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GEOCHEMISTRY

Forms of Concentration of Ore Elements in Carbon-Rich Metasomatites

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The problem of endogenic carbonification of rocks and related ore mineralization is topical for many reasons. The possibility of accumulation and transfer of various metals with reduced carbon-rich fluids has been proved [1–4]. However, several questions concerning the mode of transfer and forms of deposition of elements in carbonized rocks remain open. In the deep fault zones of the southern framework of the Siberian Craton, the degree of structural perfection of native forms of carbon and forms of metal concentration in graphite closely interrelate and depend on *PT* conditions of tectonite formation.

We have studied two areas with carbonic mineralization. The first area is located in the southeastern segment of the Main Sayan (MS) Fault. Graphite occurs here as veins, lenses, and pockets in the pegmatitic granite and cataclastic diopside plagiogneiss. The graphite disseminations in amphibole and amphibole–clinopyroxene–plagioclase metasomatites and silicification zones are combined with compact fine-grained graphite aggregates in intergranular interstices and fractures. The fine-grained graphite occurs as segregations in blastomylonite and mylonite zones.

The structural state of graphite was studied with XRD and Debye–Scherrer methods at the Institute of Geology, Komi Scientific Center (T.N. Popova, analyst). The XRD method, which yields averaged values of a great number of grains, allowed us to determine reflections from a flat grid: d_{002} = 3.34 Å and d_{004} = 1.675 Å. While using the Debye–Scherrer method, which makes possible to establish the structure of individual particles, it was ascertained that all studied rocks contain perfectly ordered graphite with a typical set of *d*-spacings (d_{002} = 2.36 Å; d_{100} = 2.13 Å, d_{101} = 2.03 Å, d_{004} = 1.678 Å, d_{112} = 1.158 Å, d_{110} = 1.23 Å, and d_{114} = 0.992 Å) and unit cell parameters (a = 2.46 Å; c = 6.71 Å). In other grains from the same type of rocks, the obtained *d*-spacings are characteristic of the poorly crystallized low-density graphite with a disordered structure and strongly compacted graphite (d_{002} = 3.39 Å; 3.31 Å). Thus, in terms of X-ray diffraction, the carbonic material in the graphite-bearing rocks of the MS fault zone has different degrees of crystallinity. Grains with both holocrystalline hexagonal and poorly ordered (but strongly compacted) structures can occur in the same samples.

According to the results of thermal analysis of graphite concentrates from the amphibole–clinopyroxene–plagioclase metasomatites and pegmatitic granite, the temperature of the onset of the exothermic effect are within the range of 550–615°C (derivatography was carried out at the Analytical Center of the Institute of the Earth's Crust; N.V. Nartova, analyst). Such a temperature of graphite burnout corresponds to the greenschist facies of metamorphism [5]. These values differ from the parameters of the peak of amphibolite-facies metamorphism (650–700°C and ~5.5 kbar) obtained for the main mineral assemblages of gneisses and crystalline schists in the MS fault zone [6]. This discrepancy may testify to an interval in the endogenic activity between the main tectonometamorphic transformations of this fault zone and the formation of graphite-bearing metasomatites and pegmatites.

The second occurrence of graphite mineralization is related to the Chernaya Ruda–Barakcha (CRB) fault zone in the western Baikal region. Graphite-bearing rocks are widespread here in the sequence of basic metavolcanics, marble, quartzite, and small bodies of metamorphosed ultramafic and mafic rocks, plagioclase schists, as well as products of high-temperature granitization and conjugated basification, diverse granitoids (up to pegmatites), and metasomatically altered schists and carbonate rocks as well.

Graphite occurs in metamorphic, metasomatic, and igneous rocks as isolated flakes (0.5–0.6 mm in size)

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Table 1. Composition of microinclusions in graphite from the Main Sayan fault zone, at %

Mineral	Si	Ti	Fe	Ni	Co	V	Cu	Pt	Nb	Mo	As	Mn	S	O	Total
Pyrite			32.05										67.95		100
Pyrite			26.87	3.72	1.14		0.68						67.6		100
Pyrite			31.75										68.35		100
Chalcopyrite			22.61				24.57						52.81		99.99
Chalcopyrite			22.85				24.89						52.56		100.3
Chalcopyrite			22.58				27.24						50.33		100.15
Molybdenite										35.18			66.54		100.4
Molybdenite										33.6			66.39		99.99
Pyrrhotite			52.46										48.03		99.99
Fe–Ni oxide	0.44		37.26	2.46			0.31							59.54	100
Rutile		33.12												66.87	99.99
Rutile		32.53	0.23						0.33					66.91	100
Rutile		32.59	0.15			0.42			0.11					66.73	100
Ilmenite	4.04	19.72	11.13									0.15		64.95	99.99
Native Fe			98.79	0.49								0.73			100
Sulfoarsenide			4.7	1.11	22.82		0.76				29.01		41.6		100
Sulfoarsenide			7.15	0.99	18.48		0.64	2.56			29.41		40.77		100
Sulfoarsenide			23.14	0.65	4.47		0.48			29.79		41.47			100

and their segregations. Rocks with the highest content of carbon are commonly related to destruction zones, where graphite makes up veinlets and interlayers that impart a slatelike appearance to the rocks. Almost monomineral graphite nodules up to 20 cm in diameter are also found.

Study of the internal structure of graphite from the CRB fault zone with the Debye–Scherrer method allowed us to identify the carbon phase with a basal spacing d_{002} = 3.35–3.36 Å, which corresponds to crystallized graphite, in all types of rocks with graphite mineralization. Other d-spacings are as follows: d_{101} = 2.03 Å, d_{004} = 1.678 Å, d_{112} = 1.154 Å, d_{110} = 1.23 Å, d_{114} = 0.992 Å. The samples with cryptocrystalline or almost entirely disordered graphite with d_{002} = 3.32; 3.39 Å are second in abundance.

The degree of crystallinity of carbonic substances was specified with Raman spectroscopy. The main constituents of the Raman spectra that characterize graphite from the CRB fault zone include the intense line 1582 cm^{-1} corresponding to the major oscillation of E2g class typical of graphite proper and a wide line in the region of 2727 cm^{-1}, which is regarded as a superposition of several lines and a combination scattering line of the second order. Since the spectra of the given type virtually lack lines 1350 and 1600 cm^{-1}, which are often detected in natural graphite and traditionally attributed to the admixture of finely dispersed and disordered graphite, the Raman spectroscopy data allow us to classify graphite of the studied sample as a well-ordered variety. This inference is supported by the results of thermal analysis: the exothermal effect begins at 615–780°C.

The analysis of the structural state and thermal properties of native carbon has shown that the degree of graphite transformation in the CRB fault zone is higher than in the MS fault zone. However, in both cases, the temperature of the thermal effect of carbonic substances differs from the metamorphic grade of host rocks of the granulite facies (T = 700–850°C and P = 7–8 kbar [7]). The wide temperature range of graphite burnout testifies to the considerable duration of carbonification.

The endogenic processes in each tectonic zone comprise Mg–Ca metasomatism, silicification, and melting with generation of silicic magmas. These processes included active participation of the reduced carbon-rich fluids of the mantle origin. The severely graphitized metasomatites and pegmatites in the MS fault zone are enriched in V, Sc, Ni, Cr, Co, Zn, Cu, Au, Pt, and Pd [8]. The graphitized rocks of the CRB fault zone are characterized by elevated Sc, V, Ti, Co, Ni, Cr, Cu, Zn, Mo, and S contents along with a tendency to gain Au, Pt, Pd, Nb, Rb, and Nd. The chemically purified flotation concentrate of graphite almost always contains microadmixtures of V and Nd and traces of Nb, Rb, Y, Sr, Pb, Th, U, Ni, Zn, Cu, Ti, Mo, and S[9].

The elevated contents of a wide range of elements in carbon-rich rocks stimulated us to study inclusions in graphite. Examination of graphite on a JSM 6400 (JEOL) SEM equipped with a LINK energy-dispersive

Table 2. Composition of microinclusions in graphite from the Chernaya Ruda–Barakcha fault zone, at %

Mineral	Si	Ti	Fe	Cr	Ni	V	Cu	Zn	Pb	Sn	Pt	Rh	Zr	Ca	Mn	S	O	Total
Native Ti		98.75				1.25												100
Native Ti		98.36				1.64												100
Native Ti		98.58				1.42												100
Native Cu							92.82	2.68		4.5								100
Native Cu							96.33	1.23	2.44									100
Native Fe			96.92		3.08													100
Native Pt			4.63				27.41				64.86	3.1						100
Native Sn							2.41			97.59								100
Native Pb									100									100
Native Zn								100										100
Intermetallide compound	2.83	1.1	68.78	15.46	10.33										1.49			99.99
Intermetallide compound		2.35	70.9	15.41	10.17										1.21			100
Natural brass							58.32	40.58	1.09									99.99
Natural brass							58.03	40.74	1.23									100
Chalcopyrite			23.95				25.05									51.1		100.1
Fe oxide	0.27		39.12											0.31			60.29	99.99

spectrometer (Oxford, England) at the Institute of Geology, Komi Scientific Center, revealed the presence of numerous solid microinclusions. Eighty graphite grains recovered with chemical dressing were studied (V.N. Filippov, analyst). The microprobe data were obtained for 156 points. Some of the analyzed metallic compounds had a carbon coating. On the one hand, this hindered the determination of the chemical composition, but on the other hand, these films indicate the cognate character of microinclusions with respect to host graphite. Based on microprobe data, the microinclusions in graphite from the MS fault zone contain sulfides (pyrite, molybdenite, chalcopyrite, and pyrrhotite); sulfoarsenides of Fe, Co, and Fe–Co–Pt; and oxides (Fe–Ni oxides, ilmenite, rutile). One grain of native iron was also detected (Table 1). Inclusions of noble metals (native Ti, Fe, Zn, Cu, Pb, Sn, and Pt) and intermetallide compounds (Cu–Zn–Pb ± Al and Fe–Ni–Cr) are predominant as inclusions in graphite from the CRB fault zone. Oxides of Fe and Cr and chalcopyrite are second in abundance (Table 2).

The previously obtained data on carbon isotopic composition of graphite from the CRB and MS fault zones [8, 10], the results of mineralogical studies [11], and the discrepancy in metamorphic grades of carbonic substances and host rocks established from thermal properties allow us to classify the carbonic metasomatism as a self-dependent process that postdated regional metamorphism.

The major types of metasomatic alteration and related graphite mineralization in the Baikal and Sayan branches of the marginal suture of the Siberian Craton are rather similar. However, they also reveal an appreciable difference. For example, graphite from the CRB fault zone is characterized by extremely high structural perfection. Native metals and intermetallide compounds prevail among inclusions. In contrast, graphite from the southeastern MS fault zone is distinguished by a less ordered structure and predominance of sulfide and oxide inclusions. It is evident that the carbonic mineralization in the CRB fault zone is related to more vigorous reduced carbon-rich flows of metalliferous fluids. Their effect was manifested over a longer period and greater depth [12].

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