. 1). Sulfide patches and veinlets recorded in outcrops are accompanied by

Table 2. Compositions of black (carbonaceous) silicites and limestones in tectonic zones of the Bor quarry

Component	1	2	3	4	5	6	7	8	9	10	11
	Sample 70ab	Sample 120-B	Sample 70-B	Sample 103/1b	Sample 169	Sample 175-B	Sample 176-B	Sample 178-B	Sample 122-B	Sample 121-B	Sample 71-B
SiO_2	49.5	65.6	86.8	61.9	76.2	82.8	77.2	77	84.8	64.7	64.8
TiO_2	1.03	0.6	0.16	0.44	0.66	0.39	0.55	0.7	0.4	0.65	0.69
Al_2O_3	17.9	18.9	2.8	8.9	12.6	7.7	10.3	10	8.3	23.5	19.3
Fe_2O_3	15.2	6.7	6.2	6.4	4	3.4	5.2	4.9	2.6	2.6	5.4
MnO	1.1	0.2	0.5	0.18	0.06	0.1	0.1	0.1	0.07	0.2	0.1
MgO	5.7	1.75	1.7	1.9	1.04	1.1	1.5	1.5	0.66	1.3	1.9
CaO	2.2	0.3	0.6	0.5	0.15	1.3	1.2	1.3	0.2	0.95	1.1
Na_2O	0.12	0.06	0.07	0.97	0.1	0.05	0.04	0	0.1	0.06	1.5
K_2O	5.7	4.7	0.1	2.4	3.7	2.2	2.9	3.4	2.4	6.5	4.2
P_2O_5	0.9	0.09	0.13	0.3	0.06	0.05	0.1	0.1	0.1	0.2	0.08
ëé$_2$	1.39	n.d.	0.5	0.6	0.48	0.85	0.44	0.6	n.d.	0.29	n.d.
C_{org}	0.34	n.d.	b.d.	3.73	1.57	ç.Ô.	0.3	0.2	n.d.	0.19	n.d.
Total	99.7	99.1	99.6	88.22	100.9	99.3	100	100	99.9	101	99.1
Rb	260	275	16	133	189	112	149	167	112	339	217
Zr	258	164	61	92	147	89	120	125	102	205	222
Ba	1453	1321	61	532	767	372	442	594	588	1427	1006
Cr	181	35	19	95	91	27	25	24	28	22	34
Ni	410	27	67	540	399	26	30	25	53	34	17
V	473	64	100	1552	1022	144	131	66	296	66	64
Cu	28	2147	323	3820	372	329	142	179	331	27	14
Zn	1082	1485	2271	22 157	1737	748	164	142	2020	80	56
Pb	74	7	683	2223	326	36	14	13	743	18	11
As	1264	342	4750	735	1141	3255	714	978	1575	122	18
Mo	100	b.d.	b.d.	220	200	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
S	0.1	0.03	0.3	2.4	2.3	0.3	0.8	0.2	0.2	0.02	0.02

Table 2. (Contd.)

Component	12	13	14	15	16	17	18	19	20	21
	Sample 120-B	Sample 103-B	Sample 171 B	Sample 171ab	Sample 110B	Sample 68B	Sample 69B	Sample 21S	Sample 19G	Sample 92
SiO_2	76.7	82.2	97.6	97.5	77.6	76.1	90	65.3	19	76
TiO_2	0.39	0.35	0.05	0.06	0.54	0.66	0.1	0.36	0.36	0.62
Al_2O_3	8.4	7.7	0.7	0.9	10.4	12	2.4	12	12	11
Fe_2O_3	4.4	2.4	0.4	0.8	3.2	3.1	2.3	3.3	4.4	3.5
MnO	0.14	0.17	0.02	0.03	0.13	0.05	0	0.1	0.1	0.02
MgO	1.4	0.65	0.03	0.04	1.1	1.2	0.2	2.7	7.8	1.4
CaO	0.3	0.3	0.25	0.1	0.5	0.08	0.1	0.9	2.54	0.6
Na$_2$é	0.05	0.4	0.04	0.05	0.06	0.04	0	0.2	0.09	0.1
K_2O	1.75	1.7	0.15	0.2	4.9	3.8	0.7	4.2	1.2	3.7
P_2O_5	0.27	0.17	0.02	0.01	0.34	0.09	0	0.06	0.1	1
ëé$_2$	b.d.	0.14	0.21	0.16	n.d.	n.d.	n.d.	0.03	2.18	n.d.
C_{org}	3.8	4.18	3.41	b.d.	n.d.	n.d.	n.d.	0.05	7.69	n.d.
Total	97.6	100	102.9	99.85	98.77	97.1	96	89.2	99.9	97.94
Rb	101	84	12	15	225	178	33	172	45	100
Zr	122	105	27	31	147	161	43	205	76	n.d.
Ba	267	506	172	144	1214	954	387	641		n.d.
Cr	34	14	3	3	36	34	7	41	83	n.d.
Ni	156	19	8	10	96	94	20	25	54	n.d.
V	430	86	6	7	270	240	75	100	117	n.d.
Cu	224	94		18	753	1255	80	19	38	n.d.
Zn	490	140	30	27	2800	361	120	104	76	300
Pb	390	30	n.d.	n.d.	761	1300	130	n.d.	n.d.	500
As	600	374	n.d.	n.d.	960	2036	369	n.d.	n.d.	n.d.
Mo	180	n.d.	n.d.	n.d.	n.d.	181	n.d.	n.d.	n.d.	400
S	0.2	0.06	0.02	0.01	0.5	0.3	1.4	0.7	2.4	n.d.

Note: Rocks: (1) shear zone in basalt dike with sulfide dissemination; (2) fracture zone in cherts with sulfide dissemination; (3, 4) shear zone in probably silicified siltstones with sulfide patches; (5) fracture zone in cherts; (6–8) thick shear zone at the contact of cherts and sandstones with different degrees of carbonization and hydrothermal alteration; (9, 10) shear zone in cherts with irregular sulfide dissemination; (11) foliation zone in cherts; (12, 13) carbonaceous rock from shear zone in cherts; (14) layered cherts; (15) black interlayers in layered cherts; (16–18) crush zones in siliceous sediments; (19) silty material cementing limestone fragments; (20) carbonaceous crusts on limestone; (21) siltstone. (n.d.) Not determined; (b.d.) below detection limit.

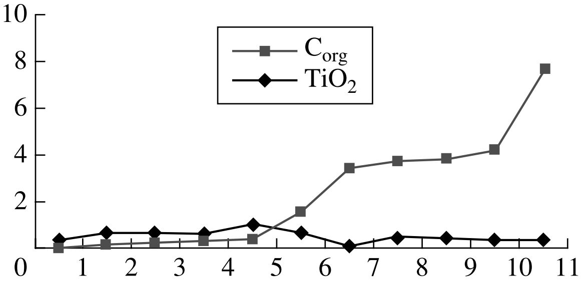

Fig. 1. Correlation between Ti and organic carbon in tectonites of the Bor quarry. The abscissa shows sample numbers ranked according to the C_{org} content; the ordinate, contents in wt %.

anomalous concentrations of Zn, As, Pb, Cu, Mo, and S in the corresponding samples. The V content is also high in such cases. However, the concentrations of ore admixtures lack positive correlation with Ti (Fig. 2). Based on the atomic absorption analysis carried out at the Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry (V.A. Sychkova and L.F. Kartashova, analysts), the Au content varies from 0.2 to 9.2 g/t. The higher Au content is confined to hydrothermally altered sectors. As in the case of Ti, ore admixtures lack any correlation with carbon. Based on analyses of the carbon isotopic composition at the Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry (N.P. Nosik, analyst), the $\delta^{13}C$ value varies from –23.8 to –32.8‰. These values match the isotopic composition of sedimentary carbonaceous rocks of the region [2, 10] and differ from the signature of the endogenic carbon (9.1–10.4‰) in deep fault zones [11].

Thus, based on the whole-rock composition, the contents of trace elements, and carbon isotopic composition, rocks from the carbon-bearing tectonite zones of the central Dal'negorsk ore district are similar to Mesozoic carbon-bearing sedimentary rocks of the region. The authors of [8, 9] define such rocks in Primorye as titanium–carbon metasomatites based on the following criteria: confinement of these rocks to shear, boudinage, and foliation zones; blastic structures of rocks; development of various forms of carbon; the presence of ilmenite and other Ti-bearing minerals; accumulation of V and Cr; a high geochemical background of noble and other metals; the development of iron sulfides; the presence of methane in gaseous and liquid inclusions; and the occurrence of accessory native metals and their microinclusions in graphite. However, all the features indicated above are also typical of carbon-bearing sediments. In particular, such features are observed in sediments subjected to the impact of submarine hydrothermal solutions, catagenesis, and tectonothermal metamorphism [4, 5, 10, 12]. At the same time, the rocks lack unambiguous signs of carbon–titanium metasomatism, such as elevated concentrations of Ti and C (relative to sedimentary carbonaceous rocks); coordinated accumulation of these components; and their correlation with ore admixtures. The carbon isotopic composition of the endogenic type is also missing.

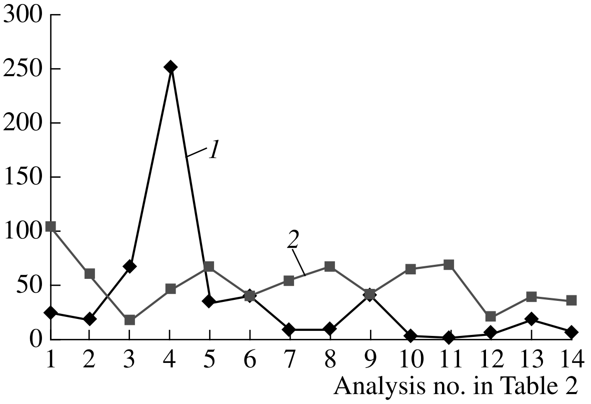

Fig. 2. Correlation between Ti and ore admixture in carbonaceous rocks at the center of the Dal'negorsk district. (*1*) (As + Zn + Pb, ppm) × 10^{-1}; (2) TiO_2, % ×100.

CONCLUSIONS

Data reported in this paper suggest that a significant part of rocks in the tectonite zone of the Dal'negorsk borosilicate deposit represents carbonaceous rocks of sedimentary framing. These rocks are probably confined to sectors involved in the crushing and dislocation of Mesozoic units of the folded basement of the region (carbonaceous siliceous and clayey siltstones and mudstones associated with jaspers and cherts). The latter rocks were subjected to diagenesis, tectonic stress, crushing, thermal metamorphism, and superimposed mineralization. The carbonaceous rocks are marked by the preferential precipitation of sulfides of Cu, Zn, Pb, and other metals. Therefore, such rocks can serve as a prospecting guide for hydrothermal mineralization nodes.

Elaboration of criteria for the differentiation of mantle-related carbonaceous metasomatites and metalliferous black shales is an urgent issue that remains to be solved.

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