

APATITE SHELLS OF THE DEVONIAN FORAMINIFERS (SAFYANOVSKY COPPER-SULPHIDE DEPOSIT, MIDDLE URAL)

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Relevance of the work is due to the possibility of a detailed study of Devonian foraminifers with apatite shells and the reconstruction of specific conditions for their formation. Foraminifer shells are morphologically similar to *Parathurammia aff. tamarae* L. Petrova, 1981, the Eifelian-the Givetian, which were found in thin sections of samples of carboniferous and chiselly aleuropelites of the ore-bearing strata of the Safyanovsky copper-sulphide deposit (Middle Urals) for the first time.

Purpose of work. Detailed study of the shells of Devonian foraminifers similar to *Parathurammia aff. tamarae* L. Petrova, 1981, as well as reconstruction of sedimentation conditions for carboniferous and chiselly rocks of the ore-bearing strata of the Safyanovsky copper-sulphide deposit.

Research methodology. Shells were studied in thin sections of carboniferous and chiselly aleuropelite samples. The detailed study of morphology and composition of the shells was carried out using a scanning electron microscope JSM-6390LV (JEOL) with an energy-dispersive spectrometer Inca Energy 450, an electron microscope Tescan and an electron probe microanalyzer Cameca SX100.

Results. Size and morphology of the shells were determined; it was also found that the walls of the shells of the studied foraminifers were represented by fluorapatite. It was assumed that initially they were calcareous, and subsequently were replaced by apatite and quartz. However, more detailed studies did not reveal traces of substitution of carbonate rock for apatite.

Conclusions. Compared with *Parathurammia aff. tamarae* L. Petrova, 1981, shells have a reduced size and a smaller number of fauces, which can be explained by unfavorable habitats in a shallow sea basin, where carbonate sedimentation was suppressed by a significant influx of volcanic material. The presence of sulfide minerals in nucleus of shells may indicate to the specific habitat (pH of the environment, salinity of supra-bottom water) of foraminifers. Findings of fossils of green, siphon algae together with studied foraminifers indicate that formation of the original substrate took place in near-surface layers (up to 200 m) of the photic zone of seas.

Keywords: Middle Urals, Safyanovsky copper-sulphide deposit, fossils, Devonian foraminifers, fluorapatite.

Introduction

The Safyanovsky deposit is located in 10 km to the northeast of Rezh (town) within the East Ural lifted block, in the southern part of the Rezhvskaya structural and formation zone. It is confined to the southern part of the Boroukhinsky tectonic block composed of igneous-sedimentary rocks of the Devonian and Mississippian period (Fig. 1).

Igneous rocks of the ore-bearing strata are represented by andesites, dacites, rhyodacites and their tuffs. The rocks of the Boroukhinsky block along the Zabolotsky thrusting of the northwestern dip superpose the limestones of the Carbonic period of the Pokrovsko-Mironovsky block. Along the Rezhvskoy mass overthrust of western dip, they are covered with limestones of the Middle-Upper Devonian, igneous-sedimentary rocks of the Upper Devonian; they also border with serpentinites of the Rezhvskoy massif (O_1). The rocks were tectonic, brecciated affected and hydrothermally altered. The main ore-shoot of the deposit is developed with an open-cut mining and a mine. The southern flank of the deposit sharply wedges out, and the northern one goes to the series of apophyses, which are represented by massive pyrite, copper-zinc and veinlet-impregnated sulphide ores. The ore-bearing strata of the deposit have a thickness of about 500 m.

Noncarbonate shells of foraminifers were found in carboniferous and chiselly rocks, as well as igneous-sedimentary rocks (Fig. 2, a, b) of the ore-bearing strata of the Safyanovsky deposit [1, 2].

Objects of research, methods of study and discussion of results

Shells those are morphologically similar to *Parathurammia aff. tamarae* L. Petrova, 1981 [5], the Eifelian-the Givetian, were studied in thin sections of carboniferous and chiselly aleuropelite samples. The detailed studies of the morphology and composition of the shells were carried out in the laboratory of physical and chemical methods of the Institute of Geology and Geochemistry of the Ural Branch of the Russian Academy of Sciences. The studies conducted using a scanning electron microscope JSM-6390LV (JEOL) with an energy-dispersive spectrometer Inca Energy 450 (S. P. Glavatsky as an operator), an electron probe The Cameca SX100 microanalyzer (D. A. Zamyatin as an operator). The places for studies are the Mining Institute of the Perm Scientific Center of the Ural Branch of the Russian Academy of Sciences and the mineralogy laboratory (Tescan electron microscope with E. P. Chirkova as an operator). By scanning electron microscopy over 10 shells were studied; some images with high resolution were obtained that allows to fix the parts of microstructure of walls (Fig. 3, c, inset); 114 determinations were performed; energy-dispersive spectra from the walls of shells were obtained (Fig. 3, c) (58 spectra from 8 sites in total).

Shells are secretory and rounded. Their outer diameter is 0.1–0.21 mm, the internal diameter is 0.08–0.18 mm. They have a threeply wall of 0.005–0.028 mm thick, short papillose (sometimes, average length) fauces of 0.01–0.066 mm in height (Fig. 3, a, b); the number of fauces varies from 1–2 to 8; in total, the sizes of 23 shells were determined. In some shells, one can see the scar of attachment of organisms to the bottom. That may indicate a benthic community of these foraminifers [6].

In contrast to carbonate shells of foraminifers *Parathurammia aff. tamarae* L. Petrova, 1981, the found shells have a reduced size and a smaller number of fauces, which can be explained by unfavorable habitats in a shallow sea basin, where carbonate sedimentation was suppressed by a significant influx of volcanic material. Good preservation and frequent coating of shells with pelitic matter, as well as traces of sedimentation, show the burial of shells in shallow marine conditions near the habitat [6].

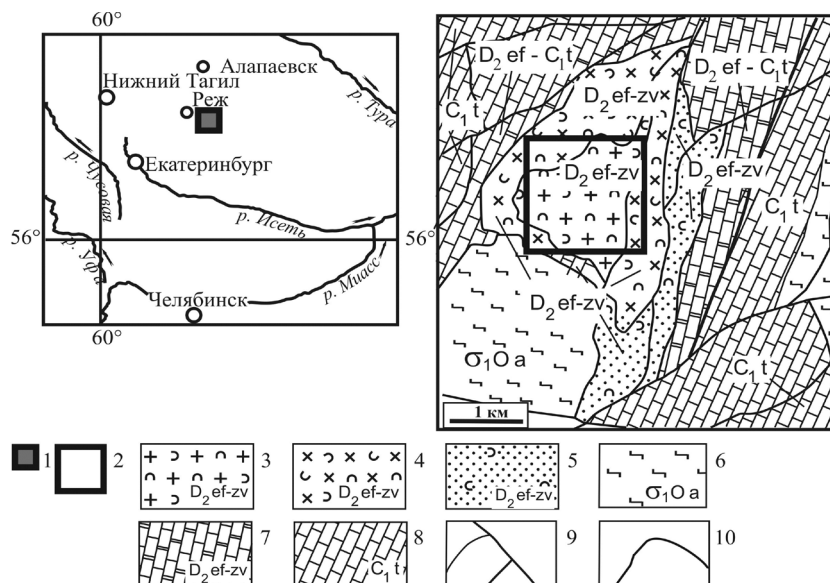


Figure 1. Areal map and geologic pattern of the Safyanovsky ore field. 1 – Safyanovsky ore field; 2 – open-cut mining; 3 – tuffs of acidic composition with beds of carboniferous and chiselly rocks; 4 – tuffs, igneous-sedimentary rocks with beds of limestones; 5 – igneous-sedimentary rocks, sandstones, aleurosandstones; 6 – serpentinites; 7 – marbled limestones; 8 – limestones; 9 – tectonic boundaries, dislocation with a break in continuity; 10 – geologic boundaries.

Рисунок 1. Обзорная карта и геологическая схема Сафьяновского рудного поля. 1 – Сафьяновское рудное поле; 2 – карьер; 3 – туфы кислого состава с прослоями углеродисто-кремнистых пород; 4 – туфы, вулканогенно-осадочные породы с прослоями известняков; 5 – вулканогенно-осадочные породы, песчаники, алевропесчаники; 6 – серпентиниты; 7 – мраморизованные известняки; 8 – известняки; 9 – тектонические границы, разрывные нарушения; 10 – геологические границы.

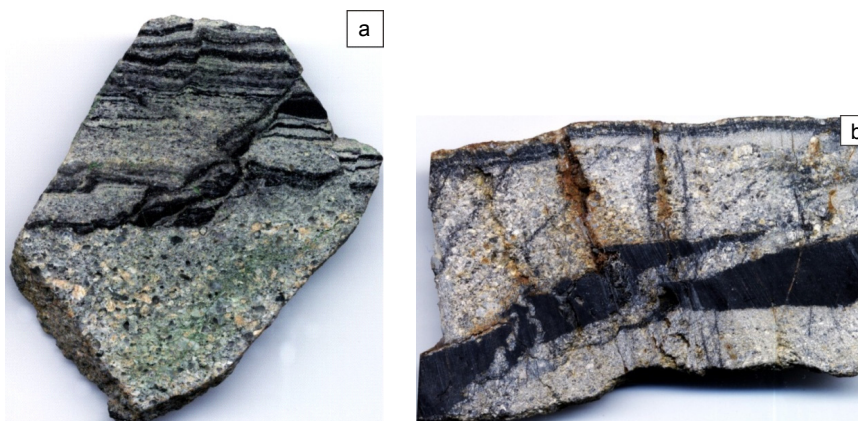


Figure 2. Graded bedding and rolling contacts in carboniferous and chiselly rocks of the Safyanovsky deposit. a – sandstone, horizon is 157 m; b – sandstone, horizon is 100 m (open-cut mining based, 200 m – mine face). The rocks occur in a section in the form of benches with a thickness from 0.1 to 1.5 m [3]. They are represented by psephitomic psammite tuffites, crystal-lithoclastic and pelitolic differences, and are composed of fragments of quartz, plagioclase crystals, subrounded fragments of rhyodacites. They contain shells of foraminifers, radiolarians, accumulations of algal residues and carbonaceous matter with definable residues of siphon algae [4]. The basic finely dispersed mass consists of quartz, chlorite, plagioclase, mica, kaolinite, and carbonates. Sandstone deposits, which are also found in the ore-bearing stratum of the deposit, have graded bedding and sometimes rolling contacts with carboniferous and chiselly rocks (Fig. 2, a).

Рисунок 2. Градационная слоистость и волнистые контакты в кремнисто-углеродистых породах Сафьяновского месторождения. а – песчаник, горизонт 157 м; б – песчаник, горизонт 100 м (отсчет от забоя карьера, 200 м – забой). Породы залегают в разрезе в виде пачек мощностью от 0,1 до 1,5 м [3]. Они представлены псефито-псаммитовыми туффитами, кристалло-литокластическими и пелитолитовыми различиями и сложены обломками кварца, кристаллами плагиоклаза, угловато-окатанными обломками риодацитов. Содержат раковины фораминифер, радиолярий, скопления водорослевых остатков и углеродистого вещества, причем встречаются определяемые остатки сифоновых водорослей [4]. Основная тонкодисперсная масса состоит из кварца, хлорита, плагиоклаза, слюды, каолинита, карбонатов. Песчаниковые отложения, которые также встречаются в рудовмещающей толще месторождения, имеют градационную слоистость и местами волнистые контакты с кремнисто-углеродистыми породами (рис. 2, а).

The presence of sulphide minerals in the shells nuclei indicate the specific habitat conditions of these foraminifers. For example, shells can sometimes be filled with framboids (Fig. 4) formed due to the vital activities of sulfur bacteria (“mineralized bacteria”) under conditions of oxygen deficiency [7].

Moreover, crystalline pyrite (Fig. 5, a), sphalerite and faded ores (Fig. 5, b) are also found in planes of foraminifer shells.

It was assumed that the shells of these foraminifers were originally calcareous, and subsequently were replaced by apatite and quartz [6]. As for the pseudomorphic replacement of fossils is concerned, the results of experimental studies of the hydrothermal substitution of apatite carbonates have revealed that poriness of initial substance plays an important role in replacement of calcite

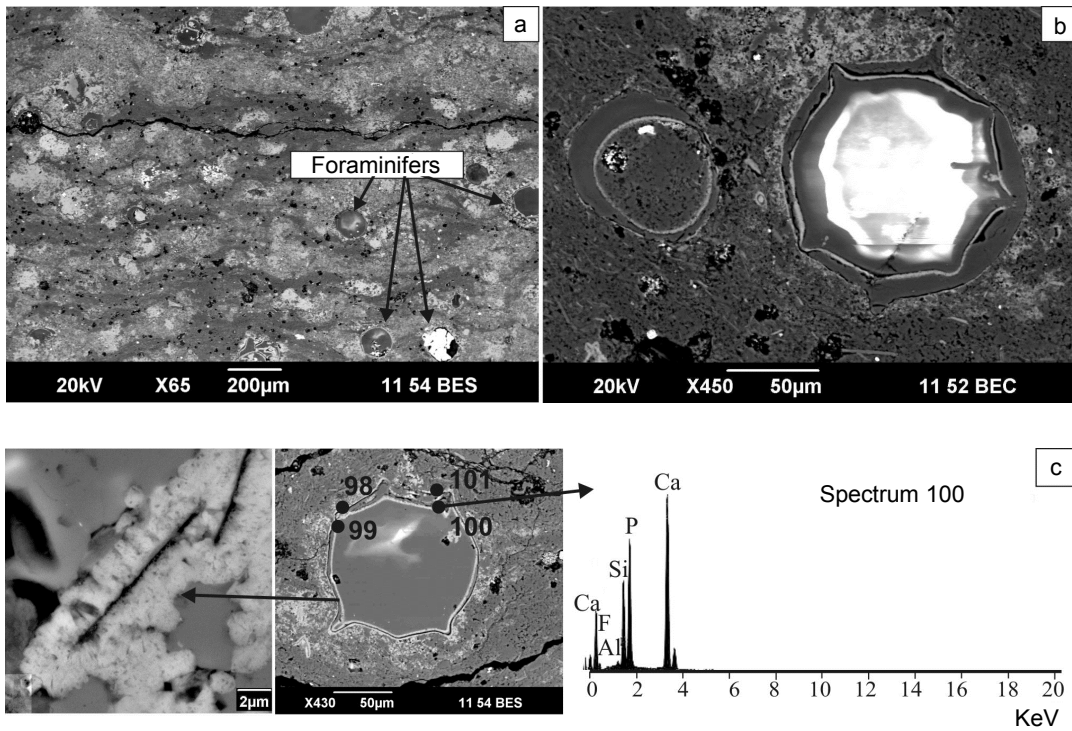


Figure 3. Photos made with a scanning electron microscope. a – foraminifer shells in carboniferous and chissely aleuropelites; b – morphological structure of the shells; c – foraminifer shells with fluorapatite wall and energy-intensive spectrum (right), fibrous microstructure of the wall is on the right inset map.

Рисунок 3. СЭМ-фото. а – раковины фораминифер в углеродисто-кремнистых алевропелитах; б – морфологическое строение раковин; в – раковина фораминиферы с фторапатитовой стенкой и ЭДС-спектр (справа), на врезке слева волокнистая микроструктура стенки.

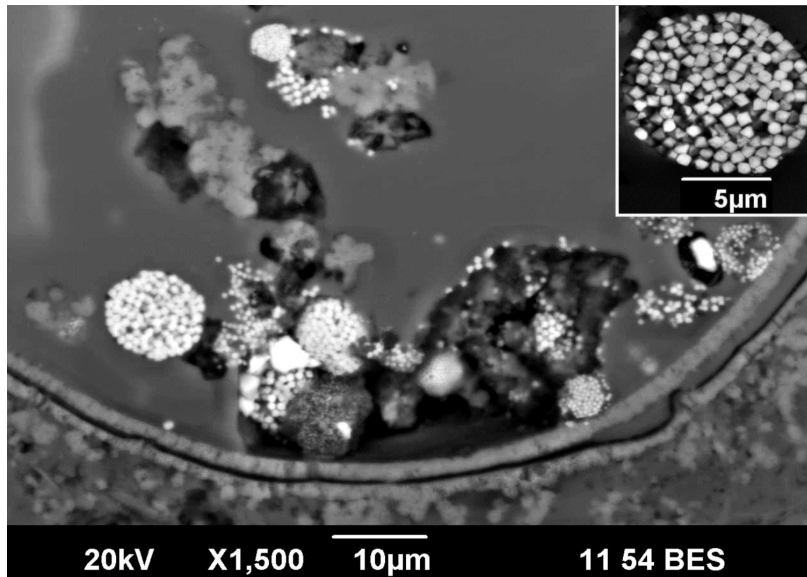


Figure 4. There is a framboidal pyrite in planes of foraminifer shells.

Рисунок 4. В полостях раковин фораминифер встречается фрамбоидальный пирит.

and aragonite [8]. Moreover, the uneven weeping of the solution in the rock is also important. With slower and uneven weeping and fragmentary substitution in aleuropelites, definable fragments of fossils can be retained, which could be destroyed in the course of sedimentation.

But the detailed studies of the found shells did not reveal any traces of substitution of apatite carbonate. According to semi-quantitative analysis, the ratio of Ca/P in the walls of shells varies from 1.6 to 1.9. Almost at all points of determinations, there is F from 7 to 3 atom per cent in the walls of shells. The studies with the use of microprobe made it possible to refine the contents of F and confirmed the hypothesis that the wall of the shell consists of fluorapatite (Table).

It should be noted that the inner part of the shell and the space between the apatite layers of the wall consist of silica (Fig. 3, b). The Table shows the wall composition of the shell, which contains a certain amount of SiO₂, as well as the analysis of fluorapatite

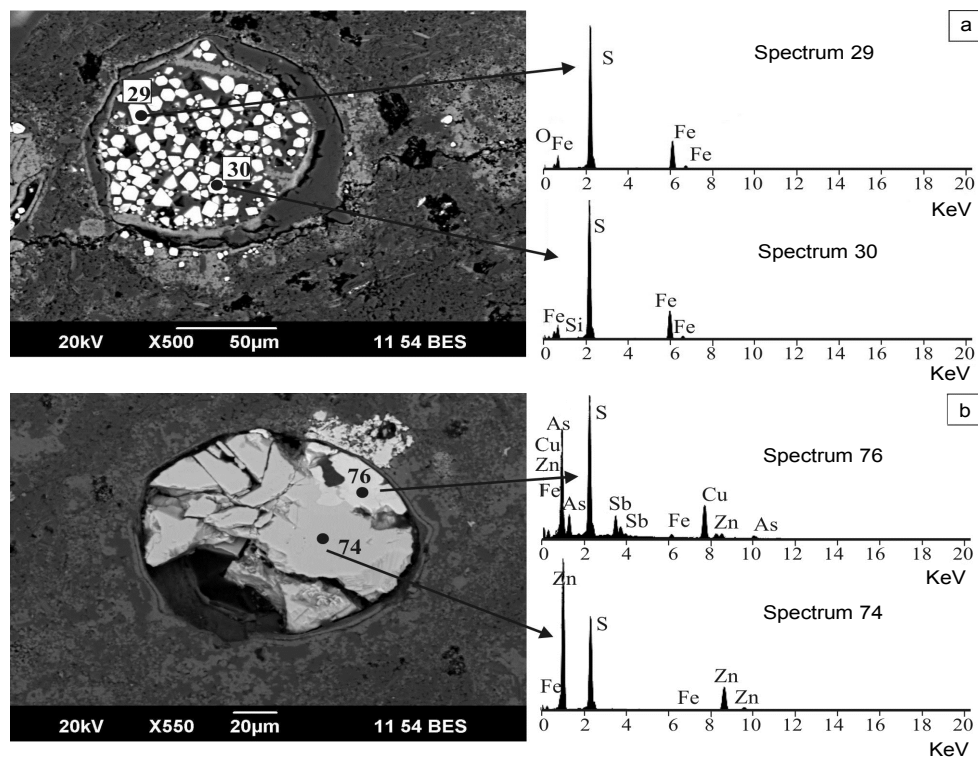


Figure 5. Sulphide minerals found in planes of foraminifer shells; composition of elements is shown on the energy-intensive spectra. a – pyrite crystals; b – sphalerite and faded ores.

Рисунок 5. Сульфидные минералы, установленные в полостях раковин фораминифер, элементный состав показан на ЭДС-спектрах. а – кристаллы пирита; б – сфалерит и блеклые руды.

Composition of the apatite wall of the shell according to microprobe analysis.
Состав апатита стенки раковины по данным микрозондового анализа.

Components wt. %	Numerical order of the analysis				
	1	2	3	4	5
SiO ₂	0.43	1.35	2.32	0.15	0.03
P ₂ O ₅	40.98	36.86	35.46	32.81	41.97
Al ₂ O ₃	0.02	0.24	0.35	0.36	0.04
MgO	0.02	0.14	0.21	0.16	0.05
CaO	53.98	52.4	51.1	46.45	55.64
MnO	0.01	0.04	0.03	0.02	0.2
FeO	0	0.06	0.13	0.96	0.55
Na ₂ O	0.27	0.25	0.35	0.35	0
SrO	0.09	0.12	0.08	0.26	0.03
F	3.32	4.35	4.13	4.01	2.29
Cl	0.43	0.05	0.03	0.05	0.41
SO ₃	0.59	0.42	0.43	1.07	0.04
Amount	100.14	96.28	94.85	86.65	101.24
	<i>Elements, atom per cent</i>				
Si	0.17	0.56	0.97	0.07	0.01
P	13.74	12.85	12.56	12.76	14.04
Al	0.01	0.01	0.17	0.2	0.02
Mg	0.01	0.08	0.13	0.11	0.03
Ca	22.92	23.13	22.91	22.86	23.55
Mn	0	0.01	0.01	0.01	0.07
Fe	0	0.02	0.04	0.37	0.18
Na	0.21	0.2	0.28	0.32	0
Sr	0.02	0.03	0.02	0.07	0.01
F	4.16	5.67	5.47	5.83	2.86
Cl	0.29	0.02	0.04	0.04	0.27
S	0.18	0.3	0.14	0.37	0.01
O	58.3	57.18	57.26	57.01	58.99

from the matrix of the rock (Table, analysis 5). Actually the SiO₂ content is low in the fluorapatite from the rock. Probably, the matrix affects the wall of the shell, because thickness of the wall is extremely small. It should be noted that the amount of P and O is somewhat underestimated compared to the standard fluorapatite (analysis 1) and apatite in the rock (analysis 5). The F content is high enough, higher than the standard one. It can be assumed that the positions of phosphorus in the apatite trellis of the shell wall can be partially occupied by carbonate ion [9].

Biologically, phosphate substance of bones and teeth is usually represented by the apatite group [9]. Hydroxylapatite exists in dentin – a solid base of human teeth – it forms the crystalline basis of hard tissue. In addition, phosphates, including hydroxylapatite and carbonate, exist in uroliths that can appear in human body [10]. It is established that pH of the solution has a significant effect on the composition of the forming stones [11].

It is known that the conodont elements, which are the mineralized remains of the parts of the conodont's mouthparts (an extinct group of marine organisms), consist of different layers of fluorapatite and collagen protein that form during the life of organisms. Fluoride hydroxylapatite of the conodont elements is well studied, its crystal structure is specified, and the features of the elemental composition are revealed [12]. The studies of the mineral composition of hard tissues of the late Devonian conodont elements showed fluorapatite with an atomic ratio of Ca/P = 1.60–1.65. In addition, some fluctuations in Sr content were noted [13]. Strontium exists in the walls of the shells of apatite foraminifers (Table) which we study.

Conclusions

According to [14], Devonian paraturamines with a secretion calcareous shell are found in the Petropavlovskaya and Turinskaya structural and facial zones of the eastern slope of the Urals in biomorphic tabular-amphipore limestones and rarely in clayey limestones and chalky clay. Foraminifers with noncarbonate agglutinated shell and siliceous and ferruginous cement are known in sedimentary deposits of the Triassic of Western Siberia [15]. Thus, Devonian foraminifers with a non-carbonate secretion apatite shell are found for the first time in igneous-sedimentary rocks of the eastern slope of the Urals. Probably, some specific conditions of sedimentation are typified for igneous-sedimentary rocks of the ore-bearing strata of the Safyanovsky deposit: pH medium and salinity of the supra-bottom water. In addition, the findings of fossils of green and siphon algae indicate that formation of initial substance took place in shallow conditions (up to 200 m) of the photographic zone of seas.

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АПАТИТОВЫЕ РАКОВИНЫ ДЕВОНСКИХ ФОРАМИНИФЕР (САФЬЯНОВСКОЕ МЕДНОКОЛЧЕДАННОЕ МЕСТОРОЖДЕНИЕ, СРЕДНИЙ УРАЛ)

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Актуальность работы обусловлена возможностью детального изучения девонских фораминифер с апатитовыми раковинами и реконструкции специфических условий их образования. Раковины фораминифер, морфологически похожие на *Parathuramina aff. tamarae* L. Petrova, 1981, эйфель-живет, были обнаружены в тонких срезах образцов углеродисто-кремнистых алевропелитов рудовмещающей толщи Сафьяновского медноколчеданного месторождения (Средний Урал) впервые.

Цель работы: детальное изучение раковин девонских фораминифер, похожих на *Parathuramina aff. tamarae* L. Petrova, 1981, и реконструкция условий осадконакопления углеродисто-кремнистых пород рудовмещающей толщи Сафьяновского медноколчеданного месторождения.

Методология исследований: раковины изучались в тонких срезах образцов углеродисто-кремнистых алевропелитов. Детальное изучение морфологии и состава раковин проводилось при помощи сканирующего электронного микроскопа JSM-6390LV (JEOL) с ЭДС-спектрометром Inca Energy 450, электронного микроскопа Tescan и электронно-зондового микроанализатора Cameca SX100.

Результаты: были определены размеры и морфология раковин, также установлено, что стенки раковин изучаемых фораминифер представлены фторапатитом. Предполагалось, что изначально они были известковистыми, а впоследствии были замешены апатитом и кварцем, однако более детальные исследования не выявили следов замещения карбоната апатитом.

Выводы: по сравнению с *Parathuramina aff. tamarae* L. Petrova, 1981, раковины имеют уменьшенные размеры и меньшее количество устьев, что можно объяснить неблагоприятными условиями обитания в мелководном морском бассейне, в котором карбонатное осадконакопление было подавлено значительным привнесом вулканического материала. О специфических условиях обитания (рН среды, минерализация придонных вод) фораминифер может свидетельствовать присутствие сульфидных минералов в ядрах раковин. Находки фоссилий зеленых, сифоновых водорослей совместно с изучаемыми фораминиферами свидетельствуют о том, что отложение первоначального субстрата проходило в малоглубинных условиях (до 200 м) фотической зоны морей.

Ключевые слова: Средний Урал; Сафьяновское медноколчеданное месторождение; фоссилии; девонские фораминиферы; фторапатит.

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