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Cell-Hosted Pyrite Framboids in Fossil Woods

J. Garcia-Guinea, J. Martinez-Frías, M. Harffy

Museo Nacional de Ciencias Naturales. C/José Gutierrez Abascal 2,
E-28006-Madrid, Spain

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Few references can be found describing pyrite in fossil wood and, to our knowledge, none as framboidal pyrite. We describe a good example of framboidal pyrite in Permian fossil wood which is clearly hosted in the wood cells. In addition, a temporal and spatial relationship exists between silica fossil wood and andesite-dacite lava flows which constitutes a complex genetic environment. Recently we have published another interesting example concerning the formation of framboidal pyrite in a cellulose environment [1].

Fossil woods can be formed by two different processes: coalification (highly condensed organic compounds) and petrifaction [substitution of organic materials by minerals, such as quartz SiO_2, Calcite $CaCO_3$, apatite $Ca_5(PO_4)_3(OH,F)$ etc.]. The recent observation [1] concerning the formation of framboidal pyrites in cellulose environments, such as ancient books (400 a), has led us to search for framboidal pyrite in other old cellulose environments. One such environment is found in Permian petrified woods (280 Ma) collected from calc-alkaline (andesite-dacite) lava flows in Palmaces de Jadraque, Guadalajara, Spain. Framboidal pyrite and silica in these fossil woods are closely related and have been formed by the same mechanism: the presence of volcanic epithermal fluids.

Pyrite is an anoxic mineral ($Fe^{2+}S_2$) which oxidizes relatively quickly at room temperature. It occurs in a wide set of geological environments, i.e., sedimentary-metamorphic rocks with organic matter, such as coal, slate, and limestones. Cellulose is a common precursor of organic matter in coal, shale, chalk, and fossil woods. During the early diagenesis of organic matter linked with sediments changes occur in organic compounds, including the formation of pyrite.

Since the work of Ferrand [2] in which the nonnecessity of bacteriogenic activity as a prerequisite for the formation of framboids was experimentally demonstrated, the term *framboid* is considered an exclusively textural (nongenetic) term to describe spheroidal aggregates of microcrysts with a maximum diameter of up to 150 µm. The formation processes of framboidal pyrite, or pyrite with a raspberrylike morphology, have recently been described in detail by Wilkin et al. [3–6] including synthesis, natural anoxic water columns, and size distributions. Framboidal pyrite appears in hydrothermal veins, modern sediments, sedimentary rocks, and it can also form directly in volcanic ash tuffs [7]. Modern organic rich sediments with framboidal pyrite from the southern Black Sea contain lignocarbohydrate with proteinaceous components, oxidized coal dust, and seeds composed of polyphenolic macromolecules derived from lignin cellulose [8].

Few references can be found which mention pyrite in fossil wood, for example, pyrite in subfossil Totara wood [9], in silicified herbaceous plants and trees from Messinian marine sediments [10], and in buried gymnosperms [11].

Petrifaction by silica preserves both framboidal pyrite and the wood structure. The process involves penetration of the wood via splits, permeation of cell walls which is favored by a reticulated system of micropores, enlargement of the micropore system as cell wall components break down, and continuing deposition of silica at a rate which maintains the dimensional stability of the wood [12]. The anoxic microenvironment of natural silica gel allows sulfide crystallization. In addition, silicified rocks such as hydrothermal veins and fossil woods are a perfect armor for protecting pyrite crystals from weathering for millions of years.

Petrified wood in this study was collected from the Permian Palmaces Formation in northern Guadalajara, Spain (Fig. 1). The volcanoclastic ash tuff rock where the silicified wood was embedded is part of the Atienza volcanic andesite-dacite emissions which fill a tectonic basin delimited by some subvertical faults [13]. The largest piece of fossil wood found weighed 56 kg and measured 25 cm in diameter; its anatomical structure was observed in thin sections. Selected pieces of silicified wood containing iron spheres were studied under polarizing (Fig. 2A, B) and scanning electron microscopy (SEM; Fig. 2C, D). The mineralogical content of samples was determined by X-ray powder diffraction using a Phillips automatic powder diffractometer with CuKa radiation. The patterns were obtained by step scanning from 2° to 64° 2θ in steps of 0.020° with a count of 6 s per step. For SEM studies the specimens were coated with gold (20 nm) in a Bio-Rad SC515 sputter coating unit. General SEM observations and specific iron profiles were carried out in a Philips XL20 SEM at accelerating voltages of 20–30 kV. Energy-dispersive X-ray microanalyses (EDX) were obtained in a Phillips EDAX PV9900 with a light element detector type ECON.

Under polarizing microscope the silicified wood cores closely resemble *Psaronius* fern medulla, and the concentric rings resemble dicotyledones. Therefore these pieces of fossilized wood could be *Pteridospermopsida* which appears to be connected to both types of plant (mono- and dicotyledones). This profile concords with the *Dadoxylon cordaioxylon* of Rio

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Correspondence to: J. Garcia-Guinea

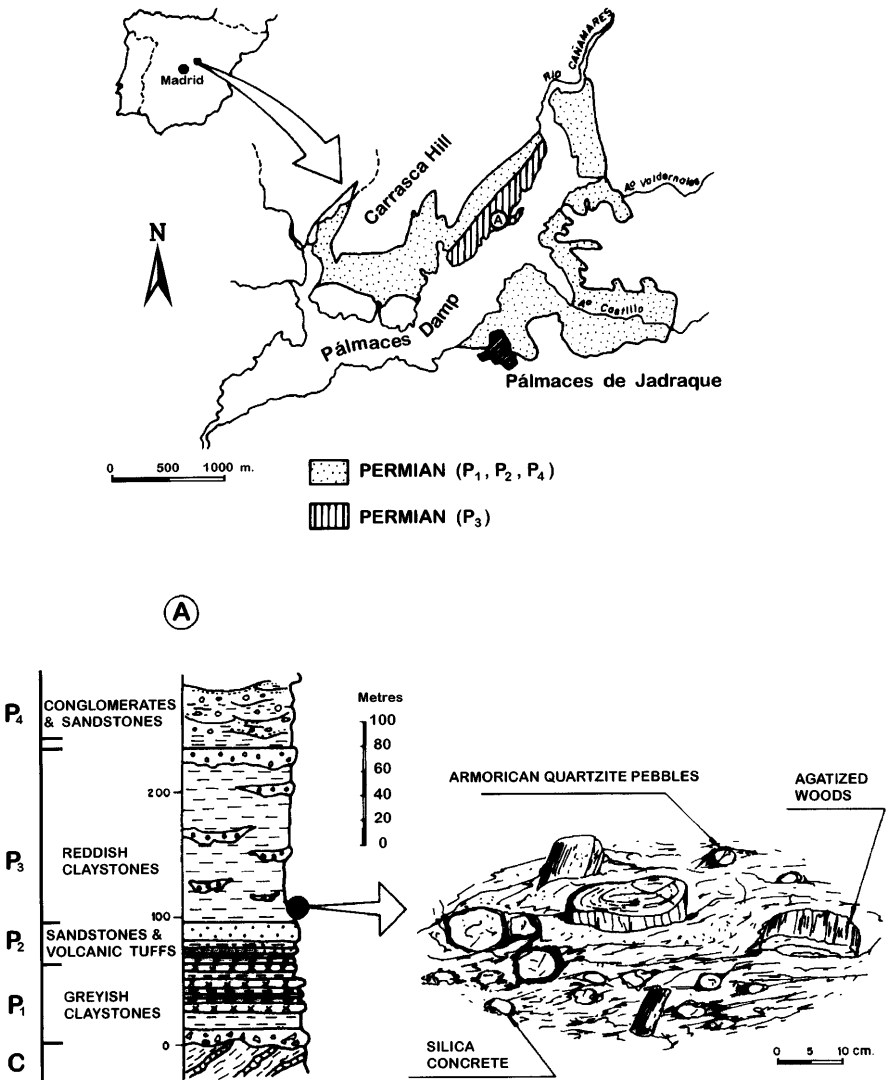

Fig. 1A–D. Geological setting of the Permian andesite-dacite lava flows which contain silicified woods with framboidal pyrite

Viar (Sevilla) Permian fossil woodland [14]. More specifically, it can be dated by the presence of *Estheria tenella* Jordan (freshwater Crustacea, subclass Brachiopoda) in the same Permian stratum as a point of reference [15].

Wood cells are sized from 2 to 20 µm; all of them are filled with quartz and chalcedony, and approximately 20% contain framboidal pyrite of about 2 µm in diameter. Figure 2C shows a framboid made up of approximately 40 microcubes of pyrite of about 0.125 µm. The original structure of the wood has been duplicated (Fig. 2); finely fibrous chalcedony replaces the cell walls. Silica microcrysts traverse the width of the walls, the angles suggesting guidance by the cellulose microfibrils. The walls are rendered more distinct by darkening which is due to the presence of iron oxide particles. Framboidal pyrite structures appear hosted in the petrified wood cells (Fig. 2A), separated from the walls and linearly distributed along the vessels (Fig. 2A).

The history of these silicified woods began 280 million years ago [16] in a *Dadoxylon cordaioxylon* rich forest. The andesite-dacite lava flow materials of the Atienza volcanism (the largest outcrop covers 1.5 km) buried and compressed the cylindric trunks producing ellipsoidal sections and internal shearing of cellular rows. These altered volcanic host rocks display porphyritic textures with a ground mass of smaller crystals and glass. The phenocrysts are plagioclase, biotite, amphibole, pyroxene, quartz, garnet, and minor amounts of apatite, zircon, rutile, and magnetite. The volcanics display evidence of later hydrothermal processes such as silicification, chloritization, and albitization with neoformed minerals: chlorite, albite, quartz, zeolites, sphene, pyrite, barite, and siderite. The hydrothermal quartz displays fluid inclusions of CO_2, CH_4, H_2O, and NaCl and homogenization temperatures (T_H) ranging from 50° to 350°C. Silica and framboidal pyrite are spatially related, and their formation can be assigned to the same genetic mechanism, for example, late-volcanic epithermal emissions [17]. Many factors must be considered to understand the complete fossilization of these Permian woods and the synchronous formation of framboidal pyrite, which in all cases involve the hydrolysis of the original cellulose. Three premises concerning these processes should be taken into account: (a) the commonest andesite volcanic gases are H_2O, CO_2, H_2, H_2S, SO_2, CO, NH_3, and N_2; (b) the fluid inclusions (CO_2, H_2O, H_2S, etc.) and homogenization temperatures (50°–350°C) of hydrothermal quartz crystals; and (c) the technological methods described for cellulose decomposition, i.e., the use of H_2SO_4 (SO_2+H_2O) to promote total cellulose hydrolysis [18] or the use of steam (H_2O) explosions (215 °C, 3 min) to obtain oligosaccharides from softwood *Pinus radiata* [19].

It has been observed that in modern plants amino acid sequences of many ribonucleases have been derived from cDNA sequences which have free cysteine compounds and disulfide bridges. In turn, sulforeducing bacteria could have lived in the fossil wood cells producing local iron sulfide supersaturations. However, these processes could not be as important as the iron and sulfur contributions from the hydrothermal fluids which

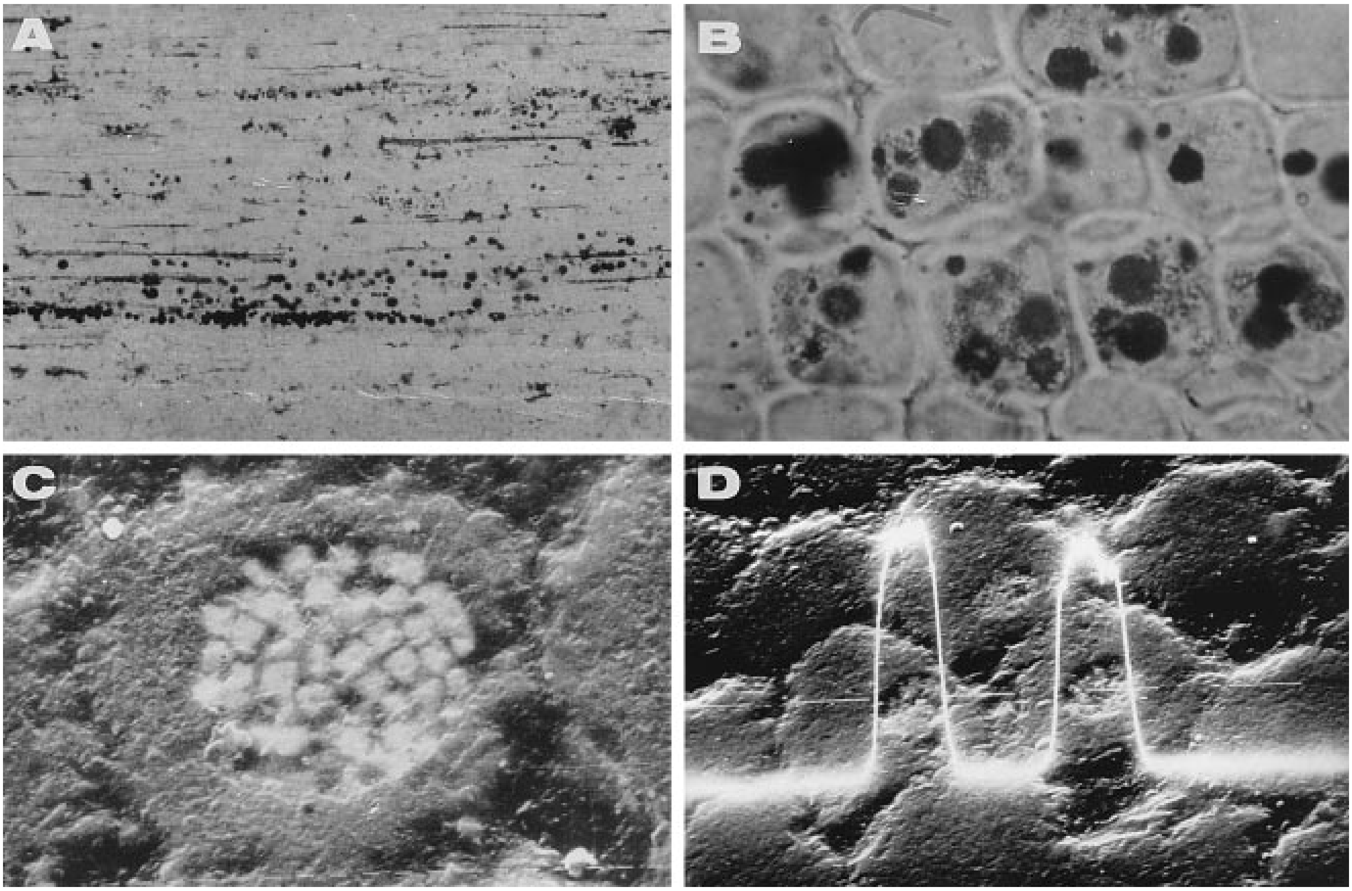

Fig. 2. Permian silicified wood from Pálmaces de Jadraque, Guadalajara, Spain. A) Cross-section of xylem displaying the linear distribution of framboidal pyrites following the wood structure (polarizing microscope). B) Cross-section of xylem with framboidal pyrite in cells (polarizing microscope). C) Framboid of 2 μm diameter made up of pyrite microcubes (SEM). D) Iron profile. Note the high content of iron within the framboid. The thin white lines represent 1 μm. SEM-EDAX

came from the volcanic source; andesite-dacite magmas can emit variable amounts of SO_2 and H_2S gases. A possible mechanism for hydrogen sulfide emissions could be the boiling of hydrothermal fluid within volcanoes. At depth, under pressure in the magma, H_2S is a stable sulfur gas. A rapid eruption and transport through the atmosphere oxidizes it into SO_2 (e.g., the 1992 August eruptions of Mount Spurr, Alaska showed a 3:1 SO_2/H_2S ratio and 6:1 in September [20].

Nevertheless, the bacteria contribution could also have been important; the thermophyllic bacteria *Sulfolobus acidocaldarius* thrive in the acid water of volcanic exhalative environments at temperatures in excess of 100°C. They may grow in anoxic environments where their energy is derived from the oxidation of sulfide ions. After death the degradation of the organic material would leave a residue of magnetic debris which could accumulate to form framboidlike aggregates. Taking into account that *S. acidocaldarius* maintain a neutral pH, the magnetic material could be initially magnetite, which upon degradation of the organic material would be liable to sulfide replacement [21].

In conclusion, cellulose and fossil wood, in conjunction with reducing conditions, are favorable environments for the growth of framboidal pyrite. Andesite-dacite ash tuffs and lava flows preserve the original wood structures, and the associated late-hydrothermal processes provide the necessary temperature (50°–350 °C), carriers (hydrothermal fluids), chemicals (silica, iron, sulfur, metals) and Eh-pH conditions (in presence of water at 25 °C the Fe^{3+} ion changes to Fe^{2+} at approximately Eh=+0.8 and pH=2) to produce framboidal pyrite armored in quartz. The influence of oxidizing-thermophyllic and/or sulforeducing bacteria cannot be disregarded. In addition, many published paleobotanical polarizing microscope photographs of wood structures clearly display opaque spheres [22–25]. These spheres, which are not described, are almost certainly metallic minerals (pyrite, greigite, magnetite, etc.) showing framboidal shapes. Judging from these observations reported in the literature, the presence of framboidal pyrite in fossil woods must be frequent. Therefore fossil wood sections which contain said opaque spheres should be analyzed under SEM and similar techniques to study details of possible framboidal minerals.

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