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Bacteriomorph Structures in Nodules, a Characteristic of Euxinic Conditions of Nodule Formation

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Abstract—Electron microscopic, spectroscopic, and geochemical study of Middle Ordovician shamosite, Wenlockian calcite, and Lower Carboniferous siderite nodules revealed the presence of organic matter and traces of microbial organisms involved in the formation of iron oxides and hydroxides and mineralized microbial films. The structure and composition of the films show high similarity to mineralized glycocalyx, which is a product of bacterial metabolism. Diversity of the framboidal micropyrite and bacteriomorph structures in size and shape indicates the formation of nodules under anoxic bottom conditions and abundance of sulfate-reducing, iron-reducing, and iron-oxidizing bacteria. The presence of authigenic minerals in the nodules, which is atypical for sedimentary rocks, suggests the influence of bottom gas–fluid seeps and, therefore, local hydrosulfuric contamination, fluctuations in salinity, and intensive development of bacterial communities.

Keywords: bacteriomorph structures, euxinic conditions, nodules, $\delta^{13}C$ and $\delta^{18}O$, Paleozoic, Chernyshev Ridge, Northern Urals, Subpolar Urals

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INTRODUCTION

According to previous studies, a wide distribution of nodules of different age and diverse genesis and composition, including modern nodules, is a good reference point for biosphere changes (Flügel, 2004). Participation of microorganisms in the formation of ores and nodules composing ores, including a wide range of mono- or polycomponent formations that differ from enclosing matter has been disputable and still remains questionable. These formations include concretions and ooids as well as their particular cases, such as oolites, microconcretions, spherulites, and globules. Previous publications suggested that oolites of iron ores were formed by chemical precipitation, with subsequent diagenetic transformations (Strakhov, 1960; James, 1966; Yudovich and Shulepova, 1973; Van Houten and Bhattacharyya, 1982; Yoshida et al., 1998; Franceschelli et al., 2000; etc.). Geobiological works devoted to extracellular polymeric organic substance (EPS) (Gerasimenko and Ushatinskaya, 2002) and lipid markers in ooids and laboratory research on biomicrospheres generating ooids, along with international projects on the potential role of microbes in ooid genesis (e.g., Duguid et al., 2010; Summons et al., 2013) appeared in recent decades. Glycocalyx (EPS) keeps cells together, forming the structure and matrix composition of the biofilm, since glycocalyx production is a natural process of bacterial metabolism. EPS is a complex mixture of biopolymers, consisting primarily of polysaccharides and also proteins, nucleic acids, lipids, and humic substances. The main functions of EPS are to mediate the initial attachment of cells to various substrates and to protect cells from environmental stress and dehydration (Vu et al., 2009). Mineralized glycocalyx was revealed in lithological objects from Precambrian to Cenozoic, which were considered chemogenic formations (*Iskopaemye bakterii* ..., 2011). The present paper provides the results of investigation of the traces of microbial involvement in the nodule structures, using an example of Middle Ordovician shamosite iron ores, Wenlockian ooids, and Lower Carboniferous concretions in the sections of the Timan–Northern Ural region (Chernyshev Ridge, western slope of the Northern and Subpolar Urals).

MATERIALS AND METHODS

Carbonate and silicate nodules were studied. These are the Middle Ordovician shamosite nodules from the sections of the Ilych River Basin (Northern Urals) (kindly provided by E.S. Ponomarenko), Wenlockian calcite ooids from the section on the Iz'yayu River (Chernyshev Ridge), and the Lower Carboniferous siderite concretions from the section on the Kozhym River (Subpolar Urals). The material was sampled in different nodule sites, using thin dental drills. The phase composition of the clayey fraction was determined by the X-ray diffraction method (SHIMADZU-6000 diffractometer, filtered Cu$K\alpha$ radiation, 2Θ range of 2°–32°). To determine the structure of organic matter in concretions, the spectra of Raman scattering were analyzed using a Horiba Jobin Yvon LabRam HR800 spectrometer. Scanning electron microscopes equipped with an X-ray microprobe analyzer were used for the study of the microstructure and chemical composition of minerals. The content of microelements was estimated by quantitative emission spectral analysis. The isotope composition of carbonate carbon and oxygen was analyzed using a Delta V Advantage mass spectrometer. The values of $\delta^{13}C$ and $\delta^{18}O$ are given in ppm relative to the PDB and SMOW standards, respectively. The error of ^{13}C and ^{18}O measurements did not exceed ±0.1‰ (1σ). Analytical studies were performed at the Geonauka Center for collective use (Institute of Geology, Komi Science Center, Ural Branch, Russian Academy of Sciences).

MIDDLE ORDOVICIAN SHAMOSITE NODULES

The first study of nodules from Middle Ordovician shamosite ores described as chemogenic oolites from the Ilych River Basin (Northern Urals) was performed in the 1970s (Yudovich and Shulepova, 1973; Yudovich et al., 1981). Micaceous hydrobiotite were recorded in oolites and enclosing clay matter from weathering crusts; in addition, oolites contained layers of siderite composition, along with shamosite concentrates.

The study of shamosite nodules and enclosing matter under an electron microscope revealed new data on their composition and genesis. The shape of shamosite nodules often does not correspond to the regularly round or oval oolites; they are distorted or fractured as a result of tectonic disruption of rocks. The nodules vary in size from 0.5 to 6 mm, although they sometimes reach 3 cm; the number of concenters in them varies from 2–3 to 20–30 or they are absent; the distribution in the rock may be uneven or dense. The concentric envelope of siderite–shamosite nodules, or more precisely, calcite–pyrite–hematite–siderite–shamosite nodules, consists of distinct or discontinuous (due to the change in the mineral composition) layers (Figs. 1a, 1b). The central part of the nodules is represented by substrate of complex composition. The presence of organic matter (OM, $C_{org} = 0.177$) in the form of spots and traces among mineral aggregates and abundant framboidal micropyrite was revealed in the nodule structure (Figs. 1c, 1d). Concenters vary in composition and contain distinct bacteriomorph structures consisting of isolated or aggregated nanotubes of shamosite (Fig. 1e), sheaflike forms composed of hematite (Fig. 1f), and shamosite nanococci on the surface of glycocalyx with an increased Ti content (Figs. 1g, 1h). The sheaflike forms are morphologically similar to biomorphic hematite from iron ores of the Kursk Magnetic Anomaly (KMA) (Merkushova and Zhegallo, 2016, text-fig. 1b) and biohematite from weathering crusts (Bortnikov et al., 2011; Novikov et al., 2016). Different mineral species were shown to compose substrates and nodules. These are shamosite, siderite, hematite, calcite, chlorite, microquartz, microzircon, muscovite, seleniferous galenite, strontium-bearing calcite–barite zones and sites, chalcopyrite, pyrrhotite, apatite, sphalerite, and magnetite–ulvite complex mineral with an admixture of kulsonite and shamosite with an apatite component, and anapaite. Many of them are characterized by the presence of titanium, while shamosite and siderite contain biogenic microelements of vanadium, cobalt, nickel, copper, and arsenic. The presence of mica, illite, titanium minerals, quartz, garnet, and epidote in the substrate composition indicates a terrigenous source from the weathering zone of igneous rocks. A significant amount of authigenic silica in nodules suggests that not only iron bacteria, but also silicate bacteria capable of processing clay minerals, play a role in the diagenetic mineral formation (Alekseeva et al., 2009). The presence in glycocalyx of Si, Al, K, Mg, and Fe microelements indicates a complex mineral composition of microbial films, which is widespread in Mesozoic concretions (Tomás et al., 2013). Bacteria use substrate as a donor of electrons and mineral substances are involved in bacterial metabolism, with further transformation into a form accessible to other organisms. This results primarily from specific reactions of cell walls in OM with particles of clay minerals (Naimark et al., 2009).

Revealed mineralized microbial crusts, along with aggregations of various bacteriomorph structures and biogenic microelements in siderite–shamosite nodules indicate participation of microorganisms in the nodule genesis. The abundance of framboidal pyrite indicates that the development and active functioning of bacteria occurred under conditions of oxygen deficiency in bottom waters and sediments, i.e., under anoxic conditions. The presence of strontium-bearing barite–calcite mineral formations, barite, sphalerite, galenite, and chalcopyrite in nodules, which are authigenic minerals atypical for normal sedimentary formations, indicates existence of bottom hydrocarbon gas–fluid seeps. The data on the isotope composition of carbonate carbon and oxygen in enclosing matter and siderite–shamosite nodules showed the greatest difference in carbon (–2.86...–0.16‰ and 0.87‰ for nodules and enclosing matter, respectively). These results indicate that nodules are isotopically lightened compared to the matrix and sedimentation occurred in marine conditions. The isotope composition of oxygen in nodules and matrix is significantly lightened (20.57–22.31‰), which may be due to the local water desalination compared to normal marine sedimentation values (28–30‰).

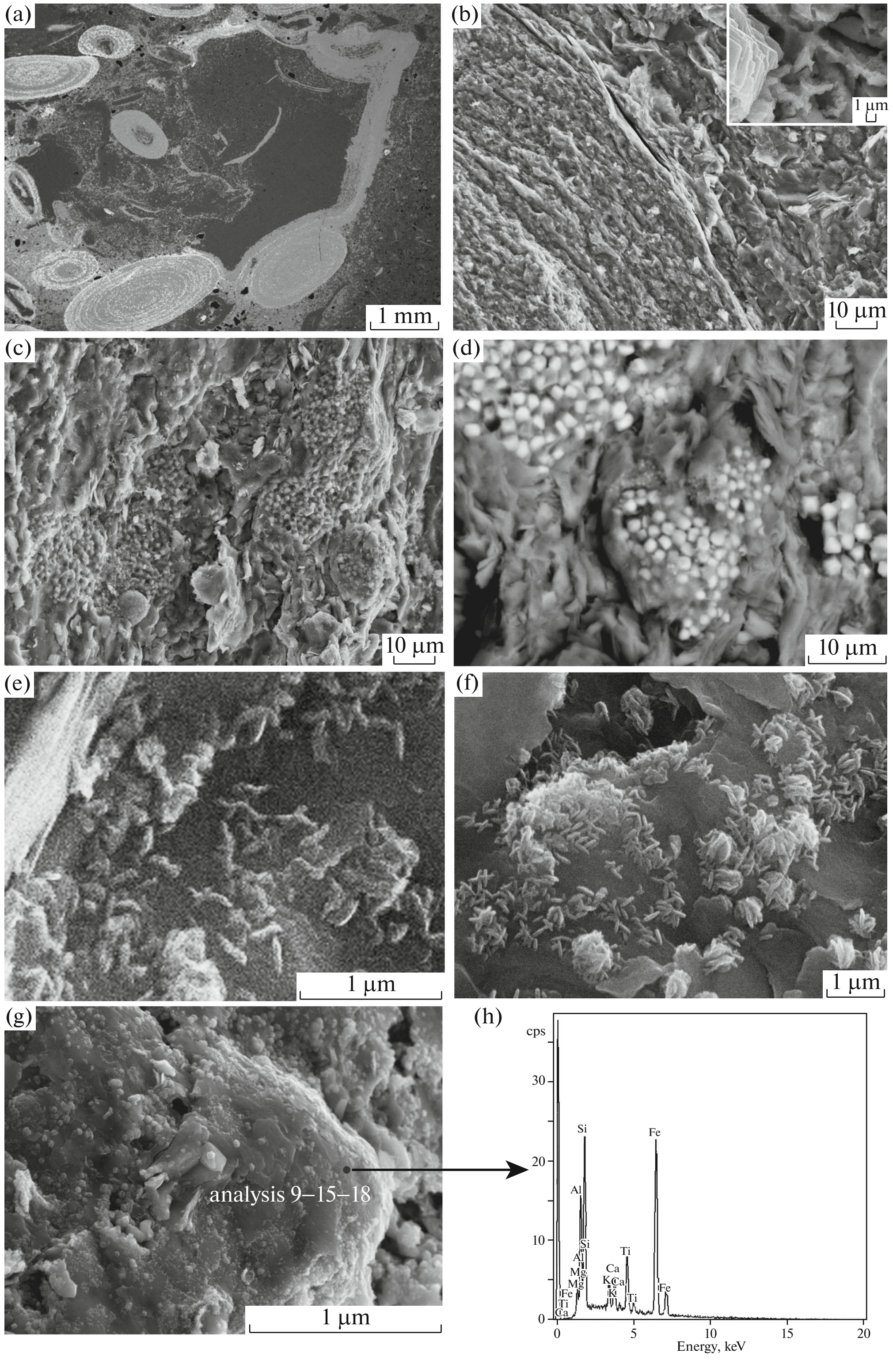

Fig. 1. SEM images in the mode of secondary electrons of microstructures in the Middle Ordovician shamosite nodules: (a) types of nodules, shape and character of their distribution, sample BK23-15-1; (b) boundary zone of shamosite nodules (left side) with a more pronounced grain orientation and calcite–shamosite substrate with titanium minerals (right side) and persistent orientation of components, sample BK23-14-7; inset shows relation of crystallomorphic calcite and biogenic shamosite; (c) character of distribution and variety of aggregations of pyrite microframboids in the zonal structure of the nodule, sample BK23-14-18 (c); (d) detail of Fig. 1c; (e) rod-shaped bacteriomorphs of nanoshamosite, sample BK23-15-22; (f) bacteriomorph structures of nanohematite in the shape of sheaflike formations, sample 9-15-18; (g) surface of mineralized microbial film with abundance of coccal bacteriomorphs in the structure of the nodule layer, sample 9-15-16; (h) spectrum of shamosite from microbial film.

WENLOCKIAN CALCITE NODULES

Ooid limestones, which are usually associated with stromatolites, are widespread in the Wenlockian beds of the Iz'yayu section of the southern part of the Chernyshev Ridge (Shebolkin and Myannik, 2014), in contrast to other coeval sediments. Ooids are formations of spheroidal, flattened, ellipsoidal, and bispheroidal shapes, which are 0.1–0.5 mm, rarely up to 1 mm in size. Nuclei (0.01–0.2 mm) were represented by peloids, lithoclasts, quartz grains, or bioclasts. Calcite envelope (cortex) varying in thickness, composition, and structure were formed around nuclei. The organogenic material (2–20%) in the fragments of ostracods, gastropods, pelecypods, bryozoans, and entire shells of micro-ostracods was recrystallized to varying degree and unsorted (0.1–2 mm). The content of C_{org} in ooid limestones is 0.03–0.18%; clarke of organic carbon in carbonates varies from 0.014 to 0.06%, according to different sources. Ooids differ in the structure of calcite grains in the envelope; they are irregularly oriented fine-grained, radially concentric, or subparallel. The envelopes and nuclei of ooids were shown to contain micrograins of monazite, zircon, orthoclase, rutile, muscovite, and alumoceladonite-like mica. This indicates a rather remote terrigenous source of weathering crusts from erosive regions. Authigenic nanohematite, pyrite, and iron oxides of framboidal nanopyrite, are revealed in nuclei and microbial films of ooids (Fig. 2f). A characteristic of Wenlockian ooids is wide distribution of ooids with one envelope zone composed of radial-subparallel calcite grains (Fig. 2a). They can be "hedgehog-like spherules," ovals, and biospheres, or unusually shaped ooids, forming one radial envelope (with densely packed crystals) around the skeletal fragments, are sometimes present; the structure consists of alternating light and dark laminae. A single-layer radial-subparallel envelope is often formed around small grains containing pyrite, which can almost completely replace the structure of the ooid. OM is present in the pelitomorphic part of the intergranular space and in the dark laminae of ooid envelopes (Figs. 2a, 2b). Calcite crystals of smoothed shape are also common (Fig. 2c); according to Summons et al. (2013), they are formed during dissolution of encrusting microorganisms with organic acids. An electron microscopic study of ooids revealed remains of mineralized microbial films with numerous nanococcal bacteriomorphs (up to 0.2 μm in size) on the biofilm surface (Fig. 2b). Mineralized glycocalyx in the shape of cellular–reticular fragments is clearly visible in the structure of the microgranular envelope (Figs. 2d, 2e). The presence of Si, Al, K, Mg, and Fe microelements in the calcite matrix of mineralized biofilms indicates their iron–mica mineral composition. The film composition and structure show high similarity to mineralized glycocalyx of Middle Jurassic ooids (Tomás et al., 2013, text-fig. 10), elemental composition of which is almost identical to that of mineralized biofilms of Wenlockian ooids. Similar glycocalyx forms are found in iron–mica ores of the Stoilenskoe deposits of KMA (Merkushova and Zhegallo, 2016, text-fig. 3). Preservation of the outer and inner structures of the envelopes of Wenlockian ooids indicates that their initial mineral composition was probably represented by low-Mg calcite, which is a stable carbonate phase. The primary low-Mg calcite composition of ostracod shells, remains of which are common in this section, and fragments of gastropods, pelecypods, and rare trilobites could have a low-Mg calcite, along with aragonite, skeleton composition (Flügel, 2004). Isotopically lightened carbon and oxygen (–5.4...–6.4‰ and 22.9–24.6‰, respectively) and a low boron content of 11–30 g/t indicate desalination of the Wenlockian basin in the territory where ooid limestones were formed. The study of freshwater ooids of Lake Geneva has shown that, prior to calcification, glycocalyx was mineralized in the form of amorphous magnesian silicate; the role of the biogenic element in their formation is the microdrilling of endolites of the ooid surface, which changes the structure and chemical characteristics of ooids during their formation (Pacton et al., 2012). Distribution of mineralized microbial crusts in Wenlockian ooids did not reveal their exclusive connection with the envelope surfaces; they were recorded in different parts of the envelope structures.

LOWER CARBONIFEROUS SIDERITE NODULES

Concretions of the Lower Carboniferous siderite-bearing terrigenous strata of ores on the Kozhym River of the Subpolar Urals were previously regarded as typical chemogenic diagenetic formations (Bagdasarova, 1966, Yudovich et al., 1979). Concretions 1–30 cm in size vary in shape (flattened, bumpy, and ellipsoidal) and structure (dense homogeneous, septarian, with fossils, and "algal pseudomorphs") and distributed nonuniformly. Studies under an electron microscope has shown that siderite is represented by bacteriomorph structures, packs of fine-lamellar aggregates, laminae with conchoidal fracture or accumulations of different forms composing larger joint units; mineralized glycocalyx, commonly containing Si, Al, K, Mg, and Fe microelements (Fig. 3d) are also present. A characteristic features are diverse forms of framboidal micropyrite (<2–5 μm) and existence of forms (up to 10 μm) with the octahedral habitus, which is rarely observed in pyrite (Figs. 3b, 3c) and considered to be a result of increased acidity of the mineral formation environment enriched in bacteria (Yushkin et al., 2013). Association of authigenic minerals unusual for sedimentary rocks, such as sphalerite, chalcopyrite, pyrrhotine, chameanite, tsumoite, fauserite, and barite, was revealed in concretions (Antoshkina et al.,

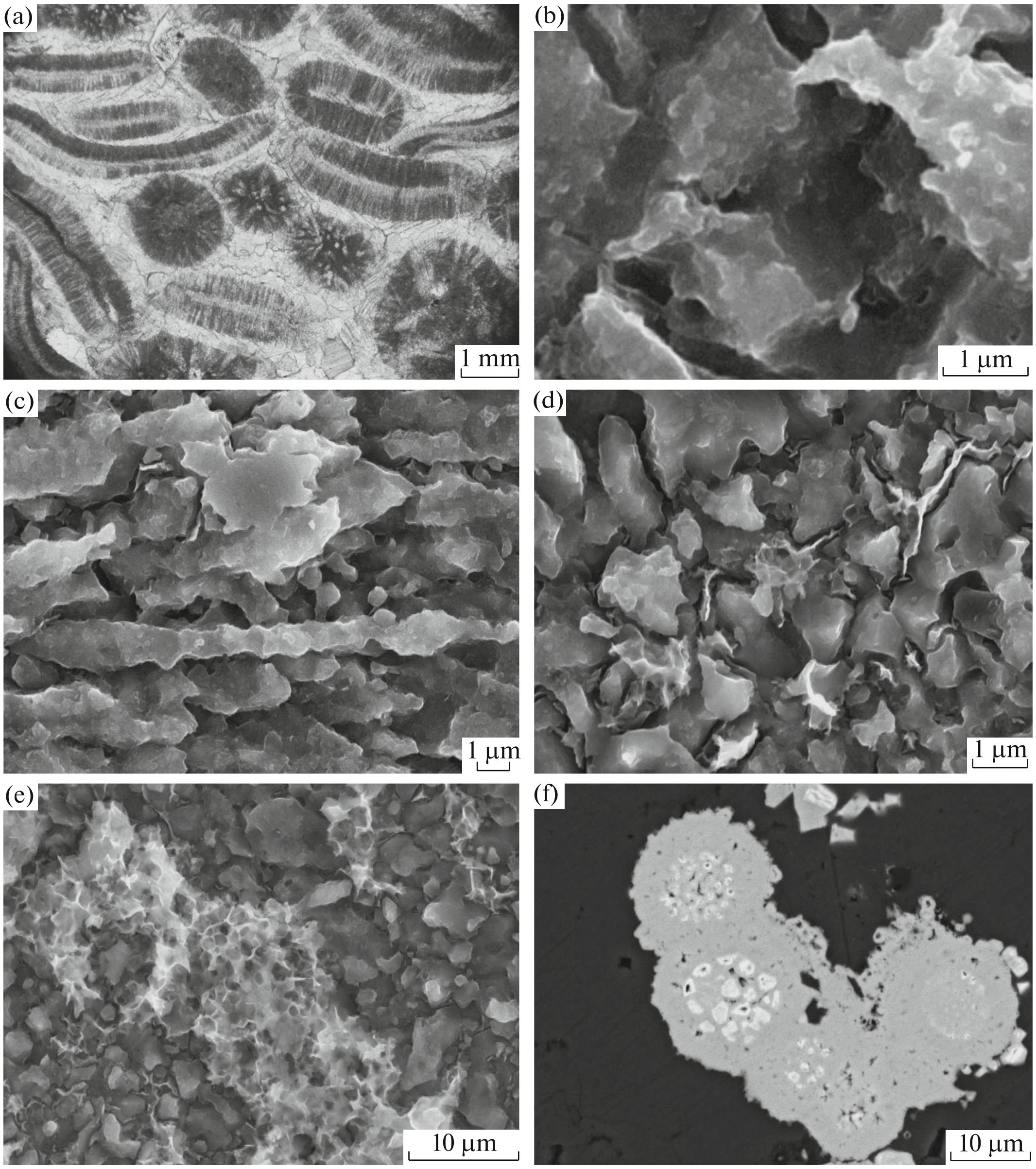

Fig. 2. Micrographs of the structure and composition of Wenlockian calcite SEM ooids in the mode of secondary electrons, sample 479/118: (a) morphology and structure of ooids and their envelopes; (b) nanococcal bacteriomorphs on the surface of mineralized microbial crusts; (c) crystals of calcite with traces of dissolution and presence of biofilm fragments; (d) fragments of glycocalyx in intergranular space; (e) cellular-reticular shape of glycocalyx; (f) iron oxides of framboidal nanopyrite aggregations in the ooid nucleus.

2017). OM envelops mineral grains and concentrates in cavities left after bacterial bodies (Fig. 3a). OM is characterized by an insignificant level of carbonation (Fig. 3e). The isotopic composition of different types of concretions is characterized by isotopically lightened carbon values of –11.2...–1.3‰ and widely varying oxygen values of 22.6–31.7‰. Such changes within the range of 9–10‰ of carbon and oxygen isotope composition indicate salinity fluctuations in the sea basin during the formation of concretions, varying from freshwater and brackish-water concretions to normal marine ones, with the participation of bacterial oxidation of OM (Christensen, 1995). In To compare the isotope composition of fossils and concretions enclosing them, scrapes of relicts of the calcite wall of goniatites, which was preserved to a greater or lesser extent, were obtained. It was possible to get a sample for analysis only from one out of fifty goniatite specimens. The data obtained on the isotope composition of carbon (–4.72‰) and oxygen (24.30‰) also show isotopically lightened values relative to normal marine sedimentary formations (2...–2 and 28–30‰, respectively).

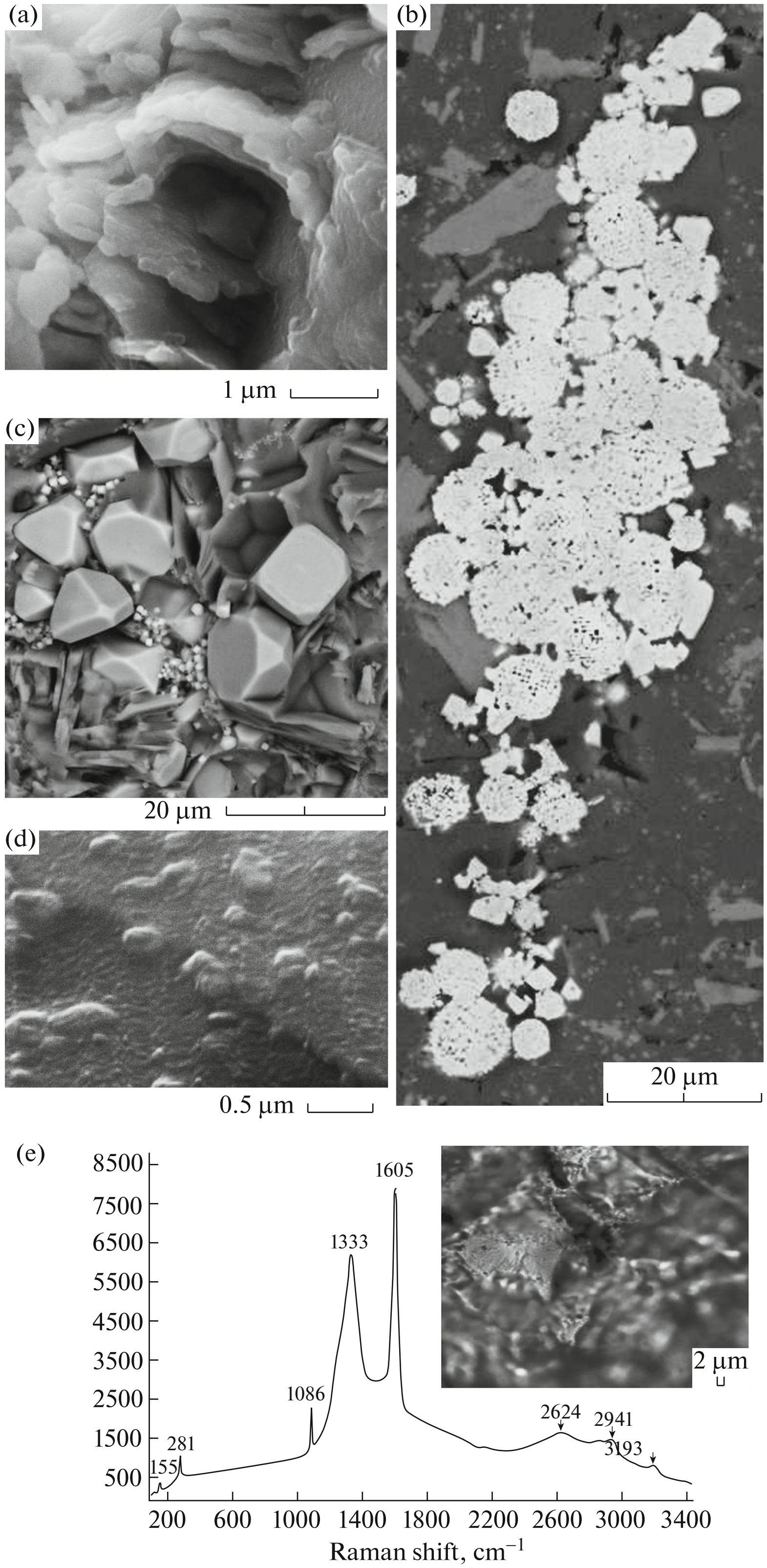

Fig. 3. SEM images in the mode of secondary electrons of microstructures in the Lower Carboniferous siderite concretions: (a) bacteriomorph structures where bacterial OM was preserved in cavities, sample Ko-V-2-06; (b) aggregations of framboidal pyrites developing after bacterial colonies of different size and structure in siderite–chlorite mass of concretion with goniatite, sample VII-16L-06; (c) idiomorphic-crystallographic forms of pyrite in siderite–chlorite mass of septarian concretion with residual microframboids, sample Ko-V-2-06; (d) spheroids on the surface of a mineralized microbial film of siderite plate, sample Ko-V-2-06. Designations: (*E*) Raman spectrum of luminescence and microstructure of condensed OM in a septarian concretion.

CONDITIONS FOR NODULE FORMATION

Investigation of nodules (differing in age and composition) from the Paleozoic sections of the region studied and of the matrix enclosing these nodules has shown that they were formed under conditions significantly differing in paleogeographical position, geological situation of the region, and sedimentation conditions.

Biologically induced mineralization of ferrolites vary due to the activity of different bacterial groups, iron-oxidizing and iron-reducing ones. The first scenario of biomineralization was realized in ferruginous oolites represented by goethite and modern ferrihydrite–shamosite ores in the seep system (Wu et al., 2009). In this case, iron-oxidizing bacteria used Fe^{2+}, O_2, or CO_2 from water and weakly ordered iron oxides for deposition outside or inside the bacterial cell wall and envelope. Fe^{3+} can rapidly be deposited on the biofilm matrix formed by iron-oxidizing bacteria (Miot et al., 2009). The study performed by Wu et al. (2009) describes the formation of ferrihydrite–shamosite ores in the seep system of the inertidal zone of one of the islands in the East China Sea. Disruption of the layers with fossil wood resulted in the formation of humic acids, which accelerated iron leaching from surrounding rocks and soil and provided ideal conditions for the survival of the iron-oxidizing bacteria *Leptothrix* and *Gallionella* in seep environments. The presence of these bacteria promoted Fe^{2+} oxidation to Fe^{3+}, along with rapid deposition of bacteriogenic iron oxides on bacterial colonies, which facilitated preservation of their morphological features.

Iron-reducing bacteria determined the process of inducible biomineralization in the siderite–shamosite nodules studied on the western slope of the Northern Urals. These bacteria, on the contrary, used Fe^{3+} in combination with oxidation by organic compounds of degradable bacterial OM. Iron oxides and ferruginous clay minerals widespread in sediments are used in the metabolism of iron-reducing bacteria. In this case, the process of microbial reduction is realized; under such conditions, siderite and shamosite could be formed. Middle Ordovician siderite–shamosite nodules were formed in a relatively calm shallow basin with hydrocarbon gas–fluid bottom seepage, with active functioning of sulfate-reducing bacteria and an abundant framboidal pyrite. The study of modern iron oxyhydroxides and framboidal pyrites under conditions of methane seeps associated with carbonates of underwater cracks in the Gulf of Cadiz (Merinero et al., 2008) showed that the activity of sulfate-reducing bacteria provided geochemical conditions for deposition of iron sulfide in the environment with low oxygen concentrations. Numerous examples confirmed that almost all ferrooxide–shamosite oolites were accumulated under conditions of prolonged existence of temperate climate, extensive transgression, and tectonic stability accompanied by a decrease in the inflow of clastic material in shallow seas, flooded continental margins, intracratonal basins, and foredeeps (Van Houten and Bhattacharyya, 1982). In the Middle Ordovician, the humid climate prevailed in the northern Urals (southern equatorial paleolatitudes, 20°–30°) (Scotese, 2000), and intensive chemical weathering with the efflux of iron into the sea basin occurred on land. The alternation of shamosite and reduced siderite layers in nodules indicates random mixture of coastal environments under conditions of a developing continent–ocean transitional zone formed during the expansion of the Paleoural Ocean (Puchkov, 2010).

The study of Wenlockian calcite nodules has shown the peculiarity of marine sedimentation in the southern part of the Chernyshev Ridge. Mineralized microbial films in the envelope of ooids and development of the "hedgehog-like" ooids in the structure of stromatolites reveal their close interrelation and interdependence of the origin under specific paleoecological conditions. The appearance of such associations in the marine basins reflects the turning points in the hydrochemistry of the marine basin and the structure of benthic ecosystems associated with regressions of the sea basin. Calcite ooids were still formed under calm water conditions, forming in the deposits envelopes around skeletal fragments, terrigenous grains, intraclasts, and inside the stromatolite formations. Even with small fluctuations in the water level, a shallow water basin facilitated the withdrawal of sediments into the vadose–phreatic environments (the presence of vadose cement around ooids) and resulted in abnormal water exchange in some parts of the basin. This promoted the appearance of euxinic conditions in bottom waters, as evident from the presence of framboidal micropyrites in ooids and pelitomorphic calcite cement. This provided occupation of calm basins by microorganisms, development of anoxic conditions in bottom sediments, disturbance of calcium balance, and prevalence of euryhaline benthos with the magnesian–calcium skeleton. The influence of microbial communities on the nature of carbonate sedimentation is more pronounced in water basins with abnormal water exchange, close location of erosive areas to the source of terrigenous material and fresh waters during regressions of the sea basin. O'Reilly et al. (2017) studied the composition of the microbial community and associated lipids in modern oolite sands on Cat Island of the Bahamas. They revealed that, among taxa that are able to promote carbonate sedimentation, those associated with the sulfur cycle are particularly abundant and proposed that some ooid carbonates are formed in the microbial film and early diagenetic degradation of biofilms could also play a role at the early stage of carbonate deposition around ooids.

The Mg : Ca ratio is known to be 5 in modern seas, resulting mainly in the formation of aragonite silts. Aragonite is not precipitated from fresh waters, since the Mg : Ca ratio in them is only 0.25 (Flügel, 2004). As unstable aragonite is transformed into calcite, the shape of crystals changes, with the formation of the pyramidal shape of crystal tips. A relatively good preservation of the external and internal structures of the Wenlockian ooid envelopes suggests that their primary mineral composition was probably represented by low-Mg calcite, which is a stable phase. A number of facts confirm the existence of an isolated inland continental shallow basin with abnormal water exchange in the Wenlockian Timan-North Ural sedimentary basin. First, in a number of sections of the Subpolar Urals (Männik and Martma, 2000) and Khoreiver Depression (Khipeli, 2005), a break at the Llandovery–Wenlockian boundary, weathering crusts, and absence of a part of Lower Wenlockian sediments were revealed. At the same time, in the south of the Chernyshev Ridge, there is a thin, but complete section of the Wenlockian (Shebolkin and Myannik, 2014). Second, euryfacial and euryhaline benthic communities in this sea were extremely poor in species composition. Third, authigenic minerals of iron hydroxides, hematite, framboidal micropyrite, and lightened isotope composition of carbonate carbon and oxygen were revealed in ooids. Similar conditions were reconstructed in the Early Triassic basin in northern Germany; they were determined as alkaline lake environments with decreased salinity (Voigt et al., 2011). Ferretti (2005) studied in detail Silurian ferruginous ooids and stromatolite-like microbiolites of the Carnic Alps (Austria) and showed that, judging from similarities in mineralogy, cell structure, and the growth and oxidation patterns, ferruginous ooids and stromatolite-like microbiolites were the products of the same biogenic activity. In addition, the Wenlockian period started with the replacement of a warm humid Llandovery climate by a cold arid climate; the bioisotope extinction events (*Ireviken* and *Mulde* events) and global regressions in the epicontinental seas (Cramer and Saltzman, 2007, Munnecke et al., 2010, Suttner and Kido, 2011). All these factors determined the specificity of sedimentary conditions in the Timan-North Ural sea basin, which was then situated in the northern subequatorial paleolatitudes.

Biochemogenic nature of siderite concretions is determined by the fact that prokaryotes can reduce Fe^{3+} in surface environments and cause precipitation of siderite (Lovley and Phillips, 1988; Fredrickson et al., 1998). Sarnchez-Romarn et al. (2014) proposed that the formation of siderite in the shallow Rio Tinto River with acidic waters (southwestern Spain) was associated with microbial ferric iron combined with oxidation of organic compounds. The iron-reducing bacteria *Acidiphilium* sp. PM promoted deposition of siderite ($FeCO_3$) in acidic environments at a low temperature (30°C). Siderite arose on nanoglobules in close association with bacteria on the cell surface; rod-shaped bacteria on the surface of siderite nanocrystals were observed. Morphological and structural similarity between modern and ancient iron-containing carbonate concretions suggests that they were formed at the bottom of the paleobasin due to the activity of iron-oxidizing bacterial communities (Johnson et al., 2013; Sanches-Roman et al., 2014). Such organisms as goniatites, brachiopods, gastropods, orthoceratids, pelecypods, and crinoids were present in the Early Carboniferous sea basin; hence, prior to the appearance of bottom gas–fluid seeps, sea waters were probably neutral or weakly oxidized. This corresponds to the pH range (7–5) in the regions with moist soil, which includes the region of humid climate in the territory of the Subpolar Urals in that epoch (Ryabinkina, 2006). Lamellar packs of authigenic siderite formed as a result of bacterial methanogenesis were found at the bottom of the Baltic Sea (Halas and Chlebowski, 2004) and developed artificially using cultures of the bacteria *Shewanella* and *Thermoanerobacter* (Roh et al., 2003). According to some authors, sedimentation of siderite occurs at a high sedimentation rate, saturation of sediments with organics, neutral pH, and increased concentration of Fe^{2+} ions in silty waters (Woodland and Stenstrom, 1979). Recent and Mesozoic siderite concretions occur in deposits formed under conditions varying from fresh ($\delta^{18}O$ = 10–14‰) to desalinated-brackish ($\delta^{18}O$ = 14–22 ‰) waters, when water contained more iron than calcium (Christensen, 1995). The most important prerequisite for such scenario is the abundance of bacterial colonies. Moreover, actively functioning microorganisms promote the formation of sulfides (mainly pyrite), phosphates, and ferruginous carbonates (Ellwood et al., 1988). The presence of bacteriomorph and lamellar structures of siderites in the Lower Carboniferous siderite nodules, associations of minerals atypical for normal sedimentary rocks, and fluctuations in salinity of waters at the continental margin indicate the influence of bottom hydrocarbon gas–fluid seeps on the development of euxinic environments. This resulted in local desalination of bottom waters, hydrogen sulfide contamination, intensive development of iron-reducing and element-specific bacteria, and in the appearance of large-scale bacteriogenic diagenesis. In the areas affected by such seeps, which contain dissolved hydrogen sulfide and methane, bacteria that served as nutrients for more complex organisms developed actively. A pronounced increase in nutrients attracted both benthic and nekton-planktonic normal marine organisms, which died in anoxic bottom conditions. Their mortmass became additional favorable environment for proliferation of bacteria and stimulated diagenetic transformations. Thus, the formation of siderite concretions in the basin with a normal marine fauna was promoted by gas–fluid seeps, the appearance of which was activated by the onset of the orogenic stage of the Urals formation.

The wide distribution of bacteriomorph structures and framboidal micropyrites revealed in the siderite and siderite–shamosite nodules was determined by the presence of various bacterial colonies in bottom sediments, the abundance of which was associated with the development of anoxic conditions in bottom waters. James (1966, p. 10) reported in his review

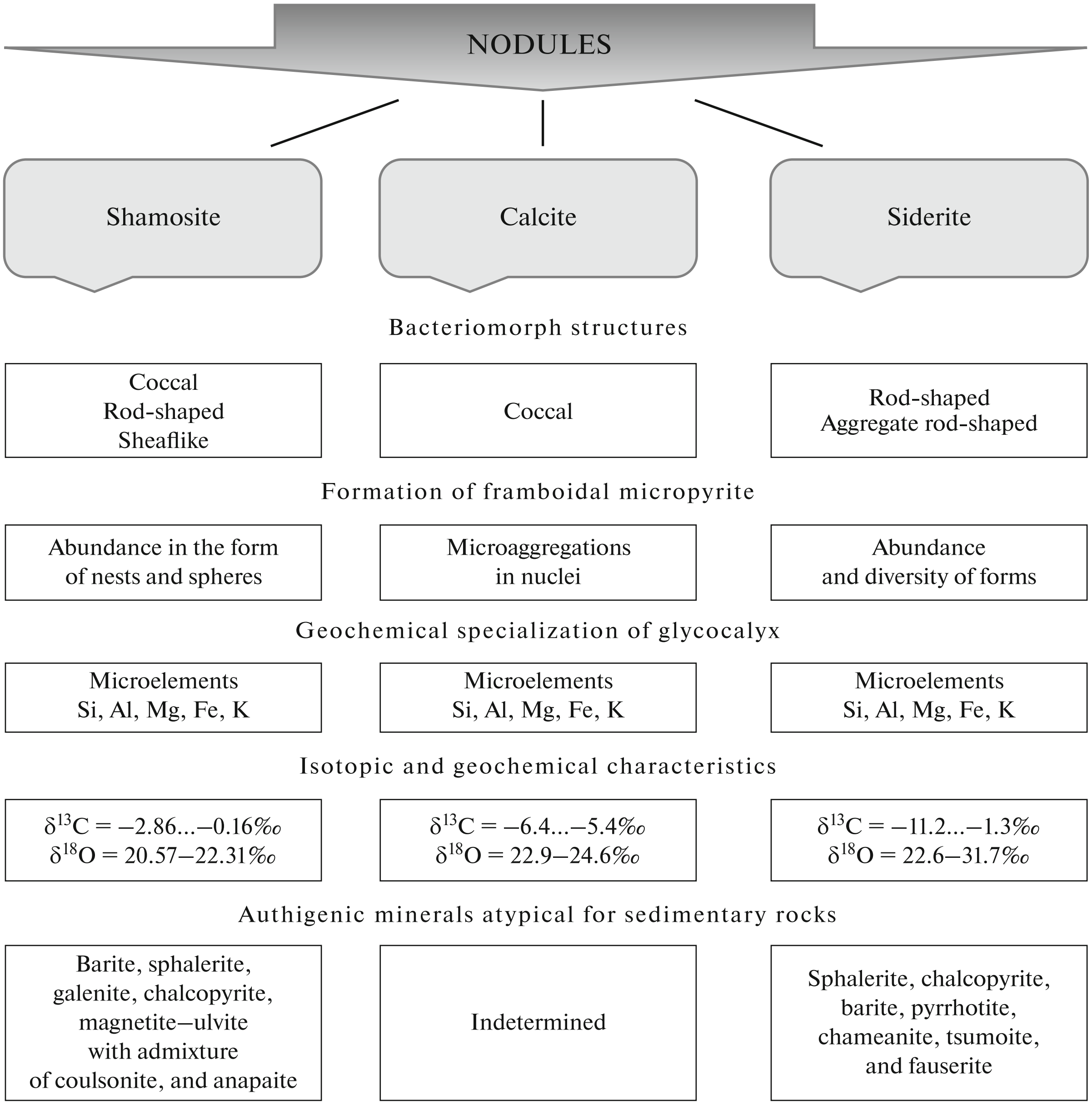

Fig. 4. Microbiological, biochemogenic, and physicochemical parameters combining conditions for the formation of Middle Ordovician, Wenlockian, and Lower Carboniferous nodules.

devoted to the geochemistry of sedimentary ferrolites that, in the second half of the 1950s, the microbiologist L.G. Love revealed the presence of microorganisms named “*Pyritosphaera barbaria*” in pyrite microspheres. Zholnovich (1990) considered the primary state of matter that precedes the formation of framboids as a biocolloid and the proportionality of microbial colonies to framboidal pyrite is one of the main arguments for supporters of its biogenic nature. While investigating framboids, idiomorphic crystals, and metasomatic masses of pyrites varying from the Precambrian to modern sediments, Folk (2004) found that their surface was commonly covered with spheroids 30–50 μm in size. These spheroids are interpreted as pyritized cells of nanobacteria and indicate that precipitation of iron sulfide was carried out by bacteria often associated with degradable organics and anoxic conditions developed in bottom waters. Similar formations of spheroids are observed on the surface of Lower Carboniferous siderite lamellae (Fig. 3d). Framboidal pyrite in fossil and modern clays and silts is closely associated with the presence of euxinic conditions in bottom waters and is interpreted as a result of direct pyritization of nanobacteria (Halas and Chlebowski, 2004).

Correlation between the episodes of formation of the studied nodules and participation of bacterial communities as well as activation of bottom gas–fluid seeps with geodynamic events made it possible to observe their interconnection and interdependence. Shamosite ores were formed at the beginning of the spreading stage, while siderite ores were formed at the active subduction stage converted into the collision stage accompanied by ophiolite allochthons shirring in the marginal area of the East European Platform (Puchkov, 2010). In the Late Silurian and Early Devonian, consedimentation depressions and swells were formed in the plate structure of the Timan–North Ural region, reflecting activation of base blocks, which was associated with the formation of the Caledonian collision belt in the northwestern European Platform. Paleogeodynamic stages are associated with the development of cold hydrothermal and gas–fluid seeps, mud volcanoes, which is evident from the modern concretions formed in the areas of conjunction of lithosphere blocks (Lake Baikal, Black Sea, Atlantic Ocean, etc.). The study of carbonate and silicate concretions differing in age and geological position has revealed common microbiological, biogeochemical, and physicochemical parameters of their formation (Fig. 4), despite significant differences between them.

CONCLUSIONS

Electron microscopic, geochemical, and spectroscopic studies of carbonate and silicate nodules revealed OM, bacteriomorph structures, and mineralized biofilms and glycocalyx of iron–silicate composition, the presence of various forms of framboidal micropyrite and authigenic minerals atypical for sedimentary rocks, such as sphalerite, chalcopyrite, pyrrhotite, barite, chameanite, tsumoite, and fauserite. Substrates enclosing siderite, calcite, and siderite–shamosite nodules are enriched with terrigenous minerals of weathering crusts. Isotope–geochemical studies revealed a significant role of bacterial organic matter in the diagenetic carbonate mineral formation under conditions when basin waters varied from desalinated brackish to normal saline ones, and bottom waters underwent oxygen deficiency. The data obtained suggest that the formation of studied nodules was influenced by bottom gas–fluid seeps, since they promoted saturation of sediments with methane and active development of bacterial colonies. In some cases, bacteria used terrigenous material entering the basin with abnormal water exchange from erosive regions during regressions, which was evident from the iron–silicate composition of mineralized glycocalyx in calcite ooids. In other cases, bacteria used clay minerals from the redeposited weathering crusts as electron donors, which resulted in the mass formation of siderite and shamosite nodules. It should be noted that participation of microbial organisms in the formation of nodules in Paleozoic sediments on the Subpolar and Northern Urals and in the southern part of the Chernyshev Ridge of the Cisural Foredeep was determined by tectonic (regional and global) and climatic (warming and cooling) events.

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