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Nodules in Carbonaceous Sediments of the Southern Tunguska Basin

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Abstract—Pioneer results of the comprehensive analysis of nodules from the Upper Paleozoic coaliferous association and the underlying Middle Paleozoic sequence in the southern Tunguska Basin (Siberian Craton) suggest the following: (1) sediments underlying the coaliferous association contain two (siliceous and carbonate) types of normal nodules and one type of allogenic nodules (redeposited chalcedony nodules in the kaolinite–chalcedony unit of the Beloyarsk Formation); (2) the coaliferous association includes four (calcite, siderite, pyrite, and goethite) types of nodules; (3) each nodule type is confined to a specific genetic type of sediment; e.g., siliceous nodules are confined to lagoonal sediments; calcite nodules, to lacustrine and lacustrine–boggy sediments; siderite nodules, to lacustrine–boggy and boggy sediments; pyrite nodules, to boggy sediments; and goethite nodules, to alluvial sediments; (4) the formation of goethite nodules is mainly related to the erosion and redeposition of siderite nodules; (5) the coefficient of carbon concentration shows a distinct positive correction with the coefficient of nodule content; (6) nodules appeared in the coaliferous association during diagenesis and epigenesis; the calcite and pyrite nodules are enriched in sandy material, as suggested by the high content of insoluble residue; (7) combustion of coal seams promoted the melting of the adjacent siderite nodules and the formation of magnetite ores; consequently, the thermally altered mudstones, siltstones, and sandstones were transformed into a high-quality building material that is used as road fill.

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Works of W. King, G. Abbot, W.A. Richardson, A. Kumm, G.I. Teodorovich, L.V. Pustovalov, J.W. Price, W.H. Twenhofel, G.I. Bushinskii, N.M. Strakhov, K.O. Emery, A.V. Makedonov, P.V. Zaritskii, and many other researchers make up the basis of the science of nodules. However, their geochemistry and genesis are insufficiently studied, particularly, in the Tunguska Basin (Russia). Nodular formations in carbonaceous sediments of the Tunguska Basin are poorly investigated. To date, only one publication has been devoted to first results concerning nodules in Upper Paleozoic carbonate sediments of the northern Tunguska Basin (Gurevich *et al.*, 1977).

MATERIALS AND METHODS

The factual material was mainly collected in the course of investigation within the framework of the international project "Correlation of Coaliferous Associations" (Pavlov *et al.*, 1990). Subsequently, our data base was constantly replenished with new materials, particularly, in the course of work within the framework of the project "Evolution of Tectonic and Paleogeographic Settings in the Middle Paleozoic in the Siberian Craton" and during investigations in collaboration with geologists from the Ugol'naya Team (Irkutskgeologiya Industrial–Geological Association) who carried out the detailed exploration of the Zheron and Zelinda coal fields. In total, we investigated nodules from 18 core-drilling holes along with 67 open pits and mine workings (Fig. 1). Thus, we collected more than 100 nodule specimens, among which 36 specimens were comprehensively examined. The chemical composition of nodules and enclosing rocks was studied at the Analytical Center of the Institute of the Earth's Crust, Irkutsk. The bulk content of oxides and minor elements was determined by the XFA method. The major components were analyzed with a SPM-25 multichannel X-ray spectrometer, while the rare (minor) elements (Ni, Co, V, Zr, Mo, Cr, Cu, and others) were determined with a VRA-30 X-ray spectrometer by E.V. Khudonogova and S.I. Shtel'makh (Revenko, 1994). Light and heavy fractions of nodule minerals were investigated by the immersion method with their preliminary separation in bromoform (T.I. Khramtsova, mineralogist).

LITHOLOGICAL CHARACTERISTICS OF SEDIMENTS

The Tunguska coaliferous basin with an area of 1.045 mln km^2 and coal reserve of 1868 Gt (as of 2004) played a unique role in the development of the Siberian Craton. The southern area of this basin is composed of

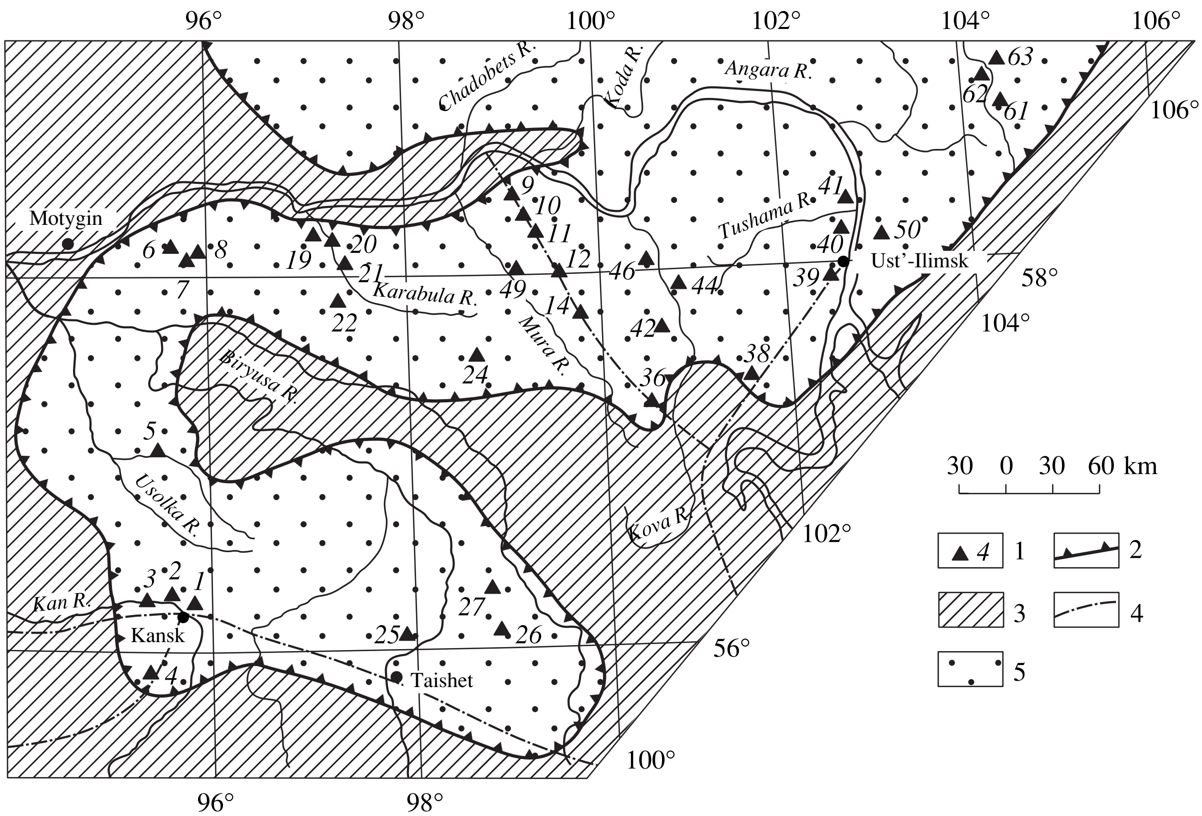

Fig. 1. Sketch map of the study area. (1) Numbers of reference sections representing natural exposures of mine workings (prospect holes, clearings, and open pits) or boreholes located in the following areas: (*1*) Settlement of Podayaisk, (*2*) Settlement of Beloyarsk, (*3*) Settlement of Antsir, (*4*) Settlement of Borodino, (*6–8*) Chuno–Karabul watershed, (*9–12, 14*) Sedanovo–Kodinsk Highway, (*19–22*) Karabula River basin, (*24*) Settlement of Kondrat'evka, (*25*) Settlement of Biryusinsk, (*26*) Settlement of Balturino, (*27*) Settlement of Bunbuisk, (*36*) Mur–Kova interfluve, (*38*) Settlement of Educhanka, (*39*) Ust'-Ilimsk, (*40*) Tushama River mouth, (*41*) Settlement of Keul, (*42, 44, 46*) Kova River basin, (*50*) Settlement of Kopaevo, (*61–63*) Katanga River basin; (2) domain of Middle–Upper Paleozoic (Devonian, Carboniferous, and Permian) rocks; (3) domain of Lower Paleozoic rocks; (4) highways; (5) domain of Middle–Upper Paleozoic rocks.

Middle–Upper Carboniferous and Lower–Upper Permian carbonaceous sediments (Fig. 2). The underlying (Lower Carboniferous and Upper Devonian) rocks are composed of lagoonal and marine (terrigenous and terrigenous–carbonate) sediments. The Lower Paleozoic lithogenesis of this area has the following specific features: (1) the wide development of lacustrine–boggy, boggy, and alluvial facies; (2) the stability of a moderately humid and cold climatic environment during the entire Late Paleozoic and the consequent low degree of weathering of clastic material; and (3) the small amplitude of basin subsidence and, consequently, low rate of sedimentation.

It should be emphasized that Carboniferous and Permian sediments of the study area were subjected to a weak hydrodynamic sorting. The sandstones and siltstones universally contain fractions ranging from the psephitic to pelitic dimension. The mudstones always include sandy grains. Such conditions of the sedimentation of allogenic material could only exist in valleys of slowly flowing rivers and in small lacustrine basins. Coals were formed in bogs, lakes, and alluvial plains. The maximal coal content is confined to marginal parts of basins and local uplifts therein.

Rocks of the coaliferous association are characterized by a rather low maturity of the terrigenous material. The sandstones and siltstones mainly belong to the arkose and graywacke groups. Units with relatively mature mesomictic quartz rocks are only encountered at the base of the coaliferous sequence. The bulk SiO_2 content in rocks rarely exceeds 70%, which is far less than the average content for sandstones in the lithosphere. The composition of the major components does not appreciably change in the vertical direction in all studied areas. Significant compositional changes are only observed in the lateral direction. This peculiarity of mineral composition of rocks is related to the constancy of provenances. Heavy minerals were accumulated in all grain size fractions of sediments. However, the maximal concentration is recorded in fractions <0.05 and 0.05–0.25 mm. The content of heavy minerals is lower in coarser fractions (0.25–0.5 and 0.5–1.0 mm).

Mudstones and the pelitic fraction of sandstones and siltstones have a polymineral composition. Montmoril-

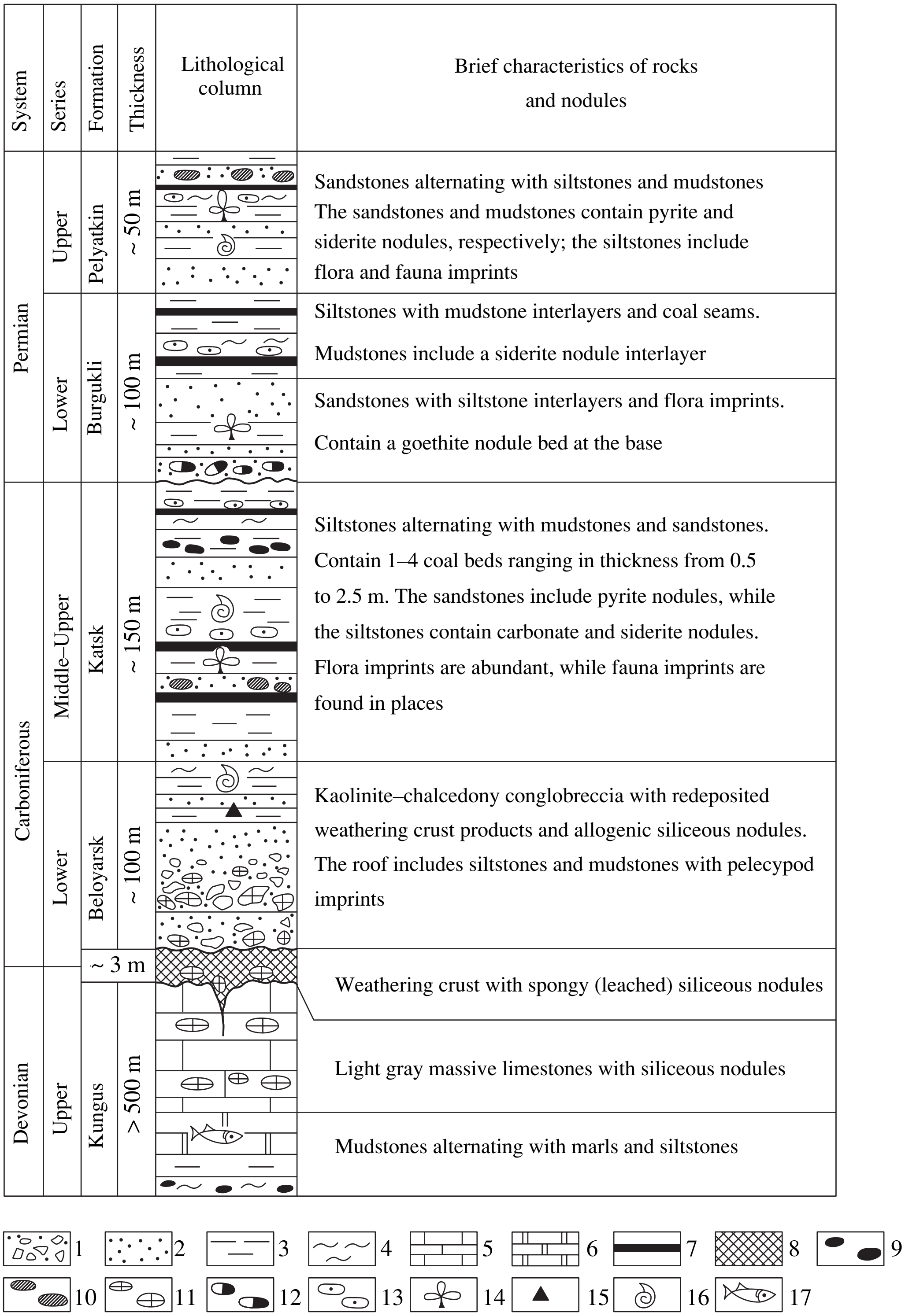

Fig. 2. Summary lithostratigraphic section of carbonaceous sediments in the southwestern Tunguska Basin with the consideration of nodule contents. (1) Conglobreccia; (2) sandstones; (3) siltstones; (4) mudstones; (5) limestones; (6) marls; (7) coals; (8) weathering crust; (9–13) nodules: (9) carbonate, (10) pyrite, (11) siliceous, (12) goethite, (13) siderite; (14–17) paleontological imprints: (14) flora, (15) spores, (16) fauna, (17) ichthyofauna.

lonite, hydromica, kaolinite, chlorite, and dioctahedral mica are the major minerals.

It is worth mentioning that the coaliferous association is underlain by a residual and redeposited weathering crust that consists of siliceous breccias, kaolinic clays, mesomictic sandstones, and siltstones. In terms of the chemical composition, the weathering crust and its redeposition products belong to the sialite type.

Karstens (1981) identified them as monosialite (montmorillonite and hydromica) rocks. The age of the weathering crust is estimated as Late Devonian–Early Carboniferous.

TYPES, STRUCTURES, AND COMPOSITIONS OF NODULES

The southern area of the Tunguska coal basin is characterized by the abundance of siliceous, calcite, siderite, pyrite, and goethite nodules (Akulov, 1983). They are mainly confined to sandstones, limestones, siltstones, and mudstones deposited in various facies settings in the Carboniferous and Permian. Assessment of the entire coaliferous association of the Tunguska Basin revealed that the averaged coefficient of nodule content therein is approximately 0.8%. Coefficients of carbon and nodule contents show a direct correlation. For example, the coefficients are equal to 12.5 and 1.24%, respectively, in the Katsk Formation; 8.9 and 0.98%, respectively, in the Burgukli Formation; and ~7.3 and 0.24%, respectively, in Upper Permian sediments of the Pelyatkin Formation.

Sediments underlying the coaliferous association in the southern part of the Tunguska Basin (Kungus and Charginsk formations) include carbonate and siliceous nodules (Fig. 2). The coefficient of nodule content in these sediments is as much as 0.05%.

Carbonate nodules are confined to limestones of the Charginsk Formation (Fig. 1, open pit 1). They have spheroid and ellipsoid shapes, grayish white color, and radial-fibrous texture. The internal zone of almost all carbonate nodules is composed of massive calcite, from which fibrous aragonite crystals extend uniformly along all directions and make up a spherical rim. The aragonite crystals are up to 3 cm in size, whereas the maximal diameter of nodules is as much as 15 cm. The nodules are mainly composed of CaO (48.5%). Contents of other components are as follows (%): SiO_2 6.36, Al_2O_3 1.47, MgO 0.37, Fe_2O_3 0.32, TiO_2 0.06, Ba 0.0046, and Sr 0.017.

Siliceous nodules composed of mainly SiO_2 (80–99%) are confined to limestones, marls, and calcareous siltstones that are exposed at the Chun–Biryusa interfluve in the Taishet district (Fig. 1, boreholes and mine workings 25–27). The siliceous nodules have rounded, flattened, ellipsoid, or irregular shapes. They are up to 13 cm long (Fig. 3a) and gray to grayish or reddish brown in color. They make up chains that locally grade into thin quartz interlayers (up to 3 cm thick). The siliceous substance in nodules often displays wavy or curvilinear colloform (gel-type) texture, suggesting their formation as gels from colloidal solutions. The siliceous nodules make up horizontal chains in whitish gray and pale brown cryptocrystalline limestones that often include numerous syngenetic quartz veinlets up to 2–3 m thick.

In recent years, various private companies are engaged in the extraction of these limestones for the production of lime. The limestone is calcined directly in open pits. The siliceous nodules and quartz veinlets considerably depreciate the quality of lime product. Therefore, the limestones are subjected to preliminary crushing (up to 10 cm) and sorting. A typical conchoidal fracture is developed on the cleavage surface of siliceous nodules during the crushing.

It should be noted that numerous allogenic siliceous nodules have been found in Lower Carboniferous kaolinite–chalcedony conglobreccias of the Beloyarsk Formation (Serpukhovian Stage) that are universally overlain by sandstones and siltstones. The conglobreccias also occur at the base of the coaliferous association. The graded structure of these rocks indicates that their depositional settings were characterized by drastic changes and the highly intense hydrodynamic activity at the initial stage of their accumulation graded into a calm regime. The conglobreccias are represented by obviously redeposited products of the sialitic weathering crust. They contain variegated (from bluish gray to reddish brown) ellipsoidal, often cavernous, intensely fractured, and locally weathered chalcedony nodules and their numerous fragments. The size of allogenic chalcedony nodules varies from 2 to 14 cm. The conglobreccias are cemented by iron hydroxides, and a coarse-grained psammitic material serves as the filler. They are widespread in the vicinity of the town of Kansk and at the Chun–Karabul interfluve (Fig. 1, outcrops, open pits, and mine workings 1–3, 5–8, 19–22).

The nodule-bearing complex in the lower section of the coaliferous association of the Katsk Formation is composed of diverse (pyrite, calcite, and siderite) nodules.

Pyrite nodules occur among sediments of the bog facies (generally, at the base of coal seams). They have been found in numerous boreholes that recovered coaliferous sediments in the Boguchanskaya hydroelectric power plant, Kodinsk airport, and Tushama River valley areas (Fig. 1; boreholes 9, 10, 40, 41). The nodules have spheroid (up to 4 cm across) or elongate-cylindrical (dumbbell-shaped) morphology up to 8 cm long. They are characterized by grayish white color, fine-grained texture, and irregular metallic fracture. Their usual composition is as follows (%): FeO 16.99, SiO_2 24.44, Al_2O_3 4.85, and S 13.53.

Calcite nodules are abundant at the Mur–Kova interfluve and in the Ust'-Ilimsk district (Fig. 1; boreholes and mine workings 11, 12, 36–42, 46, 49). The calcite nodules are confined to mudstones and siltstones deposited in lacustrine and lacustrine–boggy settings. They have a billiard ball-type spheroid shape, average size (~7.5 cm in diameter), and yellowish white color. The central part of some nodules contains small allogenic grains that served as their nuclei. The nodules have a fine-grained texture and vague horizontal or concentric-zonal structure (Figs. 3d–3g). The carbonate material (CaO) makes up 25.12% of the nodules.

The maximal content of other components is as follows (%): SiO_2 34.63, Al_2O_3 9.25, Fe_2O_3 3.56, MgO 1.59, and Na_2O 1.51.

Siderite nodules are the most widespread type. They are confined to the roof of coal seams. Their formation is governed by the development of sediments of the lacustrine–boggy facies that were investigated in the Zheron–Zelinda coaliferous area (Fig. 1; boreholes 50, 61). They are commonly observed as autonomous nodule interlayers and lenses up to 0.5 m thick. The nodules are commonly ellipsoidal and approximately 19 cm across. We assume that the flattened shape of siderite nodules is not related to vertical compression of their initial colloidal material. This morphology may be produced by the influx of the nodule-forming material along the horizontal (parallel to the bedding) direction. They have a yellowish white color and homogeneous cryptocrystalline structure on the fresh cleavage surface.

It is interesting that a vast area of siderite nodule field (~0.5 km^2) has been washed up in the river channel (Fig. 4) during the high water period in the middle course of the Nizhnyaya Tunguska River (estuary of the Bol'shaya Chaika River). This is a placer deposit of siderite nodules up to 0.7×0.35 m in size. Their edges are slightly angular (the coefficient of roundness is 1–2) and their surface contains a thin (up to 3 mm) coating of dark brown oxide that resembles the varnish. They have a grayish white color with dull tint on the fresh surface. The siderite nodules are almost always characterized by a homogeneous cryptocrystalline structure. However, their central zones are sometimes crosscut by desiccation (syneresis) cracks, and septaria are formed due to their infilling by minerals (Fig. 3l). Imprints of stems of higher plants are observed on the surface of nodules and sometimes near their central zones (Fig. 3k). It is very difficult to take specimens of nodules because of their round shape, big size, and relatively high density (the geological hammer rebounds from them as if from an anvil). Their composition is as follows (%): (FeO + Fe_2O_3) 80.69–87.92, MnO 1.87–2.77, CaO 1.18–2.75, SiO_2 5.8–9.35, Al_2O_3 1.43–1.46, and MgO 0.98–1.32.

It should be noted that Lower Permian intraformation conglomerates of the Burgukli Formation in the Katanga River valley often contain the redeposited pebbles and sometimes contain interlayers of **goethite nodules** formed as a result of the washout of beds with siderite nodules. Thin (up to 0.15 m) interlayers of goethite nodules (brown ores) occur together with basal conglomerates of the Burgukli Formation. The goethite nodules are found in the Kova River valley, near the Settlement of Nedokur, and at the Zheron coal deposit (Fig. 1; boreholes and mine workings 36, 42, 50). For example, the Zheron coal deposit contains numerous lenses and interlayers of thin (up to 0.18 m) brown ores crosscut by several boreholes (Fig. 3m). They are represented by a very hard ferruginated shell of cavernous goethite nodules up to 0.5–10 cm in size. All nodules have concentric-zonal structure that is evident from their color and hardness. The outer shell is composed of dark brown hard massive goethite, whereas the central (light yellow) shell is entirely composed of hydrogoethite (Fig. 3n). Maximal contents of the major components of shells are as follows (%): Fe_2O_3 81.99, SiO_2 14.76, Al_2O_3 2.89, MgO 1.35, K_2O 0.26, TiO_2 0.031, P_2O_5 0.26, and MnO 0.99.

Pseudonodules (false nodules) are of specific interest. This diverse group of natural segregations apparently resembles the nodules and includes blue-green pebble-shaped mudstone pellets from basal sediments of the Lower Carboniferous Tushama Formation. The brown marl and brownish green mudstone of the Kungus Formation includes spectacular calcareous gravelstones. In addition, limestones of the Charginsk Formation contain up to 5-cm-thick interlayers composed of numerous small (up to 1 mm) concentric-zonal carbonate globules. The group of pseudonodules also includes nodules produced by weathering (Rukhin, 1969). They are composed of iron hydroxides that replace fragments of sandy rocks in the coarse-grained sand during the weathering. Such nodules are developed as ellipsoid and oblate segregations, similar to the thick-walled shell, in fine-grained grayish yellow thick-platy polymictic sandstones. The goethite walls are up to 1 cm thick. The average size of nodules is approximately 5 cm. Their central zone consists of a friable fine-grained (slightly ferruginated) sand that readily falls out when the nodule is broken. Therefore, the nodule specimens resemble hollow bodies. Maximal contents of the major components in the nodules are as follows (%): SiO_2 78.48, Fe_2O_3 19.47, Al_2O_3 1.83, K_2O 0.99, TiO_2 0.12, P_2O_5 0.1, and MnO 0.013.

Thus, the nodules tend to acquire spherical shape in the case of both individual species and colonial ingrowths. This peculiarity was first noted by Baranov (1946) who established that decrease in the diameter of nodules is accompanied by the development of a more distinct spherical shape of their colonies. Long-term observations revealed that the spherical shape of nodules is a result of the tendency of the nodule-forming material to acquire a morphology that consumes the least amount of energy. This process was promoted by the homogeneity of the enclosing sediment, its high permeability, and sufficient thickness that served as a basis for the active geochemical redistribution of nodule-forming elements and did not constrain the growth of both nodules and their aggregates. It is also necessary to note that the siderite nodule-hosting siltstone beds were used as marker units during the calculation of reserves in the Zheron and Zelinda coal deposits. The bottom of the Burgukli Formation is well outlined on the basis of coarse-grained sandstones and gritstones that enclose the goethite nodules.

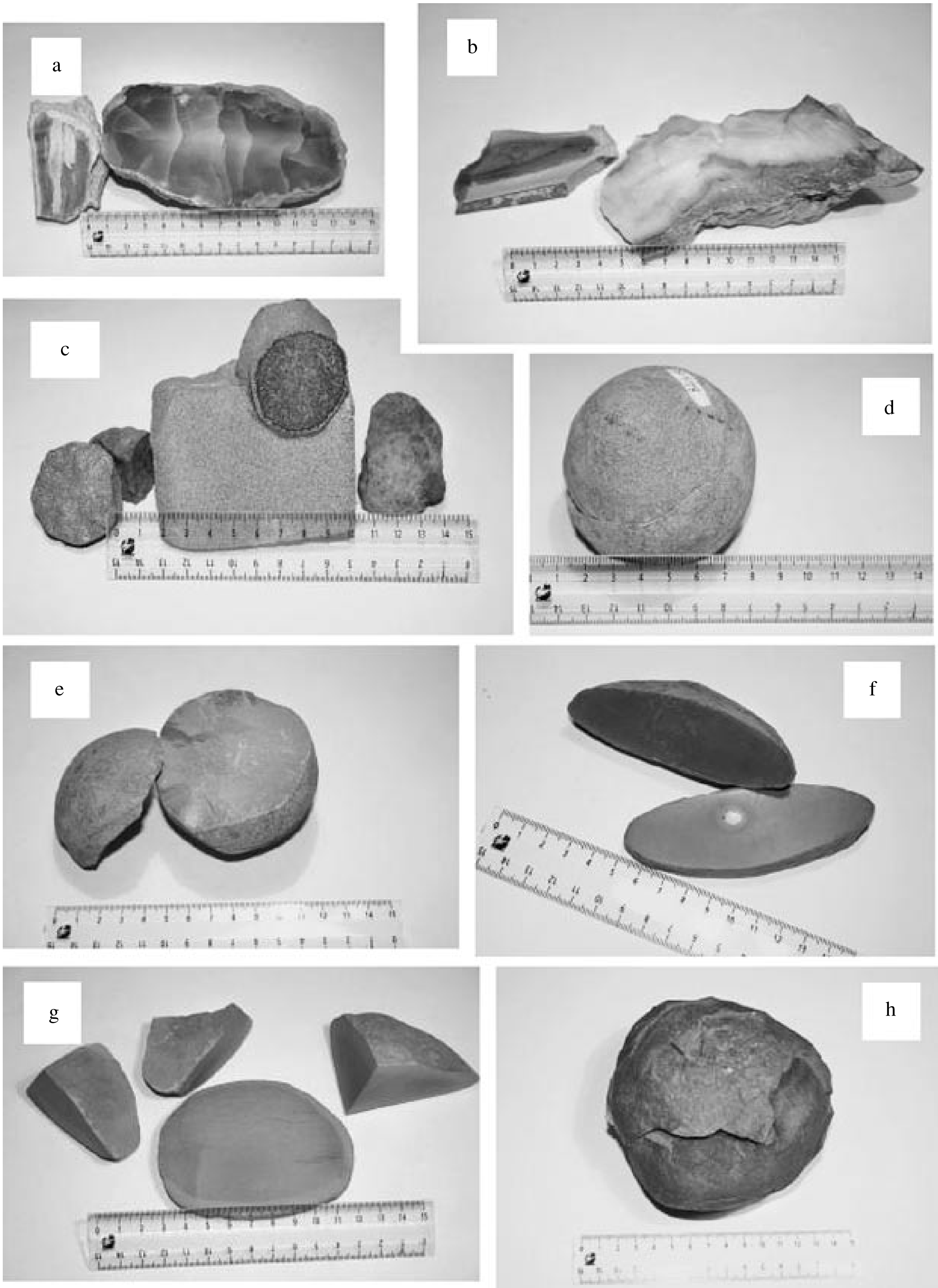

Fig. 3. Different types of nodule in carbonaceous sediments of the southern Tunguska Basin. (a) Siliceous; (b) allogenic siliceous; (c) pyrite; (d–g) calcite; (h–j) siderite; (k) siderite nodules with flora imprints; (l) siderite nodules with desiccation (syneresis) cracks; (m, n) goethite (brown ore).

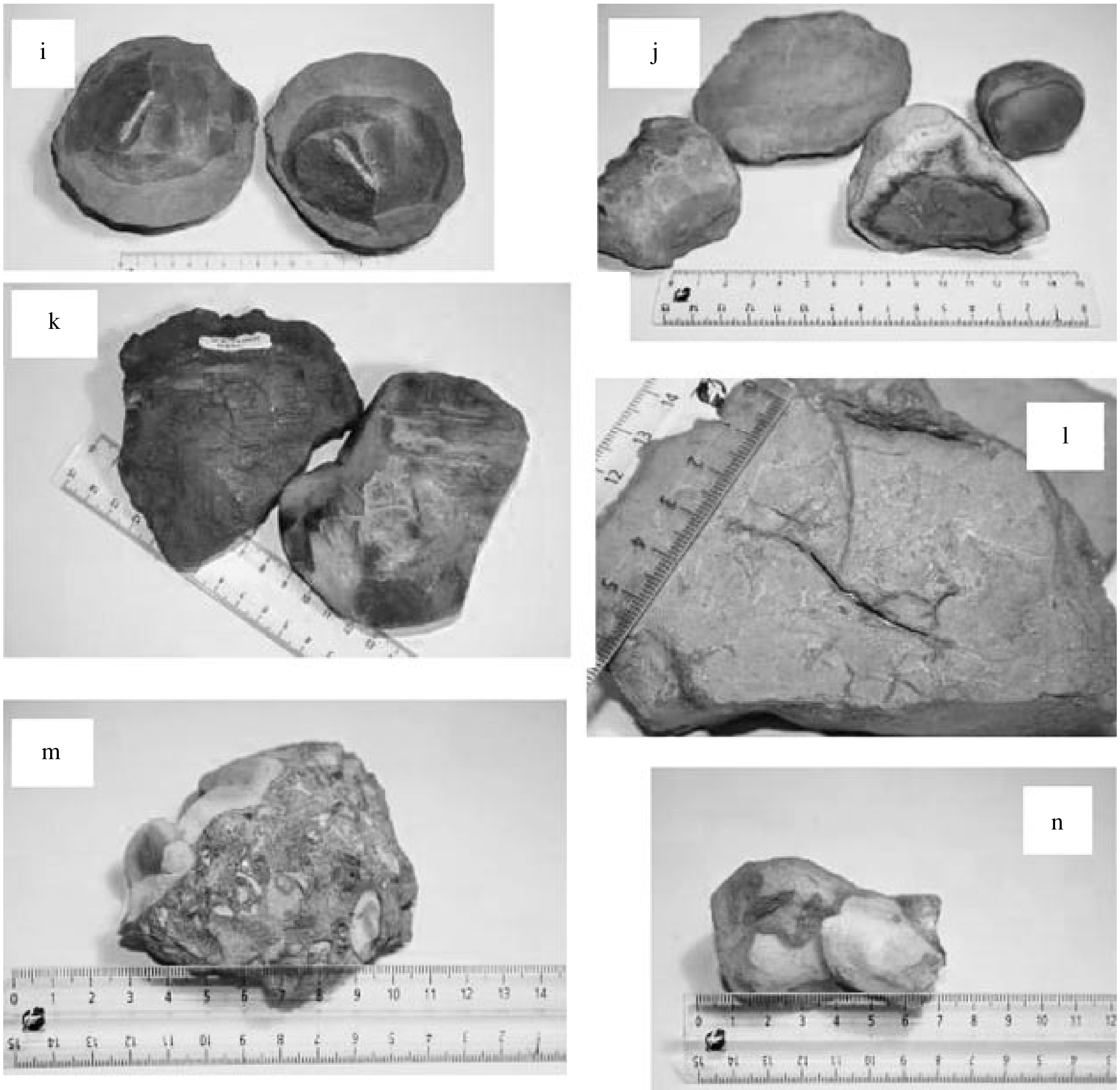

Fig. 3. (Contd.).

FORMATION CONDITIONS OF NODULES AND CHARACTER OF MINOR ELEMENT DISTRIBUTION IN THEM

Siliceous nodules formed in an aqueous medium with high concentration of siliceous compounds characterized by the absence of organic matter. Silica entered the sedimentation basin from zones of the chemical weathering of rocks that were widespread at that time in the ambient environment. The organic matter was transported with river waters and ephemeral currents. Gradual concentration of silica in the sedimentation basin (ancient Poima–Biryusa lagoon) promoted the formation of α-quartz particles and their precipitation on separate grains (seeds) on the basin floor (selective concentration). This observation confirms experimental results reported by Rottländer (1981) who established that the organic-free water in sedimentation basins are usually enriched in silica. It should be noted that the process of silica accumulation is only typical of regions with warm arid or semiarid climate. The appearance of a sufficient amount of moisture and carbon dioxide in such climatic environment fosters the formation of highly soluble alkaline silicates (e.g., $NaSiO_3$). Thus, the formation of siliceous nodules may be related to the transfer of $NaSiO_3$ into solution in the presence of exchange ion of Na or calcium carbonate and sulfate in an alkaline medium. This was indicated by V.A. Kovda as early as 1940. He experimentally

Fig. 4. Placer of siderite nodules in the Nizhnyaya Tunguska River basin (near the Settlement of Erema).

proved that silica can be formed according to the following scheme:

$$CaSO_4 + NaSiO_3 \longrightarrow CaSiO_3 + Na_2\,SO_4;$$

$$CaSiO_3 + 2H_2CO_3 \longrightarrow SiO_2 \cdot H_2O\downarrow + Ca\,(HCO_3)_2.$$

The association of **pyrite nodules** with sandstones is not accidental. During epigenesis, the sandstones served as an efficient water-conducting unit. Naturally, the circulation of waters with SO_4 ions and hydrogen sulfide along such rocks promoted the formation of pyrite. Iron was introduced into the solution as a result of epigenetic alterations of the clastogenic material. Such source of Fe has been scrutinized by Koporulin (1962) who studied pyrite nodules from Jurassic coaliferous sediments of the Irkutsk Basin. It should be emphasized that sulfate-reducing bacteria played an essential role in the formation of pyrite nodules. It is likely that their activity in circulating waters was responsible for the decomposition of sulfates and decrease of their content in the rock. The abundance of free hydrogen sulfide in the solution promoted the formation of pyrite nodules.

The formation of authigenic pyrite crystals and their aggregates in siltstones, mudstones, and coaliferous mudstones followed a different scenario. These rocks are nearly waterproof. Therefore, pyrite could form in them only at initial stages of diagenesis. They formed in shallow-water (lagoonal-boggy and boggy) basins, where the humic material was abundant in the water. Reduction of SO_4 in the sandy–clayey sediment at the diagenetic stage led to the formation of pyrite at the expense of Fe dissolved in water.

Mineral and petrographic investigations revealed that the pyrite nodules contain as much as 30% of quartz and feldspar fragments cemented by pyrite. The nodules also include as much as 1.5% of heavy-fraction minerals, such as garnet, zircon, apatite, and rutile.

Numerous data on the chemical composition of pyrite nodules and enclosing sandstones indicate that the nodules contain as much as 34.6% of FeO, while the content of other oxides in them is very low (relative to host rocks). At the same time, XFA data suggest a relatively high concentration of the following elements (%): Ni 0.004, Zn 0.0025, Co 0.0026, Cr 0.005, Ba 0.015, Sr 0.0011, Cu 0.008, and Zr 0.0054 (Fig. 5).

In **siderite nodules,** the FeO content reaches 65% in the outer shell and 55% in the central shell. Their bedding conditions suggest the formation from true rather than colloidal solutions. According to (Bushinskii, 1946; Strakhov and Zal'manzon, 1955; Gordeev, 1983; Kholodov and Butuzova, 2004; and others), Fe contained in peat bogs is transported as organic iron complexes (fulvoacids along with humic and lipidamin compounds) and is precipitated from boggy groundwaters. It is quite conceivable that some Fe migrates as molecules, ions, and inorganic complexes. The final stage of siderite formation may proceed according to the following scheme:

$$2Fe_2O_3 + 4C_{org} + 3O_2 \longrightarrow 4FeCO_3\downarrow.$$

This process is likely to be accompanied by the selective crystallization of substance near the newly formed nodule formation centers. Elements migrated from one site of the bed to another site. The element composition is as follows (%): Ba 0.0036–0.015, Zn 0.0009–0.015, Ni 0.0045–0.0062, Cu 0.0023–0.0026, Cr 0.0005–0.0007, V 0.0096–0.017, Sr 0.0015–0.0044, Co 0.003–0.004, and Zr 0.003–0.0045.

Calcite nodules of the Upper Paleozoic coaliferous association have been detected in fine-grained rocks (mudstones, siltstones, and fine-grained sandstones). The confinement of $CaCO_3$ to shore zones of ancient lakes and large bogs is caused by the intense biochemogenic precipitation of calcium carbonate from the bottom water with a high Ca content and weak diagenetic $FeCO_3$ generation due to a low Fe content in the water. The prevalence of carbonate nodules is pre-

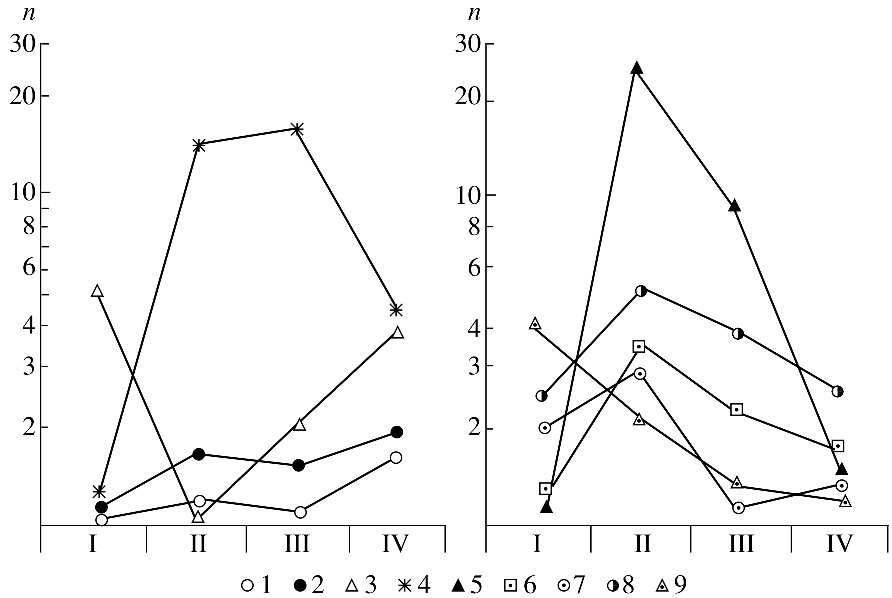

Fig. 5. Distribution of minor elements in different nodule types. (1) Ba (10^{-4}%); (2) V (10^{-3}%); (3) Cr (10^{-3}%); (4) Mn (10^{-2}%); (5) Ag (10^{-6}%); (6) Zr (10^{-2}%); (7) Co (10^{-3}%); (8) Zn (10^{-3}%); (9) Ni (10^{-3}%); (*n*) content of elements; (I–IV) nodule type: (I) pyrite, (II) goethite, (III) siderite, (IV) calcite.

sumably related to the diagenetic migration of $CaCO_3$ masses in the CO_2-rich water.

Investigations carried out by Makedonov (1966) showed that modern calcareous nodules are mainly confined to regions with a contrast seasonal pattern of climate variations. Such regions are characterized by the predominance of dry and warm seasons over the humid and cold ones, respectively.

The calcite nodules are characterized by insignificant contents of rare and trace elements, except Mn (0.12%), Cr (0.04%), and Zr (0.02%).

The composition of **goethite nodules** is as follows (%): SiO_2 17.76–22.83, TiO_2 0.031–0.23, Al_2O_3 2.89–5.2, Fe_2O_3 55.51–81.99, MnO 0.99–1.54, MgO 0.34–1.35, CaO 0.31–0.77, Na_2O 0.04–0.4, K_2O 0.26–0.89, and P_2O_5 0.26–0.3. The concentration of some minor elements is higher than that in enclosing rocks (e.g., Co 0.003%, Zr 0.033%, Zn 0.005%, and Ag 0.000026%).

Results of the investigation show that some minor elements enter the nodules as accessory admixture together with the terrigenous material during the formation of nodules of different types. For example, the heavy fraction of calcite nodules contain the following minerals (%): magnetite 2.5–2.7, leucoxene 1.3–1.9, garnet 1.9–2.5, epidote-zoisite 0.7–2.7, ilmenite 0.4–0.8, tourmaline 0.04–0.2, rutile up to 0.09, zircon up to 0.02, titanite up to 0.004, and corundum up to 0.005. The total content of these minerals does not exceed 9% of the total volume of calcite nodule.

Thus, the main portion of minor elements entered the nodules with the cementing (nodule-forming) material rather than the allogenic substance, because complex silicate and sulfide minerals gradually disintegrated during the weathering of provenance rocks. Rare elements released during this process were transported to waters of ephemeral flows. After migration in the dissolved form (partially, as absorption on the clayey and organic material transported as suspension), the rare and trace elements entered the sedimentation basin, where they were concentrated and redistributed during diagenesis and epigenesis. Calculations of the relative concentration of minor elements in various nodules based on the Strakhov method (Strakhov *et al.*, 1959) showed that the highest concentrations of Ni, Mo, Cr, Cu, and Co are typical of pyrite nodules. The goethite nodules are characterized by enrichment in Ag, Zr, Mn, and Co, while the calcite nodules are enriched in Mn. It is worth mentioning that the coefficient of relative concentration of minor elements has a positive correlation (≥1) with the amount of their input into the nodules. Conversely, the coefficient has a negative correlation with the output of elements (Fig. 6). The value of 1 indicates the geochemical stabilization in epigenesis. The distribution of the coefficient of relative concentration of various chemical elements in nodules makes it possible to vividly present their geochemical mobility during the formation of certain nodule complexes. For example, their distribution in pyrite nodules can be presented in the following form:

$$Fe\frac{Ni \leftarrow Mo \leftarrow Co \leftarrow Cr \leftarrow Cu}{Mn \leftarrow Ag \leftarrow V}, \qquad (1)$$

where Fe is the major nodule-forming element,

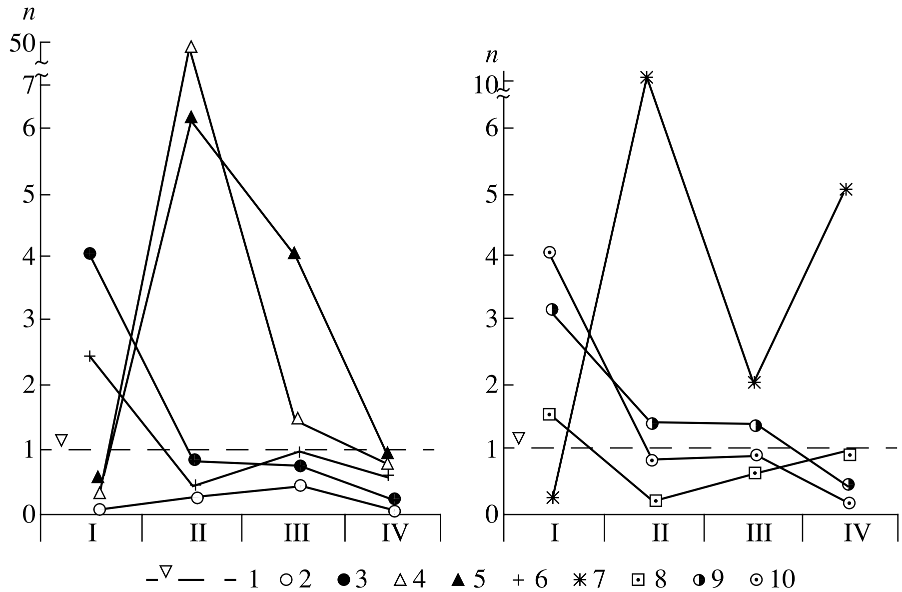

Fig. 6. Distribution of the coefficient of relative concentration of minor elements in different types of nodule. (1) Geochemical stabilization level; (2) V; (3) Ni; (4) Ag; (5) Zr; (6) Cr; (7) Mn; (8) Cu; (9) Co; (10) Mo; (*n*) coefficient of relative concentration; (I–IV) nodule type: (I) pyrite, (II) goethite, (III) siderite, (IV) calcite.

$Ni \longleftarrow Mo \longleftarrow Co \longleftarrow Cr \longleftarrow Cu$ is the geochemical series of elements introduced into the pyrite nodules, and $Mn \longleftarrow Ag \longleftarrow V$ represents the series of removed elements.

The pattern of element distribution in the calcite ($CaCO_3$), siderite ($FeCO_3$), and goethite (FeOOH) nodules is shown in relations (2)–(4), respectively:

$$Ca\frac{Mn}{Ni \longleftarrow Ag \longleftarrow Zr \longleftarrow Co \longleftarrow Mo \longleftarrow V}; \quad (2)$$

$$Fe\frac{Zr \longleftarrow Mn \longleftarrow Ag \longleftarrow Co}{Ni \longleftarrow Mo \longleftarrow Cr \longleftarrow Cu \longleftarrow V}; \quad (3)$$

$$Fe\frac{Ag \longleftarrow Mn \longleftarrow Zr \longleftarrow Co}{Mo \longleftarrow Ni \longleftarrow Cr \longleftarrow V \longleftarrow Cu}. \quad (4)$$

These relationships indicate that the geochemical mobility of minor elements during the formation of pyrite and calcite nodules was characterized by inverse correlations owing to different facies environments of their formation. The series of geochemical mobility of elements in goethite and siderite nodules almost completely coincide with each other, testifying to the identical nature of geochemical processes during their formation. However, this observation contradicts the fact that goethite nodules are formed in an oxidative environment, whereas siderite nodules are formed in a reductive medium. The contradiction can only be explained in the following way: brown ores are formed as a result of the redeposition of siderite nodules. The process is accompanied by the crushing and intense oxidation of siderite nodules. This scenario is consistent with facies constraints of sediments that enclose lenses and interlayers of goethite nodules. They are primarily associated with thin (up to 0.35 m) units of basal conglomerates and coarse-grained poorly rounded gritstones cemented by iron oxyhydroxides. These units were accumulated in a river channel with active hydrodynamic regime. In this case, the conversion of siderite into goethite could follow the following scheme:

$$2FeCO_3 + H_2O + 1/2O_2 \longrightarrow 2FeOOH\downarrow + 2CO_2.$$

Thus, the redeposited siderite served as the source of goethite nodules.

It is worth mentioning that thermally altered redrocks (zones of underground burning of rocks) have been investigated along the Sedanovo–Kodinsk Highway and in the Kansk area (Fig. 1, nos. 1, 9–12). Underground fires in these areas in the past were provoked by the combustion of coal with a high heat of combustion. Fusion is marked not only in the sandstones, coaliferous siltstones, and mudstones that were adjacent to the coal seams, but also in the siderite nodule beds. The fusion of such a nodule-containing bed fostered the formation of magnetite ore with the following contents of major oxides (%); Fe_2O_3 36.0–74.34, FeO 0.85–19.92, Al_2O_3 4.6–14.6, MgO 1.1–4.64, CaO 1.51–4.03, SiO_2 11.83–34.88, MnO 0.31–0.81, TiO_2 0.11–0.62, Na_2O 0.06–0.15, K_2O 0.27–0.99, and P_2O_5 0.22–0.53. The magnetite ore is characterized by the typical black color (with bluish iridescence), magnetism, and high density. The universally disturbed magnetite ore bed (Fig. 7) is up to 5 cm thick and represents an intricate system, because the overload pressure squeezed the fused siderite interlayers into cavities and fractures that were formed in the course of coal combustion. The thickness

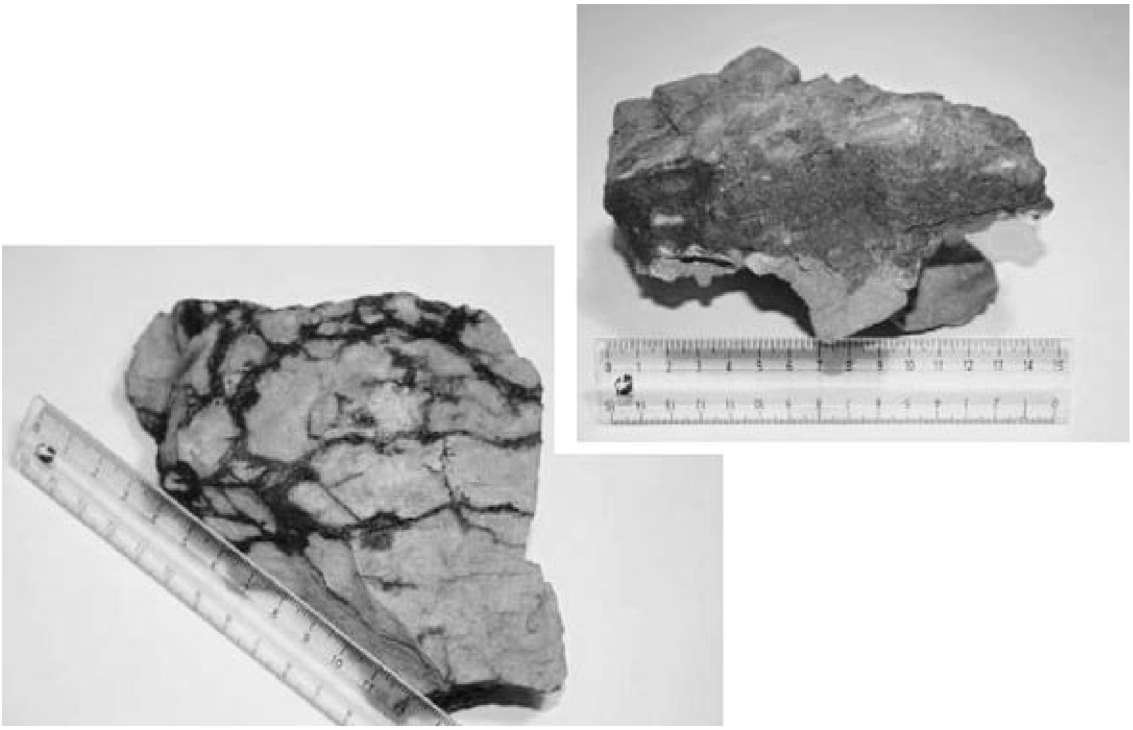

Fig. 7. Magnetite ore filling cracks in calcined sandstone.

of magnetite ore lenses increases to a few tens of meters precisely in such sites.

According to Semerikov (1977), siderite nodules were utilized for the primitive smelting of cast iron in Siberia (e.g., in the Kansk–Achinsk coal basin) as early as the beginning of the 19th century. The productivity of such smelting was as much as 500 puds (Russian unit equivalent to ~16.4 kg), i.e., 8 t/yr.

At present, the studied zones of underground burning of rocks, together with magnetite ores, are actively mined by the open pit and utilized for the construction of highways. These highways are characterized by cherry to brick-red color and high quality of the roadbed.

Statistical data on the Sr/Ba ratio in nodules can be efficiently applied for the elucidation of facies constraints of sedimentation. This indicator was first proposed by Katchenko (1959) for the description of oil-bearing sedimentary rocks. He established that the Sr/Ba ratio is <1 in continental facies and >1 in marine facies. Our calculations demonstrate that the Sr/Ba ratio is as much as 3.69 in siliceous and carbonate (aragonite) nodules from lagoonal limestones and mudstones underlying the coaliferous association. This ratio is always <1 in nodules from the coaliferous sequence (e.g., 0.57 in calcite nodules, 0.29 in siderite nodules, 0.71 in goethite nodules, and 0.07 in pyrite nodules).

CONCLUSIONS

Results of the study of nodules in coaliferous sequences suggest the following conclusions: (1) sediments underlying the coaliferous formation contain two (siliceous and carbonate) types of normal nodules and one type of allogenic nodules (e.g., chalcedony nodules in the kaolinite–chalcedony unit of the Beloyarsk Formation); (2) the coaliferous association includes four (calcite, siderite, pyrite, and goethite) types of nodules; (3) each nodule type is associated with a specific type of sediments; for example, the siliceous nodules are confined to lagoonal sediments; the calcite nodules, to lacustrine and lacustrine–boggy sediments; the siderite nodules, to lacustrine–boggy and boggy sediments; the pyrite nodules, to boggy sediments; and the goethite nodules, to alluvial sediments; (4) the formation of goethite nodules was mainly related to the washout and redeposition of siderite nodules; (5) coefficients of the contents of coal and nodules show a distinct positive correlation; (6) nodules in the coaliferous association formed in the course of diagenesis and epigenesis; the calcite and pyrite nodules are characterized by a high content of sandy material (this is suggested by the high content of insoluble residue in them); (7) the combustion of coal seams provokes the fusion of the adjacent beds and lenses of siderite nodules and the formation of magnetite ores with the transformation of the thermally altered rocks into a high-quality building material.

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