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ABSTRACT - The Dunarobba Fossil Forest, close to Avigliano Umbro (TR) in central Italy, is world registered as one of the very few locations where is documented a Middle Pliocene (about 2.5 My B.P.) forest. Lacustrine clay sediments preserved about 70 specimens, in life position, of “palaeo-sequoias” belonging to genus *Taxodioxylon*. Since its discovery, the Dunarobba site pointed out preservation problems. Natural weathering effects, of the “once buried-now exposed” mummified trunks, are responsible for significant decay effects on the exposed trees. SEM-EDX, FT-IR and XRD investigations have been carried on tree fossil samples, affected by peculiar mineralogical transformations. Reducing environmental condition transforms sulphides into Fe-oxides and prevailing hydroxides with sulphuric acid production. This diffused alteration process is responsible for these new mineralogical phases, and related volume increasing effects, probable “add-on” cause, of the exfoliating effects locally observed on the exposed trunks.

The Dunarobba Fossil Forest (Umbria, Italy): mineralogical transformations evidences as possible decay effects.

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INTRODUCTION

Geological heritage

The Dunarobba Fossil Forest represents a particular and peculiar paleontological case: it is a perfect “in situ” forest, developed along the swampy lacustrine margin during Late Pliocene (Ambrosetti et al., 1995a). A density of 43 trees/hectare was estimated and the diameter size...
of the trunks varies from 1.5 to 2.5 metres; the outcropping height of trunks is comprised between 2 and 8 metres. The basal diameter trunk is useful to estimate the real height during life: the Dunarobba forest was characterized by several giants of 31-35 m high trees that grew for about 2000-3000 years. According to the dendrochronological analyses (Biondi and Brugiapaglia, 1991) the fossil wood belongs to *Taxodioxylon gypsaceum*, an extinct species with anatomical affinities with living sequoia (*Sequoia sempervirens*).

The trunk preservation for over 2.5 My it has been possible because of the particular burial phenomenon related to a very slow sedimentation rate (estimated at about 2.6 m/1000 years). The Fosso Bianco Fm., where the trunks are comprised, is constituted mainly by clays and fine sand sediments for a total thickness of about 250 metres (Ambrosetti et al., 1995a, 1995b). The finding of trunks in life-position testifies that after death, or during life, the trees underwent conservative and reducing conditions, promoted by the continuous and slow clay sediment burial process. The evidences of this slow burial are the presence, along the trunk surfaces, of root processes, progressively developed during the soil elevation, to give stability to the tree. The soft clayey sediments developed a defence role in respect to the bacterial or fungi attacks, preventing also the mineralizing fluid circulation. So the wood decay didn’t happen and the trunks are now un-fossilized!

The Dunarobba fossil forest wood possesses also a natural durability to the attack by fungi and insect colonization, as reported by Palanti et al. (2004).

**Geological setting**

The continental deposits that include the Dunarobba Fossil Forest belong to the Tiberino Basin, a sedimentary Plio-Pleistocene intermountain basin, developed near the western margin of Apennine Chain, located in Umbria (Central Italy) and extend from Città di Castello to Perugia (Fig. 1). South to Perugia the basin subdivided into two branches, the western and eastern, forming an upside-down “Y” shape. The maximum extension estimated is of about 1800 squared kilometres. The Eastern branch, called Umbra Valley, reached Spoleto, while the Western branch, the Tiberina Valley, extended until Terni (Fig. 1). During the Miocene the area was affected by tensional tectonic activity giving origin to depressed areas on which, lacustrine and fluvial-alluvial-lacustrine environments developed. Sedimentary facies analysis and geological survey allowed reconstructing the environmental evolution of the basin: from a deep lacustrine system to alluvial plain and

![Fig. 1 - Sketch map of the Tiberino Basin and location of Dunarobba Fossil Forest (after Ambrosetti et al., 1995a, redrawn).]
finally to a system of small and little deep lakes. The total deposit thickness is of about 2300 m, with local variations related to the paleomorphology of the bottom and to the tectonic activity.

Ambrosetti et al., (1995a) identified four lithostratigraphic Units:
- the Fosso Bianco Fm. (Middle-Late Pliocene) which was deposited in a complex lacustrine system (Fig. 2)
- the Ponte Naja Fm. (Late Pliocene) formed of alluvial fan deposits
- the Santa Maria di Ciciliano Fm. (Early Pleistocene) formed of fluvial alluvial deposits
- the Acquasparta Fm. (Early Pleistocene) deposited into small isolated lacustrine carbonate basins.

**DUNAROBBA MINERALIZATION AND DEGRADATION OF WOOD: THE STATE OF THE ART**

The Fossil Forest of Dunarobba represented an important geological-site for researchers studying wood degradation and permineralization processes. Several papers were devoted to Dunarobba wood analyses spacing from chemotaxonomy (Staccioli *et al.*, 1996; Staccioli and Bartolini, 1997; Menchi *et al.*, 1997) to mineralogy of inorganic components (Staccioli *et al.*, 2001; Boyce *et al.*, 2001; Scott and Collinson, 2003) and, finally, on the rule played by organic compounds for permineralization (Nowak *et al.*, 2007). An overview of the most relevant results emerged after over 13 years of analyses is here reported.

The research team of Staccioli promoted, from the 1997 to 2001, a large field of analyses incentred on the fossil wood of Dunarobba, with the aim to identify both biomarkers of fossil extinct species and changes in the wood acid structure, and the occurrence of mineralization processes. Menchi *et al.* (1997) evidenced some important changes in the fossil woods where the free carboxylic groups disappear completely; the fossils containing only traces of holocellulose exhibit the largest amount of carboxylic groups which may be ascribed to lignin content. In all the examined fossils the initially protonated form was changed into the salified one because of the leaching carried out by water containing soluble salts. Staccioli and Bartolini (1997) reported the results of chemical analyses carried out on a sample of *Taxodium* *gypsaceum* recovered from Dunarobba subsoils: the material was much degraded because of the almost total loss of polyoses and cellulose, which are the still important constituents of forest trunks. The FOSSO BIANCO Fm

![Fig. 2 - Paleoenvironmental reconstruction from the Fosso Bianco Fm., showing the transition from wetland coastline through deep offshore lacustrine facies, to a wetland coastline again (from Ambrosetti et al., 1995a, redrawn).](image-url)
identified components were ferruginol, podocarpiol, sugiol and some long chain ketones; the phenolic diterpenes are characteristic of several modern species of *Cupressaceae*, *Podocarpaceae* and *Taxodiaceae*, which, for these compounds resemble the extinct species *T. gypsaceoum*.

Staccioli *et al.* (2001) examined two twigs coming from the site and surroundings of the DFF with the aim to assess both the degree of degradation of the organic fraction and the composition of inorganic components. Two different degree of mineralization were identified and the main minerals founded are silica, calcite, chlorapatite, chloromagnesite and clays; the goethite (major mineral in both samples) was observed in the interstitial spaces of the cell walls, whereas calcite was found in the cell lumina.

Scott and Collinson (2003) analyzed permineralized fossil woods collected in clays above the main fossil forest, and found permineralization by a combination of iron-rich minerals (iron carbonates or oxides including siderite and goethite) and ferroan calcite. In thin section, using transmitted light microscope, following said Authors, the wood showed a simple calcareous permineralization with organic cell walls preserved and cell lumina filled with calcite. The Dunarobba-site woods were found mineralized with ferroan calcite filling cell lumina, and iron-rich minerals (siderite, goethite) forming “apparent cell walls”. In some areas where calcite had not filled the cell lumina the organic walls remained. This fact indicates the importance of organic wall breakdown, in order to initiate the mineral phases precipitation, likely to be controlled by localized (sub-)cellular-scale pH-Eh conditions in the wood. Ferroan calcite deposition has occurred only in cells where there has also been an iron-rich mineral layer, deposited adjacent to the cell lumen infill and this may relate to local pH. The fact that variation in permineralization within one specimen (shown here) occurs, and that not all Dunarobba woods are permineralized (Scott and Freedberg, 2000), suggests that mineral precipitation is strongly influenced by very local changes in Eh and pH. There is a major natural variation in lignification between cells and secondary wall layers of woods (e.g. Donaldson, 2002) that, giving differential decay of celluloses vs. lignin, provides great potential for sub cellular- and cellular scale variations in Eh-Ph conditions during wood decomposition. Said Authors report that the breakdown of original organic cell walls may have locally changed the Eh-Ph conditions of the pore waters to encourage mineral precipitation.

Novak *et al.* (2007) presented spatial distribution of the primordial organic material (lignin, cellulose, pectin) remains, in the permineralized wood cells of DFF, collected using μ-Raman spectrometry. The composite nature of the petrified material, characterized by calcite in cell lumina and goethite in cell walls, was confirmed by electron, proton and X-ray microprobes. In this work goethite is essentially dominating in the former cellulose-occupied zone (secondary xylem), while the middle lamellae zone and its surroundings are relatively goethite-depleted; this suggest that the wall mineralization process was strongest in the cellulose layer and much weaker in the lignin zone. For the aforesaid Authors this is a reasonable conclusion, if one considers that the route of mineralizing solution is easiest through the tracheids, and that the wall filling continues from the lumen wall boundary towards the middle lamellae; it is also clear that the solution passing the tracheids leaves the Ca ions as calcite in the neutral to basic environment of the lumen. Fe (III) can be attracted only to the cellulose layers and is present in the wall and Fe (II) was transported inside the wall precipitating mainly in the external layers of the walls. Finally iron was oxidized forming goethite “pipes” in the external layers of the double wall, perhaps with
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bacterial activity.

It is necessary to remind that all the investigated samples, collected and analyzed in a range-time of over 13 years, by the all the above mentioned Authors, were collected in different places: in clay sediments stratigraphically above the main Dunarobba fossil forest, from soils and/or from the proper site of DFF. The totality of wood samples examined (probably belonging to different taxa that formed the various stages of fossil forest development), evidences the overall more or less diffuse presence of mineralization processes happened under different local conditions, whether under burial or subaereal situations.

Aim of this study is to present another different type of mineralizing process observed and its potential dangerous effect through time on an open air environment, thus giving also suggestions to preservation techniques. No “classic” general wood degradation effects and permineralization processes were analyzed since diffusely investigated as reported in literature data. Investigation were carried on in co-operation with the Soprintendenza Archeologica dell’Umbria.

METHODS AND TECHNIQUES

Selected fragments of the external cortex of the exposed Dunarobba trunks have been collected together with samples where hard material (mineralized one) was observed at brunch/trunk junctions (Fig. 3). Recovered materials were carefully powdered in an agate mortar and dried at 34 C°, for mineralogical and chemical analyses (XRD, FT-IR, SEM-EDX).

X-ray diffraction

After powder diffraction spectra two different types have been detected:

Samples with typical calcite diffraction patterns pointing to mineralizing processes into the wood (Fig. 4 a).

Samples with broad reflection bands centred at about 2Θ = 15°-16° and 22°-23°, pointing to not yet crystallographically ordered materials (Fig. 4 b).

FT-IR

In order to investigate the organic compounds, FT-IR analyses were performed on the same samples previously analyzed with XRD. The two samples characterized by calcite mineralizing processes, in the FT-IR spectra of Fig. 5, beside the typical peaks c, e, f proper of calcite, showed typical wood organic compounds patterns a, b, d (lignin d, and phenol compounds a, b). On the contrary, amorphous samples (unmineralized), showed FT-IR spectra perfectly overlapping the “wood-flour” standard reference pattern, thus pointing to wooden material.

The minimal differences related to height intensities of features a, b, d, in Fig. 5, may suggest decay effects of the organic matter without substitution from inorganic compounds.

SEM-EDX

Both tree-sample types have been inspected

Fig. 3 - Portion of a fallen trunk affected by mineralizing process. Particular attention is paid to the natural wood light brown-red colour (arrow). Picture May 2007.
Fig. 4 a-b – Obtained XRD patterns: top a) identical to JCPDS 5-586 calcite; bottom b) partially amorphous material.
Fig. 5 - FT-IR spectra for mineralized and unmineralized wood samples examined compared with calcite (c, e, f = calcite patterns), wood typical organic compounds (a, b, phenol compounds - d, lignin) and wood-flour standard reference pattern.
with SEM-EDX techniques. Investigations have always been carried on through BSE images on polished sections, in order to better show compositional and morphological differences. In all the investigated samples, wooden structure resulted unaltered, showing peculiar characteristics of real live wood. Investigated samples with calcite, show also variable Fe, Mn and Si content. In both sample types, small areas (μ 20-30 in size) are discernible, more abundant in the mineralized ones (Fig. 6). In such areas, areas with sulphide as pyrite and/or marcasite are found, while surrounding areas show a Fe hydroxide. This last, following BSE observations showed either a much lower contrast in

Fig. 6 - BSE image of unaltered wooden structures. Small areas (μ 20-30 in size) are discernible, with pyrite and/or marcasite (white), showing external boundaries transformed in Fe hydroxide.

Fig. 7 - BSE image of mineralized cell lumina. Sulphides and related alteration products responsible of main decay effects.

Fig. 8 - BSE image of mineralized wood. Different spots indicate sulphide filled cells (spot 2 and 3) and simple calcite mineralized ones (spot 1).

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Semiquantitative SEM-EDX analyses (%) of spots reported in Fig. 7.</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>MgO</td>
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<tr>
<td>SiO₂</td>
<td>3.5</td>
</tr>
<tr>
<td>SO₃</td>
<td>0.3</td>
</tr>
<tr>
<td>CaO</td>
<td>81.6</td>
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<tr>
<td>MnO</td>
<td>-</td>
</tr>
<tr>
<td>FeO</td>
<td>13.4</td>
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<tr>
<td><strong>Total</strong></td>
<td><strong>99.8</strong></td>
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<table>
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<th>Table 2</th>
<th>Semiquantitative SEM-EDX analyses (%) of spots reported in Fig. 8.</th>
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<tr>
<td>MgO</td>
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<td>FeO</td>
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</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>99.4</strong></td>
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comparison to that of typical Fe sulphides, and a
different chemical composition, Fig. 7 and related
TABLE 1, and Fig. 8 and related TABLE 2.

**Fig. 9 - BSE image: overview on the mineralized portion.**

| TABLE 3 |
|---|---|
| **Semiquantitative SEM-EDX analyses (%)** of spots reported in Fig. 9. | |
| | 1 | 2 |
| SiO$_2$ | 2 | 4.7 |
| CaO | 86.7 | 7.7 |
| FeO | 11.7 | 87.3 |
| **Total** | 100.4 | 99.6 |

**DISCUSSION AND CONCLUSIONS**

Two different wood types have been identified. A mineralized one, that has partially undergone to a Ca carbonate transformation, and an unmineralized one where the “organic material” has not yet been transformed. The first one is located in the external portion of the trunks, the second one in the inner portion.

Special attention must be paid to the Fe sulphides and hydroxides areas. A hypothesis points to the real original sulphide areas, which subsequently underwent - following weathering agents - to a complete transformation in Fe hydroxides. Such a transformation, originates a volume increasing as well as a sulphuric acid production following the reaction:

$$2\text{FeS}_2 + 15/2 \text{O}_2 + 7\text{H}_2\text{O} = 2\text{Fe(OH)}_3 + 4\text{SO}_4^{2-} + 8\text{H}^+$$

These transformation processes, observed in the Dunarobba fossil forest trunks, affect conservation problems too, as different trunk composition sometimes shows mineralized and unmineralized portions (Fig. 9 and TABLE 3). In fact these two different mineralized materials, show different behaviours in relations to the various environmental thermal conditions. Moreover unmineralized wood undergoes to biological agents attack.

Iron sulphides/hydroxides transformations besides changing volume variations, do produce a highly corrosive substance as the sulphuric acid, attacking both lignin and calcium carbonate. Controlling such a transformation could be a new, not yet observed, additional way to control the decay effects of the Dunarobba woods.

Future investigations could be addressed to repeated sampling in different portions of different trunks in order to confirm the preliminary results so far achieved. Final laboratory procedures to artificially reproduce decay effects for testing on small portions of

**Fig. 10 - Picture (September 2009) of the studied fallen trunk of Fig. 3. Massive loss of wooden material is present: the mineralized area is slightly enlarged.**
wood samples, could be a useful tool to obtain new information.

Pictures reported in Fig. 10 (September 2009), on the same trunk fragment previously investigated about one year before, evidenced a massive loss of wooden material and the formation of dark brown ring around the mineralized area. The size of mineralized area is slightly increased.

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