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Metallurgy and mineral processing

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KEY DIRECTIONS IN PROCESSING CARBONACEOUS ROCKS

T.N. ALEXANDROVA
Saint-Petersburg Mining University, Russia

Mathematical statistics techniques and the data from laboratory mineral and technological studies of samples were used to identify the most common natural and technological associations of microelements in carbonaceous rocks which could be of industrial value if extracted in the form of commercial products.

The discovered structures of spheroidal and ring ferrocarbonaceous clusters are respective formations of the class of metal fullerens with expressed magnetic properties. Such clusters may serve as construction blocks for new magnetic structures since each of them is a separate magnetic domain. Extracting such structures and their practical use opens the way to future technologies.

It is expected to employ such results in the future in the course of designing new techniques and technologies for benefication of carbonaceous raw materials while developing comprehensively solid mineral resources in the mining industry regions of Russia.

Key words: carbonaceous rocks, beneficiation, microelements, flotation, statistical criteria, accelerated electron beam, ferriferous carbonaceous clusters.

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Introduction. Many large and major deposits of gold, poly-metal ores, uranium and other mineral resources are associated with carbonaceous (black shale) rocks. Quite often high platinoids content is identified in them. Natural (Q_n) and technogenic (Q_t) associations of elements are identified. Ya.E. Yudovich [14] suggested calling elements "typomorphic" in case their content in the ash of carbonaceous rocks is higher than the respective clarks in sedimentary rocks. Such a term is used in this study to classify microelements (ME) in carbonaceous rocks.

The task of the study was to provide a foundation for principal directions of processing carbonaceous rocks aimed at extraction of valuable components from them. Highly promising nature of carbonaceous rocks as a source of gold and platinoids is based on two factors: wide proliferation of black shale masses in many regions of the globe and the analytical data on high content of gold and platinoids in them. Restraining factors include the extremely unstable character of analysis data (in dependence of the technique applied these may vary from quite considerable to practically zero) and lack of designs in technology of extracting mineral components from resistant highly carbonaceous raw materials. One of the possible causes of technological resistance is fine imbedding of valuable components into graphite [11, 12].

Preparation of technological samples to enrichment consisted in fracturing and reduction of samples and then selecting weighed portions for technological studies and analyses. Material washability was tested using a stage-by-stage technological scheme that included jigging, centrifugal concentration, fine tuning of narrowly classified fractions concentration desk and then flotation. Flotation based extraction of graphite containing products was executed using long chain amines, kerosene, silicofluoric sodium and pine oil in media of various pH produced by lime and sulfuric acid. The analysis of products of enrichment was conducted using atomic absorption, X-ray fluorescence and neutron activation analyses techniques. Mineral petrographic studies were done using optical techniques and electron microscopy X-ray spectral microanalysis (OEM-XSMA). Samples were studied in the St. Petersburg State University laboratory using the scanning electron microscope (Table top microscope 3000, Hitachi). To process experimental data multi-factor dispersion analysis was used and the Newman-Keuls test, their purpose to find the presence / lack of differences between the observable data(variation series) and retrieval of statistically significant differences between them [7]. Processing of graphitized float concentrates by the accelerated electron beam was done at the ILU-6 linear accelerator OF THE Institute of Nuclear Physics, Siberian Branch of the Russian Academy of Science, Novosibirsk. Accelerated electron energy was 2.7 MeV.

Identifying typomorphic associations of microelements in carbonaceous rocks. To retrieve the dependence of ME concentration on their common geochemical characteristics in shale samples we used classification [2] identifying the following groups of ME: 1) typical cation-genic lithophils; 2) cation- and anion-genic lithophils with permanent valence; 3) cation - anion-genic lithophils with variable valence; 4) typical anion-genic lithophils; 5) tiophil metals; 6) tiophil non-metals;

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7) siderophils of ferriferous group. The content of Mo, Pb, U, Re, Co, Cu, Zn, Ti, Sr in shale ash is considerably higher than their clarks in the Earth crust, clay and carbonate rocks. Due to limited availability of data on the content of Ge and Ga in ash samples, the conclusion that their average content in shale ash is higher than that in Earth crust or clay rocks is quite tentative. The table below gives systematized averaged data on ME content in various carbonaceous rocks and oil [1, 2, 4, 8, 14-15].

Microelements content in various carbonaceous rocks and oil

ME	Coals		Shales				Oil		ME groups
			Combustible		Black				
	C_{ic}	Q_{ic}^{A}	C_{ic}	Q_{ic}^{A}	C_{ic}	Q_{ic}^{A}	C_{ic}^{A}	Q_{ic}^{A}	
Li	15	1.1	60	1.77	31	0.57	–	–	1
Rb	15.6	0.53	139.1	1.95	74	0.63	337.9	2.3	1
Cs	0.64	1.42	5.0	4.42	4.7	2.57	61.5	27.2	1
Sr	103.5	1.02	270	0.97	189	0.46	450	0.88	1
Ba	128	0.7	560	1.24	500	0.69	298.3	0.33	1
Be	2.7	3.1	3	1.77	2.0	0.74	0.5	0.15	2
Sc	2.7	1.2	15	2.65	12	1.33	2.8	0.25	2
Ga	6.4	1.4	20	1.77	16.0	0.88	76.8	3.4	2
Ge	2.4	6.6	1.9	2.1	2.4	1.67	2.4	1.32	2
Ti	1,620	1.59	1,350	0.6	3,015	0.74	0.2	0.00004	3
Zr	36	0.8	160	1.42	120	0.66	7.9	0.035	3
Sn	11.0	0.49	5.0	0.88	3.9	0.43	0.14	0.012	3
V	24.7	0.82	130	1.77	205.4	1.75	39,370	268	3
Nb	2.2	0.88	17.2	2.74	11	1.11	–	–	3
Mo	2.4	5.3	2.0	1.77	20	11.1	1,216	538	3
W	2.3	5.75	2.2	2.1	2.9	1.77	–	–	3
U	2.2	2.6	3.3	1.59	8.5	2.55	20	4.8	3
Re	0.001	22.5	0.0005	4.4	0.9	4978	–	–	3
Cu	11.8	0.93	45.6	1.42	69.5	1.34	370	5.7	5
Ag	0.05	2.2	0.08	1.42	1.0	11.1	4.2	37.2	5
Au	0.03	44	0.002	1.15	0.007	2.55	0.5	147.5	5
Zn	28	1.55	100	2.2	128	1.77	2,350	26	5
Hg	0.15	15.9	0.18	6.4	0.27	5.97	2,560	45,000	5
Pb	12.8	2.8	22	1.95	21	1.15	0.65	0.028	5
As	18.8	6.4	13	1.77	29.9	2.54	248.3	16.9	6
Se	3.0	25	15.0	44	8.7	15.9	289.8	427.4	6
Cr	14.0	0.62	100	1.77	96	1.06	485.9	4.3	7
Mn	153	0.78	510	1.06	400	0.52	288.2	0.3	7
Co	4.6	1.04	19	1.86	18	1.04	320	14.9	7
Ni	10.4	0.47	60.5	1.33	70.3	0.81	14,170.2	132	7

Comment. C_{ic} is the concentration of microelement in the initial rock, g/t; Q_{ic} is the degree of its concentration in the initial rock with respect to clarks in clay rocks; C_{ic}^{A} is the concentration of microelements in ashes, g/t; Q_{ic}^{A} is the degree of its concentration in ash of the initial rock with respect to clarks in clay rocks.

Lantanoids merged into group 2 and featuring quite close chemical properties differ quite noticeably from each other in the degree of their concentration in the enrichment products; all the products are strongly enriched in Mo and Re (group 3), as compared to other ME from that group. Groups 5, 6 and 7 of ME, which are tiophils and siderophils, are pretty homogeneous in high enrichment of shales with these ME (to the exclusion of Pb and Mn), especially the ashes of black shales.

The diagrams (Fig. 1) present the comparative data on the associations of elements: $Q_{п} = Q_i / Q_{к}$, where Q_i is the content of ME, g/t; $Q_{к}$ is the content of the element in the clerk, g/t for the studied carbonaceous rocks.

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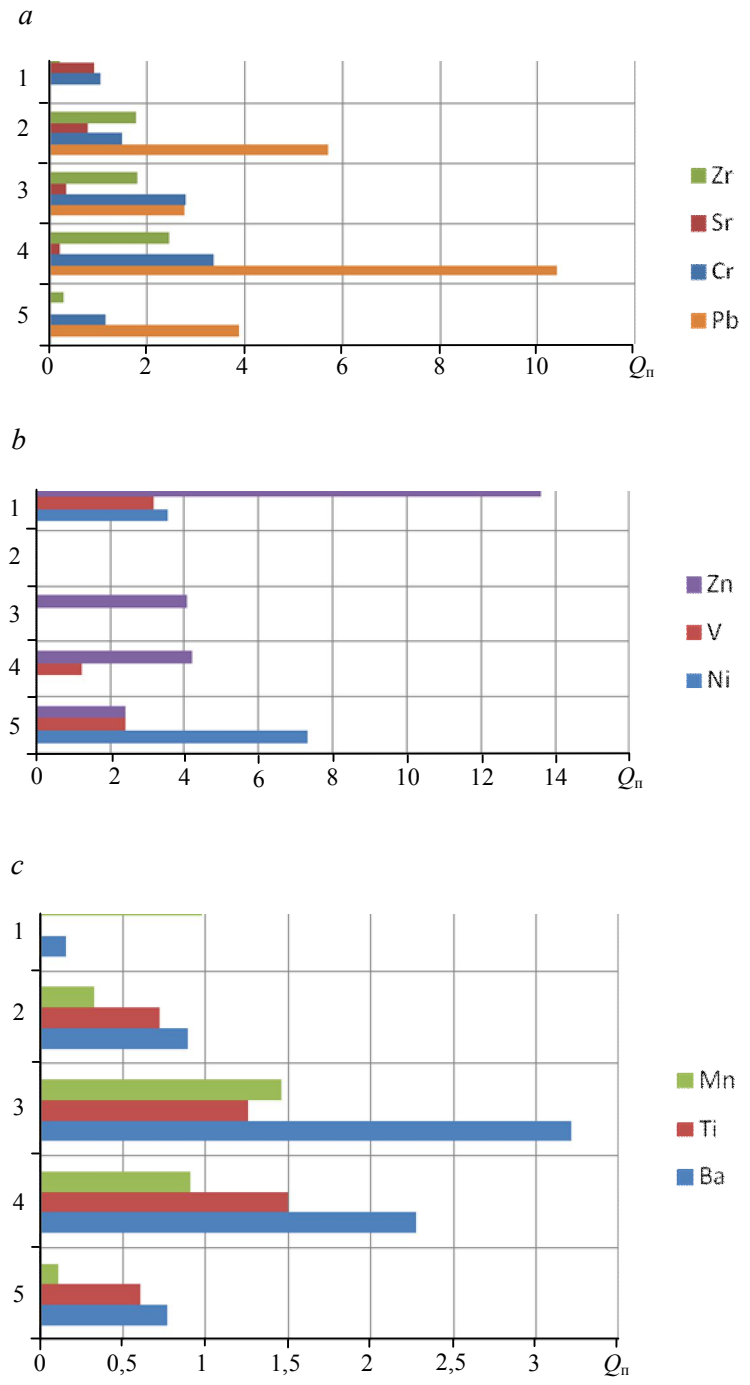


Fig. 1. Natural associations: *a* – Zr, Sr, Cr, Pb; *b* – Zn, V, Ni; *c* – Mn, Ti, Ba
1 – bituminized shales; 2 – dictyonema oil shales;
3 – Sutyrsk stratification; 4 – Kimkan stratification; 5 – Schungite

The series of flotation and gravitation enrichment products were analyzed on ME content followed by checking the series for their normality (Shapiro-Wilk's test) and calculation of the Newman-Keuls test criteria. The initial content of microelements was analyzed according the sieve analysis of samples. Technological associations of ME were identified in three series: carbonaceous flotation concentrates; sulfide flotation concentrates and gravitational concentrates.

The analysis of statistical criteria has shown that the elements Pt, Zn, Zr, As, Sn, Rb, Ag, Sr Mo, Pb, positioned following the fall-off of their correlation links are typomorphic in both their native state and the form of intermetallic compounds in the flotation graphite concentrates of the GS-1 sample. As for the flotation sulfide concentrates, such correlation links were identified for Au, Ag, Mo, Re, U, Zn [3, 5-6].

Treating carbonaceous flotation concentrates with accelerated electron beam. The results of treating flotation concentrates with the accelerated electron beam have shown that technological properties of various ores and products of their enrichment depend on irradiation dose, while their maximum changes are noted in the range of low (2-8 kGy) doses. It may be explained the following way. The initial processes taking place in solid bodies under the effect of electron beam depend quite strongly on beam parameters and the conditions of treating flotation concentrates. The decisive parameters are current density and electron energy in the beam. At low current densities and small energy absorbed by the matter (up to 1 J/g) the principal effect of treatment with accelerated electrons is the formation of radiation defects without any noticeable changes in physical properties of the substance. As the absorbed energy grows (up to 10 J/g) electric charge may start accumulating, which would eventually result in electric breakdowns. The process of charging occurs differently in the conducting (pyrite, galenite, etc.) and poorly conducting minerals (quartz, sphalerite, etc.). The discharge is of pulsating character, and a system of microfisures may start developing, which would keep growing after each pulse discharge, resulting in the material losing its strength which would work positively in the course of further hydrometallurgic re-processing. In case of irradiating the material with high energy electrons, so that the absorbed energy is high (> 100 J/g) the substance may heat and physico-chemical processes would start that differ in principle from purely thermal phenomena. That analysis of data obtained has demonstrated that there

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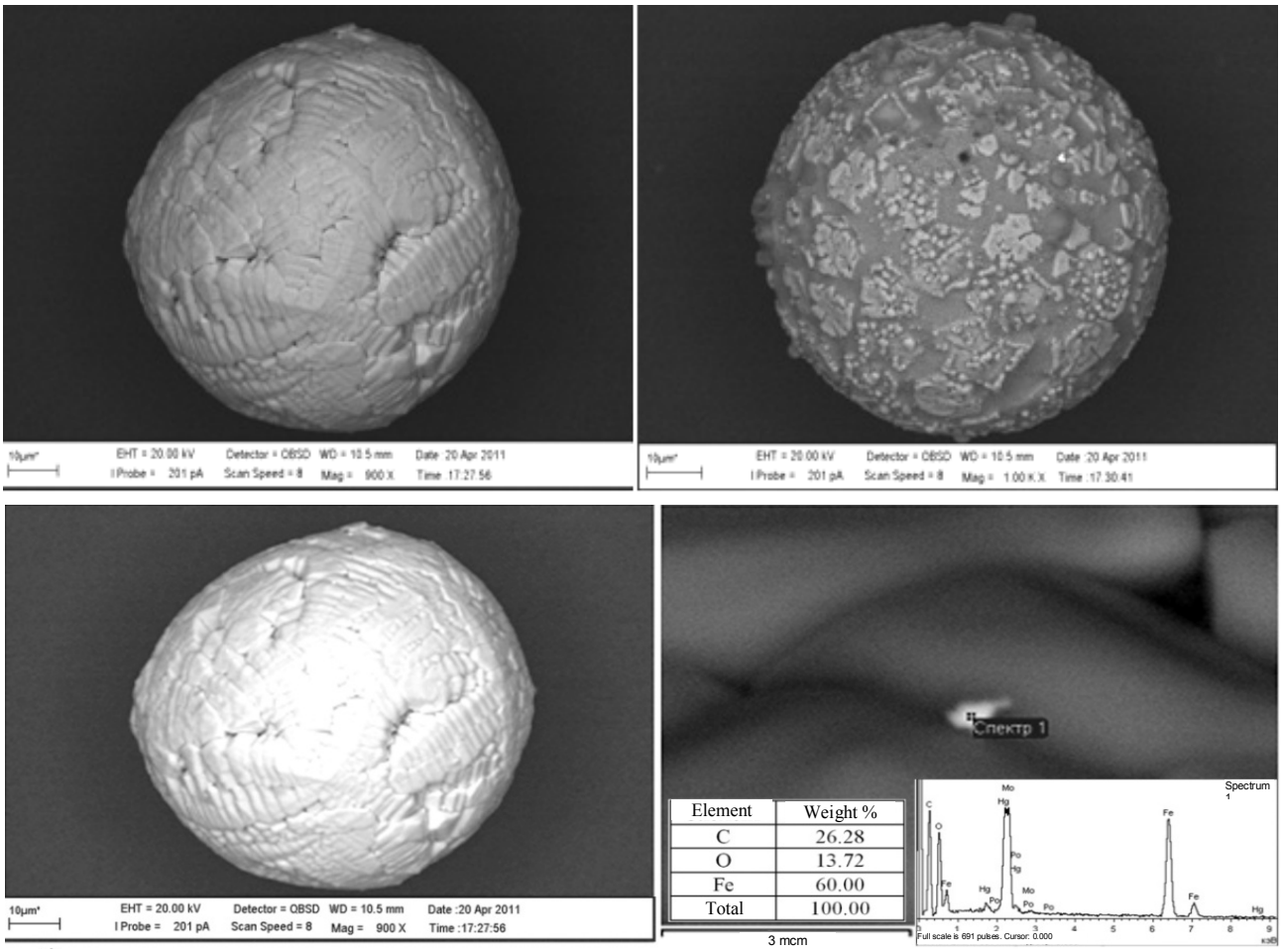


Fig.2. Regular spheroidal ferriferous structures with nano-inclusions of rare earth and noble metals

is a processing mode optimal for softening of substance and regrouping of substance structures. A particular feature of highly carbonaceous rocks (samples GS-1 and GS-2) that was detected during their mineralogical and technological studies is the presence of spheroidal and toroidal ferriferous-carbon clusters (Fig. 2). Data are available on the presence of nanotubes of carbonaceous substance in graphite bearing rocks of the northern part of Khankai terrain [12]. Properties of carbonaceous naophases are studied insufficiently yet. However, a common characteristic of nano-objects is a non-crystallographic nature of their forms, spherical nano-crystals, nanocrystal tubes, threads, toroids, etc. among them. [9]. Closing the ends of a linear chain consisting of quatrons results in the formation of a ring structure that forms into a nano-crystal toroid. The share of regular spheroidal structures increases in the treated samples (Fig. 2).

Conclusion. Using the techniques of mathematical statistics techniques and the data from laboratory mineral and technological studies of samples have made it possible to identify the most common natural and technological associations of microelements in carbonaceous rocks which could be of industrial value if extracted in the form of commercial products.

The discovered structures of spheroidal and ring ferri-carbonaceous clusters are respective formations of the class of metal fullerenes with expressed magnetic properties. Such clusters may serve as construction blocks for new magnetic structures since each of them is a separate magnetic domain. Extracting such structures and their practical use opens the way to future technologies. It is expected to employ such results in the future in the course of designing new techniques and technologies for beneficiation of carbonaceous raw materials while developing comprehensively solid mineral resources in the mining industry regions of Russia.

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Author **T.N.Alexandrova**, *Dr. of Engineering Sciences*, *Head of Department*, *alexandrovat10@gmail.com* (*Saint-Petersburg Mining University, Russia*).

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