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Pyritization of trees from the natural phenomenon Underwater Petrified Forest, Sozopol Bay, Black Sea, Bulgaria

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Пиритизация на дървета от природния феномен Подводна вкаменена гора, Созополски залив, Черно море, България

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Abstract. In the Black Sea area between the town of Sozopol and the island of St. Ivan, Bulgaria, dozens of petrified trees are exposed at a depth of 18–20 meters. This forest, probably existing in Miocene in a swampy pond, provides a unique setting to study later fossilization processes. Pyrite, a key mineral involved in the fossilization of organisms, constitutes over 80% of the studied samples and exhibits framboidal and microcrystalline textures, crucial for preserving plant cellular anatomy. Pyritization, occurring in hypoxic or anoxic environments, preserves fine details and prevents structural collapse during lithification. The transformation of marcasite to pyrite under specific conditions highlights dynamic mineralogical processes. X-ray powder diffraction analyses reveal secondary minerals including goethite, jarosite, and szomolnokite, indicating significant post-depositional environmental changes. Understanding these processes is essential for interpreting the fossilising factors that contributed to the formation of the Underwater Petrified Forest, emphasizing the importance of pyritization in paleontological studies.

Keywords: pyrite, fossilization, Underwater Petrified Forest, Black Sea.

Introduction

The natural phenomenon known as the Underwater Petrified Forest is unique to the Black Sea but globally significant as well. Initial studies focused on the petrology and formation conditions of the fossilized forest and associated coal deposits (Shishkov et al., 1988). Subsequent research by Yossifova et al. (2011) provided comprehensive insights into the petrology, mineralogy, and geochemistry of the submarine coals and the Petrified Forest. Pyrite is a key mineral involved in the fossilization of organisms, with pyritization being more common in plants than in animal soft tissues, though the process remains poorly understood (Grimes et al., 2002). Yossifova et al. (2011) characterized pyrite primarily as a component of coal mineral matter, linking it to coalification processes. This investigation aims to present new data on the mineralogy and textures of pyritized samples, and to elucidate the mechanisms underlying plant fossilization through pyritization.

Geological setting

The Upper Cretaceous volcanic types, which include some rare volcano-sedimentary and sedimentary layers from the Burgas Formation (Petrova et al., 1992), predominantly represent the geological

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formations observed in the Sozopol area. These volcanic rocks are products of multiple paleovolcanic structures (Stanisheva-Vassileva, 1980). In the coastal area between Burgas Bay and Primorsko, the Rosen Paleovolcano is exposed. A significant part of it is underwater. This structure, synonymous with the Sozopol volcano (Petrova, Simeonov, 1989), consists of external accumulative zone, the Sozopol caldera, and the ring-shaped intrusive Rosen pluton. The formation of the Underwater Petrified Forest between Sozopol and St. Ivan Island is genetically determined by the Sozopol caldera. It consists mainly of lava flows and tuffs, exposed on St. Ivan and St. Peter islands and Sozopol's northern coast. The middle–upper Miocene Evksinograd Formation, characterized by clays, sands, and sandstones (Popov, Kojumdjieva, 1987), lies uncomformably on various lava flows and sills. The Sozopol Caldera served as a favorable morphostructure for coal deposition, initially forming a freshwater lake that transformed into a waterlogged swamp with subtropical vegetation. The rapid subsidence and tectonic activity resulted in the formation of a saline lagoon, which replaced the freshwater basin (Shishkov et al., 1983). In the eastern part of the Underwater Petrified Forest area, between Sozopol and St. Ivan Island, a subhorizontal succession of clays and sandstones is observed (Velev et al., 2023). This section, about 1.80 m thick, covers Upper Cretaceous volcano-sedimentary and volcanic lithotypes at a depth of about 20 m. It includes gray-black claystones with charred plant detritus, yellow to orange claystones, and weakly cemented calcareous sandstones forming "reef-shaped" structures.

The Underwater Petrified Forest features ancient tree stumps, branches, and other organic remains, all preserved in a petrified state, and situated 18–20 meters below sea level. The silicified tree trunks were found to have well-preserved cell structures and have been identified as bald cypress (*Taxodium*). Three processes are found to occur in the Petrified Forest area. First, coal deposition takes place in a swamp setting. Later, a lagoon forms with strong water salinization and rapid sedimentation. Therefore, enhanced bacterial reduction of sulfates leads to the formation of a pyrite crust on the carbonized layer under reducing conditions. Silicification processes started after marine transgression, as silicon imitated the matrix of the cellular structure of wooden trunks and remains, petrifying them (Shishkov et al., 1988).

Materials and methods

The fieldwork is quite a complex process, as the petrified trees are located at a depth of 18–20 meters underwater. Sampling is carried out through scuba diving using the CMAS Scientific Diver Operation and Safety Standards. The samples are usually covered with marine encrusting organisms such as black mussels, sponges, etc., and need to be cleaned and dried. Selected specimens are macroscopically distinguished by the presence of a large amount of pyrite, which typically associates with carbonized material. Material has been collected both from the fossilized trunks themselves and from plant remains located on the seabed around them. Polished sections were prepared to make an optical characterization of the pyritized samples. We aim to clarify their texture, morphology, the presence of other mineral phases, and interesting relationships. Phase composition was determined by X-ray powder diffraction (XRD). The XRD patterns were recorded on a Bruker D8 Advance diffractometer. Filtered Co-Kα radiation was used in the range of 2Θ 4–80°, step 0.02° 2Θ, and exposure time per step 1.5 s.

Results and discussion

Ore microscopy of the polished sections shows that the main mineral, which replaces plant cells of the wood, is **pyrite**. According to the XRD analyses, it reaches over 80% in the samples. Typical texture is *framboidal* (Fig. 1a). The term "framboid," derived from the French word "framboise" (meaning raspberry), describes a texture with a characteristic raspberry-like morphology. Essentially, a framboid is a spherical or sub-spherical structure composed of numerous microcrystals, which are often equant and equidimensional. The crystals are mainly subhedral to euhedral with cubic, octahedral and pyritohedral dodecahedron morphology up to 100 μm (most commonly around 50 μm). This type of pyrite is closely associated with the plant cells – xylem (vessels to water transportation) and parenchyma (nutrient storage, defense against pathogenic bacteria, mechanical support, and regulation of xylem conductivity) (Grimes et al., 2002). Another observed texture is *microcrystalline*. It consists of very fine-grained aggregates and consequently looks almost compact. Microcrystalline pyrite is typically found near structures like the cell wall. It likely plays a crucial role in maintaining the structural integrity of organic matter. This preservation allows pyritized fossils to retain a high degree of three-dimensional fidelity when lithified (Grimes et al., 2002). In most of the samples, secondary iron oxide-hydroxides and sulfates are established. Goethite replaces the core, rims and infills fractures in pyrite. XRD analyses complement the supergene alteration composition and proves the presence of jarosite and szomolnokite ($FeSO_4 \cdot H_2O$) which are macroscopically observed as orange to pinkish earthy aggregates and crusts.

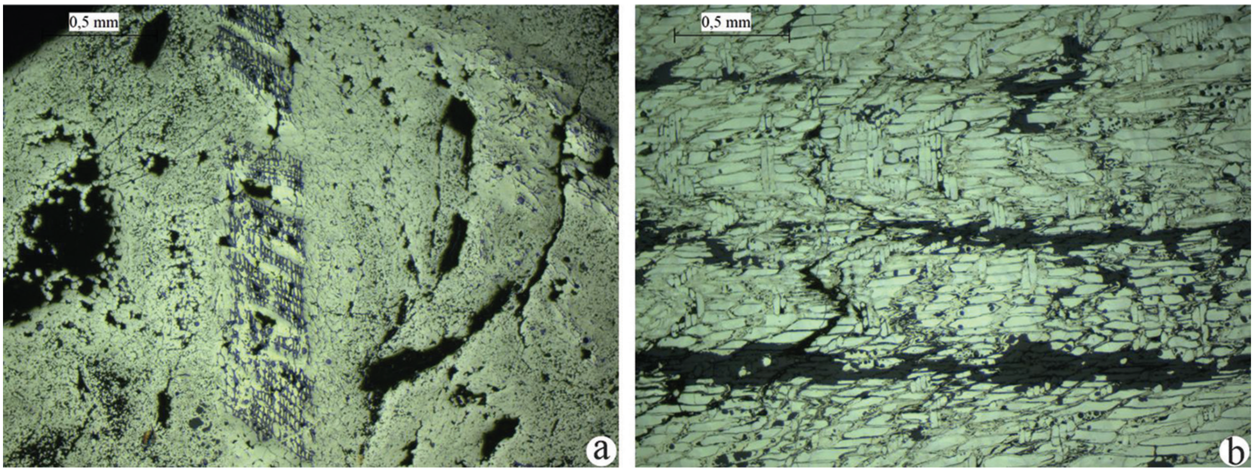

Fig. 1. Photomicrographs showing pyritization of trees from the natural phenomenon Underwater Petrified Forest, Sozopol Bay: *a*) pyrite with framboidal and microcrystalline texture replacing plant parts probably from the pyritized layer; *b*) marcasite replaces plant cells and pyrite replaces the cell walls

In some samples, the pseudomorphosis of trees parts is carried out by **marcasite**. Under microscope, this mineral shows typical strong anisotropy and it is also proven by XRD. It replaces plant cells and occurs as compact crystals and aggregates. Marcasite is enclosed by pyrite which replaces the cell walls (Fig. 1b). Marcasite aggregates, which are unstable under changing conditions, are often replaced by pyrite. This process, involves the growth of small pyrite crystals within the marcasite aggregate. The transformation from marcasite to pyrite is influenced by factors such as temperature, particle size, and the presence of water vapor. The presence of water vapor alters the nucleation mechanism and kinetics, leading to different transformation behaviors (Yao et al, 2020). Therefore, here pyrite is later and probably with secondary origin and is formed by inversion from marcasite. The marcasite-pyrite layers that follow the plant fibers are in association of quartz.

The optical characteristic of the samples shows another important aspect. Pyritization can be distinguished on the trees themselves in some of the samples, while others from pieces of plants at the bottom appear to be part of the pyritized layer above the coal, as reported by Shishkov et al. (1988). In the polished sections, various preserved plant parts (branches, bark, parts of trunks, others) (Fig. 1a) are observed as a mosaic structure. This pyritized layer likely formed after the coal deposition, with pyrite replacing the plant parts mixture from the uppermost level due to bacterial reduction of sulfates. This process resulted from environmental changes, transitioning from a swamp setting to a lagoon with strong water salinization.

Pyritization of plants can be extremely rapid process (within 80 days) and entails the precipitation of iron (II) disulfide (FeS_2) in hypoxic or anoxic environments, which typically allows for high-fidelity preservation of cellular anatomy. The lack of oxygen helps preserve fine details, while the precipitation of pyrite prevents the collapse of small structures like cell walls during lithification. Preserving the integrity of cell walls is crucial for pyrite preservation, enabling detailed studies of plant morphology. Additionally, examining the mineral microfabrics within fossils reveals the specific types of preservation that were most significant during fossilization (Grimes et al., 2002). Pyritization is essential for better understanding the processes and interpreting the fossilizing factors of the environment that form the Underwater Petrified Forest.

Conclusions

The Underwater Petrified Forest in Sozopol Bay, a globally significant natural phenomenon, offers unique insights into fossilization processes. The initial studies and subsequent research have highlighted the importance of pyrite in the fossilization of plant material, particularly through process of pyritization. The geological setting, characterized by Upper Cretaceous volcanic rocks and the Sozopol caldera, provided optimal conditions for coal deposition and subsequent fossilization. The transformation from a freshwater lake to a saline lagoon facilitated enhanced bacterial reduction of sulfates, leading to the formation of a pyritized wood trunks and pyrite layer above the coal deposit.

The results of fieldwork, optical microscopy and X-ray powder diffraction analyses indicated that pyrite constitutes over 80% of the samples, exhibiting framboidal and microcrystalline textures. These textures are crucial for preserving the cellular anatomy of the plants. The rapid pyritization process, occurring in hypoxic or anoxic environments, serves to preserve fine details and prevent structural collapse during lithification. The transformation of marcasite to pyrite under specific conditions further highlights the dynamic mineralogical processes involved. The presence of secondary minerals including goethite, jarosite, and szomolnokite, indicating post-depositional changes.

It is essential to understand these processes to interpret accurately the environmental factors that shaped the formation of the Underwater Petrified Forest. This emphasizes the significance of pyritization in preserving ancient plant structures. Future research in collaboration with paleobotanists could provide information about the types of trees and vegetation. This would enhance our comprehension of the paleoenvironment during its formation and contribute to a more detailed reconstruction of the ecosystem.

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