

Microspheres in the Silurian of the Altai Mountains: Morphology, Chemical Composition, Biomineralization, and Genesis

N. V. Sennikov^{a, b, *}, N. V. Novozhilova^{a, b, **}, R. A. Khabibulina^{a, ***}, and V. A. Luchinina^{a, ****}

^a Trofimuk Institute of Petroleum–Gas Geology and Geophysics, Siberian Branch, Russian Academy of Sciences, Novosibirsk, 630090 Russia

^b Novosibirsk State University, Novosibirsk, 630090 Russia

*e-mail: sennikovnv@ipgg.sbras.ru

**e-mail: novozhilovanv@ipgg.sbras.ru

***e-mail: khabibulinara@ipgg.sbras.ru

****e-mail: luchininava@ipgg.sbras.ru

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Abstract—The study of Silurian sediments in the central part of the Altai Mountains (Gorny Altai) by limestone dissolution has revealed two groups of spherical objects; large microspheres 90–120 μm and small nanofossils (nanospheres) 5–18 μm in diameter. Their double-layered walls are composed of standard-sized siderite microcrystals replaced by goethite. The Altai microspheres have a low Ca content (<0.5 wt %) so cannot be interpreted as calcispheres. The Altai Silurian microspheres and nanofossils (nanospheres) are tentatively attributed to biomineralized remains of loricae (shell-like envelopes) of various euglenoid alga generations.

Keywords: Silurian, limestones, microspheres and nanospheres, microcrystals, biomineralization, euglenoid algae, Altai Mountains, Russia

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INTRODUCTION

This paper reports the study of rounded micro-objects found in Silurian sedimentary rocks in the Altai Mountains. Microspheres of similar shape have long been known in the Paleozoic (Williamson, 1880; Rust, 1935). They are subdivided into two groups based on their chemical composition and morphology: calcispheres and pyrite frambooids.

Calcispheres are spherical or ellipsoidal calcareous (CaCO₃) fossils of unknown origin. They consist of a hollow central chamber (30–500 μm) and an outer shell (3–170 μm). Most researchers suggest a biogenic origin; calcispheres have been interpreted as diagenetically altered remains of radiolarians, foraminifera, reproductive organs of roundworms, acritarchs, cysts of dinoflagellates, volvox and ulvophyte green algae, and charophyte algae (Kaźmierczak, 1975, 1976; Marszałek, 1975; Servais et al., 2009; etc.).

The first demonstrations of the algal nature of Paleozoic calcispheres were published by J. Kaźmierczak and D. Marszałek (Kaźmierczak, 1975, 1976, 1981; Marszałek, 1975). They assigned representatives from the Devonian limestones of Poland to the classes Volvocophyceae and Ulvophyceae within the green algae division. Later, calcareous shells of chara algae zoo-

sporangia were found in the Ludlow–Přídolí limestones of Severnaya Zemlya (Berchenko et al., 1993).

At the end of the twentieth century, new terms were proposed for Paleozoic calcispheres such as calcareous microfossils and nanofossils (Munnecke et al., 1999). Later (Dixon, 2010), rounded carbonate formations were found within Silurian corals in Arctic Canada and were referred to as microspheres. These were examples of studying the microspheres in thin sections. The studies of carbonate microspheres with the help of chemical treatment techniques using Swedish Paleozoic material yielded new results (Munnecke and Servais, 1996, 2008; Munnecke et al., 1999, 2000; Servais et al., 2009; Versteegh et al., 2009) and allowed comparison with palynomorphs, acritarchs and other faunistic and floristic groups.

Pyrite frambooids (FeS₂: 46.6 wt % Fe, 53.4 wt % S) represent a fundamentally different category of rounded micro-objects found in sedimentary rocks. Such objects were first described by Rust (1935). Frambooids range from 1 to 250 μm in size, but, in general, their diameter does not exceed 50 μm (Savelieva et al., 2013). Frambooids consist of isometric adjacent microcrystals of the same shape and size. Frambooids can have an empty cavity inside. Many researchers believe that pyrite frambooids are mostly of biogenic

origin (Fedorova et al., 1988; Gerasimenko and Zavarzin, 1993; Astafieva et al., 2005; Savelieva et al., 2013; Reikhard, 2014; Budagaeva and Barkhutova, 2018; Lukin and Gafich, 2018). Based on the data on recent bottom sediments in the White Sea, pyrite framboids are most often formed on the silicic shells of diatoms and on the carbonate shells of foraminifera (Reikhard, 2014). Other researchers (Wilkin and Barnes, 1997; Astafieva et al., 2005) note that a spherical shape of such micro-objects is due to the formation process of pyrite aggregates and is not related to pseudomorphism over rounded micro-objects. In addition, pyrite framboids from microcrystals in the form of pentagon–dodecahedrons, octahedrons, and tetrahedrons are mostly of biogenic origin, while cubic framboids are only formed by chemical reactions (Astafieva et al., 2005).

MATERIALS AND METHODS

The Ludlow–Prídolí stratigraphic interval of the Silurian in the Anui–Chuya structural–facies zone of the northwestern Altai Mountains was studied using a range of sections (Fig. 1) and chemical treatments were used to obtain micropaleontological objects such as conodonts, ostracods and other microfossils. The Ludlow and Early Prídolí interval in the study area is represented by carbonate and terrigenous–carbonate rocks of the Kuimov Formation, while the Middle–Late Prídolí interval represented by the Chernouui Formation is composed mainly of terrigenous rocks with rare limestone interlayers and lenses. The Kuimov and Chernouui formations are characterized by representative assemblages of brachiopods, trilobites, ostracodes, tabulates, rugoses, stromatoporoids, crinoids, and conodonts (Kulkov, 1966, 1967; Polenova, 1970; Yolkin et al., 1974; Ivanovskii and Kulkov, 1974; Mironova, 1978; Gutak et al., 2000; Sennikov et al., 2001, 2008, 2019; Krasnov and Kulkov, 2009).

The laboratory chemical treatment of Altai material with acetic acid yielded numerous specimens of relatively large, rounded microspheres (from 90 μm to 120 μm) (Pls. 1, 2) from one of members of the Burtas-3 section (Fig. 2). In contrast to other light-colored calcite microspheres known from the sediments, the Altai microspheres (both large and smaller, see below) are black. In their dark color, they more closely resemble pyrite framboids than light gray calcispheres. The structure of the walls of the Altai microspheres walls and their chemical composition were studied using a TEXCAN-MIRA scanning electron microscope (SEM) (Institute of Geology and Mineralogy, Siberian Branch, Russian Academy of Sciences, Novosibirsk) equipped with an INCAEnergy 350 energy dispersive spectrometer (microprobe) to analyze the composition at various microsphere points.

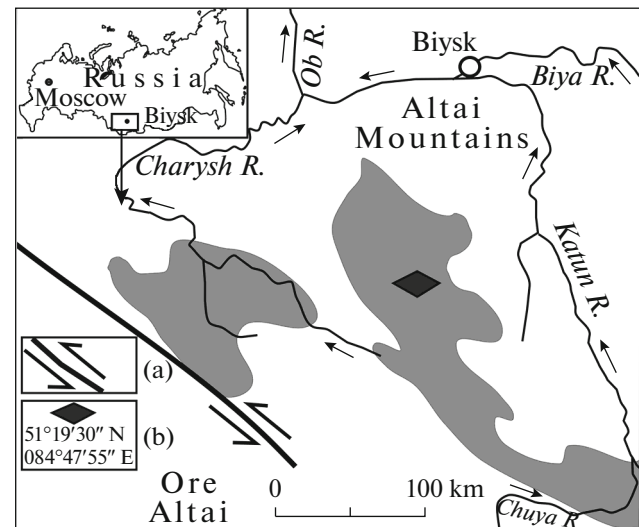


Fig. 1. Areal distribution of Silurian rocks in the Altai Mountains and location of the studied section: (a) strike-slip zone of the largest regional blocks, (b) location of Altai Silurian microspheres.

RESULTS AND DISCUSSION

According to the study results, the outer shell of the Altai microspheres is composed of highly ordered microcrystals resembling pyrite framboids in structure. Microcrystals of the Altai microspheres are largely oriented with their long axes along the sphere radius (Pl. 11, fig. 1; Pl. 12, fig. 4). Microcrystals are adjacent to each other, rarely intergrown.

Already at the first research stage using SEM, the good preservation of the large Altai microspheres indicated that they were in contact with intergrowths of larger and variable sized crystals that were different from the standard-sized microcrystals of the microsphere's wall (Pl. 11, figs. 5, 9; Pl. 12, fig. 1). It is most likely that this generation of crystals was formed from large crystals in the course of late or postdiagenetic transformation. Consequently, the generation of microcrystals that composed the microspheres' walls should have been formed at the earliest diagenesis stage, or before the sediment diagenesis.

The microcrystals which compose the Altai microspheres' walls were formed either by biogenically before sedimentation with the burial of microspheres, or at the earliest diagenesis stage during transformation (biomineralization) of already initially mineralized walls of some microorganisms. It is believed that the biomineral structures developed due to the matrices of metabolic products (Barskov, 1975; Chuvashov et al., 1987; Stanovlenie..., 2014).

Another assumption complementing and supplementing this hypothesis is that microcrystals could be formed on the walls of some organisms at the beginning of diagenesis due to abnormally high content of certain chemical elements in such walls, and higher

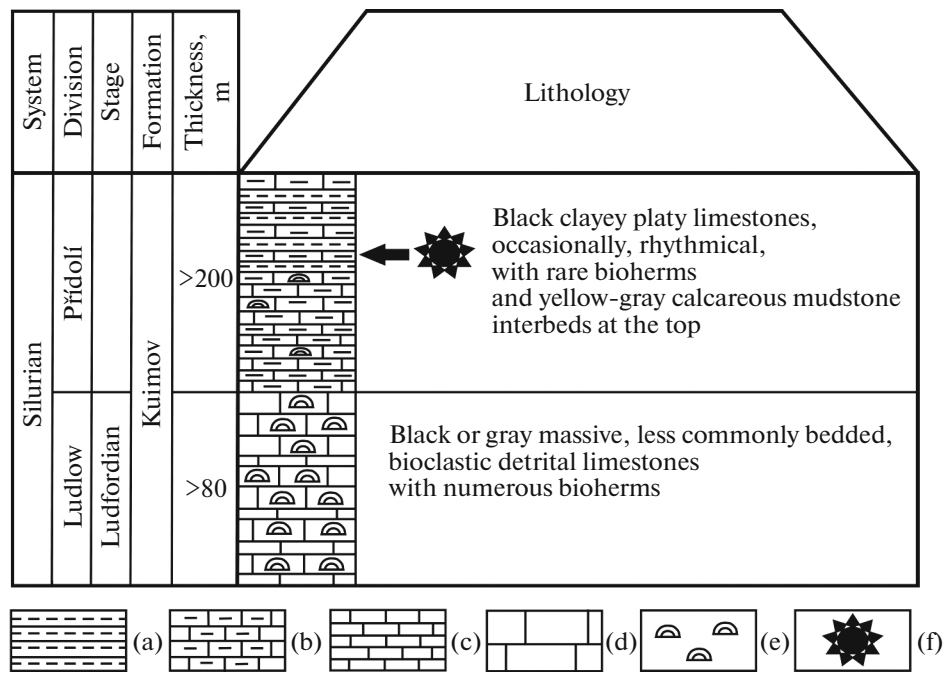


Fig. 2. Stratigraphic column of the Altai Silurian section with microspheres. The arrow shows the stratigraphic level of microsphere findings: (a) mudstones, (b) clayey limestones, (c) thin-platy limestones, (d) massive limestones, (e) bioherms, (f) microspheres.

contents of these elements in the environment. However, since the microcrystals on the microspheres' walls are highly ordered and relatively strictly standard-sized, they should have appeared on the primary organic matrix before large-scale diagenetic transformations which could and should have destroyed this matrix. It should be noted that some microcrystals occasionally differ in size, probably due to their small-scale late diagenetic transformations.

The study of large Altai microspheres using SEM made it possible to reveal a two-layered (probably, multilayered in some cases) structure of their walls (Plates 1, 2). Apparently, such a double (or multilayered) wall structure developed even before sedimentation and, evidently, before the subsequent diagenetic processes. In other words, the hypothetical maternal organisms characterized by biomineralization on their walls should have had an lifetime (initial) two-layered and/or multilayered wall composed of uniform micrograins.

Most microcrystals well-preserved after exposure to acid in the Altai "microspheres" walls are similar in form to siderite crystals (FeCO_3). According to the study results obtained for various microcrystals in the microspheres' walls using a SEM analyzer (Pl. 12, figs. 1, 2), these crystals corresponded in terms of composition (more than 50 wt % Fe, less than 0.2 wt % S) to Fe group minerals and can be attributed to goethite (FeOOH) (Table 1). In addition to being an indicator of continental conditions in oxidation zones, as well as in bogs and streams (*Geologicheskii...*, 2010), goethite is indicative of shallow sea water bodies with O-rich settings and with depths of up to 10 m (Zakharov, 2016). The Altai material comes from limestones containing typical marine organisms at various stratigraphic levels: tabulates, rugoses, crinoids, and conodonts (Fig. 2). In this regard and taking into account the habit of Altai microcrystals, it can be assumed that they are pseudomorphs of goethite (FeOOH) over siderite (FeCO_3). In terms of composition (more than 50 wt % Fe, less than 0.2 wt % S), Altai large micro-

Explanation of Plate 11

Figs. 1–11. Morphology and structure of walls of the Altai Silurian microspheres and nanospheres. Objects more or less affected by diagenetic and postdiagenetic transformations (Museum of Trofimuk Institute of Petroleum–Gas Geology and Geophysics, Siberian Branch, Russian Academy of Sciences): (1, 4, 6, 10, 11) rounded microspheres ((10) walls of an object with varisized microcrystals); (2) microsphere with two attached nanospheres (young generation); (3) multilayer wall of microspheres (shells), white arrows show the tops of microcrystals on the inner wall of the multilayer microsphere; (5, 9) microspheres composed of small microcrystals, with coarse, not standardized microcrystals intergrown with them, probably in their funnel-like apertures; (7) oval elongated specimen with a flattened top, with varisized wall microcrystals; (8) flattened oval specimen with strongly curved top.

Plate 11

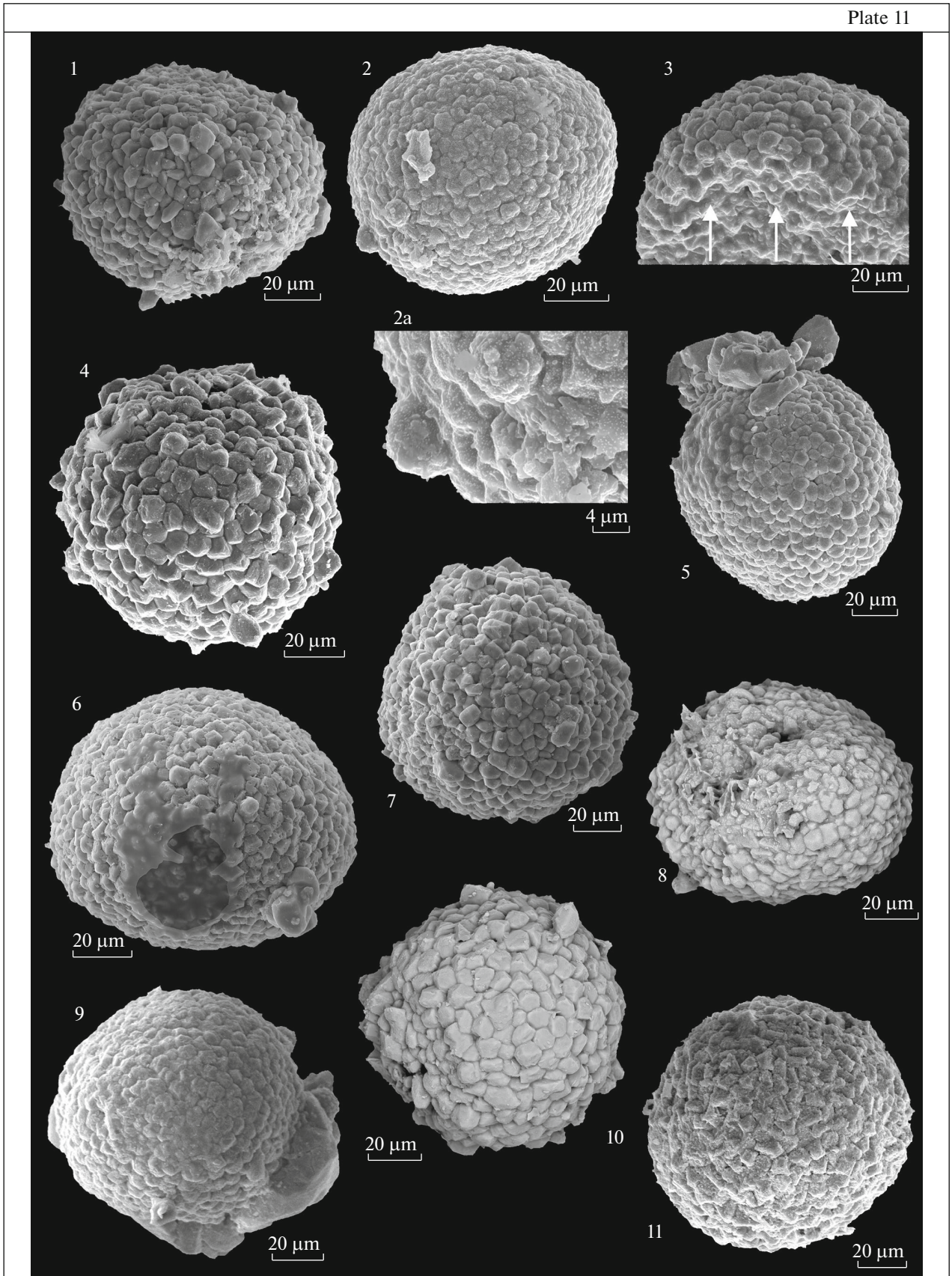


Table 1. Chemical composition of Silurian microspheres from Altai

Point	Total	Si	Al	Fe	Mn	Mg	Ca	Na	K	Zn	S	Cl	O	Mineral
1	110.77	2.53	0.64	57.05	0.21	0.74	0.36	0.31	—	0.36	—	—	46.58	Goethite
2	96.8	1.78	0.66	56.35	0.25	0.69	0.44	0.38	0.16	0.42	0.15	0.16	35.38	Goethite
3	86.94	1.86	0.86	54.64	0.21	0.6	0.47	0.69	0.4	—	0.14	0.17	26.9	Oxide
4	85.92	1.74	0.7	54.5	—	0.34	0.42	—	0.21	0.6	0.17	0.18	26.82	Oxide
5	64.79	1.22	1.84	43.53	—	0.68	0.28	0.19	0.28	—	0.19	0.23	16.34	Oxide

spheres should not be classified as classical pyrite framboids, although the shape of their crystals resembles pyrite crystals in biogenic framboids.

It is known that the diagenetic and postdiagenetic mineralization processes are directly related to the environment composition and are less dependent on the primary (including biological) substrate, although the primary substrate “contribution” to the total chemical composition of the final diagenesis product can be relatively important. Meanwhile, the chemical composition of shells of 12 species of living euglena algae of the genus *Trachelomonas* Ehrenberg (Poniewozik, 2017) is indicative of the fact that their cells almost do not absorb or accumulate Mn. In the Altai Silurian material, Mn does not exceed 0.25 wt % in microspheres and is below detection limit in some crystals. According to (Poniewozik, 2017), Fe content is 25–40 wt %, on average, in the shell of recent *Trachelomonas*, which is somewhat lower than that in the studied Silurian large microspheres (Table 1).

The micro-objects under consideration were formed during microbial activity with the formation of a shell wall of microcrystals over the “primary” microspheres. The “primary” microspheres should have been of a biological nature, as confirmed by the following two circumstances. The first circumstance: only the crystallographic mineral components on the organisms’ walls, which are formed directly during their life due to metabolic products, have a limited range of microcrystal sizes explained by the biomineralization matrix form (Barskov, 1975; Chuvashov et al., 1987; Stanovlenie..., 2014). The second circumstance: relatively small microspheres (from 5 to 18 µm in diameter) with a hard shell were found on the walls of most of the large Altai Silurian microspheres studied. Despite their relatively large size (more than 1000 nm), we will term such small microspheres as nanofossils

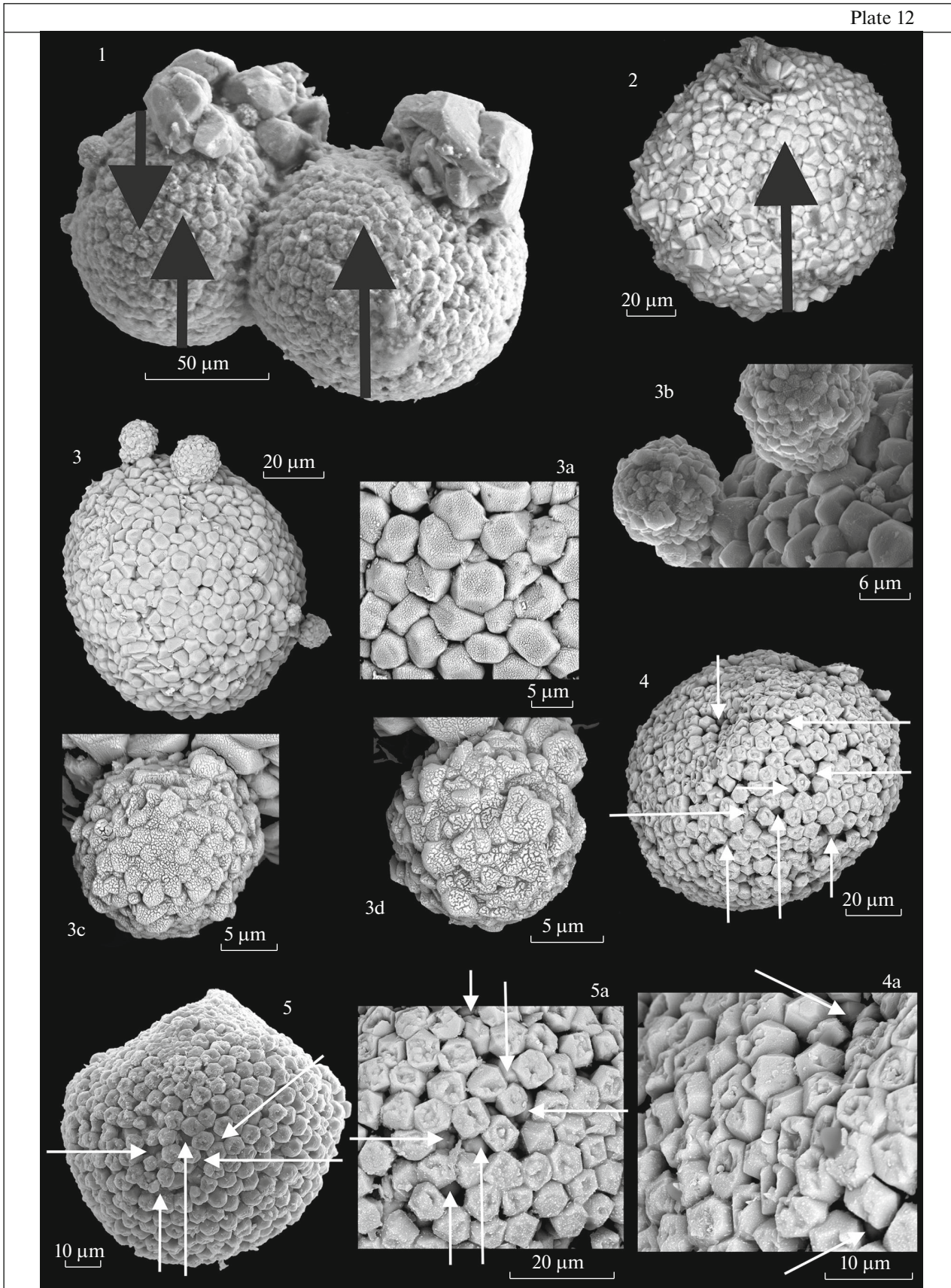
(or nanospheres), by analogy with nanoplankton (*Geologicheskii...*, 2011) and taking into account the earlier used terms (Munnecke et al., 1999, 2000; Munnecke and Servais, 2008). Most likely, these Altai nanofossils are either juvenile daughter generations of the host organisms (as large mother microspheres), or, less likely, other smaller organisms that are symbionts with them. It should be noted that the walls of such nanospheres are also composed of standardized, but much smaller microcrystals, almost nanocrystals. Such small microcrystals are formed on a matrix basis over fine grains on the wall of small biogenic microspheres (nanospheres) and do not increase further in size during diagenetic transformations. Hence, relatively large microcrystals are formed on large microspheres, while small microcrystals are formed on nanospheres. This process occurs on the walls of those host organisms which stopped growing as a result of death. In our opinion, this fact proves that nanosphere microcrystals begin to grow on the shell of the host organism immediately after its death, but before the start of diagenetic transformations. This crystallization process can be very short in time, up to several days, before burial in the sediment.

Among recent microorganisms, some algae have an outer hard (mineralized) calcite-free wall. For instance, Chlorophyta (for example, Chlamydomonadales) includes genera with a shell that is encrusted with Ca, SiO₂ or Fe salts (Chuvashov et al., 1987; Urzica et al., 2013). Some Euglenophyta (Euglenales) representatives have an outer hard shell (lorica) impregnated with Fe salts, not adhering tightly to the protoplast (Dawes, 1998; Lemeza, 2008; Poniewozik, 2017).

The investigation data on double (or multilayered) walls of the Altai microspheres consisting of Fe group minerals, together with different (large- and small-

Explanation of Plate 12

Figs. 1–5. The position of chemical composition analysis points of microcrystals of the Altai Silurian microspheres and structure of their walls (Museum of Trofimuk Institute of Petroleum–Gas Geology and Geophysics, Siberian Branch, Russian Academy of Sciences): (1) two microspheres with coarse, not standard-sized microcrystals intergrown with them, probably located on flattened tops in their funnel-like apertures; (2) elongated oval specimen with a flattened curved top; (3) relationship between microspheres and nanospheres (young generations); (4) specimen with a flattened top, with a well-defined second inner layer of the wall consisting of standard-sized oriented microcrystals (an object which did not undergo noticeable diagenetic and postdiagenetic transformations); (5) rounded elongated specimen with a poorly developed neck and a well-defined second inner layer of the wall. Bold black arrows (1, 2) show the position of chemical composition analysis points of microcrystals on the microspheres’ outer wall. Thin white arrows show the position of microcrystals’ tops on the inner wall of a two-layer microsphere (figs. 4, 5).



sized) generations, suggest the originally biogenic genesis of these rounded formations. The studied Altai Silurian microspheres and nanospheres are a mineralogical phenomenon formed on the organisms' membranes over the grains developed while alive from products of their metabolism. Probably, the "parental" organisms were Euglenophyta algae (Dujardin, 1841; Maslov, 1963; Conforti, 1999, 2010; Poniewozik, 2017).

Euglenoid algae inhabit both freshwater and marine environments (Maslov, 1963; *Marine...*, 1969; Safonova, 1984; Conforti, 1999, 2010; Moskalets and Likhachev, 2006; Lemeza, 2008; Solórzano et al., 2011; Servat et al., 2015; Jurán, 2016; Poniewozik, 2017). Under unfavorable conditions, dormant cysts with thick membranes (from two-layer to multilayer) are formed in some euglenoid plants. The fossils of several genera are referred to as euglenoid algae. The genera *Trachelomonas* and *Phacus* Dujardin are known from the Paleogene and Neogene, while the genera *Ophiobolus* Wetzel and *Dimastigobolus* Deflandre were found in the Cretaceous (Bradley, 1929; Maslov, 1963). It has been convincingly shown recently (Strother et al., 2020) that representatives of the genus *Moyeria* Thusu, formerly attributed to acritarchs (or, by some authors to euglenoid algae, Gray and Boucot, 1989) should be included in the group Euglenida. Various species of the genus *Moyeria* are known from the Upper Ordovician sections (Katian), as well as from the Llandoveryan, Wenlockian, and Ludlow sections of the Silurian in the Baltic region and North America (Strother et al., 2020). Consequently, the Altai Silurian microspheres were formed, as suggested above, over the shell-like envelope (lorica) of euglenoid algae and belong to the lower part of the stratigraphic interval of the distribution of ancient euglenids.

The division Euglenophyta includes microscopic, actively moving planktonic unicellular organisms with one or two flagella. A body (cell) of a euglenoid algae is from fusiform to spherical in shape. A cell size ranges from 4 μm to 500 μm . A cellulose membrane is absent in euglenoid algae; its protective function is performed by the outer compacted cytoplasm layer called "pellicle" (Safonova, 1984; Moskalets and Likhachev, 2006; Lemeza, 2008; Esson and Leander, 2010) or "lorica" (*Marine...*, 1969; Conforti and Nudelman, 1994; Conforti, 1999, 2010; Servat et al., 2015; Poniewozik, 2017). Euglenoids with a soft lorica can change body shape. As noted above, some euglenoid algae have a hard lorica enriched with Fe salts (Dawes, 1998; Lemeza, 2008; Poniewozik, 2017).

The genus *Trachelomonas* is the most widespread among euglenoid algae communities in recent water bodies, and the most numerous in terms of number of species (*Marine...*, 1969; Safonova, 1984; Conforti and Nudelman, 1994; Conforti, 1999, 2010; Moskalets and Likhachev, 2006; Lemeza, 2008; Servat et al., 2015; Poniewozik, 2017). The cell in recent *Trachelo-*

monas species is located more or less freely in the shell lorica (Servat et al., 2015). Such cells can metabolize, increase in size, and multiply by division (Safonova, 1984; Moskalets and Likhachev, 2006).

These are *Trachelomonas* representatives, in contrast to other euglenoid genera, which have a spherical shape and are characterized by a solid lorica in both adults and young (which is especially important in view of the study of Altai nanospheres) euglenids (Solórzano et al., 2011). The shell-like envelopes of *Trachelomonas* have a two-layer wall structure (Conforti, 2010; Servat et al., 2015). As noted above, the phenomenon of biomineralization over the initial double (or multilayer) wall of hypothetical organisms was recorded in the Altai Silurian microspheres (Pl. 11, figs. 1, 3; Pl. 12, figs. 4, 5).

Paramylon, a substance similar to starch, is an accumulated storage product of metabolism of euglenoid algae (Lemeza, 2008; Monfils et al., 2011). It composes small grains in the cytoplasm or hard grains on the outer wall (lorica), which are possible crystal growth germs as the primary nuclei of potential matrix-based biomineralization. Excessive Fe formed during life is constantly deposited in the material studied on the microspheres' walls. A calcite shell was not formed after death, as might be expected for growth of calcite crystals after the death of calcareous algae. In this case, matrix crystalline shell layers were arranged from microcrystals, most likely of siderite, with subsequent diagenetic replacement by secondary goethite.

Euglenoid algae reproduce in different ways (Moskalets and Likhachev, 2006). A single maternal cell emerging from its own shell is divided in the longitudinal direction, thus producing two individual daughter cells. In the second case, the maternal cell is divided inside the shell, yielding two daughter individuals which either both leave this maternal lorica and build their separate shells, or one uses the maternal lorica, and the other leaves it and builds its own lorica. The data on the Altai Silurian euglenoid algae made it possible to suggest the second reproduction way for the Silurian euglenoid representatives: not one or two nanospheres, but many daughter small lorica, including different generations, could be fixed on large maternal shells (Pl. 11, fig. 2; Pl. 12, fig. 3).

Newly formed young daughter cells of recent *Trachelomonas* species build solid shells in a few days around themselves as nanospheres (Moskalets and Likhachev, 2006). The shells of recent euglenoid algae are of various shapes: spherical, smooth or spiny with a simple hole; oval with a neck; and spherical with a ring-shaped collar (Safonova, 1984; Conforti and Nudelman, 1994; Conforti, 1999, 2010; Moskalets and Likhachev, 2006; Solórzano et al., 2011; Servat et al., 2015; Poniewozik, 2017). Mainly simple spherical forms were found in the Altai material, somewhat distorted likely due to the sediment compaction. There are also oval flattened and oval elongated large

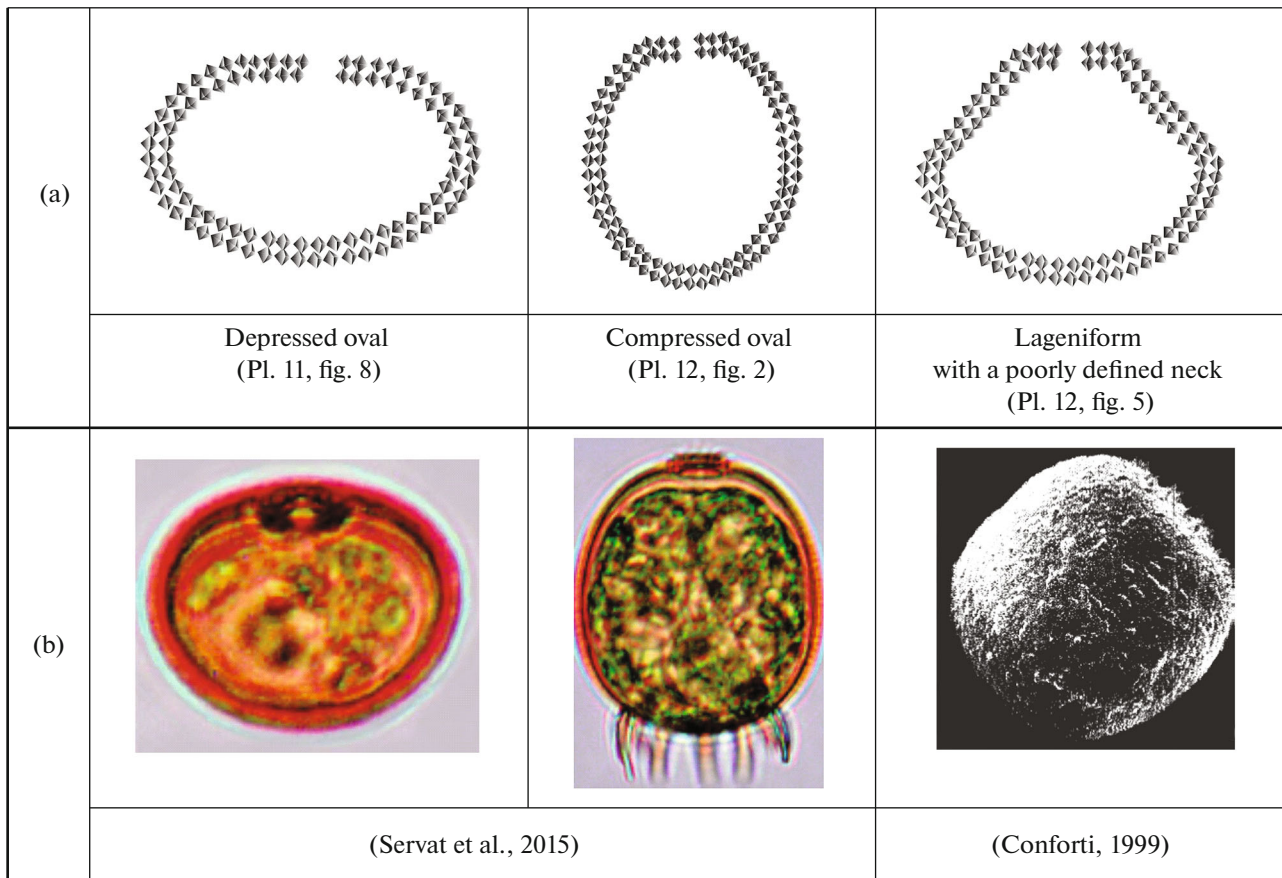


Fig. 3. (a) Shape and section of two-layered wall of Altai Silurian microspheres and (b) shape of shell-like envelope of recent euglenoid algae of the genus *Trachelomonas* Ehrenberg.

microspheres (Pl. 11, fig. 8; Pl. 12, fig. 2), as well as forms with a drawn-out top neck (Pl. 12, fig. 5). In some large Altai microspheres, deviations from the round shape are similar to holes and necks which complicate the shell structure of recent euglenoid algae. These peculiar features of the microspheres may be taphonomic artifacts. However, since such parts were recorded in several microspheres, they can possibly be interpreted as separate morphological elements, such as funnel-like apertures of the host organism's shell (Pl. 12, fig. 8). It should be noted that additional large microcrystals were formed on precisely such flattened and slightly bent elements of microspheres during diagenetic transformations (Pl. 12, fig. 1). It is apparent that evidence from additional material is required for their unambiguous interpretation. Reconstructions of the general shape and a structure of the Altai Silurian microspheres' shells, as well as comparisons with the shells of recent euglenoid algae, are shown in Fig. 3.

The studied Altai Silurian objects include two fundamentally different crystalline modifications. The entire two-layer (or multilayer) wall of the shells (loricae) is composed of adjacent, rarely intergrown, standard-sized, highly ordered microcrystals (Pl. 11, fig. 1;

Pl. 12, fig. 4). It should be noted that tops and faces of such crystals are "smoothed" to one degree or another due to the diagenesis processes.

The intergrowths of larger, different, not standard-sized and not oriented crystals in contact with the microspheres are composed of larger microcrystals (Pl. 11, figs. 5, 9; Pl. 12, fig. 1). Standard-sized microcrystals on the walls of microspheres and nanospheres were formed in underwater marine conditions before the diagenesis process as a product of transformations in granules generated on their walls during the life of euglenoid algae. Other, much larger crystals of various sizes and cubic in shape were formed during middle and late sediment diagenesis stages.

CONCLUSIONS

Numerous black microspheres of large (90–120 μm) and small (5–18 μm) sizes were obtained by dissolution of limestones from the Silurian Kuimov Formation section (Ludlow–Přídolí) in the Altai Mountains. The walls of such microspheres are composed of standard-sized highly ordered microcrystals emphasizing matrix biomineralization during the life of the organisms in individual granules of their meta-

bolic products. It is possible that this process began on a large scale immediately after their death, before burial in the sediment and diagenetic transformation. In terms of their chemical composition, the Altai microspheres should not be classified either as classic calcispheres (less than 0.5 wt % Ca), or as their diagenetic replacement products. Despite the fact that they contain more than 50 wt % Fe and less than 0.2 wt % S, we can still suggest that they were formed during diagenesis due to the pseudomorphism of pyrite framboids which, in turn, were formed earlier on the host organisms' shells.

The Altai microspheres and nanospheres are tentatively attributed to the biomineralization products of various generations of euglenoid algae fossils which had a lifetime multilayered hard outer shell (lorica) impregnated with Fe salts. The formation of such microspheres involved a few successive stages.

(1) On the outer shell (lorica) of living planktonic euglenoid algae, their metabolic products were deposited as micrograins enriched with Fe salts.

(2) The biomineralization process started on the lorica of both small (nanospheres) and large microspheres immediately after the death of the planktonic euglenoid algae (with a multilayered wall), over the matrix-organized micrograins. The biomineralization was due to microbial activity, causing growth of individual, standard-sized, highly ordered microcrystals, most likely, of siderite. It is possible that the initial part of this microcrystallization process began during the life of host organisms, but it proceeded on a large scale immediately after the death of the algae, when they had settled on the bottom substrate, most likely before burial in the sediment and diagenesis.

(3) The early and middle diagenetic transformation stages involved the pseudomorphism on the walls of microspheres and nanospheres, i.e., the formation of secondary goethite.

(4) Large, not standard-sized and not oriented cubic microcrystals, most likely of pyrite were formed in the rock in direct contact with microspheres of loricae of euglenoid algae, probably at their funnel-like apertures, at the middle sediment diagenesis stage.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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