ISSN 0024-4902, Lithology and Mineral Resources, 2006, Vol. 41, No. 6, pp. 570–575. © Pleiades Publishing, Inc., 2006.
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Pyritization of Fossil Mollusk Shells and Some Problems of Supergene Sulfide Formation

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Received February 9, 2005

Abstract—The study of specific features of the pyritization of mollusk fossil shells has provided new evidence of the relationship between the generation of hydrosulfides during the bacterial reduction of sulfates and the composition of organic matter (OM) exploited by bacteria in processes of metabolism. The OM is represented by conchiolin of the ammonite shell frustule. Interaction between the bacterial H_2S and Fe^{2+} fosters the pseudomorphous replacement of conchiolin by the colloidal iron monosulfide that is subsequently transformed into pyrite. Hydrogen sulfide and/or monosulfide migrate into diagenetic cracks and cavities formed in the clayey–carbonate matrix that fills up the interior cavity of a shell. We believe that the data reported in this communication should be taken into consideration in the study of formation constraints of vein and disseminated sulfide mineralization in sedimentary rocks during the early diagenesis and related problems of ore formation.

DOI: 10.1134/S0024490206060058

STRUCTURE OF SHELLS AND THE ORGANIC MATRIX OF MOLLUSKS

The mineral skeleton of molluscan shells is formed as a result of physiological processes in the living organism. Shells have a complex structure and composition (Lehmann, 1990). The exterior layer (periostracum) composed of OM is underlain by ostracum that consists of calcite or aragonite crystals oriented normal to the shell surface. This layer is called "outer prismoid layer." The next (pearly) layer (hypostracum) consists of fine carbonate plates parallel to the shell surface. Owing to specific optical properties and similar orientation of crystals, this layer can show color interference and rainbow iridescence. The next "inner prismoid layer" incorporates the mollusk body. Its upper part (mantle) releases mineral substance for the frustule construction. A more complicated alternation of layers can appear in the course of the shell growth.

The matrix (conchiolin)—an OM in the shell frustule—can be released as a result of dissolution of the carbonate material of shell in organic or mineral acids. The conchiolin consists of a mixture of polysaccharides and fibrillar albumens known as "albumen–mucopolysaccharide complex" (*Sovremennaya paleontologiya…*, 1988). Since the fibrillar albumen is low-soluble in water, the conchiolin can withstand the destructive impact of saprophyte microorganisms. It can be retained in the fossil state even under conditions of the aerobic burial of shells during the complete recrystallization of aragonite or replacement of shells by pyrite. The well-preserved conchiolin microstructure was detected in cephalopod shells from Carboniferous asphalt limestones in Oklahoma, United States (Drozdova, 1977). The presence of organic matrix in Devonian and Ordovician mollusks was reported in (Degens, 1965).

The conchiolin makes up interlayers between carbonate crystal layers of the shell frustule, envelopes the crystals, and penetrates them as tiny veinlets. Thus, the conchiolin plays the role of cement and fosters the strength of the shell as a single solid body. The adjacent carbonate crystals accrete after the matrix destruction. The conchiolin is characterized by variation of chemical composition and microstructure in different layers of the frustule. The conchiolin albumen has the following average composition (%): C 51.1, N 16.6, H 6.6, and S 0.75 (Drozdova, 1977).

The biochemical and morphological preservation of fossil conchiolin is governed by not only its molecular structure, but also the degree of encapsulation in spaces between carbonate crystals of the frustule. The study of Devonian and other shells revealed that they often contain aminoacids and polypeptides that are considered products of the decomposition of matrix albumens (Drozdova, 1977). The possibility of good preservation of fossil OM in mollusk shells has long ago attracted the attention of researchers engaged in problems of paleobiochemistry and evolutionary biochemistry.

The author of the present communication believes that the shell matrix is the nutrient that promoted the development of sulfate-reducing bacteria (SRB) in the example discussed below. It should be noted, however, that the conchiolin serves as a nutrient only at syngenetic and diagenetic stages characterized by retention

of the activity of saprophyte microorganisms that trigger the biochemical decomposition.

FORMS OF PYRITE OCCURRENCE IN MOLLUSK SHELL

The author of the present paper investigated the distribution of pyrite in fossil mollusk shells in the Jurassic ammonite, presumably, represented by the Lower Jurassic (Pliensbachian) *Orthosphinctes* sp. Macroscopic and microscopic observations were carried out on a polished section of mollusk chamber having the shape of a slightly deformed circle. Its interior is filled with the clayey–carbonate matrix crosscut by a network of pyrite veinlets from 0.*n* to 1 mm thick. The general pattern of shale pyritization is shown in Fig. 1 (pyrite is white in Figs. 1–8). Based on macroscopic observations refined by microscopic investigations, we can distinguish four morphological types of pyrite.

Pyrite 1 is developed in the shell frustule as serrate parallel bands (0.*n* mm wide) that mimic the outer relief of shell (Figs. 1b, 2a) and fine films between calcite crystals in the frustule (Fig. 3a). The shape of both bands and films matches the position of organic matrix layers in the frustule. The complete replacement of organic matrix produces the compact pyrite matrix (Fig. 3b, 4a). This morphological type of pyrite is probably related to the pseudomorphous replacement of conchiolin.

Pyrite 2 is developed in the inner cavity retained in the shell chamber (Fig. 1c). The cavity walls are covered with a dense pyrite layer 0.5–1 mm thick. Toward the interior part of the cavity, the layer is covered with druse-shaped pyrite crystallites 0.*n* mm in size (Fig. 1d). The chamber is mainly filled with calcite (Fig. 1e).

Pyrite 3 is observed as a systematic network of veinlets (Fig. 1). Some veinlets (0.*n*–0.5 mm thick) are filled with a dense pyrite mass. They show a nearly radial orientation (Fig. 1f). The space between the veinlets is filled with another network of nearly similar thickness. However, they have less distinct boundaries with the enclosing rock (Fig. 1g). As is evident from Fig. 5a, such veinlets are commonly surrounded by pyrite dissemination field without distinct boundaries and shapes. The density of pyrite dissemination in such a field is variable and decreases away from the veinlets. The dissemination field is several times larger than the thickness of veinlets.

Veinlet networks of both types have intricate interrelations. However, the second network apparently crosscuts the first system along the nearly normal direction.

Pyrite 4 makes up a network of disordered microscopic veinlets up to 0.0*n* mm thick (Fig. 1i).

Concentration of veinlets of various types described above produces large zones of dense pyritization in the study area (Fig. 1h).

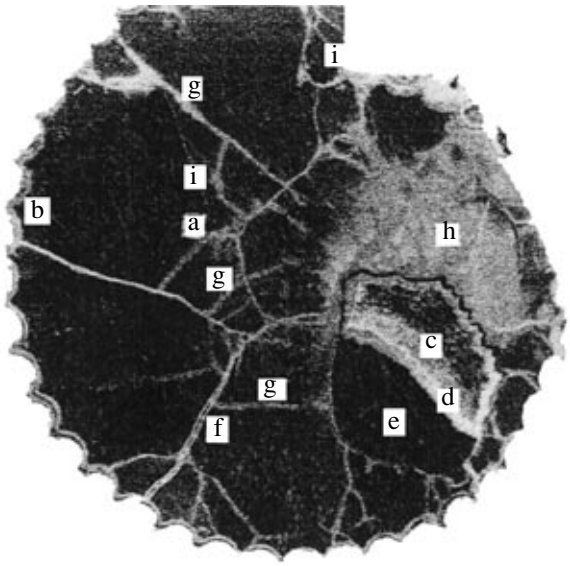

Fig. 1. Structure of the ammonite shell. Magn. 2. See the text for explanation. Figures 1–8 show reflected light images of the polished section surface. Pyrite is white.

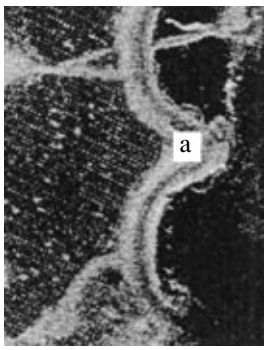

Fig. 2. Closeup of Fig. 1. (a) Pyritized periostracum. Magn. 8.

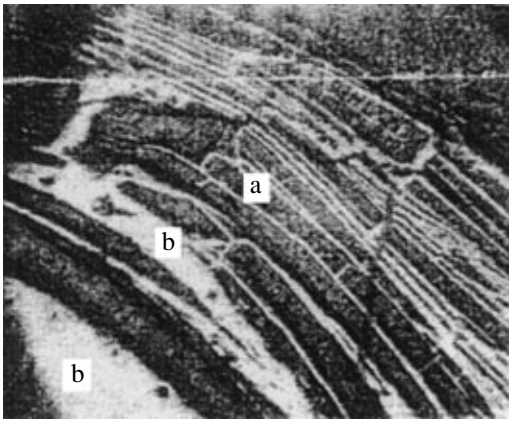

Fig. 3. Pyritization of organic matrix. (a) Pyrite between calcite crystals; (b) pyrite accumulation in the frustule cavity. Magn. 20.

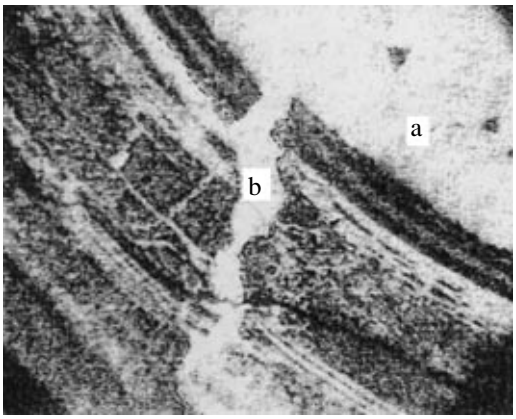

Fig. 4. (a, b) Migration pyrite. Magn. 40.

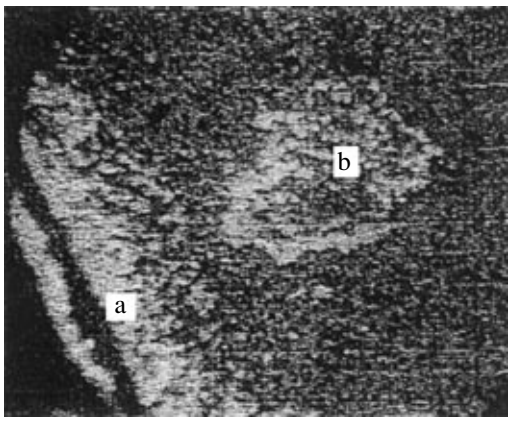

Fig. 5. (a) Pyrite dissemination near a veinlet; (b) pyrite aggregate with a common shell. Magn. 20.

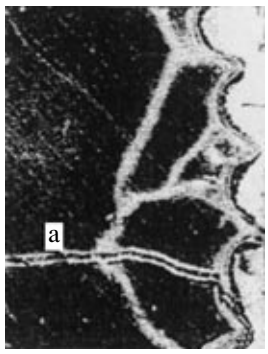

Fig. 6. Cavity within a pyrite veinlet (a). Magn. 8.

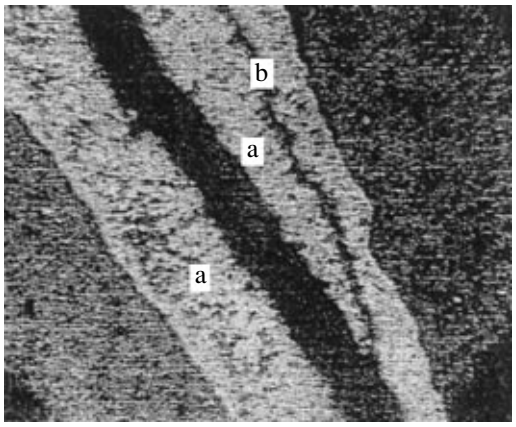

Fig. 7. Cavity within a pyrite veinlet (a, b). Magn. 30.

The proposed typification of veinlets considerably simplifies their diversity in nature. Figure 1 shows several deviations from the typification. For example, the calcite mass in the chamber interior (Fig. 1e) contains an autonomous veinlet network that is unconformable with the adjacent clayey–carbonate matrix.

Cavities in some veinlets (mainly, type 1) oriented parallel to the veinlet do not contain pyrite or any other mineral substance (Figs. 6a, 7). They divide the veinlets into parallel sectors. Such sectors contain narrower cavities in some places (Fig. 7a, b).

The clayey–carbonate matrix in the shell cavity can include pyrite grains and aggregates surrounded by a pyritic shell (Fig. 5b). Such pyrite segregations resemble pyritic pseudomorphs of microorganisms described in (Kizil'shtein, 1999; Kizil'shtein and Minaeva, 1975).

SOME EXPERIMENTAL DATA AND DISCUSSION OF RESULTS

Data presented above suggest some specific features of sulfide formation in fossil shells. We can also suppose the following scenario of vein and disseminated sulfide mineralization in sedimentary rocks in the supergene zone.

The mode of pyrite segregation in shell frustule is governed by the dependence of sulfide formation upon morphology and composition of the organic matrix. Despite the biochemical stability of conchiolin and its encapsulation in the space between calcite crystals, the mucopolysaccharide complex of this component is subject to fragmentary decomposition under the influence of saprophyte microorganisms. According to (Lehninger, 1982), the decomposition (catabolism) of albumens and carbohydrates in the conchiolin is accompanied by the formation of biochemical compounds (e.g., lactate, acetate, and ethanol) that can serve as sources of energy and carbon for the SRB. Hydrogen sulfide generated in the course of sulfate reduction interacts with Fe^{2+} ions to form the colloidal iron monosulfide or hydrotroilite ($FeS \cdot nH_2O$). If sulfur atoms are added, iron monosulfides are transformed into disulfides, such as pyrite or marcasite (FeS_2), which represent end products of the reduction of bacterial hydrogen sulfide. As

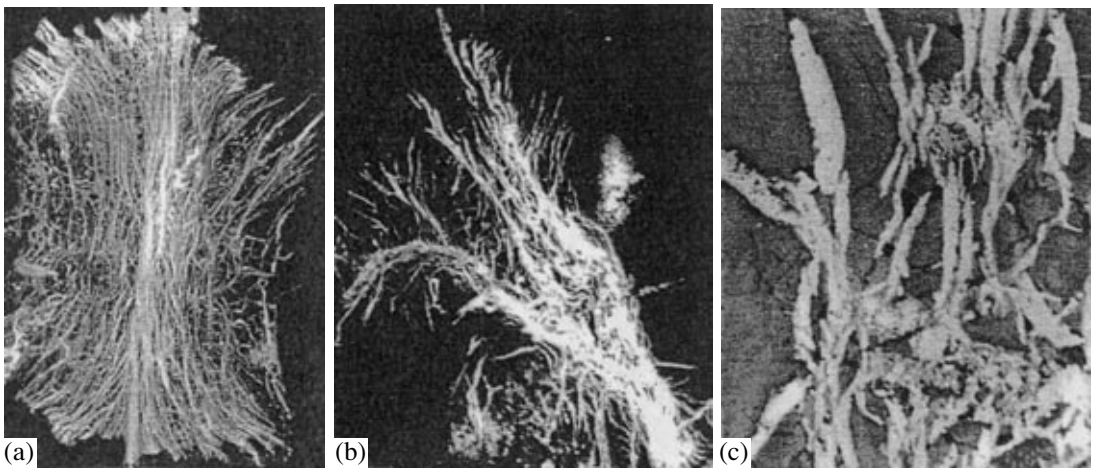

Fig. 8. Pyrite in diagenetic shrinkage cracks in coal. Magnification: (a) 2, (b) 3, (c) 100.

was shown in (*Global'nyi biogeokhimicheskii*..., 1983; Volkov, 1984), Fe is delivered to the sulfate reduction zone by mud waters and the solid phase of sediments. The $Fe^{3+} \longrightarrow Fe^{2+}$ reduction usually predates the bacterial reduction of sulfates. Therefore, the Fe^{2+} deficit is unlikely.

Thus, pyrite contained in the ammonite frustule is a result of sulfide mineralization of the organic matrix. In Figs. 1–3, one can see that pyrite segregations inherit the intricate character of the shape and distribution of matrix in the mineral substance of the frustule.

The author of the present communication investigated the formation of sulfides in Cardium shells recovered from present-day bottom sediments of the H_2S-contaminated zone of the Sea of Azov (Kizil'shtein, 1975). The formation of sulfides begins with the appearance of iron monosulfide patches and pyrite segregations on the outer and inner surfaces of shells (the monosulfide patches readily dissolve in the hydrochloric acid). The sulfides are concentrated in the conchiolin of the periostracum, prismoid layer, and pearly layer of the frustule. The conchiolin extracted by the dissolution of carbonate material of the shell contain pyrite (15–50 vol %). These observations illustrate initial stages of the formation of pyritic pseudomorphs of OM (conchiolin) of the frustule. The substitution of pyrite for the organic matrix of fossil ammonite described in the present work represents a completed psudomorphosis.

The available data indicate that pyrite can replace not only the frustule OM, but also the mineral skeleton of shells and the whole mollusk body. Examples of the complete replacement of fossil shales by pyrite are widespread as museum exhibits and souvenir imitations. Crystallochemical processes of the replacement of carbonates by sulfides are described in several works (Grigor'ev and Zhabin, 1975).

Let us dwell on the following essential circumstance. Iron sulfide formed in the organic matrix can migrate (Fig. 4b) and fill up various cavities (including cracks) in shells. Such replacements can probably take place only when the sulfide is developed in the transportable colloidal state (e.g., hydrotroilite) or when the bacterial hydrogen sulfide reacts with Fe^{2+} to form monosulfides along the conduits.

Problem of the migration of iron monosulfides was investigated in marine bottom sediments (Strakhov, 1962; Volkov, 1984). These researchers did not rule out the possibility of such process.

In cooperation with microbiologists, the author of the present communication investigated processes of sulfide formation in bottom sediments.

After filling glass cylinders with the light-colored bentonitic clay, we successively added special materials to create a three-layer medium (layers 1–3, from bottom to top). Layer 2 was supplemented with the SRB culture and a special medium accepted in the microbiological practice known as the Tauson's medium that contains the calcium lactate (OM), ammonium and calcium sulfates, and Fe^{2+} in the form of Mohr's salt. Layers 1 and 3 were composed of pure clays. Within approximately seven days, we registered the reduction of sulfates and the formation of iron monosulfides as dark patches in layer 2. The patches were well discernible in the light-colored bentonite mass. The dark patches gradually occupied the entire layer 2. However, no signs of the darkening of clays were recorded in the adjacent layers 1 and 3 that were devoid of the SRB and nutrient components. Within approximately 30 days, purple sulfuric bacteria began to appear as pink bands and patches in these layers. It is well known that the sulfuric bacteria get energy from H_2S reduction. Thus, their appearance testifies to the diffusion of hydrogen sulfide from the sulfate reduction zone (layer 2) into the adjacent clay layers 1 and 3.

These experimental results indicate that the bacterial hydrogen sulfide rather than the monosulfide migrates beyond layer 2. Evidently, the bacterial sulfide can only migrate if the Fe^{2+} reserve in layer 2 is exhausted and H_2S is not consumed for the sulfide formation.

In another experimental series, we introduced Fe^{3+} (Mohr's salt) into layers 1 and 3. Like in the first experimental series, we recorded the initiation of darkening (monosulfide formation) in layer 2. However, in this case, irregular dark patches began to form in layers 1 and 3 (at the contact with layer 2). Consequently, the dark patches completely occupied layers 1 and 3. The addition of an antiseptic (phenol) into layers 1 and 3 to exclude the probable development of sulfate reduction (due to an accidental SRB contamination of these layers) did not change the experimental results. Thus, these experiments also show that the presence of Fe^{2+} is crucial for the formation of monosulfides. Ultimately, all the clay layers revealed an intricate lenticular-banded structure owing to the irregular distribution of monosulfides (dark zones). The available data on marine bottom sediments indicate that such a lenticular-banded structure is related to the irregular spatial distribution of Fe^{2+} ion.

Migration of H_2S is crucial for the spatial distribution of monosulfides. This fact has been established for marine bottom sediments in the reducing zone of the Black Sea (Strakhov, 1962; Volkov, 1984). In this case, hydrogen sulfide migrates from the Old Black Sea sediments (an actively sulfate-reducing medium depleted in Fe^{2+}) to upper horizons of the underlying Neoeuxinian sequence enriched in this ion. However, the Neoeuxinian sequence does not contain in situ H_2S because of insufficient sulfate reduction. The counter migration of H_2S and Fe^{2+} produced the iron monosulfide-rich "hydrotroilite layer" that is well known to explorers of sediments in the Black Sea. This layer is also marked by the presence of sulfide nodules that are quite rare for marine bottom sediments (Volkov, 1984).

The pyrite veinlets, pyrite segregations in cavities, and pyrite dissemination in the mineral matrix of the shell chamber (Figs. 1, 5) are presumably related to the migration of bacterial hydrogen sulfide. The subsequent dehydration of monosulfides and their contraction could produce cavities inside the veinlets (Figs. 6, 7).

The issue of the space filled with migration sulfides (pyrite) deserves special attention. There are grounds to suppose that this space represents cracks and caverns related to the dehydration and shrinkage of the clayey–carbonate matrix of the shell. Such *neotectonic* cracks and pores may be produced by the spontaneous contraction of mineral substance during syneresis that can proceed even in a water-saturated bottom sequence (Pettijohn, 1975). Thus, the formation of cavities and their filling with the colloidal iron monosulfide could take place even at the stage of syneresis or early diagenesis; i.e., this process could coincide in time with the active bacterial reduction of sulfates and generation of hydrogen sulfide. The assumption of fissuring as a result of shrinkage is consistent with the intricate network of disordered and curvilinear cracks. The structures were deformed inside the closed space of firm shell frustules that protected the mineral substance in the interior zone from late mechanic (tectonic) impacts. Thus, we see a pure shrinkage deformation in this case.

In our previous work (Kizil'shtein and Shpitsgluz, 1998) (Fig. 8), pyrite-filled shrinkage cracks in coals were referred to as endogenous structures according to the classification in (Ammosov and Eremin, 1960). It is well known that the peat of early diagenetic stages represents an organic colloid. Therefore, this material is similar to shales in terms of the mechanism of contraction, compaction, and fracturing. Figures 8b and 8c demonstrate the successive expansion of the network of sulfide veinlets in an area located in the upper right part of Fig. 8a. Although the veinlets show a general common trend (Fig. 8a), their closeup views are characterized by whimsical distribution, blind ends, and variable width. Such a pattern, atypical of exogenous cracks related to tectonic loading, testifies to the early neotectonic formation of the network of monosulfide veinlets. However, the coals, including the sample described in the present work, show an intricate network of exogenous (tectonic) cracks that crosscut the earlier (sulfide-free) structures. Pyrite veinlets confined to active sulfate reduction zones were reported from "sulfide bioherms" in mudstones (Kizil'shtein and Nastavkin, 2003). We suggested that the veinlets are related to the filling of shrinkage (compaction) cracks in the clayey rock with a colloidal sulfide mass. As was shown above, this hypothesis should be supplemented with the hypothesis of hydrogen sulfide migration in cracks. It is quite possible that these hypotheses are not alternative versions. As for the issue of migration of substances from the veinlets, the concept of sulfide dissemination in the adjacent clayey–carbonate matrix (Fig. 5a) is in better agreement with the hypothesis of the migration of hydrogen sulfide, which has a higher capacity for diffusion into pores, relative to the colloidal monosulfide.

We believe that data presented in this work have implementation for the well-known sulfide mineralization in sedimentary rocks, including the formation of primarily sedimentary (stratiform) ore deposits. The geochemical aspect of the formation of sulfide veins and dissemination is not usually discussed for the stratiform deposits. However, the formation of such sulfide segregations requires, first, the obligatory presence of H_2S, which can only be generated in significant amounts as a result of the bacterial reduction of sulfides, and, second, the existence of a network of cavities and/or pores (caverns). Both circumstances are only compatible at the stage of syneresis or early diagenesis when the environment is optimal for the active microbiological sulfate reduction accompanied by the initial dehydration of sediments.

Of course, the emission of bacterial hydrogen sulfide fosters the formation of not only iron sulfides described above. Sulfides of other metals can also form (and are forming at present) according to this mechanism.

The preferential bonding of S_2^{2-} ion with Fe^{2+} is explained by a stronger (relative to other sulfides) force of the covalent interaction between these two chemical elements in the crystal lattice (Volkov, 1984). Other sulfide minerals can probably form if the amount of Fe^{2+} in the medium is insufficient (a rather rare situation) or the concentration of chalcophile and siderophile elements is high, as in the case of the hydrothermal sulfide formation in oceanic rift zones.

CONCLUSIONS

(1) The organic matrix (conchiolin) of fossil mollusk shells is a nutrient substrate for sulfate-reducing bacteria. Reaction between H_2S and Fe^{2+} ions, which are generated by the bacteria due to the reduction of sulfates, produces the iron monosulfide that replaces the conchiolin. The latter is subsequently transformed into a pyritic pseudomorph.

(2) A part of the biogenic H_2S or colloidal monosulfide migrates into the ambient sulfate reduction zone inside the shell chamber to form pyrite veinlets and sulfide dissemination.

(3) Sulfide veinlets and dissemination are formed as result of the monosulfide accumulation in diagenetic shrinkage cracks and pores.

(4) Results of examination of the pyritization of fossil shells can be implemented for solving issues of the supergene sulfide and ore formation.

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