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Composite structure of wood cells in petrified wood

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Abstract

Special kinds of petrified wood of complex structure were investigated. All the samples were composed of at least two different inorganic substances. The original cell structure was preserved in each case. The remnants of the original biological material were detected in some locations, especially in the cell walls. The complex inorganic structure was superimposed on the remnant organic network. The first inorganic component was located in the lumena (l.) of the cells while another one in the walls (w.) of the cells. The investigated arrangements were as follows: calcite (l.)—goethite–hematite (w.)—wood from Dunarobba, Italy; pyrite (l.)—calcite (w.)—wood from Łuków, Poland; goethite (l.)—silica (w.)—wood from Kwaczala, Poland. The inorganic composition was analysed and spatially located by the use of three spectral methods: electron microprobe, X-ray synchrotron-based microprobe, μ-PIXE microprobe. The accurate mappings presenting 2D distribution of the chemical species were presented for each case. Trace elements were detected and correlated with the distribution of the main elements. In addition, the identification of phases was done by the use of μ-Raman and μ-XRD techniques for selected and representative points. The possible mechanisms of the described arrangements are considered. The potential synthesis of similar structures and their possible applications are suggested.

Keywords: Fossil; Petrified wood; Composite biomaterials; X-ray, electron- and proton-microprobes

1. Introduction

The petrified wood, in other words the fossilized remains of once grown trees, are common in the different parts of the world. If they are found in the sedimentary geological material, they are studied to reveal the information about:

– very old populations of trees, sometimes extinct;
– climatic conditions occurring during their vegetation;
– environmental conditions characteristic of the territory under consideration, during the period between the time of burying and the recent moment;
– specific chronological information [1], much different from that extracted from the contemporary trees;
– the details of the petrifaction process, even to use the information to synthesize the similar material recently;
– not least important, to learn how such materials are organized by the nature and whether or not we can shorten and repeat the process in the laboratory.

The petrifaction process is known to occur in the limited number of materials, to mention different varieties of silica, calcite, dolomite [2], pyrite [3,4], goethite, phosphates—frankolite and apatite [5,6], laumontite [7], sapperite [8], pitchblende, sphalerite [9]. Rather extensive review of petrifying minerals was given by Buurman [10]. Tacitly, it is assumed that most commonly, only one kind of the inorganic material permineralizes everything, i.e., each detail of the primordial structure. It covers the tree ring system, tissues and cells. If one expected the differentiation in petrifying materials, it should concern seemingly the ring

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structure and this problem was under investigation [11–13]. The results indicated that there were differences between hardwood and softwood locations but they concerned the trace elements and not the essential matrix substances. Sometimes, if one inorganic compound exists in different crystallographic varieties, different phases are now located in separate places, as, e.g., opal CT in the lumena while chalcedony as the constituent of the cell wall, or vice versa [14]. This kind of differentiation is easy to explain, since the only one mineral, amorphous opal, filled the cells in and later partially crystallized with different rate on different locations.

Buurman found the samples that were permineralized or substituted by at least two inorganic substances [10,15]. Recently [16,17], we have found the information that the permineralization is possible which occurs in the way that one mineral petrifies the cell wall while another mineral locates in the internal part of the cell. Our experiments confirmed this fact. We detected the samples where the following pairs of the minerals substituted the original matter in the biological cells, in the light of the cells and in the walls, respectively:

- calcite–goethite;
- pyrite–calcite;
- goethite–silica.

The materials of such type are hardly recognized in the world literature, concerning this subject and never studied in detail. Especially, their chemical and phase composition is unknown. The application of devices of microprobe type is essential for the recognition of petrified wood of composite structure and we decide to use such techniques for the first time.

Such discovery generates next questions concerning the petrifaction process. If the petrified wood is organized in the way that the cell walls are built of one material while the interior is constructed of another one, then this kind of wood should be recognized as the natural composite material. Moreover, as it is known from the literature and from our previous studies [18], the remains of the original organic, biologically born matter can also be identified. It complicates the question further, because in this situation the petrified wood can be the sample composed of two kinds of inorganic matter supported on the organic template. It is not fully recognized how the permineralization of the wood occurs in the nature. Moreover, the transformation of the original material into a form of composite organic–inorganic copy has been hardly studied [19]. In this contribution, the microprobe chemical and structural analyses of the natural composite materials will be presented and the question of their forming will be addressed. After the recognition of the chemical and structural status of such samples on a microscale, the questions of potential synthesis of such materials and their application appear immediately. Since the apatite is one of the materials engaged in the process of wood mineralization and is associated then with the remains of the original organic material, it seems that such a combination would be useful as the implantable material, for potential bone substitution.

2. The samples

Three kinds of samples were collected for investigation. The pieces of petrified wood from Łuków (eastern Poland) were dated to be from the late Jurassic, ~ 165 million years old. Originally, the material was formed in an unidentified location in Scandinavia, but ~ 2.8 million years ago it was transported with a glacier to the recent location. The samples were mineralized in calcite and pyrite. The degree of preservation of the ring, tissue and cell structure was excellent. Unfortunately, the pieces are so small that the identification of the tree species is impossible.

The samples of the wood from the fossil forest in Dunarobba (Umbria, Central Italy) were composed of calcite and goethite. Most probably, they belong to the *Taxodioxylon gypsaceum* or *Glyptostrobus europeus* species. The fossil forest in Dunarobba is well described in the literature [20,21] and the investigation of the preserved organic matter was made. The age of the fossils was estimated as not smaller than 2 million years. The ring, tissue and cell structure were preserved here in the best way among all the samples studied in this paper. It was known from the previous investigations of the sample that some remains of the more stable fragments of primordial organic matter, especially fragments of lignin and terpens were identified.

The last kind of the samples belongs to the fossils found in the specific and archaic arkoze formation in Kwaczała, close to Cracow in southern Poland. It is a formation going from the Late Carboniferous (~ 306 millions years ago) and Permian time (286–246 millions years ago). More or less old specimens of wood were analysed only once by the microspectral methods, but this measurement concerned ferns and *Dadoxylon* species found in east German palaeontological site in Chemnitz [22]. Although some older trees have been found recently, they were not studied from the chemical point of view [23]. Our samples of arkoze wood represent either *Dadoxylon saxonicum* or *Araucarites Schrollianus* species.

3. Instrumental

Three types of microprobes were applied for getting the secondary X-ray emission, bearing the information about the chemical composition of the samples: synchrotron based X-ray microprobe, electron microprobe and μ-PIXE. The devices will be described below. The first of the microprobes, the synchrotron-based one can be rearranged in that way that the microdiffraction measurements are possible. The electron microprobe is, in turn, an attachment to the electron microscope and a collection of the secondary electron images and elemental mappings of the same location is available.