Geochemical features of pyrite pseudomorphs according to plant residues from the Upper Jurassic deposits of the Middle Volga river area (Russian Federation)

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Abstract. The study of the mineralogy and geochemistry of biomorphic ore formations has great importance for studying the processes of transformation of plant tissues during the formation of the sedimentary rocks, including ore mineralization. Forms of biogenic mineralization in sedimentary rocks are represented by various processes. The pyritization of organic residues is one of the most common forms. The purpose of this work was to conduct a detailed mineralogical and geochemical study of biomorphic ore formations collected from Mesozoic (Upper Jurassic) deposits of the right bank of the Volga river. The initial conditions for the fossilization of the objects of study were the same. Therefore, the structural and morphological features of the pyrite aggregate developing on them can be caused not only by geochemical conditions but also by the structure of the residues themselves. Samples were examined by optical microscopy, X-ray phase analysis, gamma-ray spectrometric analysis, X-ray computed tomography and X-ray fluorescence analysis. As a result of research, the stages of mineralization of wood were established, which reflect the features of sedimentation.

1. Introduction

The study of the mineralogy and geochemistry of biomorphic ore formations has great importance for studying the processes of transformation of plant tissues during the sedimentation and post-diagenetic processes, and for elucidating of the features of sedimentary ore formation. Forms of biogenic mineralization in sedimentary rocks are represented by various processes.

The pyritization of organic residues is one of the most common forms. Despite the single biochemical mechanism of the process, the mineralization of various forms of organic residues proceeds with the formation of morphological types of pyrite aggregates that are not alike [3, 4, 5]. In addition to external factors, the structural features of the fossilized fragments of animals and plants themselves have a determining effect on the course of pyritization [2].
2. Methodology

The purpose of the work was to conduct a detailed mineralogical and geochemical study of biomorphic ore formations collected from Mesozoic (Upper Jurassic) deposits of the right bank of the river. The area of the Middle Volga river near the village of Bolshoi Tarkhany in the southeastern part of the Republic of Tatarstan is contained pyritized and coalified fragments of tree stems of higher plants (Fig. 1). The initial conditions for the fossilization of the objects of study were the same. Therefore, the structural and morphological features of the pyrite aggregate developing on them can be caused not only by geochemical conditions but also by the structure of the residues themselves. Samples were examined by optical microscopy, X-ray phase analysis, gamma-ray spectrometric analysis, X-ray computed tomography and X-ray fluorescence analysis.

3. Results and Discussions

The Upper Jurassic deposits of the Middle Volga river area are represented by a shallow-water terrigenous complex, where is dominated the horizontal, thin-layered, greenish-gray clays with small interlayers of siltstones and sandstones marking the maximum regression of the Central Russian Paleomor. The absence of traces of agitation and thin horizontal layering indicates the existence of calm hydrodynamic conditions in the considered part of the reservoir that do not contribute to the active gas exchange of the water column. As a result of oxygen deficiency caused by the decomposition of organics, and inactive environmental conditions for a long period there was formed an anoxic
geochemical situation in the bottom part of the Central Russian Paleomor. The modern analogue of it is the bottom of the Black Sea.

This situation was very favorable for the development of chemotrophic microbial communities. The presence of sulfate ions in seawater determined the dominance of bacterial communities with the trophic cycle of sulfur compounds. They were based on sulfate reducers capable of using a limited number of simple compounds (lactate, acetate, H₂). In the process of their life, sulfate-reducing bacteria isolated CO₂ and H₂S, which later took part in authigenic mineral formation. Schematically, this process can be represented as follows:

\[
2\text{CH}_2\text{O} + \text{SO}_4^{2-} + 2\text{H}^+ \rightarrow 2\text{CO}_2 + \text{H}_2\text{S} + 2\text{H}_2\text{O},
\]

where CH₂O is the symbol of organic carbon, which is more accurately reflected by the Redfield equation (CH₂O)₁₀₆ (NH₃)₁₆ (H₃PO₄)₁ [3].

The established stable anoxic environment facilitated the restoration of ferric hydroxyls, which are always present in an adsorbed form on the surface of clay particles. When interacting with hydrogen sulfide, reduced iron was bound into colloidal aggregates of hydrotroilite (Fe (HS)₂ * nH₂O), which eventually turned into pyrite, less often marcasite.

\[
2\text{Fe} (\text{OOH}) + 5\text{H}_2\text{S} \rightarrow 2\text{Fe} (\text{HS})_2 + 4\text{H}_2\text{O} + \text{S} \\
\text{Fe} (\text{HS})_2 * \text{nH}_2\text{O} \rightarrow \text{FeS}_2 + \text{nH}_2\text{O} + 2\text{H}^+.
\]

At the same time, there was a competing process of biochemical synthesis of sulfide iron on the surface of the mucous membranes of bacteria belonging to the cyanobiont community. Judging by the numerous finds of phramboidal pyrite aggregates, a very high microbiological activity existed in the bottom silt sediment, which led mainly to the biogenic deposition of pyrite. Traces of the hydrotroilite in the form of black films of weakly crystallized pyrite are much less common [3].

The period of formation of the Upper Jurassic clay deposits was characterized by an intense diagenetic redistribution of iron under conditions of hydrogen sulfide infection of the bottom mud sediment of the Central Russian Paleomor. Fragments of the woody stems of higher plants, being islands of a solid substrate under conditions of an irrigated mud bottom, served on the one hand as original crystallization centers for authigenic minerals, and on the other hand, as the basis for numerous fouling organisms attached to various objects. Epibions under anoxic conditions, judging by analogy with modern species [7], represented certain groups of bacterial colonies with a sulfur trophic cycle. Accumulating elemental sulfur in the course of life, they created the prerequisites for the formation of pyrite crusts on the surface of organic residues (Fig. 2).

The mineral composition of biomorphic ore formations is mainly represented by pyrite. Smaller quantities contain quartz, barite, magnetite, illite, natroalunite. There are also areas composed of carbonified organics. The studied samples are characterized by a zonal structure, where the inner part is composed of fine-grained pyrite and carbonaceous material, and the peripheral part is composed of radial aggregates of finely and/or coarse-grained pyrite (Fig. 2). In some samples, zoning was absent, but debris particles of quartz were present in the pyrite mass, which is most likely due to sedimentation under more shallow conditions.

Pyrite in the central part of the samples is characterized by a low degree of crystallinity, which is due to its formation during recrystallization of the initial hydrotroilite particles. According to the data of [6], the formation of sulfides in the process of bacterial sulfate reduction occurs with the formation of
initially non-stoichiometric nanosized particles and their subsequent recrystallization into classical mineral forms.

Pyrite in the form of growths on the surface of the samples is a pyritized structure of microbial colonies (Fig. 2), represented by cyanobionts, originally of carbonate composition [3]. Natroalunite could be formed both at the bottom of the sedimentation basin as a result of exposure to silicates (clay and mica minerals of the host rocks), and during exogenous oxidation of pyrite. Magnetite was re-formed along pyrite in the presence of free oxygen, which indicates a periodic short-term change in the depositional reduction conditions to oxidative ones [5]. Illite, being a clay mineral that is part of the host rocks, could be in plant debris, falling into them through cracks during burial. The presence of a significant amount of barite may be due to the fact that cracks in the wood were filled with debris quartz particles of aleuritic dimension and clay material, which ensured higher mobility of the solutions in the sample. This process weakened biogenic pyritization, which accelerated the formation of pyrite by the chemogenic pathway, in which sulfur sulfate ions are not reduced. That ensures their safety and the possibility of further formation of sulfates from them (such as barite, gypsum) simultaneously with pyrite [1].
According to the data of elemental mapping of the surface by the method of X-ray fluorescence analysis, an increased content of such elements as Ge and As is noted in the carbonaceous part of the samples (Fig. 3). This distribution of elements is due to the fact that plant material, being in the conditions of sedimentation, is a geochemical and sorbing barrier that accumulates various elements from the host sediments.

![Elemental mapping results](image)

**Figure 3.** Results of elemental mapping by X-ray fluorescence analysis.

| Элемент | % весовые. | % атомарные. |
|---------|-----------|--------------|
| Al      | 0,25      | 0,39         |
| Si      | 0,18      | 0,27         |
| S       | 39,91     | 53,48        |
| Ca      | 0,11      | 0,12         |
| Fe      | 58,99     | 45,39        |
| Mo      | 0,10      | 0,05         |
| As      | 0,20      | 0,12         |
| Ge      | 0,10      | 0,06         |
| Zn      | 0,09      | 0,06         |
| Cu      | 0,02      | 0,01         |
| V       | 0,02      | 0,02         |
| Cr      | 0,01      | 0,01         |
| Ti      | 0,02      | 0,02         |

The results of gamma-ray spectrometric analysis showed a higher content of Ra²²⁶ isotopes in biomorphic ore formations and a lower content of Th²³² isotopes in comparison with the host rocks (Fig. 4). The increased content of Ra²²⁶ isotopes (a product of the decay of uranium) is explained by the accumulation of uranium in plant residues [6], which are local geochemical barriers.
Figure 4. Gamma spectrometric analysis data. Samples 1-4 - biomorphic ore formations, samples 5-8 - host rocks

4. Conclusions

As a result of research, the stages of mineralization of wood were established, which reflect the features of sedimentation. The process of fossilization of plant tissue of wood proceeded, apparently, in 7 stages:

1) the formation of wood stromatolite buildings, as a result of the life of cyanobacteria;
2) immersion of wood at the bottom of the sedimentation basin;
3) coalification and pyritization of the walls of plant tissues in a reducing environment;
4) filling the cell cavities with pyrite under the action of sulfate-reducing bacteria;
5) bio-chemogenic transformation of calcareous growths into pyrite rims;
6) chemogenic formation of pyrite;
7) hypergene decomposition of pyritized and carbonified formations, in surface conditions, with the formation of sulfuric acid and natroalunite.

Thus, the heterogeneity of the mineral and chemical composition of fossilized plant residues is due to the staged process of fossilization in the process of accumulation and lithification of sediments.

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