Mineralization of fossil wood

P. Buurman


Several pieces of fossil wood have been analyzed with X-ray diffraction and were grouped on the basis of mineralogical composition. Various mineralizations were studied in thin sections and by means of the scanning electron microscope. Wood-opals appear to show a structure preservation that points to replacement of cell walls by silica. The wood-opals are mineralogically characterized as 'disordered tridymite'. Other mineralizations, such as chalcedony, quartz, carbonates, phosphates and iron-oxydes and -hydroxydes show characteristics of filling-in. Various mineralization processes are discussed.

P. Buurman, Department of Soil Science and Geology, Agricultural University, P.O. Box 37, Wageningen, The Netherlands.

<table>
<thead>
<tr>
<th>Introduction</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental part</td>
<td>3</td>
</tr>
<tr>
<td>X-ray diffraction</td>
<td>3</td>
</tr>
<tr>
<td>Scanning electron microscopy</td>
<td>3</td>
</tr>
<tr>
<td>Thin sections</td>
<td>4</td>
</tr>
<tr>
<td>Literature review</td>
<td>4</td>
</tr>
<tr>
<td>Silicification</td>
<td>4</td>
</tr>
<tr>
<td>Phosphatization</td>
<td>6</td>
</tr>
<tr>
<td>Carbonatization</td>
<td>6</td>
</tr>
<tr>
<td>Accumulation of sulphides</td>
<td>6</td>
</tr>
<tr>
<td>Results</td>
<td>6</td>
</tr>
<tr>
<td>Disordered tridymite</td>
<td>7</td>
</tr>
<tr>
<td>Chalcedony and quartz</td>
<td>15</td>
</tr>
</tbody>
</table>
Introduction

Wood specimens were gathered for an investigation of growth-ring cycles of fossil trees by Dr van den Heuvel (Sterrenwacht – Astronomical Institute – University of Utrecht). Subsequent collecting added sufficient material for the present investigation.

Fossil wood, which occurs in fair amounts in practically all parts of the world, has been studied by both botanists and geologists for more than a century. Especially silicified specimens intrigued many a scientist and quite a number of theories on the mechanism of silicification in relation with structure-preservation, and on the source and nature of the silicifying agent, have been put forward. However, there is no general agreement on a single theory on silicification of wood. Moreover, other fossilizations, such as phosphatization and carbonatization – both quite common locally – have never been studied in detail.

The aim of the present study was to select a number of different mineralizations of wood and to make comparisons, in order to establish whether permineralization or replacement of wood structures has occurred. Also a comparison between structures in mineralizations known as ‘wood-opal’ and those of chalcedonic nature seemed important.

Specimens were obtained from several museums and private collections listed under acknowledgements. The determination of species was considered beyond the scope of the present study.

Acknowledgements

The scanning electron microscopy was carried out by Mr S. Henstra and Mr F. Thiel of the Service Institute for Applied Mechanics and Technical Physics, TFDL, Wageningen.

Thin sections were prepared by Mr G. J. van de Waal, Department of Soil Science and Geology, Wageningen.

The author gratefully acknowledges the receipt of specimens of fossil wood from the following institutions: Belgium, 1) Institut Royal des Sciences Naturelles, Brussels (Dr P. Sartenaer); France, 2) Musée des Sciences de la Terre, Nancy
Experimental part

X-ray diffraction

For the selection of specimens for detailed study, about 200 samples were X-rayed. Photographs of powdered samples were made with a quadruple Guinier-de Wolff camera.

Scanning electron microscopy

Scanning electron microscopy (SEM for short) studies were carried out with the Jeol equipment of the Service Institute for Applied Mechanics and Technical Physics, TFDL, Wageningen.

Samples were prepared as follows: small pieces of about 1 cm across, with clean fresh fracture planes were glued on sample holders, coated with a gold film and placed in the microscope.

For SEM studies the preferential cleavage of the wood specimens is of utmost importance. This feature is related to the character of the fossilization, as will be pointed out in the next paragraph.

Preferential cleavage

A preferential cleavage in either radial, tangential or cross direction is important for SEM studies. Fresh wood, monocotyledonous wood excepted, shows radial preferential cleavage; cross cleavage is prevented by the presence of long vertical tracheids, while tangential cleavage is hindered by radiating rays.
The first structures that vanish upon the death of a plant, are the middle-lamellae between the cells. When fossilization is restricted to filling of cell lumina or replacement of cell walls, the cleavage-characteristics remain essentially as before, i.e., providing good radial sections. The only connection between cells in the radial plain are pits. When replacement of cell walls occurs these connections are the mineralized pits themselves; in case of filling-in casts of pits may connect cells through the open space of the vanished middle-lamella (compare Fig. 38).

However, when partial or complete filling of middle-lamellar space occurs – or of the space of the former cell wall – most of the preferential cleavage in any direction will disappear so that samples are not suitable for SEM studies.

The same holds true when recrystallization occurs which disregards the cell walls. Although in thin section the structure may be visible, preferential cleavage plains have vanished and consequently, samples are not suitable for SEM investigations.

THIN SECTIONS

For a comparison with the generally radial sections of the SEM samples, cross-cuttings were preferred for the preparation of thin sections. When the samples were too friable they were first impregnated with plastic (isotropic). Cell-wall characteristics such as optical orientation, layering, open spaces between adjacent cells, pits, and crystallization phenomena were particularly noted.

Literature review

SILICIFICATION

Early students of silicification of wood have considered the possibility of preferential silicification of silica-rich wood. However, since cell walls in living plants are never silicified and as plants which do not contain silica turned out to silicify just as easily as those rich in silica, this hypothesis was abandoned in the 1930's. An investigation by Müller Stoll (1947) showed that preferential fossilization is not related to species but rather to circumstances of burial.

The most comprehensive studies on silicified wood were made by Felix (1897), Kraut (1933), Storz (1933), Strömer (1933) and Hellmers (1949), the latter, however, not giving much new information.

Silicified wood, occurring mainly in porous rocks, was mineralized by silica-rich groundwater. Some authors assume periodical desiccation (Hellmers, 1949), while others consider the sediments continuously water-logged (Schönfeld, 1955).

There is some controversy over the succession of decay of organic matter and silicification. Many pieces of silicified wood show remnants of lignified organic material at the site of the former cell walls. These remains may be very distorted and fractured, but in other cases show fine structures. Wieland (1930) suggested that decay precedes silicification. This opinion is shared by Schönfeld (1955). Other authors however, such as Storz (1933), suppose that decay, hampered by silicification (decay of cell walls without distortion is called ‘topochemical
Buurman, Mineralization of fossil wood, Scripta Geol. 12 (1972)

decay'), and lignification under influence of crystallization of chalcedony produces the structures encountered. In most fossil wood about 0.1-1% of the original organic matter content is preserved.

Silicification occurs both in wood buried in situ and in wood that has been transported before final burial. Although silicified wood is at present often found in enormous quantities in arid climates, the species generally indicate that their wood grew in a humid environment. Again, a humid climate is more suitable for transport of silica (Kraut, 1933).

It has been a matter of some discussion whether the silicifying agent would be colloidal silica, silica in gel-form, or silica in the form of monomeric acid. Since the appearance of Liesegang’s paper (1931) most authors agree on monomeric silicic acid ($H_4SiO_4$). It was generally accepted that silica in colloidal form would be unable to permeate cell walls, while silica in true solution could easily do so.

Schulze & Theden (1942) carried out some investigations into the transport of silica in fresh wood. It appeared that a sodiumsilicate solution was easily transported through the ray cells and thence into the tracheids.

The source of the silica is still a matter of discussion. Lacroix (1911) found wood that had been silicified in thermal springs. The wood had been incrusted and cell lumina were filled with opaline silica. However, a thermal origin of silica can be excluded for most of the occurrences of silicified wood. Other silicifications have been related to weathering of pyroclastic sediments (Schopf, 1971), by which process silica would have been set free. Processes acting in soil formation and producing free silica, have been mentioned occasionally but were never troroughly investigated. Although silicification of wood and its impregnation with calcium carbonate may occur in one and the same sample, silicification of woods does not proceed through an intermediary phase of carbonatization.

Silicified wood occurs in various habits. Wood-opal is a silification with an opaline lustre; it is famous because of its excellent structure-preservation. Felix (1897) stated that wood opal does not occur in deposits older than Eocene. Not restricted in time, on the other hand, are silicifications by chalcedony and quartz. Storz (1933) divided these into four crystallization types: 1) polyblastic: many crystals in the space of one cell, 2) oligoblastic: only one crystal in a cell, 3) hyperblastic: crystals have grown through the cell walls and consequently surfaces of two to several hundreds of cells have the same optical orientation, 4) idioblastic: well-shaped crystals in any given part of the wood.

Structure-preservation may or may not be related to the type of crystallization, although it will be clear from the preceeding observations that hyperblastic crystallization will result in a decrease in preferential cleavage.

Recently a tridymite pseudomorph after wood was found in the Lower Cretaceous of Virginia, U.S.A. (Mitchell, 1967). It was described as being of fibrous appearance (with loosely bound tracheids) and no specific orientation of tridymite crystals was found. Details on wood structure were not reported.

In German literature, three different types of silification are distinguished. ‘Verkieselung’ means replacement of cell walls by silica, or ‘silicification’ sensu stricto; ‘Einkieselung’ and ‘Durchkiesehmg’ indicate filling-in of open space in the wood-structure (cell lumina) and open space resulting from decay respectively. The last two terms are fairly synonymous with ‘permineralization’ or ‘filling’.

Storz (1933) and Schopf (1971) considered permineralization as the actual process of silicification, while Felix (1897) decided upon replacement. Many authors (e.g., Gallwitz, 1954, 1955) use the term ‘Verkieselung’ or ‘silicification’.
whenever structure is preserved, irrespective of the mechanism. Some authors, such as Kraut (1933), use the term ‘Einkieselung’ (= permineralization) when remains of organic matter are found.

Electron microscopic studies, first with replica techniques (Eicke, 1952, 1953, 1954), and later with the SEM (Alvin & Muir, 1969; Muir, 1970), revealed that excellent preservation occurs of such structural details as fibrillar structure of cell walls and bordered pits. Wood-opal shows a better structural preservation than the other silicifications. Muir (1970) concluded from this information, and also from the fact that there is open space between the fossilized cells, that permineralization has occurred rather than replacement.

**PHOSPHATIZATION**

Phosphatized wood was reported from the Pacific Sea floor (Goldberg & Parker, 1960). The age of the sample was estimated at over 28 000 years. The specimen was partly embedded in the sediment (clay) and partly in direct contact with the sea water. The buried part had not been phosphatized. Phosphorite (mineralogically francolite, a carbonate apatite) is usually accumulated in small marine basins with a low Eh and a relatively low pH, i.e. lower than 8 (Krumbein & Garrels, 1952). The decomposition of the exposed part of the wood may have resulted in similar conditions. No details on the preservation of wood-structure were reported.

**CARBONATIZATION**

Dolomitized and calcitized wood is known from Carboniferous and Permian ‘coal balls’ (Vadász, 1964). Furthermore it is reported from the Cretaceous (Higgins, 1960) and the Tertiary (Gallwitz, 1954, 1955). Structure-preservation is highly dependent on crystallization. When crystals have not extended beyond cell walls, the wood-structure may be well-preserved, while recrystallized pieces show hardly any wood-structure at all. Schwab (1959) reported dolomitized wood, in which the dolomite crystals do not extend beyond the cell walls. Cell walls not impregnated with dolomite are lignified and show cellulose fibrils.

**ACCUMULATION OF SULPHIDES**

Pyritized and marcasitized wood is fairly common and was for instance described by Gallwitz (1954, 1955) and Daber (1953). Structure-preservation is usually very poor. Muir (1970) reported wood impregnated with sphalerite (ZnS) from Tynagh, Eire. Some structural details were preserved by filling-in with sulphide.

**Results**

X-ray diffraction analysis shows the presence of the following mineralizations: quartz (SiO₂), tridymite (disordered, SiO₂), quartz + tridymite (disordered), calcite...
(CaCO₃), quartz + calcite, siderite + pyrite (FeCO₃ + FeS₂), siderite + hematite (FeCO₃ + α-Fe₂O₃), hematite + pyrite, francolite (approx. formula Ca₃(PO₄)₂O₃ (OH.F) ), goethite (αFeOOH) and goethite + lepidocrocite (α-and γ-FeOOH).

At least one sample of each type of mineralization was selected for detailed study by means of the SEM and thin sections.

In the following text, the samples are grouped according to mineralogical composition. It should be noted that collection numbers in the sample descriptions refer to the numbers listed under the acknowledgements (p. 2). Because several samples had not been numbered all samples were given a serial number, which is referred to in the text.

**DISORDERED TRIDYMITE**

**Sample-list**

24. Fibrous wood-opal with a glassy lustre, white; origin: Java, Indonesia; age: Tertiary; coll. 8: nr. 4 743.
64. Fibrous wood-opal with a glassy lustre, somewhat less fibrous than 24, grey; origin: Muffendorf near Bonn, Germany; age: Tertiary; coll. 10: RGM 39 393.
78. Massive wood-opal with a conchoidal fracture, white with a grey rim, partly distorted; origin: unknown; age: unknown; coll. 2.
94. Fibrous wood-opal with a glassy lustre, white; origin: unknown; age: unknown; coll. 2.
97. Fibrous wood-opal with a glassy lustre, white; origin: unknown; age: unknown; coll. 2.
152. Massive wood-opal with fibrous outer parts; origin: Megyaszó, Hungary; age: Mio/Pliocene; coll. 6: A639.
159. Massive wood-opal, brown; origin: Monosbéél, Hungary; age: Tertiary; coll. 6: A 1051.
161. Fibrous, soft brown material; origin: Bangla Desh; age: Tertiary; coll. 9.
169. Fibrous, white material; origin: unknown; age: unknown; coll. 10: RGM 159 993.

**X-ray diffraction**

Except for sample 24, all the above specimens show a distinct X-ray pattern of four or more diffuse lines agreeing with the strongest lines of tridymite (ASTM-card 18-1170). The X-ray pattern is the same as that of silicified chalk, described by Buurman & van der Plas (1971). All samples, nrs 24 and 161 excepted, show some additional quartz.

Upon heating, the pattern changes into that of distinctly crystalline tridymite. Although opals with some preferential orientation are known (Frondel, 1962), such as opal-cristobalite, neither X-ray diffraction pattern, nor behaviour upon heating allow classification with this group. Therefore the name ‘disordered tridymite’ is suggested. The material will be more closely studied in future.

Sample 24 is listed with this group, although it does not show a distinct X-ray diffraction pattern. Its structure and thermal behaviour however, allow its classification with the tridymite-group.
Fig. 1. Wood sample 64: disordered tridymite + quartz; Tertiary; Bonn, Germany; RGM 39 393. Cross-section, normal light, 100x ($r =$ ray; $ew =$ early wood; $lw =$ late wood).

Fig. 2. The same section as in Fig. 1 with crossed nicols, showing polyblastic crystallization, same enlargement.

Fig. 3. Wood sample 161: disordered tridymite; Tertiary; Bangla Desh. Cross-section, crossed nicols, 100x. Isotropic cell lumina and anisotropic cell walls ($r =$ ray; $pa =$ parenchyma; $v =$ vessel).

Fig. 4. Wood sample 161: disordered tridymite; Tertiary; Bangla Desh. Thin-walled ray cells ($r$) and thick-walled parenchyma cells ($pa$). Cross section, normal light, 390x.
Thin sections

Thin sections of samples 24, 64, 78, 152 and 161 show well-preserved structures (Fig. 1, 2). No remains of lignified organic matter could be found. Because of little difference in refraction between cell walls and lumina, the examination of structures may be very difficult in samples in which all open spaces have been filled with silica.

In sample 24 the cell lumina are generally isotropic, except for some places in the late wood. Most cell walls are anisotropic. Optical orientation of silica in the cell walls is the same as that of cellulose in fresh wood. Crystalline cell lumina-fillings show optical orientation perpendicular to that of the cell walls. Cell lumina are not completely filled and show botryoidal structures in the lumina-cavities (Fig. 5).

Sample 64 shows crystallized parts in both cell walls and lumina. Cell lumina fillings are polyblastic and show random orientation (Fig. 2). Cell walls show the same features as those in sample 24.

Sample 78 shows very thin cell walls the radial parts of which are more strongly anisotropic than the tangential parts. Most of the cell lumina are isotropic. Similarly oriented cell walls show the same optical orientation. The sample shows slightly anisotropic zones of distortion. Structure-preservation is splendid in the undistorted parts.

Sample 152 shows the same details as sample 24.

In sample 161 the cell walls seem to have preserved their original thickness. Fig. 4 shows thin-walled ray cells and thick-walled parenchyma cells. Most cell lumina are isotropic and of the cell walls only the outer part is anisotropic (Fig. 3). The cell wall shows the same features as in the preceeding samples.

Crystallization in these tridymitic samples never extends beyond the cell walls.

Scanning electron microscopy

Except for sample 78, which shows no preferential cleavage, excellent sections could be obtained. Electron micrographs of samples 24, 64, 94, 97, 161 and 169 show a striking structural preservation. Open space between the tracheids suggests that at least the middle-lamella between the cells has vanished. This results in the fibrous nature of many of these woods. The samples without quartz show smooth structures, while samples that do contain quartz show more crisp surfaces. Figs. 6-9 illustrate preservation of the structures. Figs. 6 and 7 show tracheid and ray cells with abundant well-fossilized bordered pits. Fig. 8 shows a cross-section, in
Fig. 6. Wood sample 97: disordered tridymite + quartz; age and origin unknown. Scanning electron micrograph of a radial section showing tracheids (t), rays (r) and bordered pits (p), 525 X, TFDL.
Fig. 7. Enlarged part of Fig. 6., showing bordered pits (either casts or replacements), 5250 X, TFDL.
Fig. 8. Wood sample 161: disordered tridymite; Tertiary; Bangla Desh. Scanning electron micrograph of a cross-section, showing cellulose fibrils of the $S_2$ layer and small pits between the parenchyma cells, 1050 X, TFDL.
Fig. 9. Wood sample 64: disordered tridymite + quartz; Tertiary; Bonn, Germany; RGM 39 393. Scanning electron micrograph: oblique radial section showing partly decayed tracheids and fossilized bordered pits (p), 525 X, TFDL.
Fig. 10. Wood sample 169: disordered tridymite + quartz, age and origin unknown; RGM 159 993. Scanning electron micrograph of a radial section showing ray cells (r) and tracheids (t) with window pits (w) and bordered pits (p) respectively, 1050 X, TFDL.
which the cellulose fibril structure of the cell wall and small pits between parenchyma cells are visible. Fig. 9 shows tracheids with fossilized bordered pits and decay structures. Fig. 10 shows tracheids and rays with bordered pits and window pits respectively; the interspace between cells has partly been filled, as is also shown in Fig. 6.

CHALCEDONY AND QUARTZ

Sample-list

1. Massive material with wood structure, brown, growth-rings, conchoidal fracture; origin: Istambul, Turkey; age: unknown (transported after silicification); coll. 12.
6. Massive and white with a glassy lustre and conchoidal fracture; origin: Istambul, Turkey; age: unknown (transported after silicification); coll. 12.
8. Brown, massive, conchoidal fracture, distorted wood structure; origin: Istambul, Turkey; age: unknown (transported after silicification); coll. 12.
42. White, fairly massive material, preferential radial or tangential fracture; origin: Hoeegaerden, Belgium; age: Paleocene; coll. 10.
71. Massive, white grey and red material with a rectangular fracture, faint remnants of wood structure; origin: Faymont, France; age: Permian; coll. 2.
88. Black, massive material with a rectangular fracture, distinct growth-rings, origin: unknown; age: unknown; coll. 2.
98. Black, massive material with distinct growth-rings and rectangular fracture; origin: Merry, France; age: unknown; coll. 2.
106. Walchiopremnnon valdajolense (Mougeot, 1852) Florin, 1940. Black, massive material, rectangular fracture; origin: Val d’Ajol, France; age: Permian; coll. 2.
114. Walchiopremnnon valdajolense (Mougeot, 1852) Florin, 1940. Black, massive material, rectangular fracture; origin: Val d’Ajol, France; age: Permian; coll. 2.
131. White, massive material with a rectangular fracture; origin: Portland, England; age: Purbeck, Late Jurassic; coll. 8.
171. Massive, white material with a rectangular fracture, coarsely crystalline and porous in its inner part; origin: unknown; age: unknown; coll. 10: RGM 159 995.
180. Taxodioxylon abrardi, massive, dark brown material with a rectangular fracture; origin: Chatou, France; age: Sparnacian, Eocene; coll. 3.

X-ray diffraction

All samples show a distinct quartz pattern. Most have an additional weak line at $d = 6.7$ Å, probably due to harmonic reflection of $d = 3.35$ Å.

Thin sections

Thin sections of samples 1, 28, 42, 71, 88, 98, 106 and 131 show that the struc-
Fig. 11. Wood sample 42: quartz; Paleocene; Hoegaerden, Belgium. Cross-section, normal light, 100x. Faint structures of cell walls (r = ray; ew = early wood; lw = late wood).

Fig. 12. The same section as in Fig. 11 with crossed nicols, showing hyperblastic crystallization, same enlargement.

Fig. 13. Wood sample 42: quartz; Paleocene; Hoegaerden, Belgium. Crossed nicols, 100x. The picture shows two kinds of hyperblastic crystallization.

Fig. 14. Wood sample 88: quartz; age and origin unknown. Cross-section, normal light, 100x. Thickwalled late wood and thin-walled early wood with rays (r).
Fig. 15. Wood sample 28: age unknown; Argentina. Both minor and large fragments of lignitic material can be found in the quartz matrix; magnification approx. 600x.

...structures are less well-preserved than in the tridymite-group. Crystallization is generally hyperblastic (Figs. 11, 12, 13) and both cell lumina and middle-lamellar space are mostly filled with silica. In some cases (28, 71, 88, 106) a fair amount of lignitic material is present (Fig. 15); crystallization in these samples is often oligoblastic. In sample 98 (oligoblastic crystallization) pit channels are visible in the thickened walls of tracheids. In several samples (1, 42, 71, 98, 131) structure has partly vanished. Cell walls do not have a specific optical orientation.

Scanning electron microscopy

Electron micrographs of samples 6, 28, 42, 71, 88, 168, 171 and 180 show a widely varying degree of structure-preservation. Samples 6, 28 and 71 lacking preferential cleavage, were not suitable for SEM studies.

Details of cell walls are not so clear as in the tridymite samples. Most cell walls look rather crumbled. Both smooth surfaces – as in Fig. 16 – and rough ones – as in Fig. 17 – show less of the original structure than the tridymite samples. A higher magnification of a part of Fig. 17, however, suggests that at least some of the finer structures of the bordered pits have been preserved (Fig. 18). In most quartz and chalcedony silicifications, preservation of bordered pit structures is much worse. Collapse structures such as shown in Fig. 19 are quite common.

By sheer luck, sample 88 broke so as to produce a cross-section. In this section (Fig. 14) open space at the site of the middle-lamellae is lacking. Silicified cell walls are quite thick and suggest differential mineralization of the different layers of the secondary wall (Figs. 20 and 21).

In a tangential section of sample 42 some of the fibrillar structure of the tracheid walls was preserved.

**CALCITE**

**Sample**

146. Black, calcitic material with lignified bark; origin: Isle of Wight, England; age: Wealden, Early Cretaceous; coll. 8.
Fig. 16. Wood sample 168; quartz; age unknown; Moscow, U.S.S.R.; RGM 159 992. Scanning electron micrograph of a radial section, 437.5 X, TFDL. Smooth structures with ghosts of bordered pits.
Fig. 17. Wood sample 171: quartz, age and origin unknown, RGM 159 995. Scanning electron micrograph of a radial section, showing casts of tracheids and fossilized bordered pits, 525 X, TFDL.
Fig. 18. Detail of Fig. 17: bordered pits showing radial structures in the margo, 3100 X, TFDL.
Fig. 19. Wood sample 88: quartz; age and origin unknown. Scanning electron micrograph of a radial section, showing a collapsed bordered pit, 5250 X, TFDL.
Fig. 20. Wood sample 88: quartz; age and origin unknown. Scanning electron micrograph of a cross-section, 1750 X, TFDL. There is no open space at the site of the middle lamella, but open space does exist between cell wall and lumina-filling. Note crystalline surface of central cells and cells at lower right.
Fig. 21. Detail of Fig. 20: distinct layering in the cell walls and crystal surfaces on the lumina-cast, 5250 X, TFDL.
**X-ray diffraction**

The Guinier photograph showed pure calcite without crystalline admixtures.

**Thin section**

The thin section shows hardly any remains of wood structure because of coarse recrystallization (Fig. 22). There is abundant lignitic material between the calcite crystals.

**Scanning electron microscopy**

Cleavage is determined by the calcite crystal planes and therefore no wood structures could be observed.

**Siderite**

**Sample-list**

70. Black, massive, coarsely crystalline material with some pyrite; origin: Siegen, Germany; age: unknown; coll. 8.

**X-ray diffraction**

Both samples show a siderite pattern with some admixture of pyrite.

**Thin sections**

Under crossed nicols the siderite appears to be fine-grained and it does not disturb cell structures. Much of the organic matter of the cell wall is preserved and has the same appearance as in the quartz samples (Fig. 23). The pyrite in sample A3 occurs as fine globular aggregates within the cell lumina (Fig. 24) while in sample 70 no pyrite was found in the thin section. Here it occurs as an external crust.

**Scanning electron microscopy**

Because of filling up open space with siderite and consequent disappearance of preferential cleavage, cell structures were scarcely encountered (Fig. 26). Siderite crystals are fairly abundant (Fig. 27).

**Francolite**

**Sample-list**

Fig. 22. Wood sample 143: calcite; Wealden; Isle of Wight, England. Cross-section, crossed nicols, 25x. The picture shows lignitic material, concentrated at the margins of calcite crystals.

Fig. 23. Wood sample 70: siderite; age unknown; Siegen, Germany. Cross-section, crossed nicols, 100x. Sideritic matrix with lignitic remains of cell walls (ew = early wood; lw = late wood).

Fig. 24. Wood sample A3: siderite + pyrite; Pleistocene; Oosterbeek, The Netherlands. Oblique radial section with crossed nicols, 100x. Sideritic matrix with lignitic cell walls and small pyrite globules in the tracheids.

Fig. 25. Wood sample 128: francolite; Upper Cretaceous; Yukon, Canada. Cross-section, normal light, 100x. Well-preserved structures of rays(r), early and late wood (ew & lw); lumina are filled.
Fig. 26. Wood sample 70: siderite; age unknown; Siegen, Germany. Scanning electron micrograph of an oblique radial section. Casts of tracheids with pits, space between casts filled with siderite, 825 X, TFDL.
Fig. 27. Wood sample 70: siderite; age unknown; Siegen, Germany. Scanning electron micrograph showing well-shaped siderite crystals, 525 X, TFDL.
117. Brown, massive material, with a crust of glauconite and jarosite; origin: St. Foy l’Argentière, France; age: Carboniferous; coll. 2.
128. Black, massive material with a rectangular fracture; origin: Yukon, Canada; age: Late Cretaceous; coll. 5.

**X-ray diffraction**

All samples are distinctly crystalline. The X-ray diffraction pattern agrees with the francolite pattern of the ASTM system (card 21-141). Sample A11 shows an admixture of pyrite; sample 117 probably contains some quartz.

**Thin sections**

Thin sections of the three samples show well-preserved wood structures, which are especially displayed in cross section (Figs. 28, 25). The francolite is distinctly crystalline (polyblastic), but crystal growth never extends beyond the cell walls (Fig. 29). At higher magnifications there is some indication that part of the cell-wall space has not been filled with phosphate. The pyrite in sample A11 occurs within the cell lumina.

**Scanning electron microscopy**

Scanning electron microscopy of samples 117 and 128 show massive, coarsely crystalline columns (casts of tracheids) on which casts of bordered pits may be visible (Figs. 32, 33). No details of cell-wall structures or bordered pits could be observed.

**IRON-OXYDES AND -HYDROXIDES**

**Sample-list**

22. Red, porous, coarse-grained material; origin: Niederpleis, Germany; age: unknown; coll. 8.
165. Red, porous, coarse-grained material with some pyrite veins; origin: Hau-trage, Belgium; age: Wealden, Early Cretaceous; coll. 1.
175. Rusty, compact material, tangential fracture; origin: unknown; age: unknown; coll. 10: RGM 159 999.
176. *Betula* sp., rusty part of trunk, showing some shrinkage, bark present, porous; origin: Siberia, U.S.S.R.; age: probably Quarternary; coll. 10: RGM 160 000.
179. Rusty, porous material, easily crushed; origin: Eickrath, near Düsseldorf, Germany; age: Late Oligocene; coll. 10: RGM 160 000.

**X-ray diffraction**

The samples consist of various iron minerals with admixtures. The iron minerals show diffuse diffraction lines, probably due to very small crystal size. The com-
Fig. 28. Wood sample A11: francolite; Gault (Lower Cretaceous); Winterswijk, The Netherlands. Cross-section, normal light, 390x. Thick-walled parenchyma cells and ray cells(r). Intracellular space(i) and part of the middle lamellae appear black in the picture.

Fig. 29. The same section as in Fig. 28, with crossed nicols, same enlargement. Polyblastic crystallization of different sizes. Central part of cell walls appears black and is probably not filled.

Fig. 30. Wood sample 22: hematite + siderite; age unknown; Niederpleis, Germany. Cross-section, polarizer at 80°, 100x. Part of tissue surrounded by a matrix of hematite (black) and siderite (white, s); o = open space.

Fig. 31. Wood sample A25: goethite + lepidocrocite; Pleistocene; Ugchelen, The Netherlands. Oblique radial section, normal light, 100x. Faint tracheid walls and accretion lines of ferric nodules.
Fig. 32. Wood sample 117: francolite; Carboniferous; Foy, France. Scanning electron micrograph of a radial section, showing casts of tracheids with casts of bordered pits, 1950 X, TFDL.
Fig. 33. Wood sample 117: francolite; Carboniferous; Foy, France. Scanning electron micrograph of oblique radial section, showing coarsely crystalline surfaces and cleavage planes of tracheid casts, 5250 X, TFDL.
position of the samples is as follows: 22: hematite and siderite, 165: hematite and pyrite, 175: goethite and lepidocrocite, 176: goethite, 179: goethite and lepidocrocite, A25: goethite and lepidocrocite.

**Thin sections**

A thin section of sample 22 shows a dark groundmass without conspicuous wood structures, and also bands of preserved wood structures. The wood structure itself is ferruginous, whereas the surrounding material contains a fair amount of siderite. Siderite occurs also in the groundmass (Fig. 30).

A thin section of sample A25 shows some preservation of cell walls and, more distinctly, accumulation-bands of iron-compounds (Fig. 31).

**Scanning electron microscopy**

Scanning electron micrographs were made of all samples, A25 excepted.

The samples show finely crystalline clusters of iron minerals, but hardly any wood structure. Some remains of this structure were found in samples 165 and 179 (Figs. 34 and 35). In sample 165 some of the fibrillar structure of the cell walls can be recognized. There is some open space between the fibrillar layer and what is apparently the filling of the middle-lamellar space.

In sample 179 too, filling of middle-lamellar space has obviously taken place (Fig. 35). This was not observed in any of the above-mentioned mineralizations.

The siberian birch (176), finally shows some fossilized hyphae of fungi (Fig. 36).

**Discussion**

When wood dies off, the first of its parts to decay are the living cell contents and the pectic middle-lamellae. Pectine is easily removed by microbiological action. Therefore both cell lumina and middle-lamellar space are open when wood is buried and fossilization starts.

Decay of cell walls under anaerobic circumstances occurs in the following order (Barghoorn, 1949, 1952): central part of the secondary wall (S₂), inner part of the secondary wall (S₃), outer part of the secondary wall (S₅), primary wall (P). When decay has acted for some time and is halted by mineralization, S₂ and S₃ are most likely to be absent.

Cellulose fibril organisation in the layers of the cell wall with respect to the long axis of the cells is: flat helical in both the S₁ and S₃ layers; steep helical in the S₂ layer and irregular in the primary wall (Meier, 1962). In silicified samples 42 and 161, in which fibrillar structures were fossilized, these show a steep helix, thus pointing to replacement of the S₂ layer or to filling of the open space originating from decay of the S₂. Decay, however, can hardly be expected to attack just one part of the cell wall and leave the other parts completely intact so as to form a casting-mould for infiltrating silica (compare Fig. 9). Moreover, the silica would have to pass through the remaining intact cell walls first. It is not known whether
Fig. 34. Wood sample 165: hematite + pyrite; Wealden; Hautrage, Belgium. Scanning electron micrograph of a radial section, showing remains of ray cells (r) and tracheids (t) with fossilized fibrillar structure (f), 1750 X, TFDL.
Fig. 35. Wood sample 179: goethite + lepidocrocite; Oligocene; Düsseldorf, Germany. Scanning electron micrograph of a radial section, showing filling of middle-lamellar space in both tracheids (t) and rays (r). Decay structures are present in some places (d), 175 X, TFDL.
Fig. 36. Wood sample 176: goethite; age and origin unknown. Scanning electron micrograph showing hyphae and spores of fungi, 5250 X, TFDL.
Fig. 37. Wood sample 97: disordered tridymite + quartz; age and origin unknown. Scanning electron micrograph of a tangential wall of a tracheid, showing two bordered pits with a concentric fibrillar structure at the surface, 3850 X, TFDL.
imprints of the structure of the $S_2$ can be found on the surface of the $S_1$ and $S_3$, but this can hardly be expected. Impregnation of the parts of the cell wall with silica or complete replacement by silica seems more likely. SEM photographs of tridymitic woods show open middle-lamellar space. In case of filling, one would expect both lumina and inter-lamellar space to be filled.

The replacement theory is also supported by observations on the optical properties of silicified cell walls made by Felix (1897) and the present writer. It appears that in wood-opals, the optical orientation of silica in the cell walls is the same as the optical orientation of cellulose in the cell walls of fresh wood. Felix (1897) noted that all parts of the cell wall ($P + S_1, S_2, S_3$) show this feature. Felix too, favoured the replacement hypothesis.

In most samples one notes very little space between the fossilized tracheids, which suggests that only the middle-lamella has vanished and that cellulose-rich parts of the cell wall have either been replaced or impregnated. This does not exclude infilling of lumina and other open space at the same time or at a later stage of silicification.

Structure-preservation is best in tridymitic samples in which hardly any filling of middle-lamellar space has occurred and even lumina may not be completely filled (Fig. 5). As is known tridymite is an unstable form of silica and it changes gradually into quartz. This is the background of Felix' remark (1897) that wood-opal – equivalent to 'disordered tridymite' – does not occur in sediments older than Eocene. At the same time it explains the change of smooth surfaces to crisp ones observed in samples without and with quartz respectively. Since the change of tridymite into quartz is a very slow process resulting in small crystals, the original structure is not much disturbed.

When external influences are different from those pertaining to near-surface conditions, for instance because of higher pressures, the 'disordered tridymite' may recrystallize into normal tridymite, as must have occurred in the case of the Virginian tridymitic wood, reported by Mitchell (1967).

Silicification does not always proceed through a tridymitic intermediary phase. Many chalcedonic and quartzose silicifications exist in Tertiary formations and it can hardly be maintained that in these cases the transformation of tridymite into silica would have been much faster. Many of the chalcedonic samples show lignified organic remains – a feature never observed in wood-opals – and preservation of structure in these lignitic silicifications is always inferior to that in the nonlignitic chalcedonies and tridymites. These observations lead to the conclusion that silicification by tridymite and by chalcedony are distinct processes.

Tridymite seems to replace cell walls, while quartz or chalcedony fossilize by permineralization (filling). This special property of tridymite may be due to some structural relationship between 'disordered tridymite' and cellulose. Excellent structure-preservation, as is sometimes found in chalcedonic silicifications (Muir, 1970), would then be due to recrystallization of originally tridymitic material.

The circumstances that favour either tridymitic or chalcedonic mineralization are unknown.

Although the question of the source of the silica is beyond the scope of this study, it will be treated briefly. Many authors think that weathering of pyroclastic rocks provides the main source of silica. Soil formation however, may liberate silica from any kind of rock and therefore pyroclastics as a source should not be emphasized. Silica liberation in soils is an especially active process in warm, humid climates.
Silicification of wood occurs mainly under terrestrial circumstances but may also happen in a marine environment. Silicified wood, transported specimens excepted, is not known from the Quaternary.

Phosphatization of wood with francolite appears to be a genuine filling of cells. It forms massive columns in the erstwhile tracheids and rays. Former cell-wall space may be filled with phosphate, but this is generally not the case.

Phosphatized wood, although not explicitly described as such, occurs in fair amounts in the Lower Greensand and Gault (Lower Cretaceous) of Southern England (Isle of Wight, Folkestone) and both the Gault and Portlandian of Northwest France (Boulonnais). Its occurrence is invariably connected with glauconitic rocks. Many pieces are severely burrowed by marine organisms.

As was pointed out before (see p. 6) phosphate accumulation will occur under slightly reducing circumstances at a pH slightly lower than 8. Decomposition of wood may give rise to these circumstances and to a high $\text{CO}_3^{2-}$ concentration profitable for the precipitation of francolite. Phosphatized wood is not known from terrestrial deposits.

Carbonatization, on the contrary, may be quite common in both terrestrial and marine rocks. It can, for instance, be observed in trees submerged in karst lakes. Generally, carbonatization will take place after burial, under the influence of carbonate-rich waters. As in the case of francolite, carbonatized wood is per-

![Fig. 38. Schematic section through a bordered pit in coniferous wood (after Harada & Côté, 1967). Cell lumina lie on either side of the pit (shaded). $M$ = middle lamella; $P$ = primary wall; $S_1$, $S_2$, $S_3$ = layers of the secondary wall; $M$ = margo; $T$ = torus.](image-url)
mineralized. Carbonates however are more apt to recrystallize than francolite and therefore, preservation of wood structure in carbonatized specimens depends on recrystallization having taken place or not.

Carbonatization is probably a more rapid process than phosphatization, and is not related to decay. As a result, lignified organic remains are common in carbonatized woods. This holds true for calcite and dolomite as well as for siderite. The formation of siderite, however, requires reducing circumstances.

Iron sulphide mineralization – pyrite and marcasite – has not been included in the present investigation. Precipitation of these minerals occurs at sites with such suitable Eh and pH conditions as may exist in decaying tissues. When open space is completely filled with sulphides, no structural details remain, but the place of the cell walls. In some cases only a small amount of sulphides is formed and embedded in permineralizing agents, such as calcite, siderite and phosphates.

Accumulation of sulphides in fossil wood occurs in both marine and terrestrial environments.

Iron-containing mineralizations form two distinct categories: the iron-oxyde group (hematite) and the iron-hydroxyde group (goethite and lepidocrocite).

Hematite occurs in both available samples in combination with a second mineral that is not stable under the same pH and Eh conditions (siderite and pyrite respectively). In both cases hematite seems to be the original fossilizing agent. Tissue remains in sample 22 do not contain siderite, the latter usually occurring at the margin of hematite masses. In sample 165 hematite structure-preservation is fairly good, which would not have been the case if pyrite had been the primary fossilizing agent. Both samples 22 and 165 therefore, were fossilized in an oxydizing environment subsequently changing into a reducing environment. The samples do not allow a choice between replacement and permineralization. The hematite supposedly formed in a terrestrial environment.

The goethite and lepidocrocite mineralizations – goethite is the stable phase; lepidocrocite is often formed in the presence of organic material – show clearly that filling of cell lumina has not taken place, but instead filling of the middle-lamellar space.

The structures suggest that mineralization took place during decay. This type of mineralization may occur in wet soils, e.g. gley soils of cold regions. Iron is derived from weathered minerals. FeOOH-mineralization is probably a terrestrial process.

The structure of fossilized bordered pits deserves closer examination. In the mineralizations with the best preserved structures, such as sample 97, bordered pits appear as flying saucer-like structures (Fig. 7) adhering to the cell wall. In other cases (francolite) only the moulds of these structures are preserved (Fig. 32).

Angiosperm and coniferous bordered pits have essentially the same structure (Harada, 1965a, b; Côté, 1967, Liese, 1965). Taking the bordered pits of coniferous wood – as given by Harada & Côté in 1967 (see Fig. 38) – as an example, an attempt is made to give an explanation of the flying saucerlike structures. The cast of the bordered pit (shaded) show a round depression, when only the cell lumina have been filled as is the case with phosphatized wood. Eicke (1954) found silicified internal casts of bordered pits. However, while pit border, torus and margo can be recognized, it seems justified to speak of replacement of structures rather than casting. In case of casting one would expect filling of the pit chamber rather than the preservation of structures inside the chamber. If the cell wall were not silicified and removed after filling of open space, pit casts would have a
disc-like form, as observed in several samples. The silica would have been supplied through the cell lumina and one would expect connections between the pit casts and the casts of the cell lumina, through silica in the pit channel (the pit-opening towards the lumen). Casts might show warts and the concentric fibrillar structure of the pit border (Fig. 37). At the site of the pit channel, however, fractures are never observed. The pit channel site on the pit casts – the flat top of the disc-like structures – is always smooth, although it may show a rim at the site of the pit border.

In the light of the above discussion on pit structures, it seems most likely that in the wood-opals replacement of cell walls by silica has occurred. In this case, cell walls are likely to split along the middle-lamella and, at the site of the pits, along the pit border, thus forming disc-like structures as well. It is clear that mineralizations of a pit irrespective of whether casting or replacement took place, may adhere to either side of the cell wall.

Such pit structures, however, cannot be explained by casting or replacement unless some part of the tonoplast material – the outer membrane of the cell plasma – is preserved during the early stages of silicification. In case of mere replacement, these disc structures must be hollow, containing the silicified torus and margo. It was not possible to check this point. But in this case too, the pit channel must have been covered during fossilization. When the covering membrane is not present during replacement, structures as described by Eicke (1954) may form.

Conclusions

1. Replacement and permineralization are two distinct processes in wood fossilization. Remains or organic matter are preferentially found in permineralized samples, irrespective of the minerals.
2. Replacement of cell walls was exclusively found in specimens consisting of 'disordered tridymite'. This group comprises the so-called wood-opals. The name wood-opal, however, is misleading with respect to the nature of the silica.
3. Chalcedonic wood with well preserved structures may result from recrystallization of 'disordered tridymite'.
4. Structures of fossilized bordered pits in silicified wood do not square with either permineralization or replacement theories when only the cell wall structure is considered.
5. Most fossilizations of wood are permineralizations (fillings). Permineralization structures (casts) are often disturbed by recrystallization. Cast structures are best observed in phosphatic specimens.
6. Silicification of wood, although it may occur in a marine environment, is mainly a terrestrial process. Carbonatization may occur both under marine and terrestrial circumstances. Phosphatized wood is exclusively known from marine sediments, but it might form under very special terrestrial circumstances. Impregnation with iron-oxyde and -hydroxyde will occur in a terrestrial environment, while accumulation of sulphides is influenced by Eh and pH conditions exclusively.
Summary

Several fossil wood samples brought together for the purpose of studying fossil growth-ring cycles provided sufficient material to investigate fossilization in relation to mineralogical composition. Samples of wood-opal, and chalcedonic, carbonatized and phosphatized wood, and finally wood impregnated with iron-oxides and -hydroxydes were chosen for this investigation. The selection was based on X-ray diffraction characteristics.

It was found, that silicified wood can be arranged in two distinct groups: 1) the wood-opals and related fibrous silicifications, mineralogically characterized as 'disordered tridymite' and chalcedonic silicifications derived from this mineral by recrystallization, 2) the silicifications in which chalcedony is the primary phase and which now show both calcenedy and quartz.

Wood-opal shows excellent structure-preservation, which decreases with increasing amounts of quartz (chalcedony) in the sample. It may show optical orientation of silica in the cell walls similar to optical orientation of cellulose in fresh wood. Both this feature and the fossilization of structural details such as cellulose fibrils induce the author to suggest that tridymite silification may well be a replacement rather than filling.

Chalcedonic and quartzose wood specimens of the second group often show lignitic remnants of wood tissue which were preserved because of enclosure during silicification, and probably lignified as a result of crystallization pressure. These fossilizations are supposed to have formed as a result of permineralization (filling).

The writer contends that the silica which causes silicification of wood does not necessarily originate from pyroclastic rocks. Silicification occurs especially in warm climates and in porous rocks.

Phosphatized wood is exclusively known from marine deposits. Accumulation of phosphate occurs in decaying tissues in contact with sea water. Phosphatized wood shows filling of cell lumina; phosphatization therefore is a permineralization. In thin section, structures generally appear well preserved. Recrystallization extending beyond the cell walls was not found. Phosphatized wood seems to occur preferably in glauconitic rocks.

The observations on carbonatized wood agree with the descriptions in the literature. Sideritic wood shows the same features as calcitic and dolomitic specimens, but it is formed in a reducing environment. Structure-preservation in carbonatized specimens depends on recrystallizations. In coarsely crystalline specimens, hardly any structures remain at all. Carbonatization may occur under either marine or terrestrial circumstances.

Samples mineralized by hematite show little structure-preservation although in some cases details of cell wall structures can be observed. Most of the wood structure has disappeared as a result of recrystallization. It was not possible to decide whether permineralization or replacement has occurred. The hematite presumably formed under terrestrial conditions.

Goethite and lepidocrocite mineralizations show filling of middle-lamellar space rather than filling of cell lumina. Mineralization supposedly occurred during decay. Several of the samples are of Pleistocene age, and the process may still take place to-day under wet terrestrial circumstances (e.g. in soils).
References


Manuscript received 4 October 1972.